

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

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Lecture 32

Depolymerization of synthetic polymers Role of organometallic and metallocene based catalysts

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Welcome. And we will be continuing that our discussion of the depolymerization of synthetic polymers. And today we will discuss about specifically about the bond breaking of the synthetic polymers, mainly, we will be dealing with polyolefins by the organometallic and with special focus on the Metallocene based catalysts. And here you will see that why we are discussing here the 2 parts one is the polyolefin and one is the Metallocene, we the terms in our course, that is one is the Metallocene based catalyst and one is the polyolefin.

And we have learned so far how to make the polyolefins by the Metallocene catalysts and today I want to give a highlight that how the same Metallocene based catalyst can also be used or the similar type of catalyst can also be used for depolymerize off the polyolefins to make either the monomers or to make the valuable feedstocks to face the demand for the energy or for fuels. So, this is this is really exciting topics very advanced topic.

And as this is very related to our main topic, this is really important to know one of the applications of the methylation catalyst or related catalyst for depolymerizations.

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CONCEPTS COVERED

- Depolymerization and recyclability. Why? ✓
- Methodologies for depolymerization. ✓
- Circular economy and Sustainable chemistry ✓
- **Strategy and mechanism of depolymerization** ✓
- **Metallocene catalysts and organometallic compounds in depolymerization chemistry**

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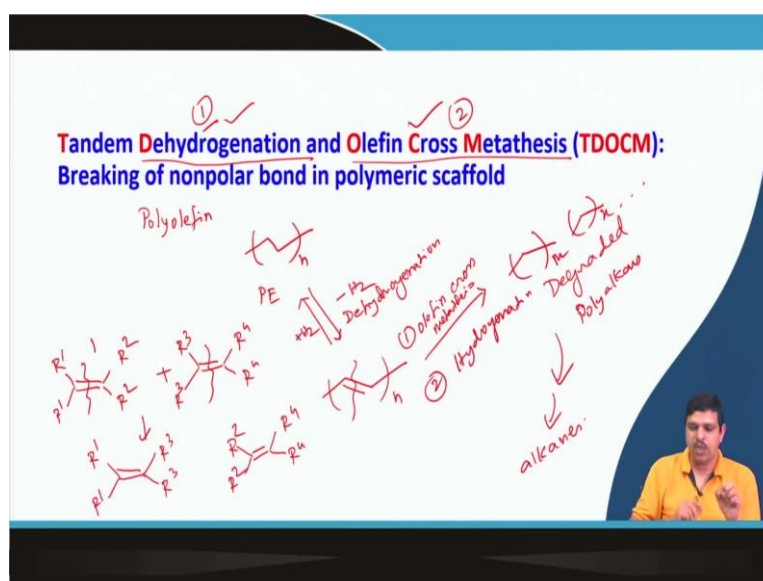
KEY POINTS

- Recyclability of synthetic polymers
- Depolymerization by chemical methods
- **Organometallic and Metallocene catalysts for depolymerization**
- **Microscopic reversibility** ✓✘

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So, in the last class, we have already discussed about these 3 concepts. And today specifically, we discuss about the strategy and mechanism of depolymerizations by these organometallic catalysts and then we will discuss about the methylation catalysts like how it can be used to break the nonpolar bonds. So, and also we will learn that how this same catalyst which is used for default polymerization can be used depolymerizations by the concept of the microscopic reversibility that is the main actually topic or main term, we will be learning today fine.

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So, but before that, we should understand that how we can break a polyolefin. As we know that polyolefins is although polyfin term means there is a unsaturated bond, but when it is a polyolefin that is there is no unsaturated bond that is the actual the poly alkanes So, this is the like that it is polyethylene, now, how you can break it?

Here is the term you will see that the hydrogenation and Olefin Cross Metathesis so 2 reactions here, one is that dehydration hydrogenation and one is the olefin cross metathesis reactions, although we will be learning in more detail about the mid cost metathesis reaction from in the next class we will be starting the metal carbon chemistry.

So here are the 2 reaction one is this one, this is the 2 one how these 2 can be combined to break the very stable and nonpolar bond, let us say carbon carbon bond, how is this possible? Very interesting. So let us see the strategy in a very, very simple way. So, how it can be done. So let us say if we did the first step that is a dehydrogenation that means u minus h2 and the reverse reaction is the hydrogenation so let us do like this one.

And this is called the de hydrogenation. Now, if we do this reaction, that is the olefin cross metathesis reaction, then what will happen? It is olefin cross metathesis reaction. See when there will be dehibernation then it will form again you will see the unsaturated bond and then after the meta thesis reactions it will and followed by the hydrogenation what will happen you will get the degraded alkenes and when it is the process will be repeated you will get the alkenes maybe with the smaller alkenes like 33456 carbon atom.

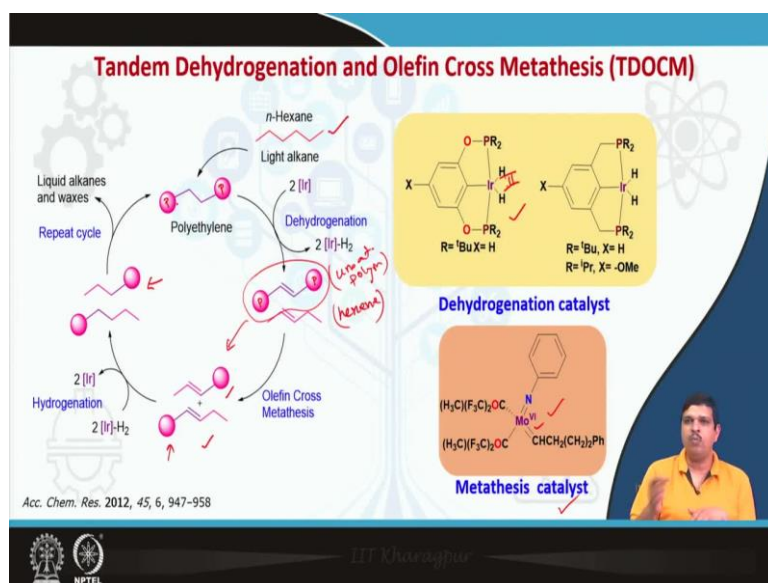
So, this category can fall in the range of ox liquid quell like that. And you know the metathesis, so what is the metathesis reaction. So, this is if you can imagine that if there is a 2 kind of so, this is 2, 2 and we will discuss in the next class onwards in more detail. So, the metathesis this is a across metathesis reactions what would happen so, is basically you will see that changing the alkyl groups, so, looks like here it is broken.

And then again it has been threaded. So, you will see this will be broken there will multiple saturated bones. So, there is a number of ways to break and then the thread and then that the way you will get a various number of like this one aim aches like that and you will get it ultimately after repeated of the process you will get the alkanes.

So, this is a strategy and how to do it, it is not easy, although, but how to do it, how to make this strategy successful that we will discuss. So, you very carefully try to understand this process that is called tandem, tandem means 2 process together in C2. And you see that 2 reactions one is the hydrogenation reaction to make the unsaturated.

And then why we are doing because we have to do for the cross metathesis reaction by cross metathesis reaction, you can only make the alkenes have different alkyl groups that means the degradation process. And then after that we have to do again the hydrogenation so that we can get a saturated alkanes that is called poly alkenes and if the steps are repeated again then the medium chains will make the smaller then very small like that, that is the strategy.

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So, here you have some of the real examples. Let us try to understand what is happening here fine. So, here you will see this is the dehydrogenation catalyst and this is the metathesis

catalyst that is the molybdenum base and this is the very famous dehydrogenation, radium 3 based catalyst the oxidation state is 3 here and this is the molybdenum 6. Now, here you will see what is happening here.

So, here this is my polyethylene or let us say these are my polymeric chain. So, in a cartoon way I have shown it, so, this is my polyethylene or poly alkanes. Now, what we are doing we are now doing the dehydrogenation reactions and we are also adding some smaller alkyne that is also another strategy or same strategy as we have already shown here same strategy but we are adding externally some XN and there is a reason why to make this process more effective.

So, we are light alkynes like hexane you can use pentane also and what will happen? You will make dehydrogenated and here you see this is from the Hexane so, that is actually Hexane, 2 Hexane and this is the unsaturated polyethylene the polymer. Now, what we are doing we are doing the polyfin cross metathesis reaction, why this metathesis catalyst you need 2 catalysts system in a single pot one is the dehydrogenation catalyst, which will be very effective and another one is the metathesis catalyst.

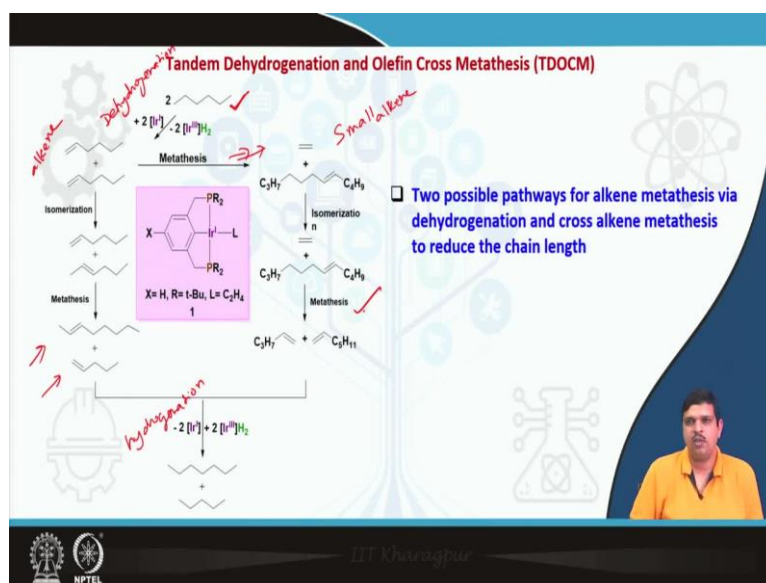
Now, what we are doing so, we are as I told so, this basically the metathesis reactions that there will be exchange of the substituents. So, what you see there will be extending, so, this is my polymeric unit this actual I have shown a particular unit of the polyethylene. Now, after olefin cross metathesis there will be degradation.

So, this you will see this unit will come here like that and this is the way it will degrade that means the polymer chain will be shorter. Now, again what we are doing we are doing the hydrogenation in presence of H_2 . So, what will be happening here you will see that this alkanes the shorter alkenes this is the shorter ligands you will see that if you see the (())(11:05) so, this is almost half from here to here is almost half.

And now, we are now doing the hydrogenation to make the alkenes, now here you see that again this one will participate in the similar reactions as it did happen for the original polymer molecules and then it will repeat it and after repeated what you will get you will get a lighter alkanes you may get liquid alkanes or the works that means, in the medium range of the medium range of carbon atoms let us like a 15 to 20 like that, if the process is very effective, you can get a lighter alkanes like hexane octane heptane like that.

So, these can also be used as if fuels or other feedstock. So, these are very effective and very new and very advanced technology which still the scientist and are trying to develop to make it more efficient and I am sure in very near future the industry people also will accept this strategy to make the monomers or the feedstock or valuable components again from the waste polymer.

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So, here again you will see that the similar mechanism same mechanism, so, this is my these are model compound, let us see like 12345 so, this is the Hexane so, what happens this is the dehydrogenation. So, there are several possibilities are there, that is why I have I am trying to tell you that in the system, there are after first or second or third degradation there are a lot of possibilities of alkenes of different number of carbons.

And then that will actually there were a lot of permutation combination and ultimately after several cycles, you get the very small alkenes with let us say like 5 to 10 number of carbons atoms. So, here this concept you try to understand. So, here it is happening the let us say the model compounds like alkyne Hexane can be treated as a model of polyethylene.

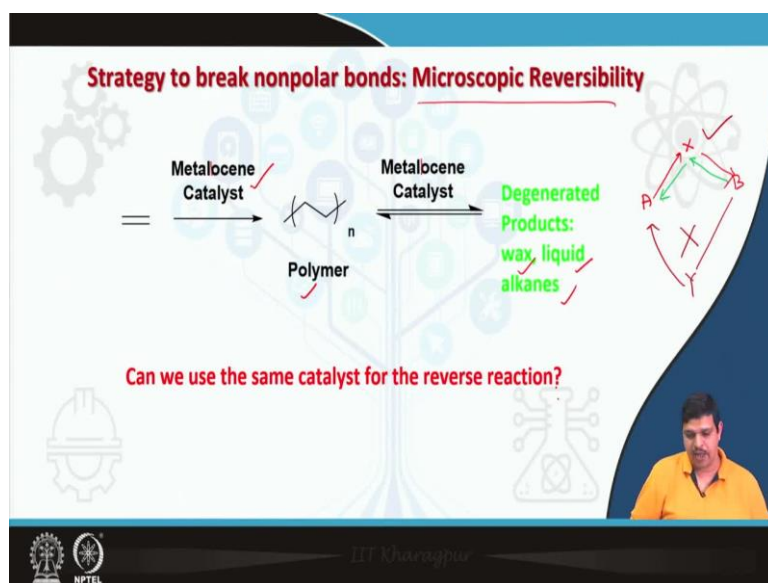
So, here when you develop a catalyst, we have to test it by a model compound like a hexane or heptane an octane and we have to study the mechanism or its effectiveness or an activity by a spectroscopic or mass techniques to understand that how it is breaking as example, like if you try with octane or oxygen or octane or hexane we can be able to take the integrated report by simple GCMs.

So, that is very important to first establish the mechanism and establish activity by a simple model compound which actually mimic the property of the poly alkanes of polyethylene. So, here you will see that after the hydrogenation you are getting the alkyne and then it may undergo the isomerization. So, this terminal to internal alkyne and then it will go to the metathesis reaction and you will see that you will get these different alkynes of different number of the carbon atoms.

And then it will undergo the hydrogenation and then you will get the alkenes of different carbon atoms. Here also before isolation there will there may be metathesis reaction first and in the meta thesis reaction again you will get a different alkenes of different carbon atoms here you see that if it follows in this way they are you will see a small alkenes that is the basically the smallest alkyne the ethylene and it can undergo the isomerization.

And then again metathesis reaction, so as I am telling that there is a lot of combinations of formulations are possible. So, the system is difficult, but eventually we will get this simpler products after repeating cycles.

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So, this strategy is very effective and although as I told that speed it is not developed to a bulk scale but in level of skill this is a very promising technology. So, by this kind of catalysts, Iridium or molybdenum catalyst it was taught by scientists who are working in this group that whether this metal ocean type of catalyst can be used by the same purpose that is the depolymerization and why it came in mind.

There is a reason and the reason is the microscopic reversibility, I am sure many of you may be aware of what is the microscopic reversal, which I will discuss in the next 2 3 slides in more depth that in a very qualitative way, simple way the microscopic reversibility is that that suppose, I am going to place a to A B. And I am going to via X. So x, so, I am going from here then there.

So, when I go back from B to A I also follow that B to X and then X to A to come to my original place I will not follow somewhere like B to Y and then to A this one is the if it follows the same path of the forward reaction then it is microscopic reversibility and I will discuss in more depth in the next 2 3 slides that what is microscopic reversibility and what is actually a concept it is. So, if we are successful to use the same catalysts which are very active and highly efficient catalysts, then our problem will be solved.

So, and then what you can get we can use the same catalyst to make the polymer and at the same time when the polymeric materials are used, then the waste polymer materials can also be converted to a useful materials like liquid alkanes wax for fuel purpose the liquid alkanes and then through the depolymerization by breaking the bonds. So, that is the fundamental aspects and the strategy.

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Microscopic reversibility

- Formulated in 1924 by the American scientist Richard C. Tolman. ✓
- It states that at equilibrium any molecular process and reverse of that process occur, on the average, at the same rate.
- The transition states for each mechanism steps are identical regardless of reaction direction.
- Accordingly, the reaction path in the reverse direction must in every detail be the reverse of the reaction path in the forward direction (provided always that the system is at equilibrium).

Principle

- In an equilibrium process, same intermediate and transition state are encountered in the forward direction and th reverse but in opposite order

$$\begin{array}{c} \text{H}_3\text{C} \\ \diagdown \\ \text{C}=\text{CH}_2 \\ \diagup \\ \text{H}_3\text{C} \end{array} + \text{H}_2\text{O} \xrightleftharpoons{\text{H}^+} \begin{array}{c} \text{H}_3\text{C} \\ | \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \\ | \\ \text{OH} \end{array}$$

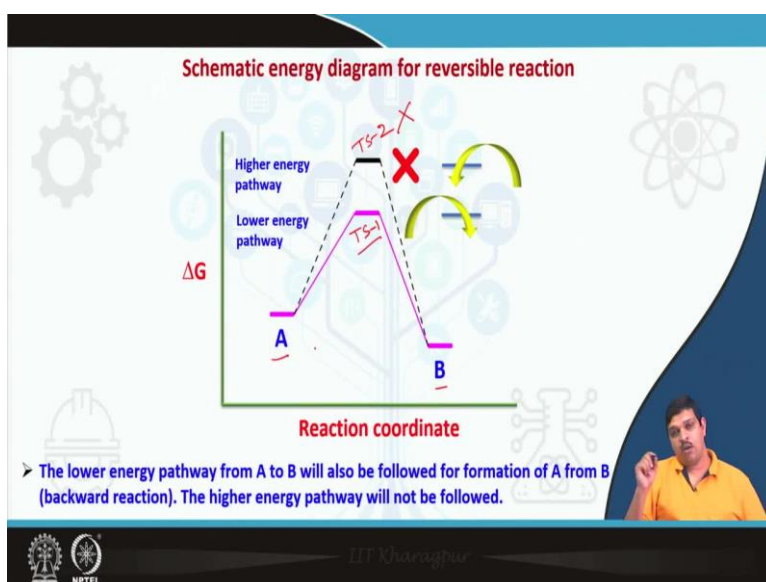
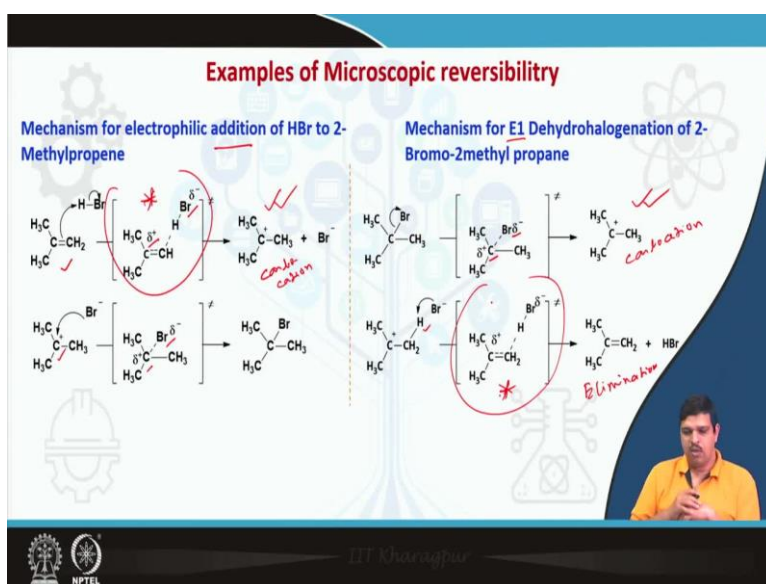
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Now, what is the microscopic reversibility? So, it tells that same intermediate and transition states are encountered in the forward reaction and the reverse reaction. So, here you see the what is the forward reaction, forward reaction is basically the addition of HOH here. So, this

is my alkyne. Now, you see that I am adding H₂O that is H and O H and what is the reverse reaction? Reverse reaction is the dehydration that is the elimination of H₂O.

The concept of the microscopic reversibility tells that the both the process should undergo through a common intermediate and this process are in equilibrium. Now let us see what is that this one actually first formulated by Richard Tolman in 1924. And it is a very useful concept and in many organic chemistry I am sure in organic chemistry when you will study the mechanism areas elimination or substitution reactions you have encountered this concept.

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I will try and discuss in more detail about that one with hydrobromination. So, here you will see that this is alkyne and I am adding the H Br. So, what is happening fast you will see that

the alkyne the π bond will attack on H and it will form that δ^+ and here the Br δ^- . So, one carbocation is formed this is called carbocation.

Now, this carbocation is formed and then the Br δ^- do the will add up on the C δ^+ and then what will happen you will see that again Br δ^- and C δ^+ and ultimately the Br will be added on the carbon. So, H is added on C_2 and Br is added on carbon. Now think about the elimination reaction. So, this one is the addition reactions and this is the elimination reaction that is the exactly opposite reaction.

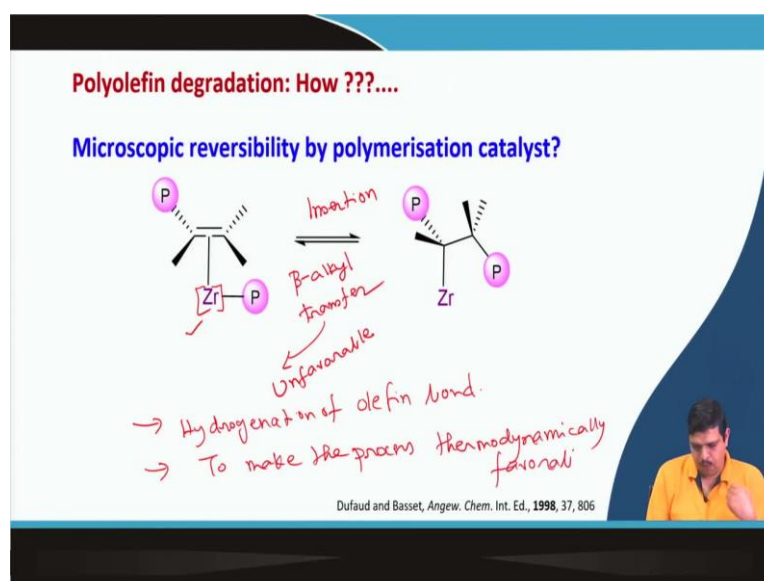
Now, how it is what is now happening in the elimination reactions. So, elimination reactions is that that now these B are so C-Br bond is polar. So, it will be Br δ^- C δ^+ and again it will form a carbocation and if you see that this one and this one is actually the same now, this carbocation is formed, so, this is my C δ^+ . And here that Br are δ^- now we will add up on this hydrogen and you will see this that is this transition state this is also the same as it is here and after that there will be elimination of the H_2 .

So, this step is the elimination, final elimination step. So, here you will see that this one and this one these intermediate sorry the transition state are the same both for the backward and forward reaction. So, this is called the microscopic reversibility that means, if you see in this diagram, that if A is the reactant B is the product.

If A is going through a transition state one to be the backward reaction that is B from B to A will also undergo through this transition state one it will not undergo through any other alternate path or other transition state. So, the lower energy pathway from A to B will be followed for formation of A from B that is the reverse reaction, no other path will be followed.

So, that is the microscopic reversibility that means, if one catalyst can do polymerization, then it should also do the depolymerization if we follow the particular strategy and condition fine.

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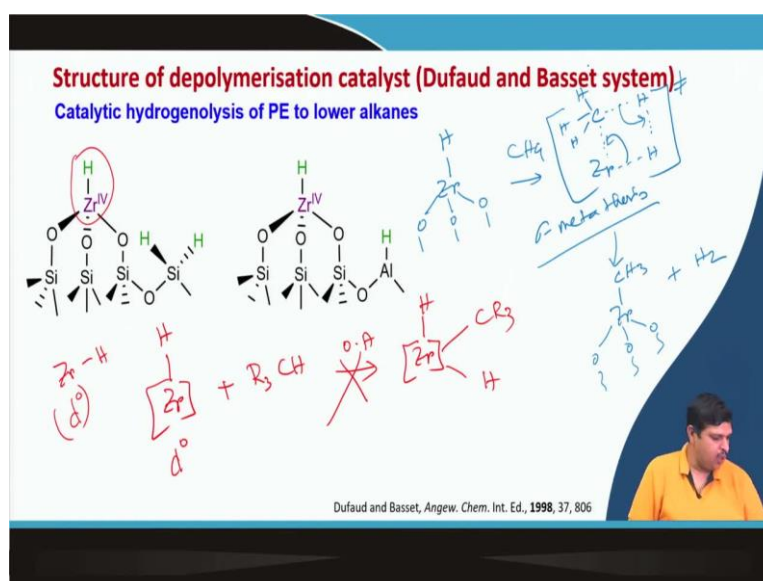


So, now, we will let us see. So, this is how it can be done. So, here you will see that this is the coordination of the zirconium catalyst are complex to alkene and here you see what is happening this is actually the beta alkyl transfer is happening. So, this instruction is happening. So, this is the backward forward reaction is actually the introduction and the backward reaction, it is actually the beta alcohol transfer.

Now, you see that according to the microscopic reversibility that these 2 reactions will undergo in a common pathway, a common transition state so, these are the actually the 2 microscopic reverse reactions one is usually the insertion and one is the beta alkyl transfer transport although the beta alkyl transfer is actually the unfavorable thermodynamically unfavorable.

So, to make this favorable post to make this unfavorable policies to favorable, we have to do some other strategy that we will learn in the next slide and what we have to do we have to do the hydrogenation of olefin bond and then to make this process thermodynamically favorable.

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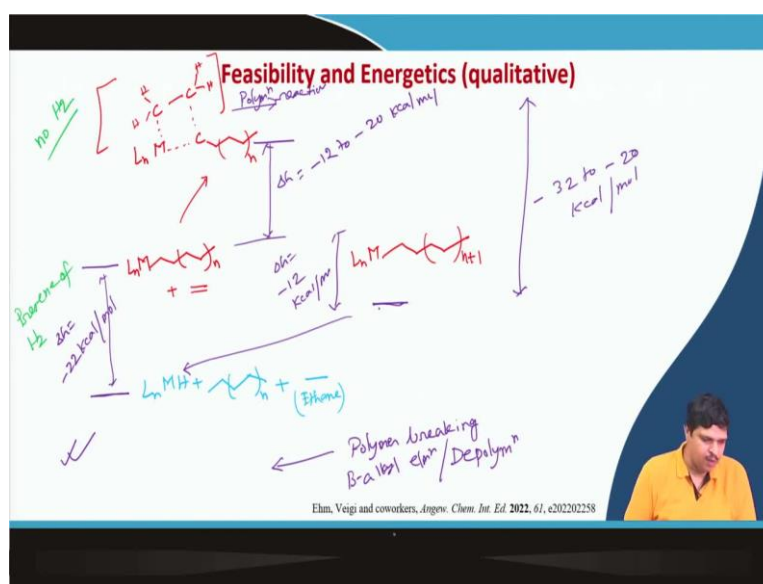
So, we will discuss with an example you will understand what I am trying to tell you. So, here you will see that this is one of the example that is developed by Dufaud and Basset that is the zirconium based compound you will see there is a zirconium hydrogen Zr-H point is there and this is d⁰ system. And you will see that if you react with R₃CH and here H and it is d⁰ and if you react to it let us say R₃CH to activate the CH bond.

The immediate thing come in our mind is like CR₃ and H that is the oxidative addition, but as we already discussed that D⁰ complex cannot do the oxidative addition reaction. So, this path will not be followed please remember that is very important. So, how it will be it will then activate the CH bond there is an alternate path how it is possible that this is possible why the sigma metathesis reactions and I will show you how it is possible.

So, if we suppose you are reacting with CH₄ that is methane molecules then CH₄ and so, this is intermediate that is through this is actually alkene sigma metathesis reaction. So, then what happens you will get the like that. So, ultimately we will get Zr-H this is to make the system heterogeneous as we already discussed in the last class that is to make the system homogeneous to heterogeneous.

So, we will get CH₃ and then you will get the hydrogen. So, this will undergo through sigma metathesis or generally D⁰ complex activates the nonpolar bonds CH or HH by sigma metathesis reactions not by oxidative addition. So, this the same strategy has been followed here.

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So, in Bluefin and vs system, you show that it is used a zirconium hydrogen bond unit and it is bounded with silica to make it more heterogeneous. And here you show that as I already mentioned that beta alkyl transport is not favorable, we have not favorable reaction. So, we have to make a strategy to make it favorable and it is done through hydrogenation.

So it is basically the hydrogen visualizes as you see here, the catalytic hydrogenolysis of polyethylene to lower alkenes and if you conceal that the energetics of this dehydrogenation reaction then you will understand why we need to do the hydrogenation analysis so, I am drawing in a very qualitative way to understand so, this is not in absolute scale.

So, first I am these are the energy and then I will show you what I am doing. Now so, this one let us say this is this is the polymer and I am reacting with let us see 3 moiety. And what would happen in this reaction it will undergo the metathesis reaction and the transition state will be like that. So, this is that it will be moiety. And here there will be 2 hydrogen.

And this is the this unit that means, there will be like that. And now, this will be possible when there is no hydrogen, so, it is in absence of hydrogen, so, no hydrogen, then so, what will be the ultimate product it will be the M L n so, this will be n plus 1. Now, if it is in presence of hydrogen then what will happen there will be hydrogen elapses so, in patients of hydrogen what will happen it will be Ln MH plus 1 2 this is and there will be Ethan.

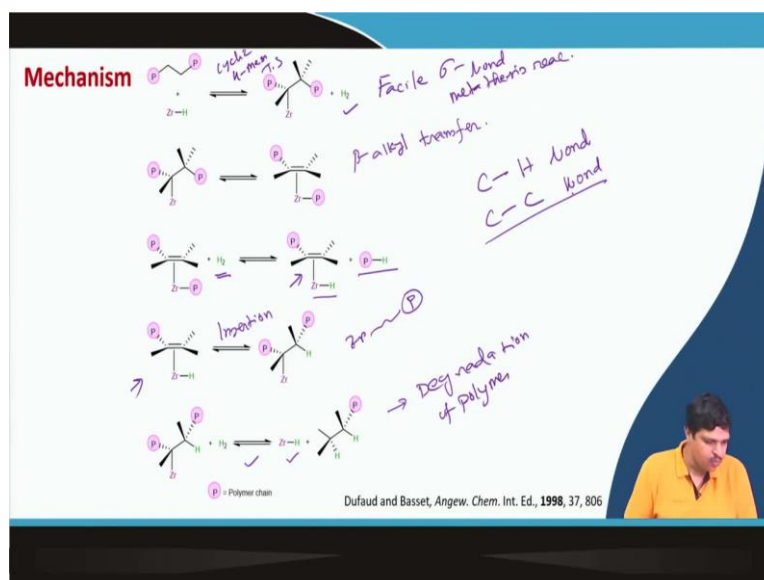
So, now, you will see if we consider the value this value has been taken from this paper and you want it to 0 to 2. So, this is minus 22 kilo calorie per mole you no need to remember this is just to have an idea and this one these value, the delta G value is minus 12 to minus 20 kilo

calorie per mole and this one is minus 12 kilo calorie per mole that is the delta G. So, this one total how much it is coming it is around minus 32 minus 20 kilo calorie per mole.

Now, you see carefully here that this one is my... these reactions from here to here this is my starting material. So, that is the alkylated and the poly poly polymer and the reaction with ethylene. So, here you will see this one you consider is the forward reaction that is the polymerization reactions. And this one is basically the polymer breaking reaction. So, that is you can see the beta alkyl elimination that is the depolymerization reactions.

So, from here it is very clear that this tape will be more feasible rather than this one. So, that is why the hydrogen (())(35:20) is better approach then the beta alkanes transport in the depolymerization reaction.

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So, that is the reason this mechanism has been proposed by the Dufaud and Basset here you will see try to understand what is happening here that this is the facile sigma bond metathesis reaction same thing I just discussed in the last slide sigma bond metathesis reaction. And similar you through a cyclic transition state cyclic core membered transition state.

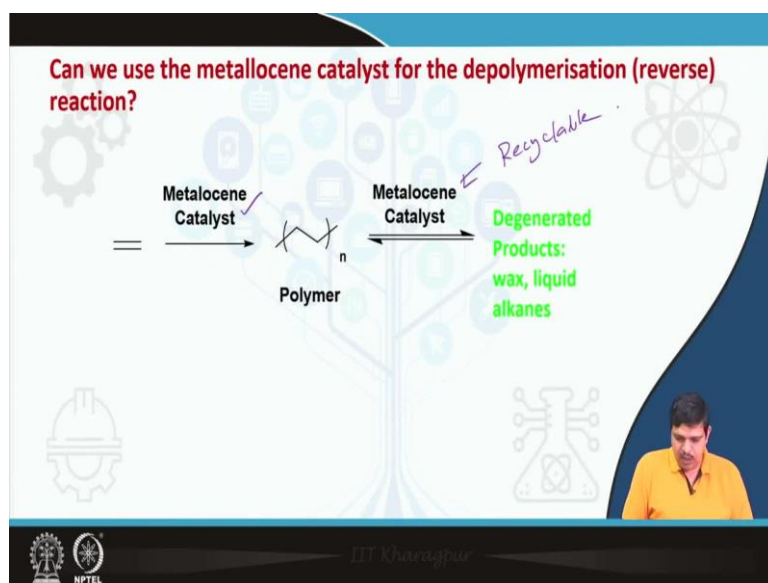
I just showed in the last slide and then ultimately you will get this H₂ and the zirconium alkylated that is the polymer attached fragment and then you will see this is a thing what beta alkyl transfer reactions and here you will see that in presence of hydrogen that is the H₂ to make the reactions visible.

So, what is happening again you will see that there will be zirconium hydrogen formation and here you will get the zirconium coordinated the alkyne fragment and the hydrogenated polymer that is a pH and then again with this one this one that is the same thing again it undergoes the insertion reactions, insertion of alkyne in zirconium hydrogen and you will get the zirconium and the polymer in grafted metal alkane bond.

Then again it is hydrogen versus happens and then you get the again generate and in that the way they are with degradation of the polymer. So, you will see how the CH bond has been activated and CC bond is activated here and how is this very stable and permanent mentally stable and nonpolar bond has been cribbed by a very strategic and UDACS approach using the organometallic compounds.

So, in the beginning if you will remember I told that this organometallic by the use concept organometallic reactions you can populate the electron density in the corresponding sigma store orbital to make that bond weak and you can prove or weaken the bond the same thing we are doing here.

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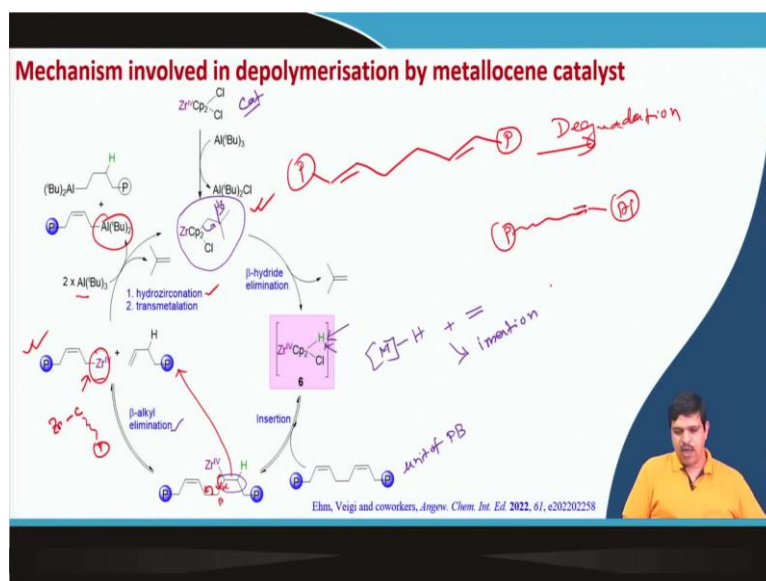
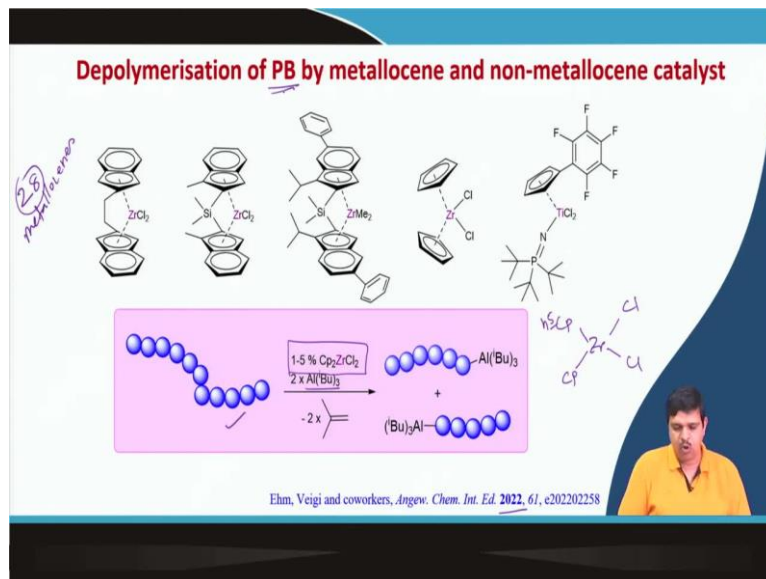


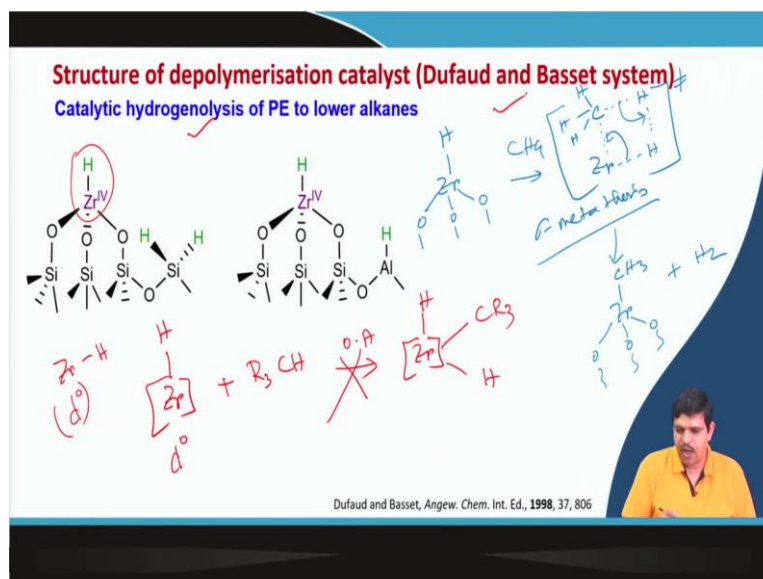
So, now, after getting the knowledge and the confidence that yes it is possible by use the concept of the microscopic reversibility with transition metal and organometallic compounds. Now, this can be applied to the Metallocene compounds which is very good polymerization catalyst is it possible let us see.

So, if we are successful then the same catalyst can be used for polymerization and then the same catalyst can also be used for the recyclable purpose. Or deforming purpose or

repurposing purpose, the purpose means the waste polymeric material can be used again to make a useful compounds or materials or as a feedstock.

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So, in this regard, very recent paper 2022 (())(39:52) that is the Ehm, Veigi and coworkers they screened 28 number of Metallocene compounds which are which have been proved as a very good catalyst, polymerization catalyst and it has been screened for various poly ethylene or similar allied polymers to crib the very stable polymers with the nonpolar bonds.

So, various types these are some representative out of 28 Metallocene compounds some Metallocene even Metallocene compounds also which are have been proved as an excellent polymerization catalysts. So, you will see here that this was the condition was used this is the polymers and here this these are the most simplest polymerization catalysts that is the CP 2 Zr CL 2 we know all these chemistry.

We have discussed very extensively in our previous classes, this is obviously top 5 and here we have to try isobutyl aluminum compound we will discuss why it is important you will understand when I discuss the mechanism and then you will see how beautifully it has been designed and how you can break a very stable bond particularly in this paper it has been screened for the poly butadiene polymer in depolymerize mechanism to break the polybutadiene.

So, here you will see that this polybutadiene has been you have been taken as a model polymer to break the polymer skeleton in a chemical means by this methylation based catalyst. So, you see that what is happening so, this is my the original catalyst and you have to use a catalyst that is the tri isobutyl aluminium and what you are getting you will be getting that zirconium with one chloride and one isobutyl and here you will see that then what is happening you are you will get a beta hydrodynamic elimination so, this is my H.

So, you will get the beta hydride elimination and then you will get the zirconium hydrogen you are very familiar with the Swatch reagent. So, very much similar kind of activity and reactions will also be followed here. So, this by after the beta elimination reactions there will be in such reactions of the alkene moiety polybutadiene. So, this is the zirconium hydrogen we know that if there is a metal hydrogen bond and if there is an alkene then the insertion reactions is very much feasible.

So, what you will get this is the unit model unit of polybutadiene PB is basically the polyphonic chain and just to write in a short replacing the big chain of the polymeric. So, just to write in a short we are writing the P as a polyphonic end and then it undergoes the insertion and you will see that this has been inserted. So, this polymeric chain is inserted in zirconium hydrogen bond and then beta alkyne elimination is happening here. So, how this beta alcohol elimination is happening? Simple.

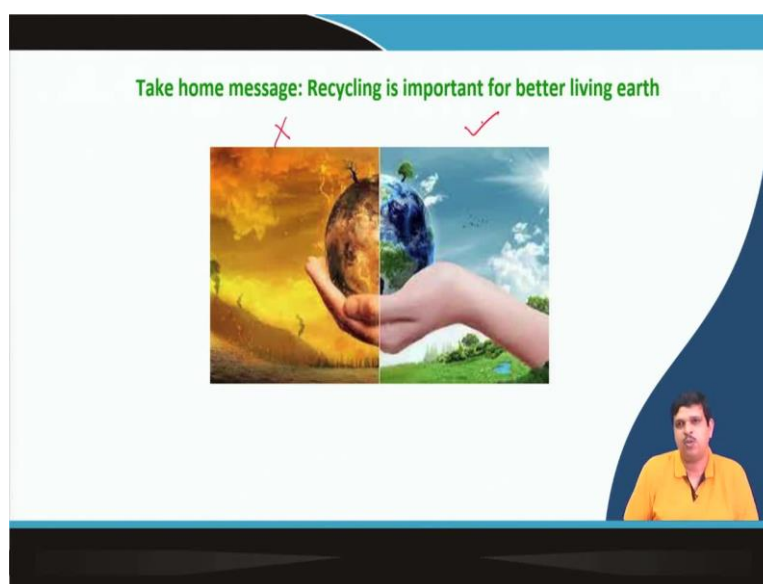
So, you will see here this is beta alkyl elimination. So, here you see that this one is alpha and this is beta. So, sorry like that, now, you see that this has been with the permission of the lower fragment of the alkyne from the polybutadiene and here another that zirconium carbon bond where you are attached with the polymer end. Now, again you will see you consider this one and this one is very much similar.

So, then again react with the aluminium precursor the co-catalyst then there will be again beta elimination reactions and then hydro zirconium reactions and then followed by transmetalation, the transmetalation means the replacing one metal fragment by another metal fragments. So, here this is basically the aluminium fragment is replacing the zirconium. So, you get back your active catalyst back and then at the last you see here, so, here there is a zirconium.

So, here you will get the aluminium so, what you are getting basically you are have a like polybutadiene moiety and what you will be getting your degradation to smaller fragments and you are getting the smaller fragment but with aluminium. So, here you will see so basically at the at the end you will be getting the aluminium kept smaller alkene and alkyne chains by this methylation catalysts. So, you will you will see the single catalyst can do polymerization and also the de polymerization by changing some minor catalytic condition.

Similarly, this Metallocene catalyst can also act as the depolymerization of the poly olefin lie as you have seen for the Dufaud and Basset system.

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So, it is really very exciting that how this methylation catalyst can act as a depolymerization by using the concept of microscopic reversibility. So, this is really fascinating, I am sure you people are very excited and enjoying that how this organometallic methylation catalyst can be used for dual purpose.

And as we discussed in these 2 last 2 classes that the recycling or repurposing of the used poly alkanes which are very robust in nature, which does not degrade easily has to be taken care of and we have to design the recycling specifically the chemical way too, because that is the most strategic most effective way to repurpose to make the valuable compounds like oil works or the same monomer or the similar monomer or even the precursors for valuable to make the valuable compounds to make the process more economic and to use the concept of the circular economy.

So, the take home message of this lecture is that Polymer we have to use definitely we cannot avoid but we have to use in a limited way and we have to recycle to make our earth better and healthy and beautiful. We have 2 options one option is this one definitely do not want and another option is this one.

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So, these are the references we already I already mentioned that. These are very new concept and very challenging concept. There are a lot of to do, lots to do to develop to make it an industrial process, the recycling process. These are very recent reviews and papers. You can read these papers and fully understand this concept. So, in the next class, this is the end of the Metallocene chemistry for the polymerization and also depolymerization.

In the next class, we will start another very fascinating system, again it is Nobel Prize our winning chemistry, that is the metal carbon and metal carbide systems, which is also used for polymerization for some of the monomers obviously, naturally these are a very beautiful system, some of the monomers to make the polyolefin and poly alkyne and allied compounds.

And I am sure you have heard the graphs catalyst, which is very famous not only for the polymerization, and also used for various value added for the synthesis of various value added compounds, even in the medicinal chemistry. So with this, thank you very much, and we will see you in the next class.