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

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## Lecture 39

## Utility of Metal-Carbene Catalysts in Alkene Polymerization

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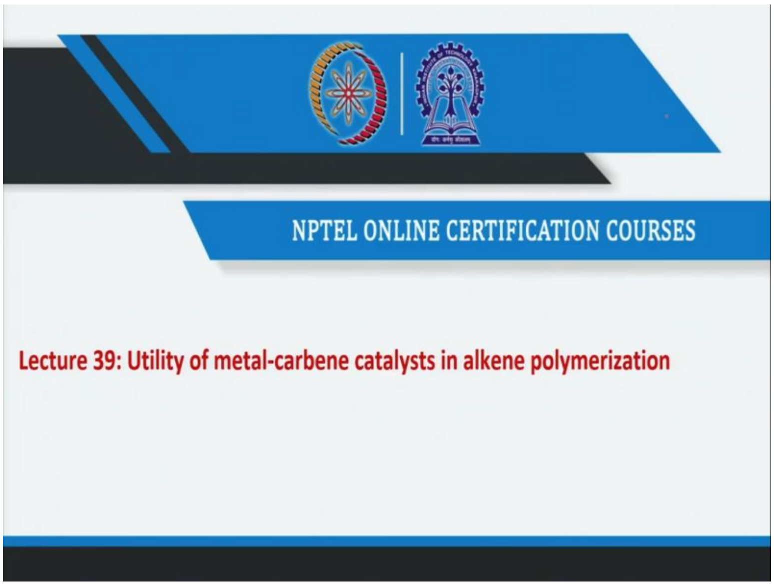

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Lecture 39: Utility of metal-carbene catalysts in alkene polymerization

Students, welcome to our class. Today, we will discuss one of the very interesting topic that is the Utility of Metal carbene Categories in Alkene Polymerizations. So, we have discussed the versatile reactions by the alkene, by the metal carbene catalysts and you saw that different type of alkene metathesis reactions is possible by a single category of metal carbene catalyst like ring opening, ring closing, cross metathesis.

And today, we will discuss the its how applicable it is a ring in the polymerizations and it is the reaction is very much similar what we have discussed in the last class. So, today, we will cover the concept like alkene polymerization by metal carbene catalysts, its scope and obviously, the mechanism.

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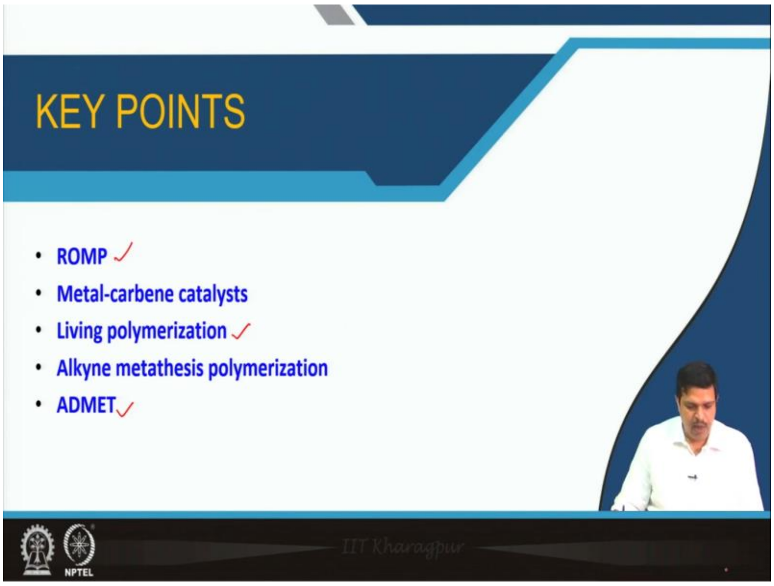

## KEY POINTS

- ROMP ✓
- Metal-carbene catalysts
- Living polymerization ✓
- Alkyne metathesis polymerization
- ADMET ✓

And the key points we will discuss the ring opening metathesis polymerization, its living polymerism nature, how it is living and what is the advantage of is a living nature of this polymers catalyzed by the metal carbene catalysts and also will discuss very much similar but not ROMP, but very much similar polymerization which is also initiated by metal carbene catalyst that is called the ADMET. So, that we will discuss.

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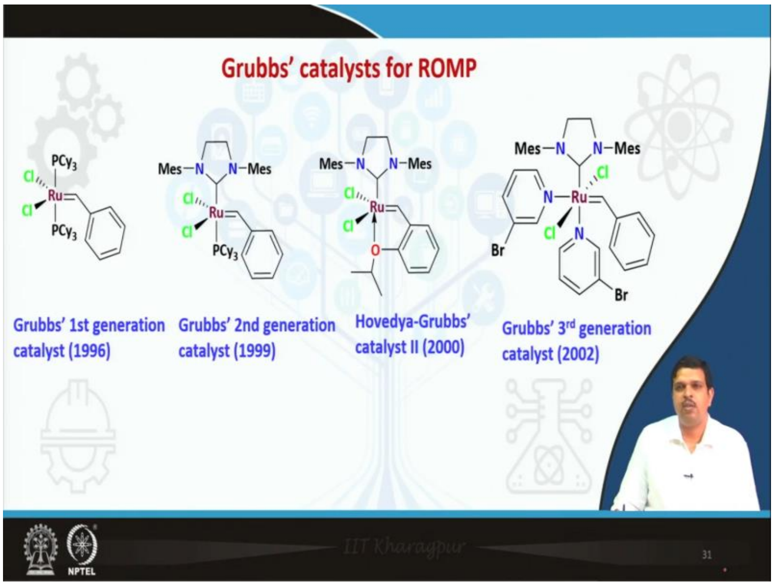

## Grubbs' catalysts for ROMP

Grubbs' 1st generation catalyst (1996)

Grubbs' 2nd generation catalyst (1999)

Hovedya-Grubbs' catalyst II (2000)

Grubbs' 3rd generation catalyst (2002)

So, let us see what are the catalysts which can do the polymerizations.

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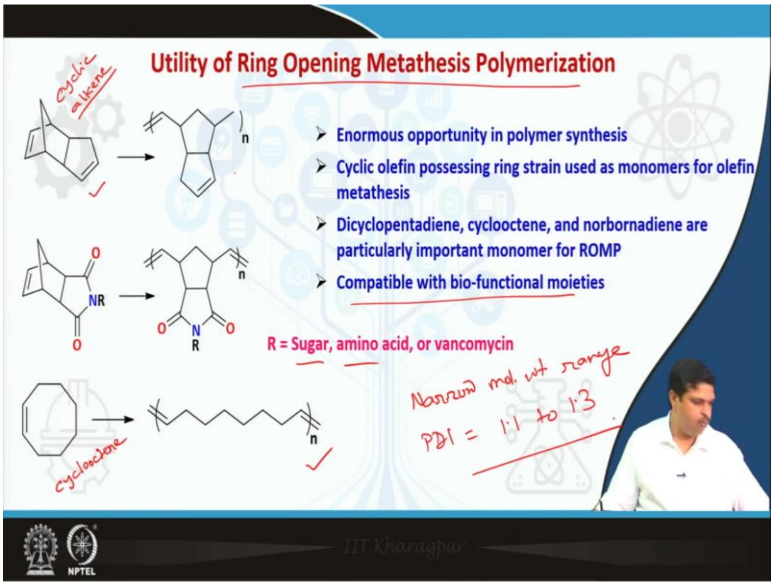


Utility of Ring Opening Metathesis Polymerization

- Enormous opportunity in polymer synthesis
- Cyclic olefin possessing ring strain used as monomers for olefin metathesis
- Dicyclopentadiene, cyclooctene, and norbornadiene are particularly important monomer for ROMP
- Compatible with bio-functional moieties

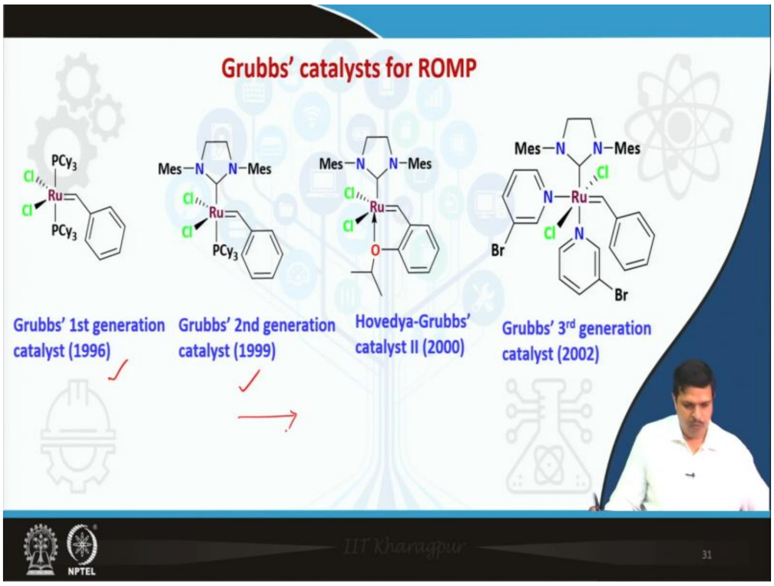
R = Sugar, amino acid, or vancomycin

cyclic alkene

cyclooctene

Narrow mol. wt range

PDI = 1.1 to 1.3



Grubbs' catalysts for ROMP

Grubbs' 1st generation catalyst (1996)

Grubbs' 2nd generation catalyst (1999)

Hovedya-Grubbs' catalyst II (2000)

Grubbs' 3rd generation catalyst (2002)

So, what is the ROMP? First we have we should discuss that ROMP is the Ring Opening Metathesis Polymerizations. So, we have discussed the ring opening metathesis reactions where one cyclic alkene can be converted to an acyclic alkane. So, where it is a very very much similar to the ring opening metathesis but here you will see that we will get the polymer.

So, one example here you see that is a derivative of dicyclopentadiene. So, here you will see that if you use the catalysts like Grubb's catalysts, you will see that it is undergoes the polymerization reactions. Very much similar here you will see that is the cyclooctene. So, this is nothing but cyclooctene.

So, if you take a suitable catalysts which can undergoes, which can initiate the polymerization and you will get this polymer. What are the catalysts? These are the most, these, the catalysts are mostly used for the metathesis polymerization. Here, you see the Grubb's first generation catalysts, second generation catalysts and the reactivity actually increases from left to right.

And you will see that after a few slides I have discussed that how you can choose your catalyst. Suppose, if one alkene, cyclic alkene is very reactive then you can use the Grubb's first generation catalyst if it is moderately reactive or less reactive, we can use the second or third generation Grubb's calories like that.

So, let us here you will see some of the examples here, and why it is so famous? Because the enormous opportunity in polymer synthesis and all it is one of the very key points that it is a compatible with various functional moieties, even the bio-functional groups such as sugar, amino acids like that.

And here you will see if it is this kind of where the R groups are sugar, amino acid then also there is no problem in the polymerization. You can get the polymers with bio-functional moiety by using the Grubb's catalyst or using the metal carbene catalysts. So, here you need, what you need?

You need a cyclic monomer is cyclic alkene and the suitable catalysts. And you have to choose the catalyst according to the ring strain associated with the cyclic alkanes, I will discuss in the in later parts. And one of the very important feature of this or advantageous feature is that the polymerization is living, that I will discuss when I will discuss the mechanism and also the narrow molecular weight range.

That means the PDI is a kind of 1.1 to 1.3, that is actually remarkable. So, by using this, so, it is actually proves that this polymerization is actually living. So, that will discuss. So, from these slides you will understand that this kind of catalyst how it can polymerize the suitable cyclic alkanes through the ring opening metathesis reactions.

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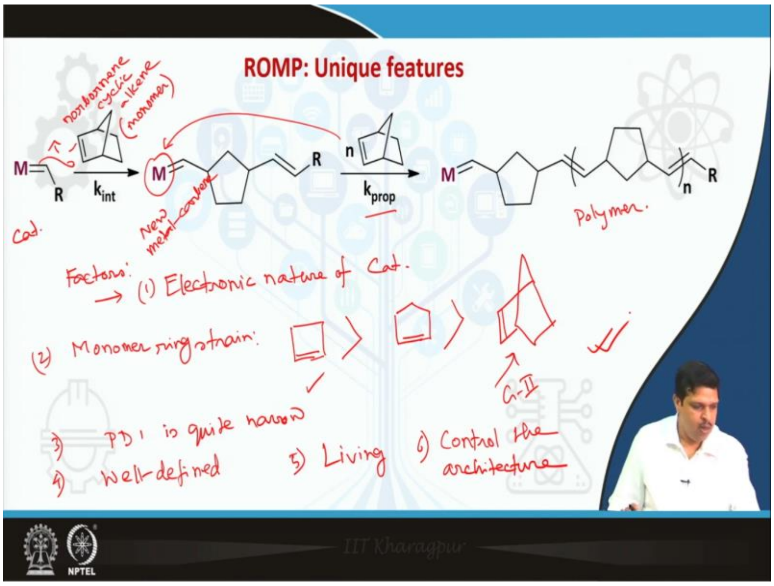

ROMP: Unique features

Factors:

→ (1) Electronic nature of Cat.

(2) Monomer ring strain:

3) PDI is quite narrow

4) Well-defined

5) Living

6) Control the architecture

So, here you see carefully that what is happening although I will discuss the mechanism after some time and here you see that this is my the catalyst that is the metal carbene catalyst. It may be Grubb’s catalyst or also Shrock catalyst and this is my this is called norbornene. This is a cyclic alkene. So, this is basically my monomer.

And what happens you will see here you this was initiated and so it is actually reacts like this one. So, it forms a metallocyclobutane first that I will discuss later and then froms a new metal carbine. The mechanism is very much the same as we discussed in the last class for ring opening metathesis.

And then again it reacts with the new metal carbene center and it forms and it repeatates, that is the propagation and forms your the polymer. As we discussed that this polymerization not only depends on the factors, on definitely the electronic nature of catalyst also depends on the monomer ring strain.

As example that if you use the cyclobutane, the reactivity is much higher than the cyclopentene or the norbornene. So, this is the trend of the reactivity. So, it clearly details that it depends on the ring strain. However, we can also polymerize this one very nicely using let us say Grubb’s generation 2 catalysts. So, it but the reactivity obviously will be little slower than the like cyclobutyl.

And as mentioned in my in the last slide, the PDI is quite narrow. Narrow that means the narrow molecular weight distribution that is definitely is very advantageous. Because you get very well-defined polymer and as it is a living, so, it is you can control the architecture. If you remember, in the very beginning of the classes that to control the architecture, the living polymerization is must then only you can make your desired block copolymers or different type of complex architectures, comb brush like that.

So, these are very much important, all that very advantageous properties of the ring opening metathesis polymerization by the metal carbene catalytics. And that is why it is becoming a very popular, even not only for academic laboratories but also in industries, the polymerization industries, various for different type of future, mainly the with the alkenes with different functional groups where we have to make a polymers or oligomers or cyclic polymers. The metal carbene is obvious choice as a catalyst where the other metal, other polymerization like alineik polymerization or free radical polymerization which are difficult in presence of the functional groups. So, that is why it is becoming very popular in polymer industries.

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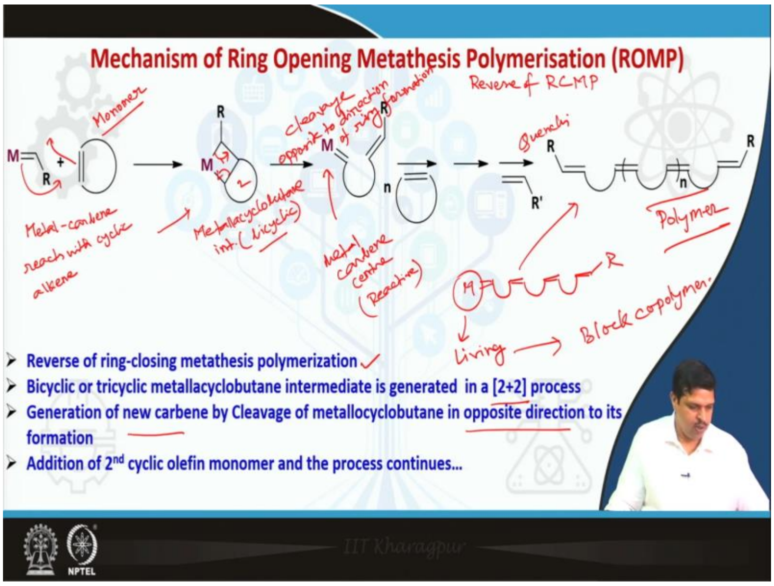

## Mechanism of Ring Opening Metathesis Polymerisation (ROMP)

- Reverse of ring-closing metathesis polymerization ✓
- Bicyclic or tricyclic metallacyclobutane intermediate is generated in a [2+2] process
- Generation of new carbene by Cleavage of metallocyclobutane in opposite direction to its formation
- Addition of 2nd cyclic olefin monomer and the process continues...

So, here is the mechanism. So, here you just check what is happening here. So, this is my the cyclic alkene that is the monomer. I have drawn it in a cartoon form to understand. So, what is happening here? You will see that the first is forming. So, this is basically the ring opening metathesis is polymerization.

Obviously, it is a just a reverse of the ring closing metathesis polymerization. So, it is basically you can think as a reverse of ring closing metathesis polymerization. So, here, what is happening here, you will see the metal carbene first reacts with, so, here what is happening?

So, here you will see that fast metal carbene reacts with cyclic alkene that is my monomer and forms a metallocyclobutane intermediate and you will see this is actually bi-cyclic. This is one and this is two. So, it is actually the bicyclic, one is alkene, one is the alkene cycle and one is the metallacyclene.

And then you will see that cleavage and this cleavage is basically the cleavage of the metallocyclobutane is just opposite to the direction of the metallocyclobutane formation. So, what actually, so, here what is happening? So, here it is basically just opposite of the direction. So, is a cleavage opposite to the direction of ring formation.

Now, you will see that this is the new metal carbene center and it is actually the appended, it is appended at the end. So, this is again reactive and then again it reacts with the another monomer and the whole process repeats, that is the propagation and then you will get basically the polymers where you have like that and here this one and as it is this metal carbene is living in nature, so, it is, if you do not quench it, it will undergo the polymerizations till all the monomers are consumed.

You can also forcefully quench it by using a very least reactive alkene, so that it does not undergo the polymerization further. And this the this that is the quenching actually, quenching step and you get a polymer and you get back your catalysts. So, here you will see that reverse ring closing metathesis polymerization obviously as I told just to reverse.

So, is basically you are get a the bicycle that is the bicyclic metalocyclobutane through a 2 plus 2 cyclo addition and then generation of new carbine by cleavage. And then it generation a new carbene and then that metal cyclobutane undergoes the cleavage by the bond breaking through opposite direction of its formation and then you it again it undergoes the cycloaddition reactions with the remaining monomers and the way the process repeats and then you get your the desired polymer.

So, very simple mechanism, very much similar what we have discussed in the last class when we discuss the ring opening reactions. And as it is a living polymer, so you can also make the block copolymers, block copolymers. So, if you that will discuss in the next class. That is the another advantage of this kind of polymers.

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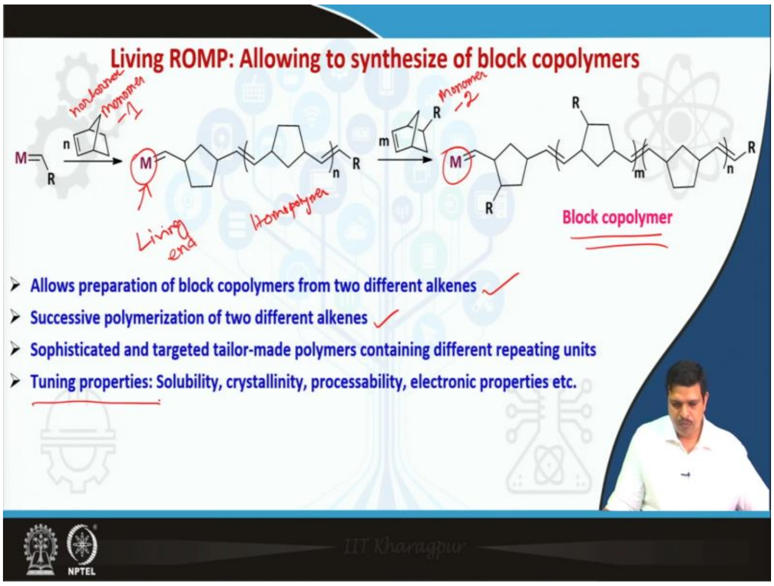

Living ROMP: Allowing to synthesize of block copolymers

- Allows preparation of block copolymers from two different alkenes
- Successive polymerization of two different alkenes
- Sophisticated and targeted tailor-made polymers containing different repeating units
- Tuning properties: Solubility, crystallinity, processability, electronic properties etc.

So, here you will see as I told that as it is living, this one, so, if you add another block. Here you will see that this is my here this is the norbornene, that is actually monomer, monomer 1 and here is the monomer 2. So, this is the substituted norbornene. So, here you will get the this is the living end and you will get your homopolymers. So, this is the homopolymer.

And once all the monomers are consumed, the monomer 1, then if you add the monomer 2, you will get the block copolymers. So, as it is a living, it is allows the formation to get the block copolymers and through the successive polymerization of the two different alkyls. And this actually gives the opportunity to make the targeted tailor made polymers of different repeating units.

Suppose, if I need a crystalline, a not purely crystalline materials or I need a flexible but the some percentage of crystalline. So, I can choose my monomor 1 and monomer 2 accordingly so that I can tune the crystallinity or fixibility or other electronic properties or solubility or possessive, or if I need to easily processible material, I can choose the monomers accordingly. So, this is very easy way to tuning as these polymers is where living polymerization as we also have observed for other like a control radical polymerization like that.

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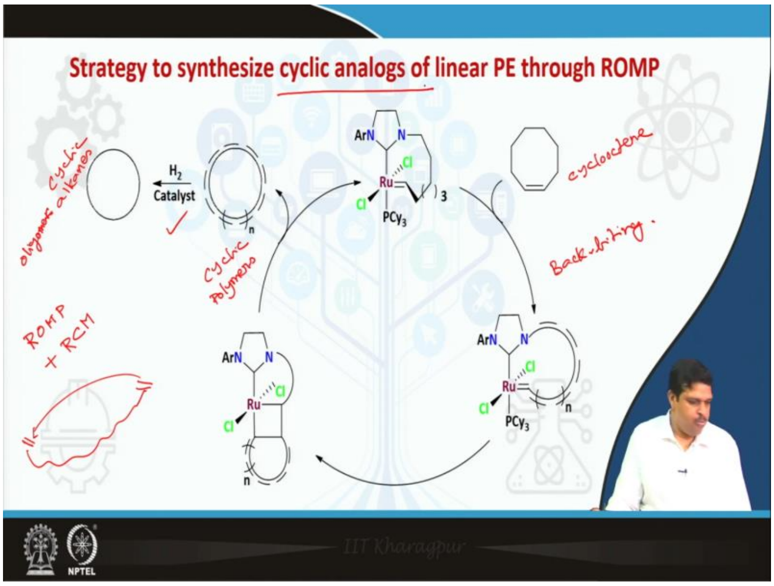
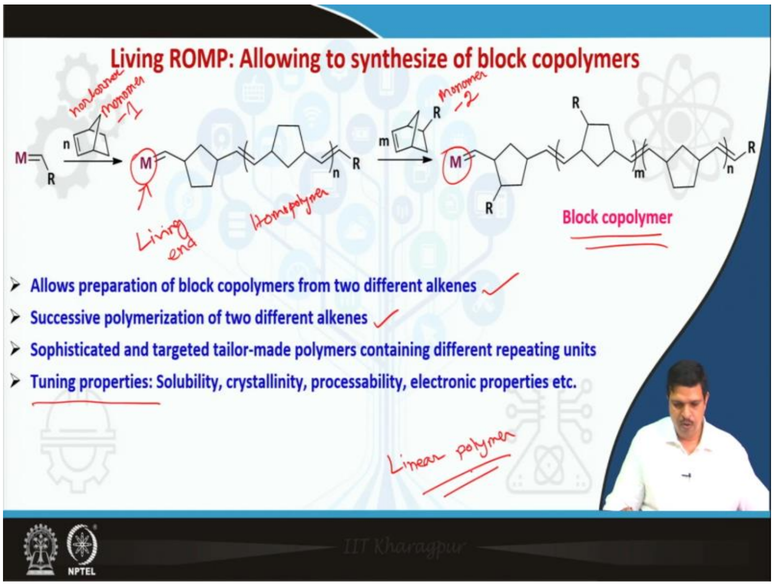


Strategy to synthesize cyclic analogs of linear PE through ROMP



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So, this is obviously a very effective way and that is why as I told that it is very popular nowadays to use this kind of catalysts. And here, one example how you can also get a different type of polymers. So, far what you see that this is the linear polymers. So, all here, whatever the linear polymers, here is one example how you can also get the the cyclic polymers.

Here, you will see that this is the cyclooctene and you will once you get the linear polymers, through the backbiting, you can also get the the cyclic polymers. Actually, this step is the backbiting step, the back biting. So, where what we are actually doing here? So, we are using the concept of ring opening metathesis polymerization and then we are doing the ring closing metathesis and then the and then we are getting a cyclic polymers. These properties of cyclic polymers are very much different than the acyclic polymer.

Sometimes, according to the desired or according to the properties, the cyclic polymers are also needed and very interesting. And this is the way how we can make a big cyclic polymers like n is equal to like 50, 60 or 80 like that. It is very difficult to make a big cyclic polymers because you will see that to thread or to make the cyclic like if you imagine that if I have a alkene here and if I have a long chain, so to thread this one, it is very difficult.

So, this is the one that very effective method to make the cyclic polymers and to make the saturated cyclic polymers, you can easily functionalize or you can do the further reaction of hydrogenation to get the cyclic alkenes. It is basically cyclic oligomeric alkenes I should tell because the number of carbons are quite huge, 50, 60, 40 like that. So, this is the another effective method of to make the cyclic analogues of linear polyethylene.

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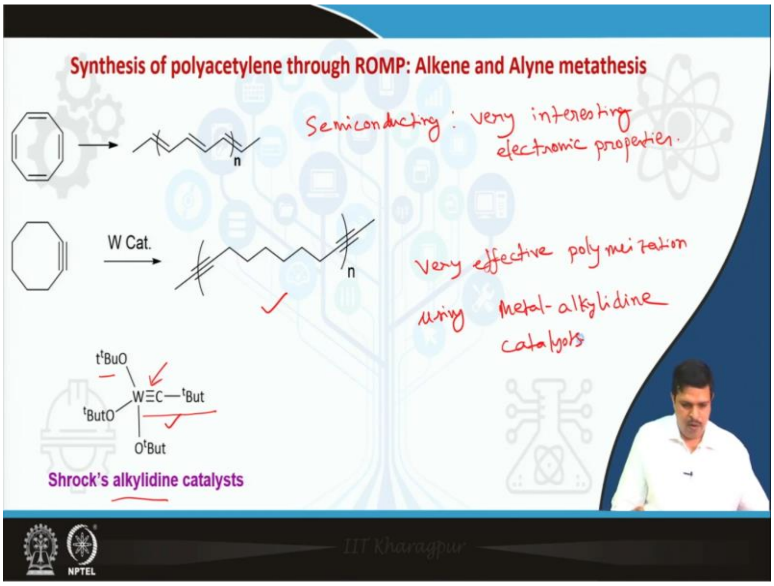

Synthesis of polyacetylene through ROMP: Alkene and Alyne metathesis

Semiconducting : very interesting electronic properties.

Very effective polymeization using metal-alkylidine catalysts

Shrock's alkylidine catalysts

So, not only that one you will see here that if you take it, you can also make the polyacetylene by choosing the correct monomers. As example, here you will see that this is the again the cyclooctotetraene and here you will see that this undergoes the polymerization by the tungsten catalyst that is the you will see that these are Shrocks alkaline type of catalyst, here, you will see that here these are the three tertiory butoxides and here it is you see that is alkylidine moiety. So, this is 1 2 3 6 W plus 6.

And here you will see that these kind of catalysts are very effective to make the polyacetylene and this kind of polymers are you know that this is semiconducting in nature. So, very interesting electronic properties. Not only that, you can also polymerize these cyclooctene by this kind of catalyst to make the corresponding the polymers like this one. These are very effective polymerization using metal alkylidine catalysts.

So, not only the strained alkene, you will see that different type of functionalized alkene or the alkyne that also can be used as a monomer to make more versatile and more functional polymers with interesting properties, which are actually limitations which for different type of other polymerization techniques, as example ionic polymerization or the radical polymerizations, controlled radical polymerizations. So, this polymerizations is very straightforward and very advantageous.

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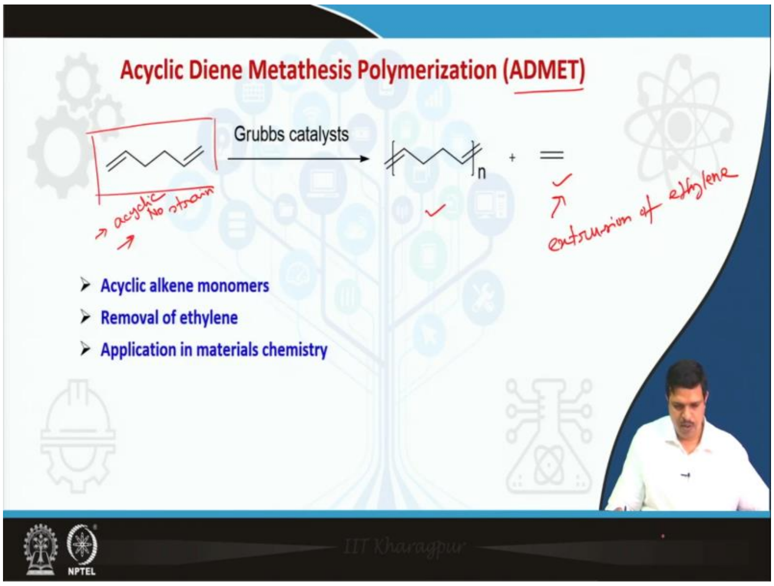
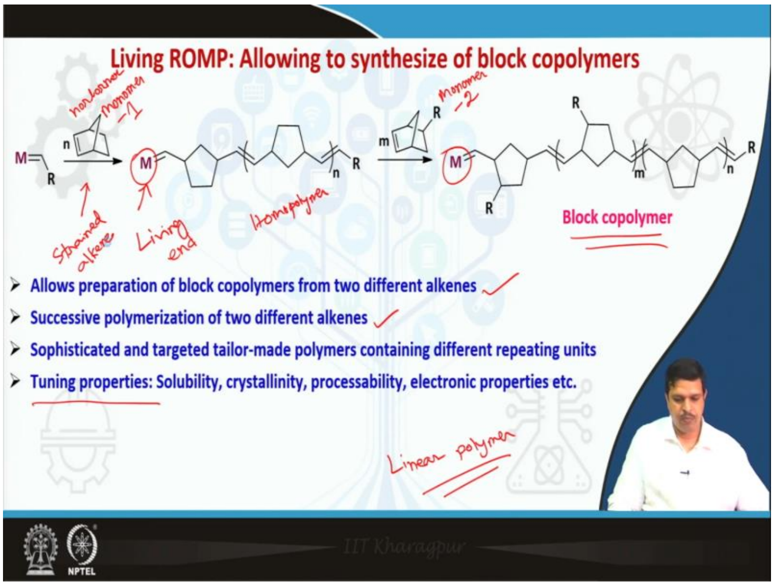


Acyclic Diene Metathesis Polymerization (ADMET)

- Acyclic alkene monomers
- Removal of ethylene
- Application in materials chemistry



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So, here another very interesting the polymerizations which can be possible by the metal, this kind of carbene or metal carbene on metal alkalidine catalyst. Here, you will see that the in this case we have used the strained alkenes. These are strained alkenes, at least some ring strain is present.

So, here in this case, you will see that these are acyclic. That means no strain here. No ring stain because this is acyclic. So, even this kind of monomer is also can undergo the polymerization using the suitable catalyst like Grubb's second generation or third generation catalyst. And this is called the ADMT that means Acyclic Diene Metathesis polymerization.

And here you will get basically the your corresponding monomer and also the the ethylene, for this case. So, this ethylene, this exclusion of ethylene is the driving, of ethylene is the driving force of this reaction. So, if we can remove the ethylene from the reaction mixture, the pollination chamber, the reaction pathways, the reaction will be more feasible towards the right and and the reaction will be more faster and more feasible.

So, this kind of reactions, the polymerizations are very much needed to develop new polymers for pi-conjugated materials. I will give some examples, how is possible. So, you will see that how this kind of a acyclic monomer is can also undergo the polymerization using this kind of carry so effective method.

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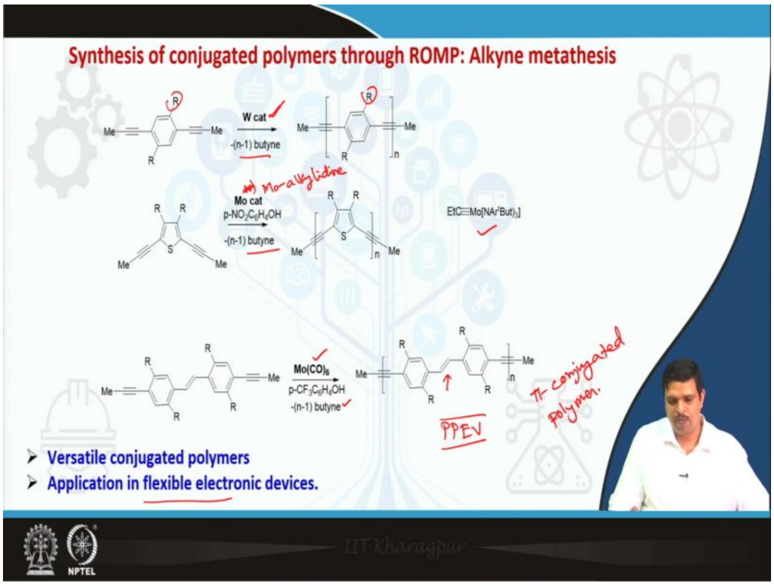
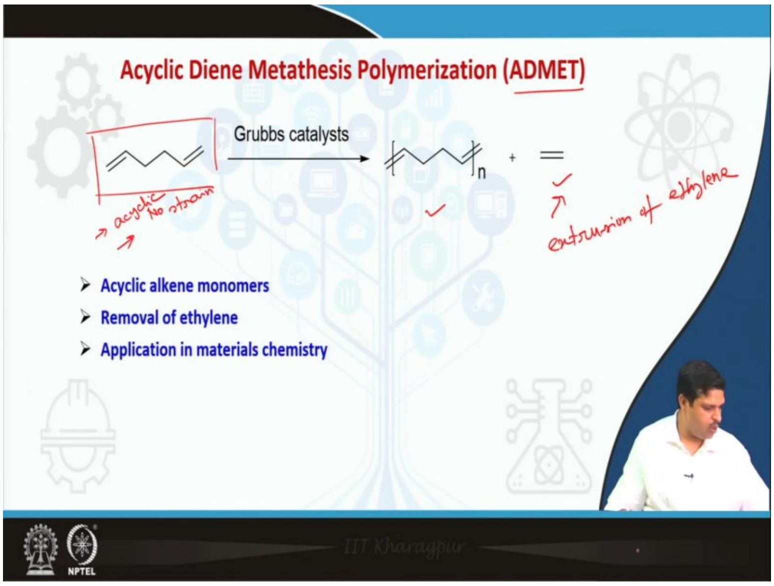


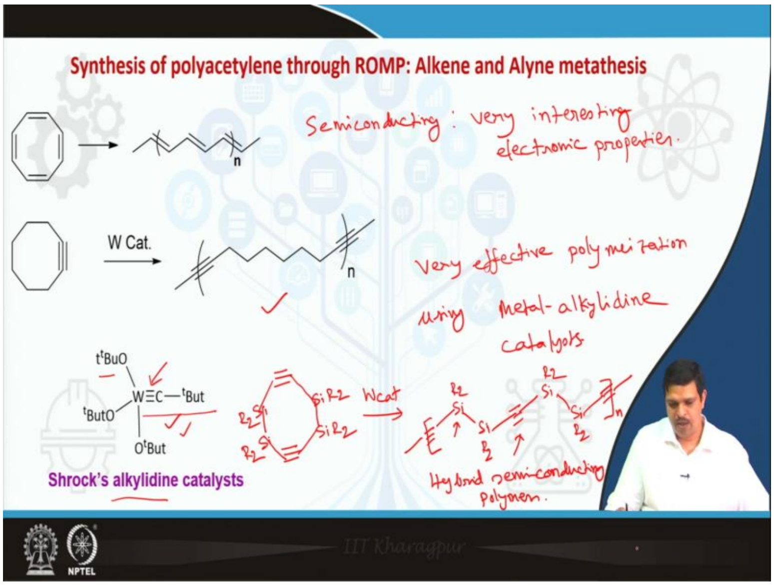
### Synthesis of conjugated polymers through ROMP: Alkyne metathesis

- Versatile conjugated polymers
- Application in flexible electronic devices.



### Acyclic Diene Metathesis Polymerization (ADMET)

- Acyclic alkene monomers
- Removal of ethylene
- Application in materials chemistry



### Synthesis of polyacetylene through ROMP: Alkene and Alyne metathesis

Semiconducting : very interesting electronic properties.

Very effective polymeization using metal-alkylidine catalysts

Shrock's alkylidine catalysts

So, here, here you will see that how the same concept of the ADMT that is the ADMT that is the alkene acyclic diene metathesis polymerization can also be applied to the alkyne version. So, as example, if you understand this one very this one the same thing is basically here also, but instead of alkene that is the alkyne.

And the tungsten catalyst is basically this, the same, same catalysts. I shall also mention here not only this one, you can also make a versatile polymers like this one. So, it is so effective. I will give another example that how you can. So, if this is and. So, is basically the hybrid polymers, inorganic organic hybrid polymers and if you use the same catalyst, you can get this kind of, and why this polymer is interesting I will tell you.

So, here, you will see that this is conjugated acetylene is there. Now, you tell that this silicon, as it is sp3 is not conjugated but that there is a special characteristic for polycelain that the sigma conjugation is also possible only for polycelain. So, polycelains is actually semiconductive in nature.

So, you can make is a hybrid semiconducting polymer. So, this kind of polymers are very interesting in the material chemistry for the industries like flexible optoelectronic devices as examples solar cells, OLED or OAFET like that. So, you will see that this kind of a new type of polymers can be possible by the metal carbene catalyst or metal alkaline type of catalyst.

This is very interesting. Still it is a kind of emerging field. So, there are lot of things to do. So, here the similar you will see that is a tungsten catalyst that I showed all of the structure and this is the molybdenum type of alkylidine catalysts. Here, you see that by using this you can get the different type of pi conjugated materials and these pi conjugated materials as I told that these are very much desired in the flexible electronic devices type application.

So, new type of pi conjugated materials are desired to tune the properties. Here, as as example, you know that polytyping is very much, very interesting material because it is semiconducting in nature. So, this also can be made by the molybdenum based alkalidine complexes where you see that this is, actually this is the molybdenum alkylidine complexes actually, alkylidine complexes.

So, here you see that you are getting a conjugated materials and obviously in this reactions, you will get the n minus number of butyne as a byproduct, in all here, everywhere. This one is called the PPEV. This is also very much very popular pi conjugate materials which are widely used for OLED type of application is also solar cell-based applications.

Here, you see that polyphenylene vinylidene polymer. So, this is the vinyl group actually. So, is and is called polyphenylene vinylidene. So, here you will see that using the molybdenum type of catalyst and this molybdenum carbene is in situ synthesized in presence of this para CH3 alcohol phenol and you get the your pi conjugated polymers. And this is very effective and you get very well defined polymers.

And these R groups, you will see that these catalysts are very compatible with this kind of R groups. That means you can change the R groups to polar or non-polar or different like ester groups alkyl, groups amino groups like that and that is why it is very emerging field in polymer industry and catalysts, organically catalysis industry to use this kind of metal alkalidine catalysts or metal carbene catalyst to develop new type of polymers.

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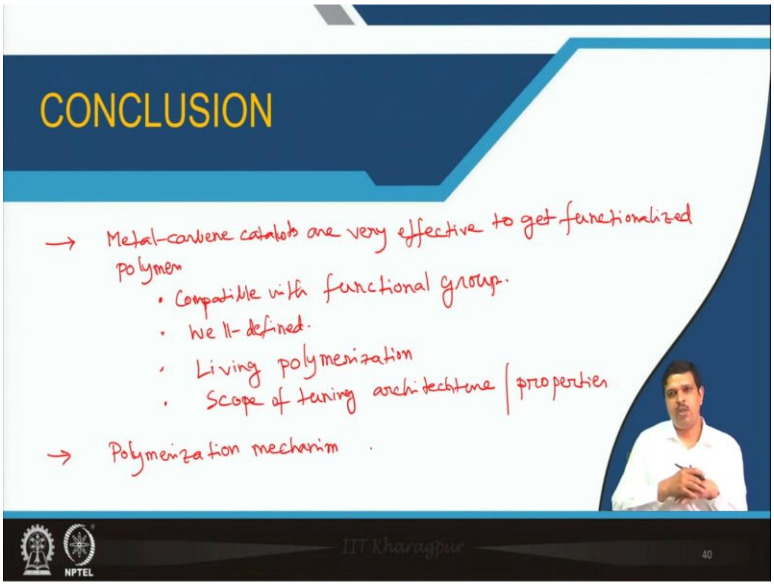

CONCLUSION

→ Metal-carbene catalysts are very effective to get functionalized polymer
- Compatible with functional group.
- Well-defined.
- Living polymerization
- Scope of tuning architechture | properties

→ Polymerization mechanism .

So, as a conclusion, what we have learned from this one? So, you will see that metal carbene catalyst are very effective to get functionalized polymers. You will see here compatable with functional groups, well defined and living polymerization. So, scope of tuning polymer architecture that is the properties.

And obviously we also learned the polymerization mechanism which actually undergoes through a mechanism. So, which undergoes through sequential formation of the repetitive formation of the metallocyclobutane intermediate and the cleavage of the metallocyclobutane.

And from here use very easily understood that how this metal carbene catalyst has can be used as a very effective catalysts for different alkene polymerization where the polymerization is not possible by other polymerization protocols due to the different functional groups.

So, this metal catalyst, you will see that it has a big future, very bright future, not only for academic laboratories or research, also for it has a bright future and bright prospect for the polymerization industry, materials industry to use as functional and tunable polymers through the alkene polymerization catalysts.

So, it is very clear that this if you choose the right catalysts and this may be a very effective way to polymerize a different type of alkenes, no matter what functional groups are there, what ring strain there or even the acyclic dying (())(37:03) or diene can also be polymerized by using this kind of metal carbene or metal alkaline catalysts.

So, I am very much sure that you are excited to know about this kind of new organometallic catalysts. So, in the next class I will try to give a summary of what we have learned in this course and what are the future prospect of this metallocenes and the metal carbene based catalysts in the polymer industries and materials industries.

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- Basic Organometallic Chemistry by Gupta and Elias, University Press, 2010. ✓

And with this one, I request to study the topics whatever you have discussed following these books. Obviously, the Crabtree book, very much effective, the Hartwig book, Astruc book and also the Basic Organic Chemistry by Gupta and Elias. So, thank you very much and see you in the next class which is actually our last class. Thank you very much. See you in the next class.