Transition Metal Organometallics in Catalysis and Biology
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Lecture - 45
Olefin Polymerization (Part 6)

Welcome to this course on Transition Metal Organometallics in Catalysis and Biology. We have been discussing a very important topic which is a noble prize award winning topic Olefin Polymerization in the past few lectures. In this regard, we have approached this topic from 2 perspectives. To start with, we have looked into it from the perspective of application point view of view.

Particularly we started talking about Polymer classification from the application perspective and we have spoken about various kinds of polymers like thermoplast, plastic duroplast, elastomers, elastoplastic materials or thermoplastic elastomers and reversible duroplast. So these were all classified based on the properties of polymers then in the same topic we have looked into polymer classification based on the chemistry perspective.

From a chemistry perspective based on the process in which by which they are synthesized and in this context we have looked at 2 kinds of classification. One is condensation polymerization, the other is addition polymerization depending on the reaction by which they are formed. For example if they use a condensation reaction where a small molecule is eliminated as a path to polymerization then these are condensation polymers.

Whereas when the monomers have just added without elimination of any molecule they are called addition polymers and for one main feature of addition polymer is that the composition of the monomer and the composition of the repeat unit of the polymer are the same, they are constant. So we have done that and again we have also looked into the classification of polymer from the perspective of the mechanism point of view.

And these are from the mechanism by which this polymers are formed. In this context this polymer can be divided into 2 types based on the pathways they take one is step growth polymerization the other is chain growth polymerization and we had seen what are the characteristic molecular weight profile of the polymer so formed in this process as a function of percent conversion of the reaction, polymerization reaction.

And what we had seen that in the step growth process the molecular weight sort of increases drastically significantly towards the end of the polymerization that is towards the end of at higher percent conversion whereas molecular weight does not have a bearing in case of chain growth polymerization on the percent of the conversion of the polymerization reaction. So in this context we have also discussed about the various types of polyethylene. Which are obtained and the types of processes which are synthesized and polyethylene are of 3 types based on their densities.

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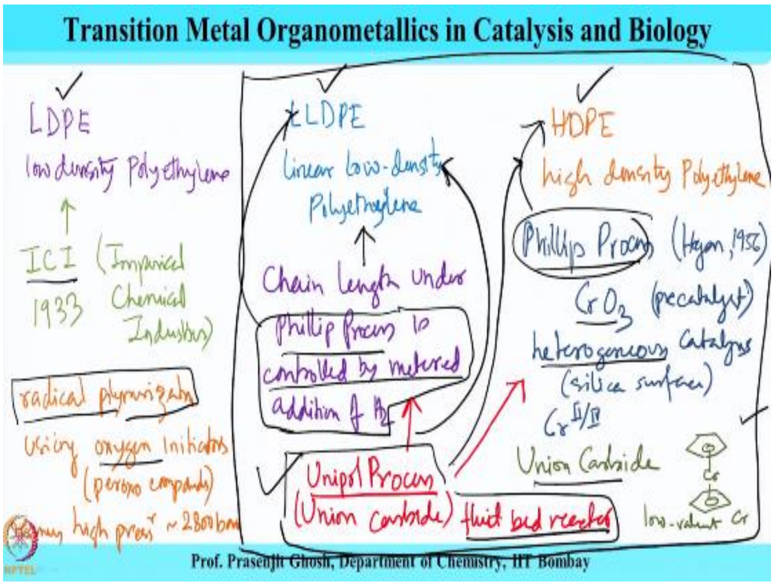

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LDPE
low density Polyethylene
ICI 1933 (Imperial Chemical Industries)
radical polymerization
using oxygen initiators (peroxo compounds)
high pressure ~ 2800 bar

LLDPE
Linear low-density Polyethylene
Chain length under Phillip Process is controlled by metered addition of H_2
Unipol Process (Union carbide) fluid bed reactor

HDPE
high density Polyethylene
Phillips Process (Hogan, 1956)
CrO_3 (precatalyst)
heterogeneous Catalysis (silica surface)
$Cr^{II/III}$
Union Carbide
low-valent Cr

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The first one is LDPE these are synthesized by these are called low density polyethylene. Polyethylene can be classified into 3 parts the first is the LDPE or low density polyethylene the next one is HDPE or high density polyethylene and the other one maybe write it later the next one after low density polyethylene is LLDPE this is linear and then is HDPE is high density polyethylene.

Or HDPE there are 3 types of polyethylene depending on the branching this polyethylene has different material properties some are soft, some are hard and brittle, some are transparent, some are opaque. Now in the last class we have also discussed about the industrial processes that are used for preparing this kind of polyethylene and the first one that we had spoken about was this ICI Imperial Chemical Industries.

First developed this process for preparing LDPE linear low density polyethylene in 1993. So this is probably the oldest polyethylene polymer to have been prepared industrially and presently this LDPE are prepared radical polymerization using oxygen initiators so like Peroxo compound. Now these radical polymerization is not good because it has several limitations requires high pressure of around 2,800 bars.

And also the reaction is uncontrolled as a result polyethylene obtained are branched has significant branching and they are soft material without noncrystallinity. So the next process are the process which is used for preparing high density polyethylene HDPE is the Phillip Process. This was discovered by Hogan in 1956 and this is sued for making this high density polyethylene.

And it was using chromium trioxide as the catalyst and pre catalyst as a pre catalyst, but the real chemistry was done and this was done on a heterogeneous fashion on silicon silica surface done on a heterogeneous fashion in a silica surface. So this Phillip Process actually uses chromium II and chromium IV as the active metal centers which carry out this polymerization process.

We have also seen that a improvement of the Phillip Process was reported by union carbide which use chromocene low valent chromium compound as precursor for this HDPE. Now there is another variant of the Phillip Process which uses hydrogen to control the chain length. So chain length under Phillip Process is controlled by metered addition of hydrogen, chain length is controlled under metered addition of hydrogen.

And that sort of gives rise to this low density polymer and this is how this LLDPE is produced. Now in context of this there was a significant discovery which is another process called Unipol Process from union carbide which uses fluid bed reactor and they have been used for producing both LLDPE as well as HDPE. So this is a interesting process. So what we see if we sum up that there are several industrial processes involved for producing various grades of polyethylene.

To start with it was ICI or Imperial Chemical Industries currently also radical polymerization is used with oxygen initiators for producing LDPE low density polyethylene for HDPE it was heterogeneous chromium trioxide process in 50s called Phillip Process which was producing

HDPE and then union carbide comes into play and produces HDPE with chromocene which is a low valent chromium precursor.

And finally by controlled metered digestion of hydrogen to Phillip Process one can get LLDPE as well as LLDPE. So Phillip Process can give both it can give HDPE and Phillip Process with hydrogen can also give LLDPE and after this there was a technological breakthrough in form of this Unipol Process which uses chloride bed reactor and then this can be used for producing both LLDPE and HDPE.

So this is a technological breakthrough from union carbide where they have gone from conventional reactor to fluid bed reactor a new technological development for producing this high molecular weight polyethylene. So this shows the chemical reactivity space for from a industrial perspective for producing the various grades of polyethylene. So, what we can see that this low density polyethylene is the one which is produced by radical polymerization.

Whereas both LDPE and LLDPE they are produced by ionic or catatonic coordination (()) (14:56) polymerization. So now we have gone on to move on to something more interesting and that during the course of development of all this Phillip Process and then Unipol process. There was a parallel development of Ziegler development towards Ziegler–Natta catalyst was taking place simultaneously and (()) (15:27) starts with this Aufbau reaction or chain growth reaction of aluminum and so we are going to take a look at this exciting development as we proceed further in this lecture.

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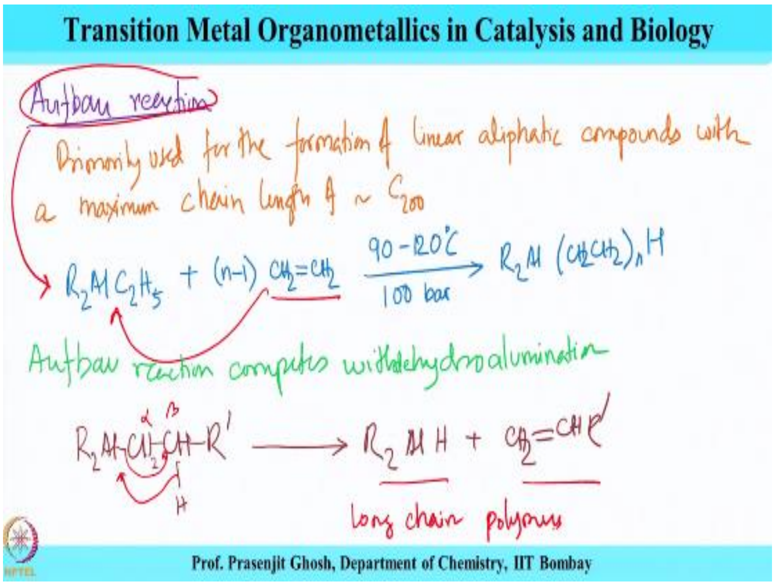

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Aufbau reaction

Primarily used for the formation of linear aliphatic compounds with a maximum chain length of ~ C_{200}

$$R_2AlC_2H_5 + (n-1)\ \underline{CH_2=CH_2} \xrightarrow[100\ bar]{90-120^{\circ}C} R_2Al(CH_2CH_2)_nH$$

Aufbau reaction competes with dehydroalumination

$$R_2Al-\overset{\alpha}{CH_2}-\overset{\beta}{CH}(H)-R' \longrightarrow \underline{R_2AlH} + \underline{CH_2=CHR'}$$

long chain polymers

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Aufbau reaction, the Aufbau reaction is this reaction is primarily used for the formation of linear aliphatic compounds with a maximum chain length of C200. So at that time this was sort of polymerization on the back of aluminum Aufbau reaction which is called growth reaction. At the back of aluminum and which could give linear aliphatic compound of maximum length of C200.

So that is really long chain compounds and the reaction of this is given as R2 Al ethyl n-1 CH2 CH2 at 90 to 120 degree centigrade 100 bar gives R2 Al CH2 CH2 n. Now what is happening is these CH2 CH2 unit it is getting adding on this metal ethyl bond in high pressure and this Aufbau reaction this is what is called Aufbau reaction and this reaction competes with another reaction called hydroalumination.

Aufbau reaction compete with another reaction called hydroalumination and this is given as R2 Al CH2 CH2 R dash giving dehydroalumination R2 Al H + CH2 double bond CH R dash and this can be explained as a beta hydride elimination and this is explained as such. So one gets; aluminum hydride and this alpha olefin. Now these are really long chain products long chain polymer and Karl Ziegler was observing this formation of this long chain polymer in his laboratory.

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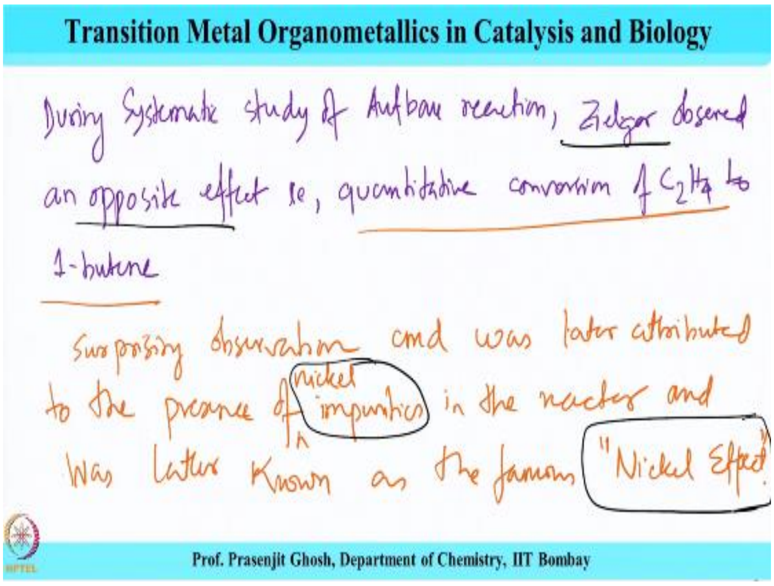

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During Systematic study of Aufbau reaction, Zielgar observed an opposite effect ie, quantitative conversion of C_2H_4 to 1-butene

Surprising observation and was later attributed to the presence of nickel impurities in the reactor and was later known as the famous "Nickel Effect"

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During systematic study of Aufbau reaction Ziegler observed and opposite effect that is 1 quantitative conversion of ethylene to 1 butene. So instead of observing very high polymer chain with Ziegler observed that in one cases he had observed quantitative conversion to just algomerise product dimerization of ethylene to 1 butene and this was a surprising observation and was later attributed to the presence of impurity in the reactor.

And this is supposed to be nickel impurities reactor and that was later known as the famous nickel effect. So while pursuing this Aufbau reaction under different condition carrying out the systemic study process Ziegler called Ziegler observed that in certain cases exactly opposite was happening that is conversion of quantitative conversion of ethylene instead of making polymer was making 1 butene.

And this was sort of contrasting and surprising observation at the time of study where the focus of the Aufbau reaction was to make long chain polymer and here they were quantitatively getting dimer. So this surprising observation was a later attributed to the presence of impurities in the reactor particularly the nickel impurities and which was famous which was later came to be known as the famous nickel effect that actually triggered the discovery of Ziegler–Natta polymerization.

So with this I stop come to an end of today’s lecture. In today’s lecture we have looked at the various industrial processes that are prevalent or well prevalent in producing or accessing various kinds of polyethylene ranging from LDPE, LLDPE and HDPE and we are also put in the perspective various discoveries and changes that were effected on individual processes to access each of these polymers.

We have also looked into the beginning or Ziegler–Natta discovery, beginning of the discovery of the Ziegler–Natta catalyst is starting from Aufbau reaction and how the opposing effect of nickel impurities led to dimerization of ethylene to 1 butene. So that was later recognized as the famous nickel effect and which even triggered the discovery of Ziegler–Natta catalysis.

So with this I thank you for being with me in this lecture. We are going to be discussing further from the point of nickel effect to Ziegler–Natta and various type of other Ziegler–Natta catalyst examples as we take this topic up in the next class till that thank you and goodbye.