Transition Metal Organometallics in Catalysis and Biology

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Lecture – 46
Olefin Polymerization (Part 7)

Welcome to this course on Transition Metal Organometallics in Catalysis and Biology. In this course, we have been discussing an important topic, which is olefin polymerization, and in this context, over the last few lectures, we were particularly focusing our discussion on poly olefin, particularly polyethylene and various processes that were prevalent in the beginning for preparing various grades of polyolefin, which can be LDP Low-Density Polyethylene or LLDP Linear Low-Density Polyethylene or HDP High-Density Polyethylene.

Now, in our discussion, we have also looked at several industrial processes starting from that of ICI or radical-based polymerization to produce LDP to heterogeneous transition metal-based chromium, centric polymerization method developed by Philips, probably known as Philips process in 1956, to be more precise, for producing HDP High-Density Polyethylene and also looked at how improvisation of the process by replacing the initial high-valent chromium trioxide as precursor with low valent chromocene by union carbide led to accessing these polymers in a more efficient way.

We have also seen how union carbide by controlling the chain length, by varying the introduction of hydrogen gas in the polymerization chamber, thereby carrying out modification of the Philip process for producing HDP and successfully use this Philip process to produce LLDP or linear low-density polyethylene. In this context, we have also noted the contribution of union carbide in a process called UNIPOL process where with the conventional reactor and used fluid-based reactor for producing both LLDP and high-density polyethylene.

Now in and around at this time, we have also discussed about the development of Ziegler-Natta catalysis or the origin of Ziegler-Natta catalysis and what we have noted that Ziegler-Natta catalysis started from investigation on aluminum-based catalysis that would produce long chain compounds of chain length of up to C 200 and which was commonly called as the Aufbau reaction.

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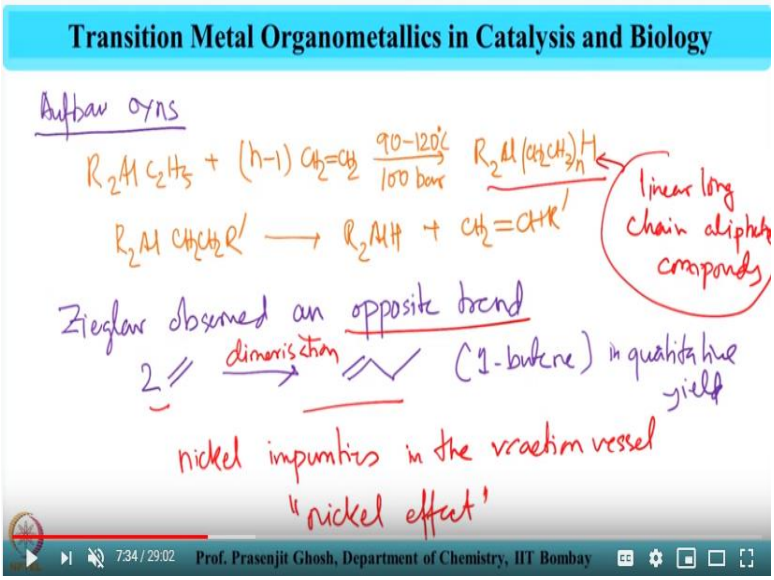

And the Aufbau reaction in short is given by 100 bar pressure produced and then there is competing reaction called the hydroalumination that resulted in aluminum hydrate compound plus alpha olefin. Now, it is while observing the production of long-chain aliphatic compounds that Ziegler observed an opposite trend and the opposite trend was that instead of obtaining polymers.

What was obtained was 2 molecules of ethylene gave away to 1-butene in quantity yields and this was a very chance discovery, which sort of showed that something opposite to what was expected was long-chain polymers, long-chain linear, long-chain aliphatic compounds. This was what was expected from this reaction, but what was found was 1-butene, which is just a dimer of ethylene.

And this is a sort of dimerization process and that was a sort of a chance discovery, which was later attributed to nickel impurities in the reaction vessel and this in short is called nickel effect. This nickel effect is what later on was the origin or source for the discovery of this famous Ziegler-Natta catalyst.

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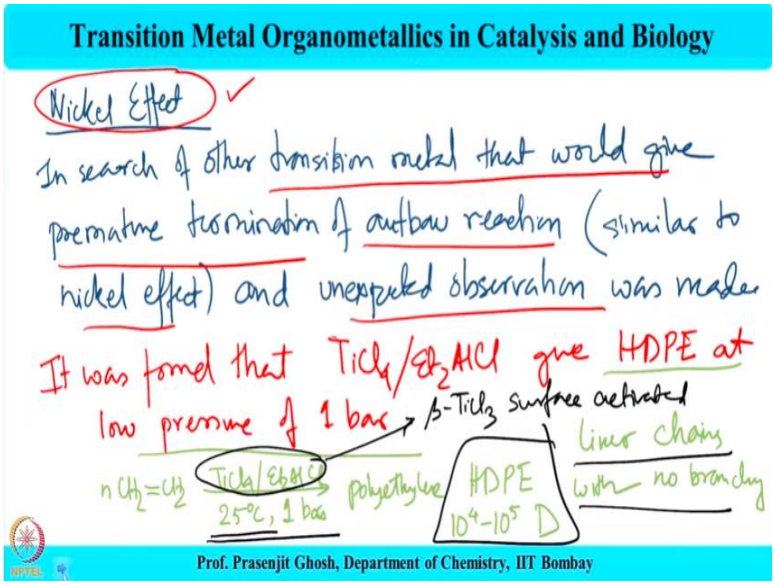

So in search of other transition metal that would give premature termination of Aufbau reaction. This is exactly similar to what was nickel effect. Another unexpected observation was made. So this is kind of very interesting, because it is sort of like two sudden (()) (09:37) led to one big Nobel Prize of award winning discovery. The first one itself was the nickel effect because people were studying Aufbau reaction and was trying to figure out ways and means to increase and make linear long-chain polymers.

However, they came across this nickel effect, which led to just the dimer. Once the nickel effect was found, they were looking for other transition metal that would behave similar to that of nickel effect and they were looking for other transition metal that would have similar effect like nickel effect on the Aufbau reaction and which would also give dimerized or oligomerized product.

However, the other expected observation was that during this search for other metal, they found another metal, which could even give a much larger polyethylene and polymer chains, which was again like going back to what they really wanted in the first place. So the way we say that two left brings us back to the same position, similarly two errors in the way of process of discovery led to exactly the same thing what they wanted in the initial stages that wanted to make long-chain polymers and that was indeed the case.

But that has to be found first the nickel effect and another unexpected observation that was made, which led to Ziegler- Natta polymerization. So let us see this unexpected polymer. It was found that Ticl4 and Et2AlCL gave HDPE High-Density Polyethylene at low pressure of

1 bar. So this is indeed a significant discovery because now unlike in radical polymerization, one could aware very extremely high pressures needed, pressure of around 2000 PSI needed to produce polymers, which are not really very long in chain like LDP.

This Ticl4 and diethyl aluminum chloride efficiently gave HDPE High-Density Polyethylene at a very low pressure of 1 bar. So this was indeed a radical discovery at that point of time because now we have a catalyst, which is a titanium-based catalyst that can polymerize ethylene to give long-chain linear polyethylene at a very low pressure of 1 bar and these are highly crystalline materials without much branching.

So that is the uniqueness about this Ziegler-Natta polyethylene discovery and this is how it came into being. First the observation of nickel effect by looking at by getting 1-butene from Aufbau reaction and then the second thing was that they wanted to see what other transition metal can give similar premature termination of Aufbau reaction, but instead they ended up finding a transition metal, which could give extremely long-chain polyethylene and then what the Aufbau reaction can give. So with this, let me just give the reaction.

This is about 10,000 to 100,000 Dalton molecular weight and this HDP obtained were almost linear chains with no branching. So, this was very important discovery at that point, which was made by Ziegler that now he has found a system, which is titanium tetrachloride with diethyl aluminum chloride at a very ambient condition 25-degree centigrade at 1 bar pressure could produce high-density polyethylene, a very high molecular rate ranging from 10,000 to 100,000 Dalton and that produce linear-polymer chains with no branching.

So, this was indeed a great discovery by Ziegler and what he found that actually the catalyst is beta surface-alkylated beta Ticl3, which is obtained from this. The really catalytic species is beta form of Ticl3, which is surface activated beta Ticl3. Now, this was the catalyst, which was producing high-density polymer.

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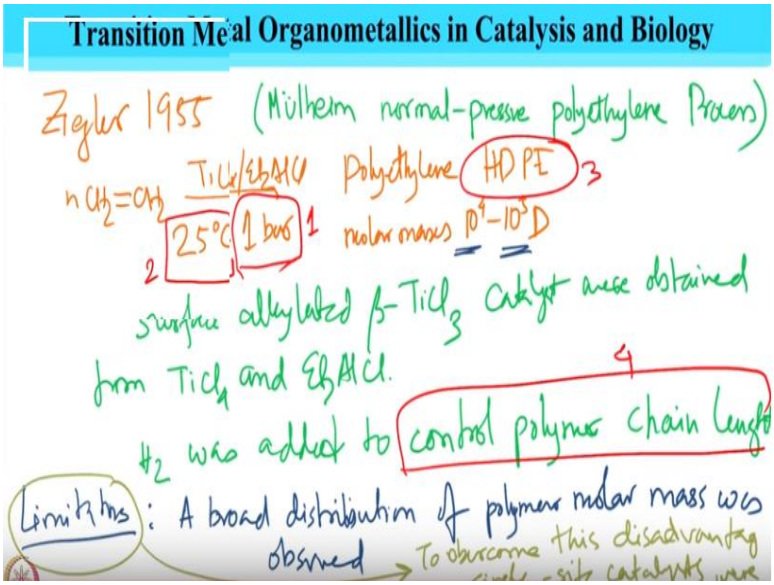

Now, this process was initially called as Ziegler 1955, discovered this polyethylene HDPE and molar mass, 10 to the power 4 to 10 to the power 5 Dalton and this process at that time was known as Mulheim normal-pressure polyethylene process. So, what Ziegler found that actually this is surface-alkylated beta Ticl3 catalyst was carrying out the process and they were obtained from Ticl4 and diethyl aluminum chloride and for obtaining the lower molecular weight, hydrogen was added to control the polymer chain length.

So, this is similar to what we had observed in case of the Philip process as well where hydrogen was added to control the chain length and then Philip process was used for making LLDPE. Now what are the advantages of Ziegler-Natta polymerization, let me just highlight. The first thing that it could produce at very low pressure, this is the number one advantage. Second thing is that the temperature is also at room temperature in ambient condition.

So this is the second advantage. Third advantage is that, it was producing high-density polyethylene, which is almost linear and without almost no branching, and fourth advantage is the control of polymer-chain length by adding hydrogen in radiation. Now, there are also limitations associated with Ziegler process. Limitations says that being heterogeneous, Ziegler process says large broad distribution of polymer molar mass was observed.

So, that means a broad distribution chain length has varied a lot as we have seen something to 4 Dalton and that means that these are martensite catalysis. So to overcome this limitation, the efforts were put into develop single-site catalysis. To overcome this disadvantage, single-side catalyst were developed and this single-site catalyst would give a narrow distribution of

molecular weight and they would give a more narrower and well behaved type of molecular weight.

So, this was the story of the first half of the Ziegler-Natta catalysis. Now, as you can see the Ziegler-Natta catalysis bears the name of two contributors, one is Karl Ziegler, and the second is Julia Natta and the first half of the story is about the ethylene polymerization, which was identified and first developed by Ziegler. So far, we have spoken about the portion of Ziegler-Natta catalysis and now we are going to move on to the second half of the Ziegler-Natta catalysis, which is about the Natta portion of the Ziegler-Natta catalysis.

Now, in terms of chemical point of view, Ziegler-Natta catalysis uses polymerization of ethylene to give polyethylene, which was Ziegler's contribution, and Natta's contribution had been extending Ziegler's contribution to polypropylene. So in that way, one can say that the real glory about the discovery of the polymerization actually lies with Ziegler, because Ziegler is the one who had first observed the polymerization of ethylene to HDP under ambient condition in 1 bar for ethylene.

So extending the same method to propylene would be obvious extension of the existing knowledge, but the way things went out is Natta came and worked in the lab with Ziegler in one of the summer, and he understood the implication of propylene that might have in the same catalysis and so he went and extended the polymerization reaction to propylene and he very well knew that propylene having a methyl group with stereoregular properties in the polymer and that he developed that aspect.

Polyethylene, on the other hand, does not have any stereoregularity issues because it is just the ethylene backbone, whereas polypropylene had stereoregularity of the methyl group. That is another dimension to the polymer that professor Natta conceived and that he applied successfully in extending the Ziegler's discovery to propylene substrate. So today with that we come to the conclusion of this lecture.

In which, we have looked into the historical perspective of the development of Ziegler-Natta contribution catalysis right from the time of the Philip process where the industrial processes were being developed for producing various kinds of polyethylene from LLDP or HDP and then we had also noted that how the study of Aufbau reaction to produce long-chain polymers

led to the observation of simple quantitative dimerization of ethylene and that was later accounted for the presence of impurity of nickel in the reactor and that was called as nickel effect.

Subsequent study of nickel effect for finding another transition metal, which would give now the premature termination of Aufbau reaction to give 1-butene, however, led to an opposing trend or opposing discovery that in presence of organo transition metal like titanium tetrachloride and diethyl aluminum chloride extremely linear long chain high-density polyethylene was obtained at room temperature at 1 bar pressure.

So this was a great discovery, again which was unexpected and that is what led to polyethylene polymerization. So this is the story, which was developed by a professor called Ziegler and the advantage of Ziegler-Natta polymerization of Ziegler polymerization is that this produces HDP High-Density Polyethylene at room temperature at 1 bar pressure and also the chain length can be controlled by metered addition of hydrogen.

And the limitation what it had is, that it has large distribution of polymer molar mass with distribution of the molecular weight and that suggested that this is a martensite catalysis and hence to improve on that, the focus changed to synthesizing a single-site catalyst for making more well-behaved polymer with narrow polydispersity index. So with this, we have come to an end of the Ziegler story of the Ziegler-Natta polymerization.

And we are going to be taking up our Natta's story next as part of the Ziegler-Natta polymerization and how we would see how professor Julia Natta translated the knowledge developed by professor Ziegler for polymerizing polyethylene and use the same propylene to produce polypropylene and how that was developed in subsequent ways. So with that I again thank you again for being with me in this class and we are going to be discussing more about this exciting story of Ziegler-Natta catalysis has been made in the next lecture. Till then, good bye and thank you.