Transition Metal Organometallics in Catalysis and Biology

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Lecture – 47
Olefin Polymerization (Part 7)

Welcome to this course on Transition Metal Organometallics in Catalysis and Biology. We have been discussing Olefin polymerization in the last few lectures and in the previous lecture, we have looked at one big discovery in the field of Olefin polymerization, which is Ziegler-Natta catalysis, and in that respect, we have seen the sequence of events starting from Aufbau reaction, the nickel effect that led to the initial discovery of Ziegler-Natta catalysis.

And subsequently we have also looked into the contributions made by Karl Ziegler with regard to the Ziegler-Natta catalysis, which is mainly centered around polymerization of ethylene. So, in today's lecture, we are going to go further and look into the contributions of Julia Natta with regard to the Zeigler-Natta catalysis, which is centered around propylene.

In this, we had observed Ziegler's work is on ethylene to polyethylene HDP molar masses, 10 to the power of 4 to 10 to the power of 5 Dalton, and the catalyst is titanium tetrachloride and diethyl aluminum chloride at 25-degree centigrade and 1 bar pressure that gives rise to this polyethylene. Now the main limitation and the active species for this is surface alkylated beta Ticl3 catalyst.

Now this had been the Ziegler's contribution in the Ziegler-Natta catalysis and he is the first one to have identified this polymerization procedure of ethylene to give polyethylene of very high molecular weight and that too under ambient condition using titanium tetrachloride and diethyl aluminum chloride at 1 bar pressure and the active species is supposed to be surface alkylated beta titanium 3 catalyst, which is generated from the reaction of Ticl4 and diethyl aluminum chloride.

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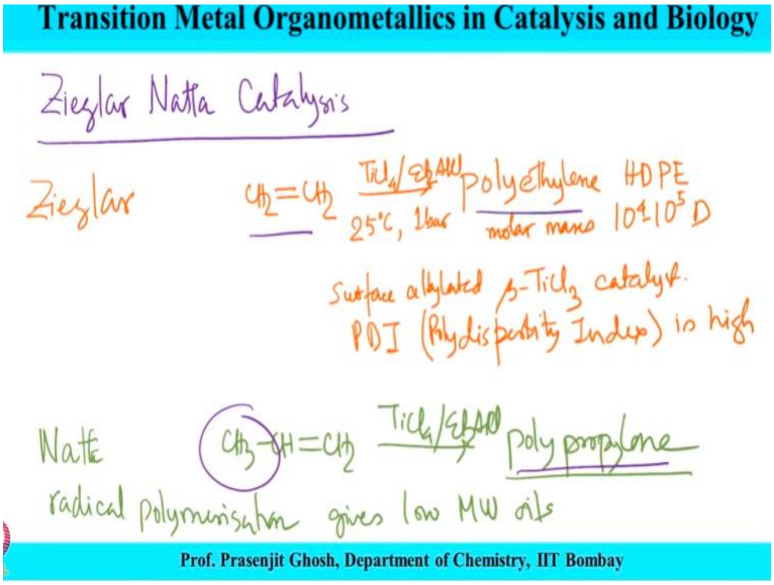

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Zieglar Natta Catalysis

Zieglar $CH_2=CH_2 \xrightarrow[25^\circ C,\ 1\,bar]{TiCl_4/Et_2AlCl}$ Polyethylene HDPE

molar mass 10^4-10^5 D

Surface alkylated β-$TiCl_3$ catalyst.

PDI (Polydispersity Index) is high

Natta $CH_3-CH=CH_2 \xrightarrow{TiCl_4/Et_2AlCl}$ polypropylene

radical polymerisation gives low MW oils

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One of the major limitations of this Ziegler's method is that they had very broad distribution of molecular weight and their polydispersity index (PDI) are very high. So, the polymers were of broad range of distribution of chain length and then the emphasis came on the developing single-site catalyst, which will have uniform active species and as a result, one can get narrow distribution of molecular weight and those are called low PDI polymers.

So, this had been the work of Ziegler. Now, the Natta's contribution had been in polyethylene to polypropylene using this catalyst and usually the low-density polypropylene were obtained by radical method. Other methods like radical polymerization gives low molecular weight oils and with respect to this, the Ziegler-Natta polymerization provided access to this polypropylene of high molecular weight and of different properties in terms of hardness, softness, and so and so forth.

Another important thing, which comes into play is the orientation of this methyl group in the propylene polymer, which is absent in case of the ethylene polymerization to polyethylene. So, there are different possibilities in which the methyl group can orient with respect to each other, that is one important thing and based on that, the polymer properties of polypropylene varies depending on how this methyl group gets stacked up.

So there are classification of polypropylene polymer based on the element of the methyl group and we are going to be looking at this different classification. The next thing which comes into play is that how different classes of polymers are produced using this titanium catalyst, so how does the catalyst site work to get this different kind of polypropylenes as shown over here.

So, now we are going to talk about the various type of polypropylene, classes of polypropylene, polymers that exist and this is termed as polypropylene classification. Now, the properties of polypropylene dependent on density, hardness, ductility, as well as the tacticity. So, the various types of polypropylene polymers that can be present depending on the methyl branching is shown below.

The first one is the arrangement like this where all the methyl groups are pointed towards one direction. These are called isotactic polymer and all the carbon atoms have same configuration, and this is called iPP. The next has arrangements of this type. This is called syndiotactic and this has regular alternation of configuration. So one methyl is coming up, the other methyl is going down and then the other is coming up and the other is going down.

So this kind of arrangement is called as syndiotactic whereas in the first one, it was isotactic where all the thing was coming up. So this is called syndiotactic polypropylene or SPP. The third one has a three region where some of them are coming up together and others are going down. So these are called stereoblock and alternation of isotactic C4 to C100 blocks with different configuration and these are called StPP.

The fourth one is called hemi-isotactic stereocenters, 1,3,5,7 are isotactic and 2,4,6,8 are atactic and this called hemiisotactic (hiPP). The fifth one is called atatic, irregular statistical change in configuration and this is called atactic (aPP). Now, all of these so many varieties in terms of polyethylene, we had around 3 varieties. LDP, LLDP, and HDP and in terms of polypropylene apart from the molecular weight, we have another variety based on stereo irregularity of this methyl group.

So, we have the first one, which is isotactic where all the methyl groups are in the same direction, followed by the syndiotactic where all the methyl groups are in alternate arrangement, then we have stereoblock of polypropylene where there are blocks of the same side oriented methyl groups followed by another block of different side oriented methyl group.

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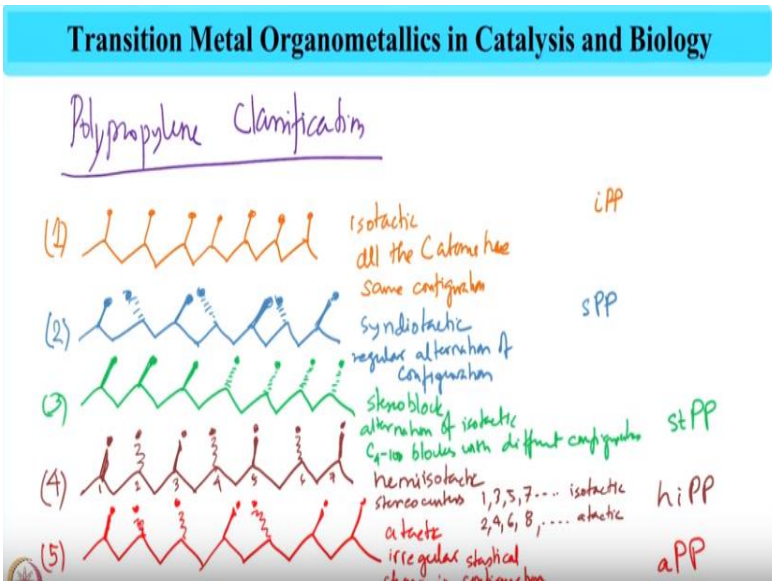

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Polypropylene Classification

(1) isotactic
all the C atoms have
same configuration
iPP

(2) syndiotactic
regular alternation of
configuration
sPP

(3) stereoblock
alternation of isotactic
C_{4-10} blocks with different configuration
stPP

(4) hemiisotactic
stereocenters 1, 3, 5, 7 . . . isotactic
2, 4, 6, 8, . . . atactic
hiPP

(5) atactic
irregular statistical
aPP

Then we have hemiisotactic in which half of the centers are isotactic, that means that occur in a regular arrangement towards one side, and the alternating other half is atactic, that means that can appear in any direction followed by the last one, which is a completely irregular statistical change in configuration, which is called atactic polypropylene. So this configuration characterization has been what was categorized by Natta in putting forward to the polypropylene polymerization.

The stereo chemical feature of this polypropylene polymer is what is seen as Natta's contribution in this whole Ziegler-Natta discovery. Hence owing to the structure of stereoisomers of polypropylene differ in physical properties and in their applications. For example, their structure relationships are also very different. For example, isotactic and syndiotactic polypropylenes are usually crystalline owing to their helical structure, whereas atactic polypropylene is amorphous.

Now this is a kind of a very interesting thing that how come the important question over here is why the polypropylene produced by Ziegler-Natta process is isotactic. Now, statistically it can form any of the five thing; so the important question, which arises at this juncture is why the polypropylene produced by Ziegler-Natta process is isotactic. The answer is lies in the mechanism and what is important is that a free coordination site cis to titanium-carbon bond is crucial.

So there has to be a cis site, which is crucial to cis site to represent two titanium-chlorine bonds and which is crucial to the formation of this. So there is a free coordination site cis Ti-C bond is important for producing this isotactic polymer.

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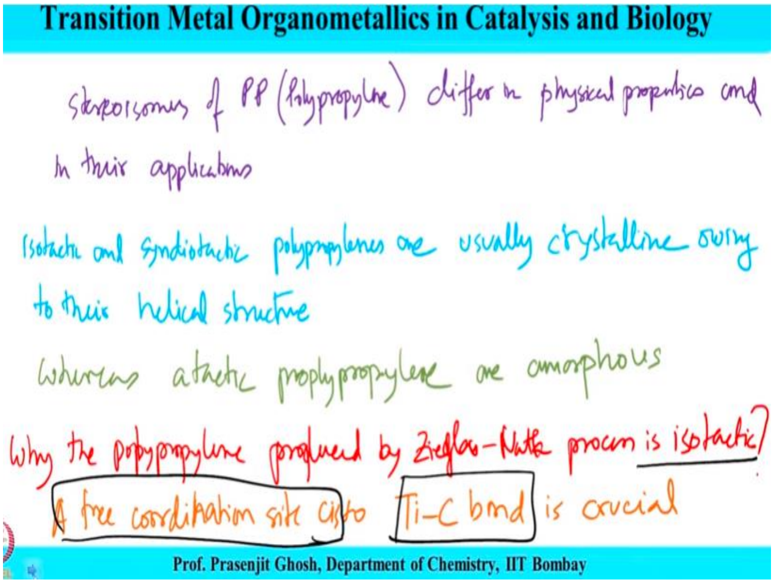

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stereoisomers of PP (Polypropylene) differ in physical properties and in their applications

Isotactic and Syndiotactic polypropylenes are usually crystalline owing to their helical structure

whereas atactic proplypropylene are amorphous

Why the polypropylene produced by Ziegler-Natta process is isotactic?

A free coordination site cis to Ti-C bond is crucial

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So with this let me just sort of take a look at how this polymerization proceeds. This is the polymer chain and to this, the propylene comes, CH3 binds, and this is the vacant site and then it goes through this four-membered transition state. So it goes through a four-membered transition state to give the product. First, there was a vacant site over here where the ethylene added, now there is a vacant site over here where another molecule of ethylene comes and sits, and then again the subsequent insertion of this into the polymer chain happens.

So, first is the insertion of this into this and then insertion of this. So, first insertion, then second insertion and then this proceeds further. This is propagation, followed by termination, which happens CH2-CH3 polymer. This is alpha beta and this gives elimination beta hydride, elimination to give titanium chloride and hydride along with CH3-CH2-P, where P is growing polymer chain, and this whole mechanism is called as the Aolman-Cossee mechanism.

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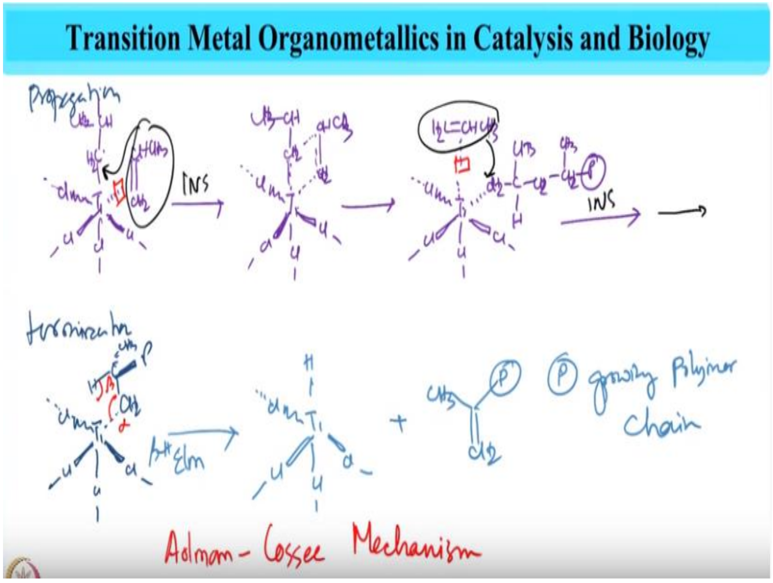

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So with this, we have come to an end of discussion of today's class and what we have discussed today in the class is that we have focused on Natta's contribution in polyethylene. We have also looked at the different classification of polyethylene that exist based on the orientation of the methyl branches and we have also looked into the question as to why this Ziegler-Natta process gives isotactic to very ordered polyethylene.

And the answer to that lies in the fact that there has to be a cis, a vacant site cis to the titanium-carbon bond, which will have the polymer chain where this propylene will come and insert and because of the presence of the cis site and the catalyst is able to distinguish between the two phases of the propane approach and selectively make isotactic polymer. So, more on this stereo regular polymerization of Ziegler-Natta process for polypropylene as we meet next.

With this, I like to thank you for being in the class. We have to be looking at the Ziegler-Natta polymerization in a bit more in detail with taking with some more complex and relevant examples with regard to this development of this catalyst as we proceed with the discussion in the next class. Till then good bye and thank you.