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

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Lecture 8

Anionic Living Polymerization, Coordination Polymerization

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Lecture 08: Anionic living polymerization
Coordination polymerization

Welcome to the course again. So, in the last classes, we discussed the common polymerization protocol of radical polymerizations and then the control radical polymerization. And where we saw that in the control radical polymerization by using the concept of dormant species, how we can control the collaborations which is not possible in the free radical polymerizations.

So, continuation to that. In this class, we will discuss the anionic living polymerization. And then we will start the coordination polymerizations.

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CONCEPTS COVERED

- Living polymerization ✓
- Metal complexes as catalysts ✓
- Catalysis
- Inorganic/Organometallic catalysts used for polyolefin synthesis

So, the basic concept, we will cover here, the living polymerization protocol, which is, we have started the concept in the controlled radical polymerization. And then here, we will mainly focus on the anionic ring opening polymerization in this class today, then we will go to the living polymerization by metal complexes, and we will briefly know the concept of the catalysis.

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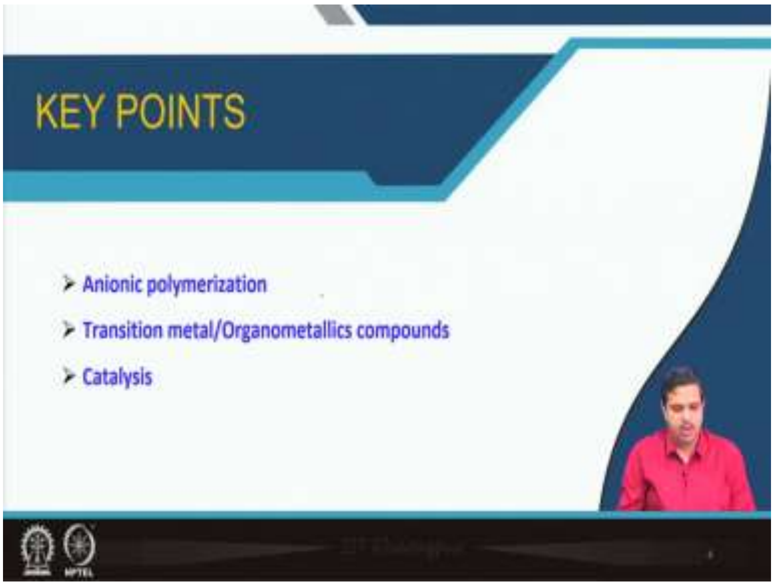

KEY POINTS

- Anionic polymerization
- Transition metal/Organometallics compounds
- Catalysis

The key words here anionic polymerization, transition metal organic compounds and catalysts and the very brief concept of the catalysis.

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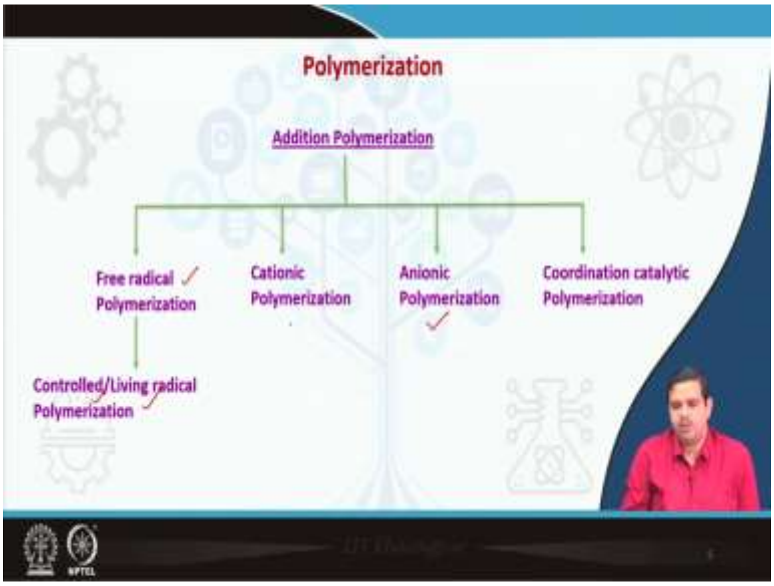

Polymerization

Addition Polymerization

Free radical Polymerization ✓

Cationic Polymerization

Anionic Polymerization ✓

Coordination catalytic Polymerization

Controlled/Living radical Polymerization ✓

So, we know about the free radical polymerization, we know now control and radical polymerization, how in a very intelligent way, how we have done the strategy of using the concept of dormant species and controlling the polymerization. Now, we will discuss today anionic polymerization, which is, which are applicable for polyolefin synthesis, catalytic polymerization is also another way, but which is not very common in polyolefin polymerization.

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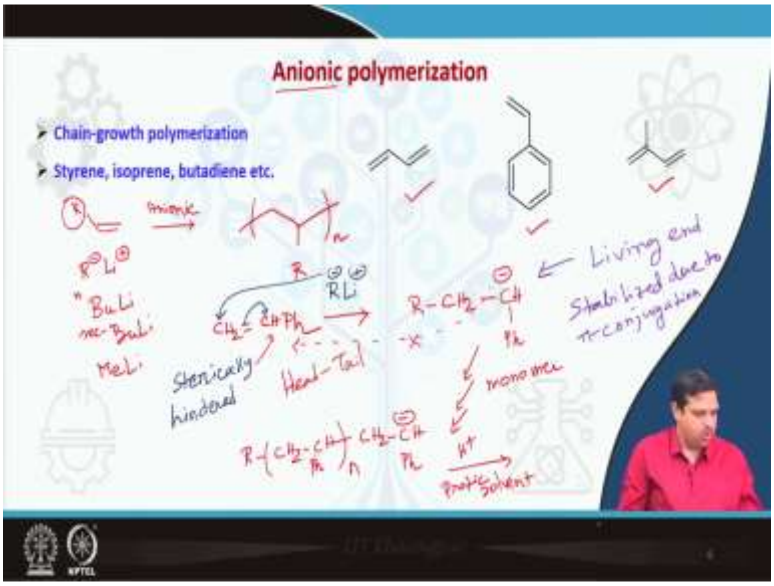

Anionic polymerization

- Chain-growth polymerization
- Styrene, isoprene, butadiene etc.

So, let us try to understand what is that? So, here the name suggests anionic polymerization. So, in radical polymerization, the active end was the radical. So, in an ionic polymerization, the active end will be obviously anion. So, let us see, what is that with a one example. So, let us see if you take this monomer and take the anionic polymerization and so, you will get like this polymer. Now, let us say how will do the anionic polymerizations. So, you have to take a initiator like this one.

So, you know that this is R Li. So, this is the organometallic reagent, and these R Li maybe butyl lithium maybe secondary butyl lithium in some cases, we can take methyl lithium like that. So, depending on the R the reaction rate is buried and also the applicability of anionic polymerization highly depends on the R. For one example, this anionic polymerization is quite possible for the styrene monomer, for isoprene monomer or for this butene polymer. So, let us see how does it proceed?

So, if we take like says styrene molecules, where R is equal to Ph here that is the phenyl. So, if you do this one and you take the R Li maybe butyl lithium SEC butyl lithium. So, this one will attack here because this is less tragically crowding, sterically hindered so this is the preferred position and then what you will get here, you will get, and you will see here this is the living end. So, this is the living end, and this is anionic is conjugated with the phenyl group. So, this is stabilized due to the pi conjugation.

So, now, what you are doing you have now initiated the polymerization. Now, this leaving end can now react to it another monomer sequentially and finally, you will get like this, like that and still here it is anion. So, this is again the leaving end, and the polymerization does not stop if you do not kill these living end deliberately. So, we use the protic solvent or H plus or any protic solvent as example water or methanol and then what you will do you will get you will get the neutral polymer by abstracting the H plus to the here.

So, you will see that this polymerization is living, why it is leaving because this end is active it does not stop or does not do any other termination which is unlike as you have done for the as you have seen for the radical polymerization. So, here again very similar to the radical polymerization, the head-to-head head to tail attack is more favoured than the head head. So, head to what is the head tail head to tail like this minus is attack to this one. So, this is the head to tail not this centre attacks to this one.

So, if it attacks this one then it is head to tail, but this is not does not happen. So, always the head to tail attack is favoured, because it is sterically because this position is sterically hindered this one. So, this attack on this side is sterically favoured. So, anionic polymerizations is always head to tail at attack.

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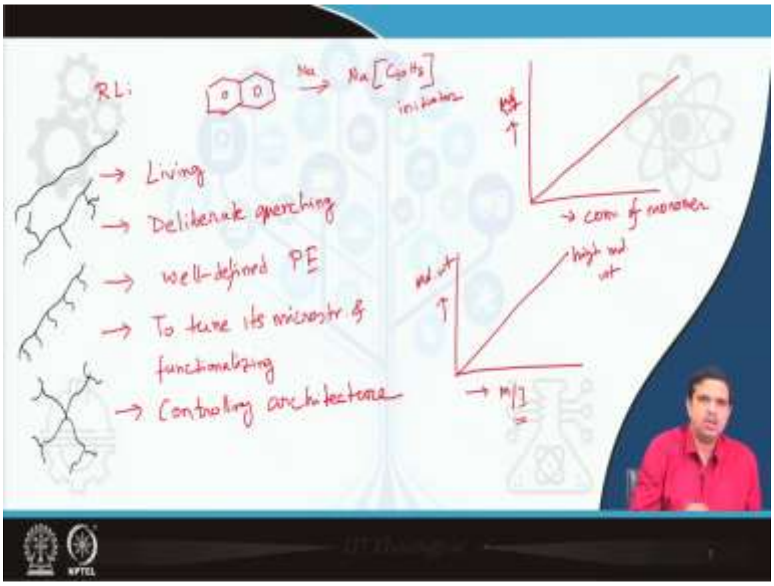

RLi

Na → Na[$C_{10}H_8$] initiator

→ Living

→ Deliberate quenching

→ well-defined PE

→ To tune its microstr & functionalizing

→ Controlling architecture

So, not only the various initiatives can be used depending upon your monomer and substrate as I show the most of the popular initiator is this one, but this is not limited to this category of this is called alkyl lithium, various initiator can also be possible as example, like aromatic initiator. So, if you react with sodium metal you will get the C10 H8 and this is a very good initiator for some of the polymers. So, the main point of anionic polymerization is the living deliberate quenching which is unlike to the free radical polymerization.

So, if you recall again the plot, if you plot this molecule weight and the conversion of monomer you will get the linear relationship. Similar way if you plot that is another way to prove that the polymerization is leaving. So, this is molecule weight and this if you had monomer initiator ratio. So, how much more you are taking the monomer and how much initiator you are taking, you will also get the linear relationship because this is living.

So, if you take less initiator, then you will get the high molecular weight polymer, if you take the large amount of initiator, you will get the low molecular weight. So, depending on the stoichiometry, you can control the molecule weight of the resulting polymers. So, that is the beauty of the living anionic polymerization. So, you will see that you can get the high molecular weight polymer by changing the initiative ratio or by taking the initiator. So, if it is living, you can predetermine the molecular weight, which we are synthesizing by changing the initiative and monomer ratio.

So, this is very good method not only to get the well-defined polyolefin but also to tune its microstructure and functionalizing sorry, the functionalizing of further functionalizing of the polymer and the controlling architecture that is the biggest advantage of this kind of living polymerization, as I told you that in many cases, you may need to have the polymers it depends on the specific applications, the linear or highly branching lying like that, many cases you will need like a grafted kind of polymer, many cases you will need like these kinds of polymers or further controlling the architecture depending on your applications and if your polymerization is not living or not controlled, you cannot make these kinds of polymer architecture.

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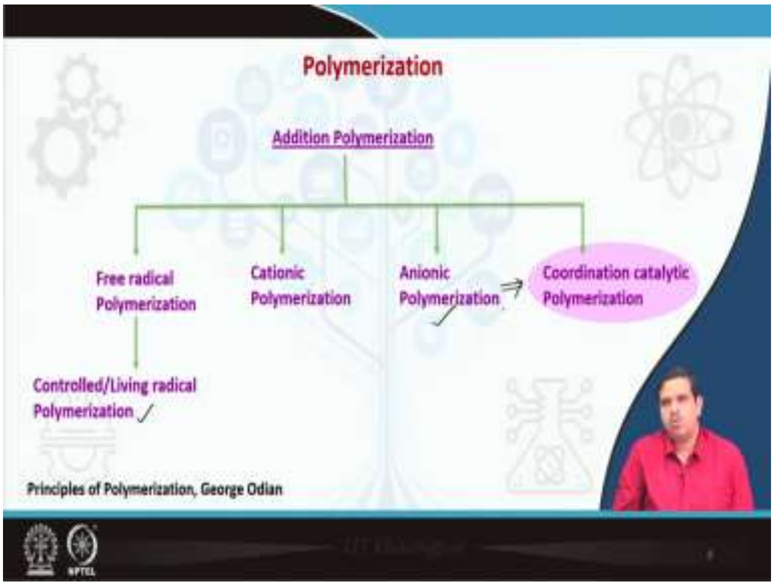

Polymerization

Addition Polymerization

Free radical Polymerization

Cationic Polymerization

Anionic Polymerization

Coordination catalytic Polymerization

Controlled/Living radical Polymerization

Principles of Polymerization, George Odian

So, this is as you see, that the controlled radical polymerization, anionic polymerizations are the category of the living polymerization. However, in the recent times, the coordination polymerization has played a major role in polymer industries for controlling the architecture and controlling the molecular weight. It has his own advantage, which we will discuss in the due courses.

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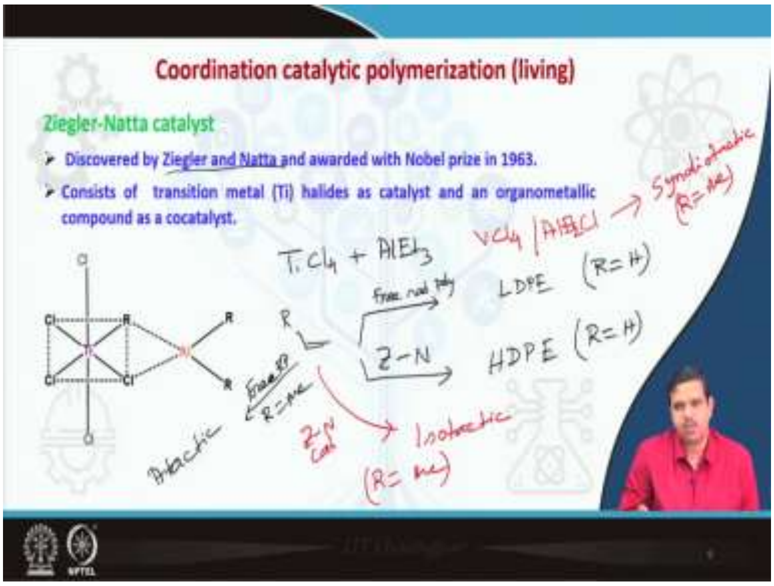

Coordination catalytic polymerization (living)

Ziegler-Natta catalyst

- Discovered by Ziegler and Natta and awarded with Nobel prize in 1963.
- Consists of transition metal (Ti) halides as catalyst and an organometallic compound as a cocatalyst.

So, if you recall, the Ziegler Natta catalyst was one of the first transition metal catalysts used for polymerization of polyethylene of Ethelyn monomer or propylene which was discovered by Ziegler and Natta and for this, they awarded the Nobel Prize in 1963. So, this is essentially a titanium chloride tetrachloride is a catalyst and this catalyst work in presence of a co catalyst, which is triethyl aluminium or other alkyl aluminium.

So, and why, what is the beauty? You will see if you do the polymerization by let us this one and if you do the traditional free radical polymerization, free radical polymerization you will get the low density polyethylene when the R is equal to hydrogen, but when you will do that Ziegler Natta catalyst, I am just writing ZN means Z just Ziegler Natta catalyst, you will get the high density polyethylene when R is equal to H not only that, when you will do the free radical polymerization, radical polymerization when R is equal to methyl, you will get atactic polymer and very surprising, if you do the polymerization with Ziegler Natta catalyst you will get the isotactic polymer, when R is equal to methyl.

So, you will see that how the different polymerization condition governs the polymerization mechanism and that you are getting the same composition of polymer, but different chemical structure. So, that we try to understand why, so, it is very clear that Ziegler Natta Catalyst has have a tremendous impact in the polymer industry as you can vary the crystallinity and the properties of the polymer by changing the chemical structure and the microstructure of the polymer.

So, it is very obvious that polymerization growth is very much different from the free radical polymerization. So, later, it was also explored, VCl4 and other co-catalyst and they are very surprising that here the syndiotactic polymerization polymer were observed when R is equal to methyl. So, you will see that how it the polymerization mechanism differs from metal centred to metal centre, I am sure you are feeling very excited, what is the reason how it governs the polymerization.

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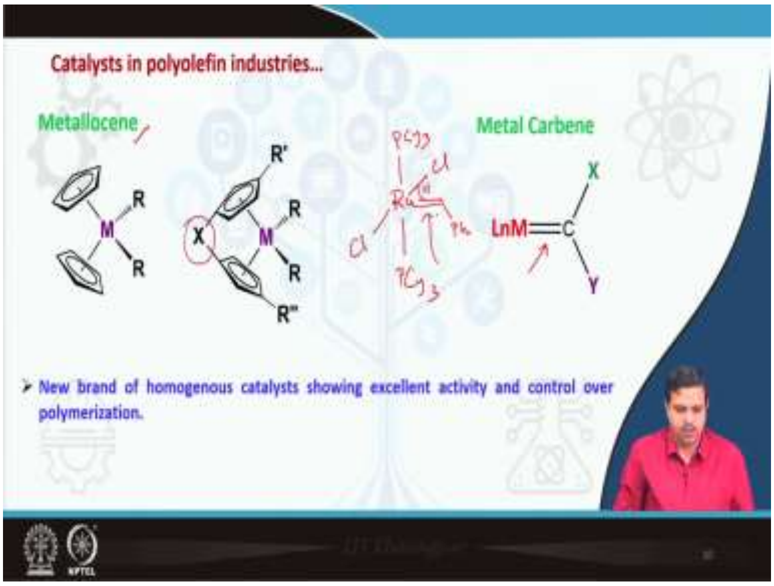

Catalysts in polyolefin industries...

Metallocene

Metal Carbene

- New brand of homogenous catalysts showing excellent activity and control over polymerization.

So, we will discuss in the due courses and after the Ziegler Natta catalyst we will discuss in very dept, what is the advantage and what is the disadvantage in the Ziegler Natta catalysts, when we will come to the lecture where we will follow a very systematic approach involved in the mechanism. So, further in the last two decades or so, this kind of catalysts have been developed, this is called metallocene where you will see this is this this metal centre each is sandwiched between these two CP groups.

And here were these two CP groups. Here it is a free not attached. And here, these two CP groups are basically threaded by a bridging atom, this bridging atom maybe silicone, maybe carbon, maybe nitrogen we will discuss in the future classes in depth and also the metal carbene catalysts where you will see this is there is a double bond between the metal and carbene. This is also very unique in nature, which were recently developed as a homogeneous catalysts showing excellent activity and control over the polymerization. I am sure you have heard the Grubbs catalyst and any idea what is the metal, ruthenium.

So, what is the basic structure of the Grubbs catalyst. So, this is like that. So, you have a, this one and this is cyclohexyl phosphene and this is two chlo. So, you will see that this ruthenium is n plus two oxidation state and you have the metal carbene bond. This is also a very good catalyst for alkyne metathesis polymerization, so, we will discuss these in a very systematic way.

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Transition metal/Organometallic complexes as catalysts

So, here, I have given a very brief idea about the organometallic catalysts, which are the recent trend in polymerization followed in many industrial polymer industries. So, obviously before going to the organometallic catalysts, it is it will be very highly benefit to understand what is catalyst because we will be I will be using the catalyst in the following classes. So, it is good to understand what is catalyst I am sure in your basic courses you have very familiar with the catalysis. The catalyst is I will discuss in a very brief way just to recall your memory.

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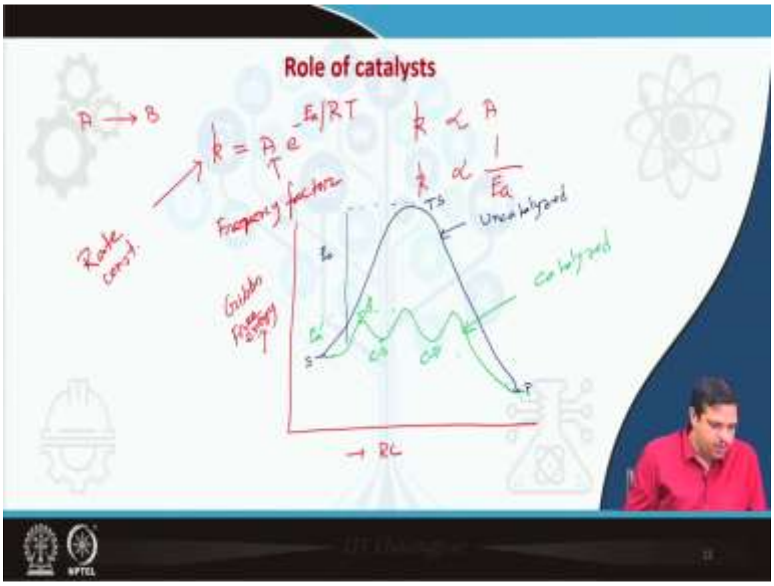

Role of catalysts

So, you know that one reaction like this one A to B, A is the substrate and B is the product. So, the rate of this reaction can be expressed by Arrhenius equation. So, A is the frequency factor all we know, the frequency factor and the small k is the rate constant and you will see here the rate constant is proportional to the A, but the rate constant is inversely proportional to the activation energy, because you see is a negative exponent.

So, that means, if the activation energy high the rate will be slow and vice versa. So, if we draw a reaction coordinate very qualitatively. So, this is your reaction coordinate and this is your Gibbs free energy, then how the reaction progress. So, I draw in a very qualitative way to understand the role of the catalyst. So, suppose this is my substrate and this is my let us say product and how is the reaction goes like this one and this is my activation energy. So, this is my activation energy and what is this, this is that transition state.

So, this black is uncatalyzed. Now, what will happen if you are facilitating the reaction by using a catalyst? So, what the major role of the catalyst is basically lower down the activation energy and how does it do, I am showing in a very qualitative way. So, here you will see that. So, here you will see that that green was green is that catalysed. Now, what will be your activation energy your activation energy will be let us say this one. So, you will see that Ea prime is much less than Ea. So, you can, this one is the catalyst and substrate transition state, this one is the catalyst substrate is intermediate, this is the transition state and this is the intermediate you will know that the lifetime of the transition state is very low.

So, it is not possible to isolate but for the intermediate complex is in many cases it is isolable. So, that is sometimes it is a good proof that yes, the mechanism is going through this purpose this way. So, sometimes we do routinely we isolate the intermediate and prove the mechanism. So, this is my catalyst and product intermediate. So, CP is my catalyst product intermediate complex, this is my catalyst substrate intermediate complex, and this is my associated transition state. Now, here you will see this is the product. So, we eventually you are getting the same product by a different reaction pathway, following the a pathway which is much lower in activation energy.

So, here you will see that this is the very simple way of looking at that how the catalysts play a role in the reactions is basically you will see that if activation energy is much low then obviously, as the rate constant is inversely proportional to the Ea. So, that means, the rate will be much higher for this catalysed reaction.

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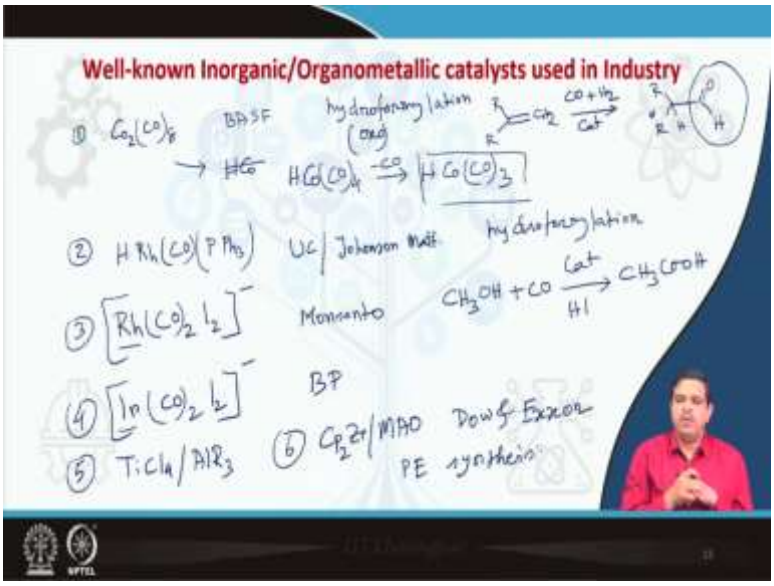

Well-known Inorganic/Organometallic catalysts used in Industry

① $Co_2(CO)_8$ BASF hydroformylation (oxo)

→ ~~HCo~~ $HCo(CO)_4 \xrightarrow{-CO} \boxed{HCo(CO)_3}$

② $HRh(CO)(PPh_3)$ UC / Johnson Matt hydroformylation

③ $[Rh(CO)_2I_2]^-$ Monsanto $CH_3OH + CO \xrightarrow[HI]{Cat} CH_3COOH$

④ $[Ir(CO)_2I_2]^-$ BP

⑤ $TiCl_4/AlR_3$ ⑥ Cp_2Zr/MAO Dow & Exxon PE synthesis

So, there are various inorganic and organic catalysts which are popularly used in industry, do you have any idea, can you tell me any one of one of them, which are routinely used in industries? I am sure you know; let us I just list out the main purpose to give a knowledge how these organometallic or transition metal complexes play a role in industries and to synthesize a value-added compounds. As example, I am sure you know that cobalt carbonyl complex which are used in hydroformylation reaction, I will also tell the specific industry which has a patent or discovered first.

So, Co2 Co cobalt carbonyl catalyst and this was discovered by BASF industry and for what hydroformylation reaction or sometimes we call oxo, what is the hydroformylation reaction. So, if you take a alkene and if you are simply using the carbon monoxide and hydrogen and this catalyst you can, sorry, functionalize this alkene by hydroformylation. So, here H and this side is. So, you will see is formulated at the terminal alkyne. So, this is radio selective specifically you will get the functionalized functionalization at the terminal alkyne, the active catalyst you may remember that this is H converted to.

So, the active species is the hydride cobalt carbonyl complex sorry, this is. So, you see here and again it is converted to the tricarbonyl cobalt hydride complex. This is the active species. I am sure you have read this in your previous course. So, this is very routinely used to get the formulated of product in industries. So, another related catalyst used as rhodium catalyst, which has more advantage than the previously complexes. So, this is the basic structure you will see that. So, this is developed by Johonson Matthew company, and which is again used for the hydroformylation for better selectivity and also you know he had there is one other problem that if this step is very much important, because to get the active catalyst, but you need the carbon monoxide in this reaction.

So, if they are you have to maintain a critical pressure of the carbon monoxide to proceed this reaction and as well as to proceed these reactions. So, this as is on a disadvantage however, it is very popular in industries. So, another organometallic catalyst used popularly used is the synthesis of acetic acid that is the Monsanto process. So, what is the catalyst, the catalyst is Rh. So, basically rhodium iodo carbon carbonyl complex. So, this is routinely used to make one of the key organic molecules which is used as a precursor to make different value added or compounds. So, here you use the methanol and you use the catalyst and you need also some iodide source HI and you will get the.

So, in all the cases you will see we are getting the organic compounds which are very important which plays a key precursor for many organic synthesis with these can be synthesized by very cheap materials like methanol, carbon monoxide, FC carbon monoxide, hydrogen, so, that is why it is very popular in industry. Similarly, very same to the Monsanto acetic acid process, Cativa which is actually developed by the British petroleum, the Cativa is nothing but just replacing the rhodium by this same similar, very similar catalyst but just replaced the rhodium by iridium.

Similarly, you will know that titanium Cl4 AlR 3. And also, you know, that which will be discussed in this course in more depth that is the metallocene based catalyst which is used by or discovered by the industry Dow and Exxon, this is used for the polyethylene synthesis. So, from here it is very clear that how the organometallic catalysts or transition metal complexes are very much related to the various industrial manufacturing process.

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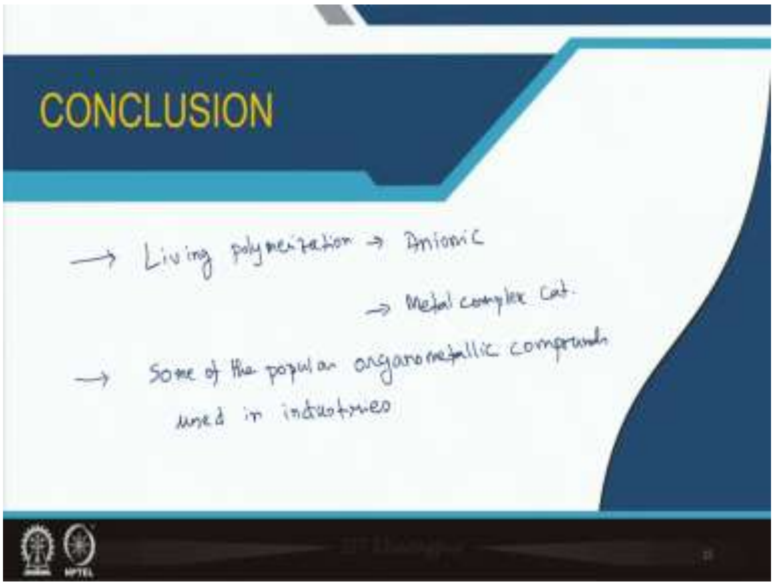

CONCLUSION

→ Living polymerization → Anionic

→ Metal complex cat.

→ Some of the popular organometallic compounds used in industries

So, here in this class, we have tried to understand the living polymerization by anionic and by metal complex catalysed and the some of the popular organometallic compounds used in industries. So, which definitely will motivate you in this course. So, in the next class, we will discuss about the unique properties of the organometallic compounds, which will be beneficial to understand the polymerization of the metal machine-based catalysts. We will try to understand that how the metal centre and the ligand governs the organometallic reactions and mechanism which will be very helpful to understand the polymerization mechanism. Thank you.