Polymer Reaction Engineering
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Lecture - 04
Gradient and Graft Copolymer, Polymer and its Compositions, Isomerism in Polymers-I

Welcome to this polymer reaction engineering aspect. Here today we are going to discuss the gradient and graft copolymer, polymers and its composition, isomerization in the polymeric system. Now here one thing is important that before we go into the either designing of any kind of a polymeric reactor or any kind of designing of a polymeric system, then the knowledge about these kinds of a copolymeric system, composition, isomerization is extremely essential.

So, in this particular chapter or in this particular lecture, we are going to deal this kind of approach, so that we can be aware that how the polymer structure being changed in due course of time. Now before we go into the detail of this particular approach, let us have a brief look at what we studied earlier.

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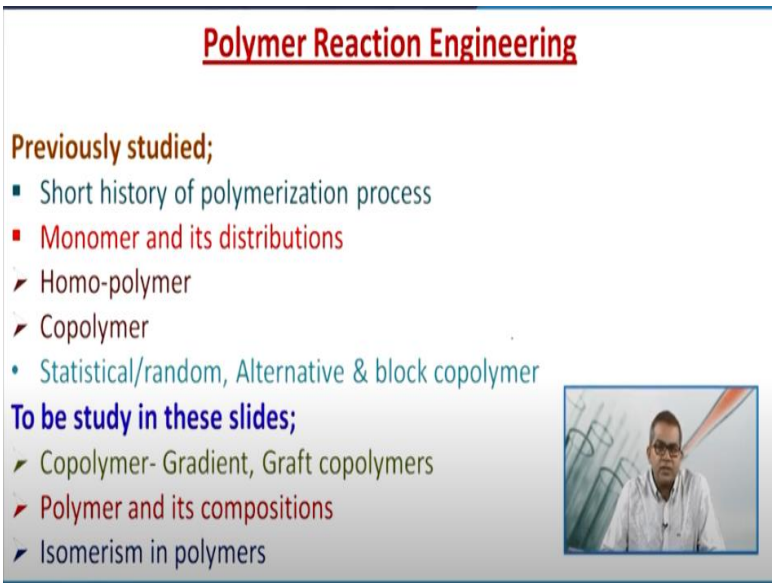

We studied about the short history of the polymerization process, monomer and its distribution especially with respect to the homo-polymer, copolymer, statistical and random alternative block copolymer etc. Now to enhance our knowledge about these

kinds of a polymeric system, in this particular segment, we are going to study about the gradient and graph copolymers.

Apart from this, we will discuss about the polymers and its composition especially with respect to the molecular weight distribution and the previous lectures if you recall, that we discussed that the polymers may have a different type of chain, may have a different type of random distribution of a chain etc. So, this type of approach affects the molecular weight of the polymeric system.

And precisely we cannot predict because of the presence of various discrete polymeric chains in the system, we cannot predict the precise molecular weight of polymeric system. So, we will discuss about that how we can analyze because the knowledge of this molecular weight is quite essential. So, in that case, we should know that how these molecular weights of polymer are distributed alongside of this polymeric mass.

Then we will discuss about the isomerization process in the polymers.

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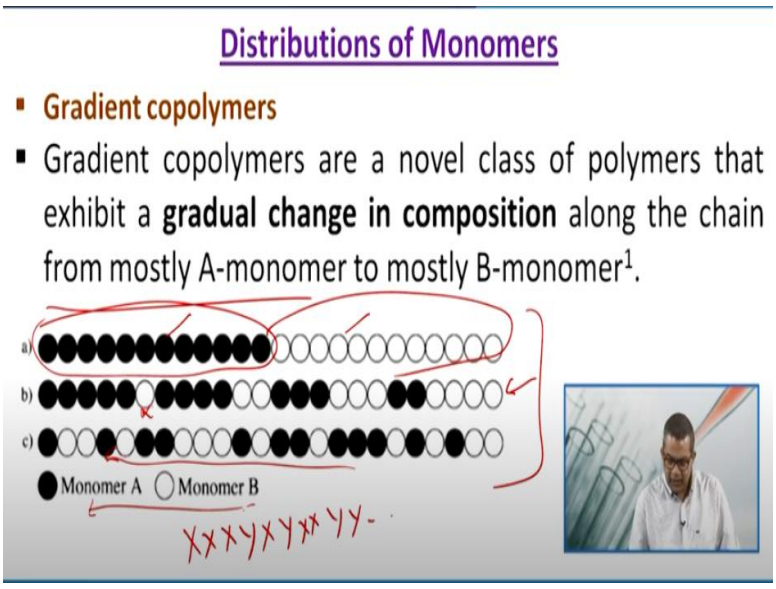

So, let us have a look about several other aspects of polymers especially with respect to the distribution of monomers. The first category in this class is the gradient copolymer. Now as the name implies that they are the novel class of polymers, that exhibits the gradual change in composition as you can see in this particular figure.

Now here you see that initially, now you can see in this particular figure, where you can imagine this scenario that this is the block copolymer type of system. And here there are two monomers, monomer A and monomer B. And if you see in this particular approach, the monomer A is just I mean shifting towards the right-hand side and monomer B is occupying its place and simultaneously there is a gradual change in the system with respect to the entry of monomer B into the system.

So, you can see that here we are having a different class of polymer and that is the called the gradient effect with respect to the copolymer system. Now in other words, if you wish to represent that it can be represented as xxx, like yx, yxx, yy and so on.

So, by this way, it gives you an enough opportunity with respect to the development of a new product, development of NC2 polymerization process, and sometimes you wish to introduce another component within the system, it gives you an enough opportunity for that particular approach too.

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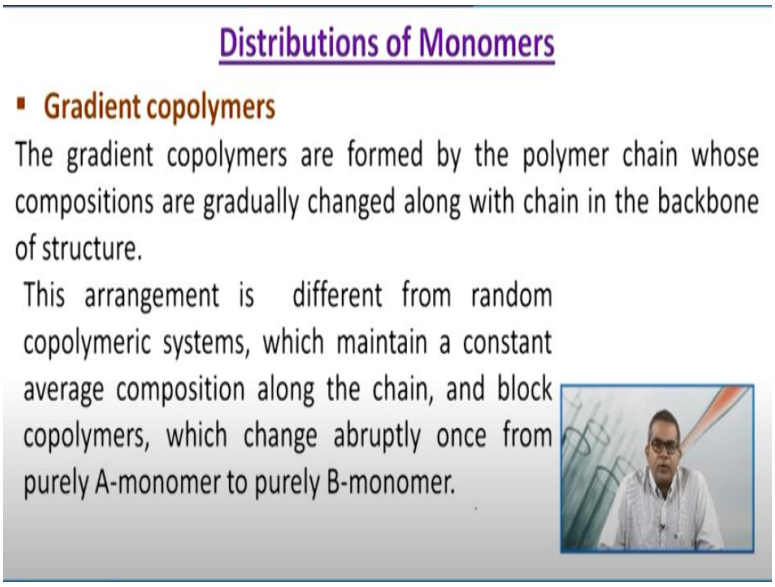

So, they are usually in other words, you can say the gradient polymers they are formed by the polymer chain, whose compositions are gradually changed alongside of the backbone of the structure. Now this arrangement if you see that it is different from random copolymeric system, which maintains at a constant average compensation along the side of the chain and a block polymer, which change abruptly once purely A-monomer to purely B-monomer.

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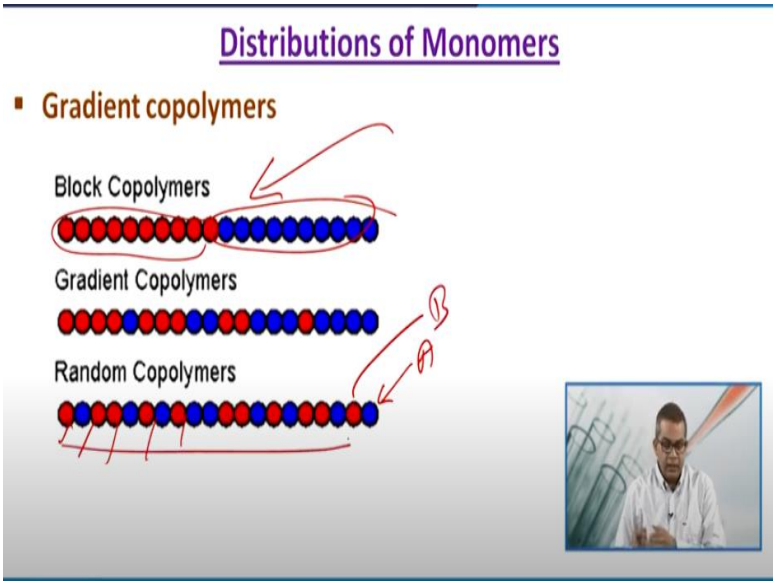

Now here you can see that the difference among all three kinds of polymer copolymeric system. Here this is the block copolymer, you can see, there is blocks of two monomers. Now here you can see this is the random copolymeric system. Here there are two monomers, maybe A and this one is B. Now you can see they are random distribution along the side of the backbone.

But here you see that there is a gradual change or this is referred as the gradient copolymers. So, this particular figure gives you enough opportunity to understand the concept of gradient copolymer system.

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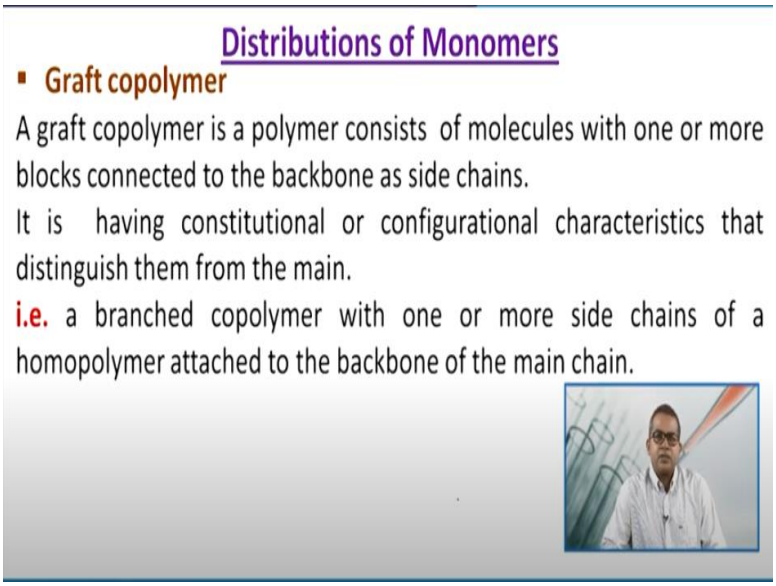

Another approach is the graft copolymer. Usually, this graft copolymer consists of a molecule with one or more blocks connected to a backbone as its side chain. It is just

like that; this is the backbone of polymeric system and you are grafting one polymer along the side of its backbone. So, it is having the constitutional and configurational characteristics that distinguish them from the main.

Now a branched copolymer with one or more side chains of a homo-polymer you can attach to the backbone to the main chain. Now just I am giving another approach about this grafting.

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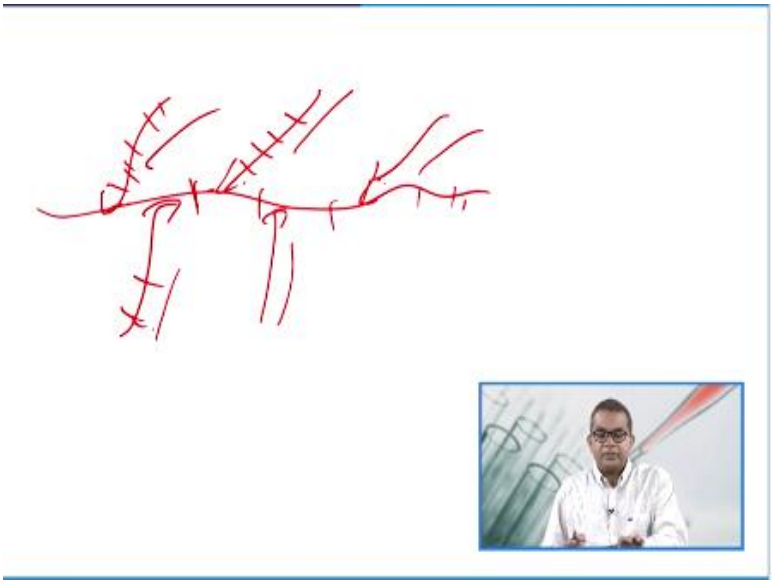

It is just like that; you are having this polymer chain and you are just introducing another polymer. This polymer may be consisting of several monomeric units and you are introducing this one. So, by this way you are implanting another polymer or maybe the same type of a polymer that depends on the scenario. And these chains, these chains along the side of this backbone may have a liberty to grow on its own.

So, this is a you can say this offers a very good opportunity to develop a new polymeric product, specialty polymers etc. So, this thing should be in our mind.

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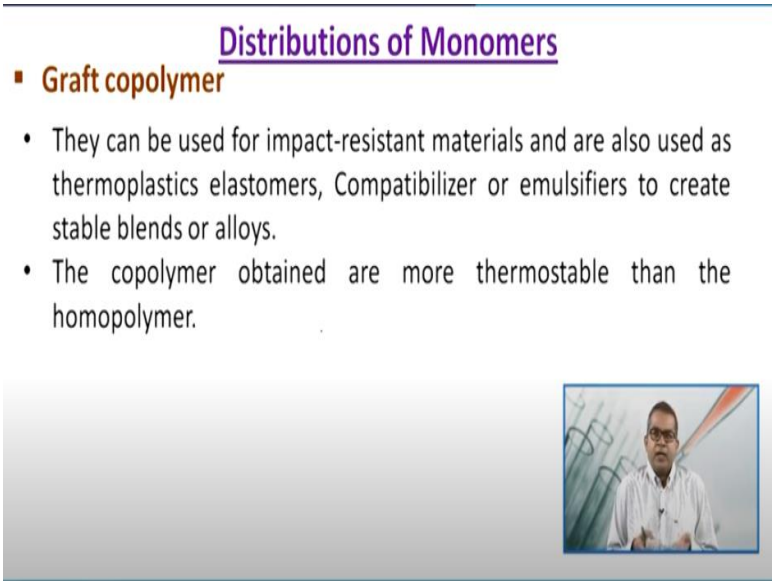

Now these type of graft copolymeric system can be used as impact resistant materials. They are also useful for the various kind of a thermoplastic elastomer, compatibilizers or emulsifier to create the stable blends or alloy. Now the reason for this kind of various approaches is that ultimately, we wish to have a polymer system or a polymer those who are having the desired property.

Maybe as I if you recall the first lecture where we discussed that it should have a flexibility, it should have impact resistance, so right from the flexible polymeric film to the automotive bumpers etc. So, we are having a discrete type of a product profile for every discrete type of a product profile, we must have a different polymeric system. So that is why we are discussing all these kinds of system.

Now thus what kind of a copolymer with the help of a grafting may have a more thermostable than other homo-polymers etc. So, this type of things are you can say that the tailor made.

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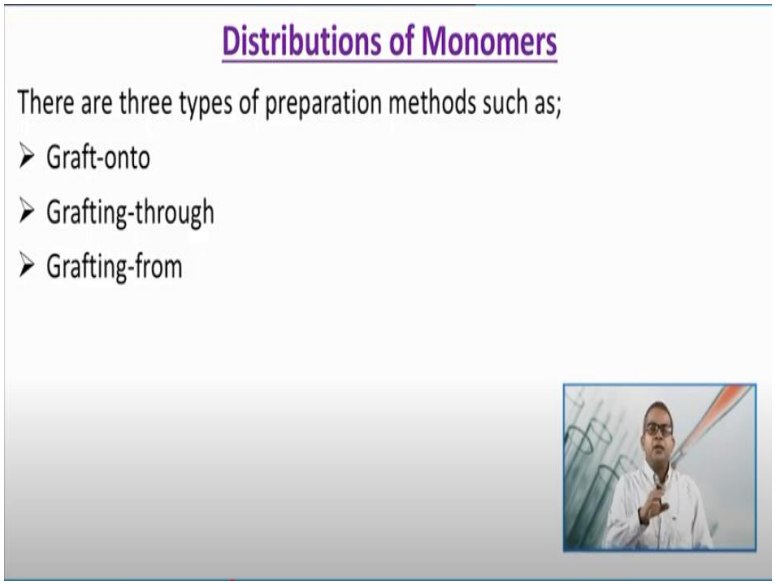

Now when we talk about the different type of graft copolymers. So usually there are three different type of graft copolymeric system. One is the graft-onto. Another one is the grafting-from and another third one is the grafting-through which are used for the grafting of the copolymer. So, this is the three-broad spectrum.

Remember everywhere these distributions or these types of a classification, it all depends on the desire, what kind of the product profile we require, as well as depends on the various operation and process conditions as per the need of this particular product profile.

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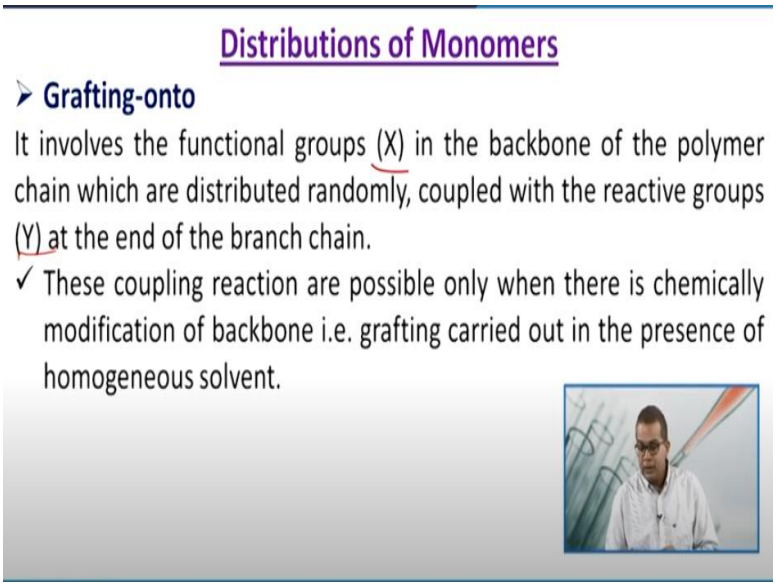

So, let us have discussion about the different classes of grafting copolymer. The first one in this category that is the grafting-onto. Now usually it involves the functional

group, let us say that X in the backbone of the polymeric system or the polymeric chain, which are distributed randomly and sometimes coupled with the any kind of a reactive group say, let us see Y now at the end of this branching.

Now this coupling reaction are possible only when there is a chemical modification of the backbone, that is the grafting carried out in the presence of any kind of a homogeneous solvent. Now remember one thing is essential at this juncture that the presence of reactive group. Now just let us see that how we are performing this type of a grafting-onto.

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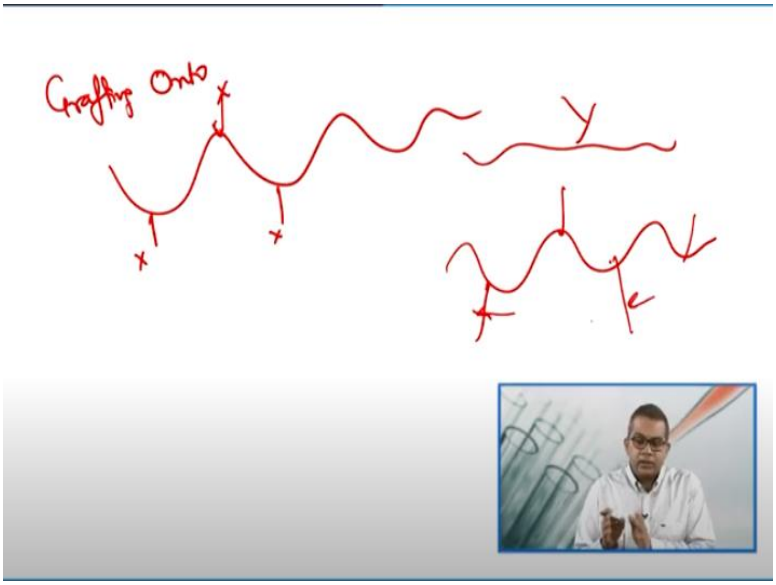

Now here see this is your polymeric backbone, I am not putting it in a straight manner. Now here the x is a monomer. Now you are performing the polymerization reaction with the help of another monomer that is called the y and it represents like this and sometimes it may represent like this. So, this is the basic approach of grafting-onto.

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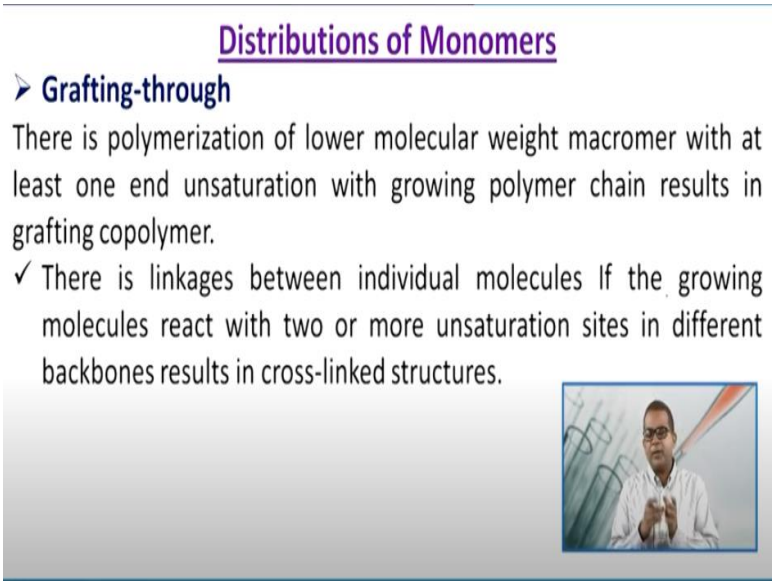

Now another form that is called the grafting-through. Now this is the polymerization system of a lower molecular weight macromer with at least one end having the unsaturation, obviously unsaturation is required for the growing of polymeric chain, because if you recall the first two lecture where we discussed that there is some there must be certain active sites or reactive site so that the chain of the polymer system can grow along the side.

So at least one end should have any kind of unsaturation with the growing polymer chain results in the grafting. Now there is a linkage between the individual molecules if the growing molecule reacts with the two or more unsaturated sites in different backbone results in sometimes it may result the cross-link structure, sometime it may refer as any other kind of a branch structure and so and so on. So, let us have a look about this particular approach.

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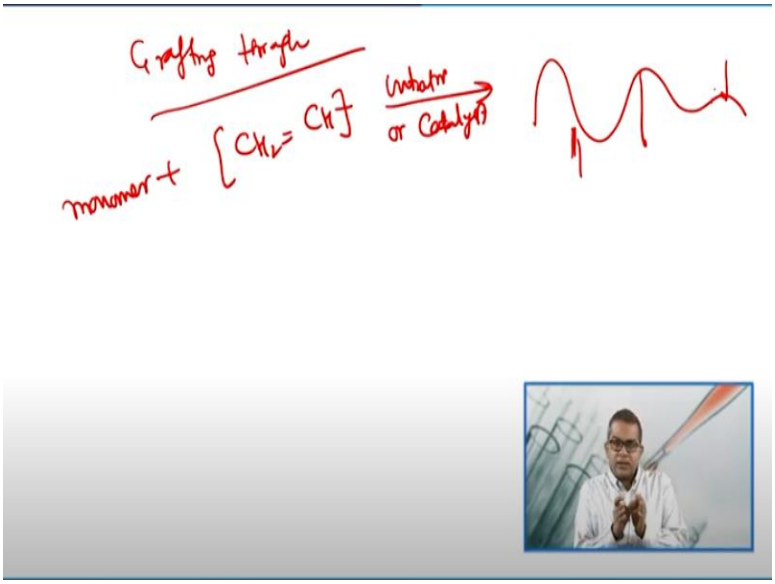

Now this is the grafting-through. I am just giving you the pictorial thing. Now let us have one monomer, maybe any kind of a monomer. Now this is, now for as I discussed previously, that for any kind of polymerization reaction, usually there are three steps; initiation, propagation and termination. So sometimes, if you cannot initiate the reaction in the suo moto, then you require certain initiators.

And these initiators are very case sensitive, we will discuss this approach later on. Or sometimes you may require any kind of a catalyst. So, this can be grafted like this, sorry like this. So, this is the grafting-through type of approach.

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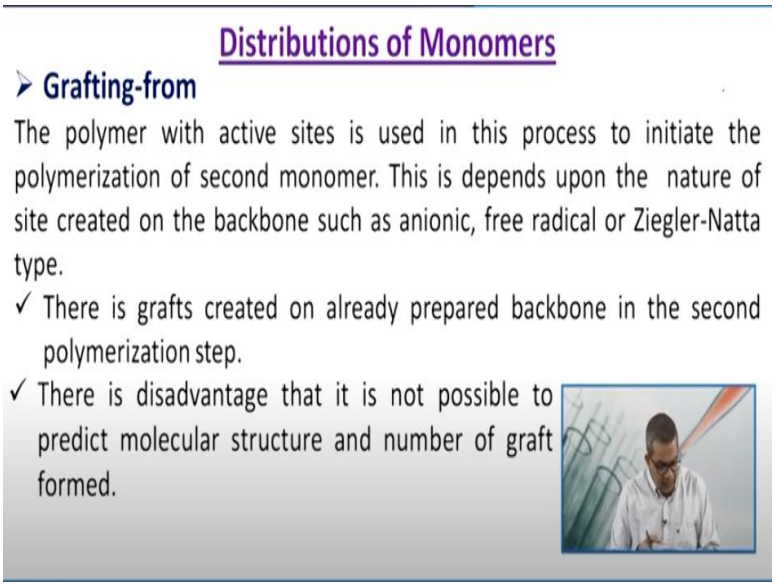

Now another the last type of the grafting copolymer approach is called the grafting-from. Now the polymer usually those who are having the active site, they are used in

this particular process to initiate the polymerization of second monomer. Usually just to make the things bit easy that the polymers sometimes they are having the active sites so that they can initiate the things on its own in its own.

Sometimes, they may have certain other things need to be incorporated during the things like in the previous slide we introduced another initiator, etc. So, in this approach, the grafting from that the polymer with active site those who are having sometimes active sites, maybe their functional group, maybe the unsaturation and maybe double bond, triple bond etc, they can be utilized.

This particular site can be utilized to initiate the polymerization of second monomer not the first one. So this depends on the nature of the site created on the backbone, sometimes maybe anionic, sometimes free radical. And as we discussed in the previous lecture, about the Ziegler-Natta type of. So usually there is the graft created on the already prepared. This is the backbone.

Now there is a there is a graft created on the already prepared backbone in the second polymerization step. Now usually, this particular approach is very beneficial as far as the industrial applications are in question. But there are certain disadvantages associated with this particular approach. Because sometimes it is not possible to predict the molecular structure and a number of grafts formed.

And thereby NC2, they you will not be in a position to predict the either weight average molecular weight or a number of average molecular weight. And these are you can say the fundamental property of any kind of polymers. But you can say precise knowledge about those kinds of a free radical, those kinds of active sites etc., may give you enough success by designing the polymeric system. Let us have a look about this grafting-through.

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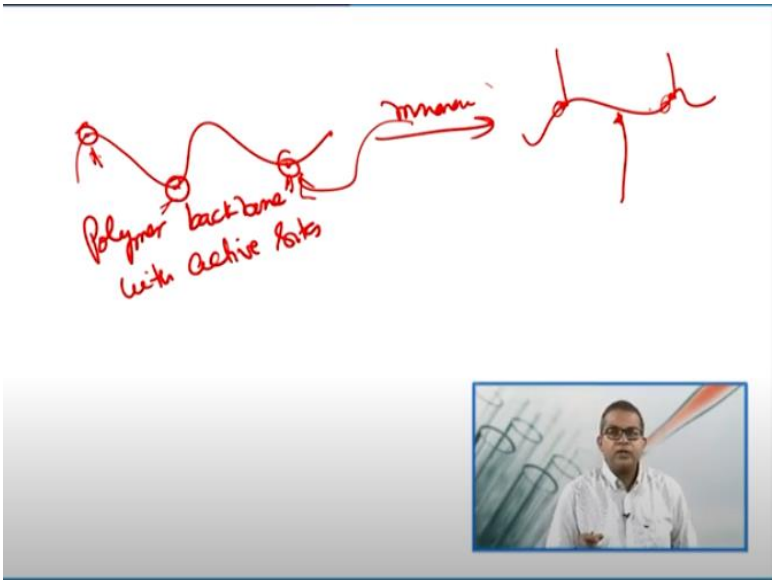

This is you can say the things where you are having the active sites and another monomer through which you would like to graft on it. You may have like this, right. This is the polymer backbone with active sites. You see that there are certain active sites and here is the monomer, probably this monomer may not have active sites. So, you are utilizing these active sites to get this monomer attached over here.

And you see that here, this particular thing is attached. So, this is you can say this is a very beautiful approach for the development of a new kind of a product or to the improvisation of other kind of product.

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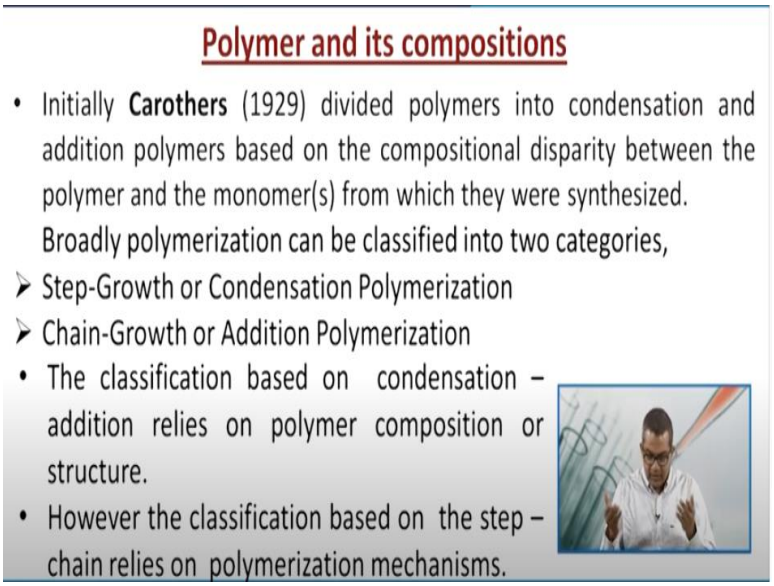

Now next is that, we would like to have a discussion about the polymer and its composition. Now it is you can say it is a very integral part of our polymer reaction

engineering, because you know that different type of a polymeric systems we have already discussed. Now how to achieve those desires, this is a big question.

Like in the previous slides, we have discussed that we are having the grafting on it, though we know that this is the principle. But how to achieve? How to go ahead with the polymerization process? That is the main important thing. Moreover, because as previously we have discussed that whenever we start the polymerization process, then it is a chain driven process.

So sometimes if you keep on going all these kinds of polymerization process, your polymer mass will become bulky. And in that case, you would not be able to control the molecular weight. And once you are not been able to control the molecular weight, then it is a very difficult thing, because you will not achieve the desired result as you require for different type of applications.

So, keeping this thing in mind, the Carother etc., they divided the polymer into polymerization process into different segments like condensation and addition. They are the based on the compositional disparity between the polymer and the monomer which they were trying to synthesize. So, whenever we discuss about the polymerization process, for the ease of our business, we classify the things into different categories.

And do not be confused about the polymerization process and the polymers. Earlier we discussed about the different type of a polymer, different type of a classification etc. But here, we are discussing about the polymerization process just to go ahead with the reaction engineering concept. So, people have divided this polymerization process into various categories, which we are going to discuss.

The more generalized categories are listed, that is step-growth or a condensation polymerization and the chain-growth or addition polymerization. So, the classification based on condensation and addition relies on the polymer composition or structure. What kind of composition do you have? What kind of the structure, maybe the network structure, maybe the linear structure etc.

Now this the classification based on step-growth or a chain-growth polymerization, it relies on the mechanism. What kind of the mechanism is there, maybe the free radical mechanism maybe there, other mechanism etc. So based on the process, based on the requirement this polymeric process polymerization process can be classified into these two broad spectrums.

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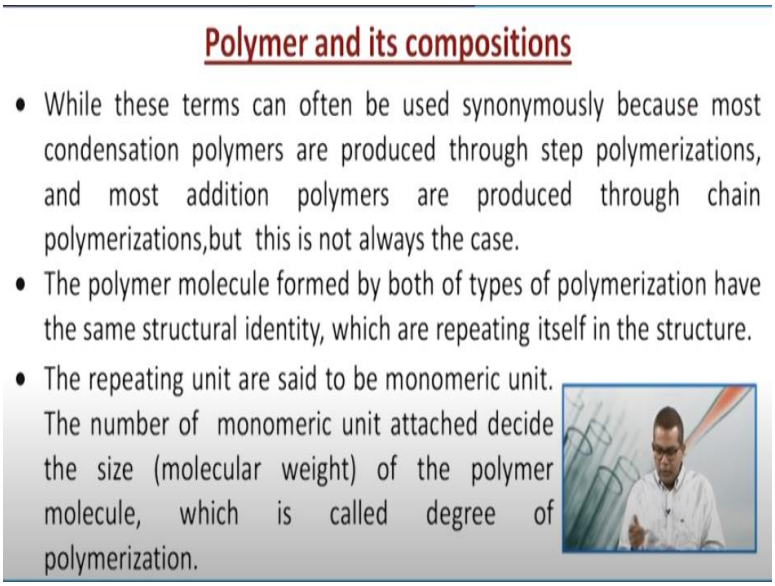

Now these terms you can say can often be used for various kind of synonymous, because most condensation polymers, they are produced through step-growth polymerization and most of the addition polymers they are produced with the chain-growth polymerization. So that is why, if you again come back to the previous slide, there are two broad spectrum, step-growth, chain-growth polymerization and condensation and addition polymerization.

So, the polymer or polymeric molecule formed by both type of polymerization may have the same structural identity which are repeating itself into the structure. Now usually, these repeating units are said to be the monomeric unit as we discussed in the previous lectures. The number of monomeric units they are attached, they decide the size, that is the molecular weight which we were discussing that number, average weight average etc., the molecular weight of the polymer.

And which is usually sometimes the these are called the degree of polymerization.

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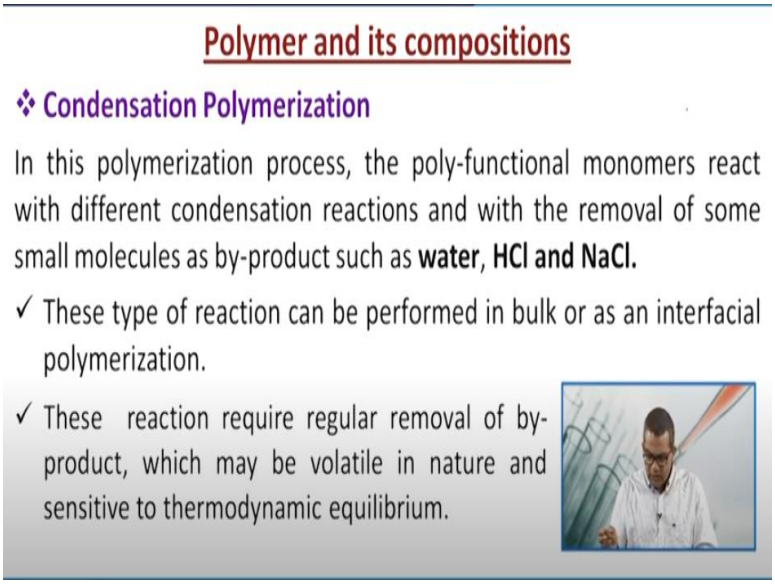

So, let us have a look about the condensation polymerization. Usually, it is a common phenomenon and we will discuss about this the step-growth and chain-growth later on. So, the condensation polymerization process it deals with the polyfunctional monomers. They react with the different condensation reaction and with the removal of some of the small molecules, maybe the byproduct etc., like water, HCl, NaCl etc.

So, you need to continuously remove these byproducts from the reaction stream. Now these types of a reaction you can perform either in a bulk or as an interfacial polymerization. And these reaction requires regular removal of byproduct. That is essential, which may be sometimes volatile in nature and sometime very sensitive with respect to the thermodynamic approach or thermodynamic equilibrium.

So, these types of things you need to take care while dealing this kind of a condensation polymerization.

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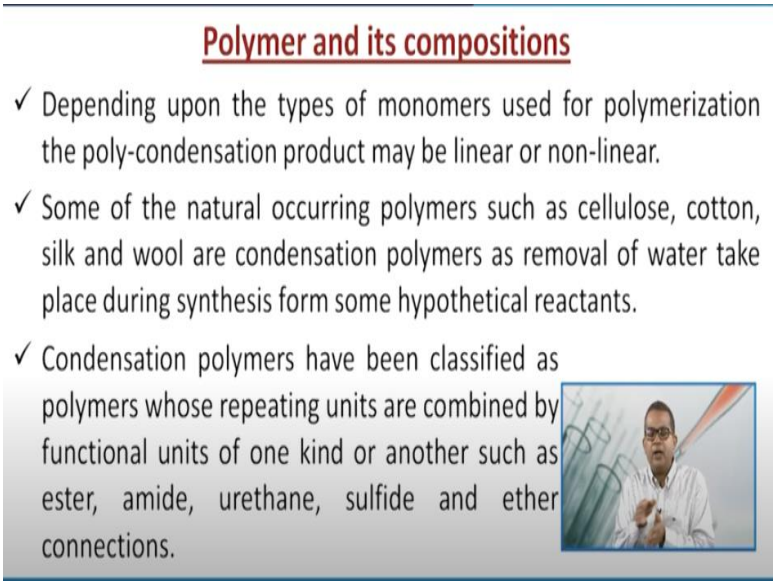

Now depending on the type of monomer, because monomer plays a very vital role while deciding the structure of any kind of a polymer. So usually, the class of monomer used for the polymerization or the polycondensation product sometimes may be linear or nonlinear, maybe the branched, maybe the cross-linked etc.

Some of the naturally occurring polymers like cellulose, cotton, silk, wool, they are the condensation polymers, as removal of water take place during the synthesis from some hypothetical reactants, because these are the natural one, that is why we are using the word hypothetical. So, the condensation polymers have to be had been classified as a polymer whose repeating units are combined by the functional unit of one kind or another, such as ester, amide, urethane, sulfide, ether etc.

So again, I am repeating the things that you require at least one functional group to carry out the polymerization reaction.

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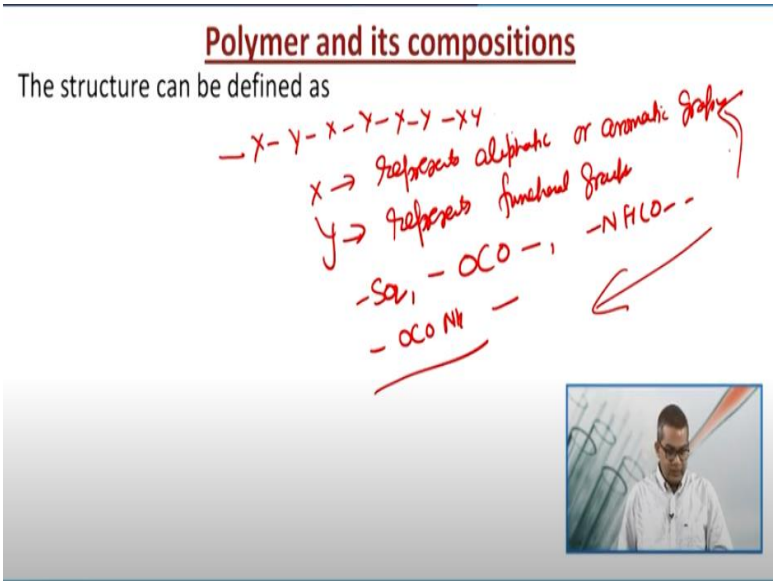

Now the structure or this particular condensation polymerization steps they are defined as like this. Now x represents aliphatic or aromatic groups and y represents functional groups. Maybe the functional group maybe like SO_2 or OCO, NHCO etc. So, you can see that easily that these functional group they play a very vital role for carry out this kind of condensation polymerization step.

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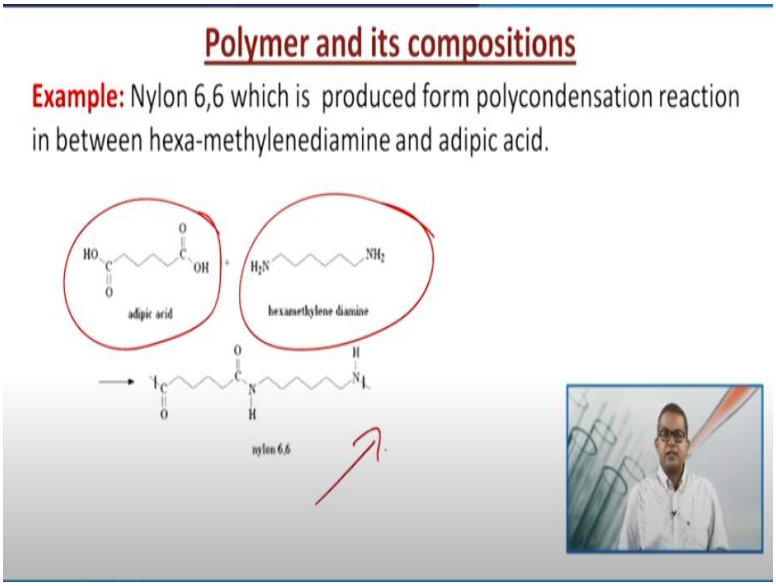

Now another example because that was a theoretical example, the best example in this category of condensation polymerization is nylon 6-6, now which is produced from polycondensation reaction between the hexamethylene diamine and adipic acid. You can see here in the figure that this is the adipic acid. It is combined with hexamethylene diamine to form this nylon 6-6.

Sometimes people refer as nylon 66, it is not the correct one. It is nylon 6-6, which is very. Now in other words, if you wish, then we can give the clear picture.

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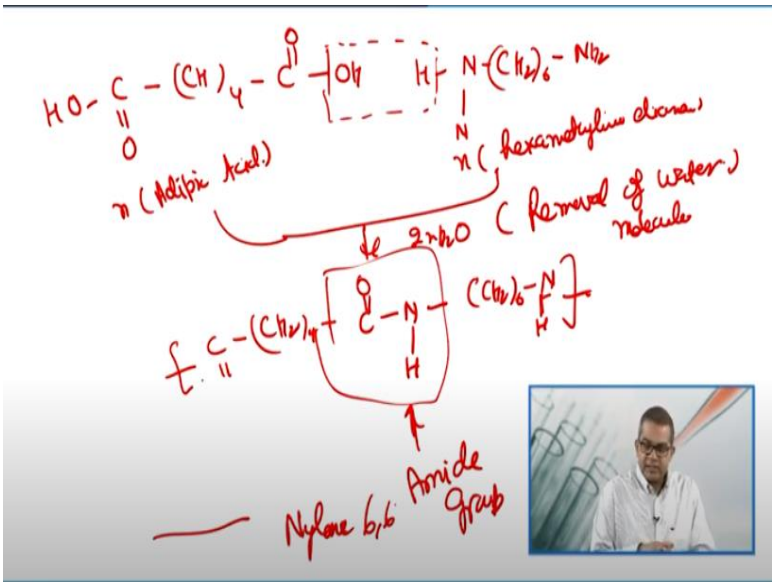

Now here I am giving you the adipic acid which combines with how this combination takes place. Now this is adipic acid. Now this particular juncture combined and this is n-hexadiamine. Now both of them they combine together and $2nH_2O$ that is the removal of water molecule that is essential as we discussed in the previous one. Then they formed the nylon 6-6.

Now this is, now you can see. Now this is the amide group and this is the structure of nylon 6-6. So, this is one example which we discussed in the previous one. Now another example that is the formation of the polyester or polyethylene terephthalate. This is again a very useful product with respect to the day-to-day affair like PET bottles maybe used for the drinking water, packaging of other thing.

So, it is again the useful product of the condensation polymerization. Now usually it is carried out with the help of a reaction between n ethylene glycol and n terephthalic acid. Now have a look about this one.

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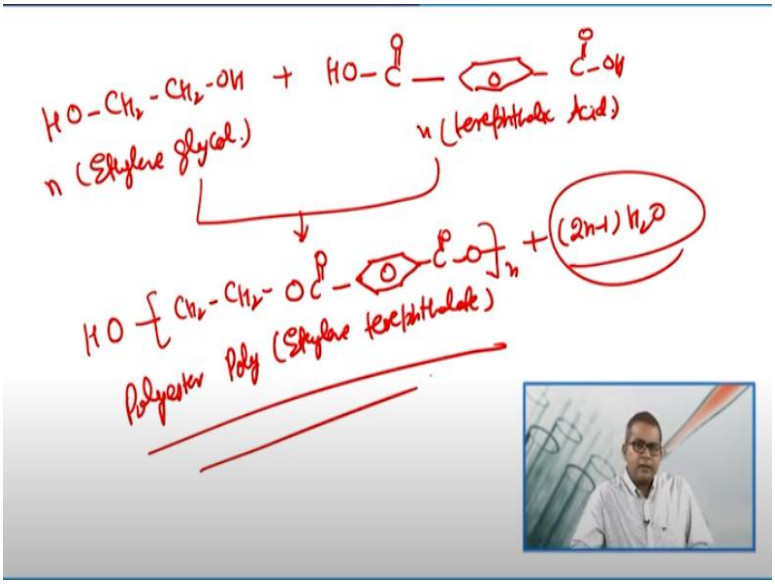

Now this is your ethylene glycol. This is the terephthalic acid. Now you see that there are enough opportunity available for polymerization. There are so many active sites available to this particular segment. Now here there is a formation of, now this is the byproduct which you need to remove continuously. Now this is called the polyester or poly ethylene terephthalate.

So, this is I can say a very useful product and it is contributing a lot to our day-to-day affair or day-to-day life.

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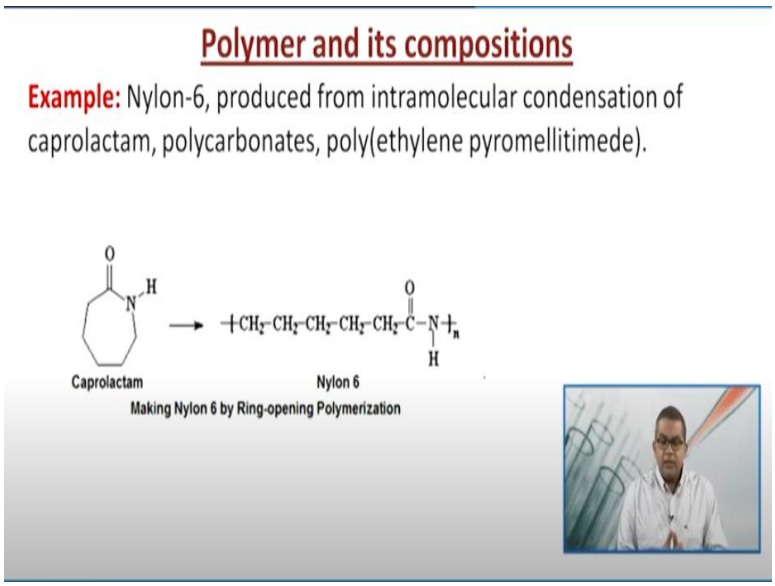

So, at this juncture, we are just aware about this one. Now here you can see another type of thing, which is quite interesting and that is the example of a nylon-6 produced from intramolecular condensation of a caprolactam, polycarbonate or polyethylene

pyromellitimede. Now here this particular reaction is again very important because this is a ring opening polymerization.

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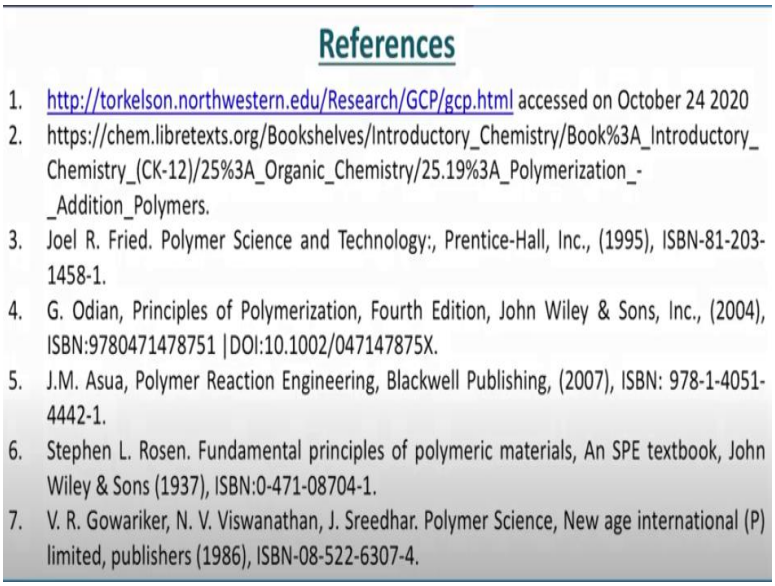

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So, we have discussed about this the formation of nylon 6-6 and PET etc., in this particular segment with the help of knowledge about the condensation polymerization. In the next lecture we will discuss about the addition polymerization which is again provides enough opportunity for the producing of production of various useful product in our day-to-day affair. Thank you very much.