Transition Metal Organometallics in Catalysis and Biology
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Lecture - 24
Ring Opening Metathesis (Part-3)

Welcome to this course on Transient Metal Organometallics in Catalysis and Biology. We have been talking about ring opening metathesis reactions in the past few lectures. In this context we have spoken about two types of ring opening metathesis reaction. One is ring opening cross metathesis and then the other one that we have partially covered or we just mentioned is ring opening metathesis polymerization.

Now one of the key features of this ring opening metathesis reaction is the fact that these reactions occur for substrates which have considerable ring strain. And as a result of this olefin metathesis, ring opening metathesis reaction, the ring strain is released and which is supposed to be the driving force for the reaction. This reaction as such is a thermoneutral and hence the ring strain release plays a considerable role in driving this reaction forward.

So continuing further, in our discussion today we are going to take up this subclass of ring opening metathesis reaction in the form of ring opening metathesis polymerization reaction.

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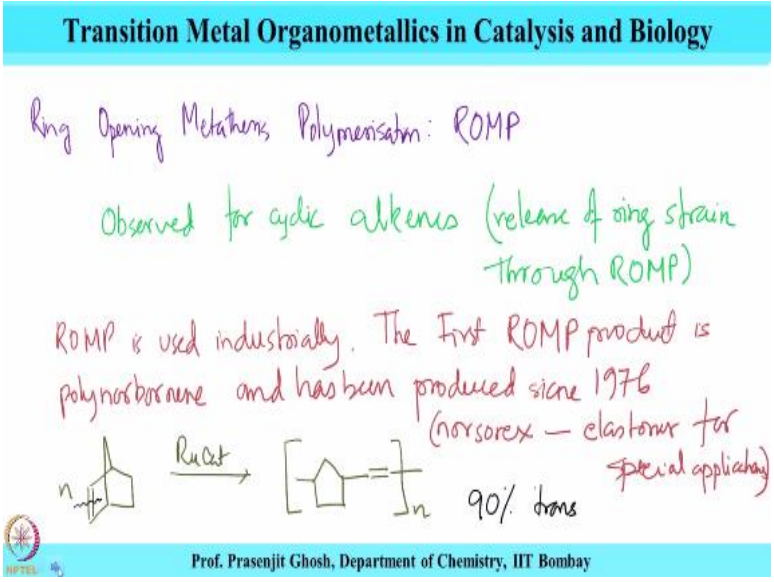

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Ring Opening Metathesis Polymerisation: ROMP

Observed for cyclic alkenes (release of ring strain through ROMP)

ROMP is used industrially. The First ROMP product is polynorbornene and has been produced since 1976 (norsorex – elastomer for special applications)

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So today we are going to be talking about ROMP. Now usually this ROMP is observed for cyclic alkanes and this is because of the fact that these possess considerable ring strain. So release of ring strain sort of provides the driving force for the reaction observed for and this is primarily because of release of ring strain through ring opening metathesis polymerization reaction.

And this reaction is of considerable interest because of the fact that this has been used in industrially in industrial scale to produce polynorbornene, is used industrially. The first ROMP product is polynorbornene and has been produced about for about more than 40 years since 1976 and has the trade name of norsorex for which is an elastomer for special applications.

So what we see that this reaction is one of the successful reactions, which have been in practice for large scale synthesis, and it is being used since a long time for about last 46 years for polymerizing norbornene. And in this regard, it is worth mentioning that in this course, as we are covering several reactions, which has been practiced in industrial scale.

So this particular reaction also falls in that subclass of reactions that we have been talking about where the applications of organometallic catalyst has made it to industry for large scale productions. So here we have norbornene in presence of ruthenium catalyst giving polynorbornene and in this case, thing that is worth mentioning that the product is exclusively a trans product which is formed 90% trans olefins are formed.

And this occurs when the two norbornene unit sort of comes together and undergo cleavage as is shown over here. So this is interesting applications for producing polynorbornene, which also go proceeds by ROMP. We are going to now take a look at several other examples which have been used as a part of ring opening metathesis polymerizations.

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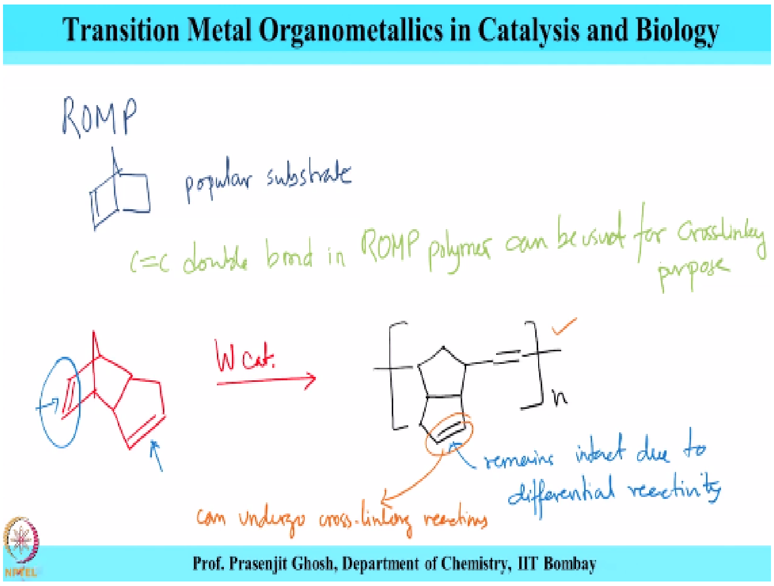

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ROMP

popular substrate

C=C double bond in ROMP polymer can be used for Crosslinking purpose

remains intact due to differential reactivity

can undergo cross-linking reactions

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And one of the popular substrate for this is norbornene. And we are going to take of another examples where there are two olefinic double bonds of differential reactivity and the double bond which is more strained or which is part of the thing that undergoes ROMP to sort of provide the polymer and the other one stays intact and be used for cross linking purpose.

So point to note as that C-C double bond in ROMP polymer can be used for cross linking making branch polymer or something of that cross linking purpose. Nice example is demonstrated in this particular substrate which has two olefinic double bond. And what is interesting is that in presence of tungsten catalyst it gives the ROMP polymer as is shown over here.

And thing to note is that of the two only of the two olefinic bond, the only the one which is more strained or this particular bond undergoes ROMP to give the polymer whereas the other bond remains intact. Remains intact due to differential reactivity. And as a result this double bond can be used for cross linking reaction.

So what is interesting about this example is that even though there are two olefinic bonds the one which is highly constrained undergoes ring opening metathesis polymerization to give the product whereas the other bond remains intact and that can be used for cross linking applications. We are going to take a look at some more other interesting applications of ROMP.

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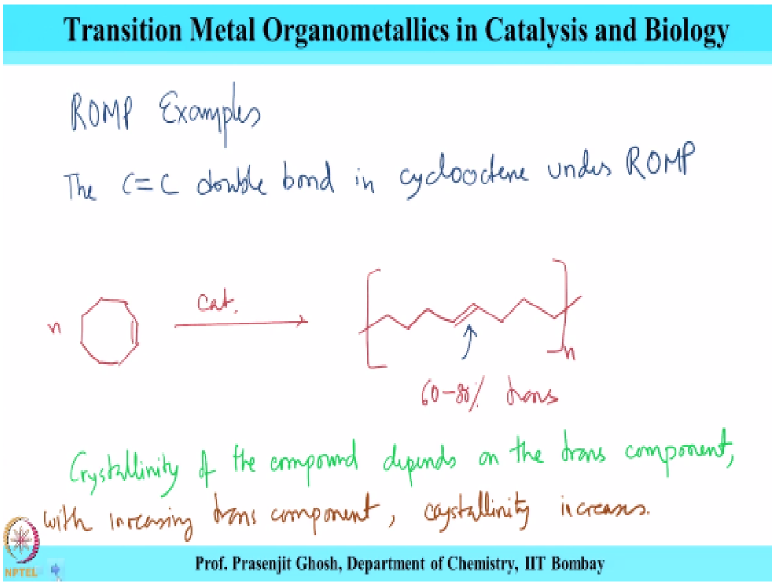

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ROMP Examples

The C=C double bond in cyclooctene undergoes ROMP

Crystallinity of the compound depends on the trans component, with increasing trans component, crystallinity increases.

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And in this case, the substrate is cyclooctane for which the C-C bond in cyclooctane undergoes ROMP as shown below. So catalyst and the product is, and as observed in the earlier case in this present case also about 60 to 80% trans products are obtained and this trans is with respect to the double bond over here.

And it seems that for metathesis polymerization, the trans, this product is the more stable product and the crystallinity of the compound depends on the trans component and with increasing trans component crystallinity increases. So this is something which is interesting correlation that the stable olefin usually is obtained as the major product, which is the trans olefin and also increasing amount of the trans olefin the substrate the product polymer product become more crystalline in nature.

Now as far as the ROMP is concerned particularly the catalytic active species for the polymer is fixed at one end of the growing chain and which sort of helps propagate the polymerization process.

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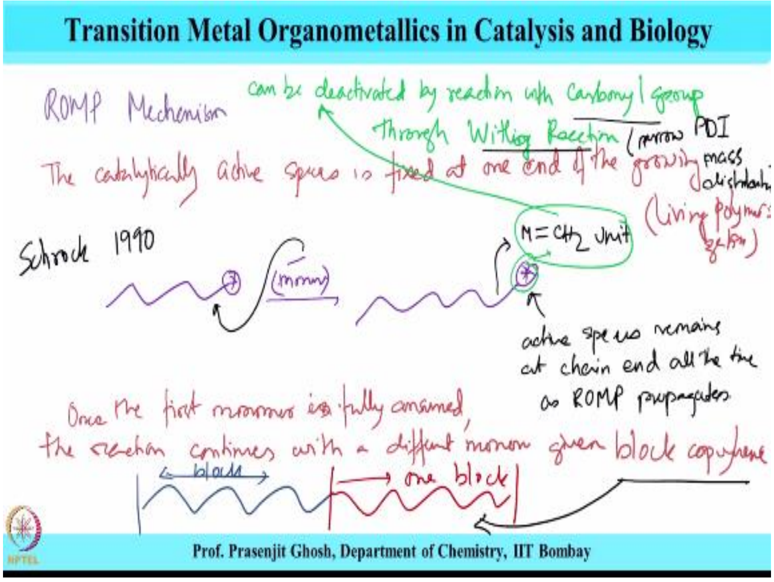

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ROMP Mechanism

can be deactivated by reaction with carbonyl group Through Wittig Reaction

The catalytically active species is fixed at one end of the growing

(narrow PDI mass distribution)

(Living polymerization)

Schrock 1990

active species remains at chain end all the time as ROMP propagates

Once the first monomer is fully consumed, the reaction continues with a different monomer gives block copolymer

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ROMP mechanism one **critic** special particular attribute about the ROMP process is that the catalytically active species is fixed at one end of the growing chain. And this sort of gives rise to living polymerization. So what that implies is shown by the cartoon drawn over Hilo. So if this is a polymer, then the catalytically active species sort of is fixed at one end.

And when another monomer comes, let us say for example, this is a monomer that gets inserted into the polymer and the polymer sort of increases in the end, but the chain the active species is always found in the end. So active species remains at chain end all the time as ROMP polymerization propagates. So that is a interesting attribute which sort of helps in different kind of applications for ROMP.

So for example, if all the monomer of one type get consumed, then the chain end is still active and it can do polymerization with a different kind of monomer and as a result, one can get block polymerization or polymers of two different types joined together, as is shown over here.

So subsequently, once the first monomer ends is fully consumed, the reaction continues with different monomer giving and this is sort of illustrated in obtaining a polymer, which is of two different types as is shown here and they would have different properties. So this is a one block and this is another block and together they would be called block copolymer. So this is an interesting application of ROMP where the active species resides on the chain end and the polymerization can proceed.

Now the this active species in the chain end is usually metal CH 2 unit which propagates the polymerization and this unit can be deactivated by reaction of carbonyl compounds and then the propagation can be stopped. So interesting thing to note is that this active species, which is nothing but this unit can be deactivated and be deactivated by reaction with carbonyl group through Wittig reaction, the famous Wittig reaction.

And so the polymerization can be stopped by reaction with Wittig reaction by reacting the metal carbene chain end with carbonyl group to give Wittig reaction and this helps to obtain narrow mass distribution, narrow PDI or narrow poly dispersity index or mass distribution. So this is a nice example, whereby the propagation of active chain end is stopped by reacting with carbonyl compound to give these (()) (21:51) compound to give deactivated chain without the active species through Wittig reaction and this was successfully demonstrated by Schrock in 1990.

So with this, we sort of come to the end of the discussion talking about various types of ring opening metathesis examples, and we have so far discussed in the last few lectures, several examples on of ring opening cross metathesis as well as ring opening metathesis polymerization. And now we move on to another kind of olefin metathesis reaction which is just the opposite of ring opening metathesis reaction and they are popularly called as ring closing metathesis or RCM.

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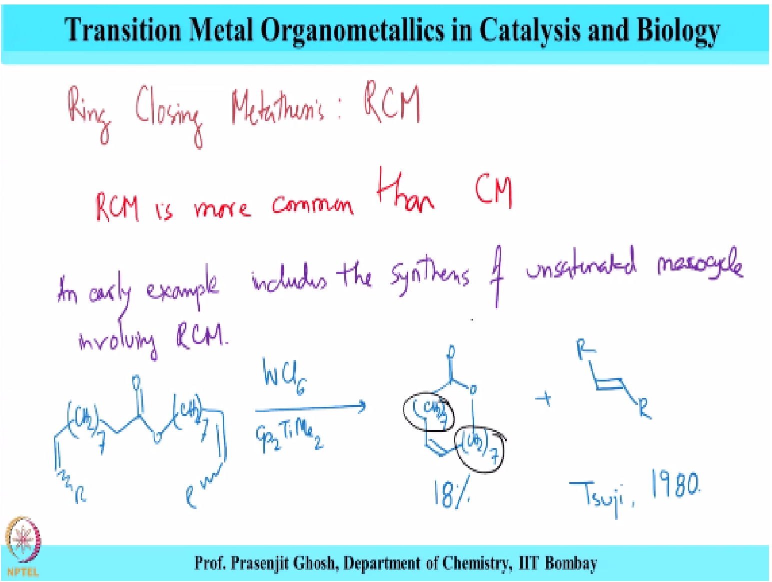

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Ring Closing Metathesis: RCM

RCM is more common than CM

An early example includes the synthesis of unsaturated macrocycle involving RCM.

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Metathesis or RCM. Now ring closing metathesis is kind of more common than cross metathesis and there are several examples. So it is a reaction which is sort of more commonly observed, RCM is more common than cross metathesis or cm and this has been successfully used for synthesizing unsaturated large unsaturated macrocyclic compounds as is shown over here.

An early example includes the synthesis of unsaturated macrocycle involving RCM and this is given by the equation as is shown here. CH 2 whole 7 is a ester CH 2 whole 7 R in presence of tungsten hexachloride and C p 2 titanium dimethyl giving this cyclic ester plus the trans olefin in 18% yield and this was reported by Tsuji in 1980.

So interesting thing to note here is that this ring closing metathesis is however opposite to that of ring opening metathesis where ring strength sort of drives the forward reaction. And in this case ring closing is just the opposite where rings are formed. But please note that these rings are really large rings, so that the ring strain are not formed as a part of the ring because the rings are really large and they are sort of like there is not much of ring strength significantly is strong to stop the reaction.

And also this probably is driven by the entropy, because from one molecule one gets two molecules. So there is a entropy factor which sort of guides the formation of RCM products. So with this, we come to the end of today's discussion, where we have started with ring opening metathesis polymerization. We have looked into various examples of ring opening metathesis polymerization.

We had looked also into the mechanism by which the ring opening metathesis polymerization propagates. And what we had discussed that there is a the active species lies at the polymer, one end of the polymer chain and as the monomer comes, it just gets inserted into the polymer with the active species always residing at the chain end.

And when and this happens in a living fashion when one polymer one monomer gets consumed a second monomer can also be inserted in the chain end through the growing polymer chain. And this results in a new type of polymer called block copolymer, which has two different polymers attached to a single polymer chain.

And then, finally one can stop even the polymerization process by deactivating the metal carbene active species in the chain end and this is done by reaction with ketone which results in a Wittig reaction. And this usually is done to control the molecular weight of the polymer to obtain a narrow molecular weight range polymer and this was successfully demonstrated by a Schrock in 1990.

So with that, we had finished our discussion on ring opening metathesis polymerization, and also initiated the discussion on another type of metathesis particularly, the ring closing metathesis which is opposite of the ring opening metathesis. And we had include examples where a large macrocyclic unsaturated rings are formed using the ring closing metathesis polymerization.

One thing to note however, is the fact that these macrocyclic rings are so large that there is no not much strain generated in the ring closing process. As a result these products are obtained as per will. However, to note that the yield was also not too large, about 18% as was discussed. So with this, we come to the end of today's discussion on various types of olefin metathesis reaction.

We started with RO ring opening metathesis polymerization and we ended our discussion on RCM and we are going to be taking up a lot more examples of ring closing metathesis when we meet next in the course. Till then, goodbye and thank you.