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

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Lecture 26
Metallocene to Post-metallocene catalysts for olefin polymerization (Contd.)

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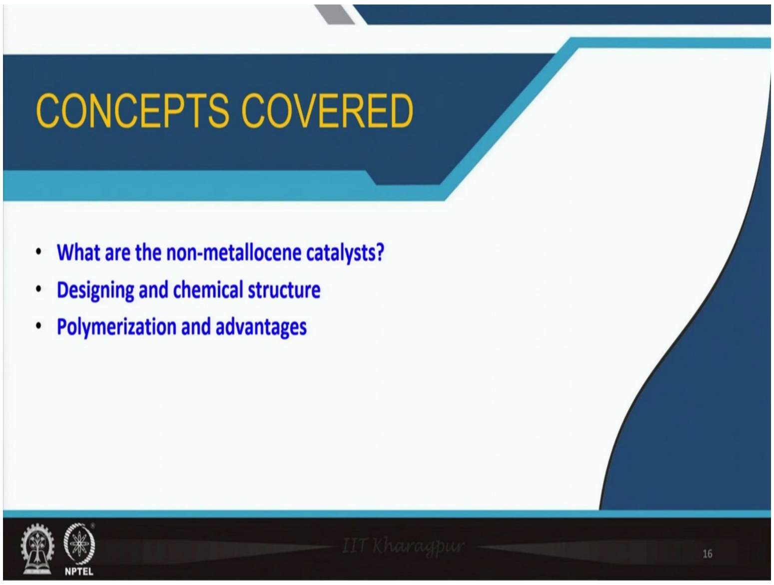
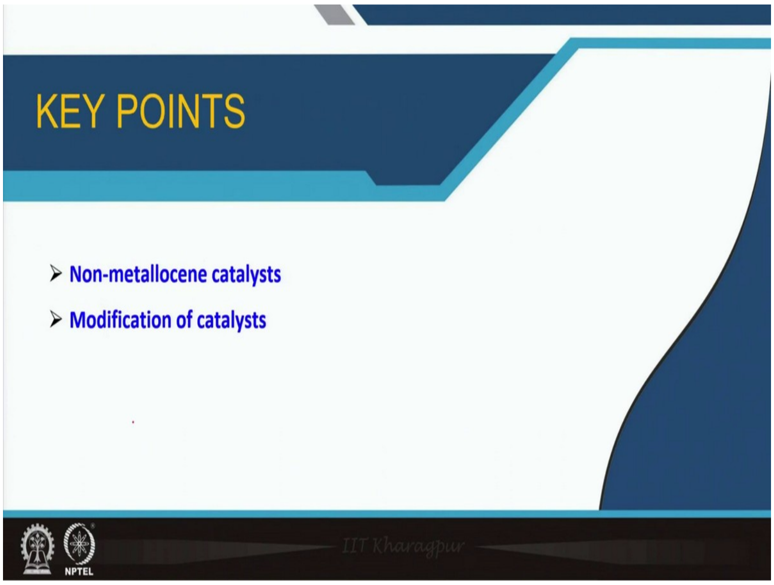


CONCEPTS COVERED

- What are the non-metallocene catalysts?
- Designing and chemical structure
- Polymerization and advantages



KEY POINTS

- Non-metallocene catalysts
- Modification of catalysts

Welcome once again to our classes, so we will continue our discussion on the post metallocene catalyst for olefine polymerizations and we will cover the concept like non-metallocene catalysts and this designing and chemical structure and its polymerization activity and obviously the advantage over the other metallocene catalyst and Ziegler Natta catalyst.

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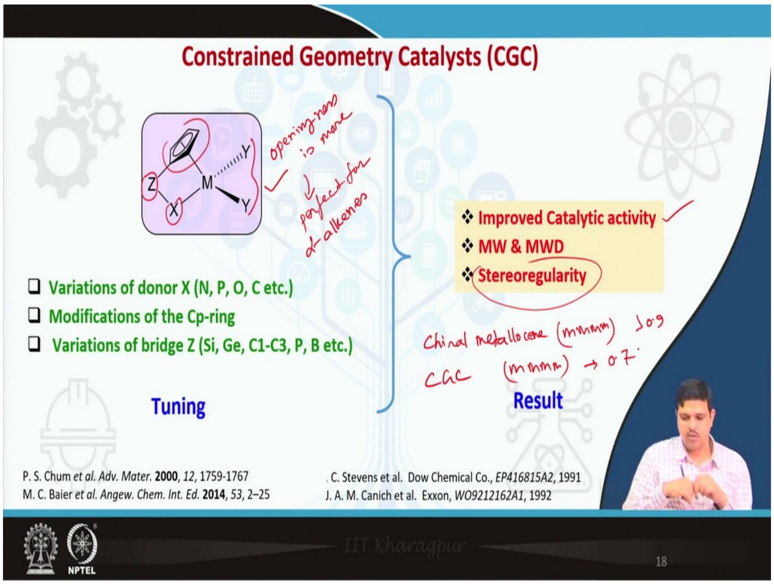

Constrained Geometry Catalysts (CGC)

opening ness is more
↓
perfect for α-alkenes

- ☐ Variations of donor X (N, P, O, C etc.)
- ☐ Modifications of the Cp-ring
- ☐ Variations of bridge Z (Si, Ge, C1-C3, P, B etc.)

Tuning

- ❖ Improved Catalytic activity ✓
- ❖ MW & MWD
- ❖ Stereoregularity

Chiral metallocene (mmmm) >0.9
CGC (mmmm) → 0.7

Result

P. S. Chum *et al. Adv. Mater.* **2000**, *12*, 1759-1767
M. C. Baier *et al. Angew. Chem. Int. Ed.* **2014**, *53*, 2–25

C. Stevens et al. Dow Chemical Co., *EP416815A2*, 1991
J. A. M. Canich et al. Exxon, *WO9212162A1*, 1992

IIT Kharagpur

So in the last class we discussed, we started our discussion on the constrained geometric catalyst that is the very successful that the general structure of this one you will see that that CP this may be different simple CP or substituted CP and this X is the donor that may be nitrogen phosphorus or oxygen based donors and the bridging units may be the boron phosphorus carbon or nitrogen or silicon but however it the bridging unit should be smaller so that the openingness on this side is more and that is why it is perfect for the high molecular weight polyethylene or the copolymerization of the ethylene and with the other copolymer as example like longer alkenes, alpha alkenes.

So perfect for other alpha alkenes not only the just ethylene and you will see that due to the advantageous properties, so improved catalytic activity, the molecular weight is very huge you can get the ultra high molecular weight but the only problem is that the stereoregularity the stereoregularity is less than the metallocene based catalyst chiral metallocene based catalyst.

As example if you for the chiral metallocene it is you can go more than 0.9 but in this case the CGC type catalyst you will be maximum you can get like 0.7 that means you have to sacrifice although the reactivity or the activity is much higher than the other catalysts.

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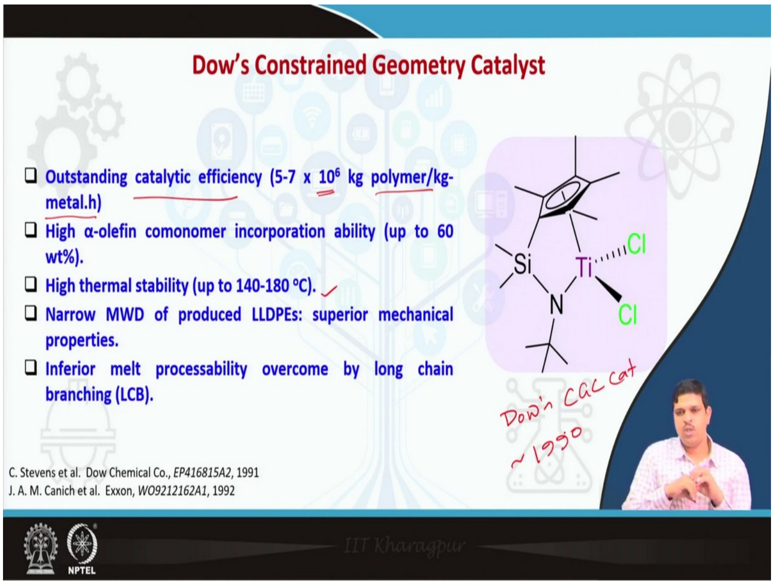

Dow's Constrained Geometry Catalyst

- Outstanding catalytic efficiency (5-7 x 10^6 kg polymer/kg-metal.h)
- High α-olefin comonomer incorporation ability (up to 60 wt%).
- High thermal stability (up to 140-180 °C).
- Narrow MWD of produced LLDPEs: superior mechanical properties.
- Inferior melt processability overcome by long chain branching (LCB).

C. Stevens et al. Dow Chemical Co., *EP416815A2*, 1991
J. A. M. Canich et al. Exxon, *WO9212162A1*, 1992

Dow's CGC cat
~1990

So but that what are the advantage here you see that is a high catalytic activity the generally the activity of the catalyst is expressed in the as the kg of the polymer per kilogram metal per hour, so that is the expression for the catalytic efficiency of a catalyst so you will see that this is in the order of 10 to the power 6 that is quite huge, high alpha olefin comonomer incorporation that I told that if it can coordinate nicely with the longer alpha alkenes as example hexane butane octane or even the styrene.

Thermal stability is much higher than the other metallocene and perfect for the low linear low density polyethylene because it can nicely co-polarized with other alpha olefins so that are the quite advantages and that is why the industry has accepted this is the one of the very famous and catalyst that is the Dow’s CGC catalyst and Dow chemicals basically first discovered or commercialized this catalyst and here you will see that this is, this was around 1990 it was first reported with this high efficiency.

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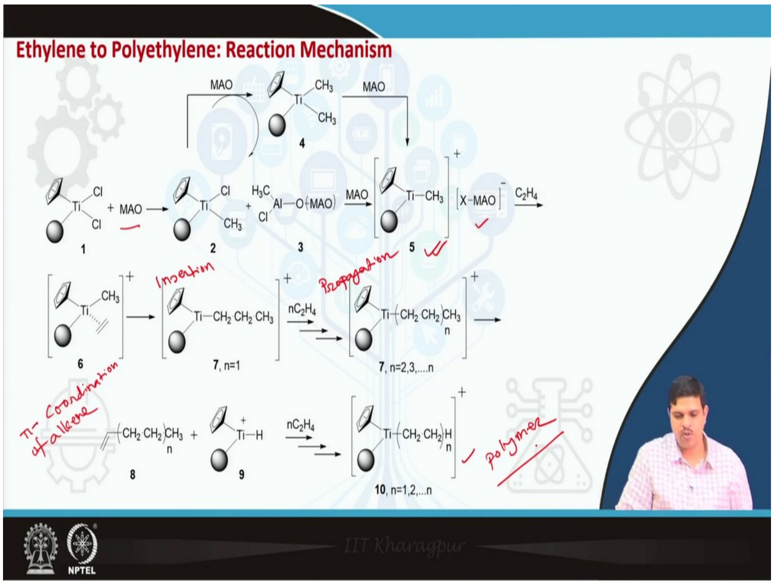

Ethylene to Polyethylene: Reaction Mechanism

And mechanism is very much similar as the other metallocene based catalyst here you see that this again you have to use a co initiative either the MAO or the phosphine based so whatever is the preferred we can use it there is no limitation on that one so here you will see that this MAO has a dual role and it will give after the alkylation and the abstraction of the methyl group you will get this the active species with the titanium and with positive charge and that X or the methyl is abstracted by the MAO and then C2H4 that is the (())(5:46) coordinate, so this is basically the coordination of 5 coordination of alkene.

And then after that it is undergoing the insertion reaction so this is basically the insertion reactions and then the following through multiple steps you will get the multiple propagation and you will get basically the propagation of the polymer chain and you will get this polymer so mechanism is same as we have seen for the other metallocene based catalyst so there is no difference on it.

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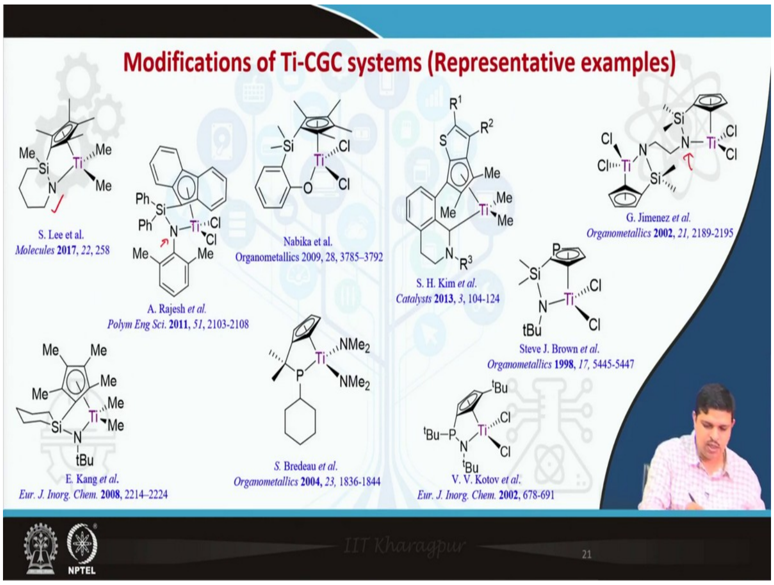
Modifications of Ti-CGC systems (Representative examples)

S. Lee et al.
Molecules **2017**, *22*, 258

A. Rajesh *et al.*
Polym Eng Sci. **2011**, *51*, 2103-2108

Nabika et al.
Organometallics 2009, 28, 3785–3792

S. H. Kim *et al.*
Catalysts **2013**, *3*, 104-124

G. Jimenez *et al.*
Organometallics **2002**, *21*, 2189-2195

Steve J. Brown *et al.*
Organometallics **1998**, *17*, 5445-5447

E. Kang *et al.*
Eur. J. Inorg. Chem. **2008**, 2214–2224

S. Bredeau *et al.*
Organometallics **2004**, *23*, 1836-1844

V. V. Kotov *et al.*
Eur. J. Inorg. Chem. **2002**, 678-691

So after that successful discovery of the Dow's CGC catalyst high molecular weight, exceptionally high molecular weight but the problem is this stereoregularity so many research groups had tried to develop different different CGC type of catalysts in time and you see some of the examples this is basically just for information nothing like, this just for information that how different type of ligands, different type of donors are possible here you see that this is basically the bridging is the cyclic bridge and here you will see that again the donor is again the amino and here you will see that this is again the amino so all are the main structural feature is same so only the bridging moiety or the CP units have been modified to induce the chirality or to induce the electronic factor which will be feasible for the polymerizations.

So there are vast scope on this kind of catalyst for the development of the new catalyst of the CGC category of the catalyst. So mainly this chemistry is dominated by the titanium, titanium 4.

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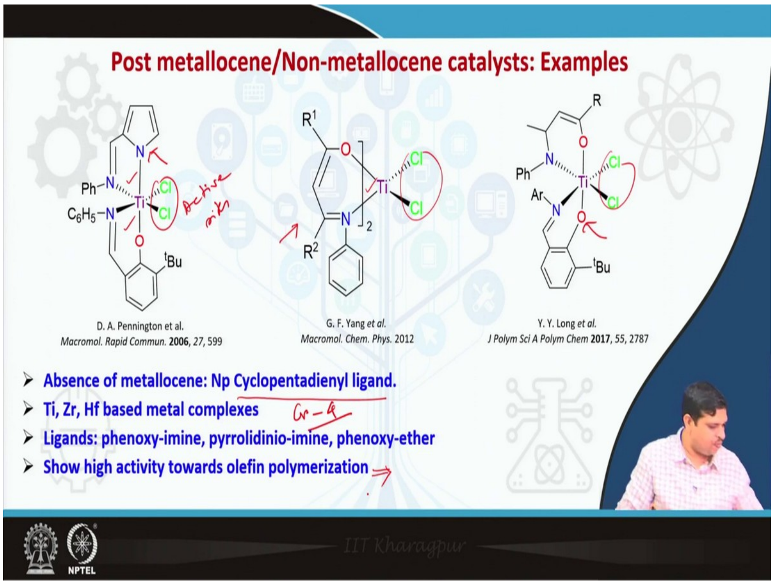


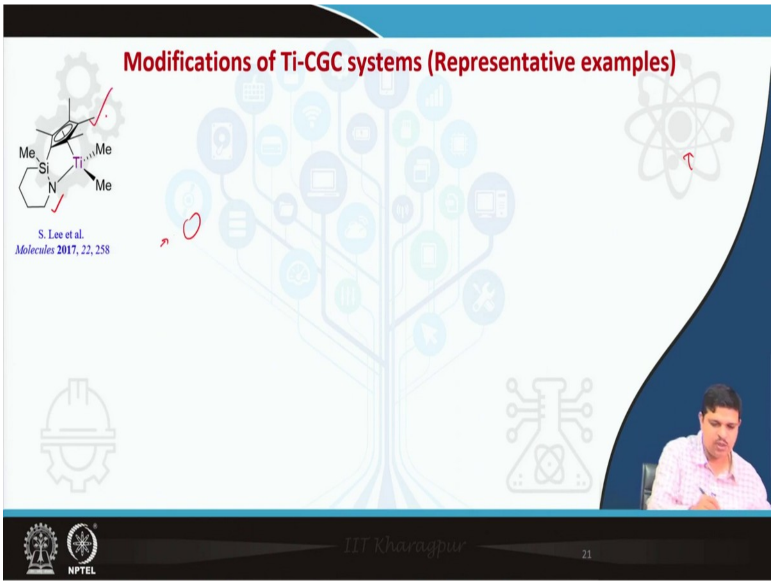
Post metallocene/Non-metallocene catalysts: Examples

D. A. Pennington et al.
Macromol. Rapid Commun. **2006**, *27*, 599

G. F. Yang *et al.*
Macromol. Chem. Phys. 2012

Y. Y. Long *et al.*
J Polym Sci A Polym Chem **2017**, 55, 2787

- Absence of metallocene: Np Cyclopentadienyl ligand.
- Ti, Zr, Hf based metal complexes Gr-4
- Ligands: phenoxy-imine, pyrrolidinio-imine, phenoxy-ether
- Show high activity towards olefin polymerization



Modifications of Ti-CGC systems (Representative examples)

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So now the recent progress of in this chemistry and that is the post metallocene based chemistry the non- metallocene catalyst you know that non CP based ligands are expensive especially if you try with the substituted CP is quite expensive like for the like this kind of ligands you see this is quite expensive, so simple ligands are always desirable, it is economic so cost effective and if the activity is good enough then industry people will love it, will accept very easily because it will be more economic so in that way the category of the non-metallocene catalyst started to develop these are basically quite new they all started around 2010 or so like that.

And you will see that here no metallocene so no metallocene based catalyst so no CP rings here no cyclopentadiene rings and all are actually titanium zirconium hafnium that is the group 4 transition metal so that means the reactivity and the polymerization mechanism will be very much similar the way we have seen for the CGC or the metallocene based catalyst and ligands are either the phenoxy imine that is you will see that that is the phenoxy imine or the pyrrolidinio imine that is the pyrrolidinio imine or the phenoxy ether, so here you will see this is the phenoxy ether.

So either phenoxy ether or the pyrrolidinio imine or the phenoxy imine so those are the chelating ligands when you I am sure you know that what is the chelating so chelating is basically multi-dented ligands and in tropically favored complexes so you can make the chelating complex very easily using the suitable chelating ligands, so here you will see that again the basic structure is same so these are the active sites so these are the active sites in all the cases and these are basically the ligands by the different type of pyrrolidinio phenoxy imine or phenoxy ether.

And this kind of catalysts have also show that good and in some cases high activity towards olefin polymerizations, there is some advantage disadvantage but these catalysts are very cost effective, very economic because there is not much really expensive ligands in this one, you can easily prepare by condensation reactions.

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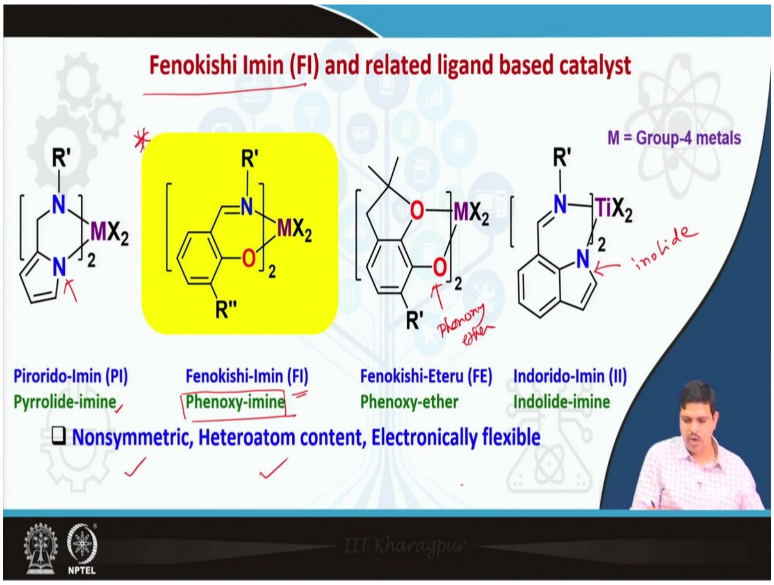


Fenokishi Imin (FI) and related ligand based catalyst

M = Group-4 metals

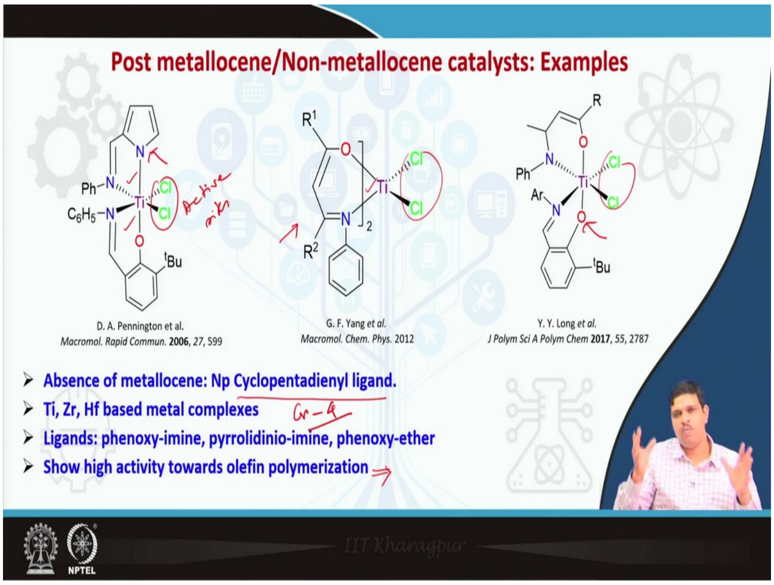
Pirorido-Imin (PI)
Pyrrolide-imine

Fenokishi-Imin (FI)
Phenoxy-imine

Fenokishi-Eteru (FE)
Phenoxy-ether

Indorido-Imin (II)
Indolide-imine

❑ Nonsymmetric, Heteroatom content, Electronically flexible



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- Ti, Zr, Hf based metal complexes
- Ligands: phenoxy-imine, pyrrolidinio-imine, phenoxy-ether
- Show high activity towards olefin polymerization

So here one of the very famous the ligand the complex system is the Fenokishi Imin so this is actually the ins in English is called the phenoxy image but in Japanese is called Fenokishi Imin so that is why it is called as FI so related ligands are like a this one pyrrolide imine so this is you will see this is the pyrrolide imine so this is the another category of the catalyst and this is you will see phenoxy ether so this is my phenoxy ether, so this is called the FE type catalyst and here you will see that indolide imine so this is the indole, so this is the indolide imine so this is called the I I.

And apart from this four category this phenoxy imine is quite popular and gives the good activity, so here see in this catalysts are non symmetric and hetero atom donors are there nitrogen oxygen so you will give a different type of isomers the regioisomers and also this stereoisomers and these are also the flexible, electronically flexible that means it can accommodate the even the sterically hindered monomers so that is that means it easily can coordinate the different type of the monomers the alkene monomers. So that is 3 criterias are very important, nonsymmetric, heteroatom content and electronically flexible.

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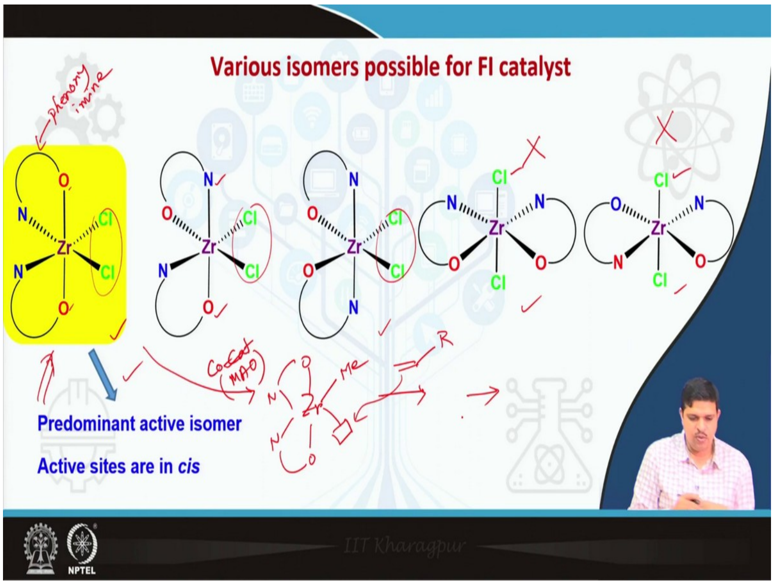
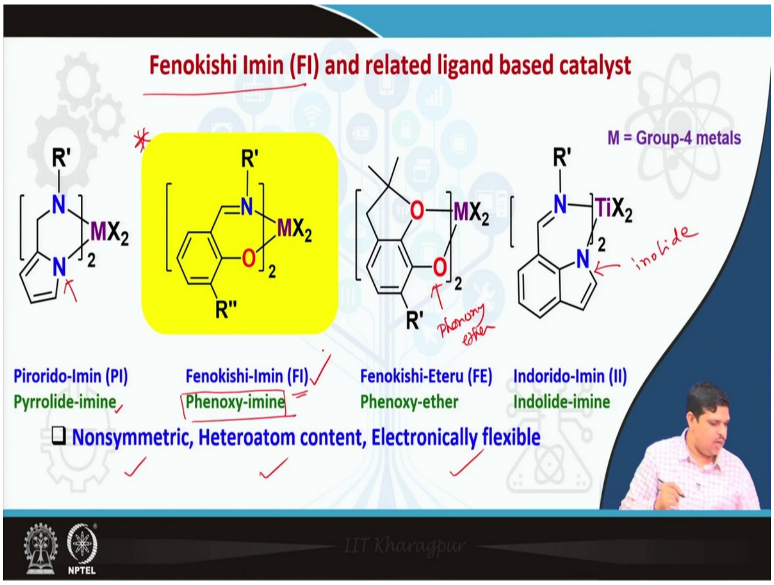

Various isomers possible for FI catalyst

Predominant active isomer

Active sites are in *cis*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Fenokishi-Imin (FI)
Phenoxy-imine

Fenokishi-Eteru (FE)
Phenoxy-ether

Indorido-Imin (II)
Indolide-imine

❑ Nonsymmetric, Heteroatom content, Electronically flexible

So here lets this one you have to like this you check the phenoxy imine, so let us take this category of the ligand first and try to understand that why, what kind of isomers are possible in solution so these are all the homogeneous catalysts, so here you see NO is basically if the phenoxy imine so this is basically NO in cartoon we have seen so this is the phenoxy imine, phenoxy imine, now here you see that this is possible one isomer that is oxygen oxygen trans here nitrogen oxygen trans so here the 2 chlorides are cis, here also cis, here also cis and this case it is trans and it is trans but think over it how the reaction mechanism the polymerization happens.

There will be alkene coordination and then the insertion, so that means this would be not effective this would be not effective for the polymerization so I am interested for this one, this one or this one it has been observed by spectroscopic method and also by crystal structure that this isomer is the predominant so this is the predominant structure and active sites of cis that is the matching and why you need the active site of cis because you have to have the if you recall you have the polymerization mechanism so you have to have the like that one so your this is using the co catalyst as example like MAO.

So what you have to get, you have to have a, you have to create a backend site and this one is let us say methyl and your alkene will coordinate here so you if you have a let us say this one so this will coordinate here and then it will undergo the polymerization, so cis positions the 2 chlorides the cis isomer is essential for the polymerizations.

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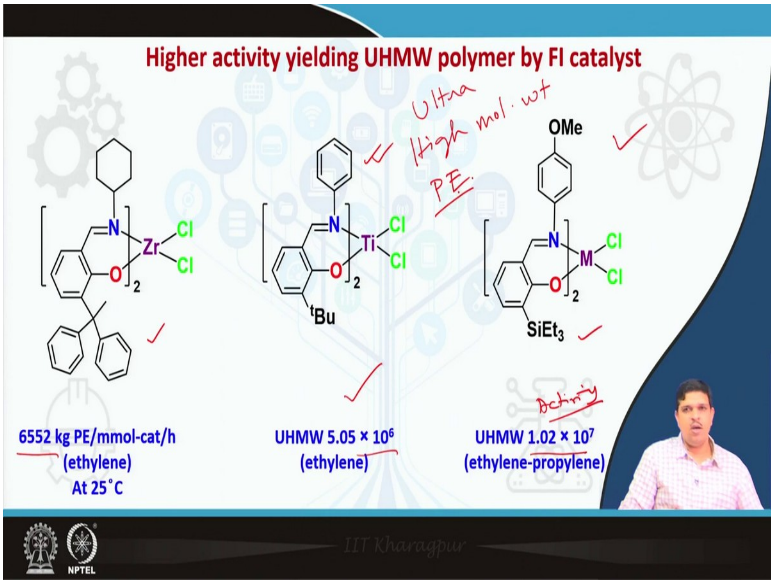

Higher activity yielding UHMW polymer by FI catalyst

Ultra High mol. wt PE

6552 kg PE/mmol-cat/h
(ethylene)
At 25˚C

UHMW 5.05 × 10^6
(ethylene)

Activity

UHMW 1.02 × 10^7
(ethylene-propylene)

So here you see that lots of poly catalysts have been developed time to time and some of the data I will try to give this is especially for the industry (())(15:47) that to understand how these poly catalysts are effective in polymerizations, so here you will see that this phenoxy imine type of catalyst here this catalyst let us see this is the 6552 or kg polyethylene per mole of catalyst per hour and this one you will see that this is 1.02 in 10 to power 7 that is the activity so this is basically the activity and you will get the very high molecular weight that is the ultra high molecular weight polyethylene and activity in the range of 1.02 in 10 to power 7 and this one is quite moderate 10 to power 6.

That means you will see that this catalyst and this catalyst is very effective for the very high molecular weight and it is called ultra high molecular weight polyethylene so this is really effective and for the polyethylene if you want targeting for the high molecular weight polyethylene these are the catalysts are suitable and perfect.

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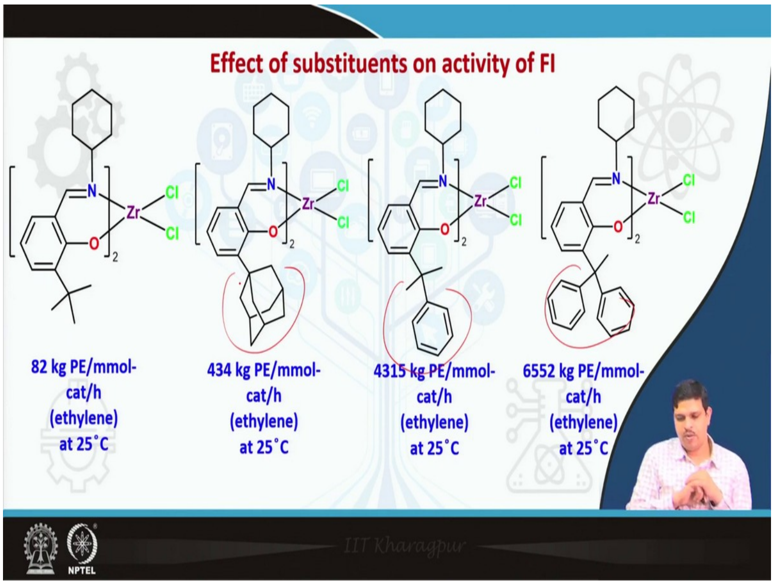


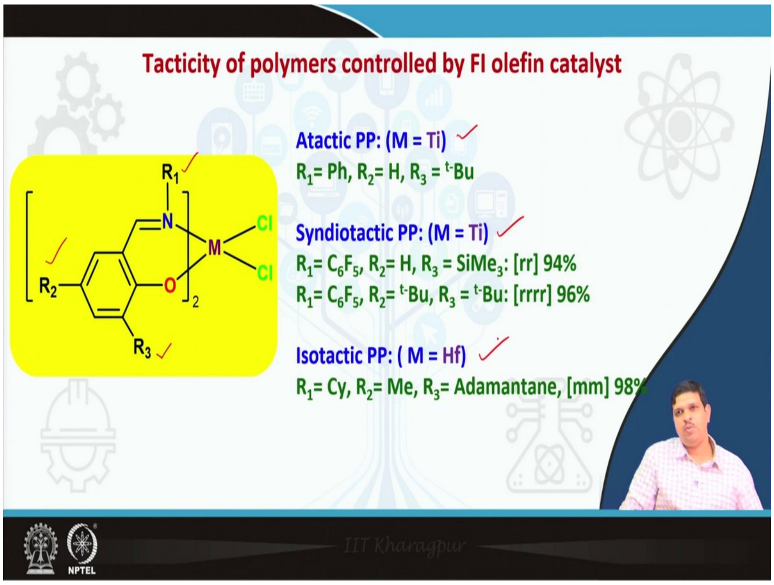
Effect of substituents on activity of FI

82 kg PE/mmol-cat/h (ethylene) at 25°C

434 kg PE/mmol-cat/h (ethylene) at 25°C

4315 kg PE/mmol-cat/h (ethylene) at 25°C

6552 kg PE/mmol-cat/h (ethylene) at 25°C



Tacticity of polymers controlled by FI olefin catalyst

Atactic PP: (M = Ti)
R_1= Ph, R_2= H, R_3 = ^{t}Bu

Syndiotactic PP: (M = Ti)
R_1= C_6F_5, R_2= H, R_3 = $SiMe_3$: [rr] 94%
R_1= C_6F_5, R_2= ^{t}Bu, R_3 = ^{t}Bu: [rrrr] 96%

Isotactic PP: (M = Hf)
R_1= Cy, R_2= Me, R_3= Adamantane, [mm] 98%

So here also see that different type of catalysts have been developed and you see that how the different substituents varies the activity so this is just for information and to see that what are the effects of the substituents and how we can tune the electronic property and also can tune its reactivity, so these are really very interesting and not only that one you can also control the tacticity by to some extent by changing this R group you have 3 option R1 R2 and R3 so depending on the different and inducing the asymmetry and or inducing or installing the different substituents you can also get the atactic, syndiotactic or isotactic polypropylene if you use the propylene as a monomer.

So highly active and also you can get the tacticity in the polymer so you are fulfilling both the criterias with the cheaper comparably cheaper catalyst so that is a perfect.

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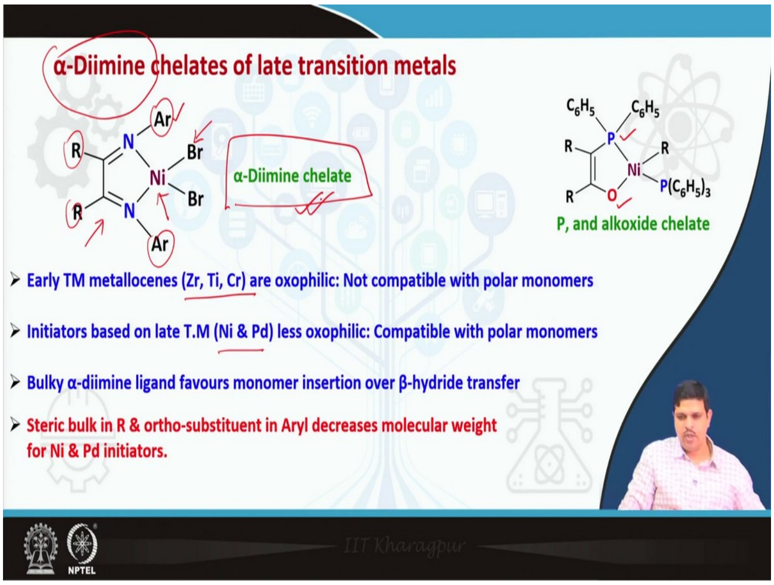

α-Diimine chelates of late transition metals

α-Diimine chelate

P, and alkoxide chelate

- Early TM metallocenes (Zr, Ti, Cr) are oxophilic: Not compatible with polar monomers
- Initiators based on late T.M (Ni & Pd) less oxophilic: Compatible with polar monomers
- Bulky α-diimine ligand favours monomer insertion over β-hydride transfer
- Steric bulk in R & ortho-substituent in Aryl decreases molecular weight for Ni & Pd initiators.

And another category and is the alpha diimine chelates of late transition metals, so first transition that is that early transition metals as example zirconium titanium all these are oxophilic that is not really compatible with polar monomers or as example acrylic monomers, acrylic monomers but for if you use the late transition metals as example nickel, palladium those are less oxophilic that means compatible with polar monomers so if we can make the similar catalyst with my late transition metals as example nickel palladium etc. then this will be much more comfortable with my polar monomers so that we can make the block copolymers or we can make the amphiphilic polymers where there would be the nonpolar part and also the polar part, non polar block and polar block using the polar and nonpolar monomers, so that will be very nice if we can make this kind of catalyst.

So here you will see that this is the alpha diimine chelate complexes and here it is nickel and this kind of ligands are very easily prepared by (())(19:39) based type of condensation reactions and not only that one this also like here you will see this is the phosphine and this is the alkoxy kind of chelate ligands are also have also been developed and reported, so bulky alpha diimine ligands favors monomer insertion over beta hydride transformation so here this one if you put the R group quite bulky it is actually favors the insertion reactions then the beta hydride transfer, so that is the you have to keep in mind while designing new ligands or the selecting the ligands from a library.

However steric bulk in R or ortho position here, see what will happen that molecular weight decreases because you are putting the streak hindrance in this side, so this side has to be open otherwise we should not put any other strict hindrance group here in this one so that should be like a simple phenyl or maybe the para substituted not the ortho substituted then there will be less activity of this polymers.

However this alpha diimine chelate complexes have now very popular and very effective and many so industries are also accepting these polymers these catalysts for polymer synthesis.

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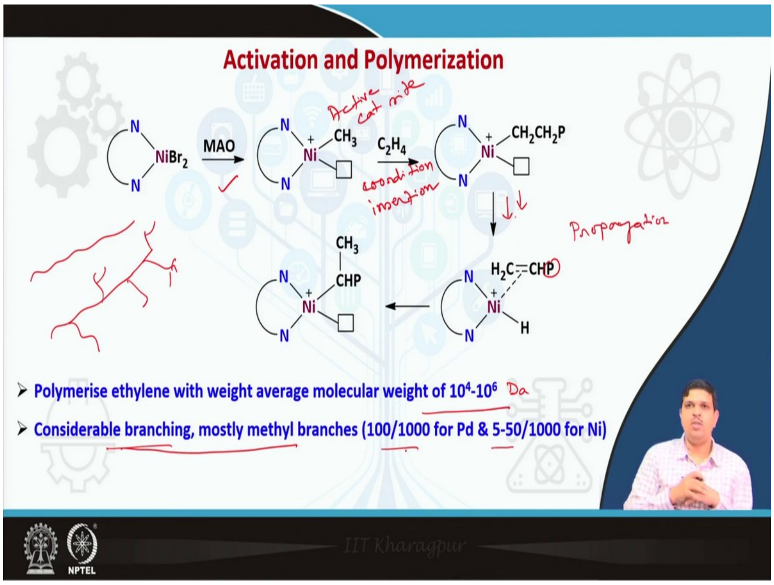

Activation and Polymerization

- Polymerise ethylene with weight average molecular weight of 10^4-10^6 Da
- Considerable branching, mostly methyl branches (100/1000 for Pd & 5-50/1000 for Ni)

The mechanism is very simple here you will see that MAO is again activating the catalyst so and then we would see here that after activating this is the active species, active catalytic site and then ethylene is coordinating so and then it is insertion reactions again so ethylene coordination and insertion as it happened in the previous catalysts and then the way it is actually propagating, P means polymer so it is now like that propagation.

So multiple steps and the propagation like that so this kind of polymers or catalyst starts very effective you can get the molecular weight of around 10 to power 6 molecular weight that is Dalton that is quite good and not only that you can get considerable branching so as you know that we also sometimes purposively put the branching in the polyethylene to induce a different properties and for getting a particular applications.

So like for like linear polyethylene this is the linear polyethylene and if you need a quite good branching this kind of catalyst will be perfect because you will see that it can induce the considerable branching, branching is like see this one 100 per 1000 of ethylene units or for the palladium and for nickel it is up to 50 per 1000 ethylene moieties.

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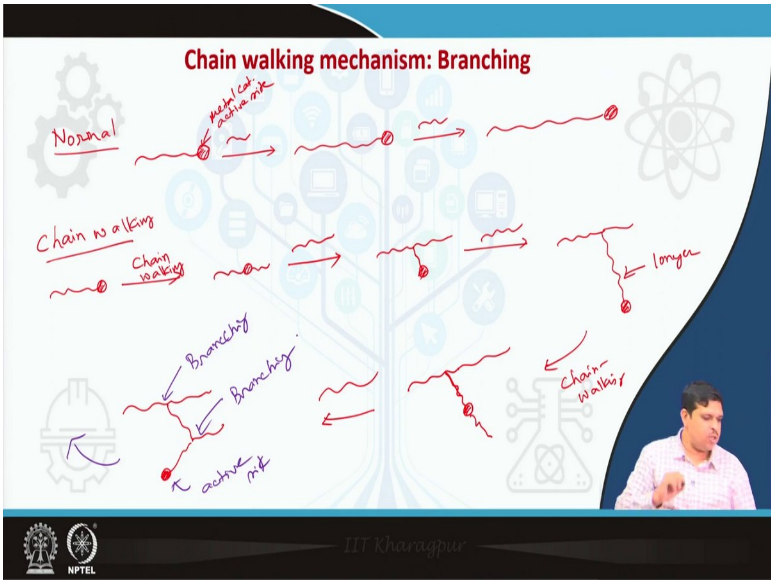
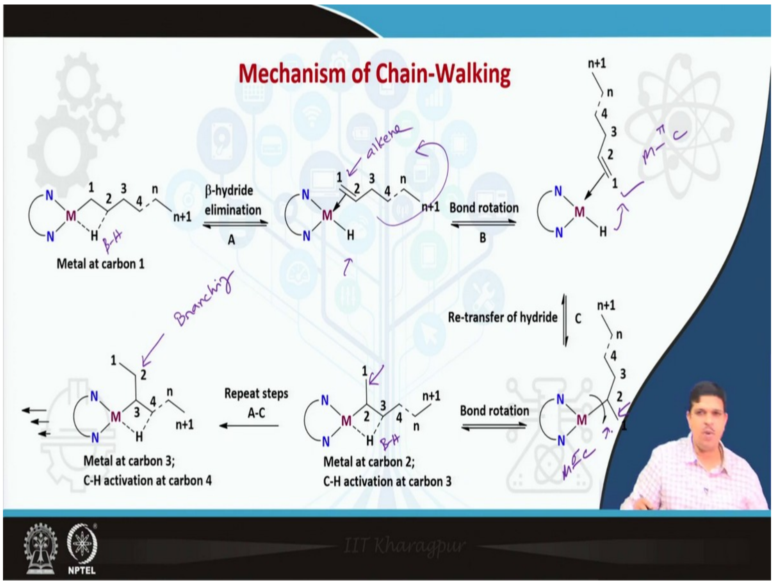


Chain walking mechanism: Branching



Mechanism of Chain-Walking

β-hydride elimination A

Bond rotation B

Re-transfer of hydride C

Bond rotation

Repeat steps A-C

Metal at carbon 1

Metal at carbon 2; C-H activation at carbon 3

Metal at carbon 3; C-H activation at carbon 4

So how this branching happens that is really very interesting I will show you, so what is the branch, how the branching happens this is actually by chain walking mechanism, I will give a very cartoon diagram first to understand so in first I will discuss that what is the normal cases so like you see this is my the metal center and if I have now monomer so what will happen it will just increase in the length so this is my active site that is the metal active catalyst, catalyst active site and now if I put another monomer then what will happen so it will like that so it will longer, so it will be longer, longer and longer.

Now in case of chain walking what is possible, very interesting so this is my polymer with active catalytic site, now chain walking what will happen so there will be this active site is now here like this one so it is basically active site is moved, how it is moved I will show you, now first you see the pathway what are the chain walking, now if we have a monomer so what will happen, so this is like that, so now I have now another monomer now what will happen?

Now this one is the longer so this is, this monomer inserted here now this has become longer now again the chain walking let us say, first chain walking, now what will happen here so here and now here now again what will happen, now you see that so this is now my active site, this one, so this is now my active site, so similarly it will give, go again the chain walking and you will see basically the branching, here branching, here branching, you will see now this is the cartoon diagram how it is possible by chemistry by bond breaking and bond making you will understand here.

So here you will see that this is my beta H and undergoing the beta hydride illumination so what is happening so this is you were getting the alkene here again and this is the hydride you are getting by beta hydride elimination and then there is a bond rotation so here you will see that what happens this bond is basically rotated this alkene bond then this is the bond rotation step, now due to the bond rotation hydrogen now has been re-transferred so here what is happening you see that this hydrogen now has the alkene has been inserted and now you have a metal carbon single bond metal carbon sigma bond or and this is the metal carbon pi bond.

Now due to this rotation what will happen now this methyl group you see this methyl group this one is now here and now this hydride, this beta hydride is now interacting with the metal like the agostic interaction and this will repeat so now after repetition see you are here we will getting the branching here, so what are the steps mechanistically, so this is the beta hydride elimination and the bond rotation by through the single and then the another beta H is coming in close proximity to the metal center and then again it is forming the metal hydride and then again the insertion again the rotation in that way you will getting the chain walking and you will get the hyper branching sometimes branching is quite considerable amount.

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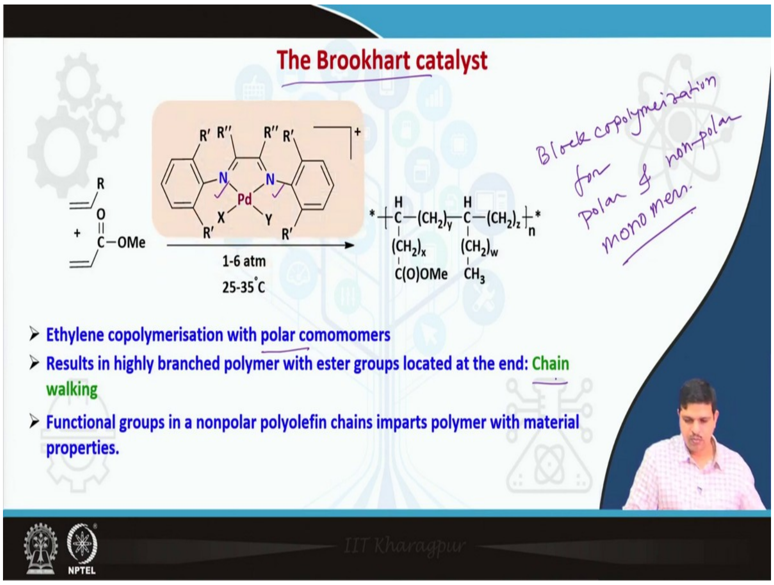

The Brookhart catalyst

Block copolymeization for polar & non-polar monomers.

- Ethylene copolymerisation with polar comomomers
- Results in highly branched polymer with ester groups located at the end: Chain walking
- Functional groups in a nonpolar polyolefin chains imparts polymer with material properties.

Similarly the other catalyst very famous catalyst that is the Brookhart catalyst, this is actually palladium based and again it is a imine based diimine based so this is you will see that again the imine are ligands or donors are there and this is very good because this is compatible with the monomer with the oxygen atoms as example like aquarius type of monomers and you can make a, make block copolymers you will see here perfect for the block copolymerization form polar and nonpolar monomer.

So this is the another breakthrough in the non-metallocene based catalyst so it is a results in highly branched polymer with ester groups located in that is the chain walking you are getting the amplific copolymers sometimes we need for different purpose and is a highly compatible with versatile number of the olefine monomers so not only for the olefine, alkyl olefine it also like a styrene, acrylic monomers and barriers.

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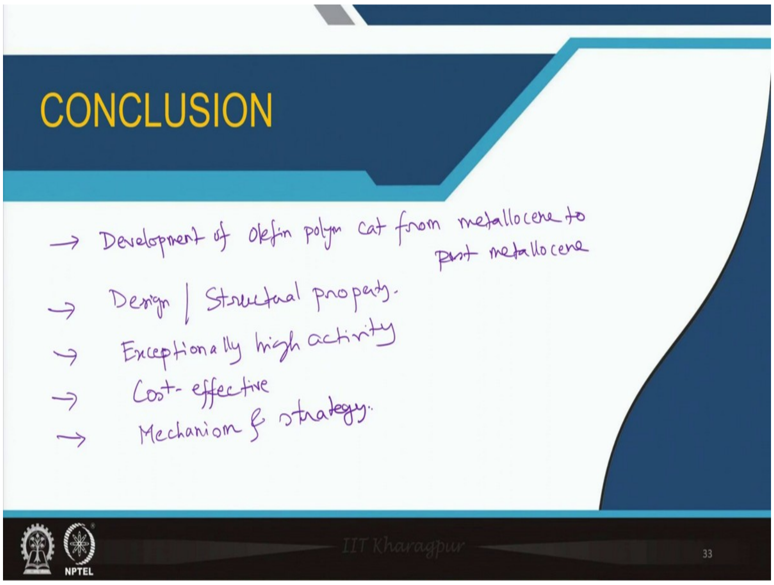

CONCLUSION

→ Development of olefin polym cat from metallocene to post metallocene

→ Design | Structural property.

→ Exceptionally high activity

→ Cost- effective

→ Mechanism & strategy.

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So in conclusion what we have learned today, we have basically learned that the development of olefine polymerization catalyst from metallocene to post metallocene and we learned the design structural property and exceptionally high activity and definitely the cost effective we also learned the mechanism and the strategy so here we are now very clear that not only the metallocene the non metallocene with more cheaper and economic ligands are also possible for olefin polymerization however, there is a disadvantage is that we have to sacrifice this stereoregularity so if you see that post metallocene are good for the high molecular polymers for branching inducing the branching for LLDP polymers.

How about if you want to get a pure tacticity or the specific tacticity then it certainly it is a disadvantage and in this case the metallocene based chiral catalyst as example like C2 symmetry or C1 symmetry actually wins and if you get a like a syndiotactic polymers then CS wins, so this is very clear that how this catalysts are exciting and why the different industry who are basically the polymer manufacturers have accepted these catalysts.

In the next classes we will discuss that how this catalyst have been transformed from lab to industry because we know that we here all we have discussed the homogeneous catalysts but homogeneous catalysts had advantage and some disadvantage mainly for the economic factor and purification factors and reusability factors so that actually the industry personals does not, do not like, they all like the reusable and which will be most cost economic method, so how we can transfer this catalyst to the heterogeneous catalyst so transformation from the homogeneous to heterogeneous that we shall discuss in the next class.

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REFERENCES

- Organotransition metal chemistry from bonding to catalysis by John Hartwig, University science books, 2010
- Principle of polymerisation by George Odian, Jhon Wiley & sons, 4th edition, 2004
- Polyolefins: 50 years after Ziegler and Natta II by Walter Kaminsky, Springer, 2013
- Basic Organometallic Chemistry by Gupta and Elias, University Press, 2010.

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So these are the references, you can consult the various books and thank you very much and see you in the next class.