Transition Metal Organometallics in Catalysis and Biology
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Module No # 06
Lecture No # 39
Alkene Oligomerization and Polymerization

Welcome to this course on transition metal organometallics in catalysis and biology. In this regard we have been discussing olefin oligomerization reactions in the past few lectures. And today we are going to finish up the discussion on olefin oligomerization or alkene oligomerization. And if time permits we start with the topic alkene olefin polymerization as well. So with that let me just give a brief overview of what we have been discussing in the previous lectures as mentioned earlier that we had started off with ethylene oligomerization in the context of shop process sell higher olefin process.

And then we had looked into ethylene trimerization using tantalum catalyst. This was a work by professor Ayusman Sen where one could produce one hexene selectively by trimerizing ethylene. The third that we have spoken about in this under this topic is this propylene dimerization in terms of producing various kinds of branched hexanes. This also is a industry applicable reaction which is used for application in auto industry particularly this branch hexanes when hydrogenated very good anti knocking agents and used in petrol for their attributes.

So after trimerization of propane dimerization of propane are producing branched hexanes we then looked at trimerization of butadiene which gives this a cyclododecatriene which is cycling compound ring with 3 olefinic 3 unsaturated olefinic bonds. And each in a trans configuration and subsequent that we have also looked at the Ziegler Natta way of preparing this cyclododecatriene using Ziegler natta catalyst titanium catalyst. And today we are going to discuss butadiene dimerization.

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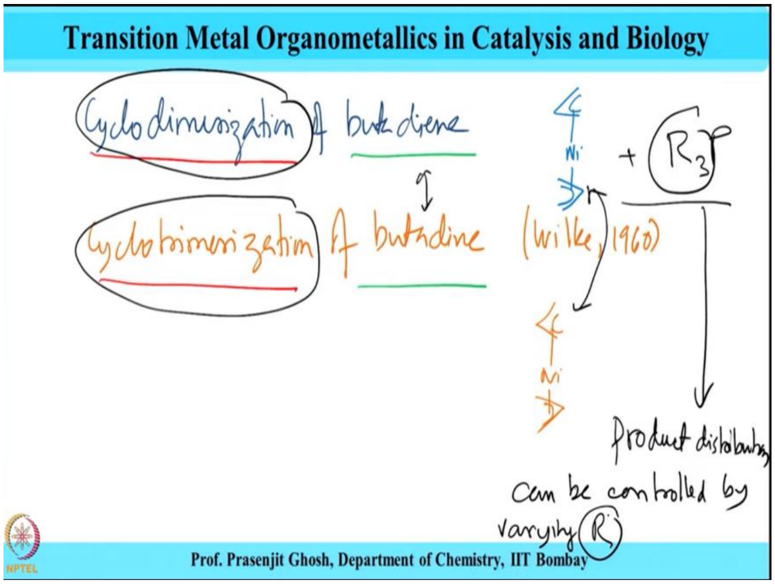

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So the one that you had spoken about earlier was butadiene trimerization and today we are going to talk about butadiene dimerization cyclodimerization of butadiene. Now in order to take up this topic we should refer to the earlier discussion of cyclotrimerization of butadiene. And this was reported by Wilke in 1960. Now the difference between these 2 process is that the earlier one was a cyclotrimerization process where do decatriene was obtained and this today what we are going to be discussing is a dimerization process where is we are going to make a octadiene in cyclic octadiene.

So there is a difference in the product which would be formed because of dimerization and obvious trimerization process. However there is lot of similarity in the process as well for example both involves a substrate butadiene. So the today's one is a dimerization of butadiene and the earlier on we had discussed trimerization of butadiene and furthermore the other similarity is that the catalyst precursor is same for both the catalyst precursor is same for the both. The one which is the dimerization and the one for the trimerization as well.

And let me just draw the catalyst precursor. So this be allyl nickel complex is the catalyst for cyclone dimerization process. And also the same is true for the nickel butadiene cyclo trimerization butadiene process. Now the difference lies in the final product one is for the dimerization the other is the trimerization. Whereas the similarity is the both are of butadiene and both require the same catalyst.

The only other difference is that these di butadiene dimerization proceeds in presence of phosphenes and they results in dimerization. So when phosphine is present with nickel allele catalyst and with butadiene as a substrates then primarily the dimerization product of butadiene is observed. Whereas when nickel allene with butadiene is present exclusively then the trimerized product observed.

So in this case when phosphenes are present then the product distribution the dimerist product distribution can be controlled by varying R the alkyl group of the phosphine. So that gives a useful handle on how this dimerization process occurs.

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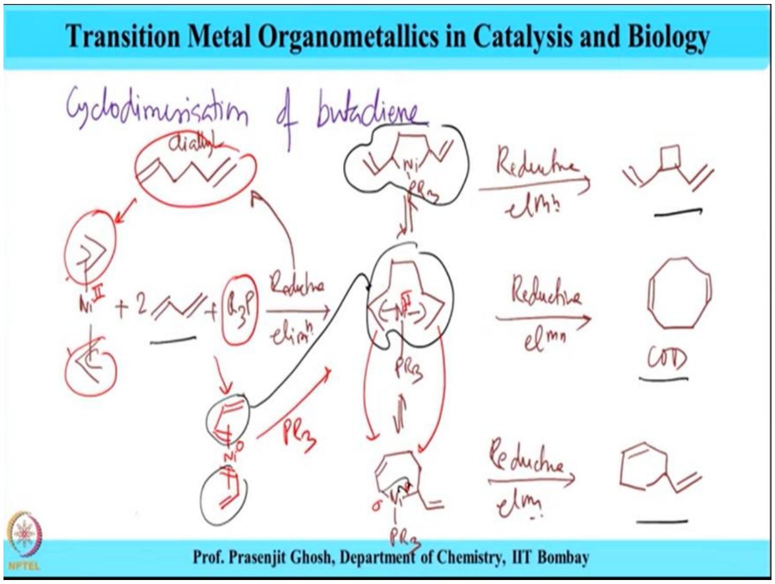

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So now let me just give the scope of this reaction in terms of the different products being formed and this is shown over here. This reacting with 2 butadiene in presence of phosphine we had observed similar reductive elimination. So this over here nickel is in +2 oxidation state and reductive elimination of these 2 species occurs to give the di-allyl compound as is shown over here and this is quite similar to what had been observed for during the cyclotrimerization of butadiene process where 2 di allyl compound was evolved.

But please note that these (()) (09:38) allyl phosphine was not present during that time and resulting in this product. This allyl nickel product again the oxygen state of these has a +2. But like last time this reaction sort of can proceed as is shown over here these would go via the formation of this nickel 0 and that in presence of PR3 would give this nickel 2 compound that would involve this oxidative addition of these 2 to form this ligand and then nickel become nickel 2.

So this process sort of is a 2 step process where an nickel 0 is formed followed by that now these ones this is formed then that can reductively eliminate to give called cyclooctadiene polymer or these can be in equilibrium to give this compound. So here the allyl moiety has just become a sigma donor and the other allyl moiety also has become sigma donor as it is shown here. Now this can again undergo reductive elimination to give these 6 membered compounds that reaction compound as is shown over here.

Similarly this are the central species can also become this nickel metallocycle as is shown over here. And that undergo reductive elimination to give an interesting compound cyclobutadiene compound of this type. So what is seen over here that this dimerization of butadiene dimerization of butadiene as is shown over here can occur to give the cyclooctadiene in presence of phosphine.

However in presence of the different substituent of phosphine there can be a other products which can be also obtained from the reaction. For example if there is this particular kind of 2 sigma a allyl reagents are formed sigma bonds to nickel are formed then one 6 membered ring can be obtained. Whereas if this nickello cycle 5 membered ring is formed then cyclobutane with 2 vinyl substituent are obtained.

So this is a nice demonstration again of the ability or scope of organometallic catalysis where a variety of substrates can be obtained depending on the sterics that one uses. So with these we come to this end of our discussion on cyclodimerization of butane and also we concluded our discussion on alkyne oligomerization reaction. So to summarize we have looked into a variety of alkyne oligomerization reaction started with ethylene oligomerization for in the context of shock catalysis.

Second one is ethylene trimerization to obtain 1 hexene third one that we have looked at propane dimerization fourth one we had looked at is cyclotrimerization of butadiene and fifth one again we have that we have looked at in this context is cyclodimerization of butadiene. So we have looked at 2 reactions of butadiene dimerization and trimerization. We have looked at one reaction of propane dimerization and we have looked at 2 reactions of ethylene trimerization and oligomerization.

It is important to mention that in all of these cases the catalyst which have used is nickel except for in ethylene trimerization where tantalum was used for catalysis. So these further range states nickel plays as a metal of choice for producing oligomers of different degrees of cyclic and acyclic from olefins. And that reason being that more electron rich electron metal are good for alkene oligomerization.

Whereas allyl transition metal are good for electron deficient allyl transition metal are good for olefin polymerization. So with these we move on to another interesting topic which is olefin polymerization. So now we are moving on from low molecular weight oligomers of olefins to high molecular weight polymers of olefins.

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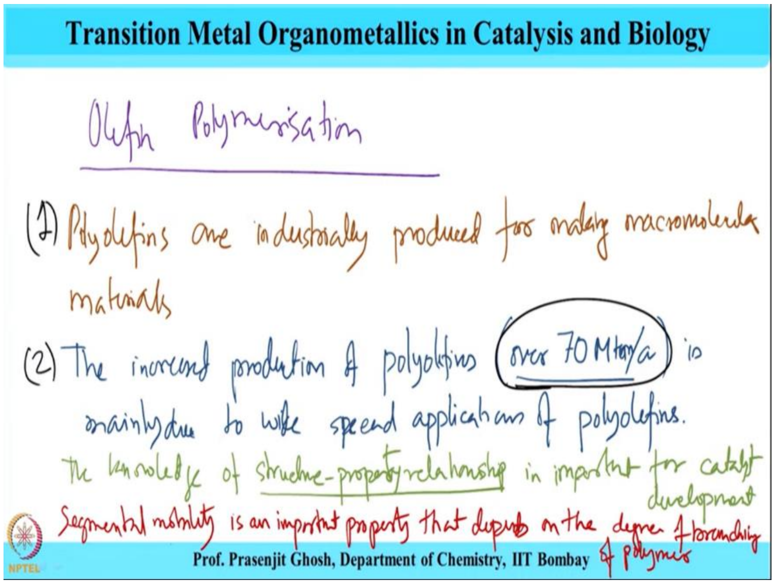

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Olefin Polymerisation

(1) Polyolefins are industrially produced for making macromolecular materials

(2) The increased production of polyolefins (over 70 Mton/a) is mainly due to wide spread applications of polyolefins.

The knowledge of structure-property relationship is important for catalyst development

Segmental mobility is an important property that depends on the degree of branching of polymers

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Now olefin polymerization is an important reaction in terms of producing poly olefins and it is very sort of synonymous with synonymous with Ziegler Natta catalysis. However there is more to olefin polymerization then Ziegler Natta catalysis and different types of polymerization that are possible for olefin and Ziegler Natta though constitute a primary portion of it. So this is a application which has seen the light of the day in terms of the application moving on from the discovery in the within the confines of the laboratory to being practiced in large scale industry.

So poly olefins are produced in this theory for making macromolecules poly olefins are industrially produced for making macromolecular materials. Now the importance of this poly olefins can be gauged by the extent of production that is required to meet the our daily need or the need for this plastics. So the increased production of poly olefin's over 70 mega ton annually is mainly due to wide spread applications of poly olefins. So these is mainly due to large scale applications of poly olefins are applied for various purposes.

And demand for poly olefin is met by increasing the production and really a large amount about 70 mega ton of poly olefins are being produced annually to meet the demand. So because of its large scale application the mean the knowledge about the structure property relationship and the development of new catalyst for polymerization is important. The knowledge of structure property relationship is important for catalyst development.

Now these is important attribute because this is where the mechanism insights about the mechanism come into play because if one word to know the mechanism fully well then one can come up with modifications which will enhance the catalytic attribute of this catalyst performance for this process and produce improved polymers. So there is a research primarily in this direction are focused in understand the structure property relationship or structure activity relationship as a function of catalyst structure.

And another thing about poly olefin is that is not only it is polymers are important but also the segment mobility or degree of branching is important with regard to determining what kind of polymer it material would be. Whether it would be a hard-brittle kind of polymer or would it be soft ductile kind of polymer. So important term over here is segmental mobility depends mobility is an important property that depends on the degree of branching of polymer.

So what we see that the poly olefin is a important area overall this is what the take home message from here in the sense that these has gone big and went on to be become as one of the biggest industrial process for making large macromolecules and then the demand for poly olefins or poly olefinic materials are so high that annually of about 7 t megaton there is a huge amount of polymers being produced.

Now this widespread application of polymers in different application for examples from furniture to bottles to other 2 devices to utensils to everything that depends on the nature of the polymers and to understand that the mechanism of the polymerization is very important and for obtaining insights of the mechanism this structure property relationship as a function of the catalyst structure is important for developing better catalyst which will produce more controlled and better polymers.

And lastly the segmental mobility of the polymer is an important property that is dependent on the extent of the branching of the polymer and then the need comes to make polymers which are branched and then exclusively make polymers which are non-branched or linear. And their overall property would depend on the extent of branching or the linearity. For example if a polymer is branched highly branched then it will be more soft material whereas if the polymer is long chain linear polymer then it will be a very brittle and hard.

So depending on the application there is a need for producing each of these types of different polymers. So with these I come to an end of today’s discussion on olefin oligomerization as well as olefin polymerization reactions. To begin with we had finished our discussion on the topic of olefin oligomerization by discussing a cyclodimerization of olefin using an nickel allyl catalyst. This is very similar the catalyst is very similar to that of the reactions cyclotrimerization of olefin.

The only difference is that in the cyclodimerization of olefin the phosphines are used and depending on the types of the phosphine used or the steric bulk of the phosphine one can not only produce this cyclooctadiene which is the cyclodimerized part of a butadiene. But also can one can obtain cyclic 4 membered cyclobutane or 6 membered cyclohexane rings depending on the nature of the R group of the phosphine we have looked into that and then we have looked into this important process of olefin polymerization we have looked into the need for large scale production of this process and how they are being met by organometallic catalyst.

We have also noted the importance of the knowledge of structure property relationship in respect to catalyst development. And lastly with respect to the polymer properties we have discussed about the importance of branching or segmental mobility of the polymer which sort of defines the very nature of the polymer. So with these I come to an end of today’s discussion. We are going to be talking more on olefin polymerization particularly about various types of polymer and their attributes when we mix next and then look into how what are the various examples and the types of the polymers that are there for these under this topic of polythene polymerization.

So with this I once again like to thank you for being with me in this class and I look forward to be discussing this olefin polymerization in great more detail when we meet next till then good bye and thank you.