Polymer Chemistry
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Lecture - 1
Introduction to Polymers

Welcome to this course on Polymer Chemistry, I am Dibakar Dhara. I belong to the Department of Chemistry of IIT, Kharagpur. In this course I planned to cover the following topics.

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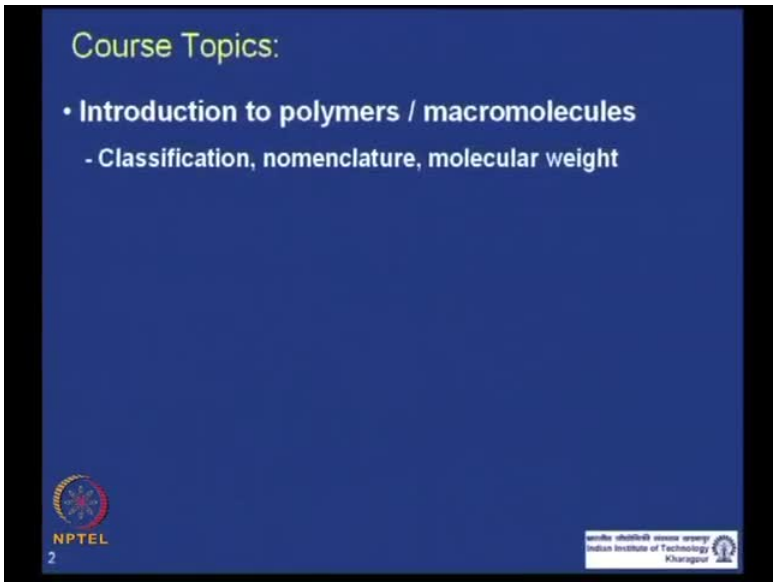

At the start I will be giving you a thorough introduction about the polymers which includes the classification, nomenclature and perspective of molecular of polymer molecules. Then I plan to cover in details various polymerization processes. I talk about, I will talk about the kinetics and the mechanism of different polymer processes which includes step growth and chain growth polymerization.

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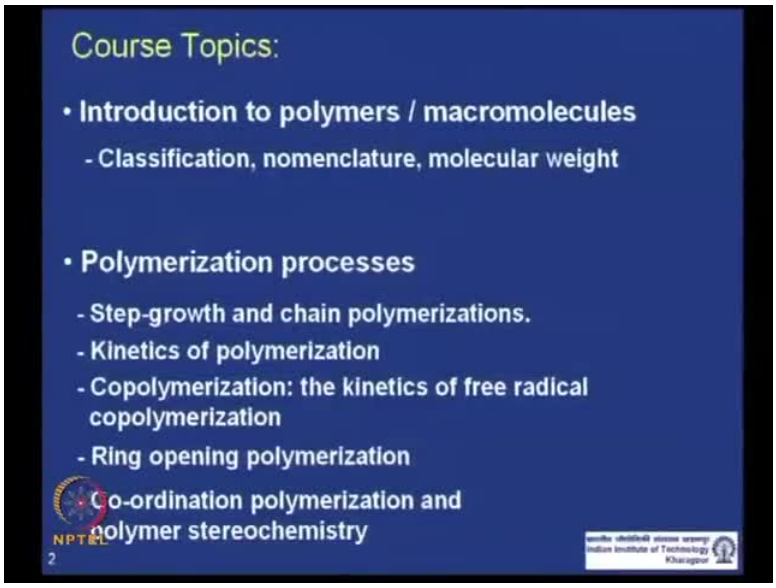

I also will cover copolymerization specially the kinetics of free radical copolymerization, and then I will also cover other important polymerization techniques such as ring opening polymerization, and coordination polymers.

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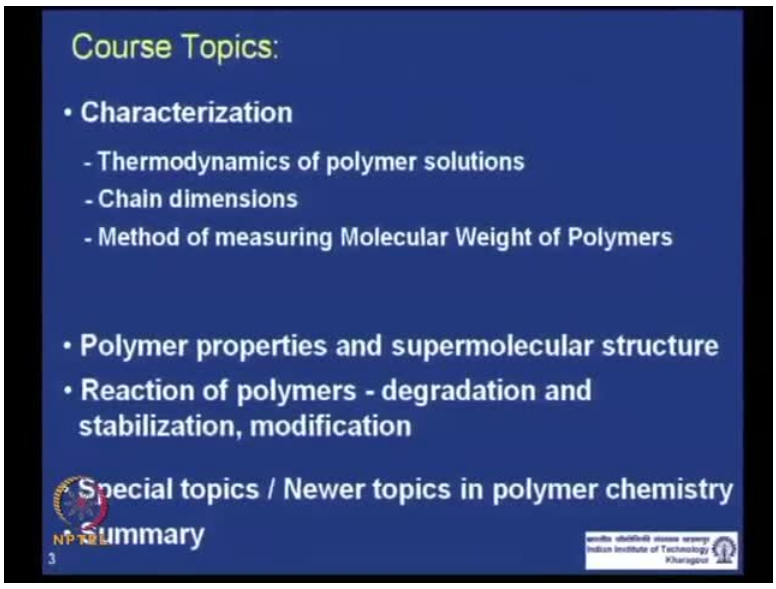

In the characterization, I will talk on detail about the thermodynamics of polymer solutions and then polymer chain dimensions, and I also will cover in detail about various methods for measuring molecular weight of polymer, polymers. And then I will cover polymer, important polymer properties and how the structure of polymer molecules

correlates to these properties. I will also cover both the chemical structure as well as physical structure of the polymers and how it relates to the polymer properties.

I will cover in brief the reaction of polymers which include polymer degradation, stabilization and also polymer modifications and at the end I have planned to brief you about few new topics, and special topics and new development in polymer chemistry and at the end I will complete with a summary of this course. Now, after learning what are the topics, we planned to cover in this course, let us introduce polymer to you, what are polymers? We we listen everywhere about the polymers, but what are polymers?

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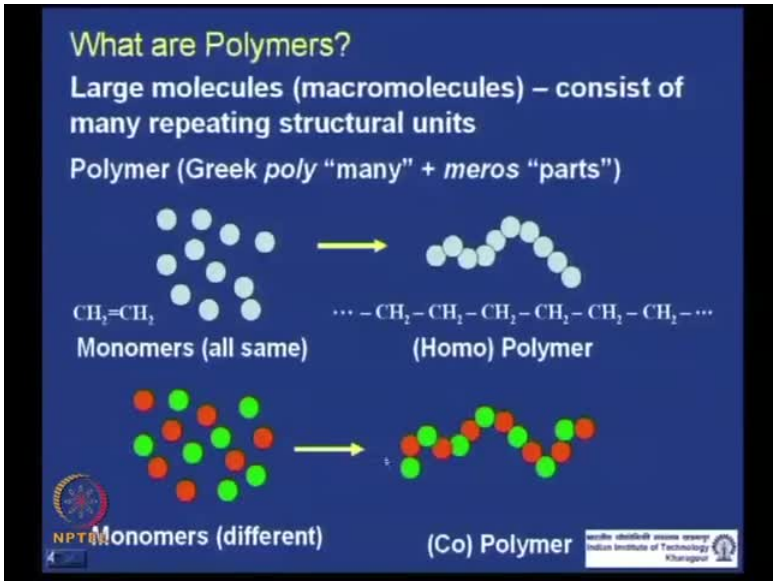

In a very simple term, in a single sentence polymers can be defined that they are large molecules that is why sometimes they call macromolecules synonymously. They consist of many repeating structural units, the term polymers derived from Greek words poly and meros, poly means many and meros means part. If I want to just show you pictorially or schematically this is the representation of polymers, you have this structure units monomers and on polymerization its gives you a linkage between the polymers making a large molecules.

So, you get a polymer for example you have ethylene here and in this side after polymerization you have polyethylene. In this case all the monomers are same so we name these polymers; we term these polymers as homo polymers. Polymers can be made from more than one monomers as well, different monomers which is showed in pictorial

in two colors and in that case you get a polymers consist of two different structural units, you and we call them as copolymers.

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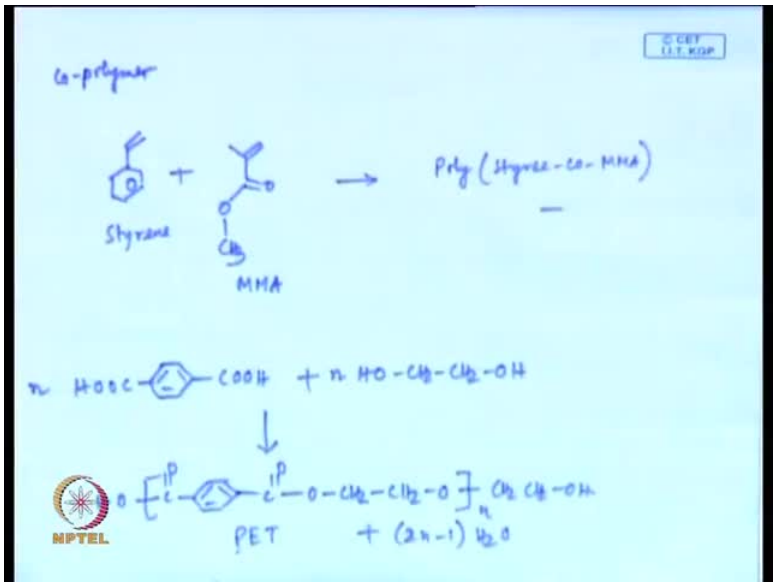

To just give you a example of copolymers I have a say I have a molecule like styrene and I also have a molecule like methyl methacrylate. Now, this two can be polymerized to give you a poly styrene co MMA, this is a copolymer of poly styrene and methyl methacrylate.

Now, this term copolymers are used generally when you have a polymers which are synthesized from two different monomers where the monomers can be polymerized independently, which means in this case styrene as well as the MMA can be polymerized to, individually can aim to polystyrene and poly methyl methacrylate. There is other type of polymers which are also synthesized from two different monomers. For example, if I take a example of terephthalic acid and ethylene glycol, I have n molecules of this, n molecules of this which on polymerization gives you a polymers which is known as polyethylene terephthalate. We get this pet bottles they are this, they are made of this polyethylene terephthalate.

So, in this case this polymer pet is also made from two different monomers terephthalic acid and ethylene glycol and we make a polymer, but generally generally we do not call this polymer as a copolymer whenever, because as I said earlier this monomer terephthalic acid or this ethylene glycol cannot be polymerized independently by all or

individually, this terephthalic acid cannot be made polymers by itself or a ethylene glycol cannot be made polymer by this process.

If if we have say more than one diol in this case ethylene glycol and say butylene glycol, that case we will have a mixture of two structure unit where you have terephthalic acid and ethylene glycol and also a terephthalic acid and butylene glycol in this, that case we call this or we name this polymers as a copolymers. To just repeat about this copolymers generally, we use the term copolymers where the polymer is synthesized form to different monomers where the monomers are or can be (( )) polymer individually. There is another case where polymer is made from two different monomers, but in this case we do not call this as a copolymers, because the constituents monomer usually cannot be homo polymerized independently by the same process.

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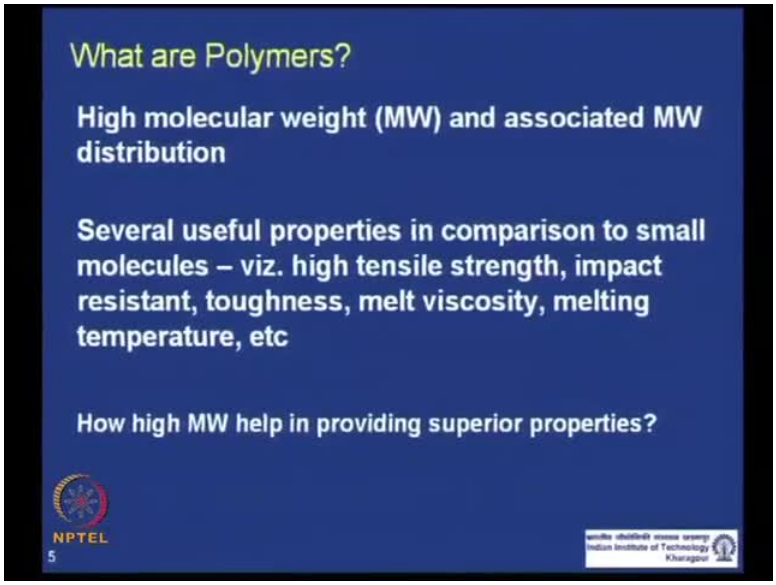

And when you make polymerization polymers, we invariably land up in distribution of molecular weight while a polymer is a high molecular weight, but it also gives you a distribution of molecular weight that means it has several length, the polymer mixture is consist of different molecular weight chains and this is, this high molecular weight of polymer which gives you or which enables a polymer to have this useful properties where, for which the polymer is known for for example, it gives you high tensile strength impact resistant, toughness, melt viscosity and and so on. Now, you might ask me why and what

is the reason this high molecular weight help in giving the, a polymer this superior properties compared to this small molecules.

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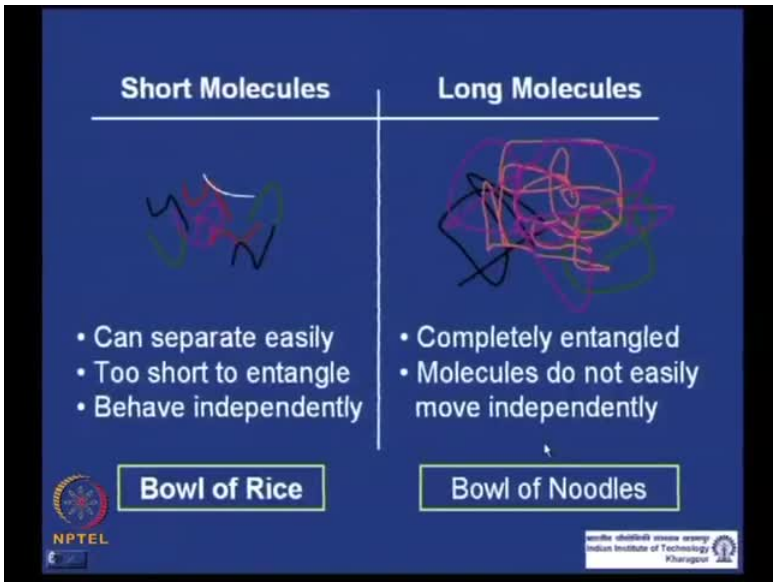

Let us look at this cartoon, if you compare as collection of small molecules or short molecules like a sugar and a long molecules which is a polymer sample. This is individual colors; individual chains represent a individual molecules in this case as well. Now, this is a case where the individual molecules are small in size, they are not entangled with each other. So, given a stress from outside they can be separated easily, in other word these small molecules behave independently. If I just give you a example of real life, say I have taken a bowl of rice and you want to take out rice with a spoon, you can easily take out because each individual rice units behave independently.

So, you can easily take out rice from a bowl by a spoon. Whereas in case of polymers because of the large size and its flexibility they are present in a mixture in a entangled well. That means the polymer chains are entangled to each other and as they are entangled they cannot be moved independently with each other for example, real life example if I have a bowl of noodles and I ask you to take a spoon, no, one spoon of noodles, you cannot independently take out as a noodles to the spoon because they are entangled. So, chains come together so when you take out a noodles you get a junk of polymer or no no pieces of noodles which you take out.

So, in this case where it was very easy to deform or set up small, mixture of small molecules in this case because of the large molecules it is difficult to deform a polymer molecules which gives you high viscosity, which gives you the high strength of the polymer molecules, high impact resistant, toughness and all other good properties of molecular polymer samples and that is why polymers is so popular now a days.

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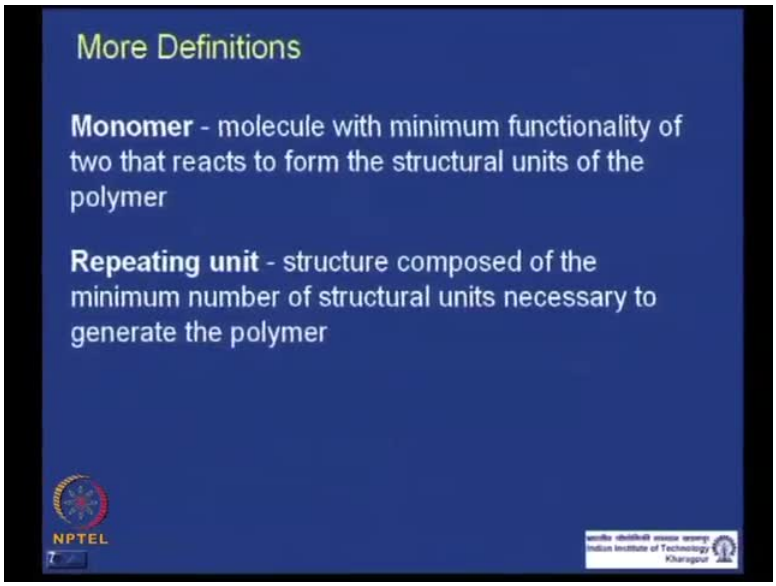

Okay, coming to the more definitions relevant to our course of polymer chemistry as such. Monomers, we talked about several times monomers. Monomers are molecules from which polymers are made. They must have at least or functionality of two to that means they can be, no, reacted at least from two sides for example, we talked about styrene molecules or ethylene molecules which means they can be extended from two sides.

If you have a molecules which have only one functionality for example, instead of ethylene glycol you have a phenol molecules, then once this weights of phenol is reacted you, the chain does not goes, you you cannot make a polymers. So, for making a polymers you require monomers which have at least two functionality in them. Repeating units it is a structure, a a polymer is formed from repeating units which means that when you write a polymer structures, the repeating unit is the unit which gets repeated.

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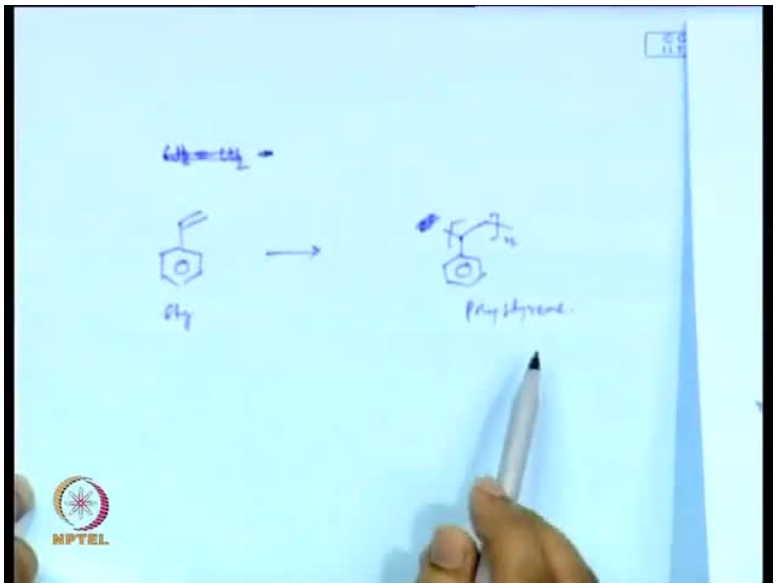

For examples I talked about the ethylene molecule in or say simple example of say polystyrene molecule. This is styrene and when it polymerized its gives you polystyrene. In this case this is the unit which is repeated which means and this is called, this is the repeat unit for polystyrene case. Now, if I go back the example I gave in the few minutes back, in this case for example, for polyethylene terephthalate this is the unit which is represented in the bracket. It is subscript of n, this is the units which gets repeated. So, if I want to write a structure of PET then I can take these units and put one after one to build the polymer units or the polymer molecules.

So, just to clarify one more time, in case of styrene we have the styrene unit as as a repeat unit and in case of PET you have this unit away with a repeating unit. We talk about oligomers. Oligomers are you know during the process of polymer synthesis, you get the small chain units which are consist of 2 monomers, 3 monomers, 4 monomers and so on, dimer, trimer, tetramers and these are called or termed as oligomers.

Now, you can ask me till when, till what time we call a molecule as a polymer or oligomer? Whether it is after 10, 11, 12, 20, 50, 100 you know after how many repeat units, you call a polymer as a polymer and before that you call as a oligomer. Now, it depends it depends upon different polymers, the easiest way to think a molecule, a long molecule as a polymer not a oligomer if you add another unit repeating unit or you take out another unit and by doing this addition of one unit or taking out all unit, if the

property of the polymer or the molecule does not change you call it as a polymer, but if change significantly then you still call it as a oligomer and that will depend on the chemical structure of the polymer.

So, some cases if you increase from a repeat unit number from 20 to 21 or decrease from 20 to 19 you might see there is a change in the property, you cannot call that chain as a polymer you have to call that as a oligomer, whereas in some cases some some cases you do not see any changes say after 20 to make 20 to 21 and 20 to 19 then you call that as a polymer.

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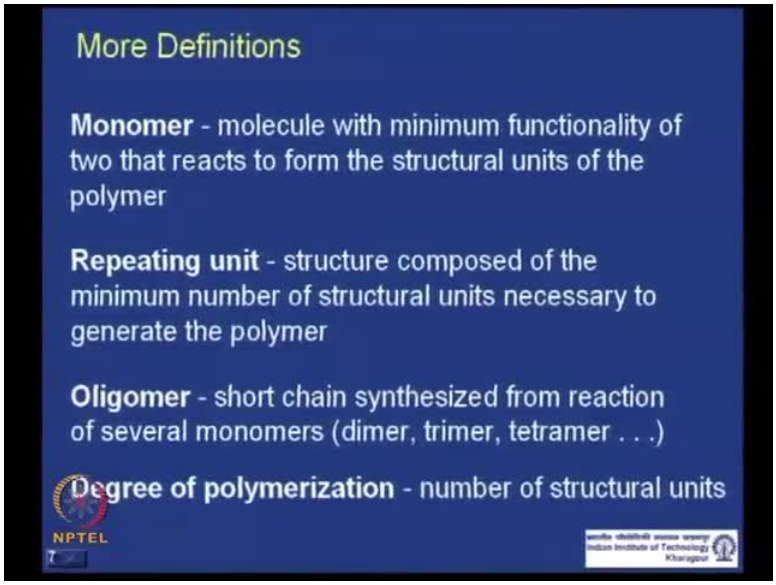

Define degree of polymers, its, it is the number of structural units present in a polymer molecule. What is structure units? Let us talk about the example I just showed you before. In the case of polystyrene this is repeating unit and this is also a structure unit because structural units is the unit which is derived from a monomer. So, in this case this unit is coming from a single monomer of styrene which where double bound is replaced by a single molecules.

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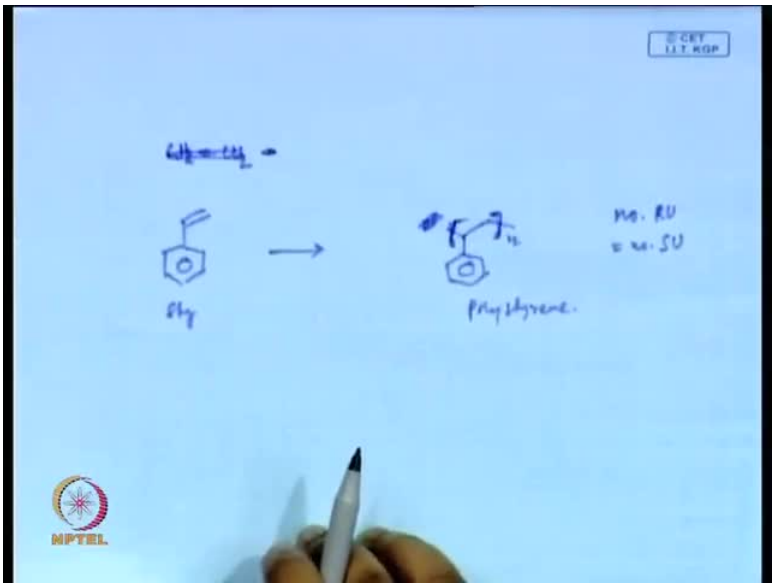

So, in this case number of repeating units RU repeating units is same as number of structural units SU is structural units. Whereas, in this case, case of polyethylene terephthalate individual monomers which are coming here and making the polymer they are called structural units. So, in this case if n is number of repeat units then it each unit consist of two structure units because in this repeat units is derived from two monomers, one terephthalic acid unit, one ethylene glycol units.

So, whereas in earlier case the number of repeating units were same as number of structural units. In this case number of repeat units is actually half of the number of structural units. So, when you define degree of polymerization it is the number of structural units not the number of repeat units present in a polymer.

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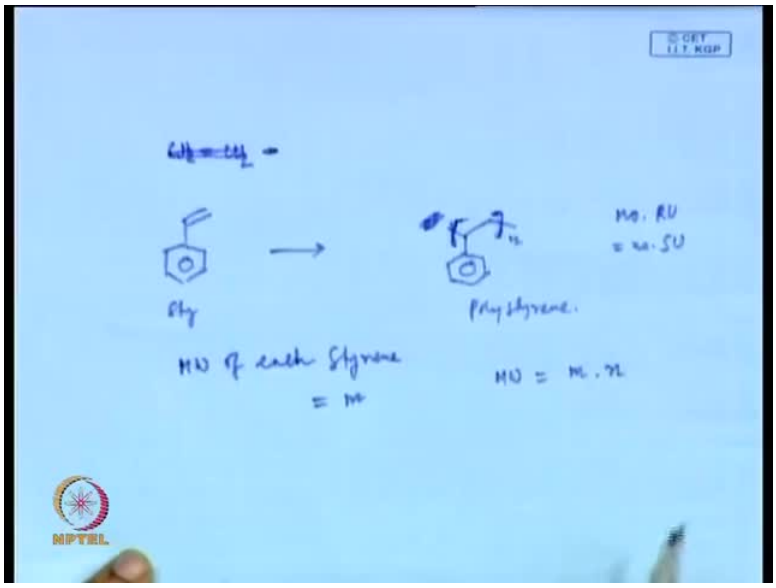

So, in this case if the molecular weight of of each styrene, molecular styrene is m and you have a polymer with n number of repeat units same as structural units then molecular weight of this polymer would be m multiplied by n. Now, what happened in this case? In the case of PET.

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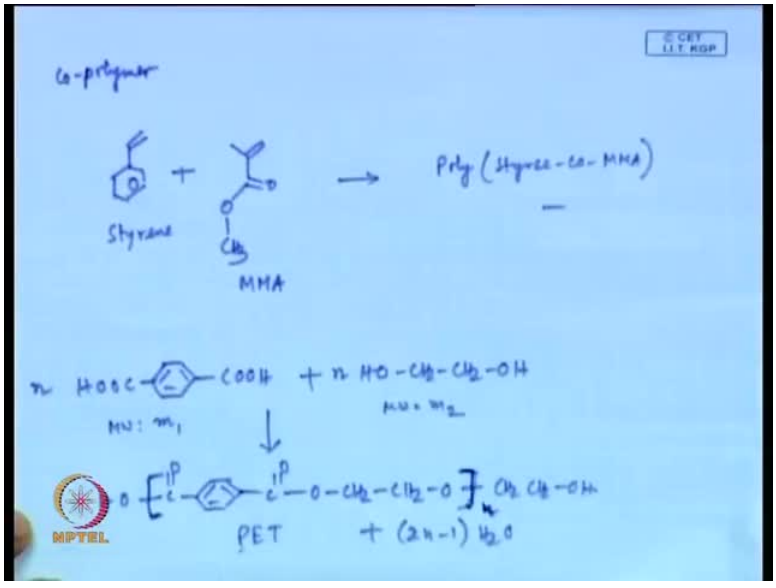

For example, if I take the molecular weight of this as m 1 and this as m 2 then how do you get the polymer molecular weight? How do you define? How did you define the degree of polymerization is the number of structure unit.

So, in this case the polymer molecular weight will be degree of polymerization multiplied by the average of these two monomers minus the water molecules which have been eliminated, I will show you a example, real example in coming pages. So, that it will get clear little bit more, if it is not clear already.

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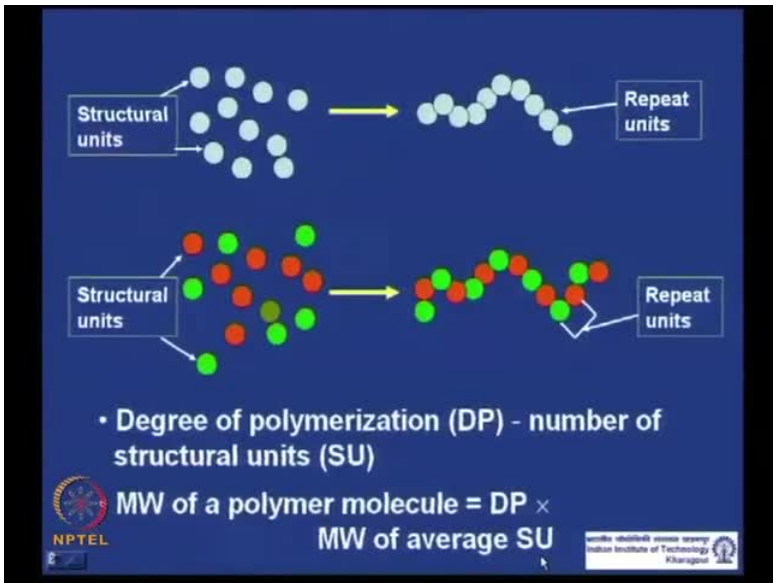

So, let us see whether it get clarified to you in this cartoon. You know in this case of styrene you have polystyrene in this case. So, structural units is same as repeat units and in this case whether you have a say example of poly terephthalic acid PET terephthalate PET to it is the polymer is derived from two different units then the repeat units is this whereas, this consists of two structural units.

So, if I take this this part then it this consist of four structural units, but only two repeat units and as I said degree of polymers is number of structural units, and the molecular weight of polymer molecules is degree of polymerization that means number of structural units multiplied by the average structure unit.

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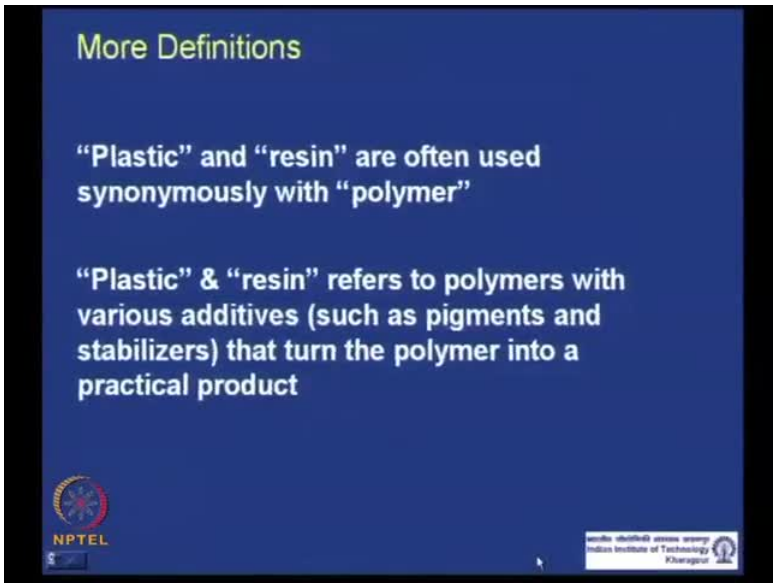

Now, before going forward let us clarify one thing in a more often or not you know in commonly polymers are referred as plastics. People ask for banning plastics, plastic bag, plastic shoes, plastics bottle everything you know, most of the applications of polymers are referred to as a application of plastics.

Now, there is certain difference between the term plastics and polymer. Polymers are the molecules which we synthesize from the monomer, they are individual molecules or a mixture of molecules, but we do not use when you synthesize a polymer from, in the lab or in a plant we do not use, in a seldom use as the polymers as synthesized. In most cases what happened we add some additives like pigment, stabilizers and then process that polymer mixture, you know polymer with the mixture to turn this polymer into a practical product.

So, if I talk about pet bottle when you synthesize pet in the lab and that is not a plastic material or when you take a pet molecule poly terephthalate molecule in the plant and then mix with the stabilizer and other things and form that bottle, that is called plastics. Plastics has also more, have more scientific definitions which we come later, but at at this point you must remember that plastics are made of polymers, but not all polymers are plastics like there are several other applications where polymers are not used as plastics.

So, when you talk about you know, but in commonly, in common man whatever they see is applications of polymers, they see in daily life is a plastic, you know applications are

visible as a plastics application. So, that is this common term that is why this common term is appearing. Just one more time plastics are polymers, but not all polymers are plastics.

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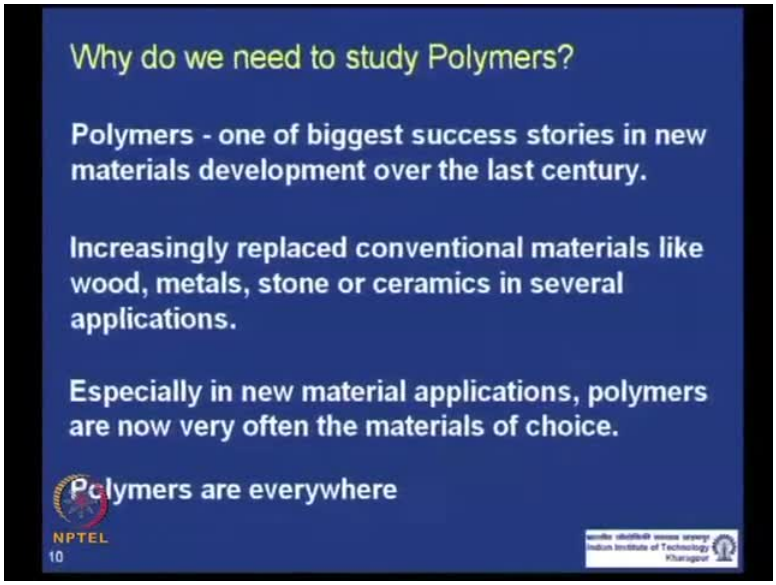

Now, this knowing, what are polymers, what are plastics and what brings the good properties in polymers? Now, why why you are, you will ask me why you are, why you need to study polymers, why we should be interested in studying polymer or polymer chemistry. If you think yourself or if you read magazines and talk to the older people then you will find that in last century whatever new material development has happened polymers will rank as one of the top.

So, in last century polymer is one of the biggest success in terms of new material development and as a results more and more applications are existing or coming up where this polymers are replacing the conventional materials like metals, glass, wood and so on for example, I am wearing a spec. Now, earlier, few years back for a decade back or so this spec was used to be made from glass, but now a days you will hardly find any spec is made up of glass, they are all made up of either polycarbonates or the cheaper ones are formed acrylics.

There are hundreds of such examples I can give, maybe I will give in later classes, but I hope you are convinced that polymers is finding applications in several places and now a days when we talk about you know we, a scientist or the developer you know application

specialist with thing for a new material application. First thing comes into mind is a polymer and more often not a polymer becomes very often the material of choice for new applications.

So, I have, hope you are convinced that polymers are you know a useful material and replacing the conventional materials. If you are still not convinced, if you think what you do once you wake up from bed you take a brush which is made up of plastic material, you use the toothpaste which contain polymer molecules, you take food, foods are also having natural polymers, the container sometimes we use, disposable plastics and you wear shirts, clothes which are made of polyesters, cottons these are all examples of polymers.

Then you come to office by a car or a bus or a cycle. There are hundreds of polymer goes in those applications. You name, you know wear shoes, everything. Now, you can argue me that these are very common common materials and these are no need for main development work for this. So, you do not need to study polymer because the knowledge or technical knowledge for this common applications are well established, but if you think about examples of polymer like a artificial valve which is made of polyethylene.

Talk about a oxygenator which is used during a heart, open heart surgery or talk about applications in car head lamp, aircraft windows and and several high end applications like very high capacity DVDs. Now, these are also application of polymers which it does not come to your mind immediately, but like this there are hundreds of very high end applications of polymers. For examples polymers are used in medicine, as a drug delivery vehicle, as a conservation with drugs, molecules and so many. So, in this case you require a definitive knowledge about polymers which will enable you to develop or innovate new polymer molecules or new polymer applications.

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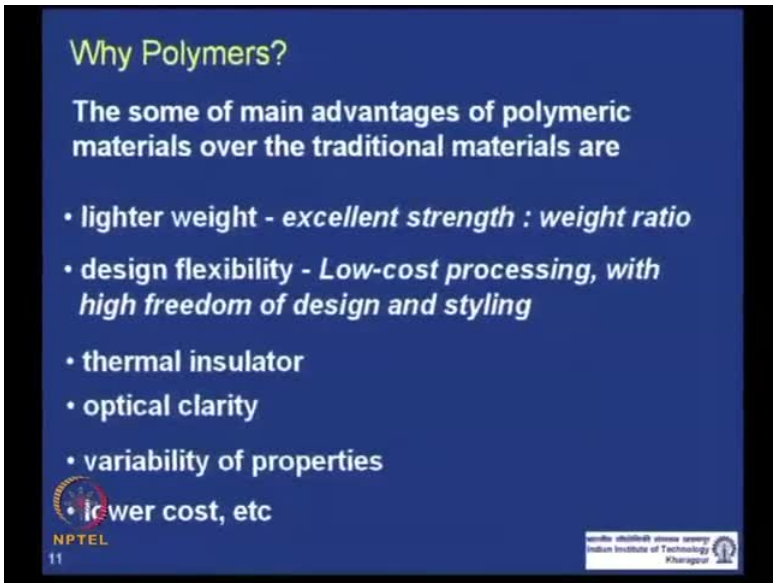

Now, why why people use polymer compared to this conventional materials or traditional materials? There are definitive, there are some definitive advantages for example, I just gave you example of the spec. Now, when you use a plastic material like polycarbonate compared to a glass this becomes much lighter, you know its gives you lot of comfort than the glass.

Now, because of the lighter of weights polymers used heavily in transportations like car automotive, in trains and all these things because the light you travel that will consume less fuel. This is one of the most important advantages of using polymers which gives you excellent strength to weight ratio. It gives you design flexibility, you know there are and also various you know the option of giving you modern styling you know. You buy a cheap processing you can make, take the polymers which is comes in after from the lab or in a plant and you can do the polymer processing, do a process and make or give that polymer a very nice shapes of your choice and give good style which is not possible with the traditional materials like glass and metals.

Polymers are most cases thermal insulator which makes it or enables polymers to use in electronic industry and unlike the conventional materials like wood, metal they are optically clear which enables application of polymers in media, and optical devices and one more important that there are so many polymers available in market that you can choose a definite polymer for your particular applications. So, that you have, you do not

have to limit it with number of polymers available, there are so many polymers available now in market. So, it gives you the option of choosing a definite polymer or particular polymers for your choice of applications and of course, you know not more often and not it comes with a lower cost. Some polymers are of course, very costly, that gives you very good performance, but more often not the polymers gives you, comes with a lower cost.

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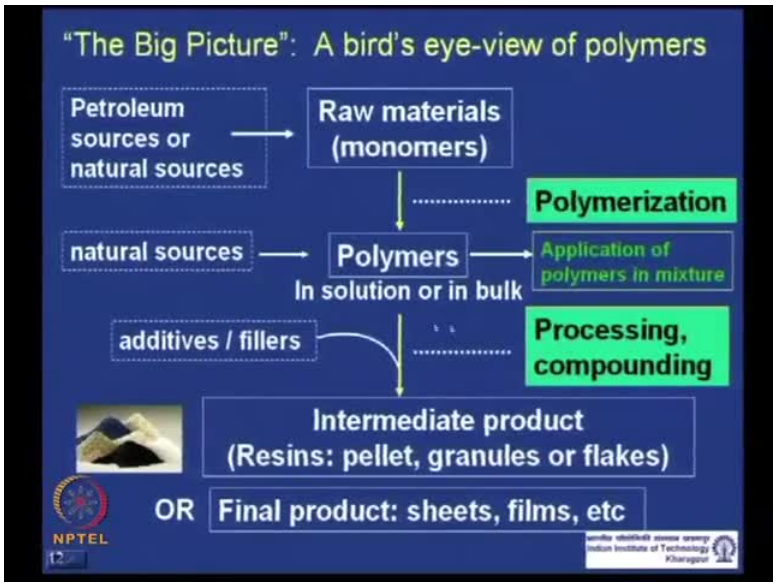

Now, before I come to the introduction of polymers or polymer chemistry, I just want to give you a big picture, a view on the top, a bird's eye view from how you look at polymers. You know different stages, life stages of polymers and how it get transformed where they induce of polymers.

So, you have a polymer molecule which you synthesized in the lab. Now, when you synthesized you get it in solution or in a bulk. So, you have a polymer which is prepared in the plant which is coming either in solution or in a bulk. Sometimes, it come other form as well like in emulsions. So, if it is solution you have to take out the polymers from the solution in a powder form and if it is in a bulk or in a melt form you can use as such and if it is in emulsion cases like some cases it is in emulsion. So, you can use the emulsion as such.

Now, where how do you get these polymers? There are some polymers or few polymers which comes from natural sources like polysaccharide cellulose and more often not these natural polymers, the polymers which comes from natural source are very useful. So, in

most cases to find a polymer, these polymers are synthesized in a plant from raw materials which are monomers by the process, which are termed as polymerization.

So, you have polymers which you can get from natural source, but in majority of places a polymer is synthesized from raw materials, monomer by process called polymerization. How, where from do you get this monomers or the raw material? Most cases you get from petroleum resources, ultimately from a crude oil or in some cases you also get a monomers from renewable resources or bio resources. As I said most cases synthetic polymers are prepared or synthesized from monomers which are derived from petroleum resources. So, now we have know where from a polymer is made. Now, you have to take the polymers towards application side. There are minority of polymers are taken to the applications where polymers are used along with the other ingredients like in detergents. In a detergent formulation you have surfactant polymers and other ingredients. If you talk about say eye drop you have polymer in aqueous solutions with salt and other ingredients.

So, in this case this are the applications which are which are where the minor, there is a minor fraction of polymers going, where polymers are used in a mixture in a solution or some other form whether polymers is either a you know active ingredient or is just act as a support role like enhancing the viscosity (( )) enhancer and so on.

But in majority you know the major volume of polymer comes out in from the manufacturing plants, goes in the application where polymer is the major part you know, is a application of polymers is major. You can have the other ingredients along with the polymer like a stabilizer fillers or pigments, but it is the polymers which is the major ingredient and other additives acts as a support which either enable the polymer to have you know better performance.

So, in that case what is done the polymers as comes out from plant is taken to a step, taken through a step, a polymer processing step which are commonly called compound where the polymer either in a melt form or in powder form is mixed with the required additives or property enhanced enhancing fillers or sometimes with other polymers as well to make polymer blends and you get a intermediate product, is like pellets. We call this as resins; you might have seen this granules or pellets yourself in sometimes in the market and if the final applications is does not require very complicated geometry then in this process itself you can make the final product for example, like sheets film where in

this processing step itself, the polymers are taken and the additives or fillers are added and it is given a shape of the final products like sheets and film etcetera, but this is not the major application this is the minor applications. In most cases the polymer manufacturer makes this as a intermediate products and they sell this to its customer who makes the final product.

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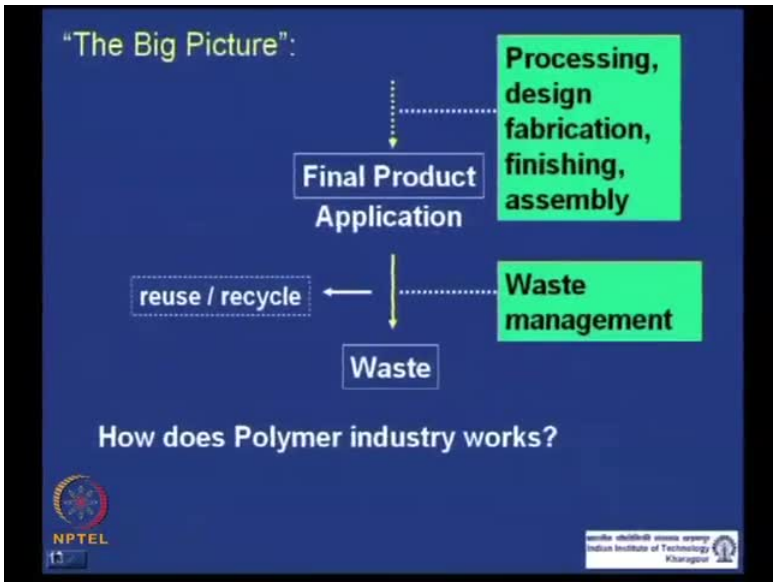

And once the polymer and this pellets are supplied to the equipment manufacturer, they do a processing steps to give you or to give the final shape, design fabrication step or in a finishing shape and you get the final products which gives you the, which goes into the final applications.

I will give examples which will clarify these points more in, once the final application is done the, this life cycle of the polymers does not end. Once the application of over polymers become a waste and its very important is as important as the earlier steps that we have a very good waste management system by which we can either, we use or recycle the polymers and if you cannot recycle or reuse the polymers then this waste of the polymer, the polymer waste has to be handled very carefully. So, that it does not pollute the environment.

So, if I repeat this life stages and various transformation step you have a monomer which most often we get from petroleum products and from monomers by doing a step called polymerization we get the polymers in the plant or in a lab either in solution or in bulk or

in some cases in emulsion form. If it is a solution you have to take out the polymers as a powder form.

So, you have now the polymers. In minority of application this polymers are taken and added to other ingredients like the examples I gave in detergents, but in major cases the polymer is mixed with the other ingredients like additives, pigments, stabilizers and it is by a process called polymer processing, compounding and you, it is transformed with granules or flakes or pellets to form intermediate product. These intermediate products are taken by the equipment manufacturer and by doing another processing step for example, injection molding they give the proper shape of the final applications where this polymer goes in.

How this, how the polymer industry works? Now, if we talk about the big polymer manufacturers like DuPont, Dow Chemicals, SABIC, Bayer they are manufacturer of polymers.

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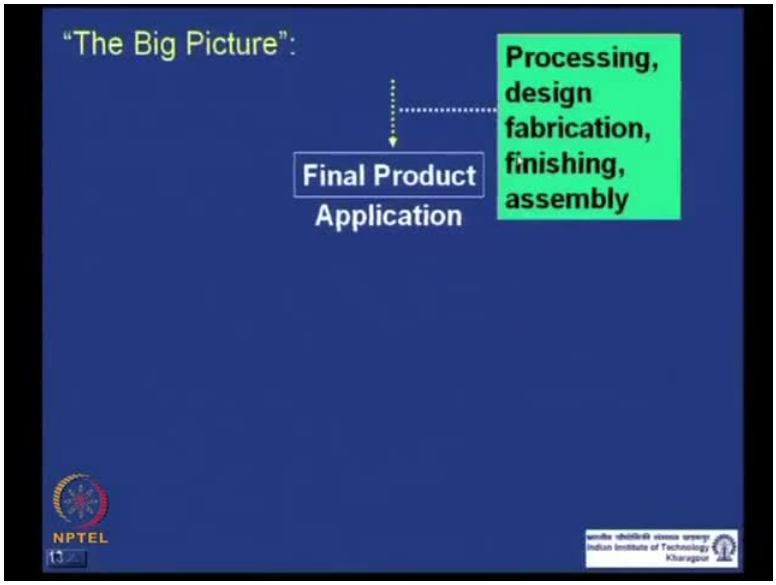

They get the monomers from other source or they might make themselves as well and they, after making the polymers in the plant they also do this steps themselves, from this intermediate product. And then sell it to some original equipment manufacturer which do this processing step, molding step to make the final product, which goes into the final applications. Now, let us come to a specific example.

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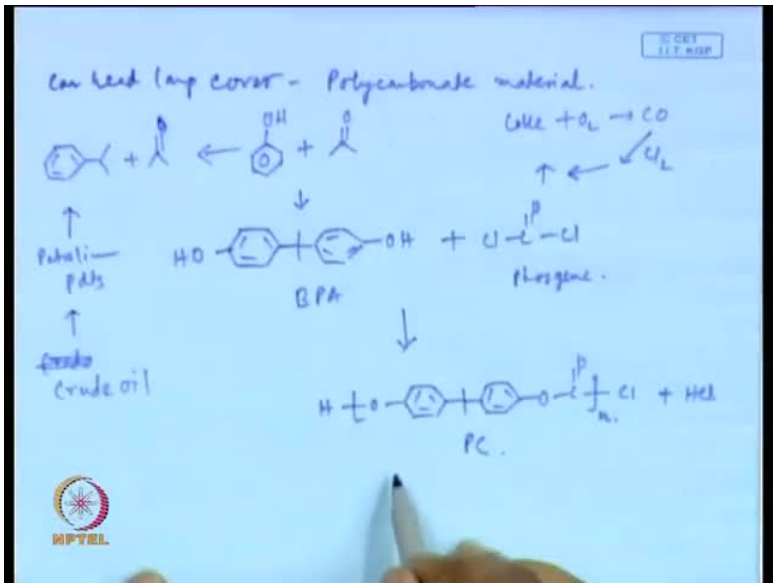

For example if I take a car head lamp cover, the cover of the car head lamp is nowadays made from polycarbonate material. Polycarbonate is synthesized from two monomers this phenol A and phosgene to give you polycarbonate. Now, how do you get, how this this is produced? This BPA molecule, this is produced from phenol and acetone and this is produced from coke getting oxidized to carbon monoxide which one react to it chlorine gives you phosgene. Where from this phenol comes from? It comes from cumin plus acetone. Where from this cumin comes from? This comes from petroleum products, which is eventually coming from crude oil.

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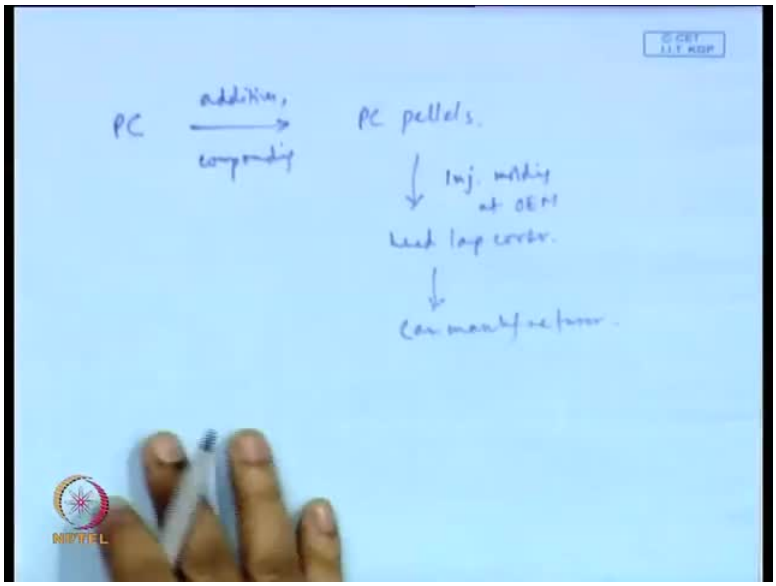

You take this polycarbonate as synthesized in a plant or in lab, add these additives, pigments etcetera and we are compounding strips and you get PC pellets. You you sell this PC plates to a cumin manufacturer which will make say injection molding and make the head lamp cover at OEM which will be sold to the car manufacture. Let us just go back to earlier page and repeat this.

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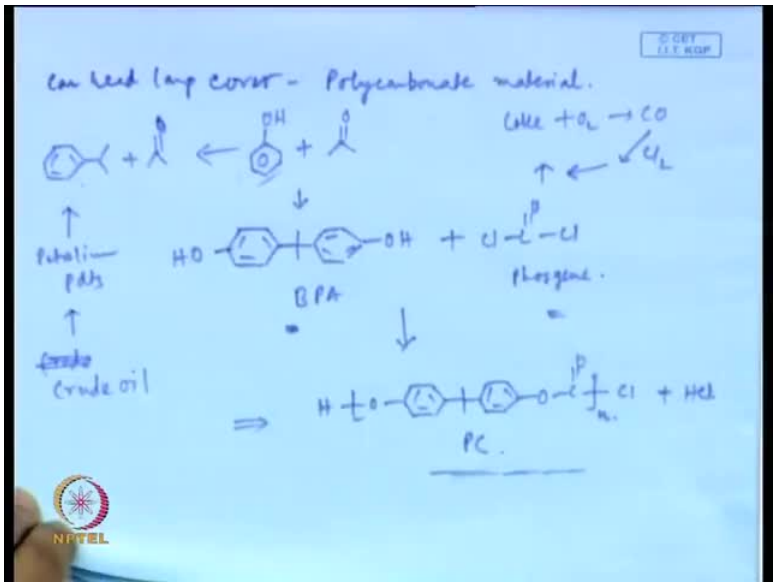

Now, a company which makes polycarbonate, which sells polycarbonate like say Bayer or SABIC. They make this process definitely, they make or they synthesize the polymer in the, polycarbonate in the plant them self. They can source the monomer at any stage, they can buy BPA and phosgene, they can buy phenol and make BPA them self or they can buy a cumin and they make and they can phenol from which they can make BPA and and then PC.

They also do this step, this step compounding step them self. Now, after making these pellet they sell it to original equipment manufacturer. This original equipment manufacturer buy this pellets, polycarbonate pellets from any of these big companies and they mold it to, they mold it to give a form of a head lamp cover which they then supply and sell it to a car manufacturer who assemble these head lamp along with other things and have this product in the market.

So, this gives you idea about a different stages of polymers and how the industry work. There are some smaller industries which make custom polymer products. These are the

examples of big polymer industry where the the companies make the polymers in very large quantity, where the the applications where polymers find you know minor like examples I said where polymers are synthesized and added as a active or secondary ingredient in other formulations, those polymers are typically made by the smaller companies and they are taken, they are synthesized by the smaller companies.

Now, what is the present focus of in a polymer research? If I go back to the earlier slide as I said that most of the current synthetic polymers are made up from monomers which are ultimately sourced from petroleum products as there is a increasing interested interest to make polymer from the monomers which are not source from petroleum products, because on using the polymers or making polymers from petroleum, there is a fear of you know depletion of petroleum resources.

So, current focus in polymer research is to make monomer and subsequent polymers from a natural sources, which could be a bio source or a source which can be renewed or the source by by renewal resources. There is a focus also make this polymerization process green and environmental friendly where you avoid use of this toxic chemicals and gases like solvents and other things. There is also emphasis of making new polymers of complicated structures which will find applications in newer especially in medicines and also this this is a continued research interest where you take existing polymers and add additive fillers, new additive fillers or different processing step, now improve processing include polymer processing where you you make this different improved application of or newer applications of the existing polymer.

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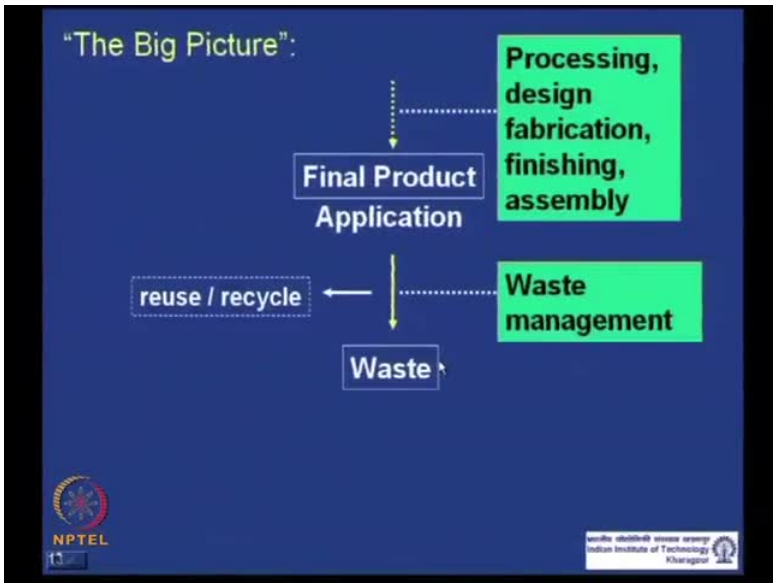

And of course, there is a very highly important you know the more importance given specially from the government side about the waste management of polymers specially recycling of polymers and find the ways where you can we use the polymers and of course, the there is a need for research how to properly manage the polymer waste. With this I we will stop this class. In the coming class I will start with classifications of polymer.

Just to repeat what what I covered in this class, we talked about the definition of what are polymers? Polymers are large molecules, which is made from repetition of structural units. We also learned why we should study polymers, polymers as you by now convinced that find applications in conventional applications as well as very newer applications, very high end applications and we also learned why nowadays polymer is used more and more applications, what are the good properties of polymers and why polymers are different, you know why polymers are get what what are the structural features of polymer gives you this is improved properties and then we also learned big picture.

Now, what are the different stages of polymers and then how the polymers are transformed from one stage to another and ultimately where how the polymer industry works and then we talked about finally about what are the important research areas in

currently researcher focusing in polymer chemistry. We will start in next class, continue the introduction and we start from the classification of polymers.