Metallocene and Metal-Carbene Based Organometallic Compounds as Industrially Important Advanced Polyolefin Catalysts

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Lecture 40

Industrially Important Polymers by ROMP: Recent Development and Scope; Overall summary of this course

Hi students. Welcome to our last class of Metallocene and Metal-carbene Based Organometallic catalysts for Industrially Important Polyolefin catalysts.

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NPTEL ONLINE CERTIFICATION COURSES

Lecture 40: Industrially important polymers by ROMP: Recent development and scope.

Overall summary of this course: What did we learn?

Today, we will discuss the in some of the industrially important polymers which are synthesized by ring opening metathesis polymeration by different metal carbene catalysts. And so far, what we have discussed? We have discussed very elaborately about the different type of ring opening, different type of alkene metathesis reactions. Then we have discussed that what is ring opening metathesis polymeration, what are the catalysts involved.

And we very deeply we have discussed that what are the metal carbene complexes, what are the category of the complexes, what the electronic properties, what is the designing of the different ROMP catalysts. And we have extensively discussed the mechanism of ROMP polymers. Today we will discussed mostly some of the industry important polymers which are actually achieved by reopening metathesis polymerization reactions. So, let us start.

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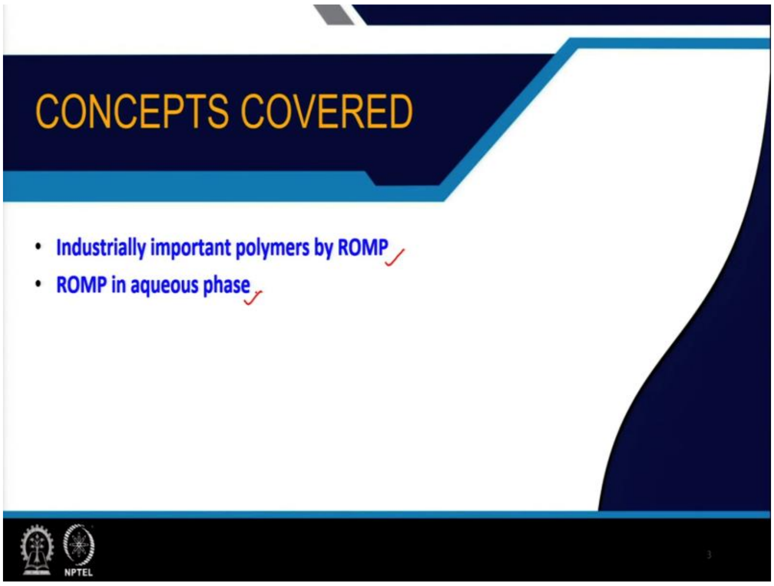
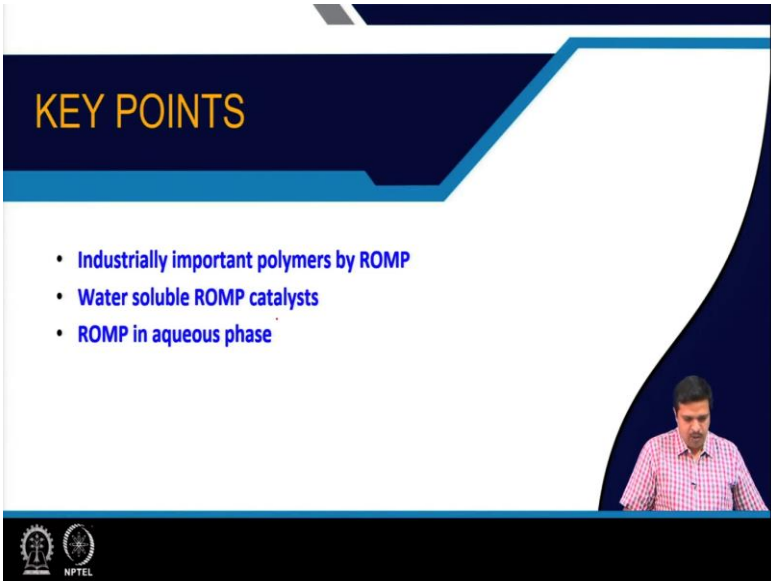


CONCEPTS COVERED

- Industrially important polymers by ROMP ✓
- ROMP in aqueous phase ✓



KEY POINTS

- Industrially important polymers by ROMP
- Water soluble ROMP catalysts
- ROMP in aqueous phase

So, today we will cover the concept of industry important polymers by ROMP and another very interesting and industrially viable processes that ROMP in aqueous phase. Why it is important? Because you know that organometallic catalysts are generally not water, not air stable or moisture stable.

So, it actually limits our uses in at ambient conditions and which are basically kind of a negative of, if you want to sell it as a industrial method. So, we have to for a practical implications, my catalyst should be stable at ambient condition and the reactions or polymerization reactions if we can do in the universal solvent like water then our process will be much cheaper and it will be more greener. So, the recent development and how we can convert or how we can design the catalysts for aqueous phase polymerizations that we will discuss. Very interesting and very just a little bit tuning of the catalysts we will discuss.

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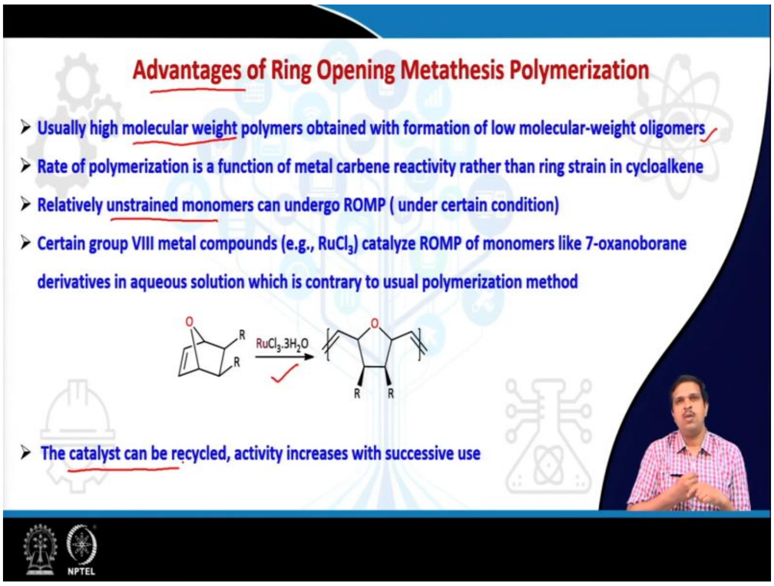

Advantages of Ring Opening Metathesis Polymerization

- Usually high molecular weight polymers obtained with formation of low molecular-weight oligomers
- Rate of polymerization is a function of metal carbene reactivity rather than ring strain in cycloalkene
- Relatively unstrained monomers can undergo ROMP (under certain condition)
- Certain group VIII metal compounds (e.g., RuCl$_3$) catalyze ROMP of monomers like 7-oxanoborane derivatives in aqueous solution which is contrary to usual polymerization method
- The catalyst can be recycled, activity increases with successive use

So, you know that we have so far discussed what are the advantage of the ring opening metathesis polymerizations, we have realized that ROMP one of the very versatile method in polymerizations. There are a lot of advantages which are and that is why it is becoming very popular, not even in the academic, in the lab but also in the industries.

So, many industrial process are based on the ring opening metathesis polymerizations by different type of catalysts. So, there are some points I have here pointed out like usually as we have already discussed that this polymers is living in nature. So, you can get a high molecular weight polymers.

And not only that, you can also tune the architecture because as it is living, you can make the different type of architecture polymers like block copolymers or other type of functional polymers. These are also you will see that these ROMP by that metal carbene categories are compatible with other functional groups attached in the monomer.

Another you will see relatively unstrained monomers can undergo reopening metathesis polymerization, you will see that metal carbene reactivity is more important than the ring strain because if the ring strain is the prime factor then norbornene or octane which have a very less linked strain should not undergo the ROMP, but we have seen obviously yes, the monomer, cyclic alkene, cyclic olefin monomer which has more ring strain that obviously we will go polymerase easily but it is also shown that the monomer with less ring strain can also undergo the polymeration.

So, metal carbene reactivity is one of the prime factorial here and that is why you different type of catalysts have been developed time to time like first generation Grubb’s to second generation like that. And you will see that many simple or cheap catalyst have also been developed because you see if you want to make a process industrially viable then the catalyst will be cheap, synthetically should be ease and also the handling of the catalyst should be very easy, otherwise, it will not be industrially viable process.

So, time to time, you will see that is one of the example which you will see that methane alkyl can also do the polymerization easily to get this kind of a ROMP polymers. And most importantly, to make it a industry vaiable, the catalyst must be reused, recycled and here yes, this also qualifies this criteria. So, it is basically you will see this is one of the most of the criteria to be industrially vaible is qualified by the this kind of metal carbene catalysts.

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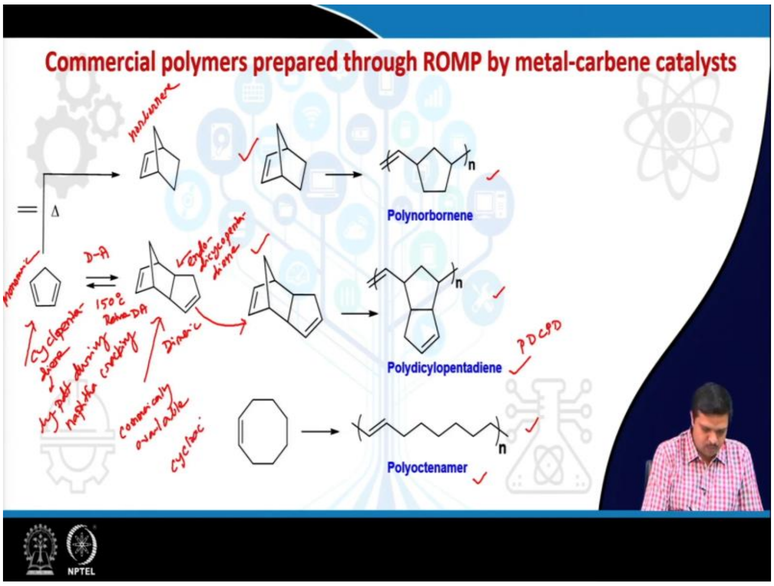

Commercial polymers prepared through ROMP by metal-carbene catalysts

So, these are the, today, as I told that I will highlight, although we have discussed in other in previous classes in discrete way the monomers like this, I want to highlight how and why these are industrially important. And these actually produce this, particularly, these three polymers are produced commercially by different polymer’s industries.

First one is you see the polynorbornene, we all know. This one is the polydicyclopentadiene and this is the polyoctenamer. We will discuss in more depth. You will see that in very interesting and why these polymers are so important, first two polymers, why these are so industrially viable because you will see that this the monomer, for the two monomer, this one and this one, you will see, these two monomers are actually linked with the cyclopentadiene.

So, this is actually cyclopentadiene. And how do we get it, any idea? We actually get it as a byproduct during naphtha cracking or petroleum isolation industry. So, that means it is actually by product. So, if this can be used for to have a other valuable products like here you will see that commercially important polymers then the whole process will be much cheaper.

However, the cyclopentadiene you cannot really buy commercially because it undergoes a disorder reactions. This is you know that in you have a disorder reaction. So, say it undergoes a cyclaeration and make a dimeric. So, this is a monomoric form and this is actually diameric form.

However, you can convert to dimeric to monomoric very easily just by heating 150-degree centigrade temperature, you will get the, so, it is basically that happens the retro disorder reactions. So, this is commercially available. That means why it is commercially available? because although we get the cyclopentadiene by the cracking of the naphtha process, it actually spontaneously diverges into dicyclopentadiene and this is actually the isomer you know that it is a two isometer, one is the indo one is the exo.

So, this is actually the indo dicyclopentadiene. So, you will see that this one is the monomer for the polydicyclopentadiene. This is also called the PDCPD, polydidicyclopentadiene. And here you will see that this cyclopentadiene, if you react with ethylene, it undergoes the reactions and forms the norbornding.

So, this is actually normally, so, you see that from a single substrate I am getting the two different monomers and the main precursor is actually obtained from a as a byproduct of nafta process. And another one you will see that this is also commercially important that is the polyoctenamer. And here what is your monomer? This is actually cyclooctane.

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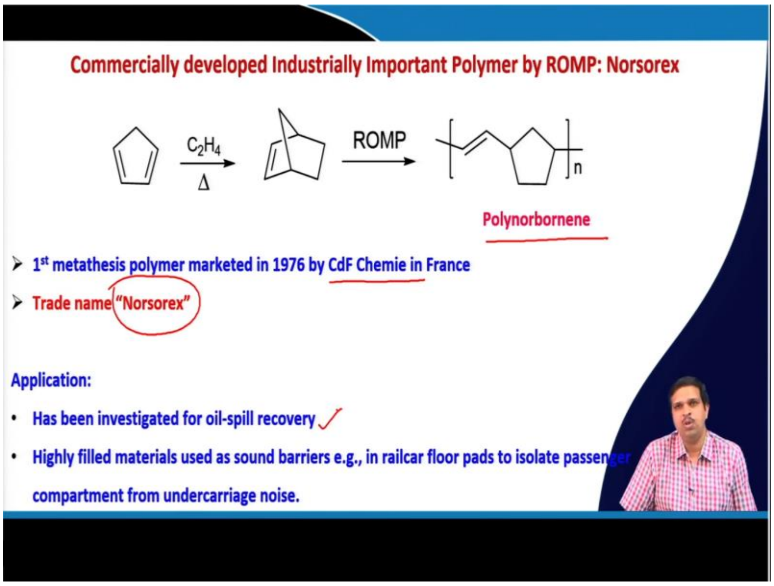

Commercially developed Industrially Important Polymer by ROMP: Norsorex

- 1st metathesis polymer marketed in 1976 by CdF Chemie in France
- Trade name "Norsorex"

Application:

- Has been investigated for oil-spill recovery ✓
- Highly filled materials used as sound barriers e.g., in railcar floor pads to isolate passenger compartment from undercarriage noise.

So, let us discuss in little more depth about this commercial available polymers, commercially important polymers. These are as I told this polynorbornene, this is first marketed by the France chemical company is called CdF Chemei back in 1976 and the trade name is Norsorex. So, this is actually named as the polynorbornene is nothing but the Norsorex. This is the trade name.

And you see that there are a lot of different applications, even though it is very important and valuable. Most of the, one of the interesting and important application is used in the oil-spill recovery and also it is sound, it is used as a sound proof materials, very good sound properties it has. And this is one of the heavily produced polymers by ring opening metathesis polymerizations.

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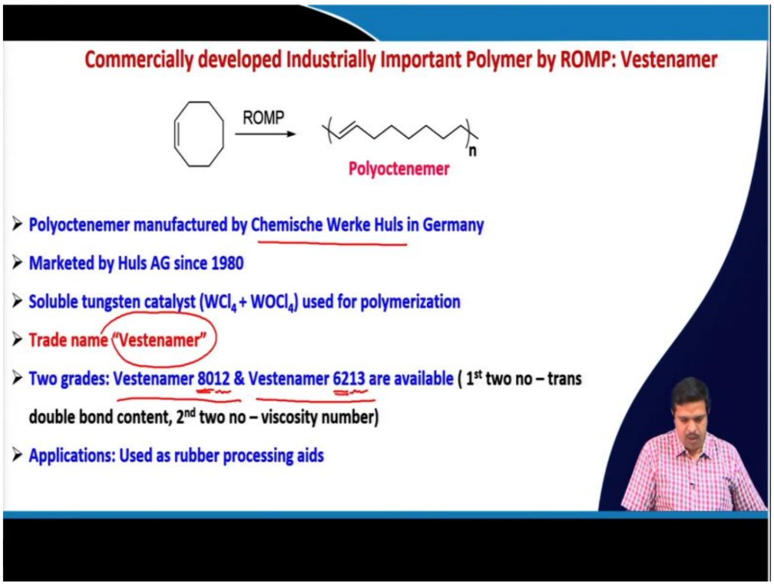

Commercially developed Industrially Important Polymer by ROMP: Vestenamer

- Polyoctenemer manufactured by Chemische Werke Huls in Germany
- Marketed by Huls AG since 1980
- Soluble tungsten catalyst (WCl_4 + $WOCl_4$) used for polymerization
- Trade name "Vestenamer"
- Two grades: Vestenamer 8012 & Vestenamer 6213 are available (1st two no – trans double bond content, 2nd two no – viscosity number)
- Applications: Used as rubber processing aids

So, this is one of the another polyoctenamer. So, this the trade name is the Vestenamer and this is actually marketed by first synth structure by Chemische Werke Huls in Germany and marketed by Huls AG since 1980. The catalyst is basically molybdenum-based catalysts. And you will see that there are different type of polyoctenamer are produced.

There are some typical trade names like Vestenamer 8012 Vestenamer 6213. So, here the first two digit actually you see it is actually tells the double bond character, how much percentage of development character, how, so the here it is like 80 percent and this one you will see 62 percent like that, average double bond percentage. And the last two number is the viscosity number.

So, this is the viscosity number, you would see. So, this is the kind of a convention to identify the different type of Vestenamer polymers and is used as a rubber processing aids and different type of like we have previously discussed that the applications of polyisoprene, polybutadiene, those kind of. So, a similar category of the polymers, the polyoctenamer.

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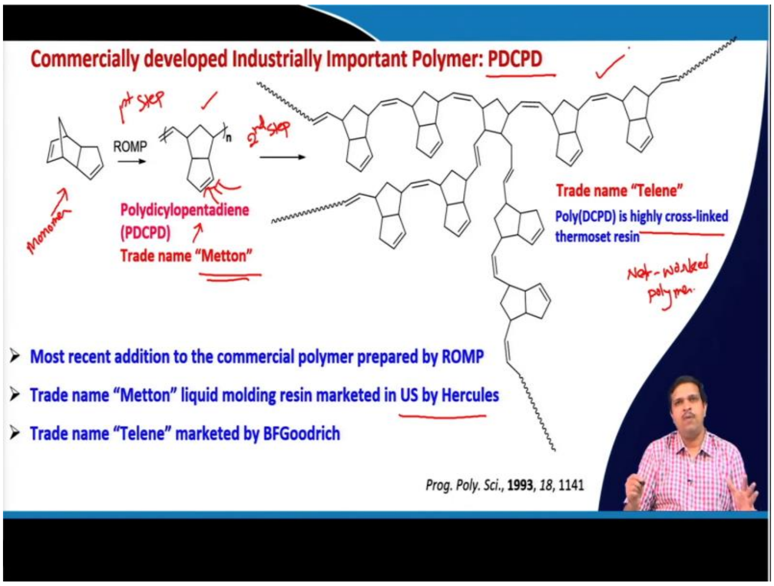

Commercially developed Industrially Important Polymer: PDCPD

Polydicylopentadiene (PDCPD)
Trade name "Metton"

Trade name "Telene"
Poly(DCPD) is highly cross-linked thermoset resin

Net-worked polymer.

- Most recent addition to the commercial polymer prepared by ROMP
- Trade name "Metton" liquid molding resin marketed in US by Hercules
- Trade name "Telene" marketed by BFGoodrich

Prog. Poly. Sci., **1993**, *18*, 1141

And most important and the recent addition of the ROMP polymers is basically PDCPD that is the polydicyclopentadiene polymer. So, the you will see that this is the dicyclopentadiene monomer and this is my polydicyclopentadiene PDCPD, the trade name is as Metton and this is marketed by the US companies Hercules and you will see that and this is very interesting in nature because you will see that this one is polymerises but you have a another alkene bond.

This alkene bond you can further take a advantage of this alkene bond and you can make you can make a different type of polymers functionalize or you can take the advantage of the alkene for fine tuning of the property, fine tuning of the synthesized Metton polymer that is the one type of PDCPD.

Now, this is you can consider as the first step, and the second step if you have catalyst is quite active then it can also do the second step and here you will see that it is actually you will do the polymerizations here. So, you will make a highly networked, highly cross linked or network polymer. The trade name of this one is Telene.

So, first one is the Metton, this one and this one is the Telene. And the properties as you see that these are the Telene is nothing but the cross-linked version of the Metton that is the PDCPD. So, the obviously, the properties will be different. The most important property of the this kind of PDCPD is the stiffness and the toughness.

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Commercially developed Industrially Important Polymer

Property	Units	"Metton"	"Telene"
Tensile strength	Psi	6200	6500
Modulus	Psi	2,61000	240,000
T_g	°C	138	155

- ✓ 1.5 inch thick poly-DCPD resin prepared with ruthenium technology is impenetrable to 9 mm bullets
- ✓ Block copolymers made up of polynorbornene and decaborane useful in the synthesis of nano structured boron carbonitride
- ✓ Possess excellent resistance to creep

- Uses of Poly-DCPD resins

Body panels for truck

Agricultural and earth moving equipment

Cell cover for chloroalkali plants

Large waste containers

So, here you will see that this is the Metton and this is the Telene. Telene is the cross-linked. You will see that inside strength is quite different for this one is 6200 Psi; this is 6500 and last transition temperature you will see that this is 138, this is 155. These polymers are heavily used in different segments like automobiles, mechanical industries like that.

Here you will see body panels for truck, cell cover for different type of industrial plants, different types of equipments and most importantly that you will see that 1.5 inch of poly-DCPD resin is actually can prevent from the bullet. You will see that 9 mm bullet. So, it is so strong in nature.

And even you will see the block copolymers of polynorbornene and decaborane useful in synthesis of nano structured boron carbonitride. That means the polymer you will see that how stiff and strong it is. So, these are polymers are very much used in our daily life, the PDCPD category and all are synthesized by the metal carbene based catalysts.

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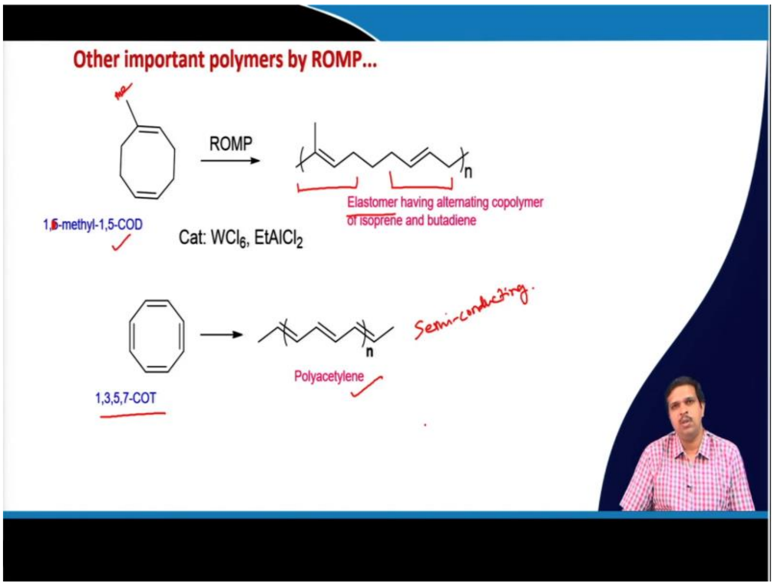

Other important polymers by ROMP...

Other important polymers like you will see that the first one very much similar like norbornene, here you will see that the 1 5 methyl, this is the methyl group, 1 5 methyl, 1 5 cyclooctadiene, sorry, this is not 1 methyl, 1 5 cyclooctediene. So, here you will see the ring opening polymerization will give a elastomers having alternate copolymers of isoprene and butadiene.

Here, you will see this part is isoprene and this part is the butadiene. So, is a kind of a you will see that you no need to may no need to charge to monomers, that is the isoprene and Butadiene. You are taking a single monomer and you are getting a alternating copolymers of isoprene and butadiene which is a good elastomeric, have a elastomeric properties. Catalyst are again the tungsten base catalysts.

And here you will see that 1 3 5 7 cyclooctatatraene because you have a four bonds and you are getting a polyacetylene type polyacetylene polymers. You know that these polymers are semiconducting in nature. And one of the what research topic is the developing the semiconductive organic polymers for flexible photovoltaic devices or OLED devices.

So, these are you will see that semiconductive polymers can also be synthesized by ROMP, Ring Opening Metathesis Polymerization. So, these are really you will see that there is no doubt that these are versatile polymers with versatile properties, and functional groups can be synthesized by the ROMP catalysts.

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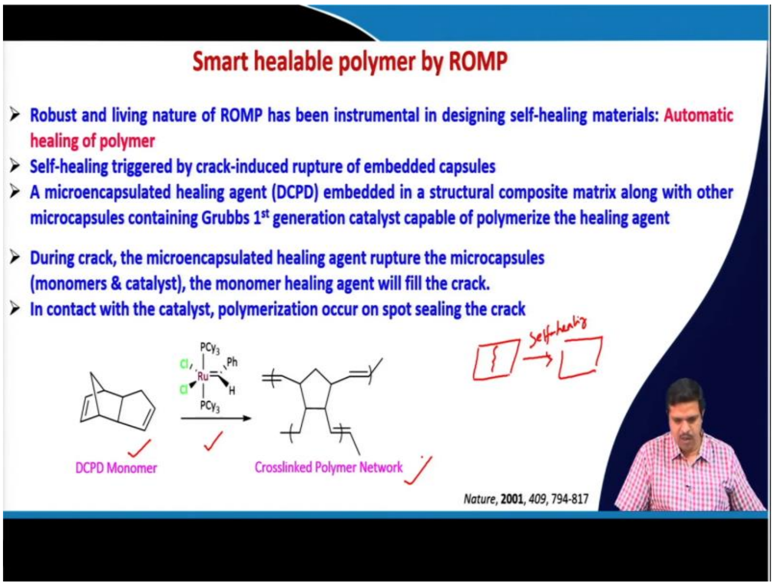
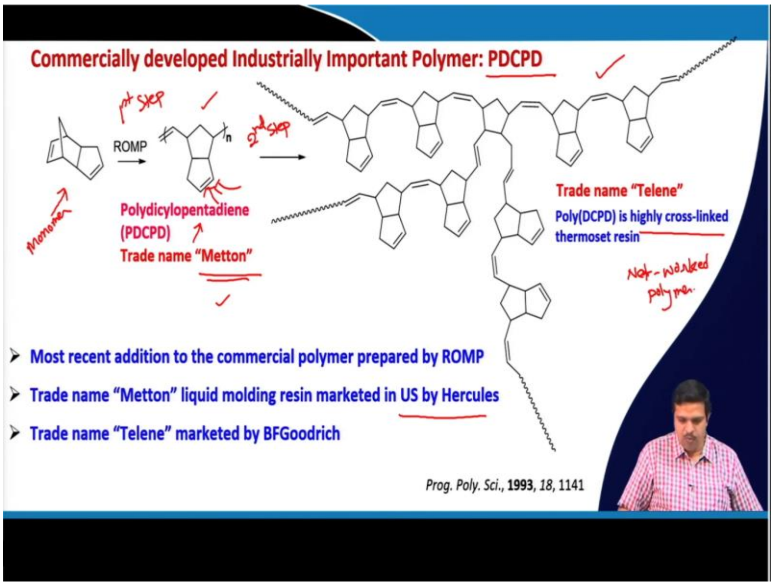


Smart healable polymer by ROMP

- Robust and living nature of ROMP has been instrumental in designing self-healing materials: Automatic healing of polymer
- Self-healing triggered by crack-induced rupture of embedded capsules
- A microencapsulated healing agent (DCPD) embedded in a structural composite matrix along with other microcapsules containing Grubbs 1st generation catalyst capable of polymerize the healing agent
- During crack, the microencapsulated healing agent rupture the microcapsules (monomers & catalyst), the monomer healing agent will fill the crack.
- In contact with the catalyst, polymerization occur on spot sealing the crack

Nature, 2001, 409, 794-817



Commercially developed Industrially Important Polymer: PDCPD

- Most recent addition to the commercial polymer prepared by ROMP
- Trade name "Metton" liquid molding resin marketed in US by Hercules
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Prog. Poly. Sci., 1993, 18, 1141

And not only that one, you will see that there is one very interesting and what is I call that applications or the thought process, how we can make my polymer is smart. Here, you will see that this is the cyclodipentadiene monomer and synthesized you will see PDCPD that is the Metton and then you can use utilize the leftover alkene moiety to make it say kind of a grafted polymer or cross linke polymers.

Now, with these fantastic properties, we can also make a self-healable smart polymers. What is self-reliable? You will see that many times what happens the polymer surface like if we have a polymer surface like that one, it may give a crack like that. Now, this is dangerous because if it happens in a very kind of a sophisticated applications, as example, lets if it is like a aircraft or let us say in a space craft. Then what will problem?

There will be permanent damage. So, there will be some mechanism to heal it, self-heal it so that this again it become a normal things. This is called the self-healing and becomes. So, this heal will be cured automatically. So, with this one, you will see if I incorporate this monomer in my main polymer skeleton and then if I treat it like this kind of a catalyst then due to the network structure, then again it will be healed.

So, that means, suppose, this is initially it was my a homogeneous surface and then due to cracking, it cracked like this one, and then if I have a self-healing properties then again it will be cured. So, this kind of a design you can do to make the polymers as a self-healable polymers. So, this idea is really I mean fantastic and nowadays different type of smart self-healable polymers are being developed.

This is another one of the very successful strategy by incorporating the Ring Opening Metathesis Polymerizable group and charged with the ROMP catalyst. Because ROMP catalyst you know that is this metal carbene catalysts are very efficient and does not really undergo any deactivation very easily. So, this is very kind of a fruitful. So, this is one of the very recent development using the ROMP.

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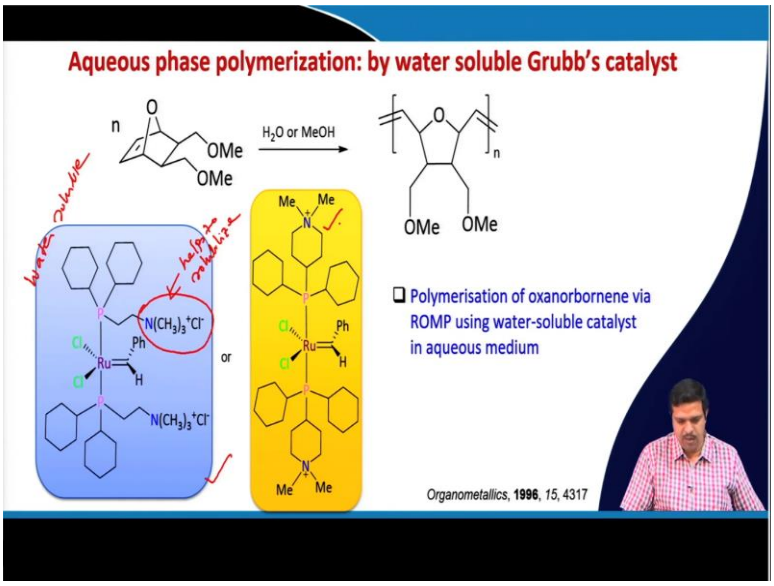

Aqueous phase polymerization: by water soluble Grubb's catalyst

- ☐ Polymerisation of oxanorbornene via ROMP using water-soluble catalyst in aqueous medium

Organometallics, **1996**, *15*, 4317

Another as I told that development in this domain is the aqueous phase reopening metathesis polymerization. This is again is very important because if I can do the polymer, polymeration in just aqueous phase, avoiding the expensive solvents like tetrahydrofuran, chloroform or other stallowing, hexanes then that whole process will be cheaper. So, like here, so what you have to do? I have to make my catalyst water soluble. And how I can do?

I have to make the neutral complex to a ionic complex then only the, so like a salt, then only it will be should be soluble in aqueous phase and it can be used for aqueous phase polymerization. Obviously, your monomer, if it is soluble in aqueous then the process will be more viable and easy.

One of the basic design, you will see how beautiful it is designed. So, here, you will see that it can it the water nerdinary amine have been used so that it actually helps to solubilize. So, the Grubb's catalysts have been, the Grubb's first generation catalyst have been modified to make the water soluble catalyst. So, many this kind of catalyst have been developed like you see this one, this again, the quaternary ammonium centers which actually helps to solubalize in water. And this is one of the very recent development and achievement by these ring opening metathesis.

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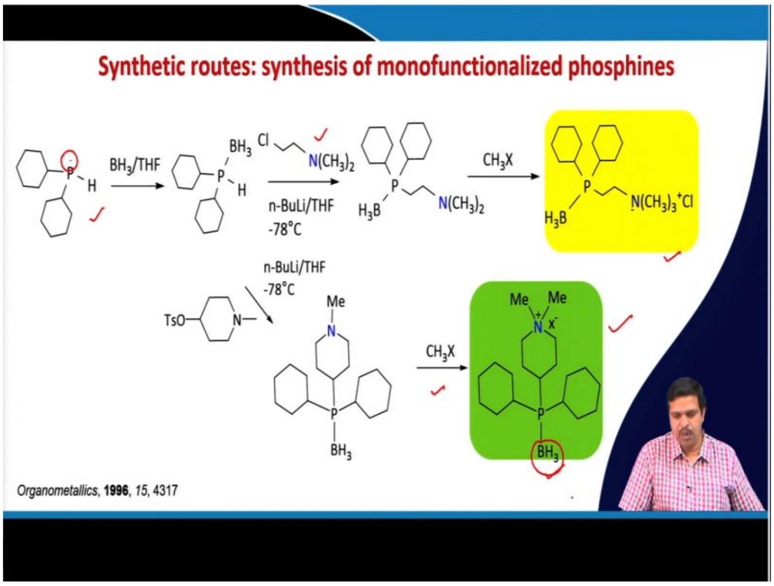

Synthetic routes: synthesis of monofunctionalized phosphines

Organometallics, **1996**, *15*, 4317

These are one of the pins strategy to how you will modify your complex, modify your ligand and then you can make it water soluble. So, like this one you will see that this phosphine you can functionalize by these chloramines and then you make this one and then ultimately you will get the, after the methylation, the last part, you will get that this amino functionalized phosphine ligands. So, after that.

So, this part, the BH3 is basically to make it stable during the whole functionalist process because it has a loan pair. It is like a protective group. So, if you do not charge with BH3, there may be side reactions. So, it is better to protect with BH3 to kill the basicity of this first of the phosphine and then you make the protected version and then you quarterize.

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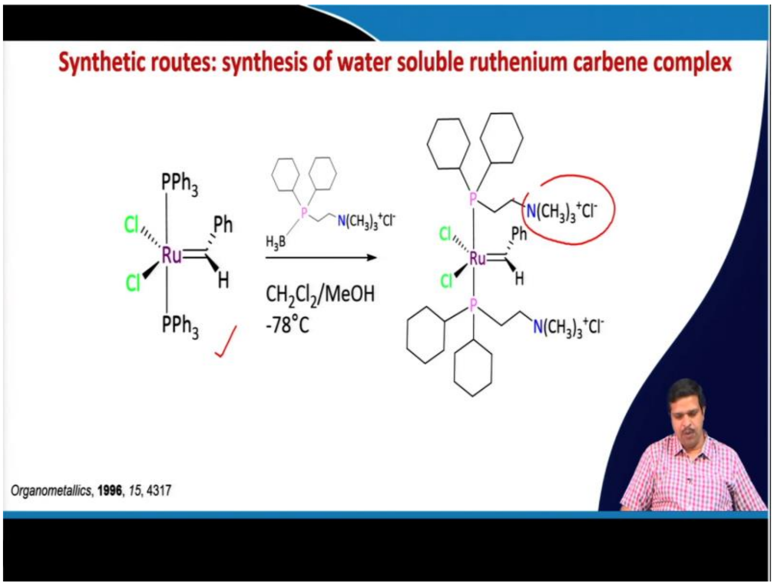

Synthetic routes: synthesis of water soluble ruthenium carbene complex

Organometallics, **1996**, *15*, 4317

And then this ligand, the protected version of this phosphine ligands, now you charge with the precursor of the Grubb’s first generation catalyst and then you will get the catalyst which is water soluble in nature due to this ionic complex. So, this you will see that how a just a fine designing of the catalyst can make it water soluble and this one then can be used for the ROMP polymerization in aqueous phase.

So, so far what we have discussed? I had just give a principle how you can make the catalyst or convert the ROMP catalyst from organic phase to the aqueous phase. So, now I am sure that you have realized that how metal carbenes have versatile reactions and applications. In the beginning of the metal carbene I told that this is a like a single key of different locks. You will see that how this a one single catalyst or modified catalyst can be used for different purposes.

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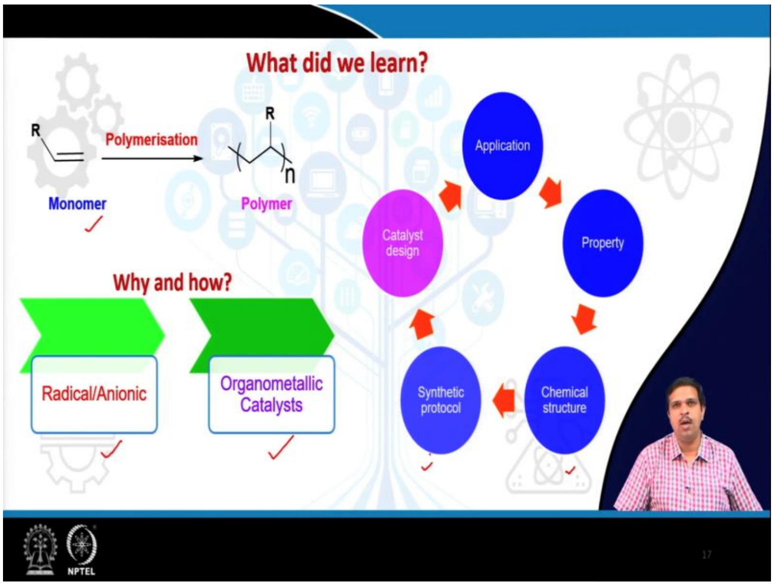

What did we learn?

R

Polymerisation

R

n

Monomer ✓

Polymer

Why and how?

Radical/Anionic ✓

Organometallic Catalysts ✓

Application

Property

Chemical structure ✓

Synthetic protocol ✓

Catalyst design

So, in just a next two minutes what I want to do, I just want to give a overall summary of what we have learned in the whole journey of this course. So, the whole concept of of this course is basically to discuss the polymerization of this type of monomers, that is the alkene monomers to make the polyolefin.

You will see that different type of catalysts we have discussed and why to develop the different catalysts, because you know that we already there is a lot of catalyst or a lot of initiators for radical, anionic and then why suddenly we needed to develop the organometallic catalyst.

The reason we discussed in beginning of our class that the application and property are very much interrelated. And you know that property again it is very much related to the chemical structure and chemical structure again is very much connected to the synthetic protocol. So, what actually we are getting from a radical or ionic that may not be the same with the orgonomettalic catalyst and actually it is true. We have realized. We have now learned that how the orgonomettalic catalysts give a different type of polymers, although the chemical structure is same but the properties are different. So, those we have learned successfully in this course and I hope you have enjoyed it.

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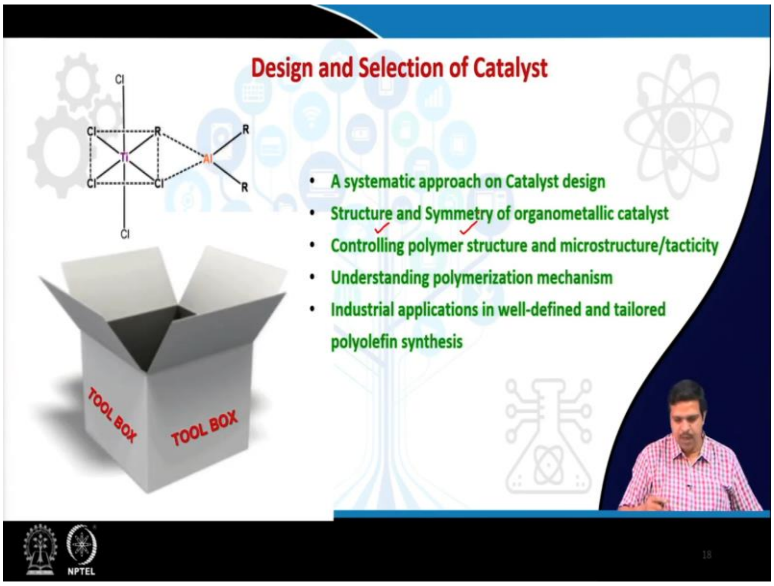
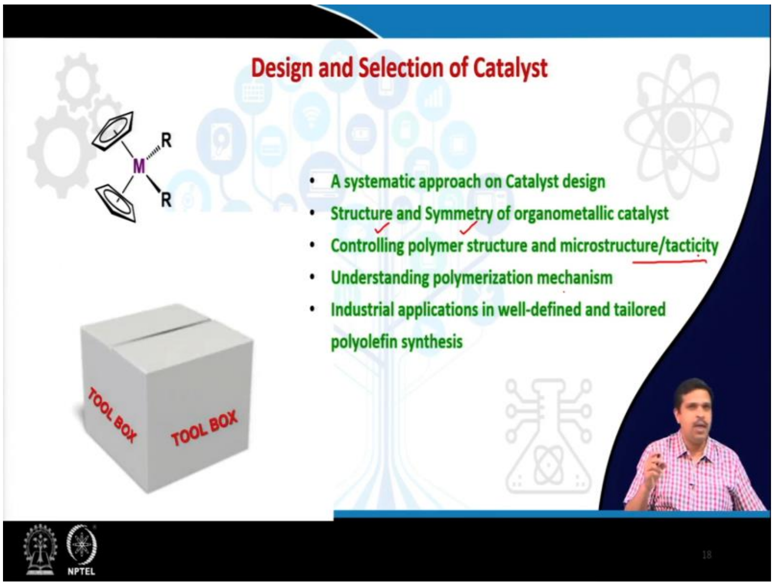


Design and Selection of Catalyst

- A systematic approach on Catalyst design
- Structure and Symmetry of organometallic catalyst
- Controlling polymer structure and microstructure/tacticity
- Understanding polymerization mechanism
- Industrial applications in well-defined and tailored polyolefin synthesis



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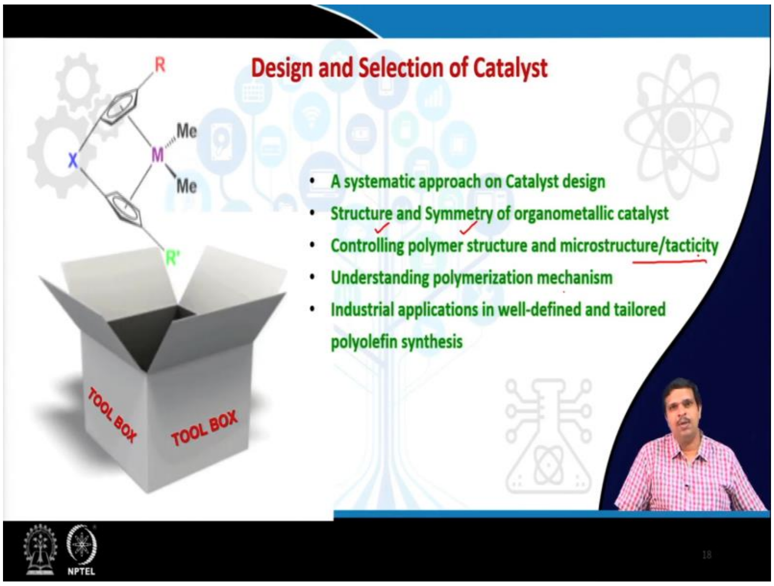

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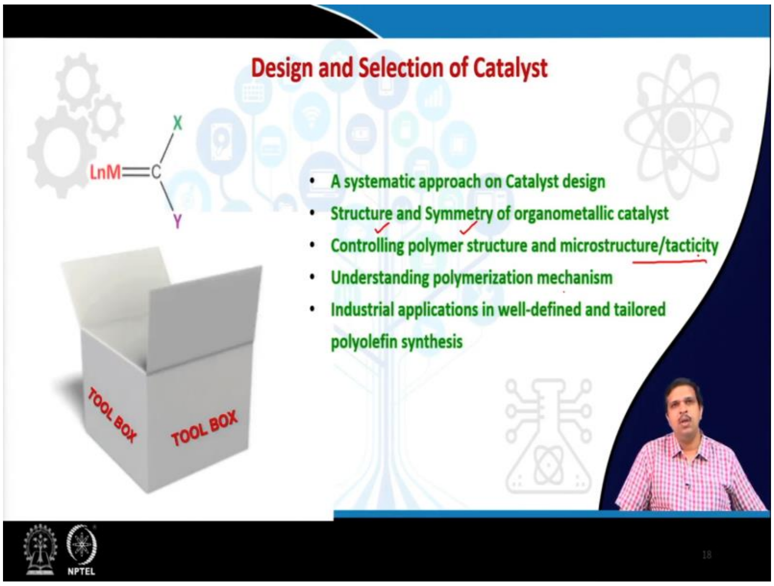

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So, very specifically I can tell that we have discussed more the catalyst design, what is the chemical structure of the catalyst, what are the metalas ion presents there, what are the ancillary ligands are there, what is the basic relation between the structure and symmetry and the properties of the synthesized polymer.

The properties brings here the chemical structure of the resultant polymers. Or more specifically, the the stereo selectivity and tacticity of the polymers. So, you now that many most of the catalyst in the orgonomettalic catalyst can very nicely tune the properties, the tacticity of the polymers. As example, if you use a prochiral monomer, as example like propylene or polystyrene, those are the prochiral molecules. And you can see that how tacticity you can control by using different type of catalyst. So, this one we have discussed extensively.

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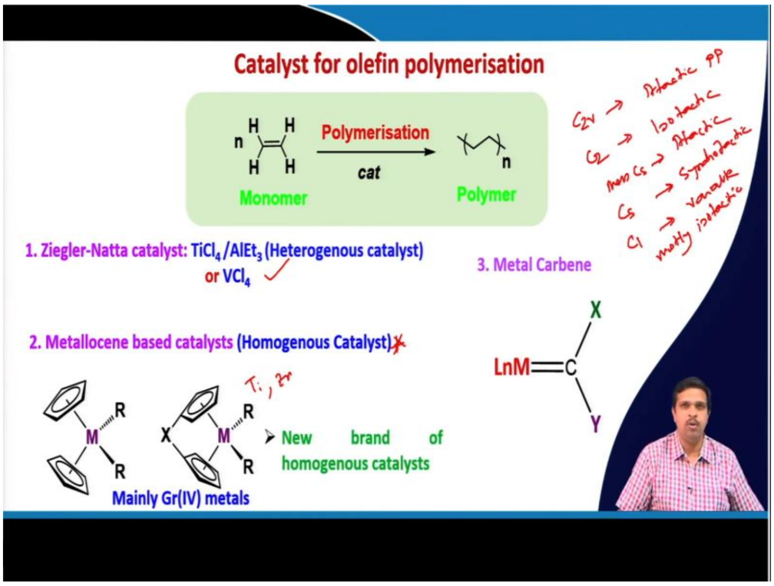

Catalyst for olefin polymerisation

1. Ziegler-Natta catalyst: $TiCl_4/AlEt_3$ (Heterogenous catalyst) or VCl_4 ✓

2. Metallocene based catalysts (Homogenous Catalyst) ✗

Ti, Zr

➤ New brand of homogenous catalysts

Mainly Gr(IV) metals

3. Metal Carbene

C_{2v} → Atactic PP

C_2 → Isotactic

meso C_s → Atactic

C_s → Syndiotactic

C_1 → variable mostly isotactic

As example, you will see that here different type of catalyst we have discussed. Obviously, the Zigler-Natta catalyst discussed to have a basic idea that why it is, although it is very successful but why exactly it is a lacking and what is the necessary to develop different type organometallic catalysts. So, here you will see this is the new brand of organometallic catalyst as a homogeneous mostly. Those are actually dominated by the group 4 metal catalyst like titanium or zirconium and we have discussed extensively that what is the basic and unique properties of bent metallocenes.

The chemical, the bonding, the electronic properties and you will see that how this kind of metallocene compounds are successful in polyoleafin synthesis. And most importantly the controlling the tacticity and stereo selectivity. As example, you will see if you have a C2V then the C2V point group we got the attactic polypropylene. If we have a C2 then we got the isotactic. If we have the meso CS then we got attactic. If this CS then syndotactic.

And if you have a C1 then it is actually variable but mostly isotactic. So, I can choose my catalyst according to symmetry, the metallocene catalyst according to the symmetry, as per my requirement. If I need a atactic, I will choose a catalyst with C2V symmetry. If I need isotactic, I will choose the category which C2 symmetry. If I need to have a syndotactic polymer, I will choose the metallocene with CS symmetry.

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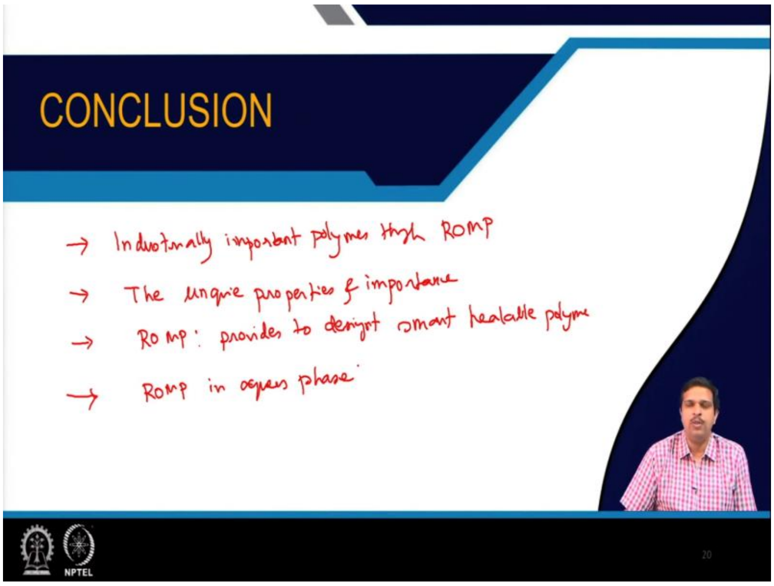

CONCLUSION

→ Industrially important polymers thrgh ROMP

→ The unique properties & importance

→ ROMP: provides to design smart healable polyme

→ ROMP in aqueous phase

So, in conclusion today, we have discussed the industrially important polymers through ROMP, the unique properties of the polymer and importance, why those polymers are so important like PDCPD, polynorbornene, still those are used heavily. And the how ROMP provides to design smart polymers, smart healable polymers and very interesting and that is actually the scope, future scope of this kind of catalyst is the ROMP in aqueous phase. So, industry will like it to make the polymers aqueous phase because it will be more industry vaiable, more economic, more easy to handle.

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REFERENCES

- The Organometallic chemistry of the transition metals by Crabtree, Wiley, Sixth edition, 2014
- Organotransition metal chemistry from bonding to catalysis by John Hartwig, University science books, 2010
- Organometallic chemistry and catalysis by Astruc, Springer, 2007.
- Basic Organometallic Chemistry by Gupta and Elias, University Press, 2010.

So, for this course, these are the most important reference books like Organometallic Chemistry of Crabtree, by John Hartwig, by Astruc, by Gupta and Elias. And with this one I am very much hopeful that you all have enjoyed this course and you have now understood that how, what is the journey.

It is a long journey. It is not like it 3 years, 4 years research. It is a long journey, how to have a efficient organometallic catalyst for the olefin polymerizations and how the industry has been accepted for different type of organometallic catalysts over the time. So, with this, thank you very much and best wishes for your exam. Thank you.