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

Professor. Sanjib K. Patra
Department of Chemistry
Indian Institute of Technology, Kharagpur

Lecture 03

Polyethylene and Polypropylene: Chemical Structure and Properties

So, welcome once again to the the course Metallocene and Metal-carbene based Organometallic Compounds as Industrially Important Advanced Polyolefin Catalysts. If we recall, in the last two classes we discussed and tried to give a flavor of the socio-economic impact of the polymers in our life. And we discussed the demand of the polymers, mainly, polyolefins, a different type of polyolefins we tried to classify and we tried to understand the basic structure of the polymer.

And also, we tried to understand what is the basic difference between the polymer, polymeric compounds and the small molecules compounds. As you recall that in we tried to discuss about the crystallinity of the polymers associated with polyethylene, mainly, because this will be important to in our further classes, where we will see that we can contour the crystallinity by using the different polymeration protocols.

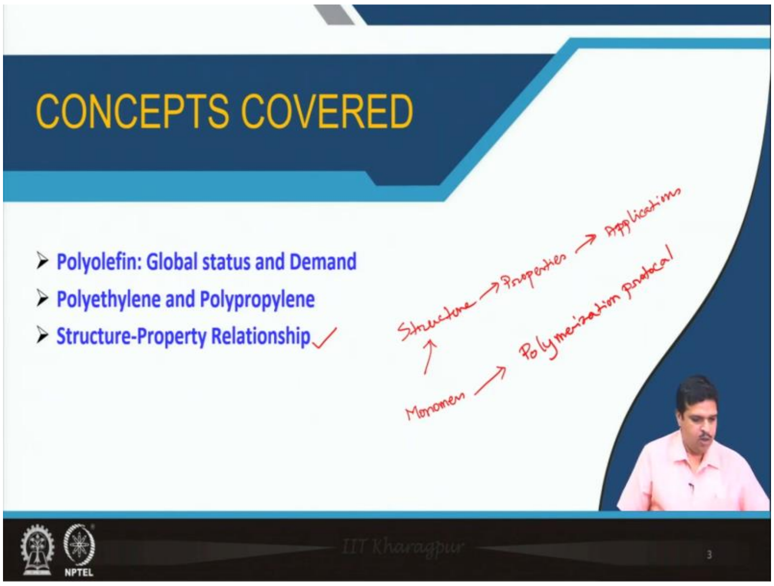
(Refer Slide Time: 01:52)

NPTEL ONLINE CERTIFICATION COURSES

Lecture 03: Polyethylene and Polypropylene: Chemical structure and properties

So, in this class, continuation with our last classes, in this class that in lecture 3, we will discuss in more depth about the polyethylene and polypropylene polymers and we will try to understand the chemical structure and its properties. So, let us start.

(Refer Slide Time: 02:09)



CONCEPTS COVERED

- Polyolefin: Global status and Demand
- Polyethylene and Polypropylene
- Structure-Property Relationship ✓

Structure → Properties → Applications

↑

Monomers → Polymerization protocol

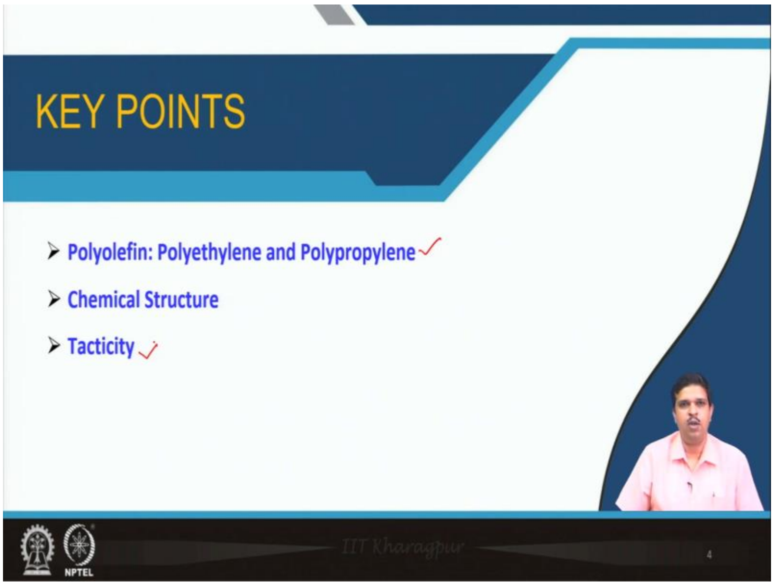
IIT Kharagpur

So, in this lecture we will try to cover the polyolefin, the global status and demand although we have discussed in the last classes. I will just try to give some data so that you will understand how much demand of particularly for this polyolefin category. Then we will try to discuss the polyethylene and polypropylene and then we will discuss the structure property relationship because this is very important.

Because suppose, if I need a particular applications, I need to understand the structure which actually can give the specific properties for a particular application. So, structure, then property and then applications. So, these one are interrelated. And again, the structure again depends on the definitely on the monomers and also you will see that in the last class we saw with that same monomers can give the same polymers of the same composition but with different architectures or different structures.

So, the monomers and the polymerization protocol. So, we need to select a specific a suitable monomer, suitable polymerization protocol to get our desired properties with the desired structure, for a specific applications which we are targeting for.

(Refer Slide Time: 04:03)

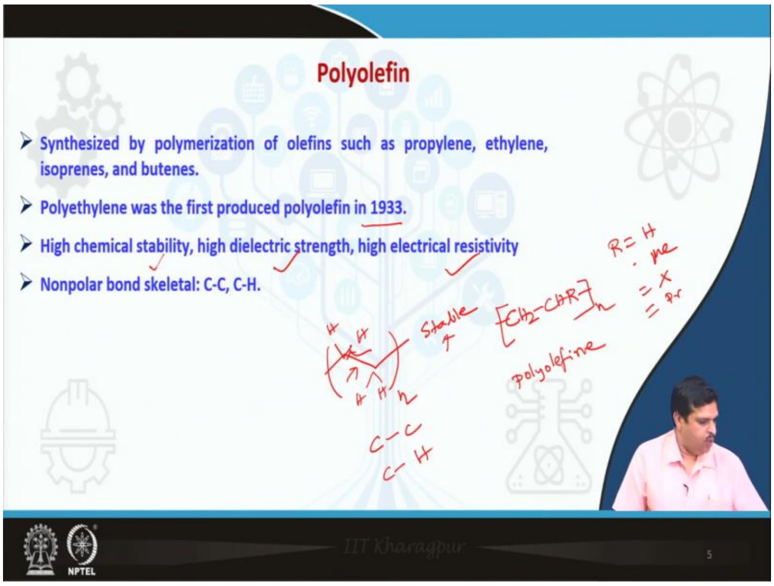


KEY POINTS

- Polyolefin: Polyethylene and Polypropylene
- Chemical Structure
- Tacticity

So, here, the key points we will try to cover and will try to understand the polyethylene propylene chemical structure and we will try to understand the tacticity. We will discuss in more detail in this class what is the tacticity and how these are related with the properties and definitely for the applications.

(Refer Slide Time: 04:25)



Polyolefin

- Synthesized by polymerization of olefins such as propylene, ethylene, isoprenes, and butenes.
- Polyethylene was the first produced polyolefin in 1933.
- High chemical stability, high dielectric strength, high electrical resistivity
- Nonpolar bond skeletal: C-C, C-H.

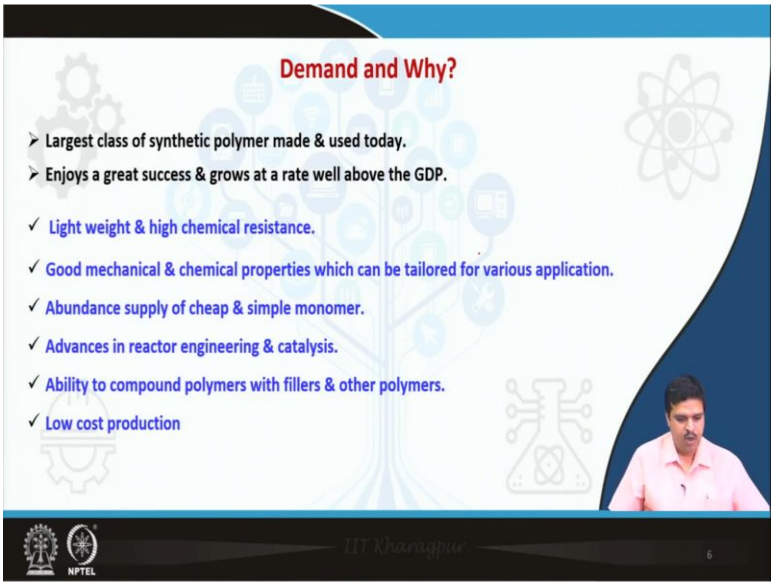
So, now, let us before going to the specific structural relation, structure property relationship, let us understand why this polyolefin is in high demand and what is the advantages properties, although we have discussed in the last classes in a very brief way. First thing that you see that this kind of polyolefin are quite stable, thermonically stable, chemically stable and quite robust and this robustness is basically due to the non-polar bond skeletal, as examples, carbon-carbon, carbon-hydrogen, those are very stable.

As example, you see that polyethylene, polyethylene is this one. So, you have here like that. So, the polyethylene is basically the chemical structure, the composition of polyethylene polyolefin is this one. So, this is the polyolefin. So, here you will see that this R can be many things, may be hydrogen, may be methyl, may be any halides like that, may be propyle, anything like that.

So, these are the polyfin category. And you will see here that two type of bonds, one is the carbon-carbon, that is the this one and here C H that is the this one, both the bonds are non-polar and very stable. You cannot really do any reaction in easy way. Although you can do in a very special way that is the C H bond activation or carbo-carbon bond activation but you need extra effort.

So, here, what is the, why I wanted to tell that these are very stable skeleton which cannot be broken in easy way. So, that is why it is very stable and that is actually prompted to use in our daily life applications. So, this one was actually first reported in 1933, quite long ago and these associated properties, as I told, the chemical stability high dielectric strength, high electric resistivity. That is why it is used as insulating materials. You will see that in electrical appliances.

(Refer Slide Time: 07:18)



Demand and Why?

- Largest class of synthetic polymer made & used today.
- Enjoys a great success & grows at a rate well above the GDP.

✓ Light weight & high chemical resistance.

✓ Good mechanical & chemical properties which can be tailored for various application.

✓ Abundance supply of cheap & simple monomer.

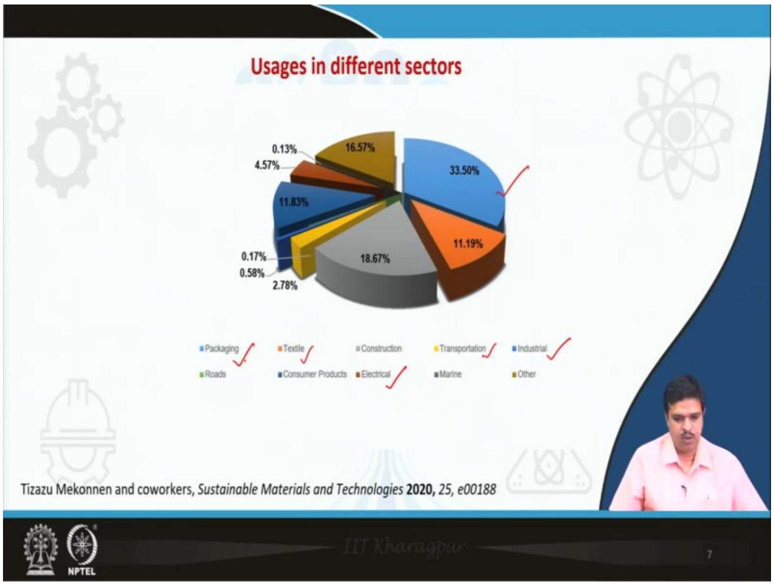
✓ Advances in reactor engineering & catalysis.

✓ Ability to compound polymers with fillers & other polymers.

✓ Low cost production

So, these the application is huge. You will see that many domains, various domains this is used and one of the main reason is that apart from the stability is cost is very low and easy synthesizable, you can make it very easily without any complications.

(Refer Slide Time: 07:40)

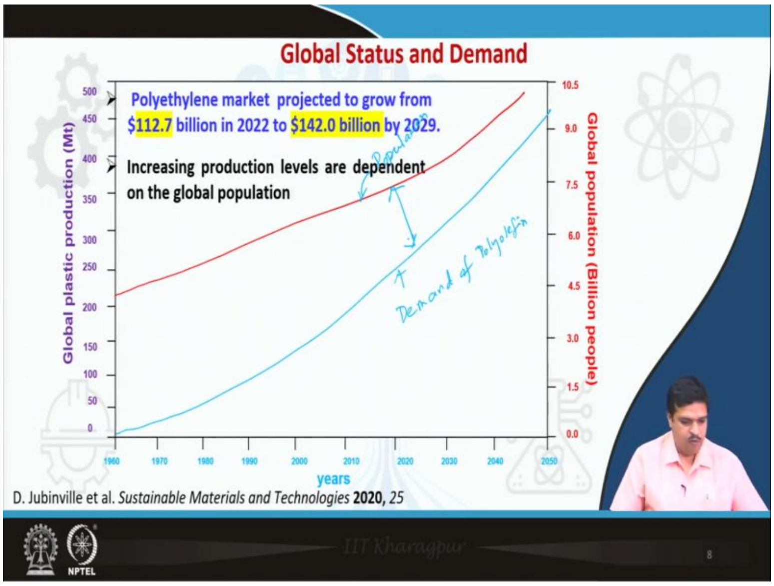


Usages in different sectors

Tizazu Mekonnen and coworkers, *Sustainable Materials and Technologies* **2020,** *25, e00188*

And this you can see that you, this pie chart you can get a, from this pie chart you can get a feel that in which domains this kind of polyolefins, mainly the polyethylenes are used. You will see that one of the major use is in the packaging industry. You will see that this one, the packaging industry. Then you will see this construction domain. Then you will see that in various applications in the industry of electrical, mainly, it is used as a insulating materials. Transportation, textiles and as I told the packaging is one of the major domain of using the polyethylene or allied polymers. So, it is the demand is huge.

(Refer Slide Time: 08:42)



Global Status and Demand

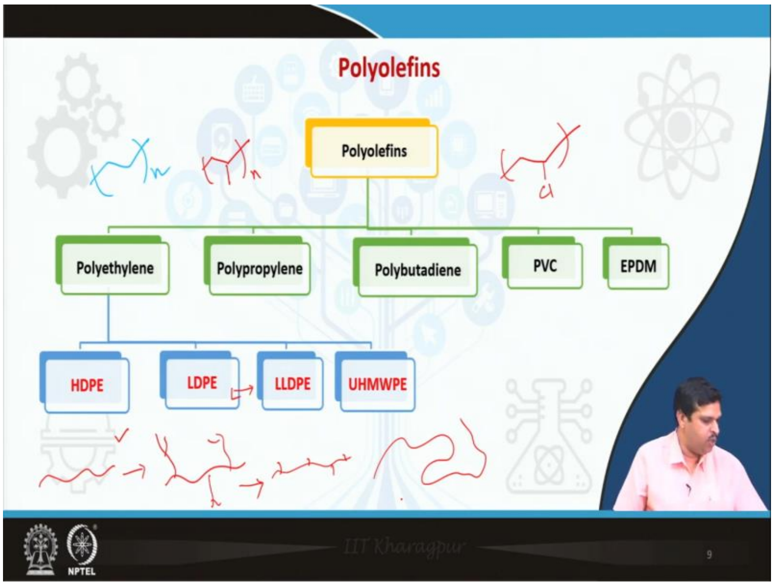
- Polyethylene market projected to grow from $112.7 billion in 2022 to $142.0 billion by 2029.
- Increasing production levels are dependent on the global population

D. Jubinville et al. *Sustainable Materials and Technologies* **2020,** 25

And if you see from this report that is the very recently published Materials and Technologies 2020 that you will see that if this is the population if like that this is a very roughly I am drawing. So, like that and if this is the population and this is the demand of the polyethylene. So, this is my demand of polyfin polymer and this is the population.

So, you can see that this is directly proportional, the demand of the polyolefin polymers is directly proportional to the populations. So, its demand is huge and you can see that it is projected that in 2029 the market will be 142 billion dollars. So, it is a huge. Fine.

(Refer Slide Time: 09:59)



Polyolefins

So, this is I am sure now, it is quite understandable and now you can understand that how the demand it is. Now, let us go to the chemistry part. Please, go to the polymer science. Before that I just want to give overview that what are the polyolefins again and what are the different type of polyolefins depending upon the structure and the depending on varying the substituents. As example, you will see here, this is polyethylene, this is we know. So, this is this one.

Now, the polypropylene, as the name suggests that this is. So, there is one methyl. So, this is polypropylene, polybutadiene, polyvinyl chloride, simple. Say instead of methyl this is chloride and EPDM is basically a combination of the different monomers to tune its physical properties, I will show the structure later.

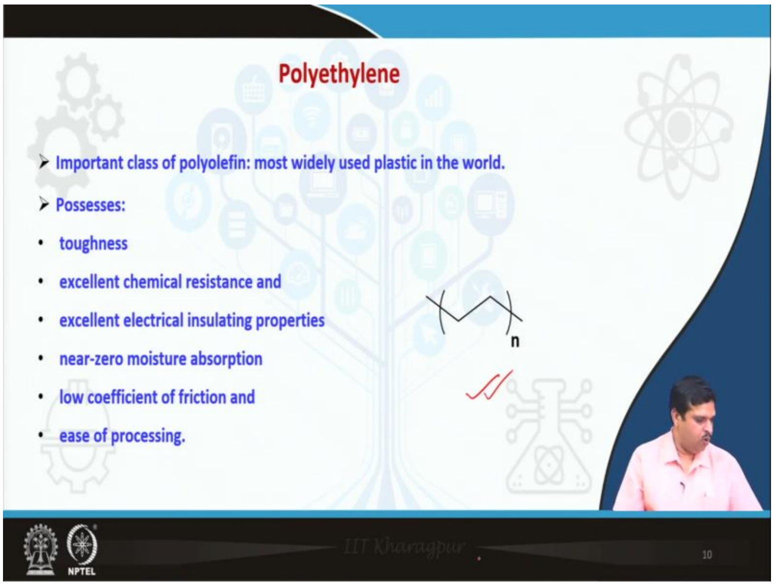
As I told that beauty of the polymers is that even though the same composition but depending on the structure, the chemical structure, the properties varies a lot and this can be advantageous to develop a different polymers of the same composition but with different properties and for different applications obviously.

As example, you see like for polyethylene, this is high density polyethylene. Normally, this polythene is four types, HDPE, one is the low density polyethylene LDPE, only the linear load density polyethylene and one is the ultra high molecular weight polyethylene. So, here, the name suggests, the high density polyethylene is basically is looks like this one. That means the there is no branch in the polymer skeleton of the polyethylene.

And LDPE is like that. So, there will be lot of branching, lot of branching like that. And in LLDPE is basically that you have a mentioned and you have a small branching. So, you see the name LDPE and LLDPE. So, this is the low density, this is the linear load density that means the reduce amount of the branching or the controlled amount of branching. And this is the property is quite different from this to this, from this to this one and also synthetic protocols are also different.

That is why it is very important to understand that what kind of polymers I need to use for a particular applications and what kind of chemical structure or engineering I have to do and for that what polymeration protocol I have to follow. And this one, the ultra high molecular weight. So, you can regard is like very high kind of things. So, let us discuss in more detail about the high-density and low-density polyethylene.

(Refer Slide Time: 13:56)

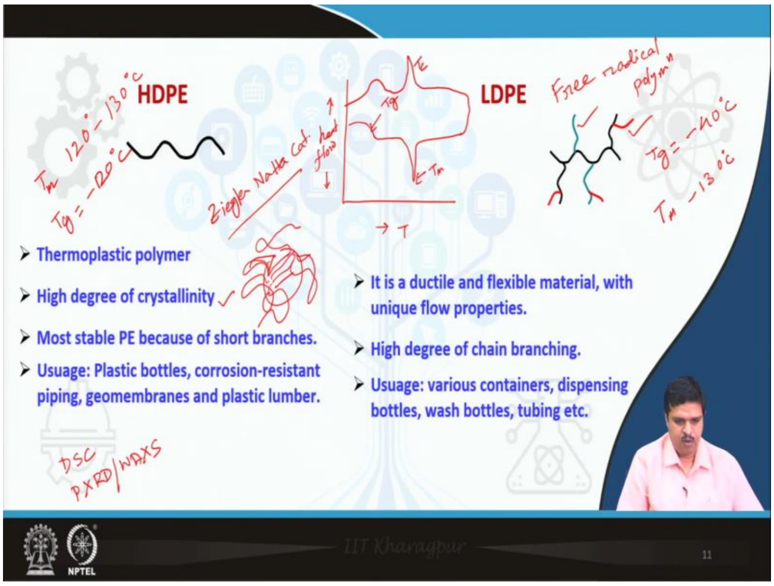


Polyethylene

- Important class of polyolefin: most widely used plastic in the world.
- Possesses:
  - toughness
  - excellent chemical resistance and
  - excellent electrical insulating properties
  - near-zero moisture absorption
  - low coefficient of friction and
  - ease of processing.

So, as I told that this is one of the heavily used polymers and the reason, the properties I already explained. This I have just pointed out for your reference. Excellent chemical resistance, excellent electrical insulating properties, ease of processing, toughness and obviously the properties are tunable, that is the mechanical strength, stiffness, toughness are tunable by changing the chemical structure and the polymerization protocol.

(Refer Slide Time: 14:38)



HDPE

- Thermoplastic polymer
- High degree of crystallinity ✓
- Most stable PE because of short branches.
- Usuage: Plastic bottles, corrosion-resistant piping, geomembranes and plastic lumber.

LDPE

- It is a ductile and flexible material, with unique flow properties.
- High degree of chain branching.
- Usuage: various containers, dispensing bottles, wash bottles, tubing etc.

So, let us discuss in more depth. So, I already in the last class explained the classification of the polymers depending on the properties. The rubbery state, thermoplastic state, glassy state, all those things. So, here you see that high-density polyethylene, the chemical structure, the cartoon diagram is like that as I showed in the last slide.

So, this is basically the branching in the high polyethylene is almost zero or very less. That means obviously as discussed in the last classes that the crystallinity that is the more orderness, the crystalline domains will be higher. And that is why this kind of polymers that is the high density polyethylene will be more steep and will show the thermoplastic nature.

The use is this kind of HDPE are kind of more steep more hard and used is household materials. And this one is generally prepared from the Ziegler Natta catalyst, although I will discuss in the following classes about in more depth about the Ziegler Natta catalyst, the polymeration and the unit properties of this kind of catalyst before coming to the metallocene catalyst.

So, Ziegler Natta catalyst, to make the high density polythene you generally follow the Ziegler Natta catalyst. And here you will see that is these are more crystalline nature. So, if you will get a sharp T M that is the melting point in, if you do the experiment, that is the DSC, Differential Scanning Calorimetry.

As discussed in the last classes that crystallinity you can measure by in a two common ways, one is the DSC and one is the WAXS or powder XRD. P X R D or WAXS. So, in DSC you will get the DSC is like that. So, this is basically Y axis is the heat flow, and x axis is the temperature.

So, you will get with temperature like that. So, this is the Tg and this is the melting temperature. Here x o up and endo down. And if you cool it then you will get like this one, like this one. So, that that is basically the crystallization temperature. So, when you are increasing the temperature, you will get the melting temperature and then when you cool down that is you will get the crystallization temperature.

Although, this polymer crystallinity is depends on the thermal history, as I very briefly discuss in the last classes that the polymer properties is little different than the small molecules. So, what happens that if suppose you are synthesizing the polymer and if you normally we isolate by precipitation, so if you do the phase separation in very rapid then the crystalline temperature can show the amorphous nature.

And then if you hit it, what is called we and generally called annealing, just below the melting temperature and keep it for some time and then you cool it, you can, then you can get the melting temperature if we perform the DSC experiment. So, you have to be careful for that one. So, for HDPE you will get the nice crystallization temperature if you do the DSC.

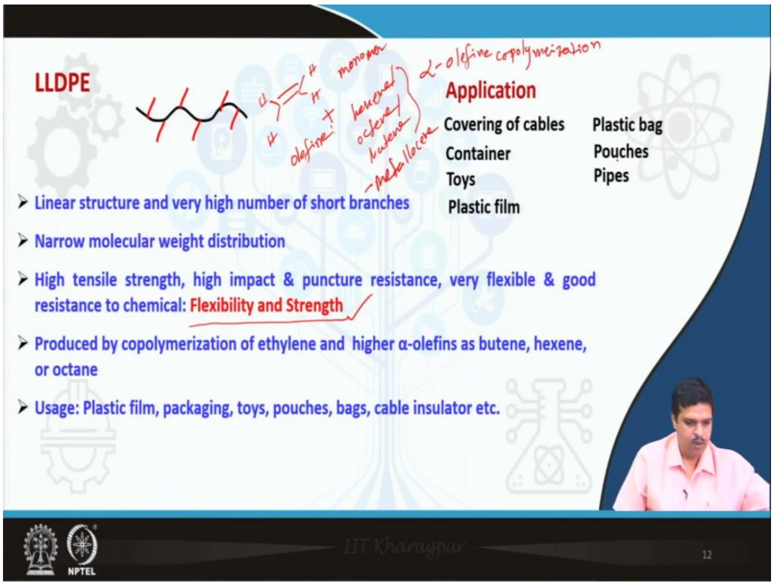
So, here you will see for Tm, you will get 120 degree to 130 degree centigrade for HDPE. For and where the Tg you will get the minus 120 degree centigrade. Let us come to the LDPE, what is the difference. So, as I told that for a LDPE, you will get, you will have the in the polyethylene you have a quite branching. So, these are the branchings. The branching is quite long, relatively longer and number of branching will be quite good in number.

So, that what will happen that in this case, if you discuss like that this is. So, you remain like that one. So, but if it is, the branching is less, then you can get some crystalline domains. That is the origin of the crystallinity. But in this case, this kind of scenario is not possible and you will get the low-density polyethylene.

And here you will see that these polymers will be quite soft because the Tg is around minus 40 degree centigrade and Tm, melting point temperature, you will in many cases it may not be visible but if the chain, side chain is less then you can get the melting point temperature at around minus 130 degree centigrade, something like that. But again, I am telling that depends on the number of branching and the length of the branching.

So, this is about the, and obviously this low density polyethylene depends on the polymerization protocols, for this one you cannot make by the Ziegler Natta catalyst. So, here you have to we generally follow the free radical polymerization. Why? Reason is very obvious that we for free radical polymerization we do not have any control about the chain length and the branching. So, generally for free radical polymerization, we get the LDPE, and for for HDPE, we have to follow the different polymeration protocol. Fine.

(Refer Slide Time: 22:15)

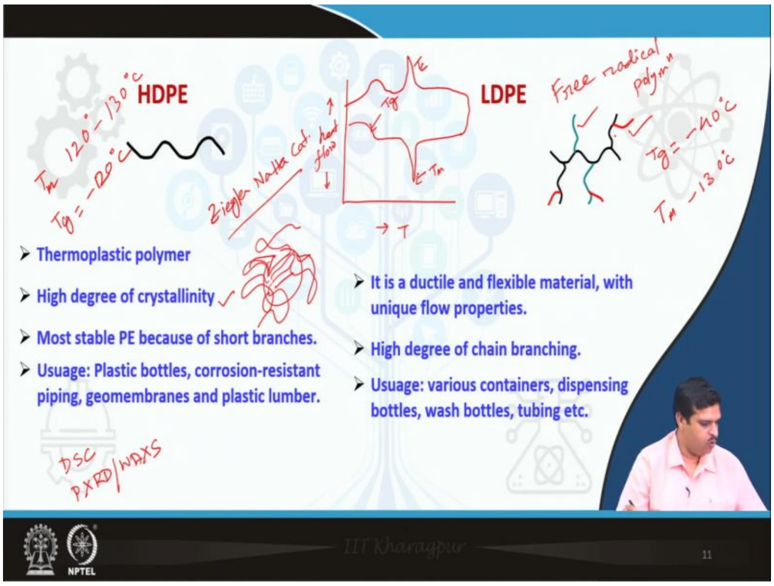


LLDPE

Application

Covering of cables
Container
Toys
Plastic film
Plastic bag
Pouches
Pipes

- Linear structure and very high number of short branches
- Narrow molecular weight distribution
- High tensile strength, high impact & puncture resistance, very flexible & good resistance to chemical: Flexibility and Strength
- Produced by copolymerization of ethylene and higher α-olefins as butene, hexene, or octane
- Usage: Plastic film, packaging, toys, pouches, bags, cable insulator etc.



- Thermoplastic polymer
- High degree of crystallinity ✓
- Most stable PE because of short branches.
- Usuage: Plastic bottles, corrosion-resistant piping, geomembranes and plastic lumber.
- It is a ductile and flexible material, with unique flow properties.
- High degree of chain branching.
- Usuage: various containers, dispensing bottles, wash bottles, tubing etc.

So, LLDPE is little different and it is more kind of a chemical structure is more fine in nature. Here you will see, you will have a long polymer chain and you will have a shorter small chain like is not like this one, this one. So, shorter and this is quite small compared to your main skeletal chain. And obviously, the synthesis protocol is different than the others.

Here we normally what we do? We use the ethylene that is the main monomer, that is the your main monomer and we used another olefin, as example hexane, octane or butene sometime and we do the co-polymerization, basically with any of this one. So, we sometimes we call this the alpha olefin copolymeration. So, this is actually in this case what I do we use only one monomer that is the ethylene but in this LLDPE we use the ethylene and also another monomer hexane or hexane olefin or butane. These are the alpha olefin.

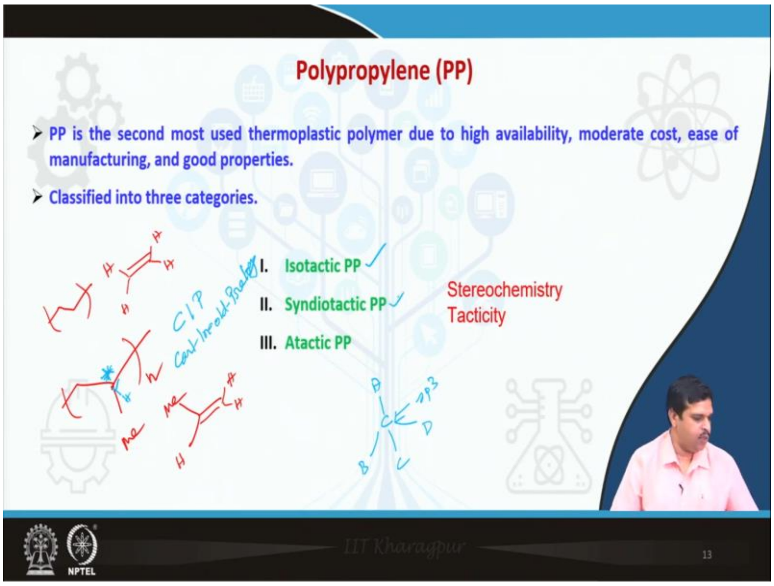
So, this depending upon the ratio, how much you are giving or feeding the number of the small branches will be varied. So, this is you see is a very well-defined LDPE, low density which is basically linear low density polyethylene. And this kind of polymerization protocol, it is quite recent, we use normally the metallocene based catalyst that is the what which actually our prime focus to study in more depth what is the how this kind of catalysts have been involved, what is the mechanism, what is the chemical structure, what is the structure property and what is the development.

So, mainly the coming see (())(25:15) actually developed this kind of metallocene based catalyst which we will discuss from the next week classes in more depth. So, the beauty is that or the most advantageous properties that you are basically maintaining the flexibility and strength in one polymer. Why I am telling?

Because in this case here you see this is quite steep due to the crystalline nature and this one is more flexible. But here you will see that this is, basically I am putting these two properties in a single system and that is why it is more flexible, the flexibility and strength are on the same materials.

And that is why you will see that this kind of polymers are heavily used nowadays, mainly in packaging industry where you need the flexible material as well as you needed quite strong material. As example for food packaging pouches, bag, cable insulator where you need a flexibility and also at the same time need strength. So, applications is huge. Among these three polymers, the LLDPE use of the demand of the LLDPE is quite high nowadays in different domains as I showed in the last pie chart.

(Refer Slide Time: 26:59)



Polypropylene (PP)

- PP is the second most used thermoplastic polymer due to high availability, moderate cost, ease of manufacturing, and good properties.
- Classified into three categories.

I. Isotactic PP ✓
II. Syndiotactic PP ✓
III. Atactic PP

Stereochemistry
Tacticity

Now, the next polymers very interesting, we will discuss in quite depth about the chemical structure is the polypropylene. So, the name suggests that this is ethylene and, so this is the polypropylene. So, obviously, this is for this one monomer is ethylene and this one monomer is propylene. So, that is the difference.

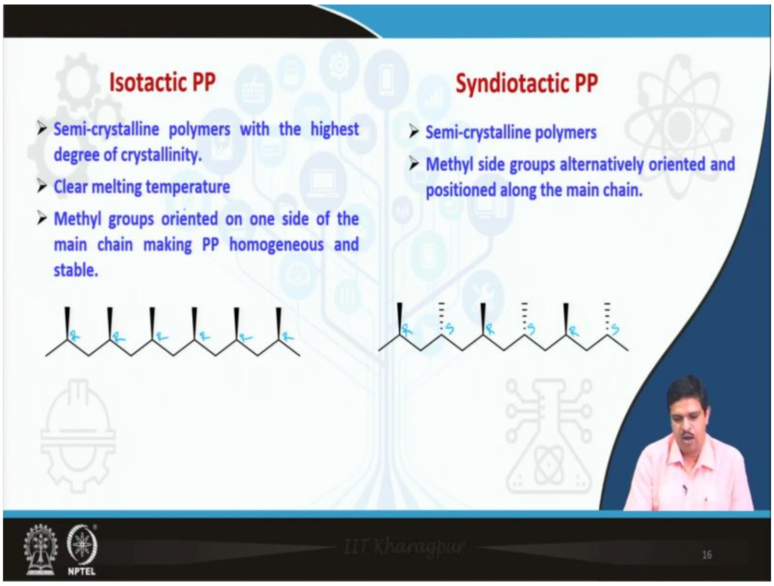
Now, very interesting that if you see that this one, this one here, if you recall the requirement of the chirality in organic molecules for SP3 carbon center as example like let us say for this kind of system where this carbon is SP3. So, a b c d that is the four arms, that is the four substituents on the carbon should be different. I am not going to the symmetry operation, I am very qualitatively I am discussion.

So, here, now here you will see that I have methyl here, I have hydrogen here and in this case the number of carbon atoms will be different. They are number of carbon atoms in this case could be different. Now, if you recall the CIP, the rule for assigning the absolute chirality, I am sure you know that what is the CIP in organic chemistry you have studied and if you forget, no problem. This is basically to assign the stereochemistry center on a chiral carbon.

So, this is called in gold, sorry, in gold prelog priorities rule. So, here according to that one, you see that this one is methyl, this is hydride, hydrogen and this one will be carbon or different length and they are all carbon will be different lengths. That means this center will be sterogenic, stereocenter.

So, that is why a different type of different configurations are possible for the polypropylene. So, one is the isotactic in where all the cases, all the centers that particular methyl group will be, this carbon will be at the same configuration according to the CIP, R or S. So, everywhere may be R R R R and this may be alternate R S R S like that.

(Refer Slide Time: 30:52)



Isotactic PP

- Semi-crystalline polymers with the highest degree of crystallinity.
- Clear melting temperature
- Methyl groups oriented on one side of the main chain making PP homogeneous and stable.

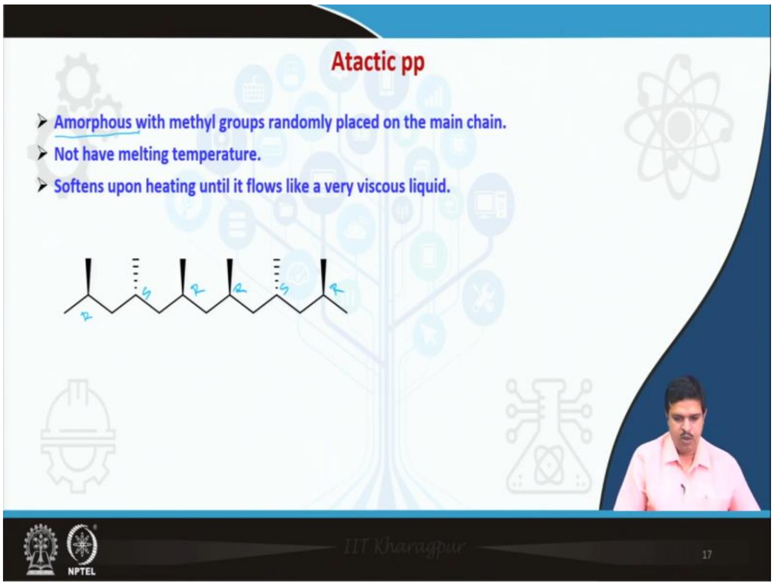
Syndiotactic PP

- Semi-crystalline polymers
- Methyl side groups alternatively oriented and positioned along the main chain.

Like this one you will see, here the methyl are arranged on a particular direction. So, this let us say if it is R then this is R, this is R, this is R, this is R, this is R, according to the CIP priority rules. Now, if it is R, then one scenario may come, this may be R, this is S, this is R, this is S, this is R, this is S. So, here methyl is up and here the adjacent one, the methylene up up but in the adjacent carbon you will see that methyl is down. So, in this case, this is called isotactic polypropylene and in this case syndotactic propylene. That means there is an alternate arrangement of the methyl groups.

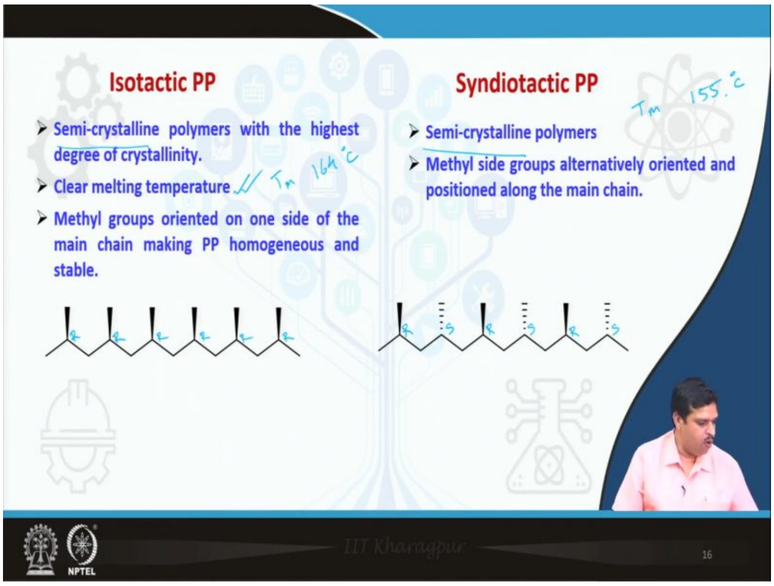
Now, another possibilities is that there is no order. In both cases there is a order R R R R R R and in this case R S R S R S means there is a some pattern, some order.

(Refer Slide Time: 32:08)



Atactic pp

- Amorphous with methyl groups randomly placed on the main chain.
- Not have melting temperature.
- Softens upon heating until it flows like a very viscous liquid.



Isotactic PP

- Semi-crystalline polymers with the highest degree of crystallinity.
- Clear melting temperature. // Tm 164 °c
- Methyl groups oriented on one side of the main chain making PP homogeneous and stable.

Syndiotactic PP

Tm 155 °c

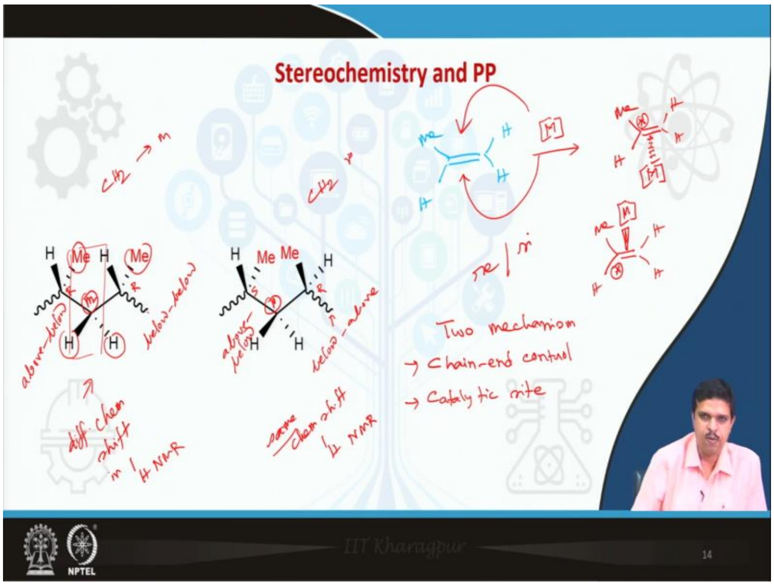
- Semi-crystalline polymers
- Methyl side groups alternatively oriented and positioned along the main chain.

But in this another situation, there is a possibility that here R here S R R S R. So, there is no pattern at all, there is no order at all. So, this kind of polypropylene is called the attractic polypropylene. Both are polypropylene but here it is you see this is attractic and here it is called syndotactic where the alternate arrangement of the methyl groups and here you will see that isotactic where the methyl groups are oriented in one side of the main chain.

So, polypropylene that is why it is very interesting that it can give three kind of polymers based on the orientation of the methyl groups in the polymer skeleton. And the most beauty is that that in this kind of structural variation you will get the different properties. As example, you will see the as these are ordered so isotactic and syndotactic are semi crystalline in nature, here and here.

So, that means you can get the clear melting temperature, if you do the differential scanning calorimetry, DSC measurement. As example. So, this is the Tm is around 160 degree centigrade and for syndotactic the Tm is around 150 degree centigrade. But for attactic you will not get any a crystalline tempered Tm is a amorphous material, this one, because there is no order in the polymer skeletal. So, this is very interesting and.

(Refer Slide Time: 34:16)



Stereochemistry and PP

Two mechanism

→ Chain-end control

→ Catalytic site

Now, let us try to understand in more depth why this stereo genic center comes. Now, you have to understand that this is a prochiral molecule m and H that is the propene. Now, if you recall that if the reactant or let us say the metal center. So, two ways it can react, one is the let us it is reacting with metal center. Suppose, I am doing let us say Ziegler Natta catalyst polymerization.

Now, it can react in two ways. Let us assume that this propane, the plane of the propane is the plane of my computer screen. Now, so this one, so this is the plane. So, my methyl, my metal center can react with this way or can react with this way. So, that means through the below of the plane and above the plane. That means it can attract is a Re face or Si phase, both ways.

And depending on the attack, you will get two different, so, if let us draw this one, how it is happening. So, here you will see that this is my methyl, this is height, this one. So, this can, if it is down. And another possibility is like that. So, eventually, you will get this one and this one, a different configuration depending on the how this metal center is attacking, whether it is from the below the plane or the above the plane. And depending on that this, one you can get the different stereocenters.

Although in later classes we will discuss the two main mechanism how you can control the stereocenter of the polymers that is the chain-end control mechanism and one is the catalytic site mechanism. So, that chain-end control that is the CEC and catalytic site mechanism that will discuss later in more depth.

Now, let us try to understand this is a part of the polypropylene polymer. Let us say is just a small part. So, this is the polymer chain representing the spring kind like the bond. Now, here you will see, this is my methyl, this is my hydrogen. Now, here this hydrogen and this methyl, you will see both are below, both are below and here this hydrogen and this methyl you see that is the below the plane, in this case both are below the plane. So, I am writing below and below and here you will see the above and below.

And in this case you see that this hydrogen and this methyl are here, the below and above and this hydrogen and this methyl here again you will see that this is above and below. So, you will see below above, above below, below below, above below. That means these two hydrogens will experience different chemical shift, different chemical shift in proton element spectroscopy.

But in this case, it will experience the same here in proton NMR. Why I am discussing? That this microstructure what is called tacticity, this you can detect by proton NMR spectra, high resoluation proton NMR spectra like 400 megahertz or 500 megahertz is good enough to detect this kind of tacticity in the polymer backbone. So, here you will see that in case of here. So, this is R, this is also R, and this R you will see this is if is S, this is R.

So, in this scenario, you will get the different chemical shift where you have a same configuration on the two carbons, adjacent carbon center. And in this case you will have a different configuration in the two adjacent carbon center. So, here you will see the same chemical shift.

Now, there is an another one here. So, this one you will see, if you this methyl and this methyl below the plane. So, if I draw the plane diagonally like this one, so, this one and this one is basically the mirror image. So, that is why this is we sometimes called the meso m and this is we called the racemic R.

So, this is the m, this is the R where the meso where in this kind of scenario this CH2, we call meso, m and this CH2, we call the r. So, if you go in this convention then what will be here? So, this one the r r. So, this one will be m, this one will be m, this one will be m like that. And this one, again this one will be r, this one will be r, this one will be r. So, for syndotactic, this CH2 will be m r r r r r and for isotactic this will be m m m.

Now, what about the atactic, can you guess? So, this is r s. So, this one, this is r s. So, can you guess what will be there for this one? Sure. So, this will be like you see from the isotactic. So, this will be m. So, what will be this one? This will be r. what will be this one? Again r, because different arrangement of the methyl. So, here this one again r, here this one again r.

So, this is also another convention to represent the tacticity in the polypropylene, type polypropylene or similar type of polymers. So, I will continue the tacticity on the, and the microstructure of the polymers where the monomer is prochiral in nature in the next class. Thank you very much.