Principles of Polymer Synthesis
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Lecture - 01
Historical Development of Polymer Science

Welcome everyone to this first class of NPTEL course Principles of Polymer Synthesis. In this particular course I am going to cover as the title suggests the basic principles of the synthesis of polymers. So, lot of chemistry aspects will be covered, and of course considering the constraints of the course for example, 20 hours certain special applications also will be covered. And so, most of the important aspects will be discussed as far as the principles of the synthesis are concerned; the way I have structured this course is like this.

In this first class I am going to give you an idea about the historical development of polymer science, how it came about, everything just did not appear out of blue. So, it took decades of honest a force from scores of scientists in order to establish what we now know as polymer chemistry and what we now take for granted as the structures of polymers.

So, basically the main focus of this particular course will be on the structure property relationship. What are the structures and what are the kinds of properties that could be generated from these kinds of structures, the kind of predictions that we could make out of them. And not only that; as the title again as the title of the course suggests it is how do you synthesize this polymers? The general principles of some of the most important polymerization processes will be discussed.

So, we will now start with the first class the topic of this class is historical development of polymer science.

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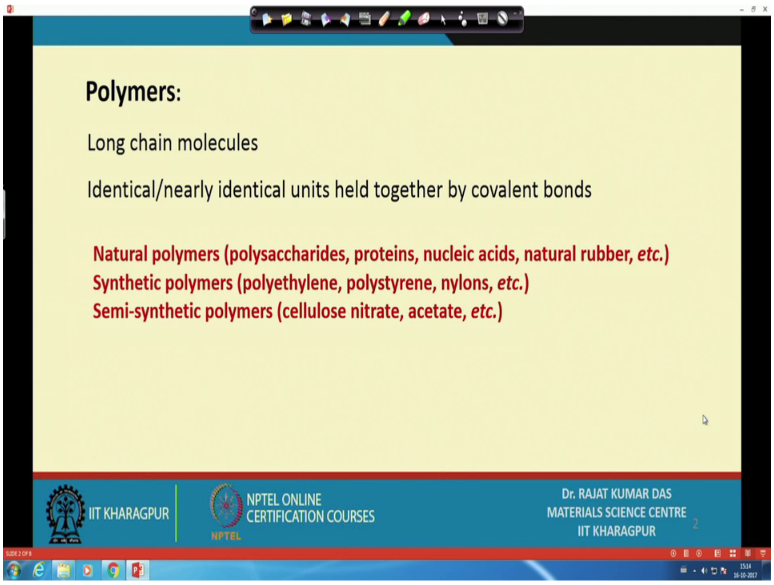

Polymers:

Long chain molecules

Identical/nearly identical units held together by covalent bonds

Natural polymers (polysaccharides, proteins, nucleic acids, natural rubber, *etc.*)
Synthetic polymers (polyethylene, polystyrene, nylons, *etc.*)
Semi-synthetic polymers (cellulose nitrate, acetate, *etc.*)

So, what are polymers these are long chain molecules and identical or nearly identical you needs held together like covalent bonds. So, basically we have many units hundreds of units or may be thousands of units, which are termed as monomers as you know now these are termed as monomers and these are all connected through covalent bonds. For traditional polymer materials, there are materials which are supra molecular polymers where all these units are connected through you know supra molecular associations reversible bonds or pie pie stacking interactions you could have hydrogen bonding interactions so on and so forth which can be broken and reformed reversibly.

We are not in general concerned with those kinds of polymers, more traditional polymers covalently bound, monomer units, strung together to form polymers. Those are the polymers we are going to discuss. So, this is the general definition that I have actually framed here identical or nearly identical units that are held together by covalent bonds.

Now, here I have actually classified the polymers based on their sources, like you know we could have natural polymers which could be based on say polysaccharides lot of sugar units, covalently bound, they could be based on natural polymers they could be proteins, based on amino acids or they could be nucleic acid natural rubber so on and so forth or based on the source we could prepare the polymers in a completely synthetic you know in the laboratory we can make polymers, which are not natural synthetic polymers it could be polyethylene polystyrene nylons etcetera.

Some of this you probably already know as far as the names of these polymers are concerned. Or it could be semi synthetic polymers, like natural polymers we modify them with different groups functional groups say for example, cellulose nitrate acetate etcetera. Now by no means this is the only way to classify polymers. There are different ways to classify polymers to which we will come slowly, but the reason I am talking about polymers to start with I mean I have not yet talking about historical development, I have started with polymers themselves some examples of them, this is just to illustrate what are the recent things that we talk about in polymers, means what we know about polymers.

And then, we will try to impress upon in the fact that some of these things which we know all now as very simple things like the covalent bonds and all between small mono molecule units which you have come to accept as the facts where not very easy to establish even 100 years back we will come to that slowly.

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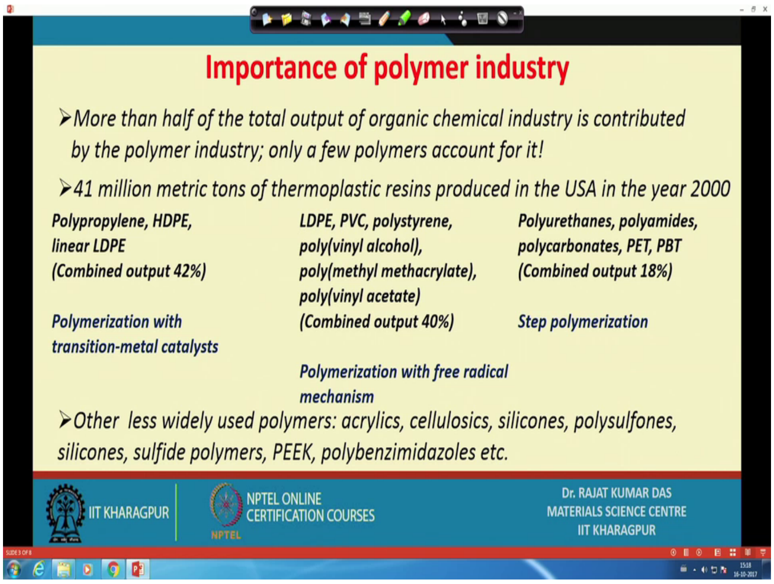

Importance of polymer industry

- *More than half of the total output of organic chemical industry is contributed by the polymer industry; only a few polymers account for it!*
- *41 million metric tons of thermoplastic resins produced in the USA in the year 2000*

Polypropylene, HDPE, linear LDPE (Combined output 42%)

Polymerization with transition-metal catalysts

LDPE, PVC, polystyrene, poly(vinyl alcohol), poly(methyl methacrylate), poly(vinyl acetate) (Combined output 40%)

Polymerization with free radical mechanism

Polyurethanes, polyamides, polycarbonates, PET, PBT (Combined output 18%)

Step polymerization

- *Other less widely used polymers: acrylics, cellulosics, silicones, polysulfones, silicones, sulfide polymers, PEEK, polybenzimidazoles etc.*

Now, this light is about the importance of polymer industry as the title suggest for this particular slide. Now more than half of the total output of organic chemical industry, if you look at organic chemistry the industry, it is contributed by the polymer industry more than half of the total output only a few polymers actually account for this.

So you can understand; what are the importance what is the importance of polymers. Here are some data forty one million metric tons of thermoplastic resins produced in the

USA in the year of 2000 only and there is polypropylene high density polyethylene, linear low density polyethylene, out of say for example, more than half of the total output of organic chemical industry, for what we say as the polymer industry. In this around 40 percent already is contributed by some of these polymers and as you can see these polymerization are affected with transition metal catalysts. Then combine the output of 40 percent is provided by LDPE low density polyethylene, poly vinyl chloride, polystyrene, poly vinyl alcohol, PMMA which is poly methyl methacrylate so on and so forth and these polymers are produced by free radical pathway or you can say some of these polymers basically are produced by chain polymerizations we will talk about that in detail as we go on.

And rest of that which is a combined output of 18 percent polyurethanes polyamides polycarbonates PET, PBT so on and so forth, those are from step polymerization. Here as you can see that this kind of distribution that I have made. So, different synthetic procedure used for preparing some of these different polymers, which are most commonly used and other less widely used polymers are there acrylics cellulosics, silicones, polysulfones, etcetera and there are also speciality polymers like you know polyether ether ketone, which is termed as peek polyether ether ketone or poly benzimidazoles those kind of things.

Here what I would like to tell you also is that you know this this is, but the kind of things that we are going to discuss in the course, are going to be something like this.

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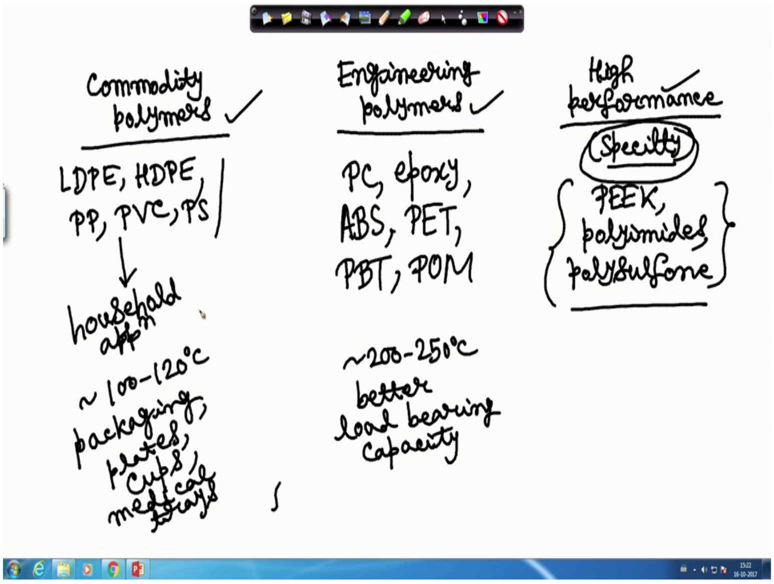

Commodity polymers ✓

LDPE, HDPE, PP, PVC, PS

household app

~ 100-120°C

packaging, plates, cups, medical trays

Engineering polymers ✓

PC, epoxy, ABS, PET, PBT, POM

~200-250°C

better load bearing capacity

High performance

Specilty

PEEK, polyimides, polysulfone

So, these are the classifications we could made of different kinds of polymers say we have what you call as commodity polymers, we have engineering polymers, and we have high performance polymers. So, in commodity polymers, under the class of commodity polymers, we could talk about low density polyethylene, high density polyethylene, then polypropylene, polyvinyl chloride, polystyrene etcetera. General household applications these polymers are used for general household applications and these are not you know mechanically very robust polymers and the temperatures that they can with stand are also limited say 100 to 120 degree Celsius approximately. Now and some of the applications for example, they are used for packaging they can be used for clothing materials or they can be used for say you know plates making plates or cups medical trays so on and so forth.

Now, engineering polymers they have more robust mechanical properties and they basically can with stand higher temperature, say in the range of 200 to 250 degree Celsius again, they are like approximate temperatures and they basically have better load bearing capacity if you compare with commodity polymers. The production cost is generally higher and some of the polymers that will come in this category are polycarbonates or epoxies acrylonitrile butadiene styrene co polymers, which is ABS or polyethylene terephthalate which is PET or polybutylene polyoxo methalne so on and so forth. And lastly there are high performance polymers which can also be called speciality polymers speciality polymers, those could be like peek polyether ether ketone or polyamides or polysulfones, they can with stand even higher temperature, they have very good mechanical properties generally and they are very costly to make. So, only in case of special applications so these are the 3 separate classes of polymers, that we are going to discuss later on as far as the synthesis of these polymers are concerned as far as the structure property relationship of this polymers are concerned.

So, after this kind of background after giving you this kind of background now it is the time to talk about some historical development, because as you can see the polymer industrials come a long way we can actually prepare whatever structures we want we can actually generate many properties engineer, many different properties it may be requiring more cost depending on the class of applications that we can research, but we can do that and we can characterize the structures also very well those kind of things we are not (Refer Time: 11:07) even 100 years back. So, I am going to give you a little bit of peak into that kind of history that is how I have designed this particular class. So, I will go back to that.

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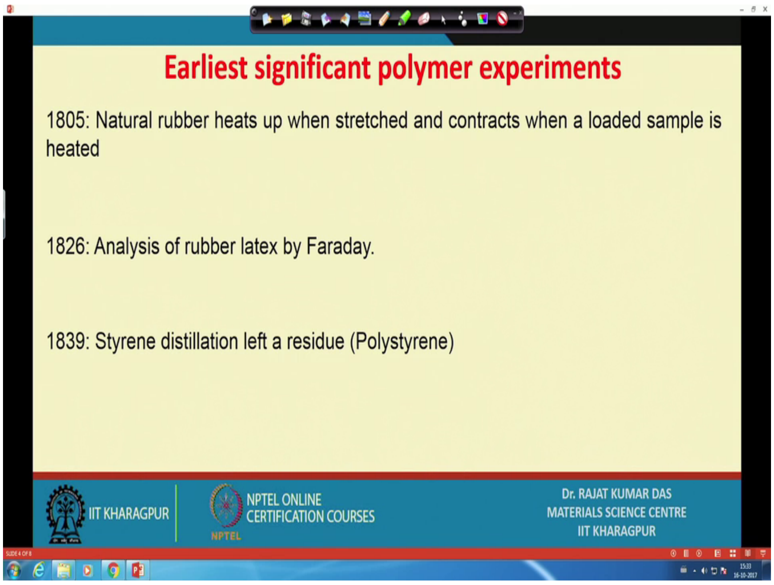

Earliest significant polymer experiments

1805: Natural rubber heats up when stretched and contracts when a loaded sample is heated

1826: Analysis of rubber latex by Faraday.

1839: Styrene distillation left a residue (Polystyrene)

So, in this slide I have listed a number of experiments that could be considered as the earliest significant polymer experiments. For example, in 1800 and 5 it was observed that natural rubber when it is traced it generates some heat and when it is under stretched condition; that means, it is loaded with a with a load, then it will contract when you are heating this material. At that point of time it was believed that an absorption of calorific fluid occurs, when you are heating a loaded sample an absorption of calorific fluid occurs and that helps the material to contract much in the same manner as for example, when you put water into the ropes they will contract.

And the next event that I wanted to mention was in 1826 when faraday analysed a an aqueous suspension of rubber lattice. So, he was correctly able to show that this phase contains proteins and he was able to comment on the elemental composition of rubber also and not only that amazingly he did an experiment, where he heated this rubber with sulphur and he observed the generation of hydrogen sulphide gas, but this is something that he explained a way as you know it is a way to reduce the amount of hydrogen in a material when you heat it with sulphur.

So, this was one of the greatest opportunities missed you know now that this is nothing, but vulcanization of rubber where you can put sulphur into a generally taki natural rubber material and then it has cross linking and that renders it elastomeric; that means, it can be stretched to a higher length you remove your force and it comes back to it is original configuration. And afterwards in 1839 it was shown that when you distil styrene there is a residue lift, which gains thickness with time and it was believed that it is nothing, but styrene oxide. And later on it was also confirmed that in absence some oxygen also this particular observation was there. That means, it was not styrene oxide, but it was some compound of styrene.

They fail to realise that it was actually a polymer of styrene. So, with these kind of introduction now I would like to tell you something else, how this particular field developed in a way that lot of other experiments were done these were some of the main experiments lot of other experiments where done lot of other polymers where made, in the 19th century which where you know commercially viable, but they did not realise that they where polymeric materials. So, I am going to give you an idea of what occurred around that point of time.

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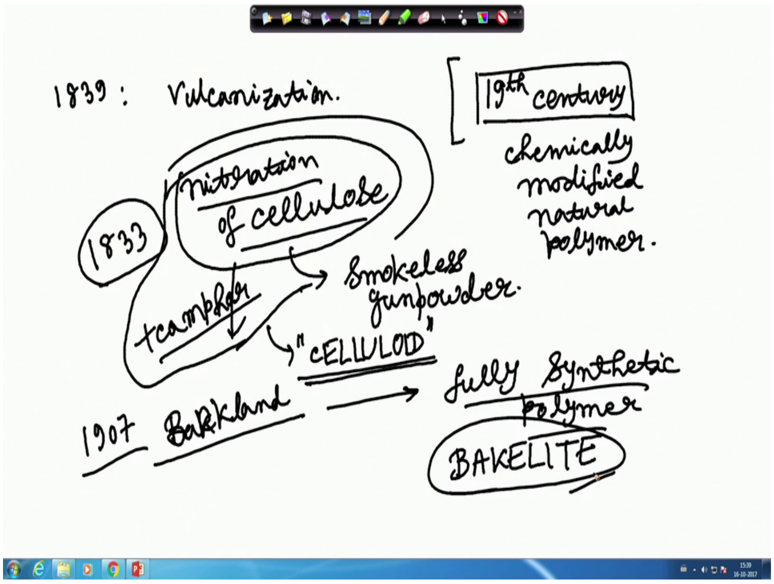

So, around 1839 Charles Goodyear he actually described the vulcanization of rubber vulcanization of rubber. So, that was the birth of rubber industry. Now, something I want to mention here that up to late 19th century up to late 19th century whatever polymers where made they were actually modification of natural polymers.

So, chemically modified natural polymers all of them were like that. An example could be the nitration of cellulose is a natural polymer. Now this nitration was described way back in 1833 and afterwards in 1847 this was controlled in a controlled fashion this nitration was done and then you know smokeless gunpowder was developed, which was used as explosive. And later on it was found that if you add camphor to this to nitrocellulose, if you add camphor this camphor has a plasticizing effect on nitrocellulose and that renders the nitrocellulose melt easily processible.

And these kind of materials where later used for the fields for the cinema and you know these were very highly flammable. So, it was not a coincidence that there were many incidences of fire that were reported from the cinema halls. And these class of materials this nitrocellulose plus camphor this class of materials are known as celluloid you may have heard about this particular term. So, celluloid films were in woke at that point of time.

Now, first major discovered as far as the synthetic polymers were concerned was in 1900 and 7 I have a slide for this after that was by Baekland, where he discovered a way to control the condensation of phenol and formaldehyde and he generated the first fully synthetic polymer first fully synthetic polymer. Which was known as Bakelite, now this Bakelite that he had generated this he commercialised this under the trade name Bakelite and this material was an excellent electrical insulator. So many different uses where (Refer Time: 17:20) for this particular material.

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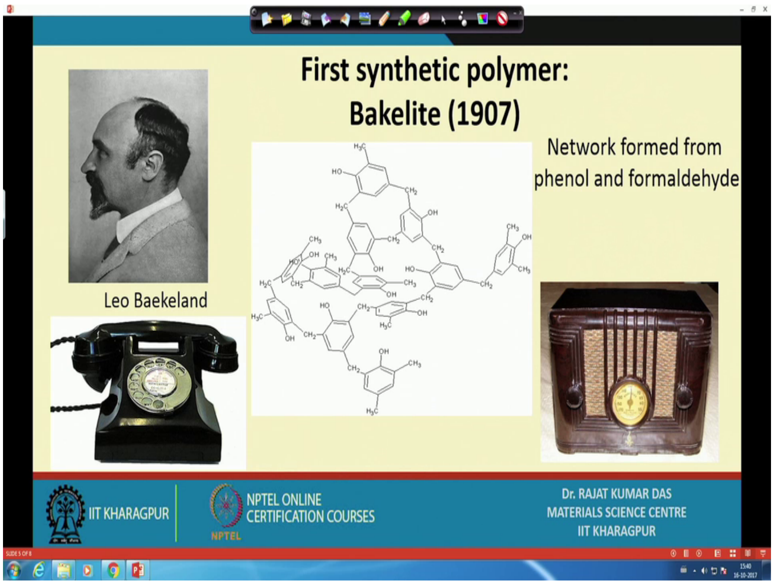

First synthetic polymer:
Bakelite (1907)

Network formed from phenol and formaldehyde

Leo Baekeland

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So, say this is the slide which describes actually the material. So, it is a network formed from phenol and formaldehyde and you know from starting from telephone to radio many of these materials where made from Bakelite. So, this was the first synthetic fully synthetic polymer that was made, but what about the name polymer, if you look at this particular name this name was coined long time back in 1833 by Berzelius.

So, at that point of time what he talked about is polymers are compounds of the same chemical composition they exhibit different properties. So, those are not in a traditional sense of way the polymers that we know now. So, they included isomers they included homologs they included polymorphs. So, those were not the now real polymers that we talk about now.

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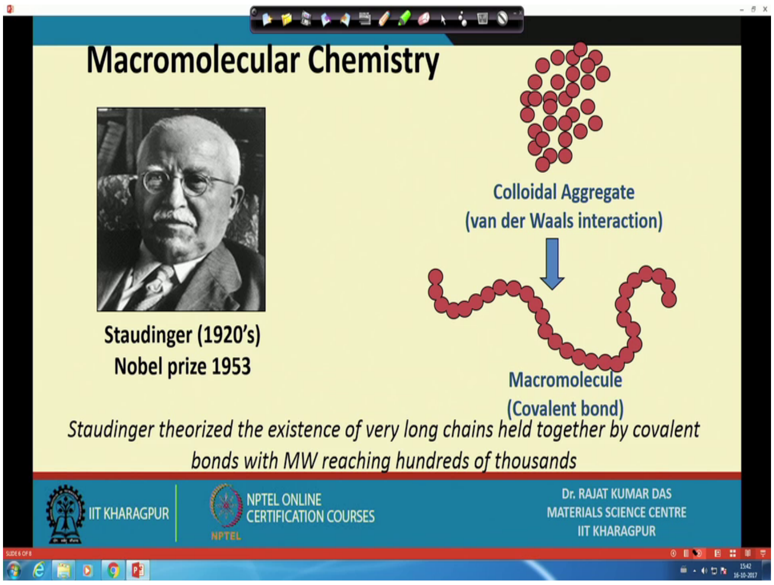

Macromolecular Chemistry

Staudinger (1920's)
Nobel prize 1953

Staudinger theorized the existence of very long chains held together by covalent bonds with MW reaching hundreds of thousands

The real evolution happened when, Harman Staudinger entered that field. So, in the early twentieth century all these properties of polymers like they are highly viscous, like they have low diffusion, coefficients or some of them are very difficult to crystallize they were all explain the way by saying that this could be you know you can explain this by the formation of Coloda aggregates, small molecules could associate and they can form aggregates and these aggregates can explain everything. And this is something that all of this changed when Hermann Staudinger a German chemist he came into the picture in 1920's he theorised the existence of very long chains, that are held together by covalent bonds with molecular way treating hundreds of thousands.

So, this is something this particular concept this is something that mate with lot of resistance at that particular point. Now I will give you an example of how you know the structure of natural rubber was basically explained without considering that it was a polymer. So, if you consider say for example, natural rubber.

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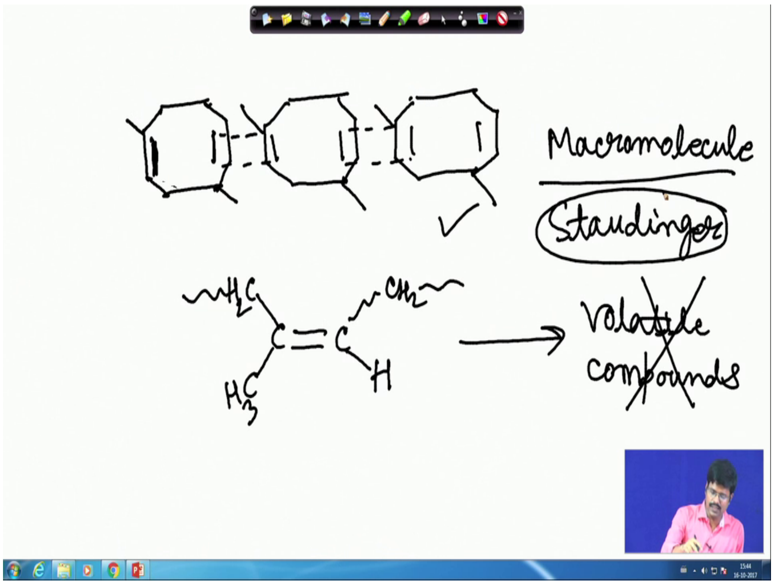

In 1900 and 5 sorry it was described as a material that consists of this molecule cyclooctadiene dimethyl cyclooctadiene. So, several of these molecules can come together several of this molecules in this fashion and they can have this kind of interaction through partial valency and this material. So, you know this kind of association of small molecules not necessarily a polymer and this could explain the properties of rubber that was what was claimed, but what Staudinger showed, basically is like this you have a double bond here.

So, if you hydrogenate this double bond and if this particular theory is true then you can actually get small molecules, but that was not the case now we know of course. So, this is rubber we have polymers of C is a isoprene this is what we know. So, what you did is that a hydrogenation of the double bond and when you do a hydrogenation we did not get any volatile compound or any cyclic product and this material has similar property as natural rubber. So, what we concluded is that the material that is produced after hydrogenation of this natural rubber has very similar properties and they are also macromolecular in nature. So, I am using this term macromolecule here this is the term that was introduced in 1920's by Staudinger himself to explain the properties of these materials.

Now, some of these things actually encountered lot of resistance and rightly. So, because at that point the understanding of structures where very much limited.

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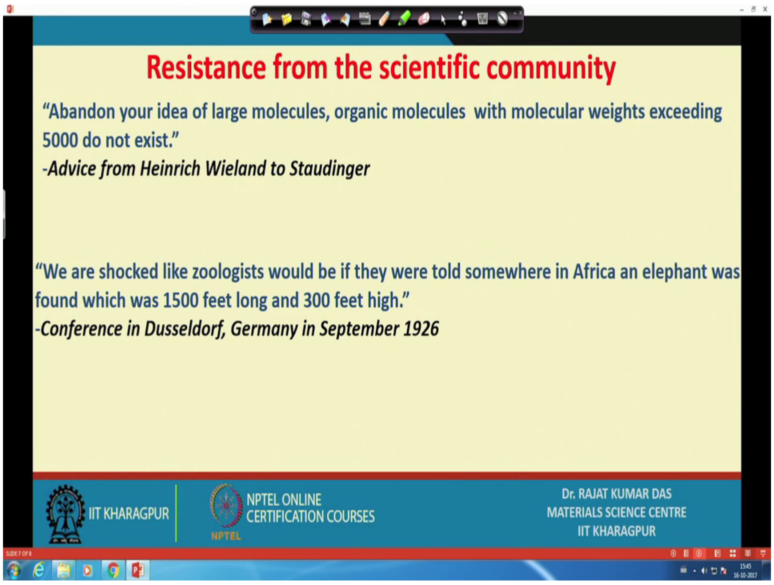

Resistance from the scientific community

"Abandon your idea of large molecules, organic molecules with molecular weights exceeding 5000 do not exist."

-*Advice from Heinrich Wieland to Staudinger*

"We are shocked like zoologists would be if they were told somewhere in Africa an elephant was found which was 1500 feet long and 300 feet high."

-*Conference in Dusseldorf, Germany in September 1926*

I will go to the next slide and I will explain to you if you comments. So, Heinrich Wieland who got Nobel Prize in 90's 1927, he told Staudinger he friendly advised that abandon on your idea of large molecules organic molecules with molecular weights exceeding 5000 do not exist, what Wieland believed is that at that the rubber that you have if you it is basically a an impure material. If you try to purify this material and you can purify it properly then you will get crystallize materials with small molecules.

So, he advised Staudinger that large molecules do not exist, in a public debate at a conference in Dusseldorf in Germany September 1926 one of the chemists actually mentioned that zoologies will be shocked, if they found that in Africa somewhere an elephant was found which is 1500 feet long and 300 feet height. We are also shocked the same way the idea of polymers like this long chain with all these molecular in which connected together by covalent bond is pure nonsense.

But later on of course, you know after all these resistance as you know Staudinger showed through hydrogenation that of course, this cyclooctadiene theory is not is not right for rubber. So, after high hydrogenation what you get is the same compound and one of the things the crystallographers believed also at that time is that the polymer molecules are. So, big they cannot fit into a small unit cell, but it was shown through crystallography the Staudinger himself showed this for polyoxomethelenes, that part of the molecule can actually be accommodating in unit cell and still it can be a polymer.

So, it is not a problem full molecule need not be in a unit cell and so crystallography aided actually Staudinger's hypothesis a lot.

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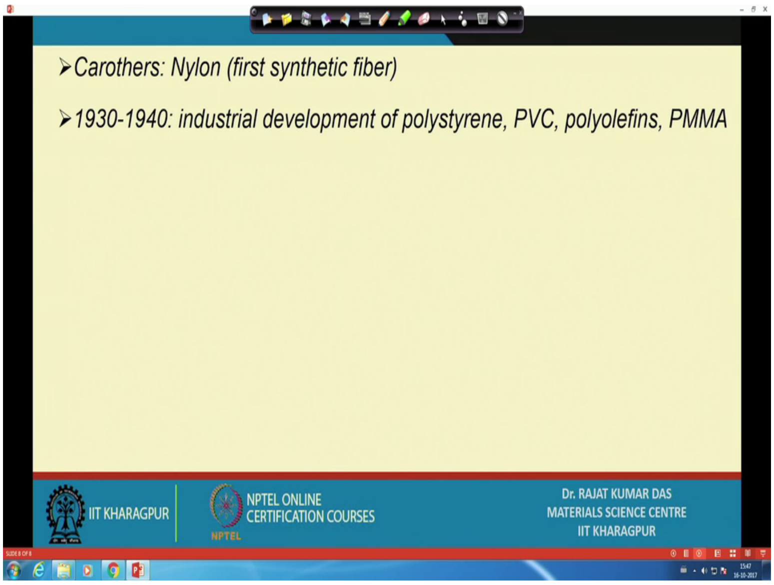

- *Carothers: Nylon (first synthetic fiber)*
- *1930-1940: industrial development of polystyrene, PVC, polyolefins, PMMA*

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An in 1930's in between 1930 to 1940 Carothers made nylon the first synthetic fibre hundreds of molecular units where joined together through covalent bonds, it was unambiguously proved and also there where industrial developments of polystyrene PVC poly vinyl chloride polyolefins poly methyl methacrylate.

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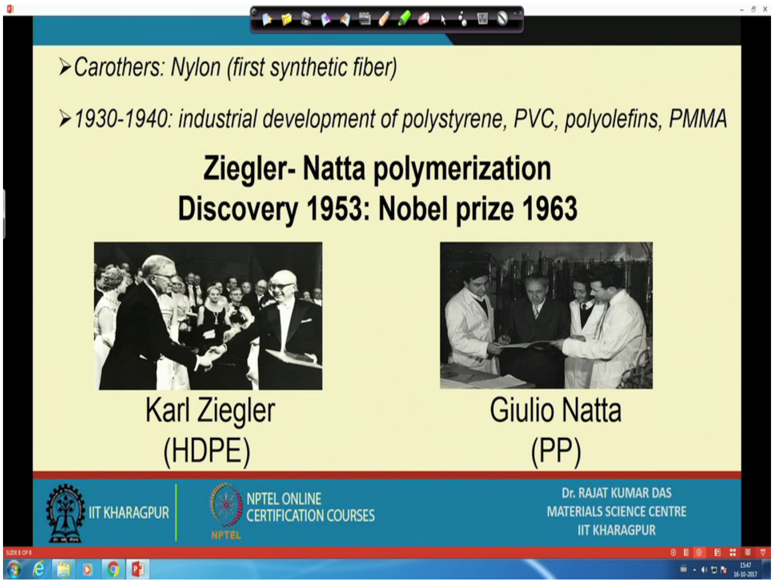

- *Carothers: Nylon (first synthetic fiber)*
- *1930-1940: industrial development of polystyrene, PVC, polyolefins, PMMA*

Ziegler- Natta polymerization
Discovery 1953: Nobel prize 1963

Karl Ziegler
(HDPE)

Giulio Natta
(PP)

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And that also calumniated into Ziegler Natta polymerization which was discovered in 1953, you know for high density undressed polyethylene and isotactic polypropylene with specific stereo regularity those things were also discovered and the Nobel Prize was awarded in 1963.

So, ultimately all of this things tell us that Staudinger himself and some of the other chemists at that point of time, they had to undergo lot of struggles and I would like to conclude this class by coating from the coating from the Nobel committees announcement, for Staudinger in 1953 actually he got Nobel Prize, for his enormous contribution to the development of polymer chemistry. So, professor (Refer Time: 25:32) a member of the Nobel committee he actually summarised his achievements, by these words it is no secret that for a long time many colleagues rejected your views and this was understandable perhaps in the world of high polymers almost everything was new and untried longstanding established concept said to be revised or new once created. So, the development of macromolecular science does not present a picture of peace full (Refer Time: 26:00).

So, I hope that I have given you a glimpse of how the polymer chemistry was developed, how for long time people had been actually working on polymers without actually understanding the structure of it, they were thinking it was composed of small units, but they could be held by non-covalent forces like colloidal aggregates. And later on Staudinger came and in front of lot of criticism and lot of resistance he established his theory and it was actually ultimately shown, that polymers with long chains can be created. And the final example that I would like to give is of evil fissure in the early 1900’s he was a pioneer of protein chemistry.

So, he had made a long polypeptide I guess 17 to 18 amino acids join together to a tedious synthesis. So, that itself should have shown to him and others that polymers are indeed possible, but even he was sceptical of these kind of ideas and he thought that molecules exceeding molecular weight of 4000 could not exist. Nowadays we know hundred hundreds and hundreds and thousands of Dalton of molecular weight of polymers are available.

With this, I would like to conclude this particular lecture. And, what are you do in the next lecture is to go into the classification of polymers and slowly try to talk about how you can determine the molecular weight of these polymers.

Thank you.