Transition Metal Organometallics in Catalysis Biology

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Lecture - 44
Olefin Polymerization (Part 5)

Welcome to this course on Transition Metal Organometallics in Catalysis and Biology. We have been talking about olefin polymerization in the last few lectures. More specifically, we have been talking about various classification of polyolefin polymers that are available from various perspectives. In this regard we have looked into polymer classification from application point of view particularly from materials perspective.

We have also looked into polymer classification from the process point of view, from the chemistry point of view and then as well as from the mechanism point of view. So having discussed various forms of polyolefin classification we are going to now focus on polyethylene and start discuss discussing the various aspects of the polyethylene chemistry particularly with regard to the preparations, their productions as well as their discoveries.

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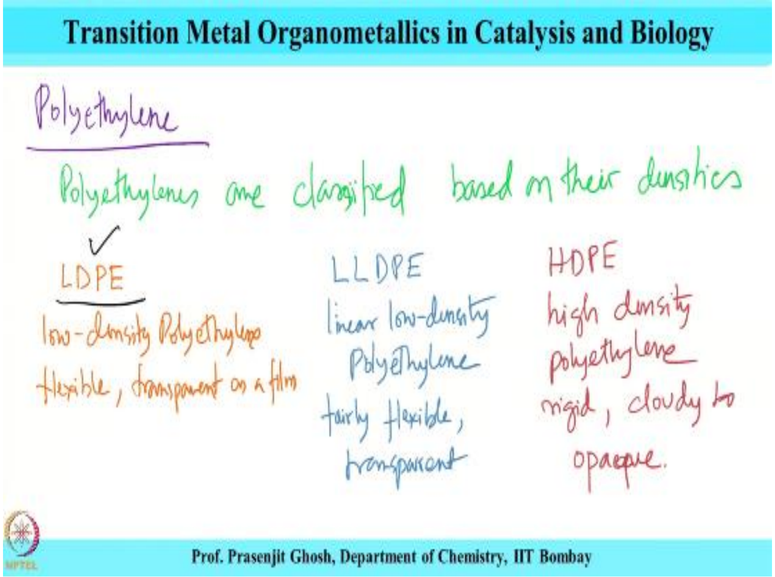

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Polyethylene

Polyethylenes are classified based on their densities

✓
LDPE
low-density Polyethylene
flexible, transparent as a film

LLDPE
linear low-density
Polyethylene
fairly flexible,
transparent

HDPE
high density
polyethylene
rigid, cloudy to
opaque.

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As we had discussed in our earlier lecture that polyethylene primarily are classified based on their densities and they come in 3 grades. One is called LDPE the other is LLDPE and HDPE. Polyethylene to be more precise are classified based on their densities and they come in 3 varieties which is low density polyethylene and these are flexible, transparent as a film then comes LLDPE and they are also fairly flexible.

These are linear low density polyethylene and they are also fairly flexible and transparent and the last in this classification terms HDPE. These are high density polyethylene, they are rigid and appear cloudy to opaque. Now with regard to the historical perspective on the development of various processes producing each of this polymers. The first actually it goes back to this LDPE which is the first one to be synthesized.

Or there were processes for this to be synthesized and Ziegler–Natta catalyst is actually came long after that about two decades later than the first process first few processes those were used for making this LDPE. Now as we had spoken about this classification of polymerization, that polymerization from a mechanistic perspective can go by step growth or chain growth mechanism all this metal mediated polymerization.

Like Ziegler–Natta they are coordination insertion polymerization or Cationic polymerization and they are they belong to the group of chain growth polymer. Now this chain growth polymer not only can happen with cations, but they can also be equally happen with anions or even radicals which will lead to polymer through this chain growth pathway and the oldest low density polyethylene was in deep synthesized using the oxygen as the radical initiator by a company called ICI Imperial Chemical Industries way back in 1933.

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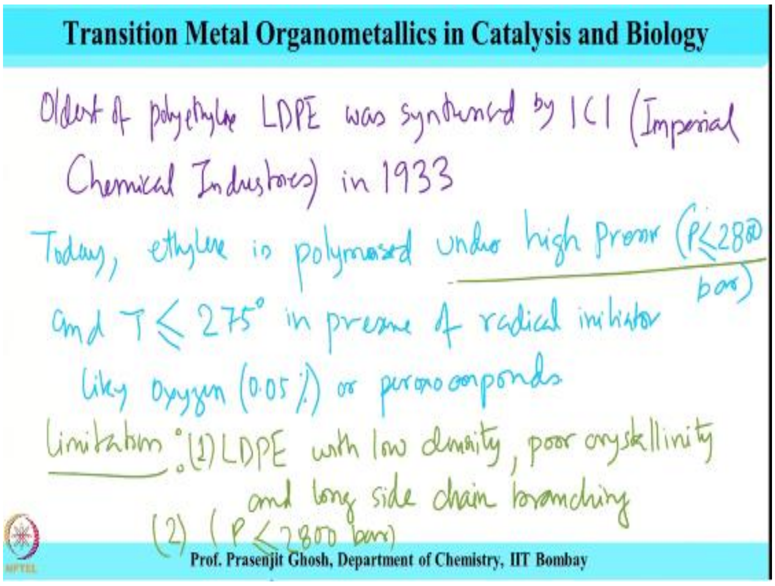

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Oldest of polyethylene LDPE was synthesized by ICI (Imperial Chemical Industries) in 1933

Today, ethylene is polymerised under high pressure ($P \leq 2800$ bar) and $T \leq 275°$ in presence of radical initiator like oxygen (0.05%) or peroxo compounds

Limitation: (1) LDPE with low density, poor crystallinity and long side chain branching

(2) ($P \leq 2800$ bar)

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Oldest of the polyethylene. It was synthesized by ICI which is Imperial Chemical Industries. So in 1933 even today ethylene is polymerized under high pressure < or = 2800 bar and temperature < or = 275 in presence of radical initiator like oxygen 0.05% or Peroxo compound. Now these one of the main limitations of a radical process is that this radical process is uncontrolled usually goes without control.

And as a result there is a lot of chain transfer and leading to chain branching and short size chains they appear in the polymer backbone as a result this LDPE low density polyethylene has a poor crystallinity and flexible long side and chains. Radical limitation LDPE with low density poor crystallinity and long chain long side chain branches long side chain branching. So by this radical process there are 2 limitations obviously this is the first limitation is that this has very long side chain branching, low density so on and so forth.

And the second limitation is extremely high pressure for 2,800 bars. So that is tremendous pressure under which this radical polymerization of ethylene is taken care of and because of such tremendous amount of pressure the reaction also goes uncontrolled and this is done in presence of a radical containing oxygen or any peroxo compounds. However, later subsequently Philips Process came into place. Where in 1956 using a chromium trioxide catalyst they could prepare this LDPE under much less pressure in heterogeneous fashion catalysis fashion.

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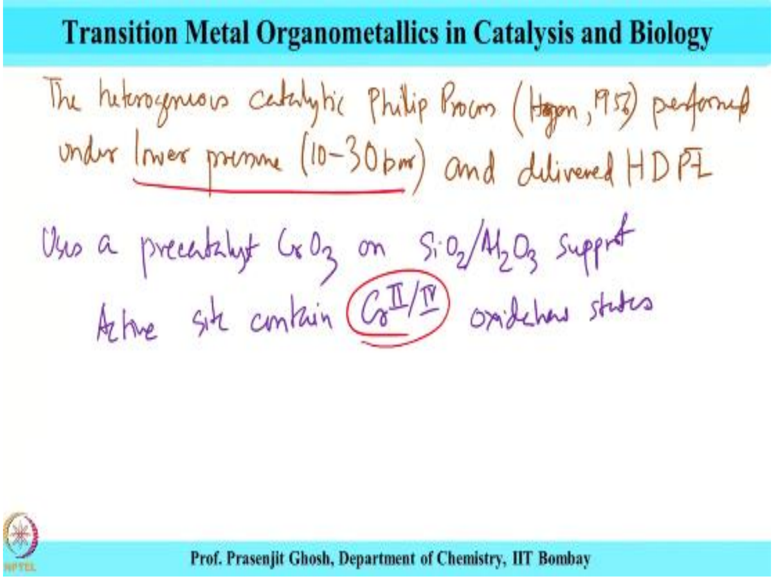

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The heterogeneous catalytic Philip Process (Hogan, 1956) performed under lower pressure (10-30 bar) and delivered HDPE

Uses a precatalyst CrO_3 on SiO_2/Al_2O_3 support

Active site contain $Cr^{II/IV}$ oxidation states

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The heterogeneous catalytic Philip Process by Hogan 1956 performed under lower pressure about 10 to 30 bar and delivered HDPE high density polyethylene. So there is improvement in the catalyst structure because HDPE is rigid, high density polyethylene it has long chain and they are cloudy to opaque and no branching. So this Phillip Process is improvement over the existing radical process which are used for making the LDPE.

The Phillip catalyst uses the applicant list which is chromium trioxide on a silicon support uses precatalyst Cr o3 on silicon Si O2 Al2 O3 support. Active side contains chromium II and chromium IV oxygen states. So in this process the take home message is that a flexible oxygen state change from chromium II to chromium IV is observed in the process which could polymerize ethylene at much lower pressure of about 10 to 30 bar.

As opposed to the radical polymerization which required about 3,000 bar, 2,800 bar to be more precise and that too producing polymer which of low crystallinity and low density like LDPE whereas this heterogeneous process using chromium successfully gave HDPE in 1956 and this is known as the Phillip Process. So before we go into details of this Phillip Process let me just note that so far the titanium of Ziegler–Natta catalysis has not entered the arena of ethylene polymerization and other metals like chromium in this particular case is successfully producing HDPE.

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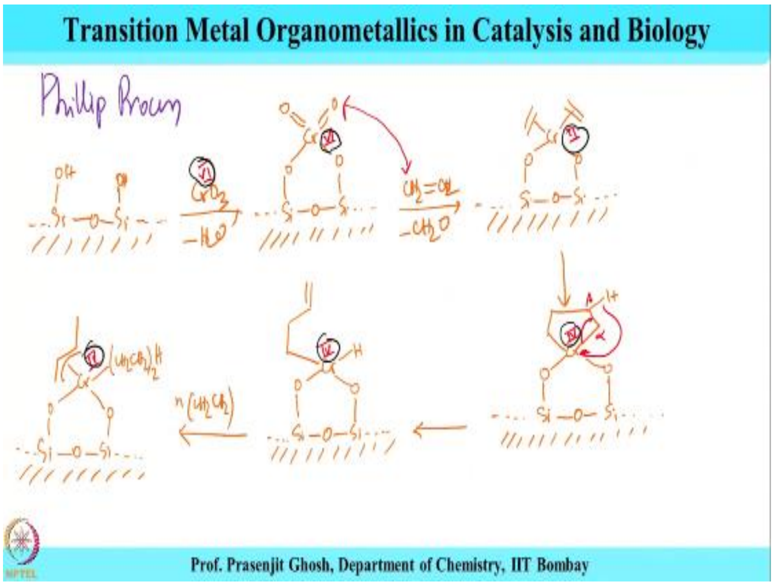

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So Phillip Process and the process sort of proceeds as follows on a silicate surface chromium Cr O3 would eliminate in water to give and this in presence of ethylene would give out formaldehyde and reduce the oxygen state of chromium from VI to chromium II as is shown here and then once this (()) (17:56) is formed so this is in chromium II and this formaldehyde is obtain by oxidizing this CH2 units for each of this ethylene to give formaldehyde.

And chromium getting reduced to chromium II which is then coordinated by ethylene and subsequently these gives five-membered chromium metallacycle as is shown over here five membered chromium metallacycle that then beta hydrogen eliminates the way it is shown to give the chromium compound as is shown here and this is a chromium hydride species and during the formation point to note that chromium now of this (()) (20:40) ethylene has changed to chromium IV.

Here also it is chromium IV hydride (()) (20:49) species and that gives in presence of ethylene it gives the following corresponding complex as is shown here. So this is an allylic compound with and the oxygen state of these remains (()) (22:18) as well. So the take home message from this mechanism is that the oxygen state of chromium initially was chromium VI that changes to chromium IV.

Then goes to chromium II comes back to chromium IV and after that it is chromium IV all the way. So this is a heterogeneous process in which this high density polyolefin can be obtained at very low moderate pressure about 10 to 30 bar and give well behaved high density polyethylene this chemistry is being done by chromium which is also early transition metal.

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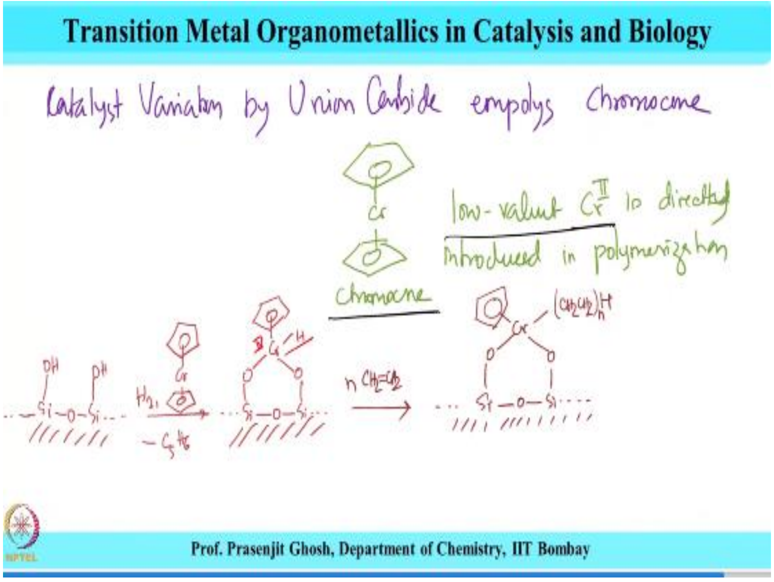

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Catalyst Variation by Union Carbide empolys Chromocene

low-valent Cr^{II} is directly introduced in polymerization

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Now a variation of this catalyst is reported by union carbide by union carbide that is also a chemical company employs chromocene. Chromocene is nothing but a ferrocene equivalent and this is useful in the sense that low valent chromium this is (()) (24:47) II is directly introduced in polymerization. So this chromium II which was forming from chromium trioxide in the Phillips Process is replaced with chromocene.

Because that will allow chromium in the divalent state right in the beginning and the Phillips Process so that sort of cuts down the reduction of chromium VI to chromium IV. So the Phillips Process is shown over here. So in presence of hydrogen chromocene is introduced and this results in elimination of cyclopentene C5 H6, but anchoring the chromium compound on to the silicon surface.

So in this case the chromium has become chromium IV directly and also found this chromium hydride and hence upon reaction with ethylene the corresponding polymer product corresponding from product is formed. So this is nice improvement where a low valent chromium is directly used for carrying out the catalysis in the union carbide process by starting the reaction with chromocene.

So with these we come to the conclusion of today's lecture. In today's lecture let me sum up what we have done is we have looked into various industrial processes that were available or known at that time for preparing this different grades of polyethylene. For example, the earliest known method for low density polyethylene or LDPE was reported as earlier as 1933 in which and later on they are still produced by oxygen as the initiator through radical polymerization.

But this requires very high pressure of about 3,000 bars and hence the reaction is extremely uncontrolled with several long side chains being generated on the polymer backbone. As a result, it gives to low density polyethylene. However, more improved and more tolerable amiable conditions for high HDPE was reported by Phillip Process which was done in a heterogeneous condition silicon aluminum surface using chromium trioxide as the catalyst.

Chromium trioxide got reduced to chromium IV and chromium II and then to chromium IV resulting in a chromium metallacycle and then subsequent coordination insertion polymerization leading to high density polyethylene were obtained by Phillips Process. So after ICI process for LDPE then we discussed Philip Process for HDPE and then we looked on a improvement made by union carbide for this chromium catalyst.

And instead of using chromium trioxide which is a high valent chromium precursor to enter the catalytic cycle the union carbide process uses directly the low valent chromium precursor in form of chromium chromocene which sort of anchors on the silica surface and that carries out the ethylene polymerization. So with this, I come to an end of today's lecture we are going to be looking at some more examples at the developmental stage for ethylene polymerization.

And then we will cover the most important of all this ones or so called the star of ethylene polymerization the Ziegler–Natta Catalysis when we meet next. So once again I would like to thank you for being with me and I look forward to taking of this topic of Olefin Polymerization or mainly ethylene polymerization in great more detail when we meet next till then goodbye and thank you.