Transition Metal Organometallics in Catalysis and Biology

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Lecture - 49
Olefin Polymerization (Part 10)

Welcome to this course on Transition Metal Organometallics in Catalysis and Biology. We have been discussing olefin polymerization over the last few lectures. In particular, we have been focusing about various topics, various aspects of propylene polymerization or polypropylenes. In this regard, we have noted that in the previous lecture that Ziegler-Natta catalysts can also polymerize propylene.

And one of the main questions that remain about Ziegler-Natta or remained at that time about Ziegler-Natta polymerization propylene, catalyst polymersizing propylene is the fact that the polymers obtained were isotactic in nature and the polymers where connected in a head to tail linkages. Let me illustrate these as follows:

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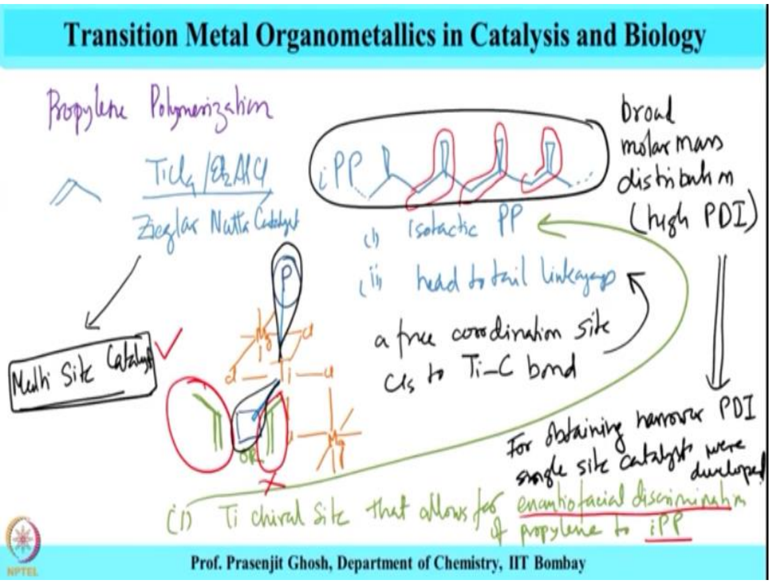

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Propylene Polymerization

$TiCl_4/Et_2AlCl$

Zieglar Natta Catalyst

Multi Site Catalyst ✓

iPP

broad molar mass distribution (high PDI)

(i) Isotactic PP

(ii) head to tail linkages

a free coordination site cis to Ti–C bond

For obtaining narrower PDI single site catalysts were developed

(i) Ti chiral site that allows for enantiofacial discrimination of propylene to iPP

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So what is important to note is that propylenes were polymerized with aluminum chloride or Ziegler-Natta catalysts to give isotactic polypropylene which is a stereoregular polymer. So polypropylene or IPP and the second thing, which at that time was difficult to understand is this hate to tail linkages, that is a propylene units. So these can be illustrated. This is one unit, this is another unit. So these are head to tail linkages of this propylene unit.

So these are the two aspects that needed explanation in trying to understand Ziegler-Natta polymerization of catalyst and the explanation came in the way of two things that these TiCl3 crystals are supported by MgCl2. So the active catalyst actually is chiral in nature where it has a sigma, a hole or sigma vacant site adjacent to a transition metal polymer bond. So this can be explained as such.

So titanium chloride is supported on a magnesium chloride crystal, where there are two sites. One is the polymer chain, which is bound to titanium, the other is a vacant site. So overall what is to notice that overall the titanium site is chiral, a site that allows that allows for enantiofacial discrimination of propylene to give isotactic polypropylene. So this is the first explanation, which provides explanation to the observation that polypropylene is isotactic in nature.

And this is illustrated by the approach of olefin, which can be either this with the methyl group on this side or it can be this with. So these are the two possibilities of which one possibility is favored. This one is favored and this approach is not favored resulting in room for enantiofacial discrimination of propylene to give isotactic polypropylene. Now the other thing, which we had discussed that leads to the formation of head to tail linkages is the fact that there is a sigma hole.

There is a vacant site present or cis to the polymer titanium carbon bond. So now, there is a presence of a free coordination site cis to titanium carbon bond and this is what allows for this head to tail orientation. So head to tail linkages is dictated by that. Now one thing about Ziegler-Natta polymerization is that the polymerization happens on TiCl4 supported over MgCl2 crystals and hence this is Ziegler-Natta polymerization one attributed.

This is the multi-site catalyst that means that there are many active catalytic centers which are present, which carry out polymerization. As a result of this presence of multi-site catalyst, the polymer so obtained become broad molar mass distribution or high in short, high PDI polydispersity index. So that means that the polymer has a wide range of molecular weight distribution that is what it means in short.

Now to have more well behaved polymers of uniform property, then the need became for developing single site catalyst. For obtaining narrower PDI polydispersity index, single site catalyst were developed. For obtaining a narrow distribution, a single site catalyst were developed and that led to another set of discoveries geared towards developing single side olefin polymerization catalyst.

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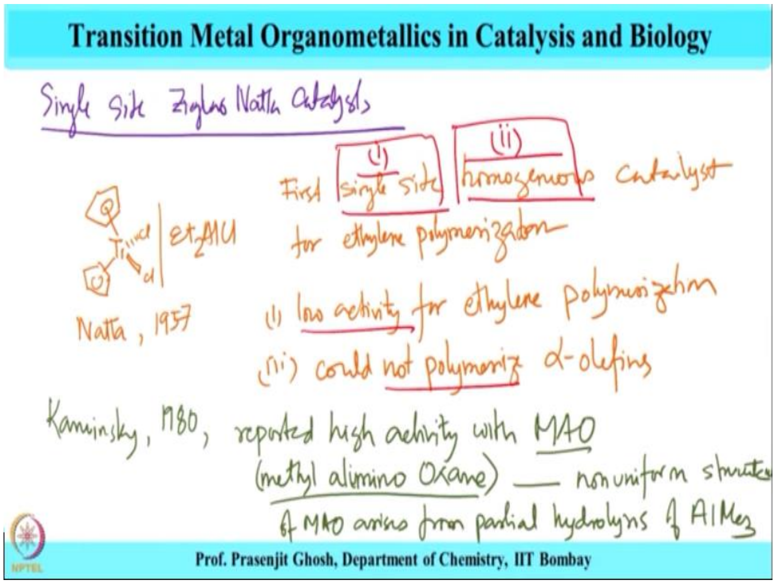

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Single Site Ziegler Natta Catalysts

Et_2AlCl

Natta, 1957

First (i) single site (ii) homogeneous catalyst for ethylene polymerization

(i) low activity for ethylene polymerization

(ii) could not polymerize α-olefins

Kaminsky, 1980, reported high activity with MAO (methyl alumino Oxane) — non uniform structu

of MAO arises from partial hydrolysis of $AlMe_3$

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So in this context Natta catalyst, in this context the Natta system of bis titanium dichloride is what provided the first initiation towards this end. The catalyst was titanium with Al2 Et2AlCl. So this was provided by Natta in 1957 and this is the first single site homogeneous catalyst for ethylene polymerization, the activity and now this catalyst had low activity for ethylene polymerization and could not matchup to the heterogeneous Ti4 TiCl4 diethyle aluminum chloride catalyst which is the Ziegler-Natta original system.

So it has low activity and second thing is that this also could not polymerize alpha olefins. So this thing was like no matchup for the Ziegler-Natta heterogeneous TiCl for diethyl aluminum chloride catalyst, but nonetheless there are two advantages to this system, which are to be noted here. The first is that this is the single site catalyst. This is the advantage number one and the advantage number two is that, this is also a homogeneous system.

So that means that the polymer were of low PDI and much well behaved. So these are the two advantages of this system, despite the fact that it had its own problem like the activity was very low and could not polymerize alpha olefins. These are sort of the drawback for this system. Then another following Natta's observation, there was another noted contribution was made by Kaminsky in 1980 who reported high activity with MAO or methyl alumino-oxane.

So at that time MAO, the structure of MAO was not known and this MAO was obtained by partial hydrolysis of non-uniform and structurally it was not uniform, non-uniform structure of MAO arises from partial hydrolysis of triethyl aluminum. So at that time, this is what led to enhancement of reactivity for homogeneous catalysis, which is originally reported by Natta.

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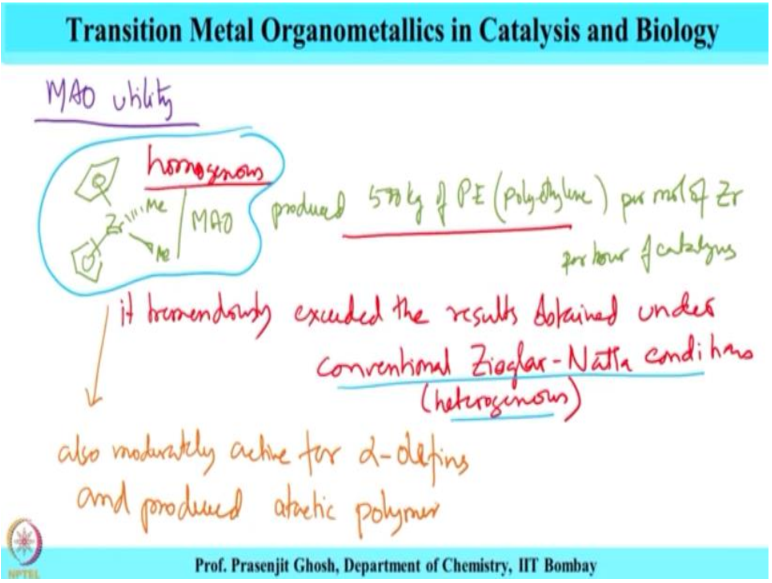

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MAO utility

homogenous

produced 500 kg of PE (Polyethylene) per mol of Zr per hour of catalysis

it tremendously exceeded the results obtained under conventional Zieglar-Natta conditions (heterogenous)

also moderately active for α-olefins and produced atactic polymer

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Now following this discovery MAO applications, it can be very much gauged from the fact that the corresponding zirconium dimethyl catalyst produced 500 kilogram of polyethylene per mole of zirconium per hour of catalysis. So this is a tremendous, highly active catalyst with MAO, the zirconium dimethyl thus became highly active catalyst that could produce 500 kilograms of polyethylene per mole of zirconium per hour. That is a huge activity.

And this was even, it tremendously exceeded the results obtained under Ziegler-Natta conditions, conventional conditions. In contrast, this convinced the (()) (19:41) under Ziegler-Natta condition. So here now we have a which is a heterogeneous system. So here we have a homogeneous system catalysis, which could beat the heterogeneous system. So this zirconium MAO dimethyle could beat this conventional Ziegler-Natta conditions under homogeneous system.

Now this catalyst was also moderately active for alpha olefins and the product was atactic. The catalyst also moderately active for alpha olefins and produced atactic polymer and this was not surprising, given the fact that this is a achiral monitor molecule. Now the next important discovery was made by Brintzinger as well as Ewen, who produced isotactic polymer using like chiral resolution one at low temperature and other using achiral derivative.

So now that was the first development towards using homogeneous catalysis to produce isotactic polymer as was obtained is using heterogeneous Ziegler-Natta system.

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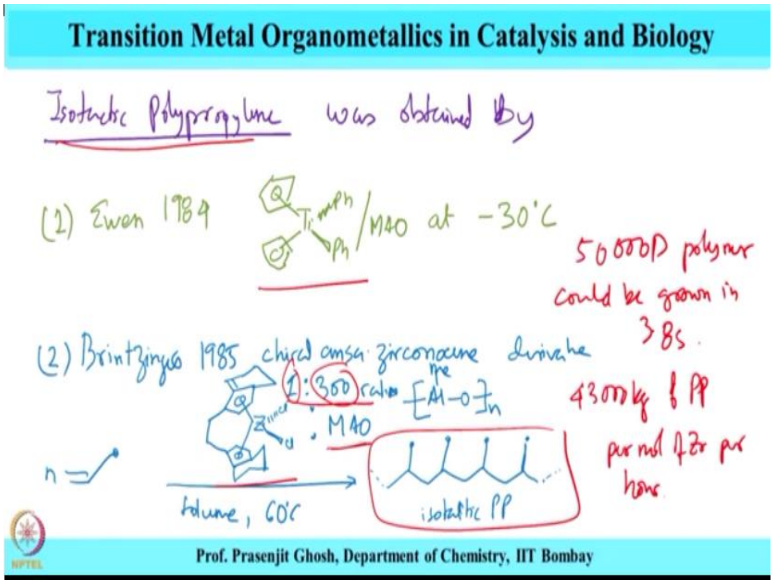

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Isotactic Polypropylene was obtained by

(1) Ewen 1984 /MAO at −30°C

50000D polymer could be grown in 38s.

(2) Brintzinger 1985 chiral ansa zirconocene derivative

1:300 ratio $[\overset{Me}{Al}-O]_n$

MAO

toluene, 60°C

isotactic PP

4300kg of PP per mol of Zr per hour

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So isotactic polypropylene was obtained by first Ewen in 1984 in presence of diphenyl titanium catalyst at minus 30 degree centigrade. So the low temperature was given, so that more ordered formation could be formed and the second by Brintzinger in 1985 using chiral ansa zirconocene derivative. So this is given as polypropylene in toluene 60 degree centigrade and the catalyst is this is ansa catalyst zirconium chloride.

And this gave isotactic polypropylene with the catalyst is to MAO 1 is to 300 ratio and MAO is given as methyl and so with this we come to conclusion of today's talk, where we saw that the development of chiral homogeneous metallocene catalysts that could give isotactic polypropylene under homogeneous condition in presence of this chiral catalyst and MAO in large excess of MAO, about 1 is to 300 ratio and could be used to make this isotactic polypropylene.

Isotactic polypropylene also could be obtained using this catalyst under very low temperature as reported by Ewan. So with this, we come to the end of today's discussion on the development of catalyst for producing polypropylene. What we had seen that which started off from a simple basic question as to why the heterogeneous Ziegler-Natta titanium tetrachloride diethyl aluminum chloride was producing atactic, isotactic polyethylene.

That led to the understanding of which led to the understanding that it is a multi site catalyst and that a result of the polymer obtained were broad and less well behaved, which led to the focus on a single site catalyst and the first single site catalyst were Italian, though of low activity was reported by Giulio Natta in 1957 using titanium dichloride and diethyl aluminum chloride, which could polymerized ethylene, but could not polymerize any alpha olefin.

Subsequent contribution by Kaminski which who came up with this aluminum oxane reagent, but this is a non uniform structure obtained by partial hydrolysis of diethyl aluminum led to high activity reported for ethylene polymerization using BCP zirconium dimethyl, which could even surpass the results obtained from homogeneous-heterogeneous Ziegler-Natta conditions and they could also polymerize alpha olefin.

Now subsequent to that, further development as reported by Ewen for propylene polymerization at minus 30 degree centigrade or the famous Brintzinger 1985 chiral as a zirconocene catalyst, which in conjunction with MAO in 1 is to 300 ratio could give isotactic polypropylene similar to that with obtained with Ziegler-Natta system. So these catalyst is extremely active and could produce about 43,000 kilogram of polypropylene per mole of zirconocene per hour.

And as a result about 50,000 Dalton polymer could be grown in 3.8 seconds. So this is a tremendously active catalyst, which was producing so huge amount of polypropylene under such conditions. So with these, we come to an end on today's discussion, where we have seen how the evolution of single site catalyst from multi-site catalysis took place during polypropylene polymerization.

How the focus shifted and how eventually the homogeneous catalyst could make a more well behaved narrow distributed polymer with much more activity higher than that of the heterogeneous conditions using suitable modifications on the metallocene system. So more on the catalyst development, this will highlight some of the interesting struggles that have been taken up by organometallics chemist in coming up with ideas that could lead to further enhancement of this polypropylene catalysis attributes, which will be discussed in the subsequent class.

So more of this interesting stuff ahead, as we go on discussing about the catalyst development in polypropylene polymerization chemistry. So with this, I once again thank you for being with me in this lecture and I look forward to have some more interesting discussion on propylene polymerization, when we meet next. Till then, good bye and thank you.