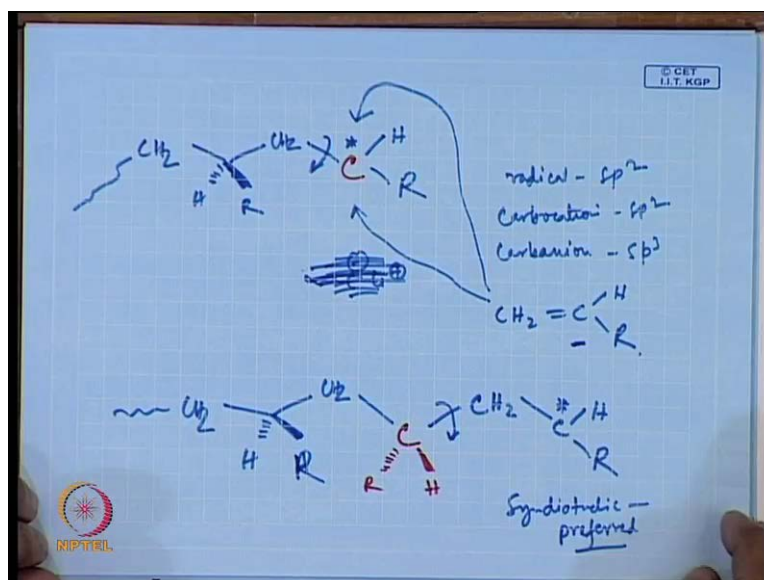


**Polymer Chemistry**  
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**Indian Institute of Technology, Kharagpur**

**Lecture - 24**  
**Polymer Stereochemistry and Coordination Polymerization (Contd.)**

Welcome back to this course in Polymer Chemistry. And in this lecture we will continue our discussion on Polymer Stereochemistry and Coordination Polymers, which we began in the last lecture.

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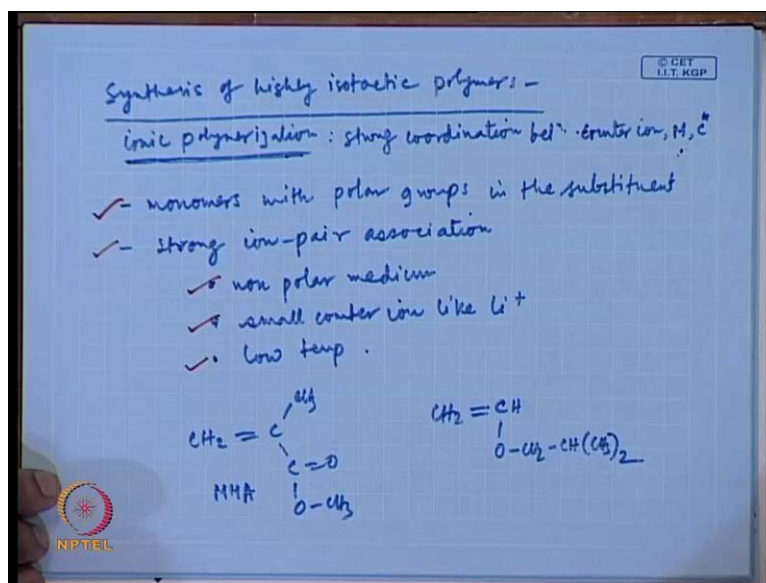
Now, in last lecture we had discussed this page, and remember we discussed this that if this active chain end in a propagating chain, polymer chain, if this carbon is radical or it is a anion or cation with a counter ion which is not strongly binded.

If the counter ion for anionic or cationic case they are free, then what happens? This carbon atom is a planar molecule and then when you, when the next monomer approach, it can approach from either side. So, the configuration of this carbon is determined by the configuration of the penultimate carbon with this case, this carbon. And obviously it is always preferred that this bulky group will be or the group substitution group will be the other side of the R group which is in the, in this penultimate carbon; which means syndiotactic polymers will be always preferred; syndiotactic addition will always be

preferred than a isotactic addition. And these preferences will always go up if you increase the temperature.

Now, how to synthesize a highly isotactic? And we also said that if we increase the temperature, obviously the tendency for syndiotactic and isotactic will be significant. So, we will be going to get a atactic polymer at higher temperature. So, basically we know how to get a syndiotactic polymer and we know how to get a atactic polymer.

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So, how to get a highly isotactic polymers? Now, we can get a highly isotactic polymers if we do a ionic polymerization such that, we have a very strong coordination between the counter ion, the monomer, the incoming monomer and the active chain and which could be a cation or an anion.

So, if I carry out a ionic polymerization where we have a strong coordination between the counter ion with the cationic or anionic chain end and the incoming monomer, then the approach will be from, always from the same side of the same side, so you will get a isotactic polymerization.

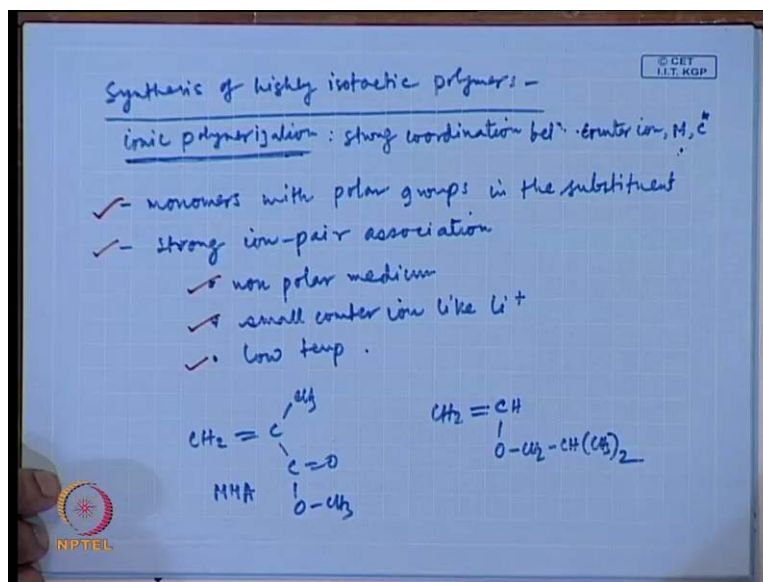
Now, how do you get or create a condition where this thing, this coordination, strong coordination between the active chain end, the monomer and counter ion happen? Now, if we have a monomer which have a polar group as a, in the substituents like, say you

have a methyl chlorate or ethyl group in the backbone, where this is a polar molecule. So, this can actually coordinate with a with a cation in this case.

So, monomers with polar groups in the substituent will help in coordinating with the counter ion and the monomer; the incoming monomer. Now it is said that, if the monomers or if the chain end, the active chain end whether it is a cation or anion, if they are free with the with the counter ion and the active chain end, if they are free, then we have seen what are the types of stereochemistry we are going to get. But if they are very tightly bound, then they can coordinate.

Now, how can we make sure that this counter ion and the active chain end are tightly bound? If you can carry out the reaction in a very nonpolar medium like hydrocarbon, and if we have a counter ion which is small in size, so that they will be tightly bound. For example, like Lithium. And if we can carry out this reaction at low temperature, what happen? Then we can get coordination; strong coordination between monomers and the incoming the active chain end and the counter ion.

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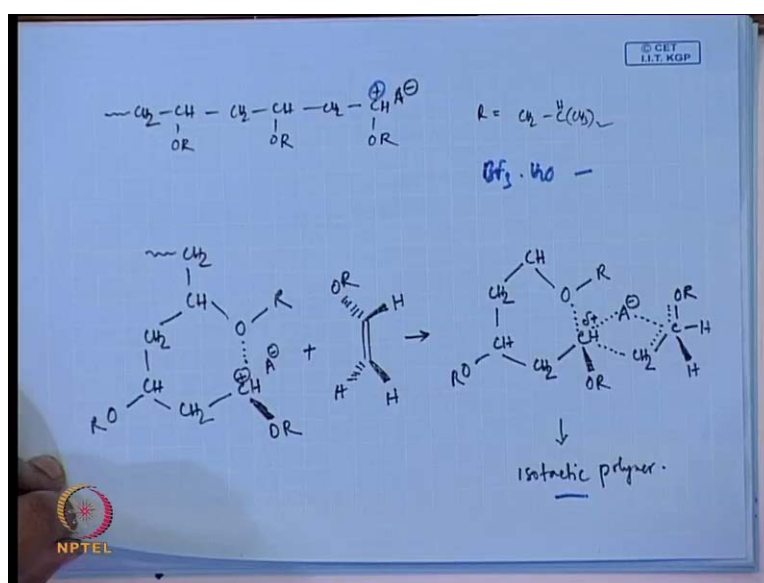
Now, let us take an example of methyl methacrylate. If we do the reaction, if we take the methyl methacrylate and do the reaction with a anionic initiator, say for example, butyl lithium in say toluene at a lower temperature. So, if we consider say n butyl lithium as a initiator and toluene as your medium, nonpolar medium and set minus 78 degree

temperature. So, this condition will satisfy that the carbon ion chain end and the lithium counter ion are tightly bound, strongly bound each other.

And if that is the case, then you can imagine the situation like this; where because of resonance, these ionic charges are distributed can in the three atom. So this can, this counter ion help in strong coordination between the active chain end and the polar substituent of the another monomer residues present in the chain. Now if such thing happens, then what happened? One of the sides is blocked.

So the new monomer, the incoming monomer can approach from only one single side. So, there is a loose cyclic intermediate formation and one side is blocked by lithium. So, monomer can approach; the incoming monomer can approach only from a single side and always producing an isotactic polymer. So you, if you do this reaction in lower temperature, nonpolar medium with a lithium plus type small counter ion, you can get highly isotactic polymers.

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Now, if you can do the same thing with isobutyl vinyl ether and make a cationic polymerization with say  $\text{BF}_3 \cdot \text{H}_2\text{O}$  and  $\text{H}_2\text{O}$  type initiator, then you have a cationic group, and again now an anionic counter ion which are tightly bound; because you are carrying out. This is a nonpolar medium. Again you can think of a similar MMA type situation, where in this case the counter ion is actually giving a strong coordination between the... this is monomer substituent and the incoming monomer forming this type

of intermediates. And again all the sides is blocked. So the monomer, incoming monomer can add to the chain from only single side. And you can get a isotactic polymer always.

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<u>Monomer</u>	<u>Condition</u>	<u>Structure</u>
<u>MMA</u>	n-BuLi in $\text{C}_6\text{H}_6$ at $-78^\circ\text{C}$	<u>Isotactic</u>
<u>MMA</u>	n-BuLi in THF at $-78^\circ\text{C}$	<u>Syndiotactic</u>
<u>Isobutyl vinyl ether</u>	$\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ in propane at $-60^\circ\text{C}$	<u>Isotactic</u>

Radical  $\rightarrow$  Syndio  
ionic

So, if we look at some data; let us consider methyl methacrylate as a... This is a normal butyl lithium in toluene at minus 80 degree 78 degree centigrade. That is the example I gave in the last page that produce isotactic poly methyl methacrylate. Look, if we have the same polymerization, same temperature, same initiator, but if you increase the polarity of the medium, obviously if you increase the polarity of the medium, T H F is highly polar solvent. So, the counter ion is not tightly bound; so strongly bound with the active anion end.

They are free they are free ion; the lithium ion is a free ion, which means the chain end has a planar geometry. And as we discussed it will give you a syndiotactic polymer, syndiotactic methyl methacrylate. Now, if you increase the temperature it will be the same reaction with butyl lithium in T H F. And do it in a much higher temperature, then you are going to get a mixture of isotactic and syndiotactic component. In the polymers, you are going to get a atactic polymerization.

This is the example of cationic polymerization which has B F 3 threat in propane as minus 60 degree centigrade. That is the example; cationic example just gave and which gives you a isotactic polymer. So, what we know that that radical polymerization will

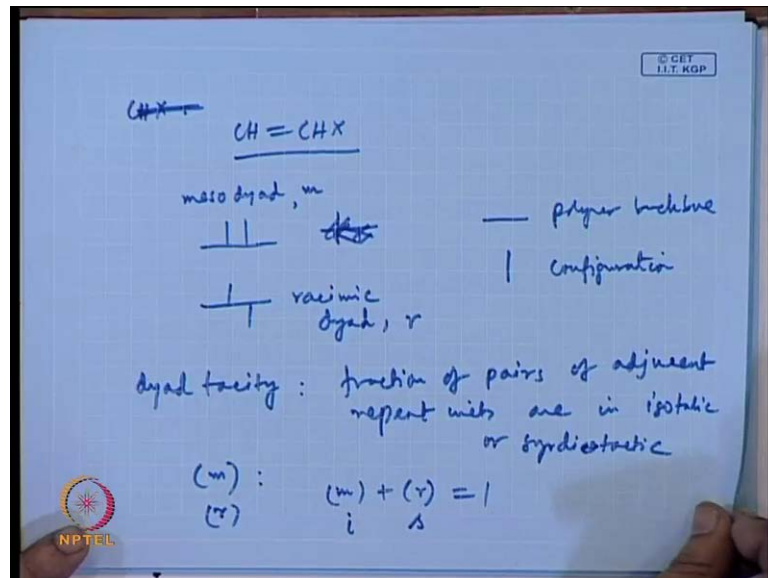
always give preferably syndiotactic syndiotactic polymers. And this do not get dominated if you increase decrease the temperature.

Now if you, for ionic polymerization if we do polymerization in condition where the ionic chain end and counter ion they are present as the free ion, then they will be ... as a radical polymerization..

And, if we do the reaction in conditions so that, the counter ion is strongly bound with the active chain end, then what happened? That, which we get, if we do reaction in the nonpolar medium at low temperature and with a, as a small counter ion, then there will be a possibility of a strong coordination between the monomer and the active chain end and the counter ion; which will makes sure that the monomer, the incoming monomer gets into the chain from one side and which will produce a isotactic polymerization, isotactic polymers.

So, I know; we know, what are the strategies? We should do to synthesize isotactic, syndiotactic and atactic polymerization. Now, let us see how do you analyze how do you analyze these polymers.

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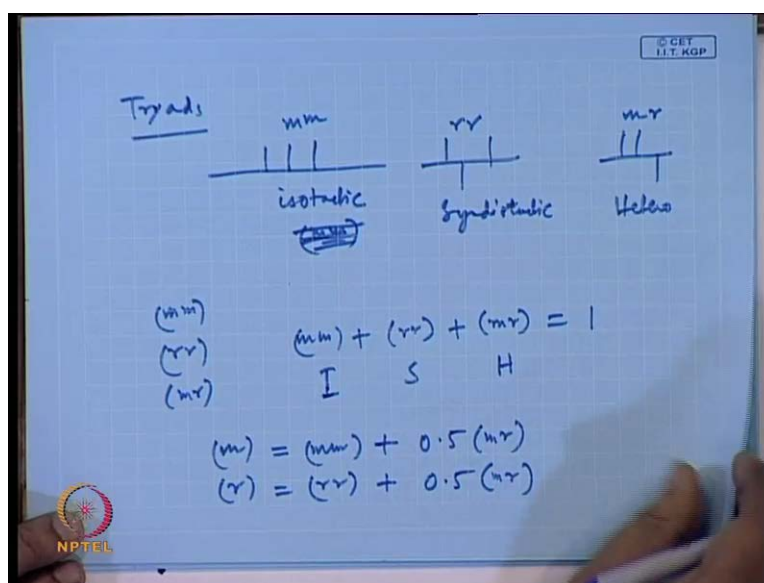


Now, let us consider a simple molecule; again same thing. Now, if we write two pair; two asymmetric pair of carbon atom, now this is the horizontal line. This is your polymer backbone backbone. And this line gives you the configuration of the carbon atom.

So this, in this case both the carbon atom, the asymmetric carbon atom has same configuration. So, we call this as a mesodyad. And if they are in opposite direction, then we call this is as a racemic dyad. We write m; we write r for this. Now dyad tacticity; this term dyad tacticity is defined as the fraction of pair of fraction of pairs; these are pairs, this is another pair; so fraction of pairs of adjacent repeat unit are in a particular Stereochemistry, say isotactic or syndiotactic.

So, if we write m; m is the fraction of pair adjacent repeat units that are present in a isotactic geometry. And r is the fraction of pairs of adjacent of repeat units that are present in syndiotactic geometry. And of course, m plus r would be equals to 1. Now, sometimes few people write this is as a meso gives you isotactic, so they write as a 'i', and the which gives a syndiotactic as small 's' as well.

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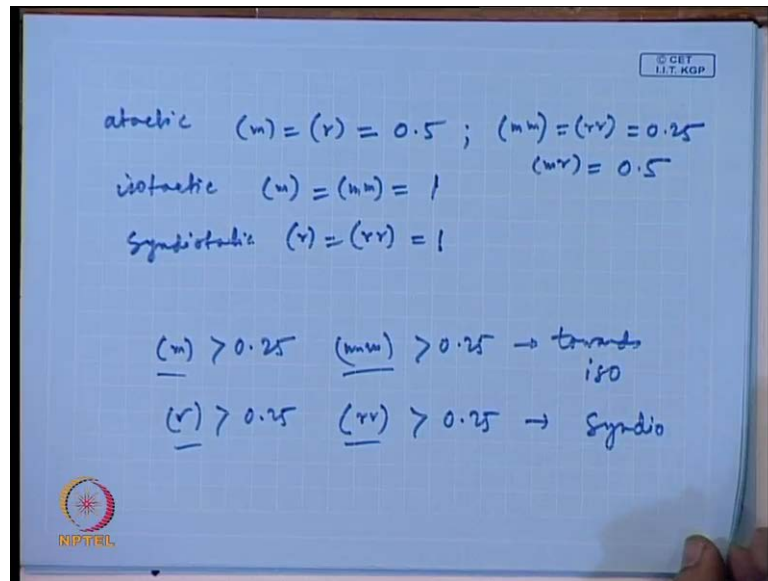
Now, we also can imagine Tryads. Tryads, where we are talking about the three... center adjacent to each other; like in this case, you have a meso pair and another meso pair. So, which actually gives you isotactic polymers and we write this as m m; so meso pair and another meso pair. So, what will be? This is a racemic pair, this is also another racemic pair; so gives you r r. and this gives you a syndiotactic rearrangement. Now, in this case you have another possibility where you have a meso dyad; another is a racemic dyad.

So, you can have a meso, m r; which gives you a heterotactic or atactic stereo arrangement. Again, we define in a similar way; m m is a fraction of these three and r r is



fraction of syndiotactic tryad and m r is a fraction of heterotactic tryad. So, we can write  $m m + r r + m r = 1$ . And sometimes, some people write this is this gives you isotactic, so they write I; they give you syndiotactic, so they write S and this is heterotactic, they write H. Now, we can easily write other from this expression. You can do yourself; plus  $0.5 m r$  and  $r$  as  $r r + 0.5 m r$ .

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Now for isotactic or atactic polymer, both fractions for r will be equals to half. So, half of the dyads will be in racemic form. So, basically it is a fifty-fifty mixture of isotactic polymers, dyads and racemic dyads; which is a completely atactic polymer. If you have an isotactic polymer, then m and m m, both the dyad and tryad would be equals to 1. And if it is syndiotactic, then r and r r also will be 1.

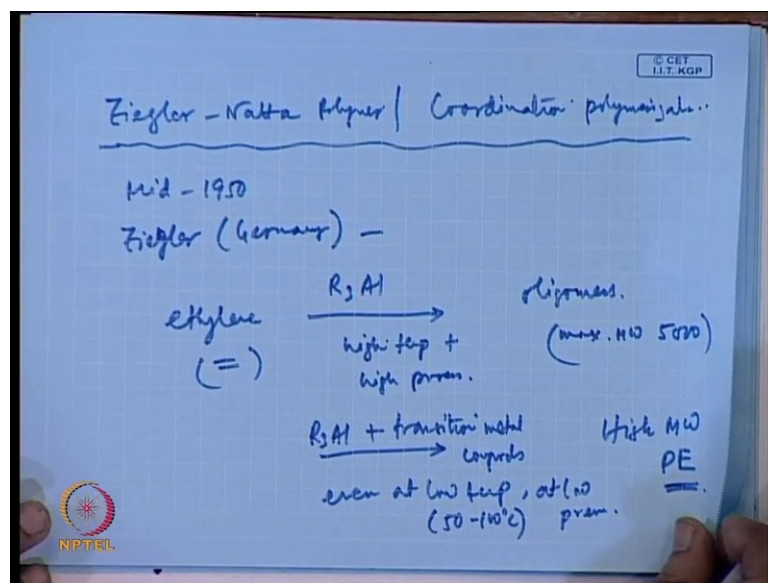
Now in case of atactic you also can you can also write m m and r r is one fourth; whereas m r, if you have this fifty fifty, then obviously this m r, the combination of m and r tryad will be half. So, you can write this. So, what we can do? We can identify this m and r from spectroscopic techniques like m m r. We can use m m r techniques to find out the fraction of m, r or m r in the... All this we can find out quantitatively from m m r experiment. And if we can find out this, we will be able to determine what is the extent of isotacticity, and syndiotacticity in the polymer.

If m is greater than one fourth, so as the m m tryad; then obviously, it is predominantly towards this giving going towards a isotactic. It is more isotactic, rather than



syndiotactic. If  $r$  is greater than 0.25 and  $r$   $r$  greater than one fourth, then it is towards a syndiotactic. That you can, yourself, this is what happened. If there is a mixture it is always a isotactic polymerization. So, these are the... So we can, what we can do? We can take the polymer which is synthesized and get a quantitative  $m$   $m$   $r$  done. And from that we can get the values of  $m$ , this one  $m$   $m$ ,  $r$  and  $r$   $r$ . This we can get. And from that, the values for individual values we can actually estimate or we can predict or we can quantitatively get the amount of say tacticity; which is the  $r$  fraction, which is the  $m$  fraction in the polymer itself.

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Now, what we will do it? It will go and move to the next topic of Ziegler-Natta polymerization or coordination polymerization. Now, it was first started around mid-1950s mid 1950s where first Ziegler, Scientist in Germany, he was doing ethylene polymerization; So, ethylene and in pressure Trialkyl aluminum. Say for example,  $R_3Al$  at high temperature high temperature plus high pressure, you only can get Oligomers; so oligopoly ethylene or oligo ethylenes; the maximum molecular of, maximum M W of around five thousand.

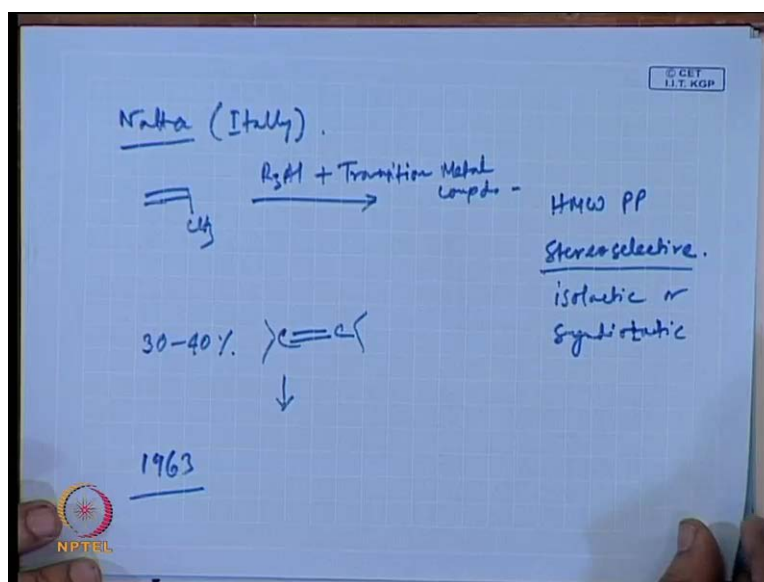
So, he was carrying out a polymerization reaction of ethylene in presence of a alkyl aluminum, Trialkyl aluminium and at high temperature and high pressure you only got oligomeric species, not a polymeric species. What happened? When he added with this alkyl aluminum plus some transition metal compounds? When he added, then even at

low temperature, say like low temperature means 50 to 100 degree centigrade and at low pressure, he got very high molecular weight polyethylene.

So basically, only... what is the change here? It is only the change of addition of transition metal compounds along with this alkyl aluminum. Then, it was dramatically... The polymerization nature was dramatically changed. You get a high, very high molecular polyethylene. Now, this polyethylene is not branched like the polyethylene. We discussed, while discussing the radical polymerization that, in case of radical polymerization you get a polyethylenes, which are branched because of chain transfer to polymers. As we discussed, we recall from our discussion of chain transfer on radical polymerization.

In this case they are not branched; they are linear high molecular polyethylene and that can be achieved even at low temperature, which is very means achievable or very comfortable temperature 50 degree to 100 degree centigrade, and even normal to low temperature, low pressure.

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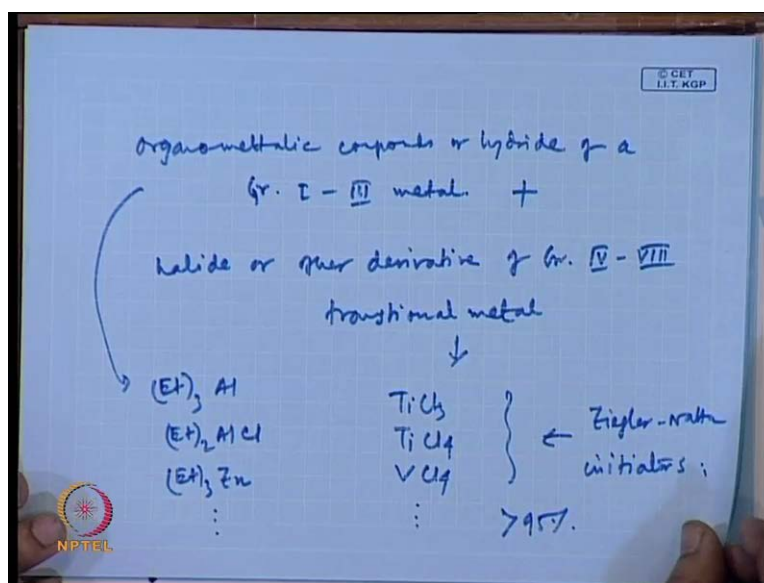
Now what happened? The same sort of catalyst was used by Natta. He was from Italy. What if... he used instead of ethylene, he has taken say alpha or say in this case propylene and used the same sort of catalyst; alkyl aluminum plus transition metal compounds.

Now, what he got? He got high molecular weight polypropylene, definitely. In addition, what he found that that was very stereo regular, stereo selective. Depending up on exact polymeric conversion, it could be a completely isotactic or syndiotactic depending up on the exact condition. But what he found that it not only gives high molecular weight polypropylene, but it also gives a very high stereo selectivity; whether it is a isotactic, completely isotactic or syndiotactic. Now these two discoveries has a tremendous effect in Polymer Science.

And even at nowadays, say more than thirty to forty percent of the carbon carbon, the polymers which are made from carbon carbon double bond, polymers which are made from carbon carbon double bonds, they are synthesized by these coordination polymerization technique. See, imagine how, what is the tremendous effect it has this discovery by Ziegler and Natta has made; a huge huge importance in Polymer Chemistry, which has given recognition to them in 1963. And they are jointly awarded the Noble prize in Chemistry.

Now, later on the large number of catalyst was discovered, developed. And basically what happens? In... basically it is the combination of again the similar type of compounds and there has been a lot of research happened in this field.

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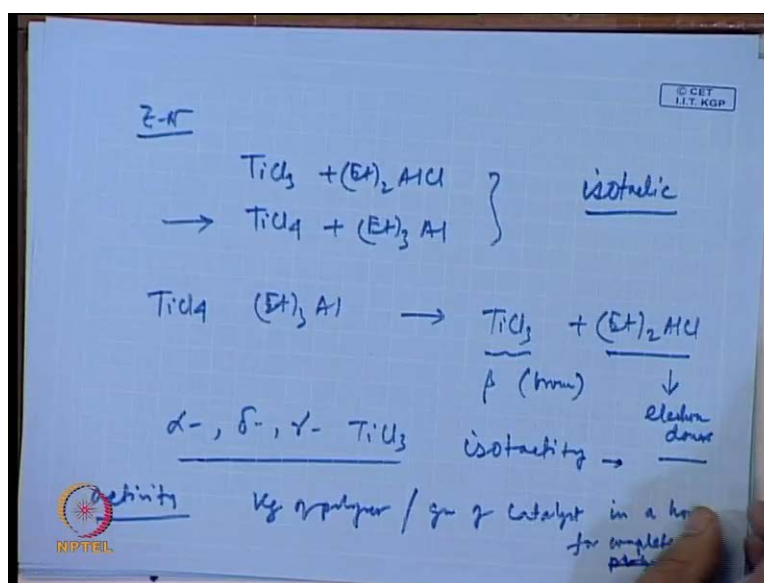


And, most cases are organometallic compounds; so organometallic compounds or hydride of a group one to three metal plus a halide or other compounds or other

derivatives of group four to eight transition metals. So, basically this are the... this is, this they would take one from here and one from here and constitute the catalyst, which is generally called Ziegler-Natta initiator or Ziegler-Natta catalyst. For example, we can choose; from this set, we can choose say triethyl aluminum or tri diethyl aluminum chloride or diethyl zinc, and from this we can say titanium, titanium chloride, tetrachloride, trichloride. And we can use so many things and these mixtures take one from here and one from here and constitute the Ziegler-Natta initiators.

Until 2000, more than ninety five percent of the Ziegler-Natta polymerization used combination of this sort of catalyst before the discovery of the metallization catalyst. Where, instead of transition metal catalyst, metallocenes are used as a catalyst along with a co- initiator; which we will discuss in a minute.

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Now, most of the examples of Ziegler-Natta catalyst, let us put this Z-N, are titanium, from these two the titanium trichloride or 2 Al Cl or say titanium chloride plus... Most of the important industrial polymers are made from this.

And, this is the original polymer catalyst combination used by Ziegler. And what happened when these things are mixed, Ti Cl 4 and triethyl aluminum? They have taken in a nonpolar solvent and they have mixed; now it produces a titanium trichloride and this. Now when you mix this two, as it was mixed by Ziegler what happens, this forms

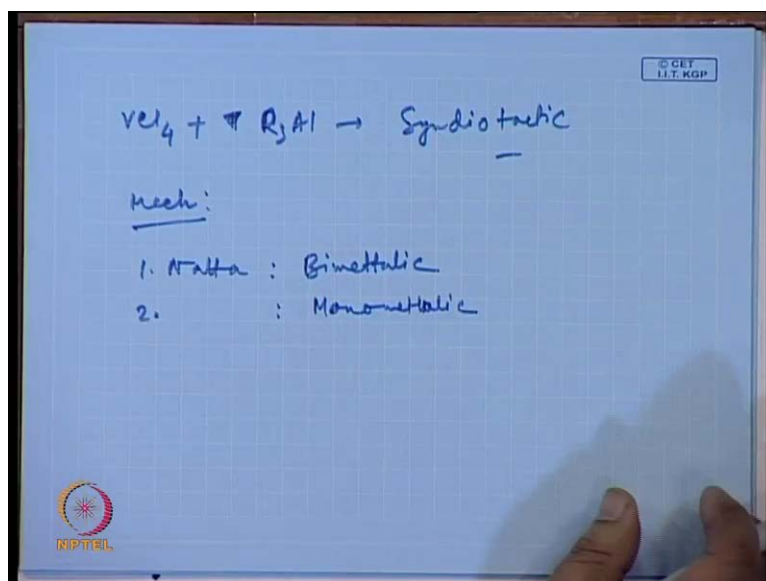
beta form of titanium chloride which is brown in color. Now, that this particular catalyst form - beta form of titanium trichloride does not have very high selectivity.

What Natta found that, instead of using beta, other forms of titanium chloride like alpha or delta or gamma form of titanium trichloride; if you use this sort of trichloride, then you get a very high stereospecificity, very high amount of isotacticity in this case. Now, what happened? These two are, generally when the polymerization made these two polymers are mixed and ball milled that will mechanically grinded so that, that also increases the surface area of this catalyst. We will see in a minute how the surface area is actually important for this catalyst and also it actually help in increase the activity of the polymerization.

Sometimes giving the development of the catalyst this titanium trichloride or tetrachloride, they are used along with a support like say magnesium chloride, where this titanium compound is either coherently bonded or they are occupied a crystal position in the lattice of the magnesium chloride support. So, that actually helps the activity and the stereo specificity. And sometimes with this sort of Trialkyl aluminium chloride or say dialkyl aluminum chloride, sometimes these electron donors are added. Electron donors, like Lewis acids are added to increase the reactivity and the specificity stereo specificity of the catalyst.

Typically, the activity of the catalyst is measured as a k g; k g of polymer produced per gram of catalyst in an hour or completely or at the end of the or at end of the your or for a complete polymerization. So, the activity of the catalyst is defined as the k g of polymers per gram of the catalyst used; we can use in other, per hour or at the end of the polymerization.

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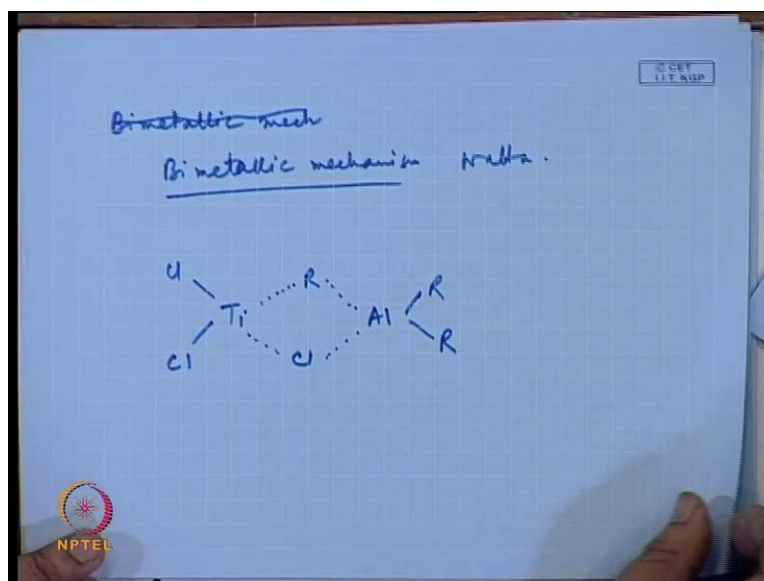


Now most cases, this type of the combination is your transitional metal compounds and alkyl aluminum compounds. They produce completely isotactic polymers except few cases; where there are few exceptions like vanadium chloride plus trialkyl compound, which gives syndiotactic. These are exception; few exceptions, rather than a regular case. Most cases, in almost exclusively all the cases it is the isotactic, which get formed.

Now, what is the mechanism what is the mechanism by which these polymerization happen and all the stereostaticity is maintained? There has been lot of studies and lot of mechanism proposed during last several decades. And till there is no mechanism, you know, which has been which has been accepted by all the Chemists, Scientists working in this field.

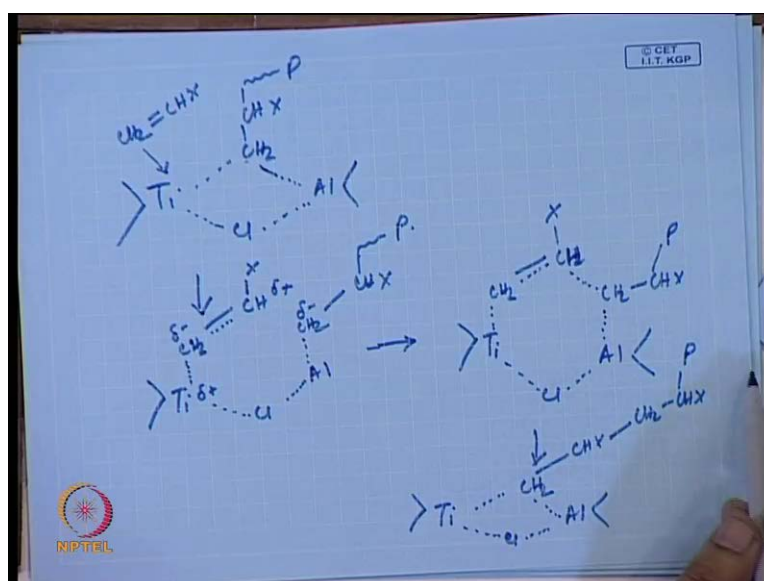
And, so what happened? Still this is, this Zeigler-Natta polymerization is not completely understood. So, what we will discuss here in this lecture, we will basically talk about two mechanisms. One was proposed originally by Natta and which is a bimetallic mechanism. And second, where majority of has actually accepted this mechanism which is a monometallic. We will discuss these two in a minute.

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Now, let us talk about first the bimetallic mechanism. This was originally proposed by Natta himself. I mean, this case the active side is an electron deficient. The active side is electron deficient, bridged complex formed by chemisorption of the alkyl aluminum; the electropositive alkyl, metal alkyl with a small ionic radius on the co-catalyst surface. Let us first draw. And this is the active side which is electron deficient than that formed by the chemisorption of the electropositive metal alkyl, which has a small ionic radius on the surface of the co-catalyst. Now, once this is formed which is electron deficient, what happened? The monomer approaches this active side and coordinates.

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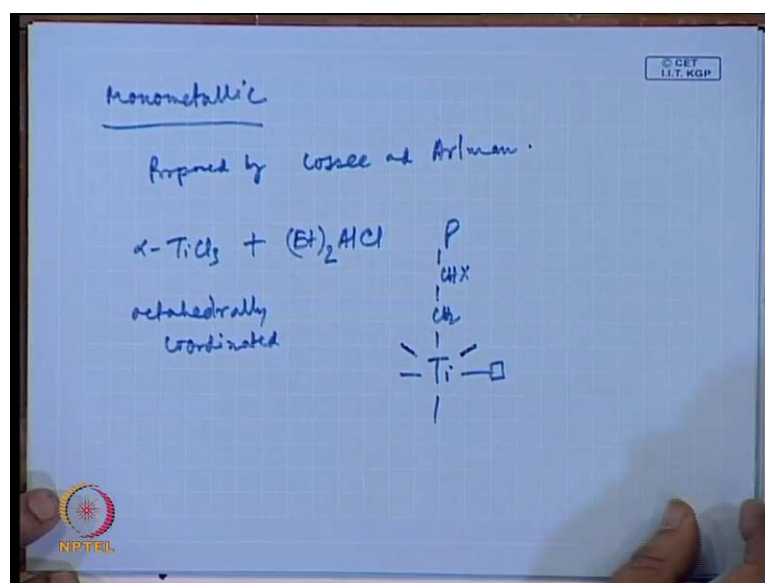
So, we can write the next step. Now instead of R, we are writing a propagating chain because that is the that is the steps get repeated. So, we are not writing the first step, first addition. We are writing any general addition of the next monomer, where P E is the polymer residue.

And, what happened? First, the monomer formation of complex between, formation of pi complex between the, with the nucleophilic olefin... So, they and this is electro deficient. So, this approaches and forms a pi complex with the titanium center and which gives you... Then, next what happened? This is followed by partial ionization of this olefin as well as this alkyl bridge. So, let us draw that.

And, there is a partial ionization of these alkyl bridge and also polarization of this monomers, which produce this intermediate, which then form a six membered ring transition state; which basically form a six membered ring transition state. You can draw yourself. And so that is the six membered ring transition state. And what happened now? There is a insertion of this new monomer; this new monomer in the alkyl carbon linkage alkyl aluminum linkage and forming again the original titanium... which will now add to the next incoming monomer.

So, we have now. So, insertion inserting this monomer, a new monomer in the aluminum alkyl aluminum carbon bond, which will form the regeneration of the bridge complex. So, again what happened? The next monomer comes and get inserted here same mechanism and you get a linear poly olefins in this case.

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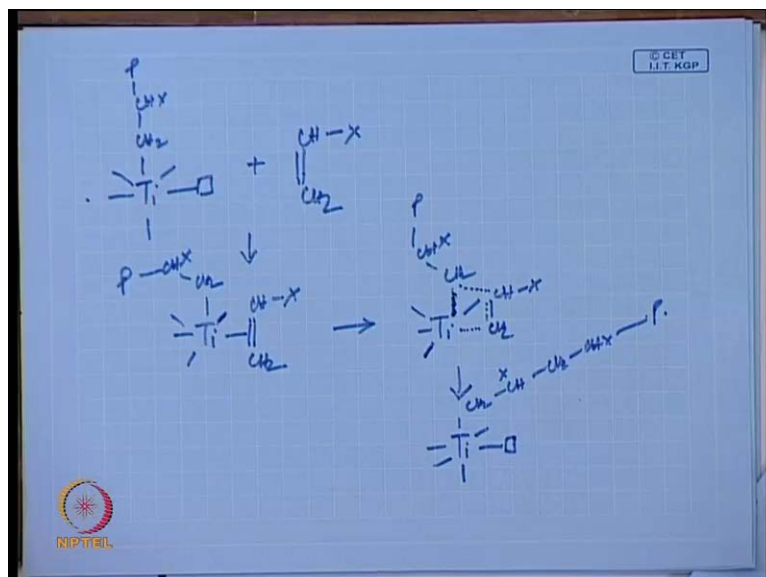
Now, the second mechanism, which is a monometallic which is proposed by Cossee and Arlman. Now this case, the vacant d-orbital present in the transition metal is the main source of catalytic activity. And the chain growth occurs in titanium alkyl bond. In this case, you have seen the chain growth, of course in aluminum bond. In the monometallic case, we are talking about the chain insertion or the chain growth happening in the titanium carbon bond. And in this case, the vacant d-orbital present in the transition metal is the main source of catalytic activity

And as we said and as I said, that insertion happens in between the titanium and carbon bond. So, if we consider the example, we given earlier. Let us take the same example to get the or discuss the mechanism. Now, this is the octahedrally coordinated crystal and because it has to maintain electron neutrality, the titanium or the surface is five coordinated titanium and have a vacant d-orbital. And what happened at the beginning? At the active center, the formation happened by addition of a alkyl to this vacant d-orbital of five coordinated titanium three plus.

So, there is a... let me draw that. Now, in this crystal as I said, this is a octahedrally coordinated. So the surface, the titanium which is present at the surface is that is five coordinated titanium three plus and that has a vacant d-orbital. We are writing this as a vacant d-orbital. Now the initially what happened? This alkyl aluminum compound gets chemisorbed. In that, vacant d-orbital and titanium gets alkylated. And this now is a

active center. This initiates the polymerization. We will let me drive the draw the mechanism in a separate page.

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So, now we have this vacant orbital. And these are all chlorine atoms, which are firmly embedded in the crystal of titanium alpha titanium chloride, again which we are writing the polymer residue here; 'p' as a polymer residue. Now, the monomer gets coordinated form pi complex with the vacant d-orbital. Monomer gets coordinated to the vacant or empty d-orbital. And then it forms a cyclic transition state.

So, it forms a four membered cyclic transition state. And then, this new monomer gets inserted in the titanium carbon bond. In earlier case, in bimetallic case we proposed... the mechanism was proposed where the new monomer is getting inserted in the aluminum carbon bond. In this case, the new monomer is getting inserted in the titanium alkyl bond and regenerating the vacant d-orbital. So,  $\text{CH}_2\text{-CH X-CH}_2\text{-CHX-P}$ .

So, now this is regenerated. This active center is regenerated. So, again one more monomer comes and the cyclic four membered cyclic transition formation takes place and the monomer gets inserted in the titanium carbon bond. So, the polymer, linear polymerization takes place.

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**Features of Ziegler-Natta Polymerization (monometallic)**

- An octahedral vacancy (d-orbital) of  $Ti^{3+}$  is available to complex with incoming monomer
- Orientation of the coordinated monomer is determined by its steric and electronic interactions with the ligands around the transition metal atom
- The propagation step is completed by insertion of the coordinated monomer into metal-C bond. The growing polymer chain is always attached to the transition metal.
- Orientation of the monomer as it inserts into metal-C bond determines the configuration of the stereo center in the newly formed terminal repeat unit
- Isotactic polymer is formed when the preferred orientation for coordination of monomer is of much lower energy than others.

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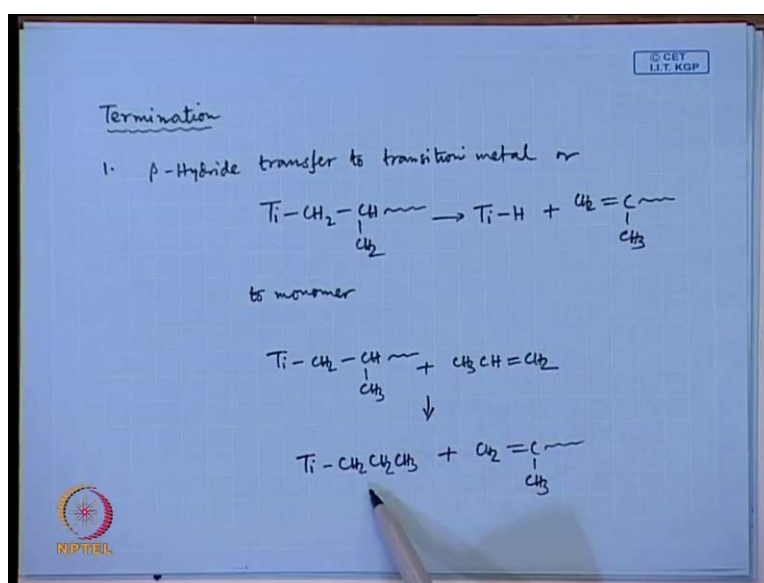
Now, let us discuss few features of Ziegler-Natta polymerization which is the mechanism, we just talked about the monometallic mechanism. We all talked about that. Let me just summarize one more time the features. This is the important mechanism. So we just, one more time let us discuss. So, basically an octahedral vacancy of the d-orbital of titanium three plus is available to complex with the incoming monomer. So, in this case there is a vacant d-orbital, which is available for complexation with the incoming monomer.

The orientation of the coordinated monomer is determined by the steric and electronic interaction with the ligands around the transition metals. So, basically these are the ligands. In this case chloride; there, their interaction with the monomer; steric and electronic interaction with the monomer actually determines the orientation of the coordination monomers. And the propagation step is completed by insertion of the coordinated monomer in the metal, transition metal carbon bond as we discussed now.

And, the growing polymer chain is always attached to the transition metal. Remember in case of bimetallic, the growing polymer chain was attached to the aluminum metal. The orientation of the monomer as it inserts into the metal carbon bond, determines the configuration of the stereo center in the newly formed terminal unit. You know, that is obvious; what is the orientation of the monomer, when it gets complex and inserted, that orientation is determined by the stereo center, whether it will be isotactic or syndiotactic.

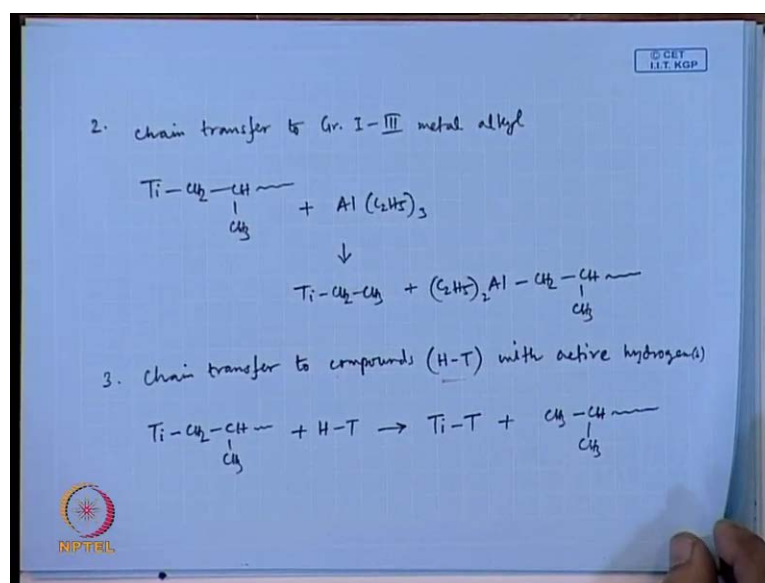
An isotactic polymer is always formed when its preferred orientation for coordination is much lower than the other. If one of the orientations is preferred, much preferred, if one of the orientations of these incoming monomer molecules is much preferred over the others, then what happens? The isotactic polymerization formation takes place. So, now, we basically know these are the mechanisms of Zeigler-Natta polymerization. So, once initiation and propagation are done, let us just glance through the possible mechanisms by which we can terminate. These Zeigler-Natta polymers or coordinated polymers get terminated. And termination actually can happen in one of the three ways, like just, am just doing it a little fast.

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There is nothing more to understand and it is just for information purpose. Termination can happen; beta hydride termination to the transition metal. These hydride can get terminated and transferred to the transition metal forming a within end group in the polymer. It can also get transferred to a monomer; a monomer forming or forming this combination.

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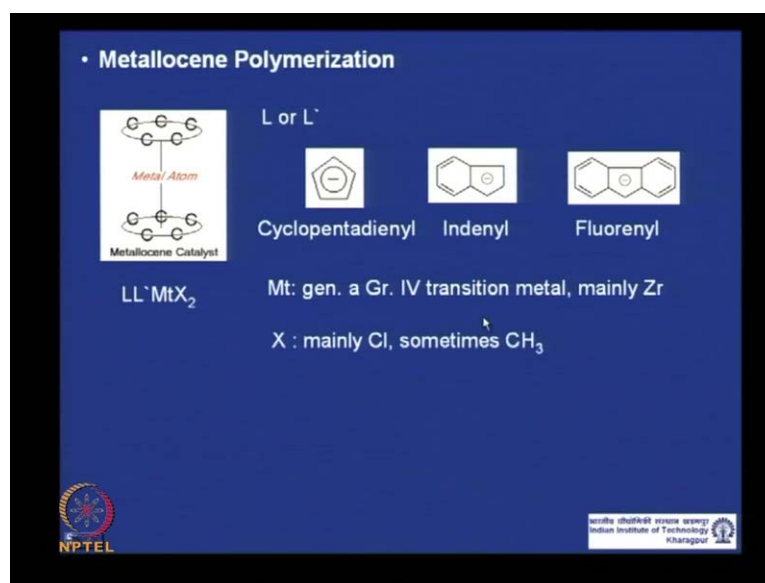


Another way of this polymers; the Zeigler-Natta polymers get terminated which chain transferred to the group one to three metal alkyl metal like aluminum alkyl, we just discussed. Basically if you take this example, propylene by titanium catalyst; now, this can get transferred and you can have the chain get terminated. The chain can terminate, the chain can transfer to compounds, added compounds, which are having active hydrogens. We can write this generic structure of H-T with active hydrogen. Then, this chain transfer can happen to this and the chain can get terminated. Now, so this is all about the Zeigler-Natta polymerization.

And, this is the majority of the industrial polymers. And Olefin industrial polymers was synthesized by this catalyst combination, Zeigler-Natta catalyst, till the discovery of metallocene catalyzed coordination polymerization. Now in case of metalist, now what I have not talked till now that this is heterogeneous polymerization. When you mix this alkyl aluminum and titanium chloride, the catalyst actually gets precipitate from the solution and when you add ethylene or propylene, it is a heterogeneous polymerization.

Now metallocene, you can actually do the polymerization in the homogeneous medium. Metallocene polymerization can be done in solution in a homogeneous medium. And the advantage is that at the end of the reaction, you can isolate the metallocene catalyst and then purify and reuse.

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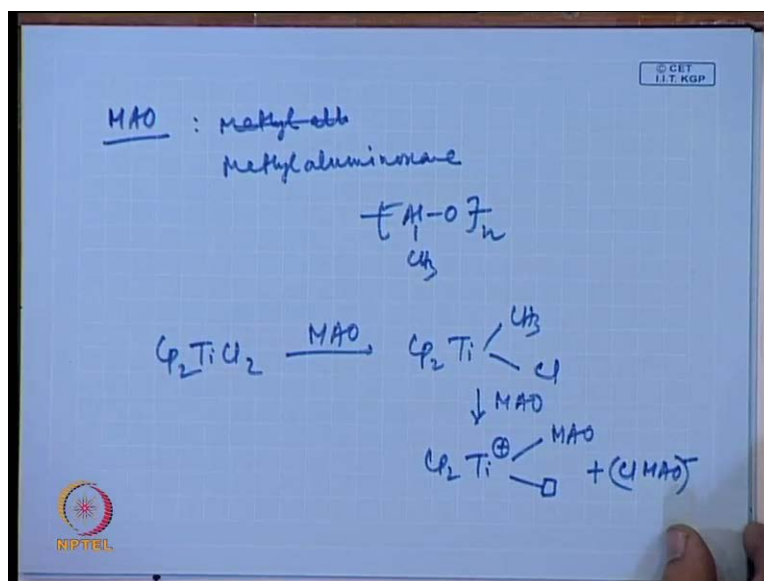


Now, what is metallocene polymerization? You can give a generalized structure of metallocene catalyst like this where or you can write a structural  $LL'MtX_2$ ; where  $LL'$  are the ligands which can be equal. But the  $LL'$  can be same or different; from different metallocenes like Cyclopentadienyl or Indenyl or Fluorenyl. These are the few examples of the ligands which are present in the metallocenes. For example is example of metallocenes, where you have two side; two cyclopentadienyl coordinated with, attached with iron. Generally, this metal used is a group four transition metal and in most cases it is zirconium and so zirconocene is what is mostly used in case of metallocenes polymers. And X is a, most cases it is a chloride and sometimes it is  $CH_3$ .

Now this require, this is like this titanium transition metal in Zeigler-Natta polymerization, this requires another co-catalyst like alkyl aluminum as is in the case of Zeigler-Natta polymerization. But if we use alkyl aluminum, then what happened? The stereo specificity was not very high.



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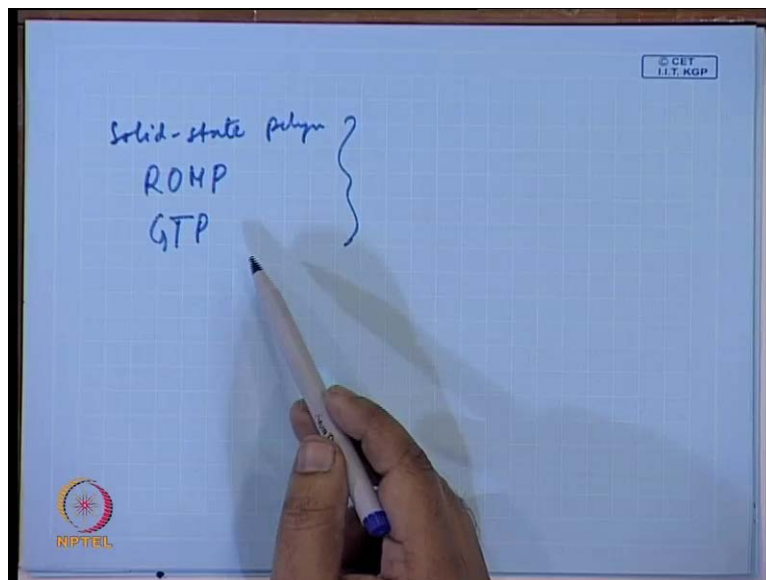
So, the most used co-catalyst is MAO which is a methylaluminoxane, which is network compound of this. Now for example, let us take a metallocene polymerization. This is a Cp cyclopentadienyl, Cp<sub>2</sub> say titanium chloride, inclination of MAO. MAO does actually two things. It is alkylate; first it is alkylate, the metal and then abstract one halogen and form metal... ion and which generates one vacant or vital.

And, rest of the mechanism is same as we discussed in case of Zeigler-Natta polymerization in, like the insertion of polymer monomer molecules. So, rest of the propagation and propagation follow the same similar mechanism as we discussed in case of Zeigler-Natta polymerization. The advantage of metallocene polymerization is that, as I said that this can happen in a homogeneous condition and at the end of the polymerization it can isolate the monomer, isolate the catalyst and purify and then we reuse the catalyst one more time.

So, with this we have completed our discussion on Stereochemistry, Polymer Stereochemistry and coordination polymerization. Now in this lecture itself, we basically completed our module on polymer synthesis. What, till now what has happ...till this twenty four lectures was except the first few couple of lectures, where we give introduction about polymers. Rest of that twenty two lectures or twenty one lectures, we discussed how to synthesize polymers. Now, what are the different ways we can synthesize the polymers. And I tried to give emphasize on the polymerization or

synthetic process which are important, which are used very frequently or which are more important industrially. And there are some specialized techniques as well, where which are used for specific techniques, special polymerization techniques.

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For example, we solid-state polymerization, ring opening method, this is polymerization or group transfer polymerization. Now, these are a not very common example of polymer synthesis or lots of industrial polymers are not used by this technique. So, it can be covered in a specialized course on polymer synthesis itself. So, in a general course like this of on Polymer Chemistry, we are not going in details on this type of specialized polymerization technique. So, you are requested, if you are interested you can go and read a or consult a specialized book on polymer synthesis to know more about this polymerization techniques.

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**Examples of commercial coordination polymers**

- **HDPE**
  - Low branching
  - High crystallinity
  - High density
  - Films: packaging
  - Sheets
  - Tubing
  - Wires and Cables
- **HMW-HDPE**
  - MW 0.25M to 1.25M
- **UHMW-HDPE**
  - MW > 1.5M
  - High abrasion resistance and impact strength
- **LDPE**
  - Copolymerized by slight amount of 1-olefin
- **PP**
  - Very high strength
  - High T<sub>m</sub>
  - Very low density

Now before we end this lecture, let us go through the commercial, a few commercial coordination polymers. And you can for example, high density polyethylene which has low branching, high crystallinity, high density. You can actually use these coordination polymers to make high molecular weight, high density polyethylene or ultra-high molecular polyethylene. You can make low density polyethylene as well by copolymerizing with slight amount of one olefin, such as one butylene or one hexylene along very slight amount with ethylene that, we will basically introduce to do branches and reduce the crystallization, increase reduce the density as well.

And, another very important point polymers which is made industrially by this technique is as we discussed several times is the polypropylene. And as we said that, stereo regular polypropylene like isotactic polypropylene and syndiotactic polymers are useful to synthesize.

So, with this we come to end in this module of polymer synthesis. In next lecture onwards, what we will do? we will study the characterizes process, characterization of process, how after making this polymers what are the ways we will characterize and even with the polymers, which we have learnt for last twenty four lecture. How we can we have learned how to synthesize the polymers.