# Metallocene and Metal-carbene based Organometallic Compounds as Industrially Important Advanced Polyolefin Catalysts

### Professor. Sanjib K. Patra
### Department of Chemistry
### Indian Institute of Technology, Kharagpur

## Lecture 20

## Olefin polymerization by Zeigler Natta Catalyst: Important features

Welcome once again to our course. So, in the last class, we have discussed that how the stereoregularity is possible using the two oil established pathway, that is the catalyst site control or chain in control. So, we have discussed that for using the, by using the chiral catalyst, we can get the selectively one isomers or even though we are not using the chiral catalyst, even though the stereoregularity is possible where your last inserted monomer dictates the stereoregularity for the second insertion of the monomer.

So, with this concept, what we learned in the last class, we will try to discuss the olefin polymerization of by Ziegler Natta catalysts and what are the important features, what the factors influencing its stereoregularity. In the last class, if you remember, we have discussed the very simple mechanism of bond forming, bond making by the using of Ziegler Natta catalyst and now today, we will try to understand its, how it tunes a stereoregularity, what are the sites, what are the mechanism. So, it will be, should be really interesting.

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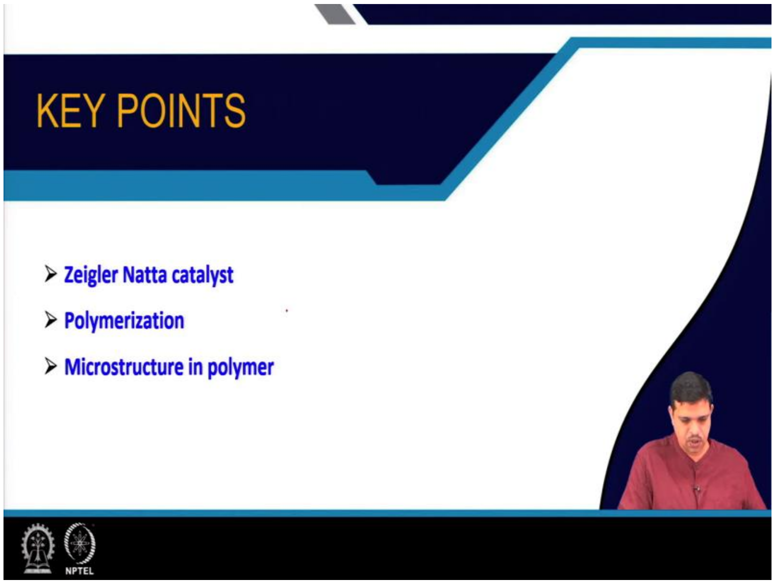
CONCEPTS COVERED

- Mechanism of Zeigler Natta polymerization ✓
- Origin of stereoselectivity ✓



KEY POINTS

- Zeigler Natta catalyst
- Polymerization
- Microstructure in polymer

So, as I told we will try to understand the mechanism of Ziegler Natta polymerization and origin of the stereoregulatory.

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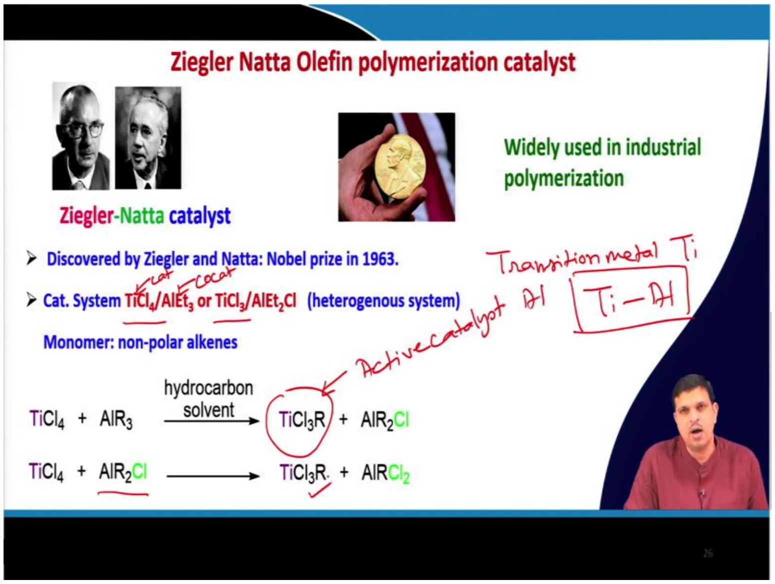

Ziegler Natta Olefin polymerization catalyst

Ziegler-Natta catalyst

Widely used in industrial polymerization

- Discovered by Ziegler and Natta: Nobel prize in 1963.
- Cat. System $TiCl_4/AlEt_3$ or $TiCl_3/AlEt_2Cl$ (heterogenous system)

Monomer: non-polar alkenes

$$TiCl_4 + AlR_3 \xrightarrow[\text{solvent}]{\text{hydrocarbon}} TiCl_3R + AlR_2Cl$$

$$TiCl_4 + AlR_2Cl \longrightarrow TiCl_3R + AlRCl_2$$

So, what is Ziegler-Natta catalyst? All we know, it is a widely used catalyst in industrial polymerizations, very popular and you know that Nobel Prize has awarded for this remarkable discovery. The system, catalytic system is TiCl4, and the transition metal is titanium. And you need another metal that is the aluminum. So, it is basically a titanium-aluminum system, the heterobimetallic system.

So, this one is the catalyst and this one is the co-catalyst. So, the catalyst and co-catalysts are both needed to initiate the polymerization. And the most of the general Ziegler Natta catalysts are either TiCl4 AlEt3, tri-ethyl aluminum or the TiCl3 di-ethyl aluminum chloride. It is a heterogeneous system, and the polymerizations are performed in hydrocarbon solvent. And the polymerization here, the preferred monomers are the non polar alkenes.

So, here, what is done, the catalyst and co-catalysts are reacted in the same condition, same solvent and then monomer is passed. So, it is in situ reactions. First, the co-catalyst formation and then the polymerization. So, these are the basic steps. You will see here, the titanium chloride and Al3, that forms the TiCl3R. We will discuss how it is formed and why it is important. So, this R is basically the active catalyst. Similarly, if you can use di-alkyl aluminum chloride, you will get the TiCl3R. So, these are the active catalyst.

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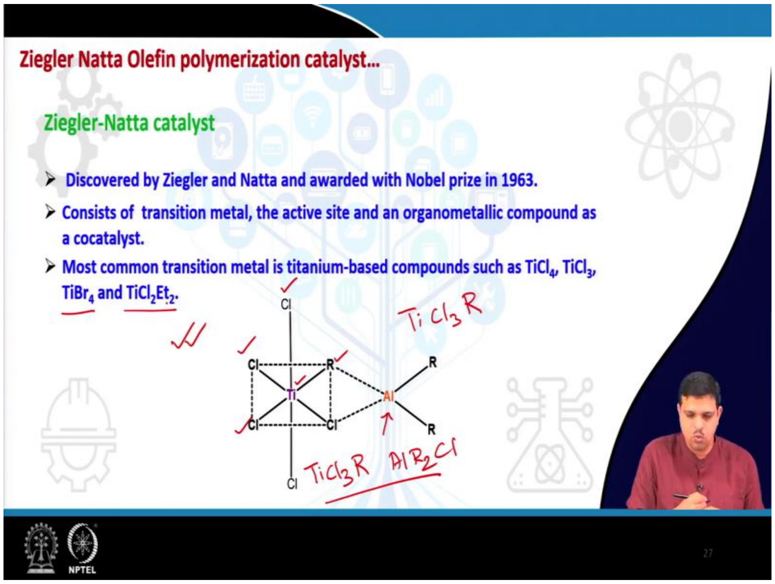

**Ziegler Natta Olefin polymerization catalyst...**

**Ziegler-Natta catalyst**

- Discovered by Ziegler and Natta and awarded with Nobel prize in 1963.
- Consists of transition metal, the active site and an organometallic compound as a cocatalyst.
- Most common transition metal is titanium-based compounds such as $TiCl_4$, $TiCl_3$, $TiBr_4$ and $TiCl_2Et_2$.

Now let us try to understand little more depth. So, this one you will see that you have TiCl3, as you see in the last, TiCl3R. So, you have titanium, you have R group here, and this one, 3-chloride, 3- chloride, and this is the co-catalyst. Here, you have AlR2Cl. And this is TiCl3R. So, most of the active site, the catalyst co-catalyst sites are generally the, if you see the discrete structure, it is looks like that one.

So, in the later part we will discuss that this is what we are drawing on the paper, it is not simple. It is very complicated structure, it is a three dimensional structure and it is not a discrete molecules as you on the pen and paper. We will discuss and we will try to understand that how it is important and to realize to understand and how the stereoregularity is maintained using the Ziegler Natta catalyst. That is why this catalyst system is very popular.

So, not only the TiCl3, we can actually use the other halides also, like titanium bromide or the mixture of the other alkyl and halides like that. So, but only, mostly in industry, it is used, this system, that is the more popular system.

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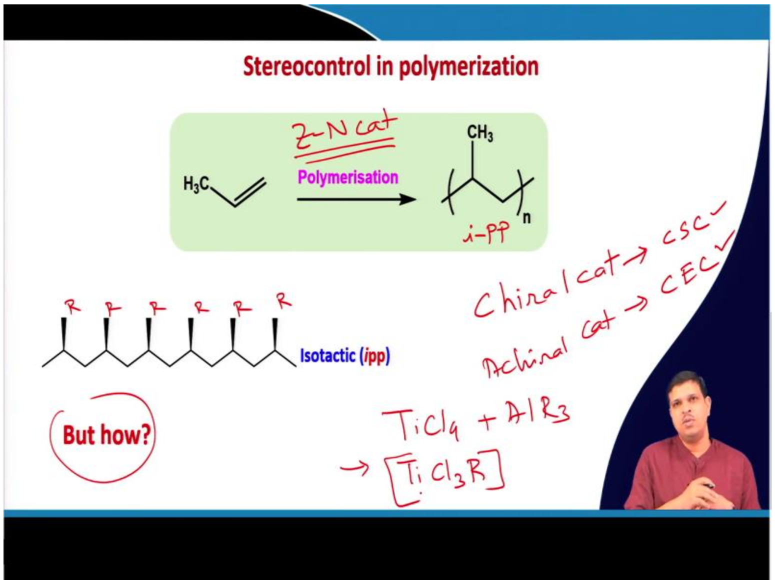

**Stereocontrol in polymerization**

Chiral cat → CSC ✓

Achiral cat → CEC ✓

$TiCl_4 + AlR_3$

$\rightarrow [TiCl_3R]$

So, as now you are all aware that this polymerization is the Ziegler Natta polymerization catalyst is famous for getting the stereoregular polymer. So, this is, you get the isotactic polypropylene. All we know that what is isotactic polypropylene. So, this, if all are same site, then it is isotactic. We discussed this one in earlier classes. Now, question is how? Now, very interesting. So, in the last classes we discussed that we have to use the chiral catalyst. So, to induce the stereoselective reaction. That is, goes through the catalyst site control mechanism. And here another way is the achiral catalyst, that is the chain in control mechanism.

Now, what do you suggest? Whether this polymerization is using the, this is catalyst site control or the chain in control, that is a very interesting question. And how we will answer whether it is a CSC or whether CIC. Let us see what is actually real pathway. That is the very interesting and quite complicated also, that how this Ziegler Natta catalyst plays the role for the stereoregularity, maintaining the stereoregularity in polypropylene either through the CSC or the CIC.

As you see that we are using the TiCl4 and AlR3. And what we are getting? We are getting TiCl3R. That is the simplified discrete catalytic, you can say active, to designate the active catalytic site. Now from here, it looks like it is achiral catalyst, but I will prove this is not achiral catalyst, this is chiral catalyst. It is very funny, no?

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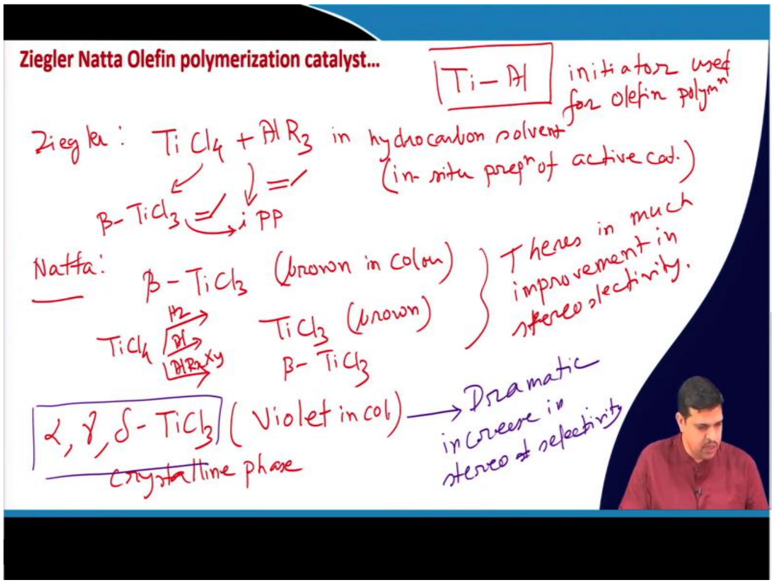

Ziegler Natta Olefin polymerization catalyst...

Let us see how it is possible. Before that, we should try to understand how these Zeigler Natta catalyst have been developed because answer is hidden there. Either it is chain control or the site control. So, let us try to understand. So, as I told this is a bimetallic system, titanium-aluminum system.

Now, this is the titanium-aluminum based initiator used for olefin polymerization, especially for to make the stereoregular IPP polymers. So, Ziegler, what he did, he made the, he charged the TiCl4 with AlR3 in hydrocarbon solvent. Try to understand what I want one to tell, because the answer is hidden, hydrocarbon solvent. So, and then, he did the polymerization. And he got the IPP polymerization.

And, so what he did is he prepared the in-situ preparation of active catalyst. It is not that first the active catalyst formed, isolated and then it is used for the catalyst, not like that. Later, Natta realized that what is formed first, actually it is first formed the TiCl3. I am not considering the alkyl part. And this TiCl3 can exist in different crystallography forms, different crystalline form, alpha, beta, this is called the crystal phase, alpha, beta, gamma, delta.

So, this is TiCl3 and then it is doing the polymerization. And the color of this one is actually the brown in color. So, after that, Natta was trying to make a different, trying to establish the different routes by reducing the TiCl4 like aluminum or hydrogenation or using other aluminum derivatives to make the TiCl3. And he saw that most of the cases, he is getting the same brown color. That means is all actually the beta TiCl3 and there is no much improvement in stereoregularity or stereoselectivity.

But later, it was realized that if you take other form alpha, gamma or delta TiCl3 which are violet in color, all the three forms are violet in color, so these are the other crystalline phase. So, these are violet in color. And a surprising result was observed. What was observed? A dramatic increase in stereoselectivity. So, what we learned from here? We learned that the crystalline phase is important for the, for this case, where the stereoselectivity is concerned.

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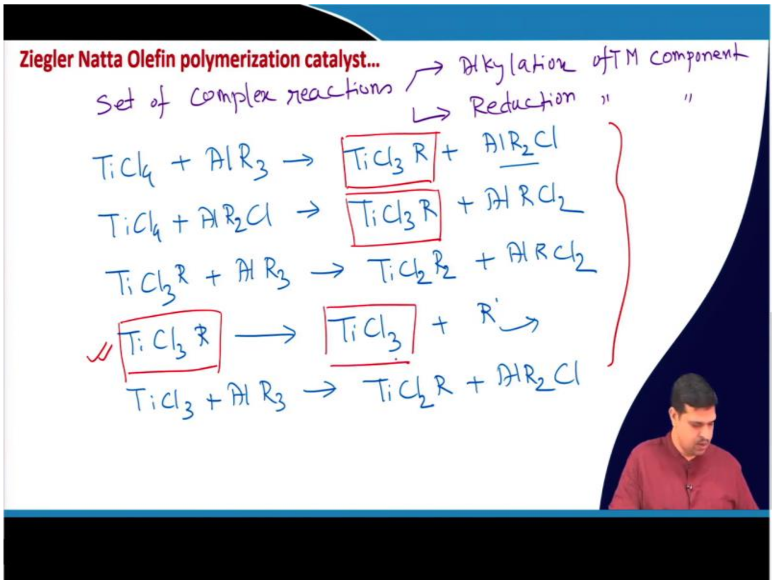

**Ziegler Natta Olefin polymerization catalyst...**

Set of complex reactions → Alkylation of TM component
→ Reduction " "

$$TiCl_4 + AlR_3 \rightarrow \boxed{TiCl_3R} + \underline{AlR_2Cl}$$

$$TiCl_4 + AlR_2Cl \rightarrow \boxed{TiCl_3R} + AlRCl_2$$

$$TiCl_3R + AlR_3 \rightarrow TiCl_2R_2 + AlRCl_2$$

$$✓✓ \boxed{TiCl_3R} \longrightarrow \boxed{TiCl_3} + R^{\cdot}$$

$$TiCl_3 + AlR_3 \rightarrow TiCl_2R + AlR_2Cl$$

Not only that, there is other very complex reactions are operated, we have to consider. As example, I, what I will list now, set of complex reactions, so what you see, as I told that we write TiCl4 AlR, AlET3 or AlR3, this is right in a very simple way, but the catalytic system is very complex. So, set of complex reactions, I will list out. This is basically based on the alkylation and the reduction of transition metal component. That is, the titanium.

So, let us see what are the possible reactions when you are charging the TiCl4 with tri-alkyl aluminum. So, TiCl3 are plus AlR2Cl. So, it is basically exchanging one chloride with the R of the aluminum. Now, again it react, it can react with this one, AlR2Cl, and form the TiCl3R plus AlRCl2. Now, this TiCl3, that is the R can react with AlR3 and form the TiCl2R2 plus AlRCl2. These are all possible reactions, and it actually happens. Then TiCl3R is reducing and forming the R dot. And TiCl3 plus again AlR3 is forming the TiCl2R plus AlR2Cl. This R can undergo the recombination with R dot and forms the corresponding alkyl.

So, no need to be worried about so much reactions. Actually, we do not need all this information to understand the reaction mechanism. But what I want to give the information, that in the reaction mixture there are possibilities, there are lot of complex reactions possibilities are there and here you will see that we will be more interested for this kind of species, like this one. Why? We will understand from the next slides where we will be discussing the mechanism.

So, there are, so you will see that the catalytic system is really complex in nature and we will see, although no need to be worried for all this set of reactions, what I am trying to tell that this species, TiCl3R, try to concentrate on this one. Let us see how, what happens.

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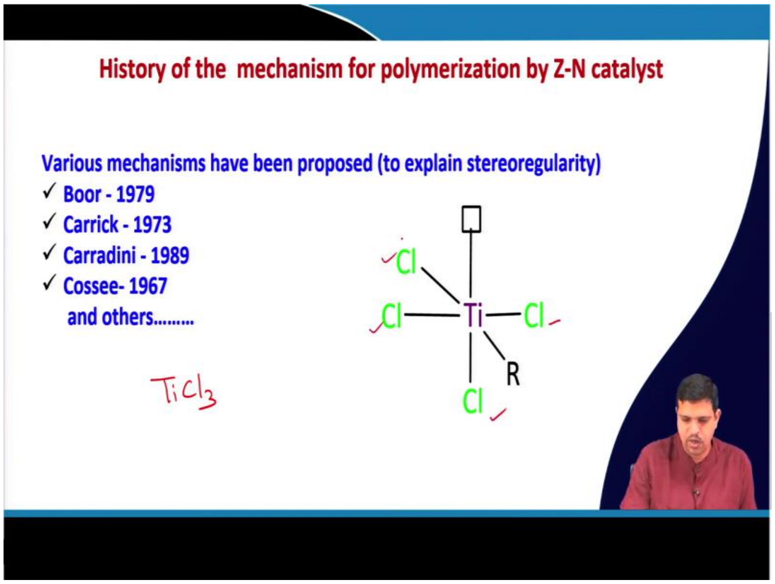

History of the mechanism for polymerization by Z-N catalyst

Various mechanisms have been proposed (to explain stereoregularity)

- ✓ Boor - 1979
- ✓ Carrick - 1973
- ✓ Carradini - 1989
- ✓ Cossee- 1967
- and others.........

$TiCl_3$

So, here, although as I told, that this, we write as TiCl3 but it is actually not simple as that that. So, it is a discrete polymeric kind of form where your, these chlorides are shared by another titanium.

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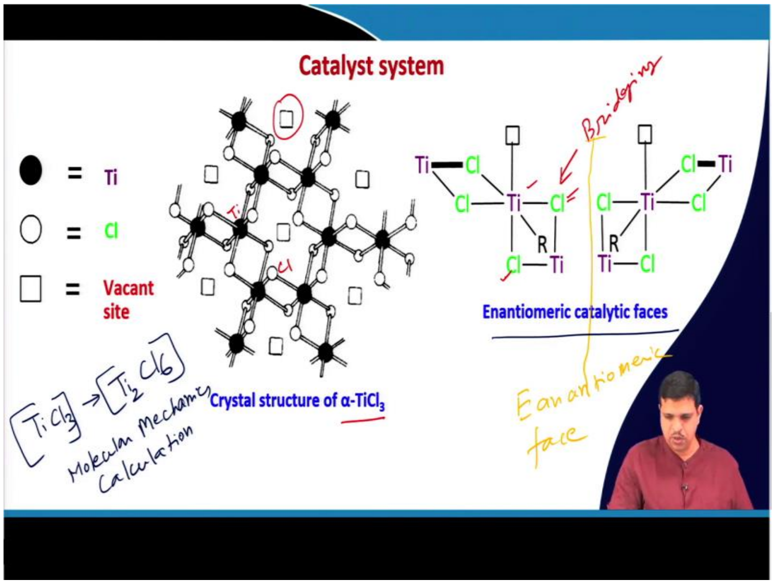
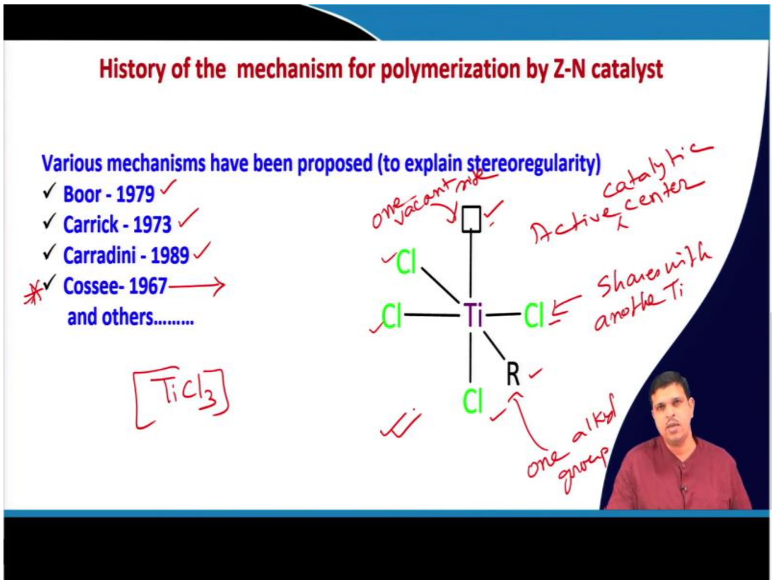


## Catalyst system

● = Ti
○ = Cl
☐ = Vacant site

Crystal structure of α-$TiCl_3$

Enantiomeric catalytic faces



## History of the mechanism for polymerization by Z-N catalyst

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- ✓ Boor - 1979 ✓
- ✓ Carrick - 1973 ✓
- ✓ Carradini - 1989 ✓
- ✓ Cossee- 1967 ⟶
- and others………

So, in, like this one. Here, you see this titanium and this chloride and this chloride is again shared by the another titanium, like that. So, different active, so this is actually the active center or rather you can say active catalytic center where you will see there is a one vacant site the all the chlorides are basically shared with another titanium and one vacant site and one alkyl group.

So, this is important to understand. So, on the titanium, if you just think as a discrete single molecule, so four chlorides which are again shared by another titanium through clobridge, chloride bridging and one site is occupied by alkyne and one is the vacant site. And this is act, this active site is proposed by Cossee.

And as I told, this is a very complex system. So, different mechanism have been proposed, different active centers have been proposed time to time to understand its stereoregularity, polymerization like Boor 1979, Carrick 1973, Carradini 1989, Cossee 1967 and so on. At least 10 mechanism have been proposed. But this is the most well accepted, easy to understand, and this polymerization is well understood by this mechanism proposed by Cossee-Arlman.

So, let us see what is that again. So, now it is clear that how this Zeigler Natta catalyst looks like, if you consider as a single molecule. So, here the picture will be more true here. Here as I told, that this chloride are shared again through the titanium bridge bond, bridging. And if you see these molecules, this, actually the crystal structure of alpha TiCl3 and how does it look like, you see that I will come, this is the this is the alpha, gamma or delta as I told, beta are possible, this is the alpha TiCl3.

Here you will see this is the titanium. And this is the chloride. And most importantly, these are the vacant sites, if you see in the crystal structure. And you see here, one very interesting, so this one, if you, this plane, you see this is a relationship of enantiomeric. So, here you will see, so this is the called enantiomeric phase. So, why it is important, it is important to understand that there is a chiral center exists, and that chiral center actually depends on the what phase you are using, the percentage of the chiral center whether it is alpha, gamma, beta and delta.

You see this moiety carefully, this is basically enantiomeric catalytic phases. Now, it is understandable that why these catalysts actually act as a chiral catalyst. So, here, so that is why, so it is always better to consider as TiCl3 as Ti2Cl6 which will give a better picture of the Zeigler Natta catalyst. And also, this has been supported by molecular mechanics calculation. So, now I am sure that you are, now you understand that what are the possibilities in the simple TiCl4 for AlTT system by pen paper, but actually, it is not that simple, it is very complex structure.

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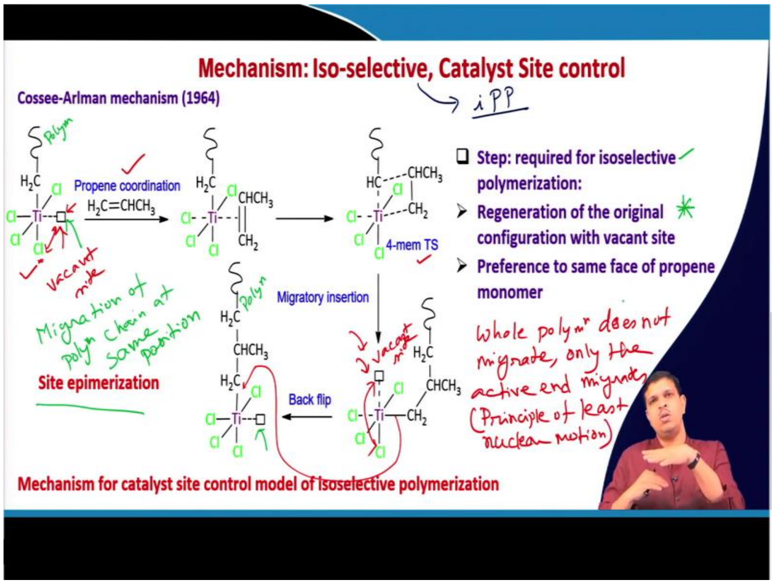

Mechanism: Iso-selective, Catalyst Site control

→ iPP

Cossee-Arlman mechanism (1964)

- ☐ Step: required for isoselective ✓ polymerization:
  - ➢ Regeneration of the original configuration with vacant site ✳
  - ➢ Preference to same face of propene monomer

Whole polymr does not migrate, only the active end migrates (Principle of least nuclear motion)

Migration of polyn chain at same position

Site epimerization

Mechanism for catalyst site control model of isoselective polymerization

Now, with this concept, let us discuss now what is the real mechanism is operated here. Why it is iso-selective, why we get the iso-selective, or isotactic polypropylene. So, see this slide, this one is very important. So, please see it very carefully and try to understand. So, this is the active center of the Ziegler Natta catalyst as we discussed in the last class, last slide, here you will see. So, this is the this one.

Considering a single discrete molecules. So, what is happening now, you will see that the propene coordination, simple. So, this is the vacant site, propene coordination is happening. And as we discussed in the last class, the bond breaking, bond forming steps. So, after coordination, there is a four-member transition state. And then what happens, you will see there is a migration, migratory insertion reactions. So, here you see that there the polymer chain is now migrated here. So, now what is happening, this is my vacant site. See very careful.

So, my vacant site was here, but now the vacant site is here. So, you see the position of the vacant site is now changed. So, it was initially, if you see that if you check this chloride, so it was, vacant site was cis to this one, now the vacant site is trans to this one. Now, if the vacant site is positionally changed, now if the alkene coordination happens here then definitely there will be no iso-selectivity because iso-selectivity will happen where? Where the addition of the next monomer will also happen on the same vacant site. Then only it is possible of iso-selectivity. If not, then it will be syndioselective.

So, here what is happening, you will see that in this step, this polymer chain is migrated and here basically, not the whole polymer chain does not, be careful here. The whole polymer chain does not migrate but only the active end migrates according to the principle of least nuclear motion. That is, the more, less energy energetic pathway. Now, you will see that now vacant site is in a different position now.

So, what it is proposed that there is a back flip. That means this chain now is again when there. Now, you will see that the vacant site was here initially. Now, the vacant site is again at the same site. So, this is called the site epimerization. So, migratory or polymer chain at the same position. So, why it is happening, back flipping, the migration of polymer chain at same position.

So, here you see that here my polymer chain and now here is my polymer chain, but the length has been increased by two carbons, after insertion obviously, but my vacant site is now at the same position as it was in the previous step. So, this is the mechanism for the iso-selective polymerization.

So, this is the mechanism for catalyst site control of iso-selective polymerization and which are the well accepted by, to explain the iso selective polymerizations which actually operated by the catalyst of Ziegler Natta, where you see that it is does not look like a chiral catalyst but actually it acts as a chiral catalyst.

So, what are the basic steps for iso-selective polymerization? Regeneration of the original configuration with vacant site. This is very important. Otherwise, if it is not, then we will get the syndioselective. And preference of the same phase of propene monomer. When we are putting the vacant site a particular position, let us say this is my catalyst here is the vacant site. So, if we create the vacant site after one addition of my monomer, then after insertion, the vacant site should be same so that the monomer can approach through here not like through here or here. Then it will be not stereoselective.

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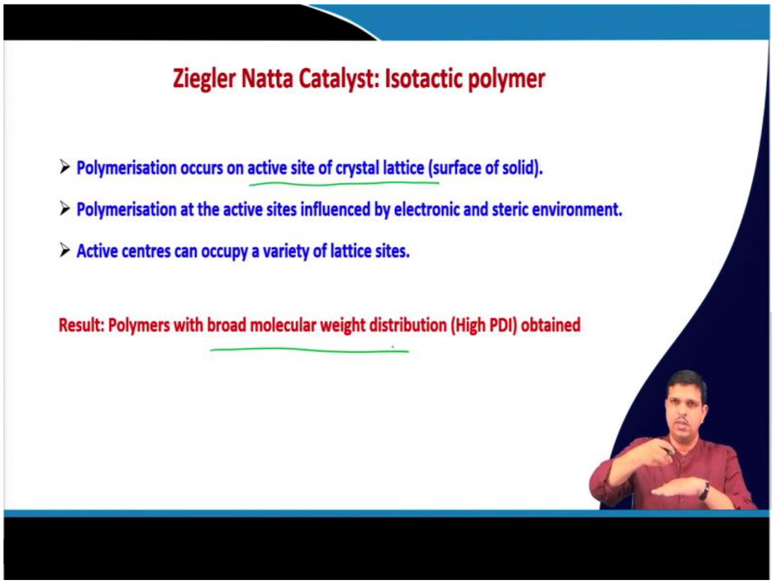

## Ziegler Natta Catalyst: Isotactic polymer

- Polymerisation occurs on active site of crystal lattice (surface of solid).
- Polymerisation at the active sites influenced by electronic and steric environment.
- Active centres can occupy a variety of lattice sites.

Result: Polymers with broad molecular weight distribution (High PDI) obtained

So, but as you see, the polymer, the catalyst, is it very difficult to understand how these chirality, chiral environment is formed. And because this is a heterogeneous system, the this enantiomeric phase, this is a heterogeneous system. So, this, all the polymerization actually happens on the surface of the catalyst, not, it is, not, it is not a homogeneous system. So, polymerization occurs on the active site of the crystal lattice, that is, on the surface of the solid.

And this active site influenced by electronic and steric environment. And that is why we get the different rate of polymerizations depending on the, where the vacant site is. And as it is a heterogeneous system, the active centers can occupy a variety of lattice sites. And as a result of these three points, most of the polymers achieved from Ziegler Natta catalyst is actually the broad molecular weight distribution.

Although these are iso-selective, but we get the broad molecular distribution because due to its heterogeneous system, because this attack of the monomer actually depends on the active centers, how the vacant space is available on the surface.

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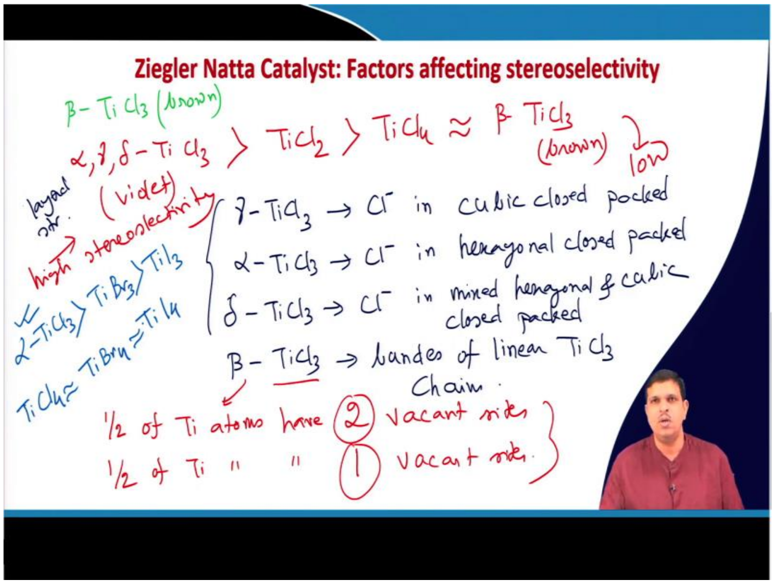

## Ziegler Natta Catalyst: Factors affecting stereoselectivity

$\beta$-TiCl$_3$ (brown)

$\alpha, \gamma, \delta$-TiCl$_3$ > TiCl$_2$ > TiCl$_4$ ≈ $\beta$-TiCl$_3$ (brown) low

layered str.

(violet)

high stereoselectivity

$\alpha$-TiCl$_3$ > TiBr$_3$ > TiI$_3$

TiCl$_4$ ≈ TiBr$_4$ ≈ TiI$_4$

$\gamma$-TiCl$_3$ → Cl$^-$ in cubic closed packed

$\alpha$-TiCl$_3$ → Cl$^-$ in hexagonal closed packed

$\delta$-TiCl$_3$ → Cl$^-$ in mixed hexagonal & cubic closed packed

$\beta$-TiCl$_3$ → bundes of linear TiCl$_3$ Chain.

1/2 of Ti atoms have ② vacant sites

1/2 of Ti " " ① vacant sites.

So, to understand in more detail about the stereoselectivity, some of the factors we have to understand, otherwise the discussion will not be complete. So, we are, we know that beta TiCl3 which is the brown in color has quite less stereoselectivity. And compared to the alpha, gamma or delta TiCl3 has much more stereoselectivity compared to the beta TiCl3. So, this is, as I told, this is violet in color and this is brown in color. And this is the high stereoselectivity and this is the low stereoselectivity.

And I will try to emphasize that what are the factors for observing this kind of difference. So, I will not go in detail on solid state. If you are interested in the solid state properties of the TiCl3, you can further study the related topic, but what I will try to explain, I will try in a very qualitative way that what are the factors for governing the different crystallinity and how this dictates the stereoselectivity.

So, let us try to list out. Gamma TiCl3, here the chlorides in cubic-close packed. These are actually the layered structure. And the alpha TiCl3, the chlorides in hexagonal-closed packed. And delta TiCl3 Cl minus in mixed hexagonal and cubic-close packed. And in the beta TiCl3, that is quite different, the, here is actually the, if you see the solid state structure, it is a bundles of linear TiCl3 chains.

So, in this case, what happens, in this case, half of the titanium atoms have two vacant sites. And here, half of the titanium atoms have one vacant site. Now, you try to understand from this structure here. So, in this case, this is a structure of alpha TiCl3. Here, you will see one vacant site is a layered structure, but in the beta TiCl3, that is a linear TiCl3 structure. And here two vacant sites are possible for the half titanium and for the half titanium, it is one vacant site.

Now you can imagine if there is a two vacant sites, then obviously there will be no stereoselectivity and that is the reason that stereoselectivity is quite less for the beta TiCl3. Now I think your, it is clear, understandable. So, this is the very important factors for choosing the system in doing the polymerization in Ziegler Natta.

Not only that, we should also know that like if you use the alpha TiCl3 and if you use TiBr3 or TiI3, the stereoselectivity will be more for the chloride, rather than iodide. And also similar for TiI4, it is almost similar for the all the cases. So, we should, this information are very much needed, otherwise we will choose the wrong catalytic system if I want to target for a particular polymers.

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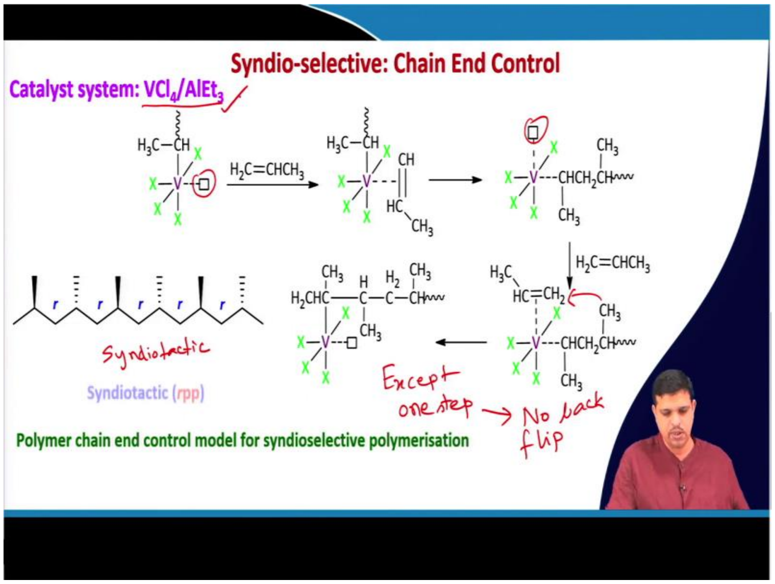

Syndio-selective: Chain End Control

Catalyst system: $VCl_4/AlEt_3$

Syndiotactic

Except one step → No back flip

Syndiotactic (rpp)

Polymer chain end control model for syndioselective polymerisation

Now, very interestingly, very interestingly if you use the VCl for AlEt3, because these are, you see titanium, vanadium. So, if we use the titanium, we may think that if we just replace by VCl4, probably we will get the same polymer but it is actually not. So, you will get the syndiotactic polymer if you use the VCl4/AlEt3 system. This is also Ziegler Natta, falls under the Ziegler Natta catalyst category.

So, here you will see that all the mechanisms are similar, except one step. Here, here no flip. So, in the, here you will see for Zeigler Natta, there is a back flip, that is the back flip. And here that the flipping, so that no back flipping occurs. And as a result, what you are getting, there is the vacant site. Now, the vacant site is here. So, alkene is coordinating here. Now, that is why this vacant site is now not getting back at the original polish position and that is why we are getting the syndiotactic polymerization.

So, for VCl4/AlEt3, if suppose you want to get the specifically, the syndiotactic polymers, then you will have to choose the VCl4/AlEt3 system. And if you want to take the, if you want to make the isotactic polypropylene, you have to use the titanium aluminum system.

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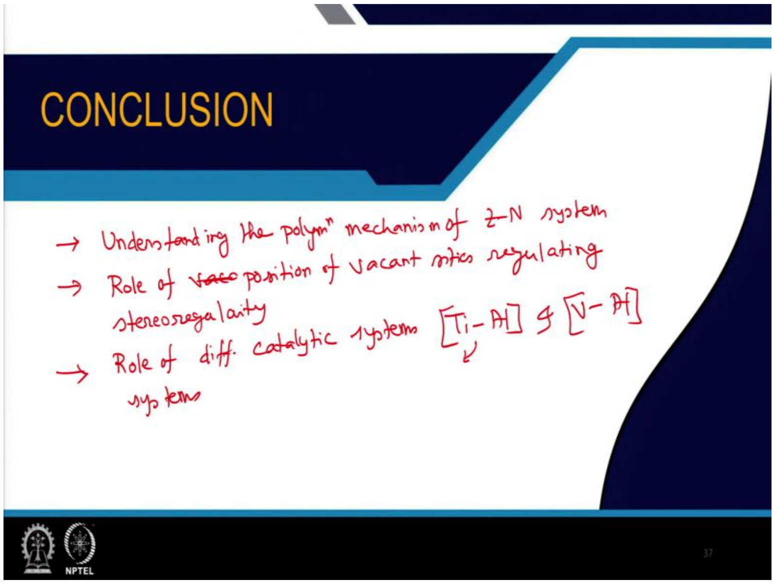

CONCLUSION

→ Understanding the polym$^n$ mechanism of Z-N system

→ Role of ~~vacc~~ position of vacant sites regulating stereoregularity

→ Role of diff. catalytic systems [Ti-Al] & [V-Al] systems

So, in the conclusion, what we have discussed, the, to understand the polymerization mechanism of Ziegler Natta system, the role of vacant site, position of the vacant site, regulating stereoregularity, the role of different catalytic systems of Ziegler Natta category, as example titanium-aluminum and the vanadium-aluminum system.

So, here you see that for titanium-aluminum, also very important to understand how the stereoregularity is maintained by using the different titanium analogues because now we are well understood that the polymerization, the stereoselectivity is maintained by the titanium analog, and more specifically, it is due to the different crystalling phase of the titanium analogues.

So, it is now very clear that how the, with one example of the metal catalyst that is the Ziegler Natta and their analogues, that how the polymerization is quite different than the free radical anionic polymerization. It is more interesting and more advantageous to have, to control the microstructure and stereoregularity in polymer.

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## REFERENCES

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So, with this knowledge, we will discuss in the last class with the metallocene catalysts where you will see that the stereoregularity again can be maintained but where the mechanism is quite similar and more easily understandable where the Ziegler Natta catalyst, the mechanism is really very complex and sometimes it is not very understandable because it depends on the, from the knowledge of the solid state chemistry.

And these are, also as it is a heterogeneous system, all the polymerization on the surface of the catalyst, so the mechanism is very complex. This is the most advantage of the Ziegler Natta catalyst. So, in the next class, we will try to enjoy a different category of the catalysts for the polyolefin polymerization. See you in the next class. Thank you.