Transition Metal Organometallics in Catalysis and Biology
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Lecture – 55
Olefin Polymerization(Part 16)

Welcome to this course on transition metal organometallics in catalysis and biology we have been discussing about olefin polymerization particularly we have looked into ethylene polymerization as well as propylene polymerization in the last few lectures and there we have looked mainly into homo polymerization of these two monomers ethylene and propylene what it means that ethylene monomer polymerized to give poly ethylene and propylene polymerized to give poly propylene.

And these are what is called these homo polymerization. Now in the last class we have also looked into the other possibilities of doing copolymerization. Copolymerization can be of two different monomers they can be both olefins like ethylene and propylene ethylene 1 hexane or Italian alpha olefins and so on and so forth or they can be of ethylene and alpha olefin baring functional groups.

Now the main challenges which we have encountered is that these particularly for ethylene alpha olefin polymerization the main challenges which was encountered was the rate of polymerization are not the same for the 2 monomers. For example for Ziegler Natta catalyst as well as the metallocene catalysis the ethylene o polymerization is much higher at a much higher rate than the alpha olefin homo polymerization.

Whereas in metallocene catalyst the difference is not that extent however still it is less acute then the difference what is present in Ziegler Natta catalyst. But still nonetheless they if they are there that rate of homo polymerization of ethylene is higher than the rate of homo polymerization of alpha olefins. Now when it comes to copolymerization of ethylene with alpha olefins bearing functional group it is even more challenging because the hetero atoms of the functional group compete with the ethylene binding for which occurs at the polymerization site.

As a result the presence of functional group also poisons the catalyst for further polymerization and this poisoning is more significant for heterogeneous Ziegler Natta type catalyst then it is for metallocene based ones and that is what was the main drawback is that the polymerization of functional monomers were in fact poisoning the catalyst. However nonetheless in the last lecture we had seen this nice example where for vulcanizing catalyst Waymouths successfully homo polymerize heteroatom bearing functional groups.

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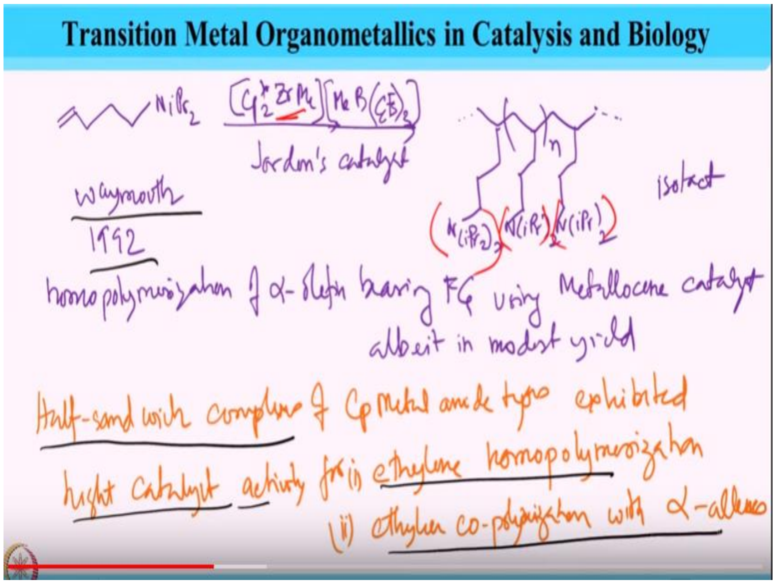

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Waymouth
1992

homopolymerization of α-olefin bearing FG using Metallocene catalyst
albeit in modest yield

Half-sandwich complexes of Cp metal amide types exhibited
hight catalyst activity for (i) ethylene homopolymerization
(ii) ethylene co-polymerization with α-alkenes

Like that it goes, and this is the repeat unit. So the good thing is this was reported by Waymouth in 1992 and what this work is about his work is about homo polymerization of alpha olefins bearing functional group using metallocene catalyst and these were isotactic albeit in modest yield. Now this is a interesting result because these for the first time showed that for using metallocene catalyst these poisoning of the metallocene catalyst with this kind of functional group did not does not happen that significantly and one is able to obtain this homo polymerization of alpha orphan functionalized polymer in large yield.

Now that is a significant discovery and that led to the discovery of an important catalyst which are called which are half sandwich complexes and which are called constrained geometry catalysts. Half sandwich complexes of CP metal amide types exhibited a high catalyst activity for ethylene homo polymerization and its highly copolymerization with alpha alkenes.

Now this was a interesting discovery the Waymouth discovery way back in 1992 which sort of said that the metallocene based complexes are indeed tolerant towards functional group and as a result of further modification led to extremely active half sandwich complexes which showed very high catalyst activity for ethylene homo polymerization as well as ethylene alpha olefin copolymerization.

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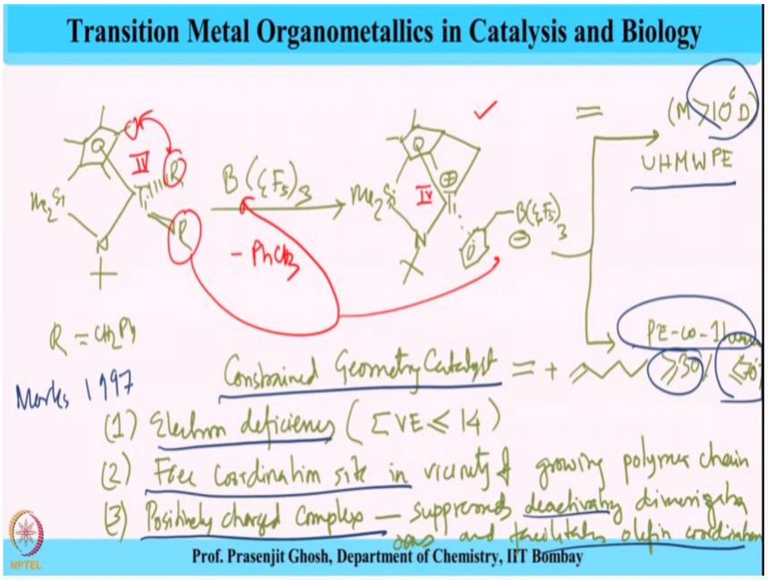

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R = CH2Ph

Marks 1997

Constrained Geometry Catalyst

(1) Electron deficiency (ΣVE ≤ 14)

(2) Free coordination site in vicinity of growing polymer chain

(3) Positively charged complex — suppresses deactivating dimerizations and facilitates olefin coordination

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Let me illustrate this with a particular example where R = CH2 pH and the here titanium is in +4 state and these gives the following Me2si t-butyl titanium actually there is a activation of the methyl group as its shown here and overall there is a positive charge and the benzyl group is abstracted on boron which has a negative charge. So overall this is a titanium 4 compound but its cationic in nature and there is this anion and in the course of formation of this the first is the benzyl abstraction which goes on to boron as is observed over here.

And the second is elimination of - pH CH 1 benzyl group abstracts activates a methyl proton the other one activates a methyl proton and eliminates as toluene to give these cationic complex now these cationic complex is extremely a good catalyst both for ethylene as well as for polyethylene which ethylene it could produce molecular weight greater 10 to the power 6 dalton and ultra-high molecular weight polyethylene and with olefins it could do polymerization.

So this is extremely good catalyst for polyethylene copolymer 1 hexene greater than 30% yield this is 30 percent incorporation and hexene less than 70% incorporation. So extremely good catalyst for polyethylene as well as alpha olefin incorporation and this catalyst is called constraint geometry catalyst. It has 3 features the first one is electron deficiency this species has total valence electron less than equal to 14 extremely electron deficient species.

The second there is a free coordination site in presence of in vicinity of a growing polymer chain and third is a positive charge complex and this prevents suppresses deactivating dimerization process reactions and facilitates olefin coordination. So now these are very important notable features of this constraint geometry catalyst that is extremely little deficient then it has a free coordination site and also being positively charged that it suppresses the activation pathway and facilitates olefin bonding.

And these are so good that it could produce ultra-high molecular weight polyethylene polymer of about a million molecular weight huge molecular weight and also it could produce ethylene 1 hexene copolymer with about 70 percent incorporation of ethylene and 30 percent incorporation of polyethylene. So this is a important example, and this was reported by Marks Tobin professor Tobin marks in 1997.

Extremely good catalyst and the fourth feature of this is that it has a steric bulk that also takes care for this alpha high molecular weight polymer. This is illustrated I have just spoken about and another important quality is that so we have spoken about copolymerization of 2 units where this constraint geometry could polymerize ethylene as well as alpha olefin and then tar polymer or polymerization of 3 units.

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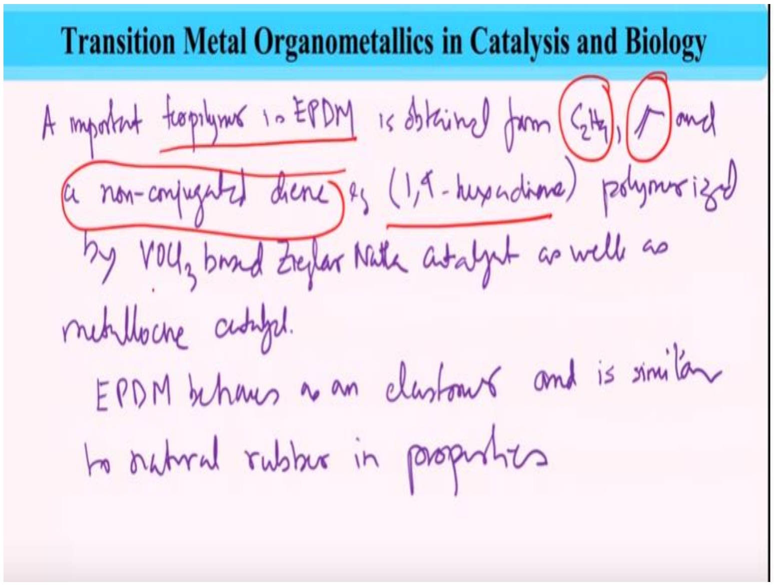

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A important terpolymer is EPDM is obtained from C_2H_4, and a non-conjugated diene eg (1,4-hexadiene) polymerized by $VOCl_3$ based Ziegler Natta catalyst as well as metallocene catalyst.

EPDM behaves as an elastomer and is similar to natural rubber in properties

Important tar polymer is EPDM is obtained from ethylene, propylene and non-conjugated diene example 1,4 hexa diene and these are polymerized by V or CL3 based Ziegler Natta catalyst as well as metallocene catalyst. EPDM behaves as an elastomer and is similar to natural rubber in properties. So here we had spoken about in the previous slide we have spoken about the polymerization of 2 different monomers one is alpha olefins and Italians and then now we are talking about polymerization of 3 different monomers one is ethylene another is alpha olefin and non-conjugated diene and I mean 3 different monomers.

And these are done can be done both as a heterogeneous way where it is your VOCL 3 basically another catalyst as well as by methylation catalyst this EPDM or the tar polymer are elastomeric in nature and we have similar like that of the rubbers. So this is an interesting example where 3 different monomers could be polymerized to obtain something which is of natural rubber. So in this regard another interesting property which we will be talking about is that of poly cyclo olefins.

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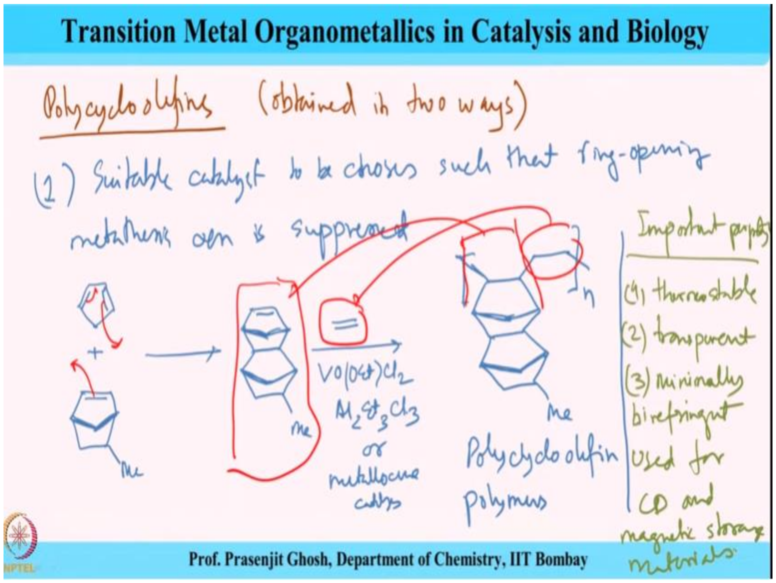

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Polycycloolefins (obtained in two ways)

(1) Suitable catalyst to be chosen such that ring-opening metathesis rxn is suppressed

Important props

(1) thermostable
(2) transparent
(3) minimally birefringent
Used for CD and magnetic storage materials

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Now they can be poly cyclo olefins can be obtained in 2 ways and the first is important suitable it should be a suitable catalyst to be chosen such that metathesis ring opening metathesis reaction is suppressed and then this was reported by Kashiwa in 1988 and the reaction is given as follows. So this the first is a Diels-alder reaction to give this not a cyclic species as is shown here and that in reaction with ethylene and VOVL2 it is CL3.

Or metallocene catalyst gives this cyclic poly olefin which is given over here of ethylene over here and what is seen over here there are 2 things first is the polymerization of the 2 units 1 unit is this alpha living and the other unit. So these 2 units are shown over here this being the first sorry these 2 units are shown over here these being the first and these being the second ethylene unit and this being the first these 2 got copolymerized to give these cyclo poly cyclo olefins polymers and the property wise important properties they are thermostable.

One is a thermo stable the second is transparent and third is minimally by refringent and advantage over poly metallic layers and poly carbonates and used for CDs compacting and magnetic storage materials. So these poly cyclo olefins again co polymerization of 2 olefins one is cyclic another is ethylene to give this and they have important properties like thermo stable, transparent, minimally birefringent and also used for CD and magnetic storage applications.

So with this we come to the end of todays discussion in todays class we have looked into the copolymerization strategy of olefins and alpha olefins and the main challenges arise in this area f from 2 aspects one is that the rate of polymerization of the 2 monomers one is ethylene as well as the other is alpha olefins are different and it so turns out that alpha olefins are more slower than the olefins in terms of conventional Ziegler Natta catalyst.

However, in using metallocene catalyst one can have less acute difference of the activity of alpha olefins as well as ethylene and what we have discussed today is about the advent of constraint geometry catalyst which could produce ultra-high molecular weight polyethylene of about higher than one-million way Doulton and also it could successfully copolymerize ethylene and hexene with about higher incorporation about 70% or greater incorporation of hexene and about 30%.

So incorporation of ethylene in its copolymer we have also spoken about moving going beyond polymerization of 2 monomers to polymerization of 3 monomers and we have spoken about our product tar polymer from ethylene propylene and one for hexa diene and then finally we have looked into poly cyclo olefins which are usually which are material of importance for magnetic applications they are thermostable transparent and minimally bi refrigerant and they are produced by 2 pathways.

We have discussed one of them which involves using catalysts that will not promote ring opening metathesis reactions and hence first there we have seen one example by Kashiwa where first Diels-alder reaction and subsequent polymerization with VOETCL2 and presence of aluminum ethyl reagent or materialism catalyst that could give these poly cyclo olefin polymers. So with this we come to an end of todays class more on discussion about various applications of these copolymerization with olefins and alpha olefins as well as with functional monomer as we continue the discussion in the next class till then goodbye and thank you.