Metallocene and Metal-Carbene based Organometallic Compounds as Industrially Important Advanced Polyolefin Catalysts

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Lecture 7

Common Polymerization Protocol and Mechanism: Controlled Polymerization

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Lecture 07: Common polymerization protocol and mechanism.....Continued
(Controlled Polymerization)

So, welcome to this course, in if you recall in the last class, we discussed about the free radical polymerization and the step growth polymerization where we show that in the polymerization, we really do not have that much control. So today we will continue, and we will discuss some of the control polymerization mainly free control radical polymerizations and anionic polymerizations, where the controlling is much better, and you can get the well-defined polymer following this polymerization protocol.

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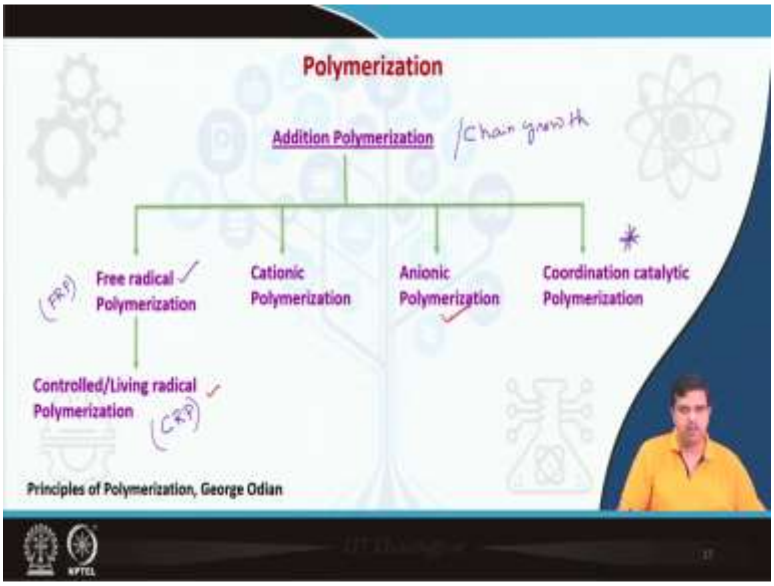

Polymerization

Addition Polymerization /Chain growth

(FRP) Free radical ✓ Polymerization

Cationic Polymerization

Anionic Polymerization ✓

Coordination catalytic Polymerization *

Controlled/Living radical Polymerization ✓ (CRP)

Principles of Polymerization, George Odian

So, the here in the last class, remember that we discussed the free radical polymerizations now, we will be discussing in this class mainly the controlled living radical polymerization and the anionic polymerization, which are actually used for the polyolefin synthesis mainly in the industry and definitely in the lab.

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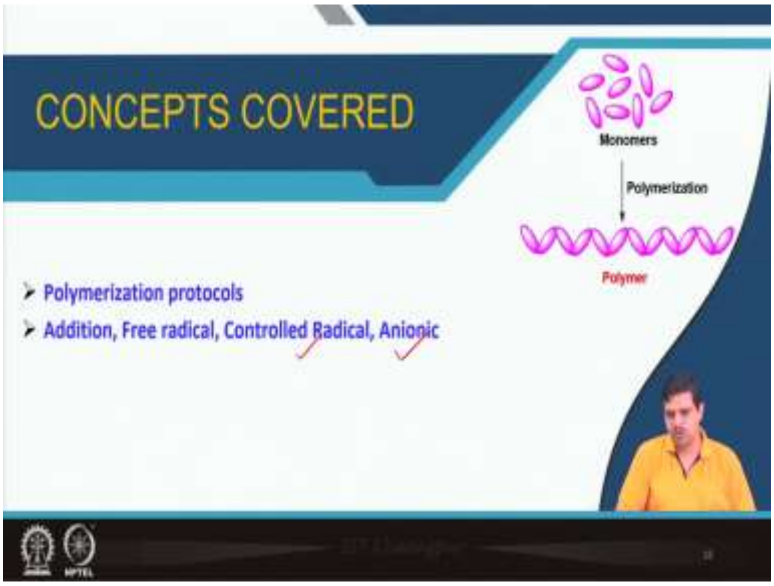

CONCEPTS COVERED

- Polymerization protocols
- Addition, Free radical, Controlled Radical ✓, Anionic ✓

So, concept I would cover here mainly the control radical polymerizations this one okay, what the way what kind of initiated you have to use, what kind of condition you have to follow.

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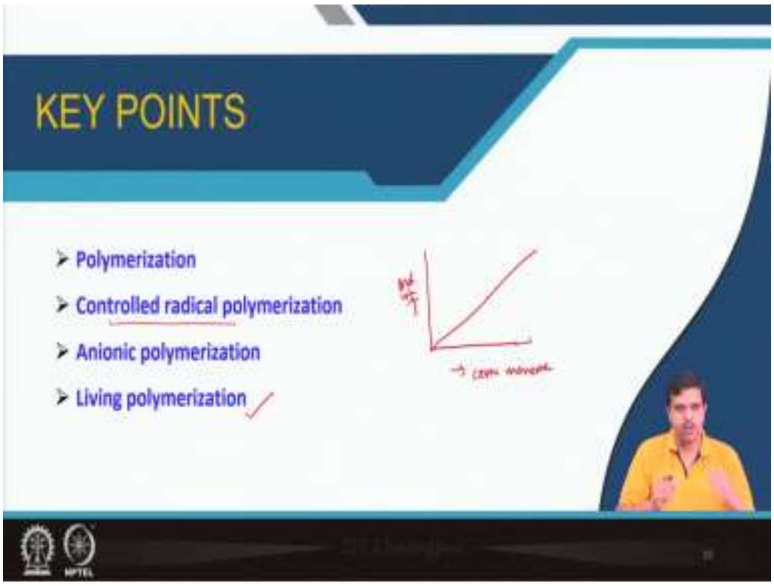
KEY POINTS

- Polymerization
- Controlled radical polymerization
- Anionic polymerization
- Living polymerization

And the key points for this lecture is as I told the control polymerizations radical anionic and the living as you know that living polymerization is always advantageous in the last class, I showed the graph that where you can basically have a control over the molecular weight and the conversion of the monomer and the relation is linear that a particular time at time, you will, you will see that the relation within the molecular weight and the conversion of the monomer is linear.

So, the molecular weight depends on the monomer concentration depends on the time. So, this is very advantageous because this is, the polymerization is very much controlled. So, that we will try to discuss what are the polymerization protocol in this class.

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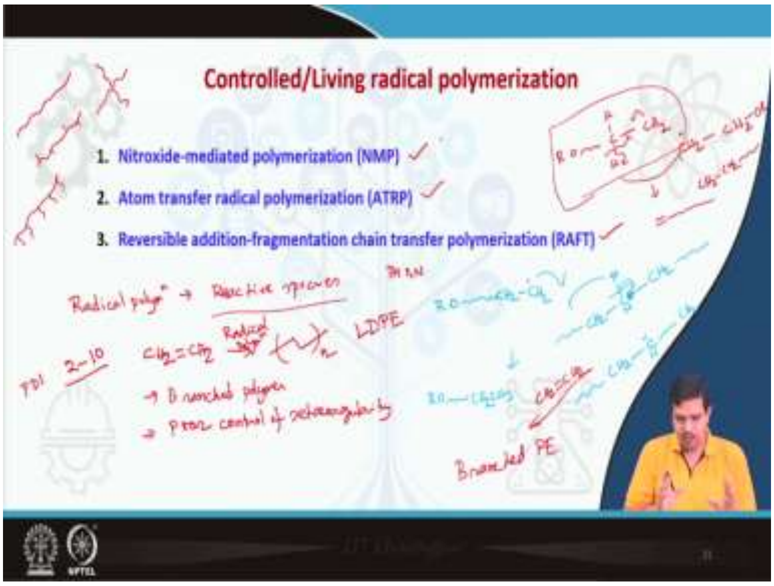
Controlled/Living radical polymerization

1. Nitroxide-mediated polymerization (NMP)
2. Atom transfer radical polymerization (ATRP)
3. Reversible addition-fragmentation chain transfer polymerization (RAFT)

These are very advanced choice that is the control leaving radical polymerization, one is the I will discuss one by one in a very brief way, nitroxide mediated polymerization, Atom transfer radical polymerization and reversible addition fragmentation chain transfer polymerizations, and why these are needed?

That is the big question. Why the routine radical polymerizations was not sufficient or what are the advantage, if you recall the last class, we discussed that in the all the radical polymerizations, we need a we need to create a species the reactive species, in basic many cases, we use the AIBN or benzoyl peroxide type of initiators which can be which can undergo the homolytic cleavage at moderate temperature and then that highly reactive radicals can react with the monomer and you will get the monomer with reactive in and then can react with another monomer to get the polymerization and that is the way the propagation happens.

So, but the problem is that in the radical polymerization if I do these reactions. So, you will get the polymer is no problem, but you may only have some control in the in the molecule weight and the linearity of the polymers that means, you will get the branched polymers I will discuss I will show you how you will get the branched polymers. So, you will get the branch polymer. You will get the pore control of stereo regularity So, this stereometry obviously it comes when you have using prochiral monomer as example propylene. So, in this case, you do not have a control on the branch and linearity of the polymer.

So, in this case that is why I cannot tell that 100 percent that you will get the high density polyethylene you will may have a low density high density allowing the low density polyethylene because they are maybe branching with which in which depends on the polymerization condition. So, here that is why if you do the radical polymerization, radical polymerization it is very difficult to get the high density polyethylene in most of the cases you get the low density polyethylene, why it is?

Because, you know, if you recall the radical polymerization discussed in the last class in quite depth, so, this is your I just show the polymer with reactive end. So, this is I am just showing the, not drawing the entire chemical structure of the polyethylene, I am just showing the active end, this chain type zigzag drying the bond means there is a, this is a polymer chain and that is actually called conventionally follow during the representing the polymer.

So, what I am doing I am just writing the radical which is, this is the your active end, which further reacts with another monomer This is my the active end with the radical now, you will see I have also same here available in the polymerization while you are doing the polymerization now, what may happen here, if I suppose these, these hydrogen, I am just removing this one I am just drawing so that it is easy to understand. Now, again the homolytic cleavage may be possible here. So, what happens these can couple these can couple and this. So, what will happen now, so this is giving your dead end, CH3, so, this is dead polymer. But now you here you what happens you are getting here like that.

So, now, see the here you please understand what happened here. So, here your radical is at the end of the polymer that means the active centre and the end of the polyethylene and here the active centre and in the middle of the polyethylene chain. So, this is the mechanism where you get your branched polymer because this one now can react with your monomer, and you will get basically branched polyethylene. So, that is the reason why you get the branched polyethylene if you follow the radical polymerization.

And obviously, other problems associated with that you will get a broad distribution of the molecular weight because there is several ways of termination as we discussed in the last class that simply coupling with this one and this one. Or there is other possibilities that this can also couple this can also undergoes another mechanism of termination that is the disproportionation, that we discussed in the last class for the polystyrene, but similar situation may happen for poly ethylene as well. So, here is my this one and here is my other chain.

Now, what will happen here you will see, that this phase then homolytic cleavage of this one, so, this is one, this forms the double one, and this comes out. So, the respond then form the H dot. So, this one now can react with this one. So, you will get eventually that two dead polymers one is with this end and one with the vinyl group descent. So, this is this kind of termination is called the disproportionation and another way it is very easy to understand this way coupled with another one so, you will get the double molecular weight, due to the just simply coupling of this of this reactive polymeric end.

So, there you see that there is a possibilities of different unwanted reactions and who is the responsible for that one, because the reactive, highly reactive nature of the polymer rate is the you can say is the culprit. So, that is why it is very difficult to control this polymerization by the free radical point and that is why he called the free radical polymerization. So, that is why you will see the polydispersity, if you use the PDI is quite high here even sometimes, you may get very high molecular PDI value 2 to 10 something like that, but you have to understand that do not think that PDI 1 or 1.5 or 1.2 is always kind of advantages.

So, that depends again, it depends on the what application you want to do it. So, sometimes purposively We make the polymer with high PDI. So, the students or the learner who are from the industrial background, you I am sure you are very quiet familiar on this one. Fine. So, the main take home message from this free radical polymerization that we do not have much control we get a (())(12:08) selectivity, chain link content is very poor, we get very branched polymer and that is why we cannot really follow this polymerization protocol, where the more finding architecture is needed for the different polymers as examples you will see that this is the linear polymers, this is sometimes we need the this is called LLDPE we discussed already.

We need sometimes like start like a polymers, we need the grafted polymers like this one, where all the side arms are should be ql space and these as I discuss these the beauty of the polymer the same polymer composition, but if you change architecture, you will get quite different properties. And obviously, you will you can apply for different applications. So, in that so, this is the problem that the very poor control of the free radical polymerization and as I told that the main culprit is the reactive species associated with the free radical polymerization.

Now, in this polymerization, you see nitroxide mediated polymerization, atom transfer radical polymerization, reversible addition fragmentation chain transfer polymerization, all were developed quite recently compared to the other traditional radical polymerizations those are all discussed all are discovered after 1992 to 2020 after 1990. So, if you understand is quite recent. So, let us discuss that what are these and what are the basic concept to make this radical polymerization to control and living.

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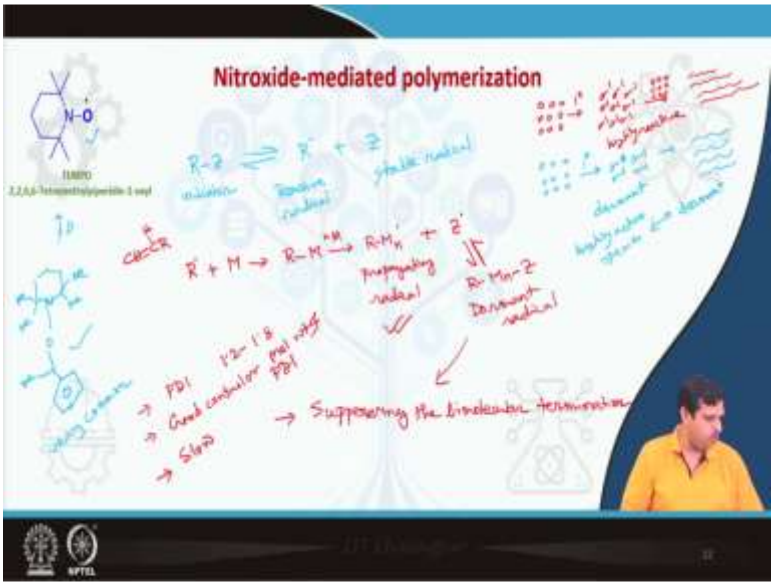

Nitroxide-mediated polymerization

TEMPO

2,2,6,6-Tetramethylpiperidine-1-oxyl

$R{-}Z \rightleftharpoons R^{\cdot} + Z^{\cdot}$

initiator

Reactive radical

Stable radical

$R^{\cdot} + M \rightarrow R{-}M^{\cdot} \xrightarrow{+M} R{-}M_n^{\cdot} + Z^{\cdot}$

propagating radical

$R{-}M_n{-}Z$

Dormant radical

→ PDI 1.2-1.8

→ Good controller mol wt PDI

→ Slow

→ Suppressing the bimolecular termination

highly reactive

dormant

highly active species ⇌ dormant

I again I will not go in depth about the kinetics, I just try to showcase that what are the basic strategy we have followed to make this radical polymerization more controlled. So, in the free radical polymerization I will just give you one another pictorial diagram here, in the free radical polymerization what happens here you have the radicals, the monomers, like that one. And you make the initiator molecules. So, you make reactive by putting the initiator okay. And so, these are now these are now you can tell the reactive with initiator. So, I am just putting like this one. So, these are now reactive monomer you can say.

Now you have a lot of monomer in your polymerization container now, what will be happening as it is quite reactive, so, what will happen you will get the polymerase polymers with uncontrolled chain link. So, ultimately what you will get, you will get the polymers with quite broad molecular distribution, but because this is highly reactive, highly reactive. Now, if we can control this polymerization then what will happen? So, here again I have monomer and here I am putting initiator and again I get like this one, but if I can control it that if I can reduce the reactivity of these active species what we can get, we can get the almost similar chain length of the polymers.

Now, how do I will do it. So, basically, we can you will use the concept of the dormant species, dormant species means, what we will do we will try to make equilibrium about the highly active species within a dormant species. So, we will follow we will apply the concept of the dormant species here, to make the highly active radical to make less reactive or whenever it is needed, it will again react with the monomer, but it will be in a controlled way, let us discuss what is this?

So, this is the initiator in the free radical you saw that initiator we are using AIBN or the peroxy type of radicals, here we will use the different types of radicals. So, actually this is prepared very easily by from here this is okay and okay. So, you will see that it is a, it is called styro, this species called tempo that is the is a piperidine derivative OC 2 2 6 6 tetramethyl piperidine one oxide. And this is called the styro tempo. So, if you just hit it, you can get this tempo radical. So, this is again initiate by a radical, but the nature of the radical is different from the radicals you are getting from the AIBN or the tempo.

So, what we are doing here, so, let us so, this is my initiator, that is that this one is the initiator, although there are various initiators are available at this moment, but this is the commonly used very common initiator we used in industry analysts in the lab, but there are several initiatives are available. So, what happens here you get the two radicals, one is the R dot and one is the Z dot, this is the reactive radical, reactive radical and this is the stable radical. Now what will happen this one so, this is the stable radical this one so, this is the Z.

Now the next case what happens so, your R dot reacts with monomer. So, here the monomer maybe polyethylene or sorry the monomer may be ethylene or any other vinyl containing. So, anything like let us say the monomer I am writing here like in the common. So, let us say this is my monomer. So, this maybe olefinic, maybe acrylic type of polymer anything. So, now, this one will react with monomer and you will get the, this is so this is basically react to with monomer and eventually you will get. So, if you have you have a lot of n a lot of monomer. So, you will get the polymer with active n. So, this is we can tell it say is a propagating radical.

So, the active n at the polymer n. Now, I have Z available that is the stable radical. So, this can react with Z dot, and you will get the R. So, Mn now Z. So, this is basically dormant radical. So, is there is equilibrium with this one. So, I actually in if I follow this one, we should write as equilibrium sign here. So, this equilibrium exists between these R dot and Z dot and it forms R Mn Z. So, this is the dormant radical is basically what we are doing we are controlling the reactivity of these very active species and that is the strategy we are following for nitroxide mediated radical polymerization.

So, here and this is by this way what we are doing, we are basically suppressing the biomolecular termination, which is if you recall which is another one of the biggest problem if we follow the free radical polymerizations, but the disadvantage is that this polymerization is quite slow. In NMP you will get a fantastic control over the molecular distribution, the PDI which is very nice. The PDI you may get almost like 1.2 to 1.8 for some of the polymers. Good control on molecular weight and PDI, but the disadvantage is that it is quite slow polymerization. And sometimes it takes two to three days like that, but the polymerase you will get a very good control over the polymerization protocol in this polymerization protocol.

So this is a one very popular method, very recent method advance method that is a nitroxide mediated polarization and it solved the uncontrolled polymer polymerizations in free radical polymerizations.

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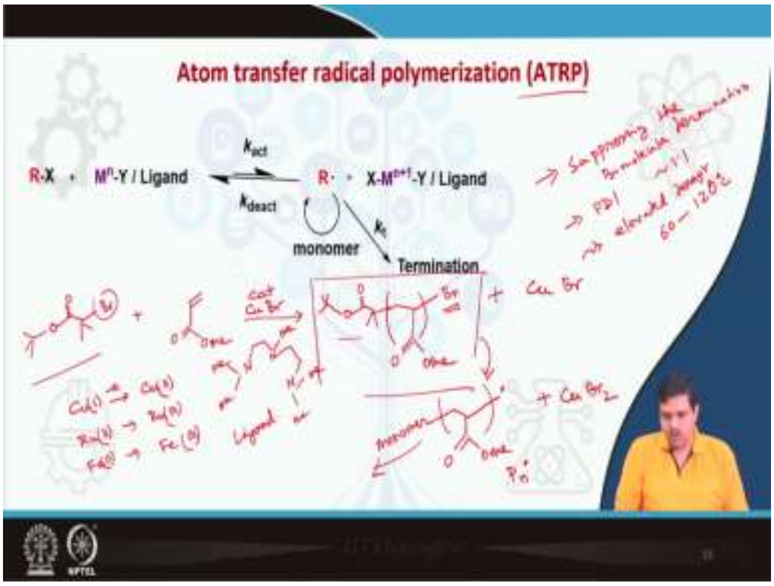

Atom transfer radical polymerization (ATRP)

So, this is another method is called atom transfer radical polymerizations. Here you will see that again we that you have to suppress the bio molecular termination by again the concept of the dormant species. So, where what we use, you have to I will give one example what kind of initiator you will use. So, this is like this one, this is (())(25:48) group and many wide varieties of vinylic containing a monomers you can use, one of the monomers is methyl methacrylate or the, sorry.

So, this is one of the I just want to give one real example of the monomer, what we can use yes, acrylic type of monomer you can use and here we will be using one catalyst and this is the metal catalyst, we will use here you will see we will use the like a copper one complex by. So, you have to choose one most previous transition metals complexes where there it can undergoes one electron oxidation and form the copper two. So, that and similarly you can use other complexes like ruthenium two or iron two like that which can undergoes the oxidation like this one.

And I will tell you in very shortly why you need it, because there is a step where that comes that catalyst would undergo the one electron oxidation to facilitate the polymerization. So, let us I you will understand why it is needed. So, now, you I needed catalyst one real example is copper bromide. And what you will get you will get the polymer of this one. So, this is your end that is this end. So, this one and this methyl and you will get your yes and here ome. And here you will see that this bromide so, we will be here.

And also, here one ligand is used to facilitate or stabilize to form this copper to complex. So, one tridentate ligand commonly used is this one and here like that. So, this ligand you can use anything we generally use anything means any chelating type good ligand chelating type ligand you can use to basically take the formation to stabilize the formation of the copper two. Now, you will see here what we are doing. So, we are now the bromo is at the end now, if when it is it will react with, when it will react with copper bromide again. So, what will happen? It will form the polymer. So, I am not writing this one. I am just straightly write getting this polymer and you will get the copper bromine two.

So, what we are doing here, now again this is your active species with radical so, I can just write as a Pn dot. So, now you see what happened. So, again this is a you can say dormant species. Now, we can again reinitiate by using properly judiciously chosen catalyst transition metal complex here to reactivate again to form the radical and then it can again react with the monomer this can again react with monomer to get the polymer.

So, you will see that again this concept of these dormant species. So, very similar concept as the nitroxide mediated polymerization. So, here again is basically I am suppressing the bi molecular termination and PDI is quite good here again you can get almost 1.1 PDI and the problem but only problem is that the polymerizations is happens quite elevated temperature, that is the one of the problem.

So, it is need around like some in some cases you need 120 degree integrate temperature. But another disadvantage that if you want to use these polymers, for any biomedical applications or any material science application, you have to be very careful about the contamination of the transition metal complex impurities. So, you have to really be very careful to purify the polymers. So, that was the advantage, disadvantage, but you see that we can have a very good control over the normal free radical formulations using the concept of atom transfer radical polymerization.

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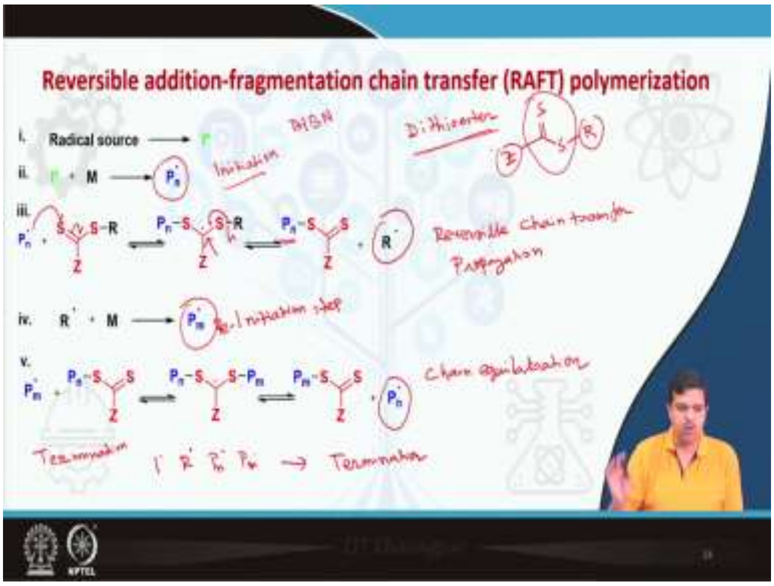

Reversible addition-fragmentation chain transfer (RAFT) polymerization

So, this is the next one is another way of controlling the radical polymerization, that the reversible addition fragmentation chain transfer polymerization. So, here what we use, we use a initiators like AIBN again and we use a very special reagent here this called wrapped reagent that is a dithioester derivative, dithioester derivative, that is basically the S this is like that. So, this is the dithioester moiety. So, now, what happens again we are also we are using the concept of the dormant species here and many a wide variety of the polymers as example monomer as example any acrylate monomer you can do the polymerization using this raft and this is also again very effective polymerization protocol to make the polymerization in a controlled way.

So, this is my initiation, initiation step and here you will see this is the reversible chain transfer. So, this is basically your propagation step. Now, how does it happen? So, this reacts this PN is react with this radical is reacts here. And from sorry, this is. So, you see that this is my initiation step you got a react a polymer with reactive n by attacking that radical initiator. Now, this one react on this one and you get the that radical here. So, this is here is now your radical.

Now, there is a again rearrangement, so, here and this is here so, this is the formation of the that radical again and you will see that your polymer end is now embedded on the this dithioester moiety and you will getting the now in this R dot you will react with monomer again and you will get the Pm dot. This Pm dot again will react to this is basically your initiation step. So, this is your, you can take re-initiation step because this one is your first initiation and there this is the polymer embedded on your diethylamide. So, this is also again can reinitiate by these R dot. So, you will get the Pm dot.

Now, this Pm dot can react with your that polymer had the n group is the diethylamide moiety and then you will get the your again this Pn dot polymer, this initially it was a Pm dot now it is a Pn dot and Pm is again embedded on the diethylamide. So, this is basically chain equilibration step you can tell, equilibration step you can tell and at the last is termination. So, all these I dot R dot Pn dot and Pm dot will get the undergo the termination by radical quenching.

So, again here this is also very nice method for to get the well-defined polymers by using the concept of the reversible addition fragmentation chain transfer polymerization and here the specialty that you have to use these kinds of dithioester moiety these called the rapt agent here again you can control the steps by appropriately choosing the R group and Z group, I will not go in depth discussion on this one I just I wanted to give the concept.

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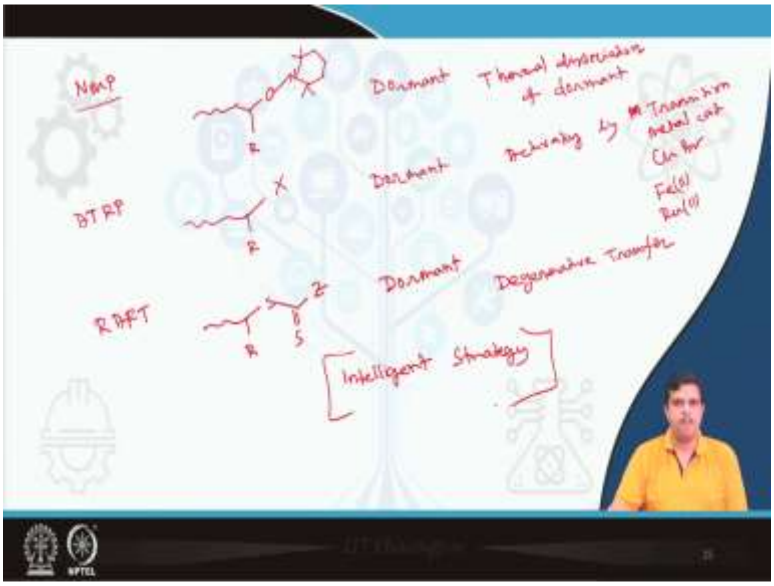

So, what is the common factor here, in this radical polymerization, the control radical polymerization, in all the case you will see that in NMP what do we did, what we did we put a we use the concept of the dormant species, here in this case if, in this case, this was the dormant species in NMP, in ATRP again we this is the dormant species if we recall because this again reacts with my let us say copper bromide to make the radical again and in the RAFT process, which one is the dormant species we are getting the dormant if you recall, you getting the S that is a diethylamide like this one.

So, you will see that these again the dormant. So, we are using the concept of the dormant species to control the highly reactive nature of the radicals. So, here you will see that thermal dissociation of the thermal dissociation of dormant. Again react or reinitiate the polymerization, here we are activating the dormant species activating by transition by transition metal complex catalyst, as example like copper bromide or any other iron two or ruthenium two complexes. And here we are doing the degenerative transfer of the dormant species to make it again active.

So, this you see a what I called a very intelligent way intelligent strategy to make in all the cases to make the controlled nature of the radical polymerization to make the uncontrolled radical nature of the polymerization to make it controlled and well defined.

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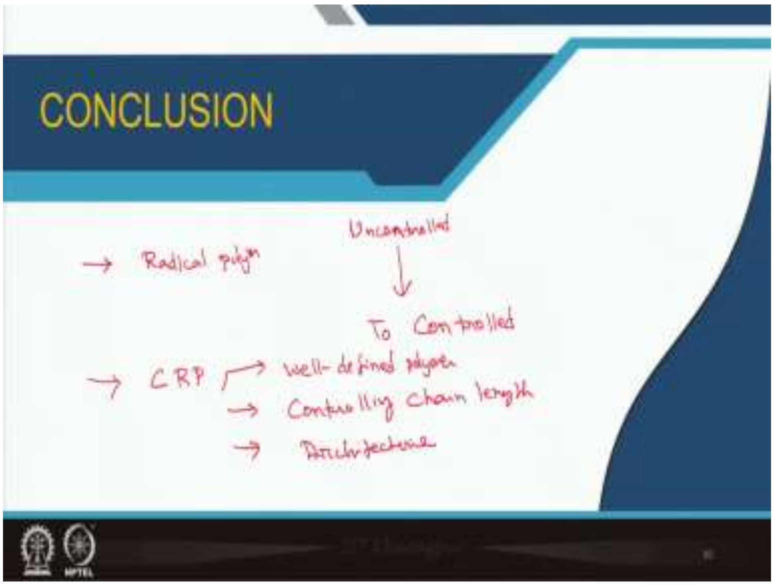

CONCLUSION

→ Radical polyn

Uncontrolled
↓
To Controlled

→ CRP → well-defined polym
→ Controlling chain length
→ Architecture

So, in here you will see that we have in the conclusion we have you see this we discussed the how we make the radical polymerization uncontrolled to controlled by following the strategy of the dormant species to make equilibrium between the dormant species and the active species in the radical polymerization, and use understood that how this radical, the control radical polymerization this is called CRP allowed us to make the well-defined polymer, controlling chain length and obviously, the architecture.

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REFERENCES

[1] Principle of Polymerization by George Odian, Wiley
[2] Introduction to polymer chemistry, Robert J. Young, Peter A. Lovell, CRC press
[3] Introduction top Polymer Chemistry by Charles E. Carraher Jr., CRC press

So, whatever the content I have discussed here you can find in a well very popular textbook like George Odian, Lovell and Young and the Charles Carraher. So, all are available easily available.

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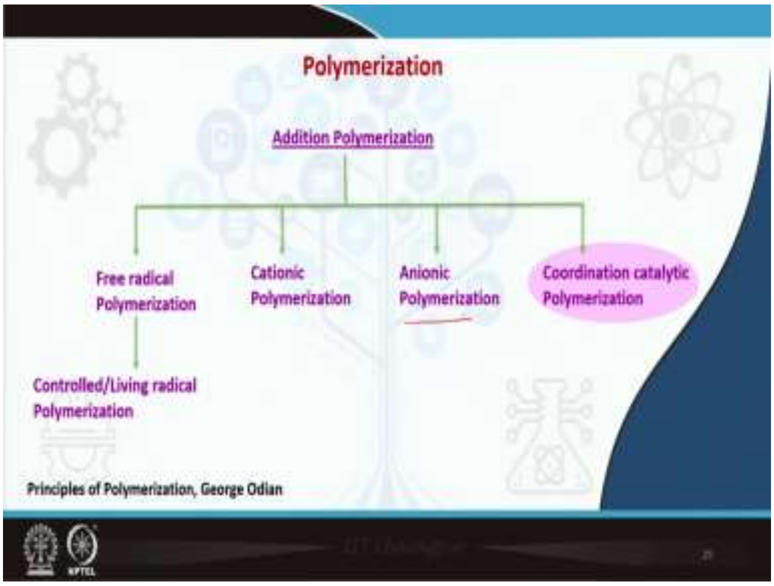

Polymerization

Addition Polymerization

Free radical Polymerization

Cationic Polymerization

Anionic Polymerization

Coordination catalytic Polymerization

Controlled/Living radical Polymerization

Principles of Polymerization, George Odian

And next class I will discuss very shortly about the anionic polymerization. And this is also another method of making the living polymerization and then we will enter to the polymerization, very special polymerization take protocol, that is the coordination catalytic polymerization, where you will be using the transition metals to make control polymers and where you will see that we can control the molecular weight and also the architecture of the polymers and also the stereo regularity of the polymers, which is very interesting, and we will use the concept of the unique organometallic reactions in this coordination catalytic polymerization.

So, that must be very interesting in, while we will discussing about the organometallic complexes catalysed polymerization, in the next class or so. Thank you very much.