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

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

Lecture 01

A Brief Introduction to Polymers

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Hello, welcome to the NPTEL course, titled as Metallocene and Metal Carbene based Organometallic Compounds as Industrially Important Advanced Polyolefin Catalysts. I am Dr. Sanjib Kumar Patra, Associate Professor, Department of Chemistry, IIT Kharagpur.

As you see the course title, so the course will be on the discussion and the recent development of organometallic compounds with a special category that is metallocene and metal carbene which has basically change the manufacturing process of the sum of the polymers as example like polyolefin which is now routinely used in industrial manufacturing process.

And, I mean there is no doubt that in the last few decades the polymer materials have revolutionized our society and changed our daily life and definitely in our widely used in our technological applications and among these polymers, polyolefin is a special category. So, in this course we will discuss how this polyolefin are being synthesized in industry by the modern catalysts like metallocene and metal carbene.

So, this course is an interdisciplinary and you see that we will have to have a knowledge of ergonometric chemistry that is the inorganic and organic chemistry. We would have knowledge about the catalysts, we should have a knowledge about the polymer chemistry. So, it is a perfect course for UG, PG and PhD students from the multidisciplinary subjects. As well as this course will be very much beneficial to the industry who are working or in associated with manufacturing the polymers.

So, let us start with the lecture 1. So, as I told that these catalysts are very special, you will see this is called the metallocene based metallocene, this one we will discuss in very depth after few class, but this I just want to show the basic structure of the catalyst which will be discussing in the future classes through a systematic approach. And this is called the metal carbene.

So, here you will see that this is the carbene bonds, this one the metal carbene like your ethylene you have seen ch two double bond ch two. Here the metal double bond carbon and here is a category of the sandwich compounds. We will discuss in depth in the following classes.

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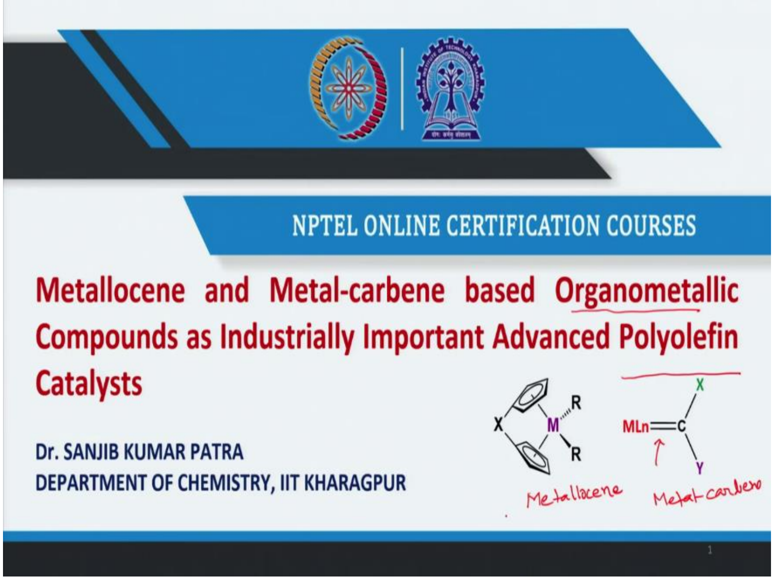

So, first what, I will try to introduce the polymer chemistry. I know that some of you may be not from the polymer background. So, there is no problem. If you take this course, even if you are not in a polymer background there will be no problem to understand this subject. So, what I do in the next 30 minutes show, I will try to introduce the polymers in a very brief and in a very lucid way.

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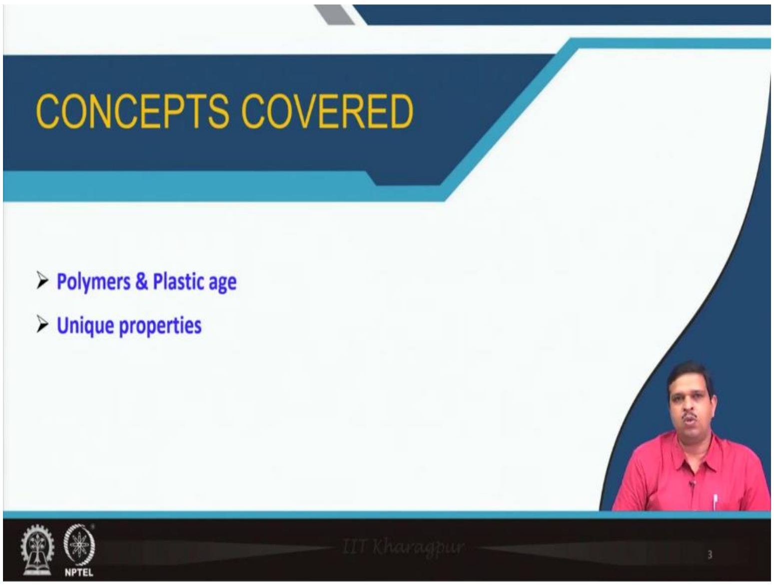

So, what is polymer that will come to your mind. So, we will cover the concept in the first class. We will discuss that what is the polymers? What are the unique properties of the polymers and what the properties and can be advantageous for a specific applications. That we will try to understand and we also try to understand how we can design or monomer polymer, with the aim of application that is basically associated with its properties.

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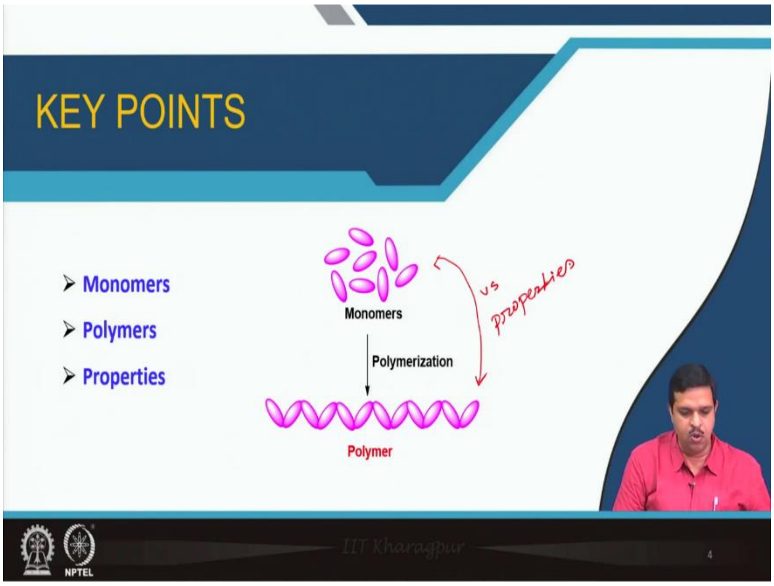

So, let us start. So, what is polymer? So, polymer is basically you see the different repeating units are connected with covalently bond. As an example, you see, this is a monomer. See this one, oval shaped species, this is a monomer and now if it is connected by covalent bond, you see that is a long chain of molecule. So, this is the polymer. So, you are basically what we are doing, we are connecting the small molecules by a covalent bond. This is the polymer.

So, we will try to discuss that what are the basic chemical structure of the polymer looks like and what are the properties associated the polymer and how different the properties it is. So, properties, we will discuss what the difference in properties between these monomeric molecules and polymeric molecules because before going to the subject we should understand the basic properties of the materials. Otherwise, we will not or we cannot develop the field or we cannot develop that what actually we want. So, for that a good knowledge of the structured property relationship is very important.

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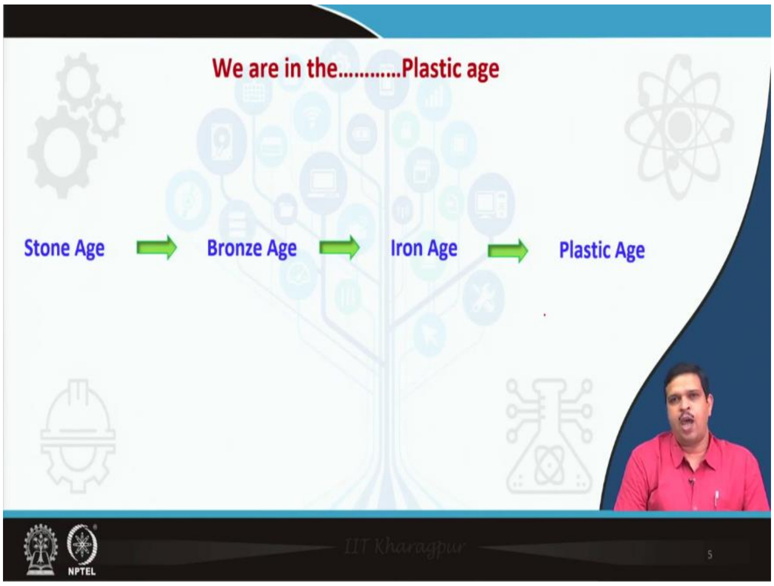

So, as you know, I in the beginning I said that we are in a plastic age. In our childhood we have learned about the Stone Age. Stone Age, bronze age and iron age and you see that how our age has been transferred according to the need or according to the development. So, now there is no doubt that we are in a plastic age because you see, even you check your bag, check your belongings. I am 100 percent sure that you are, I am sure you have multiple gadgets or equipment's or items at this moment with you.

As an example, you are writing with a pen. So, the basic material of the pen is polymer. The mobile, the electronic gadgets we are using, the outside component is the polymer. So, we are in a plastic age. We can we cannot avoid the uses of the plastics. And this has actually changed our daily lifestyle and definitely our technological aspects.

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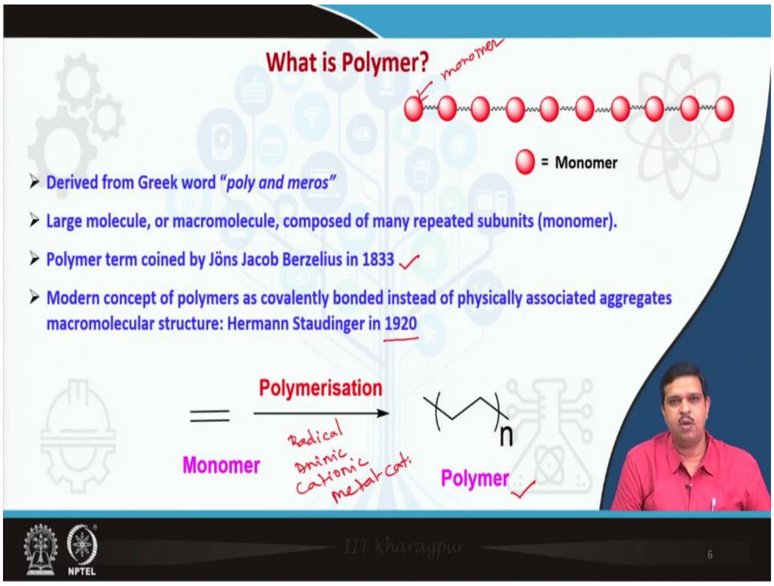

So, we are in a polymer world. So, what is the polymer as already I discussed that the polymer actually looks like this one, if you think this is a monomer and the whole molecules is the long chain is actually polymers. The monomers are connected with covalent bond. This is the polymers. So, first this… what is the meaning of the polymer? Polymer actually derived from the two Greek words, that is the poly and marrows. Polys means mini and marrows means the repeating units. That is the name came from the polymer and this is the polymer the first reported in 1833. The first synthesized polymers was in 1833.

However, the polymer field was not popular until 1920 because it was very difficult to realize that what kind of material it is because as I told the properties are very much different from the monomeric molecules. So, it was difficult to characterize, it was difficult to understand the basic properties as we understand the small molecules.

So, until 1920 polymer field was a kind of a suppressed field, you can say. And it is the great person, the Hermann Staudinger in 1920, he proposed the hypothesis that the polymers is basically a large macromolecules which are formed by through a covalent bond. So, this was first 1920 and he actually warded awarded the Nobel Prize for giving a direction to the new field.

And you know that in the last one or two years, there is a celebration in worldwide to celebrate the field of the polymers which actually, as I told that we are actually in the plastic age. So, in the last two years worldwide we celebrated it through a conference, celebrated through a special publication in high reputed journals. So, it was almost 100 years that polymer field has been greatly developed.

So, as an example this is one of the very popular polymer which has industry important, highly important industrially manufactured polymers. That is the polyethylene and what is the monomer? This is just ethylene monomer. Actually, this is the first prepared polymer in 1833. However, that time it was not very much understandable due to the lack of characterization, a lack of understanding.

So, this polymerisation we will discuss the following classes, how this polymer can be from the monomer. So, there is different procedures for polymerisations, radical polymerisations. I am sure some of you already know who have taken the basic polymer course. There are anionic polymerisation, there are cationic polymerisation and also there are metal catalysed polymerisations.

And obviously the radical polymerisations, nowadays the well-defined radical polymerisation that is called control radical polymerisation are also available. As example like, nitrox mediated radical polymerisations, ATRP polymerisation, RAFT polymerisation. That we will discuss in the following classes when I will discuss the basic polymerisation protocol.

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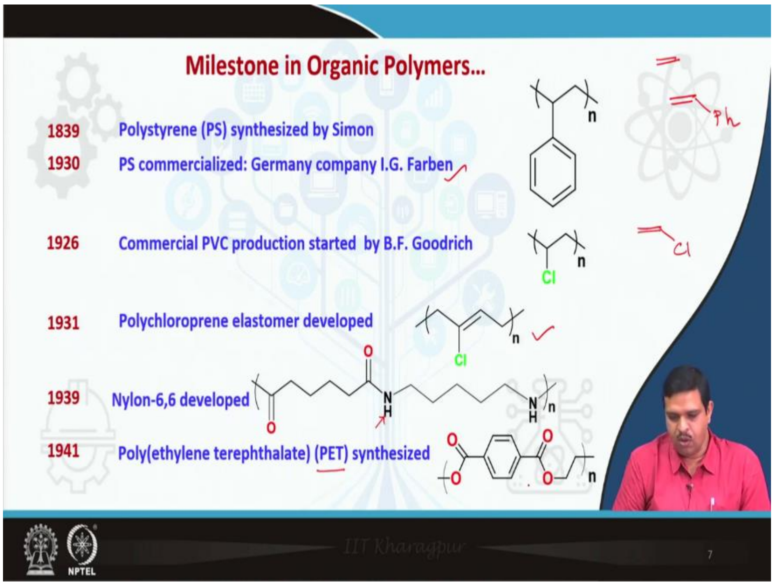

So, now we know that what are the polymers. In the next two slides or so I will discuss or I will show what are the polymers we see in our daily life. As example, you see the polystyrene I am sure many of you know that the polystyrene we use regularly in our daily life and this is the basic structure. So, what is the starting material? This is the actually the monomer that is so here, this is my ethylene and if you substitute one proton by phenyl, substitute one proton by phenyl this is the styrene.

So, this is the polystyrene which was first reported in 1839 and around after almost 100 years it was commercialized by German company, IG Farben in around 1930. In 1926 in a very similar time the another polymer was commercialized that is the polyvinyl, PVC. That is very popular, you know nowadays the floor tiles, the pipes are made of the PVC, very popular. So, this is again is you see the what is the starting material or the monomer? This is the monomer, that chloro substituted ethylene.

Then the polychloroprene, this is also heavily used in our daily life. We all know the nylon-6 this is used in textile industry. So, this you see that this is prepared by condensation polymerisation which we will discuss in the following classes when we will discuss the basic polymerisation protocol. So, nylon-6 6 developed and is heavily used in a textile industry and it is quite crystalline and that is why it makes fine materials.

And you know that this NH is there. So, it basically forms hydrogen bonding and make a like a hydrogen bonded cross linking materials which makes it more crystalline domains. We will discuss this later. This PET all you use in our daily life, although we are now government has forcing to ban this kind of materials due to the environmental issue but these are heavily used in daily life that is the polyethylene terephthalate, that is the PET. The chemical structure of the PET molecules, the PET polymers is like this one. You will see this is basically polycarbonate type of materials.

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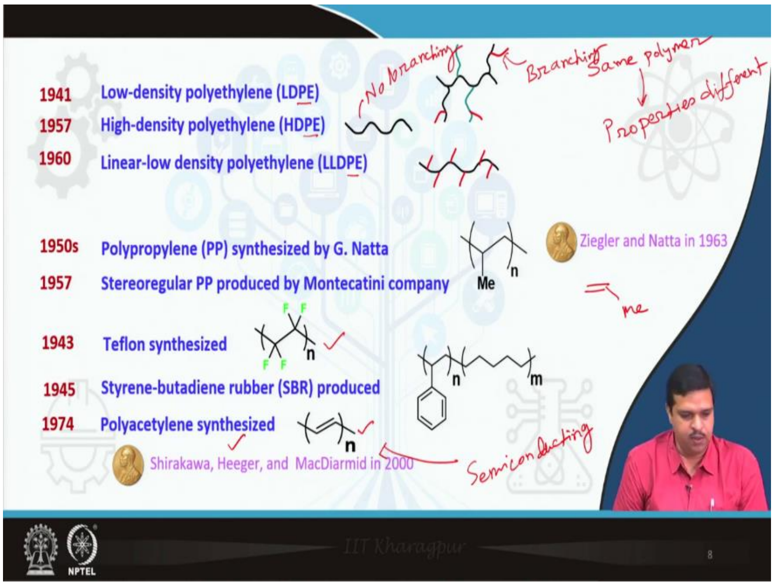

So, in following you see this in 1941 after that there was a revolution in the polymer industry. The first polyethylene polymers which was been commercialized that I already discussed that is the polyethylene. Now depending on the chemical structure that is the microstructure, the polyethylene properties can also be varied. That is really a very beautiful aspect in the polymer chemistry.

So, what I am trying to tell that you have the same polymer. You have the same polymer but the properties are different. So, that is not possible at all from the small molecules. So, you have a same polymer but the properties are different. So, here you will see what I am trying to tell the same polymer.

Here you see all are in the ethylene category, polyethylene category that is the low density polyethylene, high density polyethylene, linear low density polyethylene. All are basically polyethylene polymer but we have done some engineering of the polymer. Why we have done? To tune its properties for different applications. Like you will see this high density polyethylene that means you will see that you try to see the microstructure between the high density and low density polyethylene.

Here there is a branching these are called the branching and here is no branching. So, in high density polyethylene there is no side branching and low density polyethylene there is a quite good amount of side branching. So, depending on this microstructure the properties are different.

So, like high density polyethylene is quite crystalline whether low density polyethylene is not that much crystalline materials. When I will discuss later in more depth about the crystallinity of the polymers as you know that this is also another aspect in the polymer chemistry. We all know that small molecules crystallizes very easily and this is quite obvious. But the polymer, some of the polymers are also may be semi-crystallin in nature. As we have seen for the small molecules or the crystallinity always be much less than the small molecules but it is possible.

There is another category was developed that is the LDPE that is the linear low-density polyethylene. Here linear load density means that you see the low-density polyethylene and here linear low-density polyethylene. Here linear means that there is not that branch. So, that means compared to the LDPE, the LLDPE is more linear in nature and there will be small branching.

So, what we are doing? We are basically making little flexible and also we are trying to combine the two properties, the brittle due to the crystalline nature and also trying to make more flexible. So, we are want to induce two properties in the LLDPE, so this is the recent development in the polyethylene which is LLDPE. This LLDPE polymers we will discuss this is one of the major aspect of using the modern catalyst in the polyene industry.

Similarly, the second most popular polyolefin polymer is the polypropylene. Here you will see that instead of the ethylene, this monomer is used. So, is basically the methyl substituted ethylene that is the propylene. So, again this is the Nobel prize or award winning discovery, Ziegler and Natta where both awarded Nobel Prize in 1963 who develop independently the polymerisation of the polypropylene. The polypropylene again is very interesting, polymer in nature we will discuss in the following classes.

We all know about Teflon. Teflon again is basically the fluorine substituted ethylene monomer. So, when you polymerize you will get the fluorine substituted polyethylene. So, this is PTFE, PTFE is a very robust very hydrophobic material used in daily household including in our kitchen wires.

Then, this is again you will see that Styrene-butadiene is also heavily used and which have industrial applications and the most recent one comparative to other polymers is the polyacetylene. So, you see that most of the polymers are basically electrically insulating. So, polymers are regarded as that non-conducting materials but this is the first category of the polymers who were discovered by Shirakawa, Heeger and MacDiarmid and for that they were awarded the Nobel Prize in 2000 that is one of the remarkable and pioneering discovery in polymer chemistry.

That polymers are not all the polymers are basically the electrically insulating. Some of the polymers if you design that polymer also can conduct the electricity. So, these are actually semiconducting in nature. So, that is one of the very fascinating properties of the polymers. Now you know that we are now solar cell is one of the very hot research field because to get the renewal energy from the nature.

So, this kind of material that is the semiconducting materials are being used to develop the photovoltaic devices which actually can replace the silicon based semiconductor devices and if we can use this kind of materials that photovoltaic devices will be flexible. So, that is quite hot research field nowadays.

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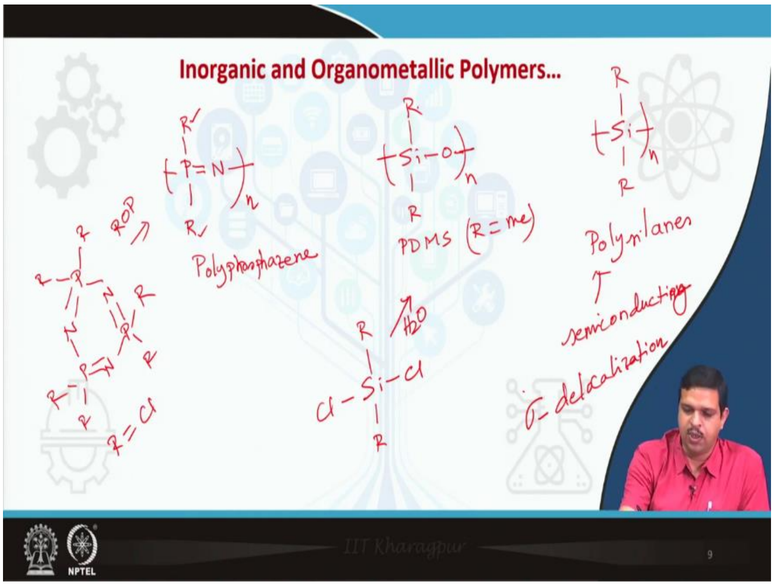

So, now we have a very brief introduction about the organic polymers which are used in our daily life. Not all the organic polymers, there are a lot of popular inorganic and organometallic polymers which are also used in daily life, not only for the bulk uses or also for some smart applications in material science and also in the biomedical applications.

From inorganic we cannot really ignore one polymer which is very famous and very popular and well developed. This is the category, this is called the polyacetylene. So, here you will see the aging, this is representing the p double bond n and poly is the polymer and phosphor means you have this phosphor, p is there and you can tune these properties by substituting the different R group.

Similarly, another polymer which is also very much important and have a wide application this is, I am sure all you know about this one the poly-dimethyl selection. Can you tell me what are the applications of poly-dimethyl solution. Especially it has a lot of application in biomedical applications. So, this is we call the PDMS when the r is equal to methyl. This is quite flexible, it is a electromatic materials. So, you can stretch it at room temperature, TG is quite low.

So, you know that this is very easily prepared by the silocotion monomer. As example, from like if you have dye alkyl di-chlorosilane and if you just do the teeth with water and do the poly condensation reactions, you will get the PDMS polymers. And for this one, if you take this kind of monomer, R is equal to generally cl chloride and you do a ring opening polymerisations, we will discuss later about the ring opening polymerisation then you will get this kind of polymers.

So, this is basically due to the strain of the ring it opens and gives the linear polymers. Similarly, another category of inorganic polymer is the saline. So, saline is also another interesting category. This is called the polycelain, this is interestingly… this is also semiconducting material. And as we know that generally the pi-delocalized materials are good for conducting the electricity but here a beautiful properties is observed that is called the sigma pi-delocalization.

So, these are the common inorganic polymers which are heavily used for sophisticated or smart application not for bulk applications. Polyphosphogene, poly di-methyls hydroxine, polycelains. As I told that you can easily change this R groups to tune the properties like glass transition temperature, the solubility, the processability. So, this is in your hand what you can, how you can tune the physical properties.

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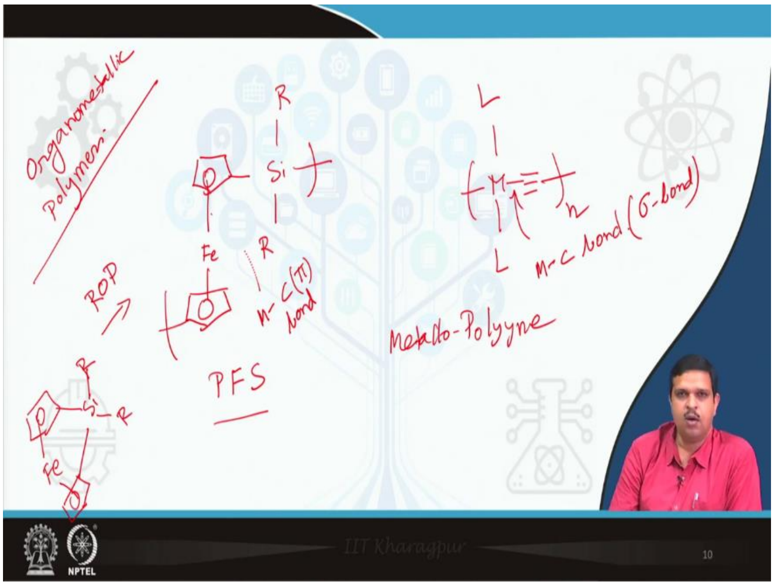

So, again I just give some organometallic polymers. As example, this is again very well-developed. So, this is called the PFS, this is called the PFS, the Polyferrocenes polymers. This is the PFS polymers, this is truly organometallic, this is truly organometallic polymers. So, we can synthesize it by reopening polymerisation again using this kind of monomers following anionic polymerisations or metal catalysed body polymerisation or thermal ring opening polymerisation.

Another category of very popular organometallic polymer is like that is this category. So, this is called the metal of poly ion. So, you will see that you have a metal carbene bond and here also you will see that metal carbene bond. So, here basically metal carbene Pi Bond and here metal carbon sigma bond. That is the different but these are kind of very quite well developed organometallic polymers which are quite new in the sense. Not very old as like a polyalkenes or polyolepine or other organic polymer. These are the emerging areas in polymer chemistry.

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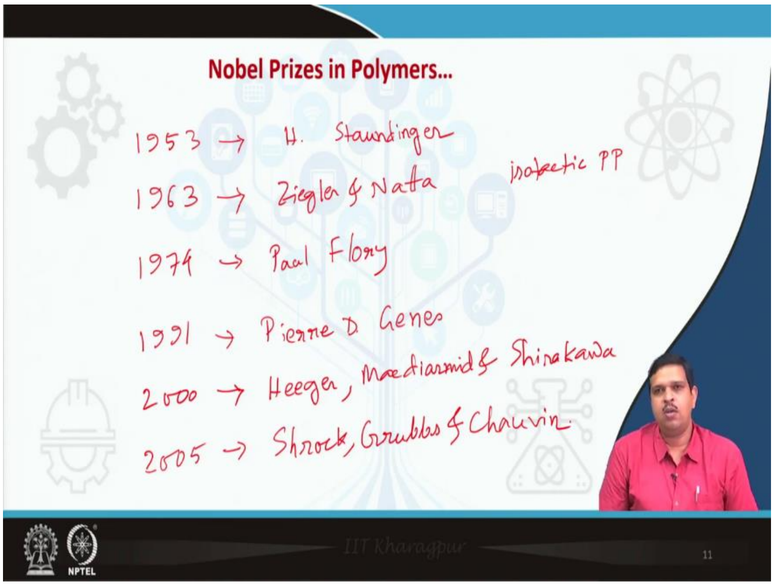

So, what I just wanted to give the flavour that these polymers has actually have a lot of applications not only for bulk uses also for the sophisticated applications in materials and biomedical aspects. In the next two minutes or so, I will just try to give a kind of a general knowledge in the polymers and which will excite you to study these subjects. So, do you have any idea that how many Nobel prizes have been awarded in the polymer chemistry? You will be very excited to know it.

Let us do the list. In 1953, the first Nobel Prize in the polymer chemistry that is by H. Staundinger who actually proposed the polymer macromolecular hypothesis. Then in 1963 all you know, any idea who got the Nobel Prize? Zigler and Natta who actually showed the polymerisation or discovered the polymerisation by that the Zigler Natta catalyst which is basically TICL for AL83, the aluminium alkyl and titanium chloride. So, this the isotactic or stereo specific. We will discuss what is the isotactic, isotactic polypropylene synthesis.

Then 1974, the Paul Flory, he proposes the random coil organization of the polymers. Then in 1991 Pierre De Genis, he worked extensively on the polymer physics. Then 2000, I already told that the trio that is Heeger, Macdiarmd and Shirakawa got the Nobel Prize for the discovery of the semiconducting organic polymers. And in 2005, Shrock, Grubbs and Chauvin he got the Nobel Prize for the metathesis polymerisations. So, you will see that how the polymerisation field was appreciated by avoiding the Nobel Prize.

So, thank you very much. In the next class we will further understand that what are the basic unique properties of the polymers and what are the advantages properties for the polymers compared to the small molecule or small molecular systems and then we try to understand the structured property relationship which we can be advantageous for the applications. Thank you very much.