# 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 21

## Coordination polymerization of olefin by Metallocene Catalysts: A new avenue in polyolefin catalysts

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

Dr. SANJIB KUMAR PATRA
DEPARTMENT OF CHEMISTRY, IIT KHARAGPUR

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Lecture 21: Coordination polymerization of olefin by Metallocene Catalysts: A new avenue in polyolefin catalysts

Welcome to this course, Metallocene and Metal-carbene based Organometallic compounds for polyolefin catalysts. So far, what we have discussed we discussed the Ziegler Natta catalysts, that is the one of the very successful transition metal based catalytic system. Although it is a heterogeneous catalyst, but it was very popular, very successful and the activity is quite good.

Today, we will discuss another category of metal based catalysts for olefin polymerization, that is the metallocene catalysts. And after discovery of the metallocene catalyst, it is basically realized that this is a new revolution in catalyst science, particularly for the olefin polymerizations. And many industries have been accepted this system. Obviously, there is a lot of reasons that we will discuss.

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CONCEPTS COVERED

- Metallocene as catalysts for olefin polymerization
- Role of initiator and co-initiator
- Mechanism

And before that we will try to understand that what is the polymer metallocene catalyst system for the olefin polymerizations, what are the components and what is the initiator system or what are the co-initiator system and why this is needed, what is the role, and obviously the mechanism, and then we will discuss very systematic way, what are the advantage, which were not present in the Ziegler Natta based, another very successful catalyst, transition metal based catalysts.

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## KEY POINTS

- Metallocene catalyst/initiator
- Co-catalysts/Co-initiator
- Mechanism of olefin polymerization

So, the key points will we will cover here, the metallocene catalyst as initiator or catalyst, co-catalyst, the concept of the activation of the initiator the mechanism of olefin polymerization. Okay, let us start.

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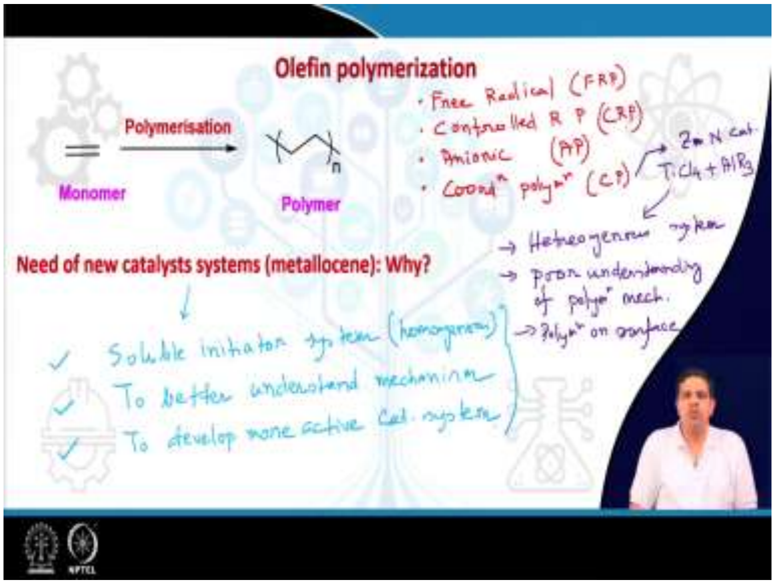

## Olefin polymerization

- Free Radical (FRP)
- Controlled R P (CRP)
- Anionic (AP)
- Coord$^n$ polym$^n$ (CP) → Z-N cat. TiCl$_4$ + AlR$_3$

→ Hetrogeneous system
→ poor understanding of polym$^n$ mech.
→ Polym$^n$ on surface

Need of new catalysts systems (metallocene): Why?

↓

✓ Soluble initiator system (homogeneous)
✓ To better understand mechanism
✓ To develop more active Cat. system

So, now we are familiar about this kind of polymerizations where you show that that if you have a monomer like ethylene or any other alpha olefin, you can go do the free radical polymerization. So, that we have already discussed in previous classes, free radical polymerization, controlled radical polymerization. Radical polymerization, I am writing as FRP. This is CRP. Then anionic polymerization, that is, we call AP. The cationic polymerizations are there but not very common for the olefin polymerization.

And then the coordination polymerizations. That is the transition metal based catalyst system for the alpha olefin polymerizations. And in the last category, that is the fourth category we saw that Ziegler Natta catalyst is very successful, and there we saw that what are the system, if you remember, is $TiCl_4$ plus $AlR_3$. And we saw that this is heterogeneous system and very difficult to understand the mechanism. The poor understanding of polymerization mechanism.

And there, if you remember, that it is very difficult to understand. Although, we have realized that there should be a back flip of the whole polymer chain in from the growth site to the vacant site. That we have, to make the vacant site at the original position where it was there before the propagation. And that is the way that we have realized that you can make the isotactic polymers.

So, the polymerization mechanism is really very complex and unclear. And also the heterogeneous system makes it more difficult to understand the mechanism. And also we saw that depending on the phase, crystalline phase of the $TiCl_3$, like alpha, beta, gamma, delta the stereoregularity is very different. So, after the discovery of the Ziegler Natta catalyst, people started to make a different system or to develop a different system where you need to make the soluble initiator system.

Why it is required? Because for academic perspective, if it is homogeneous system, the soluble system, then it is easy to understand the mechanism by different spectroscopic methods, which is not possible or very difficult either in heterogeneous system. Although, if you think in a commercial perspective or industrial perspective, definitely the heterogeneous catalyst is the more advantageous.

So, homogeneous system and to better understand, so these are the initial driving force to develop a different transition metal based catalytic system or metal based catalytic system to better understand the mechanism and obviously to develop more active catalytic system. You remember that when we discuss the mechanism of Ziegler Natta catalyst, the polymerization happens on the surface.

So, in this case, because it is a heterogeneous system the polymerization happens on the surface. The polymerization on surface. Now, if we make homogeneous system and soluble initiator system, then definitely the activity of the catalyst will be more because now, if, now the molecules are, all the molecules are available, all the catalytic system are initiator available to initiate my monomer. So, these are the three main driving force to or curiosity to develop different metal system for olefin polymerizations.

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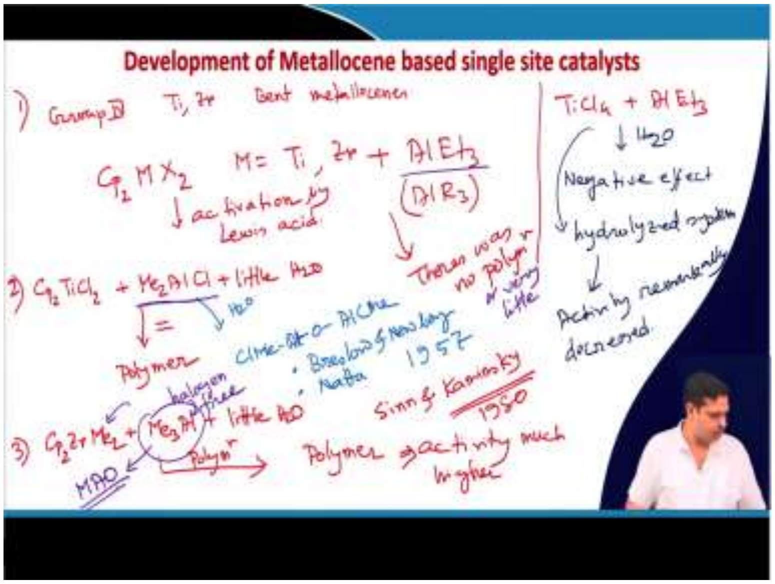


Development of Metallocene based single site catalysts

1) Group IV Ti, Zr Bent metallocenes

$Cp_2MX_2$ M = Ti, Zr + $AlEt_3$ ($AlR_3$)

↓ activation by Lewis acid

There was no polym or very little

2) $Cp_2TiCl_2$ + $Me_2AlCl$ + little $H_2O$ → Polymer

ClMe-Al-O-AlClMe

- Breslow & Newsburg 1957
- Natta

3) $Cp_2ZrMe_2$ + $Me_3Al$ (halogen free) + little $H_2O$ → Polymn → Polymer activity much higher

MAO

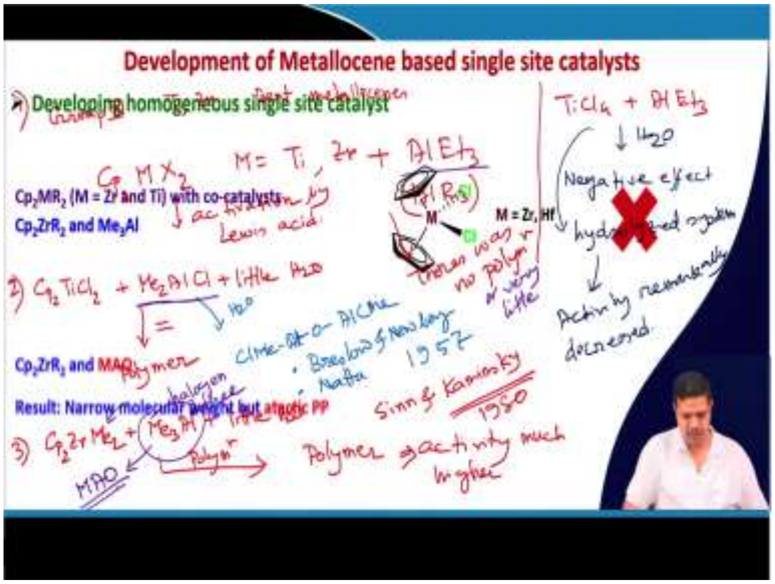
Sinn & Kaminsky 1980

$TiCl_4$ + $AlEt_3$ ↓ $H_2O$

Negative effect

hydrolyzed system

Activity remarkably decreased



Development of Metallocene based single site catalysts

Developing homogeneous single site catalyst

$Cp_2MR_2$ (M = Zr and Ti) with co-catalysts

$Cp_2ZrR_2$ and $Me_3Al$

M = Zr, Hf

$Cp_2ZrR_2$ and MAO

Result: Narrow molecular weight but atactic PP

So, before going to the main mechanism, I will just try to give a flavor how the, this transition, this metallocene based catalyst actually developed or discovered. So, after discovery of the Ziegler Natta catalyst, as discussed in the last slide, scientists jumped on to develop a different systems and the Group 4, and we discussed in very extensively, the Group 4 metals that is the titanium, zirconium and bent metallocene, we have no lone pair.

That is, there is no non-bonding orbitals and there is no lone pair. So, it is a good acceptor for different ligands as example like for ethylene, pi acceptor. So, that electronic criteria we have discussed very extensively in our previous classes. So, people started to develop new catalyst, and this the category was very successful where M is equal to titanium or zirconium. And these requires activation.

So, only this system does not work, you have to need, some, you have to do the activation of this catalyst and for that a Lewis acid system was used. And we will discuss later that what are the Lewis acid. I will just try to understand, try to discuss the strategy. So, that time as we saw that for Ziegler Natta catalyst, $TiCl_4$ and $AlEt_3$, their system what was the problem? If you have some moisture in this system, it is a negative effect.

That means the, it undergoes the hydrolysis and it actually gives the hydrolyzed product, hydrolyzed system and the activity is remarkably decreased. So, why I discussed? So, from it is here it is clear that if you have, if I have a moisture in the system then it is bad. So, same concept or same experience was also applied that if here, if I use any kind of moisture or in the system then there may be a problem.

So, here initially, what was done, Cp $2TiCl_2$ using Me 2, that was the first discovery of the metallocene catalyst or the attempt of discovered the metallocene catalyst that when this system was used in the presence of $Cp_2$ $MX_2$ plus $AlEt_3$ or you can in general, $AlR_3$, that there was no polymerization, there was no polymerization, please note it very carefully. So, what is the wrong with this one? People were confused.

Then it was the two scientists independently, Breslow and Natta reported that if you take this system and plus a little amount of water then if you do the polymerization like ethylene, then the polymer was detected. So, this was a really very confusing and at the same time, it was really funny. So, then it was realized that this water has a positive effect which is unlike in the Ziegler Natta system.

So, this one actually reacts with water and give like this kind of diameric system. That was actually Breslow, independently and Natta. Actually two scientists knew about it. This is around in 1957. Now, with this idea and this observation, Natta later observed that that if you purposively take some moisture, so his system was zirconium and dimethyl, and we will discuss this in more detail. I just want to show how it was developed, a very nice story is there.

And then if you use like, so it is a trimethyl aluminum, and then purposively little water, and you saw that if you do the polymerization, then that activity is much higher and is much higher, even is higher than the Ziegler Natta catalyst. So, from this, and this was discovered by Sinn and Kaminsky. Kaminsky was the, is the pioneer in this metallocene catalysts. And this was discovered in around 1980.

So, you see that the chemistry is not really very old. So, this was the, you can say the Renaissance in the polymerization, in the olefin polymerization chemistry. And this is after that the many industries started to follow, obviously there is a lot of reason that we will discuss. You see here in the Breslow and the new one, Natta, they took this aluminum compound. And Sinn and Kaminsky, they actually took this one that is the halogen-free, both cases. Here also halogen-free, here also halogen-free. That is more advantages than the others. So, this is a really very important observation by the different scientists.

So, here you see that if you take that only this one, there was no polymerizations or very little, you can say, negligible. But if you take that this kind of aluminum compound in with the your metallocene, titanocene, zirconecene catalyst and if you purposely add little water, then you saw that there is a drastic change in the activity. And Sinn and Kaminsky proposed that this one undergoes a partial hydrolysis and then gives a different oxo-breezed aluminum clusters which is popularly we call MAO.

We will discuss in very details about the MAO because it has a big role in catalytic activity. So, so you will see that the different, how the active different catalytic systems were developed and in a very systematic method and which was a kind of a revolution in polymer industry.

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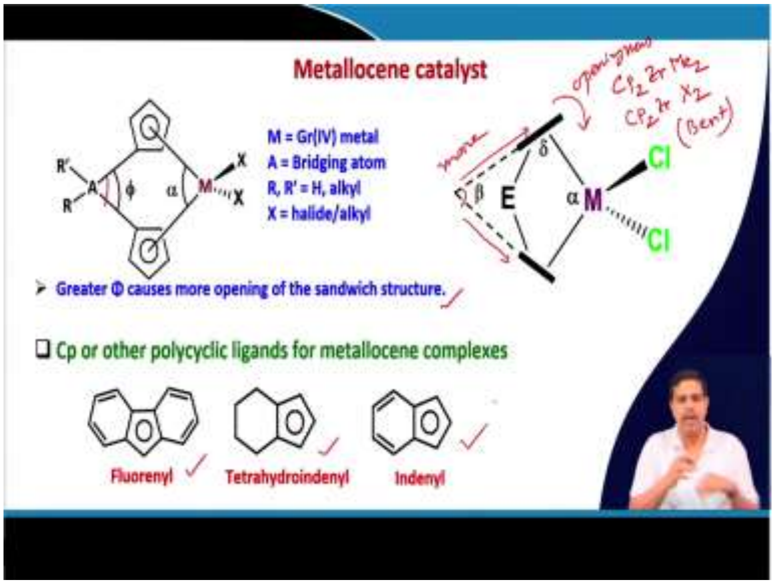

Metallocene catalyst

M = Gr(IV) metal
A = Bridging atom
R, R' = H, alkyl
X = halide/alkyl

- Greater Φ causes more opening of the sandwich structure. ✓

☐ Cp or other polycyclic ligands for metallocene complexes

Fluorenyl ✓ Tetrahydroindenyl ✓ Indenyl ✓

So, you, here if you recall, I have discussed in the previous class, so I am not going very detailed, if you just recall our last classes that there is some structural parameters. Here, this is our, if you can just think that this is my Me2 or this is the structure of Zr X2 and here you will see these are the bent metallocenes, we all discussed, and this one you will see that if you draw the plane, angle, the plane of the C p rings are meeting here and this is the beta.

Similarly, this also if you draw this one and this is the bridging atom. So, here you will see the more beta or more phi is means the more openingness of the sandwich structure. So, this, if this is more, then here is more openingness, means the steric factor is less here. That means substrate, that is here monomer can approach very easily.

So, different type of ligands we already discussed, not only the C p rings. Different fused polycycline ligands can be incorporated bridging or non-bridged and we will discuss later why we have to bridge, which is actually falls in the category of the mansion metallocene, that we will discuss.

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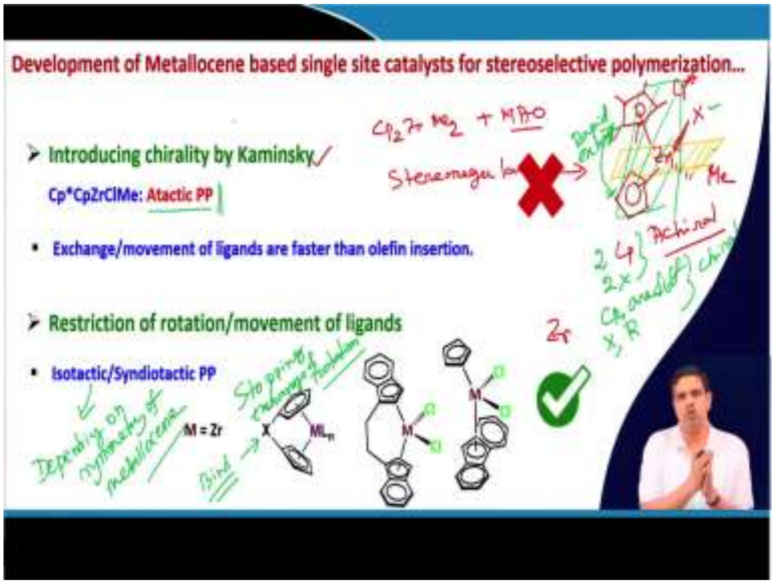

Development of Metallocene based single site catalysts for stereoselective polymerization...

- ➤ Introducing chirality by Kaminsky
  - Cp*CpZrClMe: Atactic PP
  - Exchange/movement of ligands are faster than olefin insertion.
- ➤ Restriction of rotation/movement of ligands
  - Isotactic/Syndiotactic PP

So, we now know that the Kaminsky develop the first active catalyst, metallocene based catalyst systems that is the C p2 ZrCl2 or C p2 ZrMe2. And in presence of the MAO, we will discuss in the next slide, what is the MAO. And you saw that there is a polymerization, smooth polymerization and acts as a fantastic system even in some cases, the activity is much better than the Ziegler Natta catalyst. And it is a homogeneous, so it is very easy to understand the mechanism and the complexity is not involved much as we have seen in the Ziegler Natta.

So, later after discover the polymerization, then Kaminsky and other groups where now interested how to regulate the stereoregularity. So, that is the, one of the challenge because if we make the stereoregular polymer and if we know that what is the mechanism, how, and accordingly if you can if we can design the catalyst, then we will have a kind of a toolbox that if I need a isotactic, I will use this catalyst, if I need a syndiotactic, I need I will use this catalyst, if I need atactic, I will use this catalyst.

So, with this target, so what was the concept? So, if you see that this catalyst, that is the zirconium and like if I draw like this one, if you see that these two C p rings are symmetrical. This is achiral because you have a plane of symmetry here. This is the plane. So, this is achiral. Now, if I make chiral, how we can do it? I have to destroy this plane of symmetry. And how we can do it? We can do it by using two different C p ligands. So, with this target, this one done. So, one in case C p star and one in case C p.

So, if we also different like this one, if it is my different group, this is the, let us say, I am changing now this one. Just, it will be more clear now if I put like this Me. Now, what is happening if we do, if we change substituents of the C p as well as the this one then what will happen? You do not have plane of symmetry of this one and also you do not have plane of symmetry this one. This is basically the, if you consider this two C p rings like this one, so if you consider a plane here then.

So, if you consider the plane of these two plane, this is one chloride and one is methyl, so if you consider two planes then also it is not symmetric because you have a chloride and you have a methyl. So, here now, this is now achiral. Now, you see after using this one also, the Kaminsky observed atactic polymerization, polypropylene, if you use the pro-chiral monomial. So, it is very interesting. So, even though we are using the chiral catalyst, then also you are getting the atactic polymer.

So, when 2 C p, and 2 X, it was achiral. And when two C ps are different, and when one using X and one using R, then it should be chiral. So, if you use the chiral catalyst, if polymerization should go through the catalyst site control, then my polymer should be isotactic polymerization, that is I should get the iso-tactic polypropylene. But in this case you see we are getting the atactic polymerization. So, this is also kind of a very confusing.

However, later realized that due to the rapid exchange and rotation, and this rate of exchanger rotation is much faster than the insertion of the alkene. And due to this one is actually it is undergoing the atactic polymerization. So, what to do? We have to stop this exchange or the rotation. And for that one, how we will do it? We have to bind the two C p rings. So you have to bind the two C p rings by some bridging unit. Then what will happen? You are stopping the exchange and rotation.

And by that way, you can get your desired isotactic or syndiotactic polymerization, depending on the symmetry of metallocene. So, that is the one of the beauty in this metallocene based catalytic system. So, you, depending on the symmetry and structure of the metallocene you can get your desired atactic syndiotactic isotactic in very controlled way. So, that is the one of the biggest advantage of the metallocene based catalyst. So, you have to be a good concept on the symmetry and the point groups of the metallocene.

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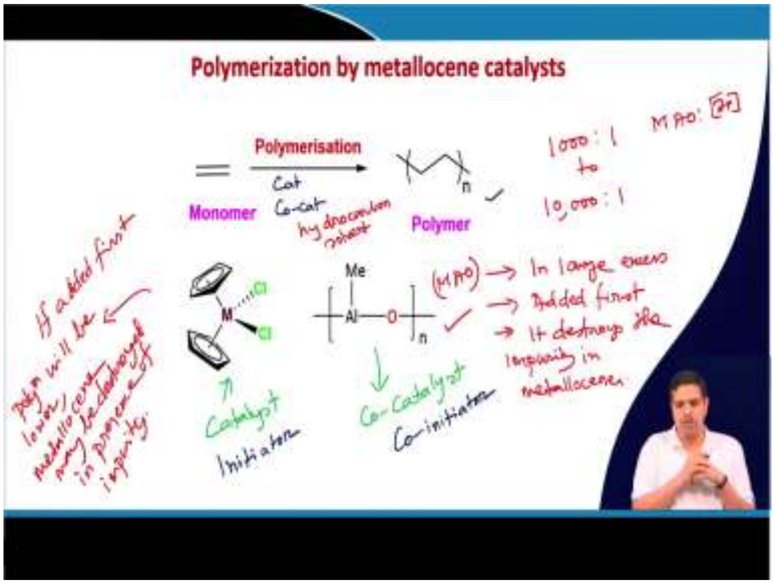

Polymerization by metallocene catalysts

(MAO) → In large excess
→ Added first
→ It destroys the impurity in metallocene

If added first
Polym will be lower, metallocene may be destroyed in presence of impurity

So, here we know that polymerization by metallocene catalyst now can be done with the two systems, one is the C p2, this is my, called the main catalyst, and this is, also it is needed, this is called the co-catalyst or sometimes it is called initiator and it is called co-initiator. First what I do I will just discuss the polymerization condition and then after, from that condition we will try to realize what is happening and what are the criteria of this polymerization.

So, if you take the monomer like ethylene, so you will get the corresponding polyethylene. Now here, two catalytic system, one is you need the catalyst and you need the co-catalyst. Now, it is very clear. Now, generally, we used a hydrocarbon solvent for the polymerizations if your monomer is gaseous. And here, this co-catalyst is used in a large excess, like 1000 is to 1 to, like that.

So, this is the ratio of your MAO, I will go detail what is the MAO. So, this is actually called the MAO. Next slide, I have discussed the detail about the MAO. And this is my, the zirconium. So, you need, so your co-initiator and initiator, real initiator ratio is quite high. So, that means this MAO is used in large excess. And this has to be added first.

This is very important. In the (catalysis), in the polymerization vessel, you have to use this one as first.

And it is believed that it destroys the impurity, if there is any impurity, in metallocene. If you use the reverse, that is first the metallocene and the MAO, then your, you can, if there is any impurity, that impurity will not be taken care of and you can get the less polymerization activity. So, that is very important. This has been realized after trial and error. So, if you take the first, if added first, polymerization will be lower, and metallocene may be destroyed in presence of impurity that come from the solvent or your the polymerization vessel. So, that is very important.

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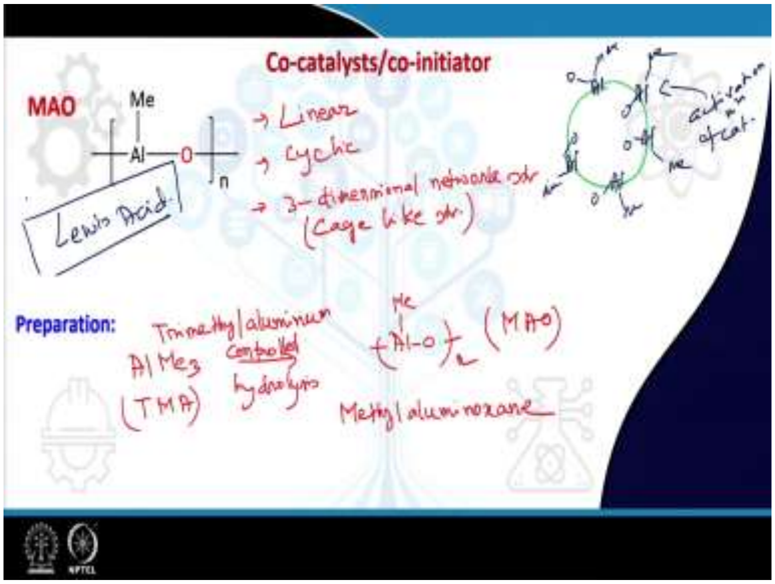

Co-catalysts/co-initiator

MAO

→ Linear
→ cyclic
→ 3-dimensional network str
(Cage like str.)

Lewis Acid

activation of cat.

Preparation: Trimethylaluminum AlMe$_3$ (TMA) controlled hydrolysis (MAO)

Methylaluminoxane

So, you realize here that you need really a very good amount of MAO. So, now let us see what is MAO. So, as I told that this is a co-catalyst. You have to use it. Only metallocene cannot perform the polymerizations. And this MAO is nothing but the partial hydrolysis of the Trimethyl aluminum, that is the, we call trimethyl, TMA. So, this is trimethyl aluminum. And if you do the polymerization, if you do the hydrolysis, that is, that has to be controlled hydrolysis, that means partial hydrolysis. Then you will get the structure of like this one. So, that is called the methylaluminoxane, that is nothing but the MAO.

The, although this is a very simplified structure, I show it is a linear, but in reality it is not that simple. It may be linear, it may be cyclic or it may be three-dimensional network structure. And most people believe that this is the, and accepts that it is a cage like structure. So, what happens, you have like this kind of cage like this, I am, just very qualitatively I am showing. And this is, you have a like aluminum here, aluminum here, aluminum here, like this one. And like that, very qualitatively I am showing, like this one. And the activation of the catalyst is, actually happens on the surface, here. Activation of catalyst.

So, you see that this is really a very complex structure although, and this is acts a very good Lewis acid. And that actually, you need to activate the, our main catalyst that is the zirconocene. So, we, so far what we have understood in this class, we understood that there is a need of more reliable and more efficient catalyst than the Ziegler Natta catalyst, although Ziegler Natta catalyst was very successful in olefin polymerization. And the disadvantages of Ziegler Natta catalyst, we have now discussed very elaborately.

To remove all these disadvantage the scientists started to develop a new catalyst and the metallocene based catalyst were proved to be one of the best substitute of the Ziegler Natta catalyst. Reasons are various that some of, we have discussed in the, this class. Some of the, we will discuss in the in the next classes. So, as you know that here, the catalytic system two component, one is the catalyst and the co-catalyst. And we have now know that what is the co-catalyst.

And in the next class, we will try to discuss the role of the co-catalyst, how the activation happens on the main catalyst and how the polymerization growth happens on the metallocene based catalyst which is called also as a single site catalyst system, and why it is called the single site catalyst system. So, in the next class, we will continue this metallocene based catalysts and its detailed mechanism. Thank you. See you in the next class.