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 31

Depolymerization of synthetic polymers - Role of organometallic and metallocene based catalysts

So welcome once again in today's class. So we will be continuing our discussion on Metallocene in polyolefin chemistry. Today's class will be little different from the rest of the classes. So far what we have learned, we have learned that the development of the Metallocene in polymerizations and we have seen that Metallocene is wonderful replacement of Ziegler Natta catalysts for its reactivity for its selectivity.

And also we have learned that how to make this homogeneous Metallocene based catalyst to a heterogeneous catalyst to make it industrially viable and to make it most cost effective. So, till date we have discussed or the use of the metallocene in bond making process that is the polymerization process, where we have seen that monomers can add to another monomer and making the polymers.

Today we will discuss the depolymerization that is the reverse and you may ask that why we are discussing this one in this class, because it is a… the title of this course is Metallocene based catalysts for polyolefin. It is important considering the time relevance and the environmental conscious and you will see at the end of the classes that how the Metallocene the same catalyst can be used for polymerization as well as depolymerization.

I will try to give a the concept and try to understand by a simple by simple mechanism and simple concept or organometallic chemistry and you will be really excited and I am very much sure to know that how the same catalyst can be used, but before starting, I want to mention that this the concept is old the organometallic chemistry of the transition metal complexes, but the use of these complexes for depolymerization that is new.

So, you will not find much information in the textbook for this one obviously, we will use the same unique reactions for organometallic chemistry that is a textbook knowledge, but the particular uses of these organometallic compounds for the polymerization you will not get in text book. So, we will use some very recent reviews and also some very recent articles published in high impact high impact journals.

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So, let us start our discussion. And here you will see that the concept will cover depolymerization and recyclability as I told that, we will be will learn here that how the organometallic catalysts and methylation catalysts are used for depolymerizations but before that, we have to understand why do we need it? What is the importance? We are making then we are breaking so, why it is needed?

So, this is nothing but called the recyclability of the polymers and why it is needed. We will discuss, we will discuss very shortly the methodologies of depolarization which are available at this moment, although we will not discuss in more depth and we will just try to give a concept of circular economy and sustainable chemistry this is very much important as I told very much important at this time, while the age in that age we are living now.

Because you know that we have the lifestyle has been improved a lot. And that is why we need we need a high energy demand. And for that high energy demand, we need wheels, we need new materials. And for that, we have to use the circular economy for that the same material is used and then again, we can use the same material for same purpose or maybe different purpose.

But it has the important purpose or which have the impact on the society as example, if I give example like lithium ion batteries now, we are very much used the lithium ion batteries because that is one of the best batteries and even in all the cases 90 percent Electric gadgets you will see that we are using the lithium ion batteries. Now, if we use excess amount of

lithium, then after few years all the lithiums will be completed I mean all will be used up because the source of the lithium (())(5:42) is limited.

So that is why we have to have the use the concept of the circular economy and the sustainable chemistry to continue an important technology or important material. So that concept I try to give you and here we will be discussing the depolymerization so it will be more concentrated on that one that strategy and mechanism of depolymerization and then we will discuss that how this organometallic and metallization based catalysts can be used in this very fascinating but very important chemistry to solve this a million dollar problem.

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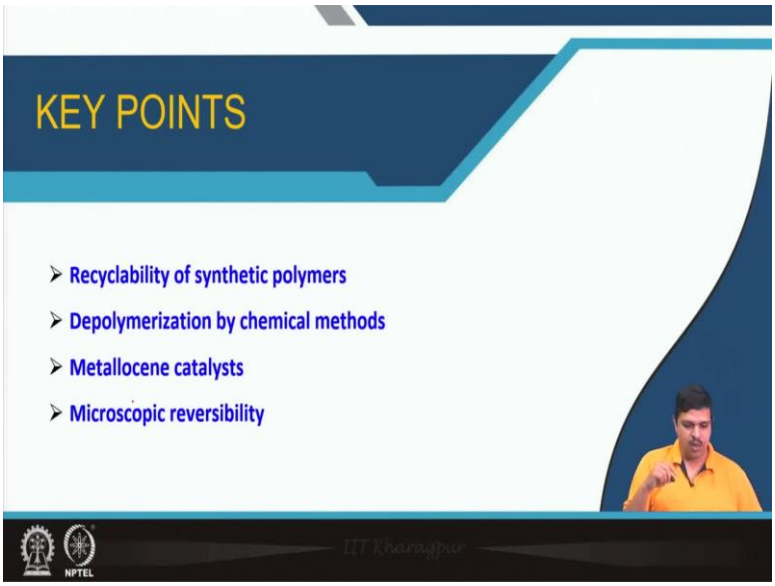

So, these are the key words recyclability we know, the Metallocene, microscopic reversibility we will know and depolymerization by chemical method that is our main interest. We will know in these classes.

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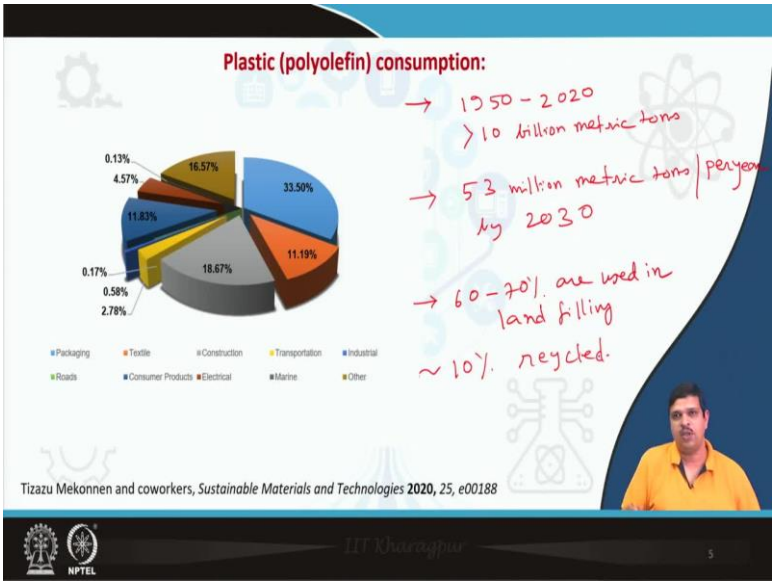

Now, as I told that why we need depolymerization? Fine in the in the very beginning of the class, I showed the same diagram and we were very excited to know that how this polyolefin or which is commonly called plastic, how it has a big market and how the big scale it is produced, because it is so popular you cannot in the beginning I told that if you just think a single day without any polymer I am sure challenge you cannot because the polymers is now so much involved in our daily life we cannot really avoid the polymer.

Now, this is good we understand the polymer. Now, it has also been effect anything if you use in excess in a long run there will be effect, so the bad effect. So I discuss all things but here probably if you can recall that the plastic is in 1950 to 2020 it is almost around or more than 10 billion metric tons have been synthesized manufactured. So, you can understand how much polymers have been manufactured.

If this trend continues then it is assumed that around 53 million metric tons will be synthesized per year by 2030 which is really really big value. Now, we the so much polymers are synthesized, now, what will happen after using it. If there will be at some time that everywhere there will be used or unused polymers polymeric materials, but what to do with this one. And exactly this alarming situation is already started.

Because if we that all the used Polymeric Materials hardly 60 to 70 percent are used in landfilling and only 10 percent that is the maximum is hardly used in for recycling purpose. So, 10 percent is recycled and you will see more most of the polymers are actually are used for landfilling, that is really bad for the environment because this is not a natural materials.

These are synthetic materials and we have already seen that the polymers like polyethylene polyurethane all these polymers have really strong bonds so, it is really does not decompose or does not degrade spontaneously. So, that is a really a big threat to our society to art or to human or to living systems.

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So, one you see here that excess use of plastics. You have you will see that this is a photograph from the sea. Now it is so common even in even in India you will see that so, many plastic materials are in the sea and it is assumed that if it is continuous that whole sea will be converted to a bean for the plastics if you are not careful on that one and you know that this that micro-plastics after partial decompositions and these micro plastics are now entered in food chain.

The living systems in the sea, they consume this micro-plastics and then it enter in the first and that fish we consume and you will see that we this is a really big threat to our to the life or human life, and different types of very complicated disease like cancers are now very common for this kind of bad effect. So, it is a really big big threat.

So, it is very easily understandable from here that excess use of plastics has caused excessive pollution in the earth. So, one of the main reason of the pollution is the excessive use of plastic apart from the emission of the toxic gas in other things, and as I told that landfill is around only 60 to 70 sorry the landfill most of the polymers are used for landfill that is 60 to 70 percent.

And only 10 percent is used for resource generation, resource generation means either it is used for used again to polymer or to other materials like fuels and to solve partially the energy demand. So, if we can convert to monomer or if you can convert or to the feedstock for variable compounds or fuels means like smaller alkanes, hexane, butane hepten that is really now high demand to make the valuable compounds or to use as a feedstock from the used polymers.

So, that will try to learn in this class that how it is possible because this is very important not only for the industry, it is also important for the citizen who are using these materials, the polymeric materials both and also definitely the Government encourages and have imposed various rules to protect the earth from the pollution caused by excessive use of the plastics that you might ensure you are out of that one.

So, you cannot really use now plastic bags as we used to do like the last 3 or 4 or 5 years. So, our government has also declared various rules about this against the excessive use of the plastics.

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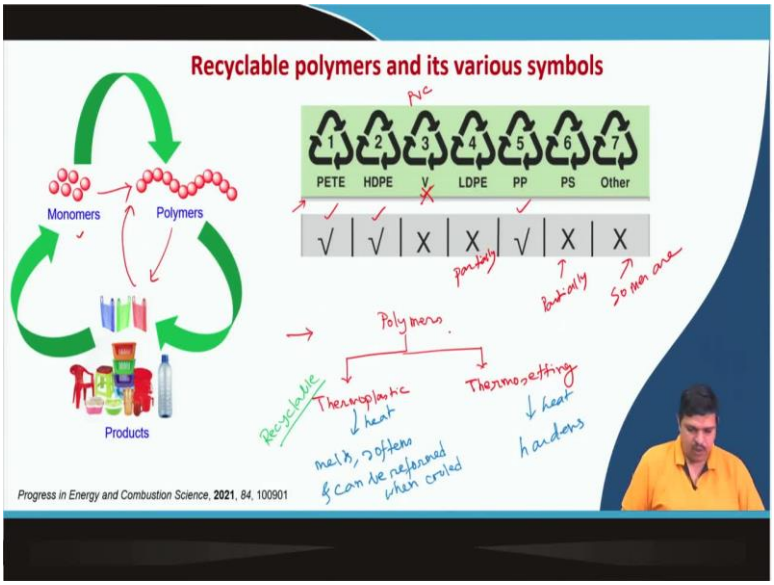

So, definitely we are the scientists we are academicians or industry peoples. We will be now with this class, we have also responsibility to develop or to think about that how these plastics can be reused to a valuable materials and to stop the excess use of the plastics as I told that you cannot avoid the polymers because polymers is so much kind of related to our life, but we should know to use in a restricted way.

So, here you will see that as I told that these are the ideal cases that the polymers like this is the monomers and from the monomers we are getting the polymers. And then we are from the polymers we are getting the valuable compounds sorry the valuable materials or the useful materials and from the polymers we are getting the material.

And then if we recover then again if we recycle to polymers or to other materials, valuable materials or to the same products like here as I showed the picture like tub, chairs all the domestic materials, if we can do that that the way we can actually reduce the use of the plastic to some extent. And I am sure that if you if any plastic material is nearby to you, I am sure you have seen some kind of these kinds of pictures like that one.

This is a triangle that 2 arrow 3 arrows in a triangle shape we should all know that what is the meaning of that one. This is a mandatory for any plastic materials the manufacture this the mandatory to show these symbols on the product. I have already taken some pictures. The materials which are available in my office, you will see that this is like it is written LDPE the 4 here you will see the cycles 3 arrows in a triangle it is written as 5 and below it is written PE here or the same thing you see that 5 and PP.

And here you see this is triangle shape 3 arrows and it is the return 7 and in the below it is others. And here also use PP what is the meaning of that one we should really understand. And accordingly we have to think for recycling these materials that is very very important as I told at this time, at this time, we are living. So, let us understand these symbols.

So, here it is, you will see that is it is called PETE we all know that this is basically polyethylene allied polymers and you will see this this can be recycled without any problem. So, this is recyclable. And you will see this is HDPE here, we put 3 arrows in a triangle shape and it is written 2 and 2 means this is HDPE.

So, many cases, products HDPE can be written or cannot be written if it is 2, you have to assume that this is actually high density polyethylene or related polymers. So, this also you see this can be recyclable. So, PETE can be that is the recyclable and the symbol is for PETE 1 and 3 triangles, 3 arrows in the triangle shape. V stand for the PVC or vinyl rated polymers. So, this is PVC or vinyl related or allied polymers.

So, here you will see that this is not recyclable, this is difficult to recycle. So, most of the PVC materials is actually not recycled, it is can be used for landfilling, but you cannot again use it and give a shape and this is you see the LDPE, LDPE the code is 4, LDPE is 4 this can be recycled, but it is actually partially polypropylene you will see here most of the materials like plastic materials.

You will see the PP these are all you will see that sort of PP almost all the plastic the packaging materials are used, which are hard, like sanitizer bottle or the Dettol bottles, all these kind of bottles are actually made up polypropylene. So here also you will see this can be recycled. 6 is for polystyrene. This is also again, it is not fully recycled but can be done partially can be recycled, fine this tick means you can reform.

Can take the same material like if it is a bottle and you can make again the similar kind of material like bottle or similar kinds of materials. So, that is the full recyclable and the last one that is the code you see is 7 that is the others, other means, these may be the acrylic, plastics polycarbonates, nylons and others like which are not included in this PETE, HDPE, PVC LDPE PP or other things.

So, this is depending again as I told that some are recyclable but not all the polymers can be recycled and these kind of symbols are mandatory for any manufacturer to put in their

respective polymeric plastic materials you can if you can check with you if you have any kind of plastic materials nearby you can check it this is very important to know.

Now I am sure if I give one symbol you can be able to tell that what kind of polymer it is and whether it will be recycled or not you can check yourself. So, another point I want to mention that here we know the 2 type of in the very beginning we have discussed that you can divide the polymers into 2 categories based on the response of on heating, one is the thermoplastic and one is the thermo setting I am sure that you can recall we have discussed already in our very earlier classes.

So thermo plastics actually what happens if you heat it, it melts and softens and can be reformed and thus it can be reformed when cooled and that is why it is recycclable, but thermosetting what happens this actually if you heat it, it hardens. So, you can imagine that this cannot be recycled however, it is by mechanical way you can make it powder and then you can use it for filling purpose.

So, any type of thermoplastic polymers you can recycle without any problem. So, these are you have you should know that what kind of material it is and that the way you can decide that whether it will be recyclable or not fine.

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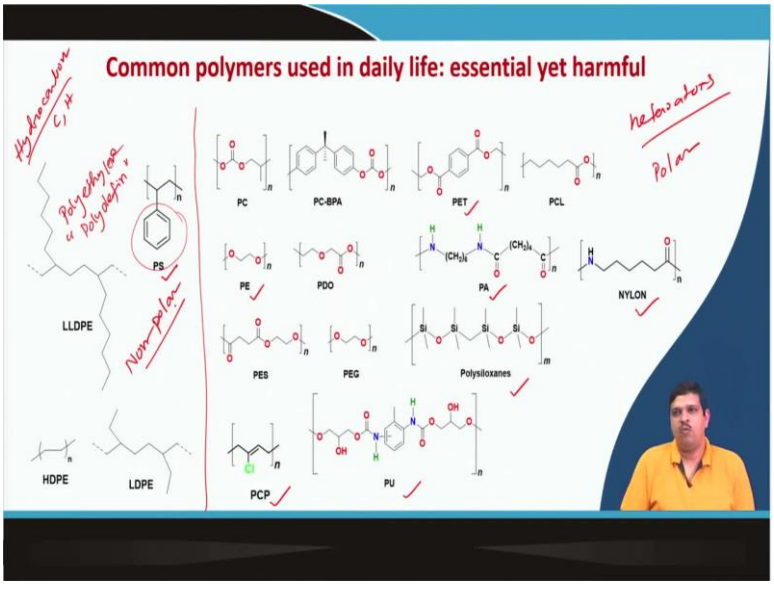

So, these are the common polymers used in daily life these are already discussed in our previous classes. These you will see that this is the basic structure of polycarbonate, this is the p polyethylene oxide this is you will see that this is basically the PCP this is the

polyethylene this is the nylon 6 6 nylon heavily used in textiles, these are the polysiloxanes this is the PET. So, you will see that this is a polyamide.

So, this is kind of similar to the nylon polynylon nylon structure and very special cases you will see that this is the polystyrene this is all the polyethylene different form of polyethylene or you can more generic name the polyolefin. So, the basic difference between these 2 categories if I divide here you can understand that here the left side or like these are all hydrocarbon polymers polymer that means there is no hitter atom all C C and H carbon and hydrogen and the polymer skeleton has the saturated bonds.

The polystyrene forget this benzene part, the skeleton I am telling that is the saturated carbon that is the 4 valency and all are the poly alkyne category. Now, in this case the right hand side you will see that the polymers with hetero atoms so you see that is why the bonds are polar and here it is nonpolar. So, we will discuss after some time after a few slides that what is the impact of this polar and nonpolar nature.

And what how difficult it is to break a polar bond and nonpolar bond having the polymers that we will discuss after a few slides, these are basically just to know to give idea that this many polymers will use in daily life and heavily used for domestic purpose.

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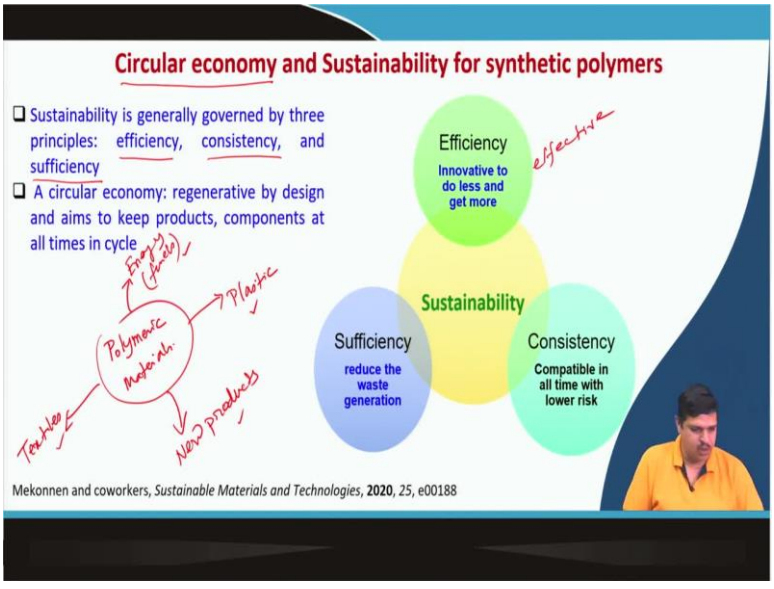

Now, this is very important, to understand now, the circular economy and sustainability. Circular economy and sustainability is a kind of a very similar concept and heavily related concept. So, as I told that, if you use one particular materials, which has a limited shorts, and after some time what will happen that that resource will be stopped, the resource will be

exhausted and then you do not have the resource to make the important materials and then your product will not be very cost effective.

So, we have to think a sustainable scenario to make the polymer or the material cost effective, so, that it can be made without any much problem and that is the concept is the circular economy that means it is cycle cycle should be should not be stopped. So, the 3 concepts of the sustainability is the efficiency, consistency and the sufficiency it is very important. The efficiency means, it has to be very efficient method without investing much money in the process should be viable and it should not be highly cost effective.

And consistency, so, that means the method should be very effective method this should be very effective. And the consistency that again it is very much related to the efficiency that it should be the process should be compatible in all time and with lower risk. So, this is very much like a similar as efficiency. And the third point is the sufficiency that means, it is basically involves to reduce the waste generation.

So, there is enough resource are available for the next batch of process. So, these 3 concepts are very much important to make a process viable and sustainable following a circular economy. So, the circular economy actually is regenerative by design and aims to keep products components at all times in a cycle.

So, most of the now industries follows the circular economy to make the process cheap, cost effective and so that the common people can buy the material otherwise it will be so expensive, nobody can buy it. And that is why the polymers used polymers used polymeric materials is high time to convert these used polymeric materials after use either to new products or to new plastic materials or the textile these I am telling the used polymeric materials or to use in the energy domain, the energy demand like to make the quiz.

So, these are the 4 domains are now peoples or scientists or industry peoples are jumping to contribute to this Domains by converting the used volumetric polymeric materials for 2 purpose to solve the demand of these valuable in these valuable domains and also to reduce the plastic pollution. So, this you see that how exciting it is and how important it is.

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So, now these are you see these are some cyclic methodology I will not go in very detail, but you just try to understand how it can be done. So, you see that this is the refinery and from the refinery we make the monomers like ethylene let us because we are in this course will be more like involved in polyethylene poly alkene, so ethylene or hexane for LLDP so, just consider like most of the monomers as basically from the refinery industries, are made from the refinery industries.

So, these are the monomers and from the monomers we make the polymers by different methods we have already discussed and then after processing we make the plastic products and this plastic product goes to the consumer and then what do we do you will see the different materials after using it and we throw it and this one, now goes to the post-consumer waste. Now, time has come to recycle this one to again to useful materials, and how to do it.

So, after collection and sorting to different type of materials as example like as I told that PETE or HDPE the symbols according to that one, this one the PETE, HDPE LDPE PP. So, according to that one you can sort it out and after sortin if it is a thermoplastic the route will be different, if it is other polymeric material. So, route will be different, and also how we are recycling whether we will be using the for making the similar plastic products or will be one to solve the problem of the oil energy or whether we will be making the monomers again.

So, that different recycling methods will be different strategy fine. So, here you will see that this one like here you will see this is from the… after sorting you if you do the mechanical recycling you will come here the plastic products. And then you will make again so, mostly

like as we discussed already like thermoplastic polymers, you can do it very easily. Now, another one, you see that (())(33:44) this is the primary recycling.

So, that means, you can again make the polymers and then you make the plastic products and then go to the consumer. Now, this one the gray one that is the more challenging and more demanding, challenging and more demanding that is you make big bonds. In other cases, we are not breaking the bonds, here you are breaking the bonds and you are making the monomer and then from the monomer you are then again you can make the polymers then plastic products and then cycle goes on.

And also from here, you can also use the other materials, valuable materials, like fuels as a byproducts or other new compounds. So, these are very much important and this can be done by chemical recycling. That means by breaking the bonds. So, these 2 are same. So, this is an this is the blue one and the gray one this can be done by the chemical recycling, this is very much challenging and very much demanding and it is also the concept twice is really exciting.

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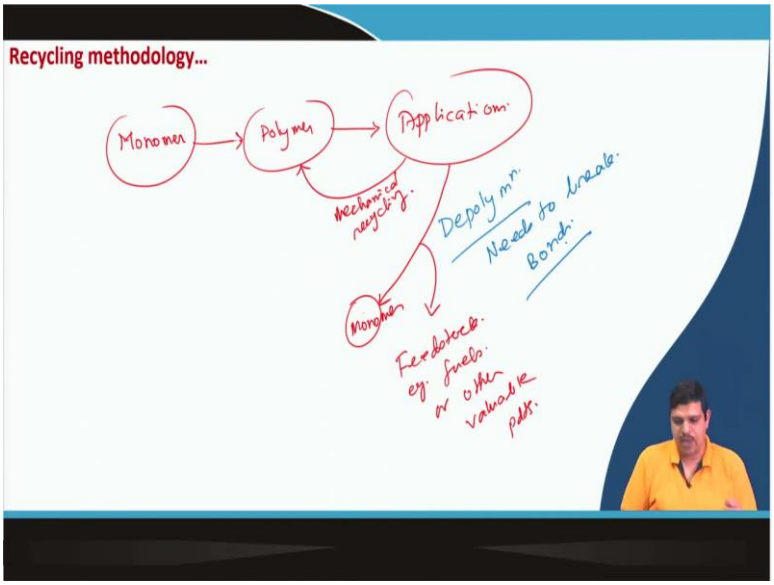

So if you see this one the cycle I just want to qualitatively I want to show once more that if it is when this is your monomer and from you are making the polymer. And then you are doing the blending and forming. So, you are the… the applications that you are making all these materials. Now, what you can do that you can do the now from here you can do 3 ways one is this one that is the primary recycling. So, this is called the primary by mechanical recycling.

And from here if you can make the monomers or the feedstock as example, the fuels or other valuable products. So, that for that you need that depolymerization. In other cases, you see that these are not depolymerization, these are basically mechanical recycling here, we need the depolymerization and that is I told that it is the challenging part that you need to needs to break the bond and how it can be done, this can be done by strategic design of the recycling methodology or strategy, that we will be discussing.

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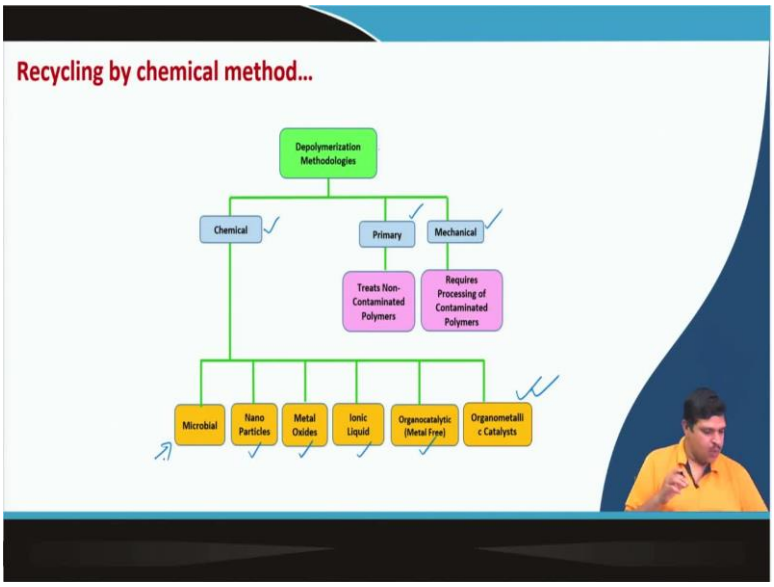

So, you will see here that if this is the… what are the depolymerization methodologies? So, you can do by chemical you can do by primary or you can do by mechanical. So, these are the… primary and mechanical is basically there is no involvement of the bond breaking process, these are chemical methods.

We will be most interesting by following the strategy of the organometallic catalysts and here you will see that this is the most demanding and most effective method conceptualize and on the basis of the concept this is really exciting and others are like you will see that by ionic liquid by metal oxide by nanoparticles by organocatalytic those are also available, but those are not really very effective process.

And some of the polymers also is the biodegradable and various micro bacteria actually are responsible to degrade although these are not very effective methods but those you cannot also ignore those are also good methods, but here we want to learn that how that organometallic catalysts which are used for the polymerase and can also be used for depolymerization by choosing the right strategy that will be our aim.

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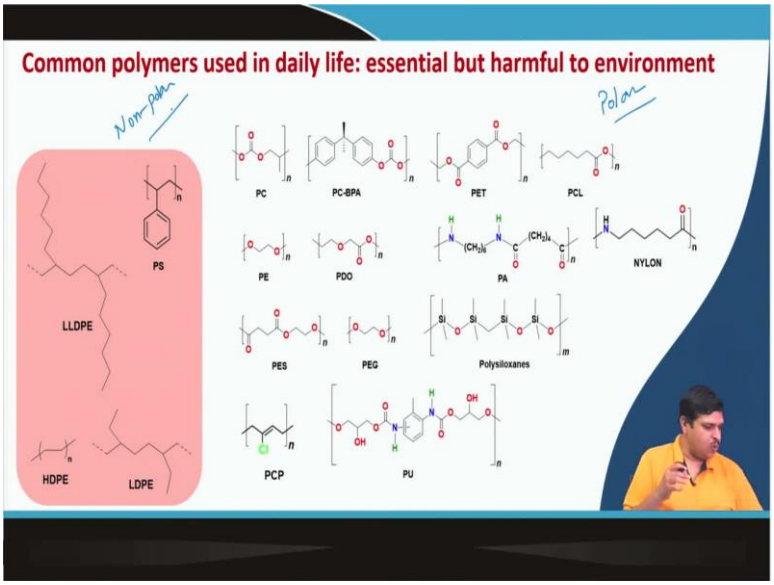

So, as I already discussed that what are the basic difference between these 2 category of polymers this is the nonpolar and this is the polar bonds. And in general, the non-polar bonds is very difficult to break the non-polar bonds, because it cannot really do any reactions with nucleophile or electrophile because these are nonpolar.

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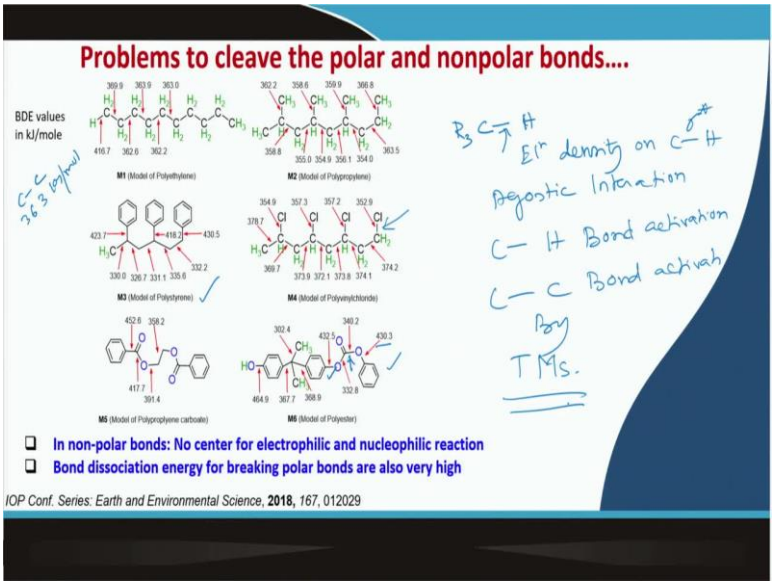

And bond strength is quite high if you use if you see this one, see for like polyethylene is a model unit of a polyethylene, the carbon carbon bond is you see here it is around 363 kilojoules per mole, so, use bond energy.

So, and for like for model propylene so it is very much similar around 360 kilojoules by more mole, this is like a polystyrene you will see that again very strong bond the CC is around CC bond is 332 kilojoules, per moles and like polyvinyl chloride, you will see that carbon chloride bond is around 353 kilo joules per mole.

So, you will see that those bonds are very strong very difficult to break the nonpolar bond because there is no center for electrophilic and nucleophilic attack. Similarly, the polar bonds as example for carbonates or polyester, these are also quite high energy that is like 430 kilojoules per mole then CO bond is around also for 32. This one is around 342 kilojoules per mole. So, this is quite high in energy however, if you design any reagent to attract nucleophilic or electrophilic way that can be clipped.

So, that is so, for that for that region that cleavage of the polar bond entity is easier than the nonpolar entity. So, you need a fine tuning of the catalysts or the breaking agent and you can react with the nonpolar bonds and you can break the bonds one will discuss these things like here, if we see that R3 CH bond we discussed in our previous classes that CH bond is a nonpolar bond and how you prove it.

You by organometallic way so, you have to populate the electron density on density on C H Sigma Star bond and how we can do it, do it this is called True agnostic interaction and agnostic interaction and this is called the CH bond activation. So, we have to follow the C H bond activation or CC bond activation by transition metal chemistry.

So that is why you need a very strategic way to break this non-polar carbon carbon or carbon hydrogen bonds in poly alkanes. And that is very challenging and very difficult to depolymerize these kinds of systems.

So, in in the next class, we will discuss very specifically about how to depolymerize, how to break the carbon carbon and carbon hydrogen bonds and what are the strategies by the organometallic catalysts with a special focus with the Metallocene based catalyst and to cleave the polyethylene or allied polymers and as we have already learned that this process is very much important to save our art and to save our environment and not only for that to make the polymerization process is viable and to maintain the circular economy.

Thank you and see you in the next class.