Transition Metal Organometallics in Catalysis and Biology
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Lecture - 43
Olefin Polymerization (Part 4)

Welcome to this course on Transition Metal Organometalics in Catalysis and Biology. We have been discussing about Olefin Polymerization and in this context we have been talking about olefin classification or polyolefin classification depend from various aspects. For example, from the polymer perspective or from the polymer property point of view we had spoken about various classification that exist for polyolefin polymers.

Namely thermoplastic materials, duroplasts, elastomers, elastoplastic material or thermoplastic elastomers and reversible duroplasts. Again from the polyolefin perspective with regard to polyethylene we have looked at how many different types they come in and they come in 3 varieties which is LDPE low density polyethylene, it can be LLDPE linear low density polyethylene or HDPE high density polyethylene.

So if polyethylene are graded based on the density of the polymer (()) (01:32) and in that there are 3 varieties. Now having discussed the polymer classification from polymer perspective or from polymer type point of view then we moved on to looking at the polymer classification from a chemistry perspective particularly from the point of view of the process through which they are synthesized as well as from the point of view of mechanism through which they were synthesized.

So in this category we have spoken for about 2 types of classification. One is condensation polymer as well as addition polymer these are from the perspective of the process by which these polymers are synthesized. Similarly, from the mechanism that is followed to produce this polymer and from this perspective there are 2 types which is step growth or the chain growth polymer.

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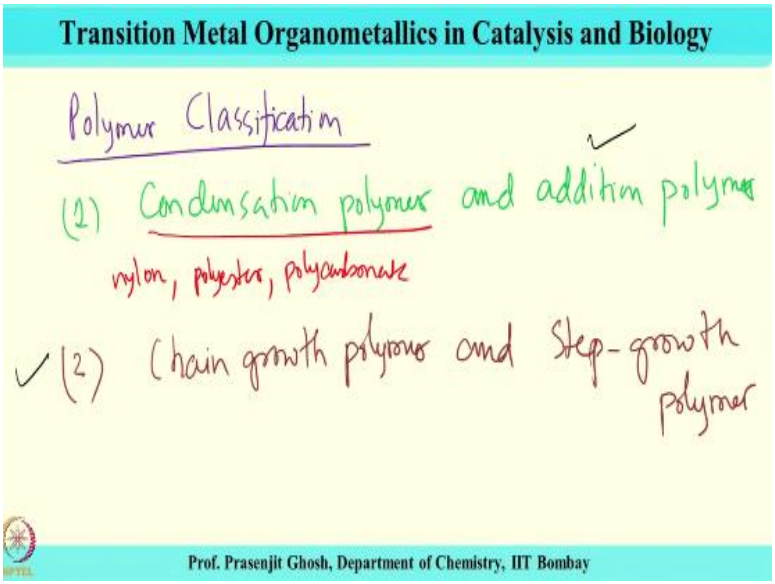

So we have been talking in the last class about the process perspective which is condensation polymer and addition polymer and from the mechanism perspective the 2 types of polymer are chain growth polymer and step-growth polymer. Now in this context we have studied the condensation polymer in great detail in the previous class and we saw that many important commercially important polymer like nylon, polyester, polycarbonate polymers are synthesized using this condensation polymer.

And these are mainly monomers which are polyfunctionalized and there can be more than one type particularly of 2 type like diamine and diacid or diol diacid or diol diacid, diamine and diacid or diol acid chlorides for making this kind of condensation polymer. Now having discussed the condensation polymer in great detail in the previous lecture what we are going to be doing today is to look into the other process based polymer.

Particularly these addition polymers and this examples and followed by the other 2 classification which is classification based on mechanism that is the chain growth polymer and the step-growth polymer.

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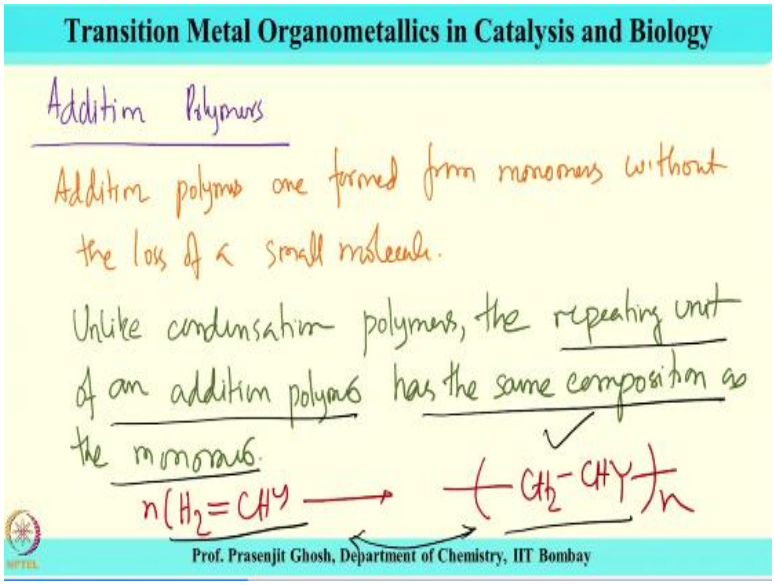

So having said this let us now move on to discuss about this addition polymer classification. Now addition polymers are the ones or the polymers that are formed from monomers without any loss of a small molecule unlike the case with condensation polymers. In the condensation polymer the condensation reaction within the monomer resulted in formation of some small molecular the bye product.

However, in case of addition polymer the reaction between monomer does not lead to formation of any bye product. Addition polymers are formed from monomers without the loss of a small molecule and the other biggest advantage or characteristics of this addition polymer is that the repeating unit has the same composition as the monomer whereas in condensation polymer the repeating unit is not exactly of the same composition as the monomer because a small molecule has come out of it.

So another important characteristics of addition polymer is that unlike condensation polymers the repeating unit of an addition polymer has the same composition as the monomer. So an example of this kind of polymerization is given below mainly the polyethylene polymerization is an example of this addition polymerization or the vinyl monomers was formed mainly through polymerized mainly through this process n CH2 CHy upon polymerization gives CH2 CHy n.

So these are vinyl polymerizations using vinyl monomer unit. So what we see is that polymers can be characterized based on the method in which they are polymerized. One mainly is a condensation method where elimination of small molecule occur, but the other is

just an addition method where the small molecule does not occur and polyvinyl polymers are polyethylene polymers are a result of this addition polymerization.

And another important characteristics of this addition polymer is the fact that their composition of the repeat unit of the polymer which is shown over here this is the repeat unit of the polymer this is exactly same as the monomer composition and that is said over here repeating unit of the addition polymer has the same composition as the monomer. So this and this 2 compositions are same.

So now we are going to look at another type of polymer classification mainly from the mechanistic point of view and these are the step-growth and chain growth mechanism and this classification is mainly based on the pathway which is used for making this long chain polymers from the monomers.

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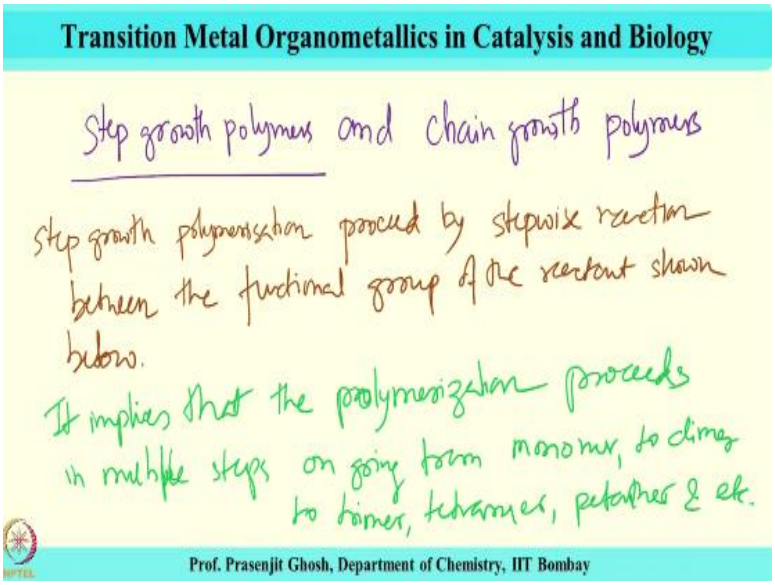

So let us first start from the step growth polymerization. So what really distinguish between the step-growth and the chain growth is the mechanism by which the step growth polymers are formed. This is illustrated or this is best explained in the definition that follows. Step growth polymerizations proceed by a step wise reaction between functional groups of the reactant between the functional group of the reactant shown below.

What it means that the polymerization proceeds slowly from monomer to dimer to tetramer, pentamer so on and so forth. It implies that the polymerization proceeds in multiple steps on going from monomer to dimer to trimer, tetramer, pentamer.

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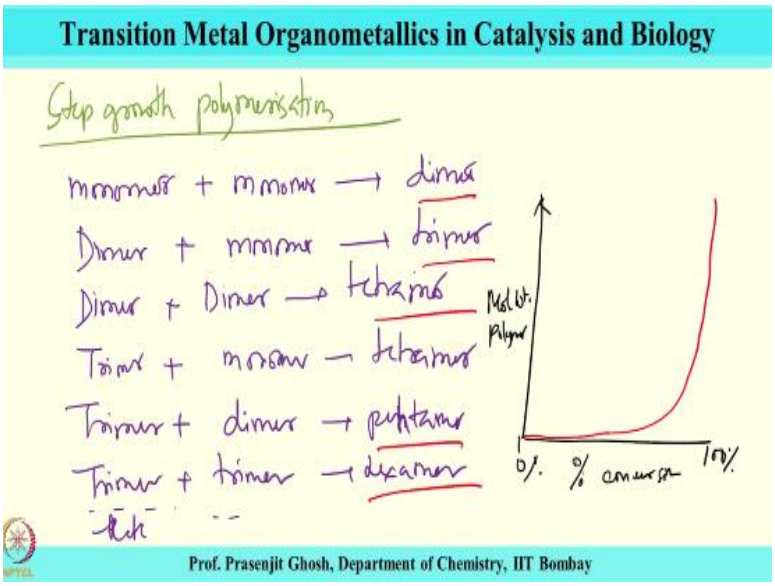

So this can be illustrated below for example first monomer will react with another monomer to give dimer then dimer can react with another monomer to give trimer, dimer can also react with another dimer to give tetramer, trimer can react with monomer give tetramer, trimer can react with dimer to give pentamer, trimer can react with another trimer gives (()) (15:54) and this thing proceeds.

So this polymerization was proceeds in steps and as a result of each steps the size of the polymer keeps increasing like the dimer then trimer then tetramer, pentamer, (()) (16:23) the size of the polymer keeps increasing and this can be reflected if one way to measure the polymer molecular weight with the percent conversion for this kind of step growth polymer. So if one were to look at the molecular weight of the polymer as a function of percent conversion of the monomer.

So this is 0% to 100% then what is observed over here is that the molecular weight sort of increases, but increases slowly. It is only in the end that there is a sharp increase in molecular weight happen when the longer chain oligomer they react with each other to give even further even further more longer chain oligomers. So there is a characteristic trajectory which is known for this kind of step growth polymerization.

Where the molecular weight increases slowly with conversion in the beginning of the reaction, but however towards the end of the reaction the molecular weight sort of increases drastically as the longer chains react and polymerize to give even longer chain. So this is a

characteristic feature of this kind of step growth polymerization.

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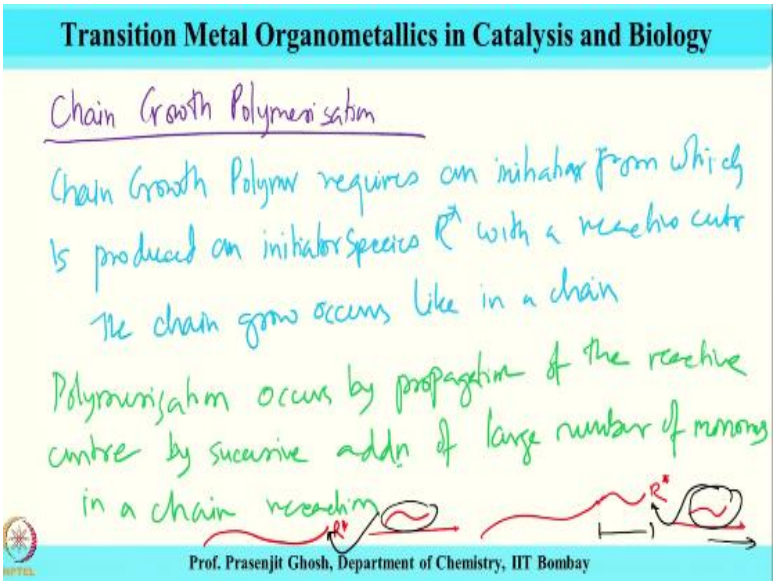

Now we are going to look at the other polymerization process which is called the chain growth polymerization. Now in chain growth the polymer does not grow like a chain where each of the chain length gradually grows with each of the monomer adding to the singular chain and the chain keeps on increasing. So this chain growth polymer requires initiator. So chain growth polymer requires an initiator of initiator from which is produced and initiator species R dash with a reactive center.

And the chain growth takes place like in a chain, the chain growth occurs like in a chain and this polymerization occurs by propagation of the reactive center by successive addition of large number of monomers in a chain reaction. So this is sort of explained in this cartoon as it is shown here. So for example if this is a chain with a reactive propagation center and to this one monomer comes along.

This monomer then gets added to this polymer chain generating another reactive center and this species would then be so this monomer would get inserted and then subsequently another monomer would come and insert. So the chain has increased by this much the monomer length when the second monomer would come and insert this and cycle propagates.

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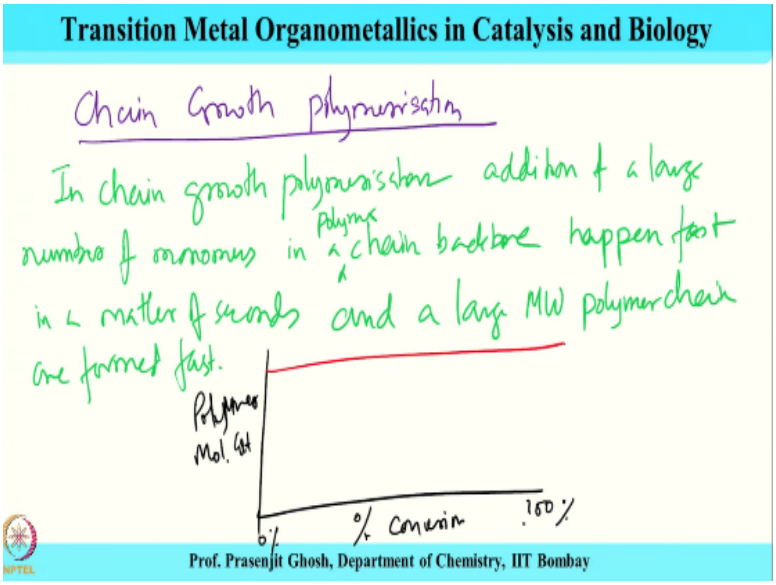

It is important to note that this chain growth polymers. It is this addition in chain group polymers growth polymerization addition of large number of molecules, of a large number of monomers in a chain reaction, polymer chain backbone happen fast in a matter of seconds and a large molecular weight chain polymer chain are formed fast. This also has a trajectory polymer molecular weight and percent conversion.

And what has been found is that the molecular weight does not change with the percent conversion because it just forms the equal length polymer no matter what how the reactions proceeds. So these 2 graphs the one in which for the step growth the other for the chain growth that sort of as a function of variation of molecular weight as a function of percent conversion of the monomer tells us inside as to what mechanism is proceeding.

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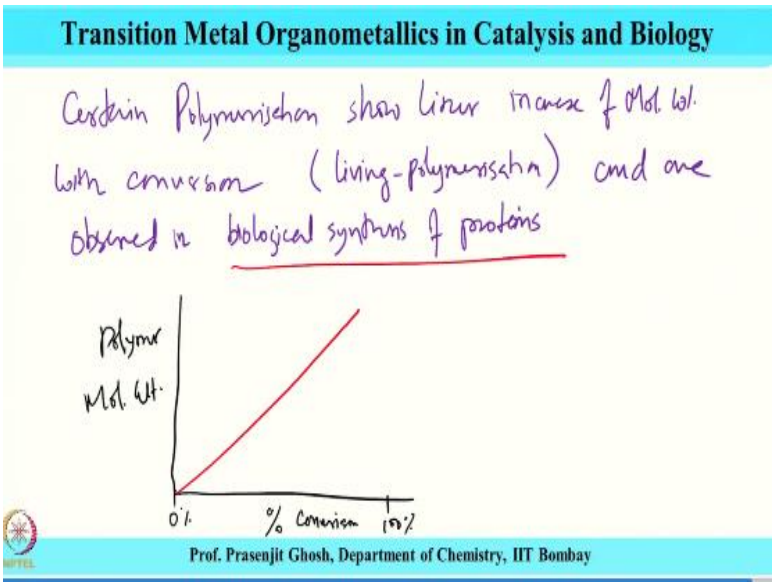

Now there is a third type of polymerization which is sort of a living polymerization and they are mainly seen in biology. Certain polymerization show linear increase of molecular weight with conversion and so these are sort of living polymerization and are seen in the biological and are observed in biological synthesis of protein and for them the characteristics plot of molecular weight versus percent conversion is slightly different.

Percent conversion and for this the trajectory which is observed of the molecular weight is something like this that the molecular weight increases with the percent conversion and these are mainly seen for biological system or where the polymerization is living when the monomer comes the chain further keeps on adding. So with this we come to the end of today's lecture which was primarily polymer classification.

From chemistry perspective particularly from a process perspective where we discussed about this condensation polymer and the addition polymer with examples then we also looked at how the mechanistic classification about polymerization would vary and in this from mechanistic classification we have seen that the polymer can be classified into 2 types. One is the step growth as well as the chain growth.

And for each of this step growth and chain growth we have discussed the characteristic molecular weight versus percent conversion (()) (29:08) in step growth polymerization. There is a sudden increase in higher molecular weights towards the end of the conversion and sort of the exponential the carve sort of stays gently increases in the beginning of the conversion whereas towards the end it lies sharply.

Whereas for the chain growth what we saw that the molecular weight is kind of fixed and does not change with percent conversion and lastly we had spoken about biological processes where certain polymerization show increase molecular weight with percent conversion and these are sort of polymerization which are living in nature and they are seen in biology particularly with regard to protein synthesis. So with this I conclude today's discussion on chain polymer classification and we are going to be discussing more on this olefin polymerization as we meet next till then goodbye and thank you.