Transition Metal Organometallics in Catalysis and Biology
Prof. Prasenjit Ghosh
Department of Chemistry
Indian Institute of Technology – Bombay

Lecture - 48
Olefin Polymerization (Part 9)

Welcome to this course on Transition Metal Organometallics in Catalysis and Biology. We have been discussing about olefin polymerization in the last few lectures. In this regard, we have covered several topics, including polyolefin classifications from material perspective, like types of different types of polymers that can be obtained from polyolefin polymerization based on their properties, the polymer material properties like somebody something which is elastic, something which is plastic, something which depends on duroplast, depends on temperature so on and so forth.

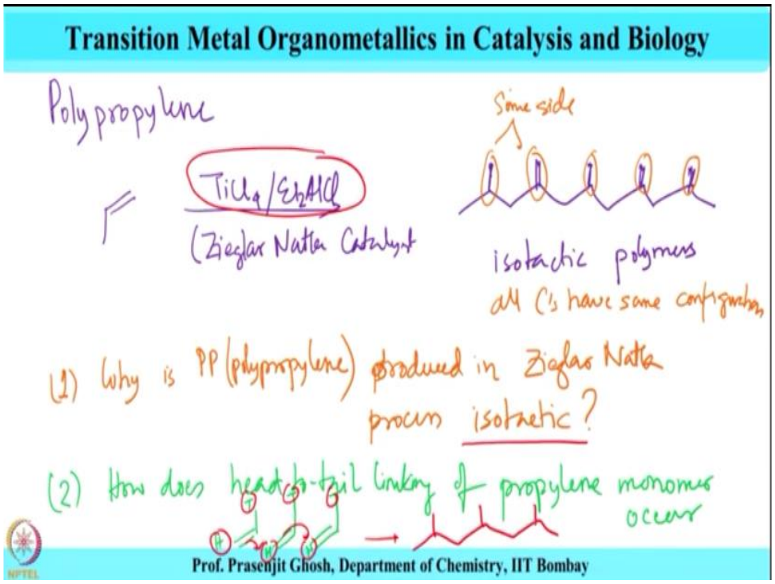
We have also looked into polymer characterization, based on the processes. For example, the condensation polymers or addition polymers, the reaction they use for making these polyolefins, polymers as well as we have distinguished or classified polymers based on the mechanism, step growth mechanism and chain growth mechanism.

And we have also looked into how the polyethylene from the perspective of their different types classes of polyethylene polymers that are known to the historical prospective of their development from Phillip process onwards to Nichol effect and then subsequent discovery by Ziegler to produce high density polyethylene at room temperature under 1 bar pressure using titanium as catalyst.

Now moving on, we have also looked into polypropylene polymers and polypropylene was polymerization of propylene, which was mainly been attributed to the development by Giulio Natta and we had seen that how polypropylene polymers are different from the polyethylene polymers, mainly from the orientation of this methyl side chains of the propylene group, which can be atactic, syndiotactic, stereo block, hemi- isotactic so on and so forth.

So today, we are going to go deep, delve deep into this polypropylene polymerization, particularly from the mechanism and the catalyst development point of view.

(Refer Slide Time: 02:40)



Transition Metal Organometallics in Catalysis and Biology

Polypropylene

$TiCl_4/Et_2AlCl$

(Zieglar Natta Catalyst

Same side

isotactic polymers

all C's have same configuration

(1) Why is PP (polypropylene) produced in Zieglar Natta process isotactic?

(2) How does head-to-tail linking of propylene monomer occur

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

Now polypropylene, so this is a Ziegler-Natta. Now the catalyst gives isotactic polymers. Now this has too many issues with it. The first is that, why isotactic polymer, which means that all the methyl groups are on the same side, stacked on the same side. They all appear in the same side and overall they sort of become chiral. All the carbons have the same configuration and these sort of led to 2 questions regarding the mechanism of polymerization with Ziegler-Natta catalysis.

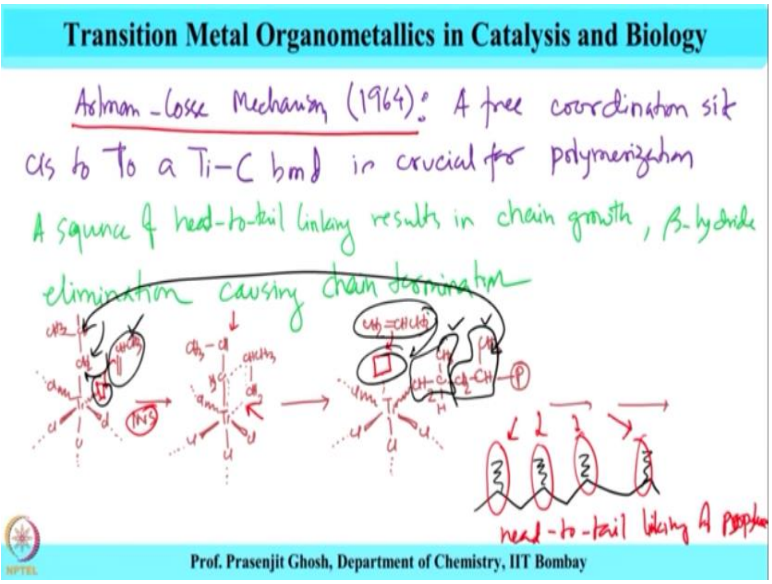
The first question being, why is polypropylene produced in Ziegler-Natta process isotactic. Now this is an important question, because it says that how come polymer, which is chiral in nature and isotactic in nature produced from a catalyst, which is a chiral or non-chiral. So there is an element of suspicion as to how come achiral catalyst produce chiral product. So this is a counterintuitive question, which does not satisfy the intuition.

That one can obtain isotactic polymer from just TiCl4 and diethyl aluminum chloride, which is the Ziegler-Natta catalyst, which itself is achiral. So this is the important question, which throws out some more insight into the process of polypropylene polymerization under the Ziegler-Natta condition and the second thing, which comes out of fate is how does head to tail linking of propylene monomer occur.

So this also is important question, because head to tell linking means that all the monomers are sort of linked in a same fashion. So if this become the head and this becomes the tail, so this is head, this is tail, this is head, this is tail. So head to tail linking happens all the time resulting a polymer of this type, whereas there can be possibility of tail to tail, head to head, other possibilities they do not occur.

So these questions throws out important challenges on the mechanistic part that should explain, why such thing is observed. Now the mechanism for polyolefin is based given by a mechanism, which is called Arlman and Cossee mechanism.

(Refer Slide Time: 08:28)



Transition Metal Organometallics in Catalysis and Biology

Arlman-Cosse Mechanism (1964): A free coordination site cis to To a Ti–C bond in crucial for polymerization

A sequence of head-to-tail linking results in chain growth, β-hydride elimination causing chain termination

head-to-tail linking of prop

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

Which was given in 1964 and which states that free coordination site CH2 to a titanium-carbon bond is crucial for the polymerization. Now this, at this juncture, with this information, this Arlman-Cossee reaction mechanism does not explain the full or explain both the questions, we had post earlier about the isotacticity of the polymer polypropylene or about the head to tail, but these sort of explains the second part the head to tail mechanism arising out of these process.

And it says that head to tail results, it says sequence of head to tail linking results in chain growth beta hydride elimination, which causes chain termination. So let us the explain these Arlman-Cossee conveniently explains that the presence of a vacant bond, the vacant site next to a growing alkyl chain is essential for the head to tail insertion resulting in the polymer growing polymer chain.

But what it does not still yet explain is the reason for isotactic polypropylene, that is observed during the Ziegler-Natta polymerization. So let us just see the second aspect first that head to tail arrangement through the mechanism as is shown over here, CH3. So this is the vacant site, which is occupied by an olefin. So this is this insertion step on this vacant site occupied by this ethylene resulting in a polymer chain on this arm and the vacant site on top as is shown here.

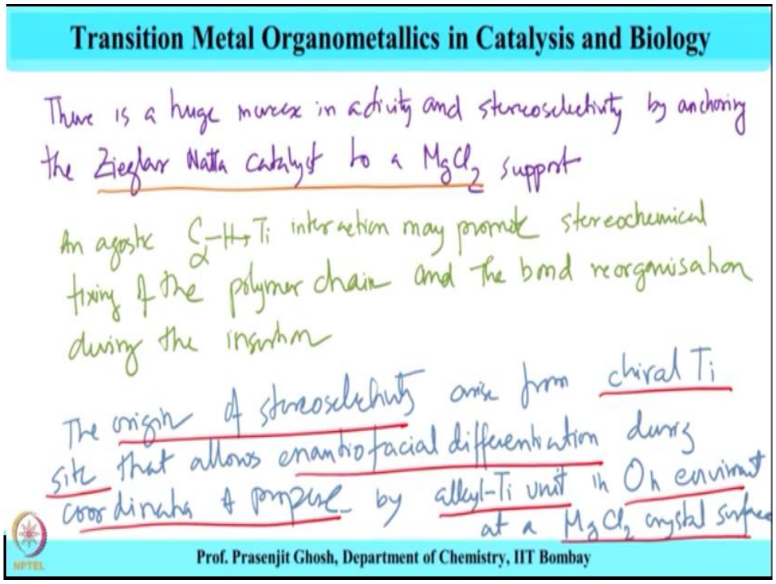
So now, the polymer chain has moved. Now the polymer chain has moved and there is a vacant site over here and that then gets occupied by another pollutant molecule and the reaction then proceeds further. So the point to note is two things. One is that, first thing is that there is a vacant site CH2 the titanium carbon bond followed by this vacant site being occupied by this propylene and then the insertion of this propylene unit into the bond.

As a result, this alkyl chain now skips to the side and another vacant site is created, to which this olefin now comes an bind. So this is called migratory insertion. There is a migration of the alkyl chain, which happens from this to this. So as a result if one were to take a look that because of this oscillatory migratory insertion, there is a head to tail joining of the propylene unit. So all the methyls are pointing towards the same.

So this explains the second question that this propylene is formed in a head to tail fashion, but still a lot more remains to be answered. The first question that why is it isotactic. Isotacticity would depend on the stereochemistry of this carbon. These are all carbon attached in a head to tail fashion. Tail linking of propylene, head to tail linking of propylene and then the isotacticity would depend on the configuration of this carbon.

And for that to happen, then the catalysts have to be achiral in nature and that can be explained this atacticity explained by the fact that the stereoselectivity or stereoselectivity of this Ziegler-Natta catalyst is enhanced in magnesium support, which are to be considered in more details.

(Refer Slide Time: 18:21)



Transition Metal Organometallics in Catalysis and Biology

There is a huge increase in activity and stereoselectivity by anchoring the Zieglar Natta catalyst to a $MgCl_2$ support

An agostic C_α–H→Ti interaction may promote stereochemical fixing of the polymer chain and the bond reorganisation during the insertion

The origin of stereoselectivity arise from chiral Ti site that allows enantiofacial differentiation during coordination of propene by alkyl-Ti unit in O_h envirmt at a $MgCl_2$ crystal surface

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

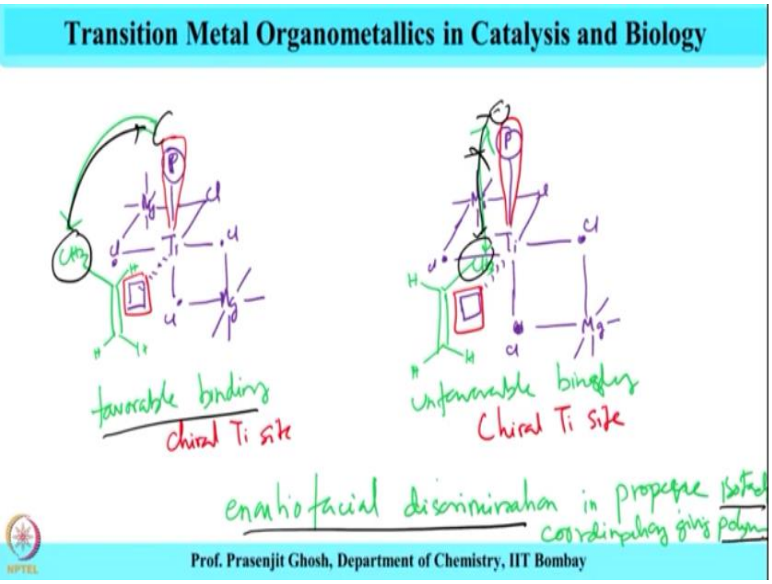
So to explain the chirality, one needs to consider the fact that there is a huge increase in activity and stereoselectivity by anchoring the Ziegler-Natta catalyst to magnesium chloride support okay. Now this is something, which is an important observation that Ziegler-Natta catalysts when attached to magnesium chloride provides isotactic polymers, which sort of indicates that there is some amount of chirality in the catalyst supported catalyst is brought about by anchoring the Ziegler-Natta catalyst onto a magnesium support and we are going to explain that.

And the second thing, which also comes into play is that agostic and agostic C alpha H to titanium. So agostic interaction between C alpha, alpha carbon, alpha proton to titanium interaction may promote stereochemical fixing of the polymer chain and bond reorganization during the insertion step and the bond reorganization during the insertion step and this more specifically is explained by the fact that the origin of stereoselectivity arise from chiral titanium site, that allows enantiofacial differentiation during coordination of propene.

And this chiral occurs by alkyl titanium unit in octahedral environment at MgCl2 crystal surface. Now this is a very powerful statement. It explains this the nature of isotacticity. It says that the origin of stereoselectivity arises from a chiral titanium site, which allows enantiofacial differentiation during the coordination of propane and that arise by the titanium alkyl unit present in octahedral environment in a magnesium Cl2 crystal.

So it says that when titanium's alkyl unit of Ziegler-Natta catalyst with the growing polymer chain is present on a magnesium Cl2 crystal, then the overall the site, the catalytic site becomes chiral and results in isotactic polymer. So this can be best explained by the orientation as is shown over here.

(Refer Slide Time: 24:05)



Transition Metal Organometallics in Catalysis and Biology

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

Titanium Mg, these are chlorine Mg chlorine, so this is the polymer chain and here is the vacant site. This is the vacant site and this is the polymer chain. Now it is draw this configuration similarly as is shown here. This is the polymer and this is the vacant site as is marked over here this is the polymer chain and this is the vacant site and this is how the titanium is supporting the magnesium chloride crystal and these are chiral titanium site.

Now when the olefin comes, then the binding of olefin happens in this fashion as opposed to, because of obvious reason this one is favorable binding. This methyl group and this polymer chain are further apart, unfavorable binding because now the methyl chain are this asterically hindering and as a result, these results in facial discrimination, results in facial in enantiofacial discrimination in propene binding coordination leading giving isotactic polymer.

So this is a very important concept, which is shown that this binding is favorable, this facial binding and that leads to enantiofacial discrimination whereas interaction between this is not favorable and that gives rise to isotactic polypropylene. So with this, we come to the conclusion of today's lecture in which we have explained the result of two things, which are not very obvious from the Arlman-Cossee reaction.

First is the head to tail by linking of the polypropylene, linking of propylene in polypropylene polymer and this is explained by the fact that there is a vacant site C's to the growing titanium carbon bond of the polymer chain and second thing is the isotactic polymer, the chiral polymer being obtained from Ziegler-Natta catalyst and this has been attributed to a chiral site by formation of the titanium on the magnesium chloride crystal, which results in a chiral environment around the catalyst.

And that successfully carry out enantiofacial discrimination of the binding propene, which result in isotactic formation of the polypropylene. So with this, we come to an end of this today's discussion on polypropylene more on the perspective of this interesting chemistry of polypropylene as we meet in the next class. I once again thank you for being with me in this.

Next class more of the exciting stuff coming up in the next class, where we see the catalyst development and walk you through the various aspects of polypropylene chemistry in terms of catalyst design and polymer activity when we meet next. Till then, goodbye and thank you.