Metallocene and Metal-carbene Based Organometallic Compounds as Industrially Important Advanced Polyolefin Catalysts

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Lecture 04

Polyethylene and Polypropylene: Chemical Structure and Properties (Continued)

Welcome to the lecture 4. This is basically the continuation of the lecture 3 where we started to discuss about the chemical structure or basically to understand the microstructure of the polyethylene and polypropylene where we started to discuss in the last class the tacticity that the microstructure associated with polypropylene or the similar type of polymers.

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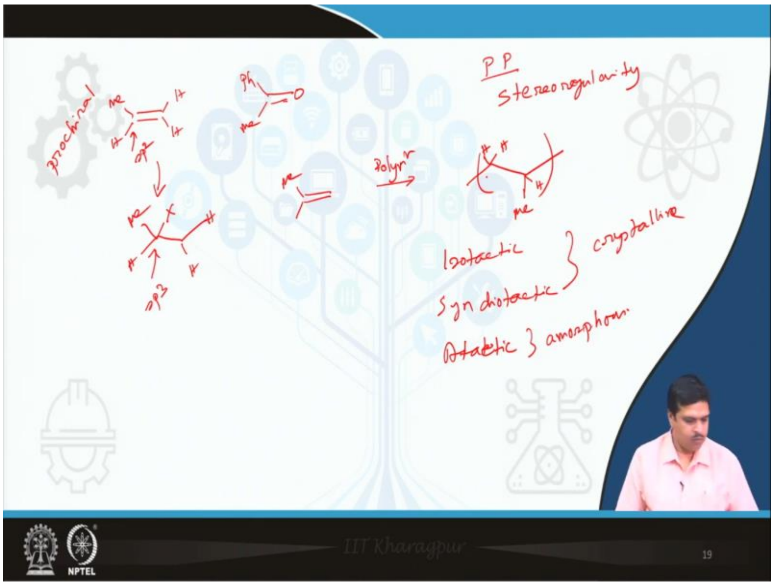

And we saw that if you start from a, like let us like a prochiral molecules like this one, that is the propene, you know that all of you know these molecules the acetophenone. So, this is also a prochiral molecules. So, this is the S P 2 center and if we can make the SP 3 centers by putting another substituents on this one then it will be like that. So, this is my C H 2 and this is my hydrogen, this is my methyl and let us say this is my X and this is H H and this is H.

So, now, you will see that this is SP 3. So, now you have the different four groups are there. So, it will become the stereo center. So, this kind of prochiral molecules will give chiral by putting another substituent. So, similar thing happens, if you see carefully that if this is your propylene molecules and if you do the polymerization and you end up with this situation where your, so, here it is methyl, here it is here another hydrogen and here the chain with different carbon, here also chain of different carbon.

So, this kind of polymers, this is the polypropylene, here you will see the stereo regularity issues. Now, depending on the orientation of the metal, of orientation of the methyl group, you will get different kind of stero regularity that we discussed in the last class. And the interesting point is that in the last class we discussed I can get the isotactic, we can get the syndotactic and we can get the atactic.

And this one is the crystalline and this one is the amorphous. And that is why you will see that this atactic polypropylene is quite, if you heat it, it becomes soft, quite soft in nature. And these are relatively harder. So, you will see that depending on the microstructure you can get the different properties and then you can basically do your applications according to the properties.

Now, we will try to understand more about the microstructure and how to detect the microstructure, the tacticity by routine spectroscopic methods. One way is the proton NMR. So, in the last class we discussed how how you can assign by simply the chemical shift of the the C H 2 protons in the repeating repeating units of the polypropylene and we explain that why the chemical shift is different for the isotactic or syndotactic scenario. So, we will discuss in more depth today.

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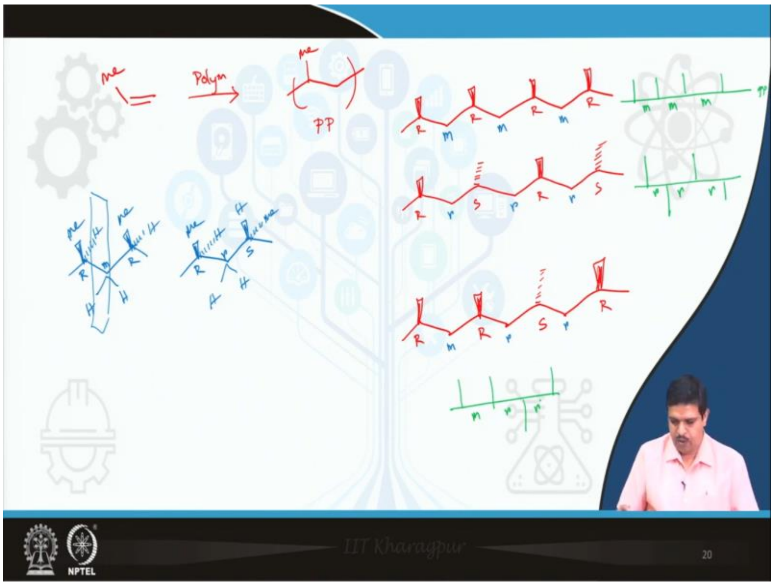

So, let us again, so, this is my propylene and I am doing the polymerization and I am getting this polypropylene polymer. So, let us the three scenario would get, sorry, it is, try to understand and please also do practice yourself. Now, here this is so, this is my R R R R R and this is R S R S. Now, another scenario like that. So, this is my R R S R like that.

Now, if you consider this C H 2. So, here we have assigned R R eight as on the basis of the stereocenter. Now, consider this C H 2. So, this one will be m, this one will be m, this one will be m like that. So, this one now will be, this is, this stereocenter is based on the R S descriptor and this is, this C H 2 is the small R racemic, this r means racemic. So, this is r, this is r, this is r. And here accordingly this convention that C H 2, so this will be m, this will be r and this will be r, is it clear. So, this is basically, if you see like that. So, this by H and if methyl group, let us say the above and this one. So, this is let us say this one and methyl is below H and this is my H H.

Now, you see that this, in this case, methyl and methyl group is above the plane. So, this is same configuration. So, R R and this is R and this is S. And this is the measure. Why? Because if you imagine a plane crossing this C H 2. So, you will see that here, so like this plane, like this plane. So, you will see methyl methyl is above H H is the below. So, you will get the meso, and like this one the scenario is different. So, that is why this is r, small r, racemic and this is m.

So, for simplicity, if we generally do, we follow the easier convention. So, we just instead of writing on to show the stereo center, we just write is a linear form like that one. So, if it is like this one, so, the like this, this, this, this, this like that and for this one, this like this one, sorry, like that and this one we write like this way, this way, this way, this way. So, this is the simple convention we follow to represent the tacticity in the polymer backbone. So, if methyl group is oriented above the plane, we just put the line, this is your mention of the P P and we just put this methyl group is upward and if it is the below then we put is the downwards like that.

Now, so, we put it like this and we write like m m in the middle, m, like that. And here same way. So, here we will put the r r r. Same way what we put? We will put m, we will put r, we will put r. So, this is the convention we follow for representing the tacticity in the polymer backbone.

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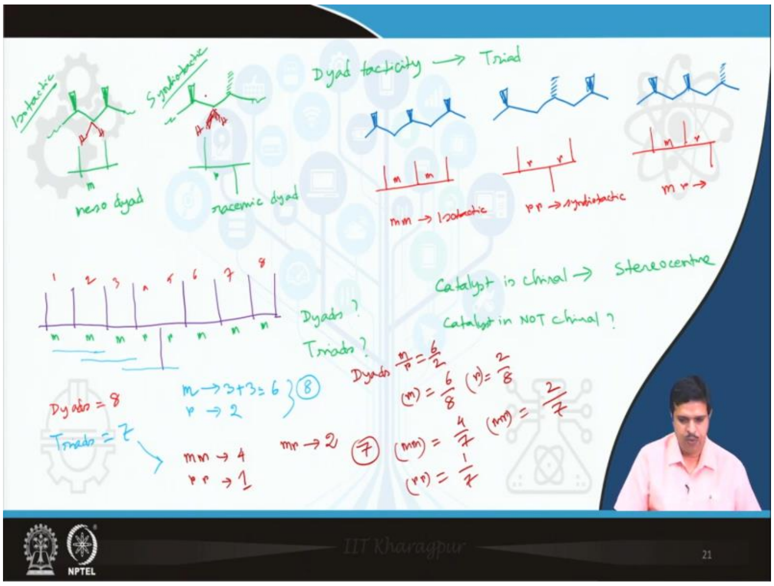

So, let us discuss in more depth because this concept will be used, will be very useful when we will do the mechanism study and to understand the mechanism by a particular polymerization protocol and here we will discuss in more depth the polymerization by the metallocene based catalyst because that is one of the biggest or you can say the biggest beauty of the metallician catalyst that how we can get the stereo regularity of the polymers if we use a prochiral monomers which are not possible if we do the other conventional polymerization like radical polymerization like that.

So, that is that is why it is very important to understand the tacticity, otherwise we cannot detect by the routine spectroscopic methods and we cannot understand that what kind of polymer it is. So, let us take various small fragment of the propylene let us say like two repeating units. So, just a two repeat units. So, one is the methyl groups are on the same orientation. So, this is called the diode. So, this is an another one I am taking like this and this one. So, this is called a diode tacticity. I am just taking only the two repeating units of the polymer, of the polypropylene backbone to understand the tacticity.

Now, so this is then if we represent like a line, so, this is meso. So, this, this is in the middle it is C H 2. So, this is called the meso diode. This is called the meso diode and this is then the opposite one, so these two methyl groups are in the opposite direction, opposite orientation, so, if this one then it is, if we represent by line, so, it would be like this one and this is this C H 2 is different as a r and this we call the racemic diode. So, this is isotactic fragmentation of a isotactic PP and this is a fragmentation of a syndotactic P P.

Now, you will see. Now, if I go to the diode to triad tacticity. Now, what will be scenario? Let us try yourself, you can try yourself. So, what will be the difference? Then you add one more unit. So, here put the methyl, then the methyl, another possibility. So, here like that alternate orientation and another one like that. Now, can you label the tacticity as I did for the diode?

You can try yourself. So, let us try, let us do it. So, first thing you represent as a line. So, here, here like that. So, here like that and here, here, here is like that. So, you can put it as a m m. So, this is r, this is r and this is m this is r, you see. So, here you will see this m m. So, this is isotactic, isotactic, isotactic triad. This is r r. So, this is basically syndotactic. And what is this? Obviously, this is atactic. This is m r.

Now, go to the, so, this we did with a very small fragment to understand. Now, in the polymer, it will be quite big. So, now let us do in a to understand in a bigger chain, to just to understand let us take a like a 8 9 or 10. Let us take 8. So, what will be the scenario? We will just draw it, just draw it with eight diodes. So, we know the diode, we know the triad, how does it happen.

Now, let us try with eight repeating units, how does it happens. So, what will be the scenario? So, let us make the first the main skeletal chain represent as a line and we put like let us take nine repeating units. So, 1 2 3 4 and let us take this one, 1 2 3 4. Now, label it, label it as a small m and small r, small m and small r convention. So, this will be your m m m, stop here this is r, this is r, this is again m, this is again m, this is again m. So, this is the scenario.

Why we are trying to understand? Because when we will discuss in later part that how we can control the stereo regularity by following the two mechanism, one is the catalyst site mechanism and one is the chain end control mechanism. So, in one case you will see that the catalyst is chiral and it will induce the stereo center because the catalyst is a chiral. And one case, chain and control, the catalyst is not chiral, catalyst is achiral. But you are getting the stereo center. This is very funny. So, in one if your catalyst is chiral, if your catalyst is chiral then obviously, you will get the chiral center for this.

We will discuss this one. This is very interesting. But if your catalyst is not chiral then what you will get if it is not chiral in many cases, if it is not, if catalyst is not chiral then also you can induce the asymmetric synthesis, in organic chemistry of heart, the asymmetric synthesis and how it is possible, we will discuss in the next classes or.

So, in our polymerization, by metallocene chiral or a chiral catalyst, you have to have a good concept of this tacticity. Because by this way only you can study or you can conclude that in which mechanism this catalyst, this polymerization is happening whether it is a catalytic site control or whether it is a chain end control. So, here you will see that now I am asking two questions.

You have to do now it is on the class that how many diodes, the question is that you find out the diodes and triads and label it. How many, first how many diodes and then you label how many now how what level according to the small m small r convention and how many triads and label it as a m r convention. Let us try it, let us do it. So, first what you have to do? We have actually done the main part we have done it. Now, you will see, this is if first you see the diode. So, 1 2 3 4 5 6 7 8. So, 8 diodes. Is it clear? So, I am getting the 8 diodes. So, diodes is number of, the total number of diodes is 8.

Now, can I tell that how how many triads from here? Let us do it. So, this is how many? This is one, this is one, this is one. Now, this is one. Now, this is one. So, like that you will have a triads total. How many? 7, like that. So, 8 diodes and triads. Now, you find out what type of diodes. So, here you will see that this diet m m m. So, m, I am first trying trying diodes. So, how many m m? 1 2 3, 1 2 3 3. So, 1 2 3, 1 2 3. So, here here total 6 m diodes. Sorry, here I have to I should not write the double m, it will be single m. Because it is a diode.

Now, total. Now, 6 assigned as a m and this leftover is the r. So, r is 2. So, total is 8, clear. So, out of 8 diodes, I have the 6 m and two 4. Now, let us set triads. So, you will see one triads is m m. So, here you will see m m, then m m, then m r, then r r r m m m m like that. So, if you calculate the triads, how many you are getting?

So, let us see, so you are getting the let us first m m, this m m. So, one m m, this is one, this is two and here this is one, this is two. So, total I am getting, the m m I am getting the 4. Now, you are getting r r, how many? r r this one and this one. So, r r I am getting only one that is triad only one. Now, how many m r, how many m r? Where m r I am getting. Here you will see m r and m r. So, again 2. So, total 7.

So, here you will see that in this case for diode, if you see the ratio for diodes m by r ratio is how much? Is it, this is the m and this is the 6 by 2, and in this, this is the m by r and we also represent in like this way. So, like m, how much the m m? I am getting the ratio with respect to the total number of diodes, the m I am getting 6 by 8. And r I am getting 2 by 8.

Similarly, m I am getting like in a first bracket that is the convention. So, 4 by 7, r r I am getting 1 by 7 and m r I am getting is 2 by 7 like that. So, as I told why you are studying because we I already discussed that the chemical shift of these protons, these two protons will be different if it is isotactic, moiety or whether it is a syndotactic moiety.

For isotactic moiety as already I already discussed that you will get here different chemical shift but in this case you will get a same chemical shift because you see this will as in the last class I have discussed that if you have like this and this you will have this hydrogen is a below. This is methyl, this is a below. And here this hydrogen, this is the above and this is the above.

So, this one will experience different chemical shift. We will experience the same chemical shift in proton NMR spectroscopy for the racemic diode that is the syndotactic fragment. So, with by calculating the number of, by carefully checking the chemical shift of these two hydrogen protons and then relating with the diodes and triads, you can calculate or you can determine the microstructure of the polypropylene or related polymers by proton NMR Spectra.

As I told obviously, it you have to use 400, 500 or 600 megahertz high-resolution NMR to get the knowledge or the information about the tacticity. So, this is as I told that this is very interesting and you have to understand the logic behind the determining the tacticity of the polymers. Obviously, as I told that you can also get the knowledge whether it is a syndotactic or isotactic or atactic by other physical properties as example for the stiffness, the crystalline nature of the polymer.

But this, the spectroscopic method the proton NMR and also C 13 definitely, as I am discussing proton NMR because this is more easy to record, easily available. So, combination of the proton and obviously combination of C 13, you will have we should we will have a good knowledge about the tacticity of the polymers. So, now, we know that what is the basic convention to represent the tacticity of the polymers where the stereo regularity exist in the polymer backbone.

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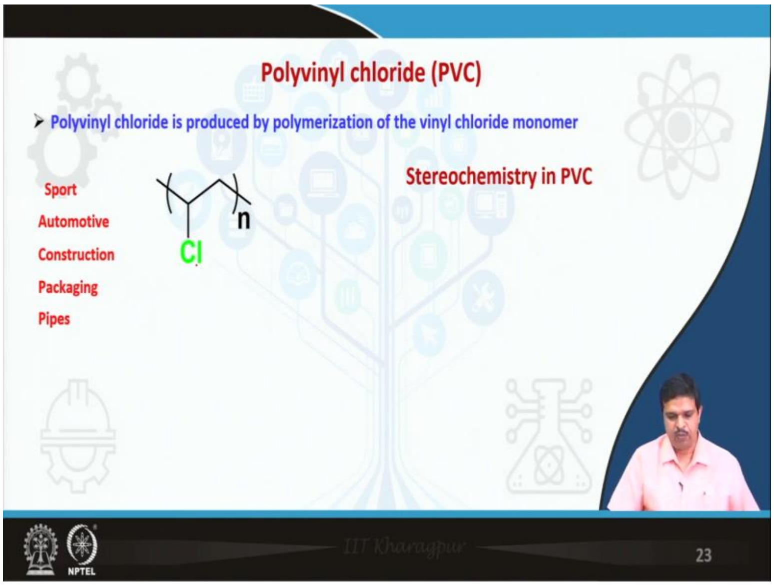

Polyvinyl chloride (PVC)

- Polyvinyl chloride is produced by polymerization of the vinyl chloride monomer

Sport
Automotive
Construction
Packaging
Pipes

Stereochemistry in PVC

So, similar, if you understand here that in the polypropylene, this was the methyl and in the polyvinyl, this is the chloride in plates of vinyl. So, obviously, the similar kind of stereochemistry is also of may be, may also be observed in polyvinyl chloride. Why we are discussing PVC?

Because you know that if you see, look around your, you look around your classroom, you will see that many cases in this room you will get the PVC material, the tiles, the pipes, all are made of the PVC. It is a very popular polymers. So, I am not discussing in depth about the application others, I am more discussing about the chemistry of the polyvinyl chloride.

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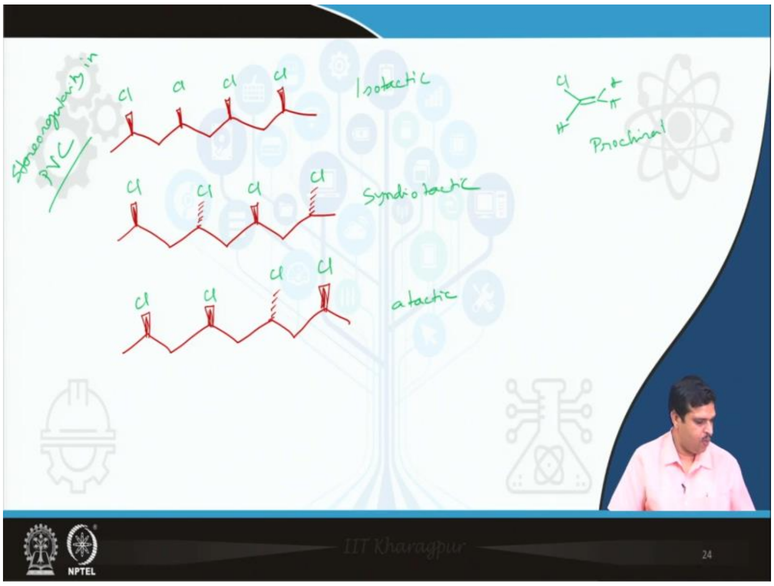

So, as I told that these also exist because you see that very similar to the propylene, polypropylene if you understand the polypropylene then you will understand the PVC. The same concept here. So, here also same concept. So, you just put chloride here in just a chloride here. So, this is basically a fragment of the PVC polymer. So, here you will see same way you can do.

So, this is isotactic, this is syndiotactic and obviously this is the atactic. So, in the PVC also the stereo regularity is possible in PVC polymers. Because here we are using again the prochiral monomers. So, this is your monomers. So, this is also prochiral. So, I think now we have a good knowledge about the microstructure, what is the origin of the microstructure in the polymers.

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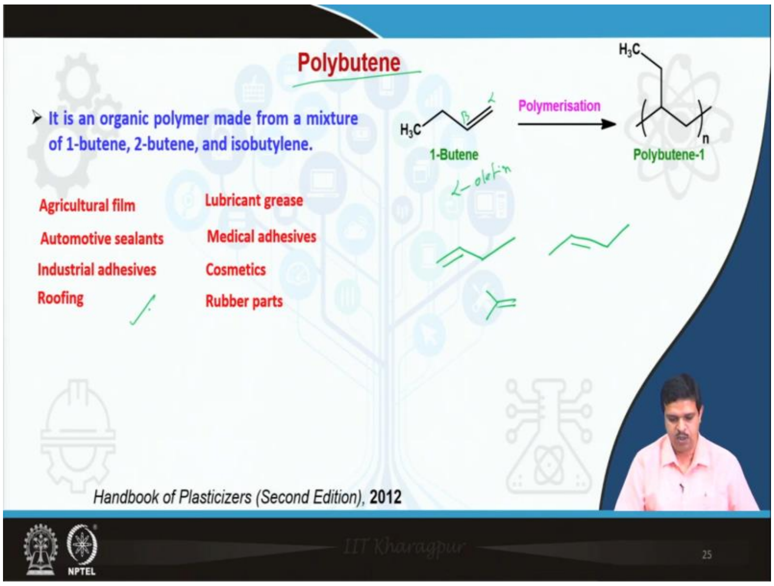

Polybutene

- It is an organic polymer made from a mixture of 1-butene, 2-butene, and isobutylene.

Agricultural film
Automotive sealants
Industrial adhesives
Roofing

Lubricant grease
Medical adhesives
Cosmetics
Rubber parts

Handbook of Plasticizers (Second Edition), 2012

So, not only the microstructure, you will see that different type of regio isomers are also possible and that is also can govern the polymeric properties. As example, if you see the polybutene, this is also another polymer, heavily used polymer in the category of polyethylene, polyolefin. So, here also you see that purposely we use is a mixture of the butene.

Here I have shown only with one butene that is the alpha olefin that is we use this alpha olefin. So, this is the polymerase like that and you get the polybutene. But if there is a mixture of the butene because you would show that you know that three kind of butene are possible depending upon the position of the double bond. So, this is one. So, this is one that is a true butene and another one, another one is is the, of course, I am.

So, here you will see, this is the one butane, this is the two butene and this is the isobutylene. So, all are basically butene and obviously depending on the monomer, the polymeric structure would be different, like this one is for the alpha butene that is one butene. So, depending on the ratio of the different monomers, you can also tune the physical properties. The applications I have listed. The applications is quite huge. I am not discussing the application. I am just trying to emphasize the chemical structure of the polymers, the common polyolefin polymers we use in daily life.

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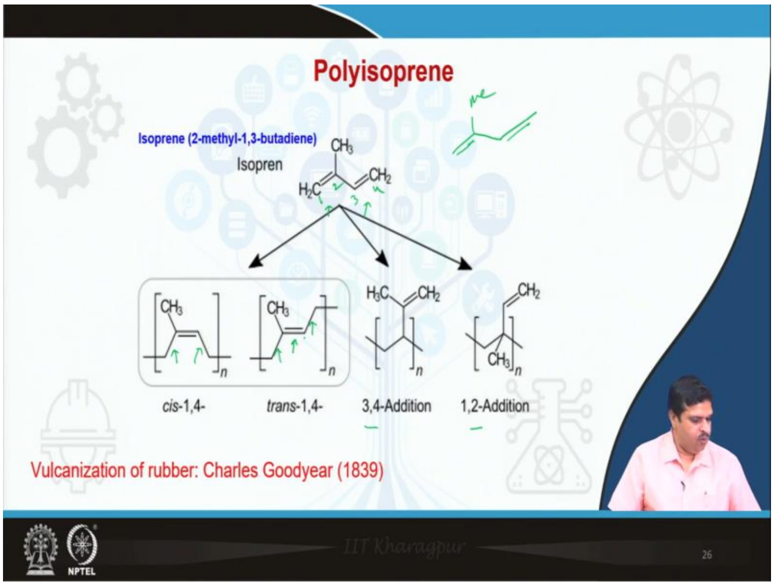

Polyisoprene

Isoprene (2-methyl-1,3-butadiene)

Isopren

Vulcanization of rubber: Charles Goodyear (1839)

So, another one is a very famous polymers and very interesting you can see it is a polyisoprene is naturally occurring polymers. You know all the rubber trees we can get the polyisoprene from there. And also, we can synthesize the polyisoprene very easily by radical or ionic polymerizations.

So, here also you see that very interesting, here two kinds of olefenic bonds are there in the isoprene. So, here you will see that here, so, here is one double bond, here in the double bond. So, polymerization may occur here or here or here. So, depending on and also you can it can undergo the isomeration. So, depending on that one, you can get a mixture of the polyisoprene.

All are polyisoprene but if you see very carefully, the chemical structure will be different and all are possibilities they are depending on the polymerization protocol. And also, definitely the stability of the olefenic bond. So, here you will see this is cis 1, 4, this is cis 1,4 because here you will see this is the cis, this is the trans 1, 4. So, here you will see, this is the trans, this is the cis. This is 3, 4 addition. So, here you will see this if I 1, 2; 3, 4. So, this is you will see that 1 2 3 4 from here.

So, if I start from here, 1 2 1 2 3 4, here all that is why it is called 3, 4 addition. This is the 3, 4, 3, 4. So, 1 2 3 4. So, this is the one to addition that means this one. So, the polymerization is through one to addition. So, this through this one. So, this is 1, 2 addition and this is 3, 4 addition, that is the this way. This is one two this way. So, you will see that depending on the polymerization protocol, this test statistical distribution will be different and the polymerization properties, the polymer properties also will vary to some extent depending on the ratio.

And you know this polymer was very famous from quite earlier days because this is heavily used in the tyre industry, particularly, when the Charles Goodyear discovered the vulcanization of the rubber using sulfurate and basically he used to took the advantage of this extra the extra olefenic bond and did the change the physical properties of the polymer to make the more stiff in nature. Because you know that this, the polyisoprene is rubbery which is quite soft, the T g is, temperature is quite low.

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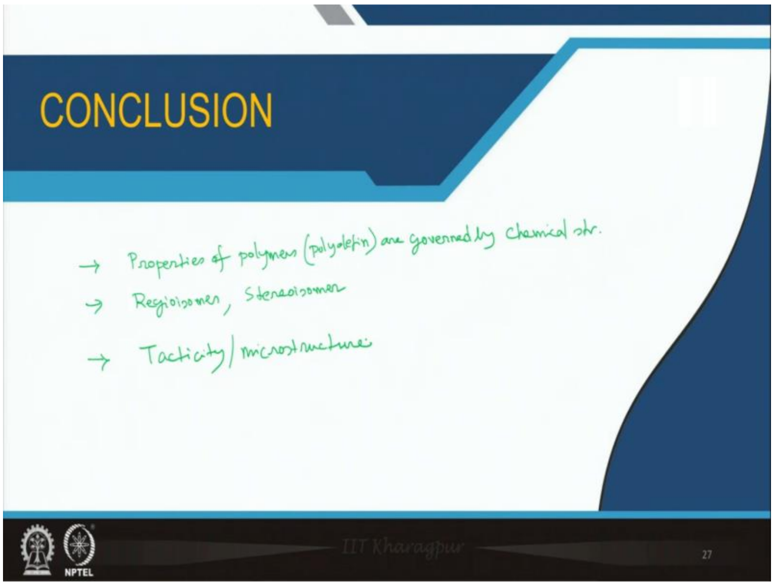

CONCLUSION

→ Properties of polymers (polyolefin) are governed by chemical str.

→ Regioisomer, Stereoisomer

→ Tacticity / microstructure

So, from here it is very clear that depending on the polymeric chemical structure, the properties of the polymers are highly varied. So, we you will see that the properties of polymers here specifically we I restricted on polyolefin, polyolefin type of polymers are governed by chemical structure. This chemical structures may be two types, one is the ragioisomeric and one is the stereo regularity.

So, we discussed the ragioisomers, we discussed the stereo isomers or stereo regulatory and we discussed the tacticity that is basically coming from the stereo regularity or stereo isomers of the polymers where the monomer is the prochiral in nature. And we try to understand the microstructure present or possible in the stereo type of polymers. So, why it is important? Because these are important because this see if you target for a applications, you have to know about the properties of the polymers and you have to know that how to engineer the polymer backbone.

So, with this knowledge, in the next class we will try to understand the polymerization protocol. Because as I told that the polymeric, the chemical structure you can control by the polarization protocol by using the same monomer. So, that is very important to understand the different available polymerization protocols and then the common polymerization protocols.

And then we will go into the our main content of the of this course that is the organometallic catalysts are used for making the polyolefin in industry, that is the metallocene and the graphs type of catalysts. So, thank you very much and we will see in the next class.