

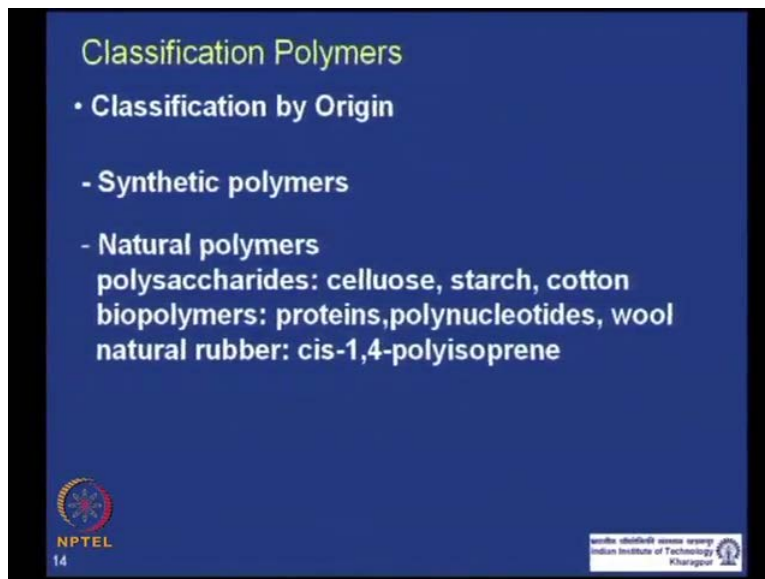
Polymer Chemistry
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Lecture - 2
Introduction to Polymers (Contd...)

Welcome back; in this class, I will continue with the introduction of polymers. I will begin with classification of polymers. Now, at the very beginning, you should remember that there has not been or still there is no single method for polymer classifications, which is generally accepted, but I will do, I will list all the various ways of classifying polymers.

Now, I do not expect student to remember a question, how many ways a polymer can be classified, but students should be aware of the terminology, which are used in this various classifications, so that when they come across these terms, they should be able to relate the meaning of this term.

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Classification Polymers

- **Classification by Origin**
 - **Synthetic polymers**
 - **Natural polymers**
 - polysaccharides: cellulose, starch, cotton
 - biopolymers: proteins, polynucleotides, wool
 - natural rubber: cis-1,4-polyisoprene

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Let us start with the classifications. Classifications can be done. How? Nowhere from a polymer is originated. In the last class, I have said that polymers can be originated from a natural sources and I also said that those are minor class of polymers. Majority of polymers are synthesized in the lab or in a plant from most cases, petroleum resources and some cases form natural resources.

Natural resource derived monomers. So, we can classify as a synthetic polymers. The polymers, we synthesize in the lab or we can classify as a natural polymers in which case, polymers come from nature. For example, polysaccharides which represent cellulose, starch, cotton, biopolymers, proteins, nucleic acids, wool, silk and so on and say, natural rubber, cis- 1, 4-isopropylene. Some cases, we take these natural polymers, and we modify this polymer synthetically for a particular reason, for specific applications. Those cases we can term those polymers as semi-synthetic or semi-natural in any of the ways.

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Classification Polymers

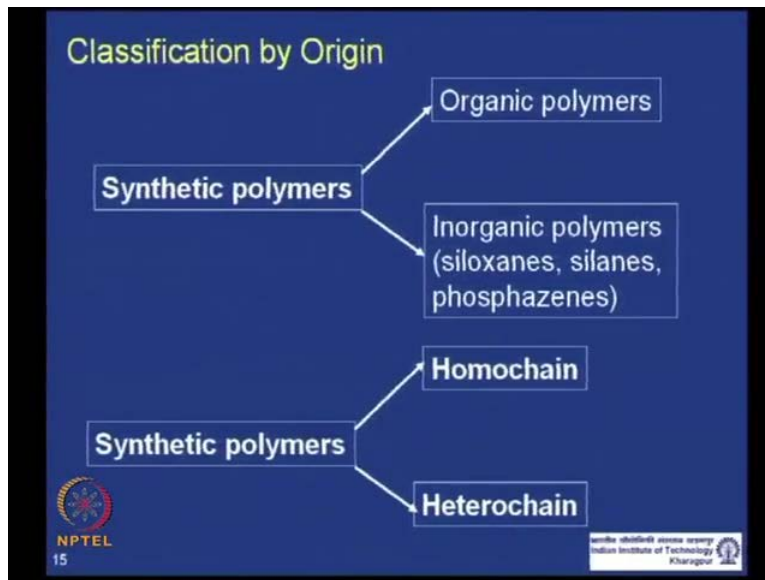
- **Classification by Origin**
 - **Synthetic polymers**
 - **Natural polymers**
polysaccharides: cellulose, starch, cotton
biopolymers: proteins, polynucleotides, wool
natural rubber: cis-1,4-polyisoprene
 - **Semi-synthetic polymers**
chemically modified natural polymers

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So, third category could be semi-synthetic polymers, where chemically, which is chemically modified natural polymer.

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Synthetic polymers can be classified as the organic polymers. The polymers which are made from carbon, nitrogen, oxygen and hydrogen and as inorganic polymers, where beside this elements, carbon, hydrogen, nitrogen, oxygen, you have silicon, phosphorus, boron, sulphur, such elements in the polymer molecules for example siloxanes, silanes, silicon, phosphazenes. These are the examples of inorganic polymers.

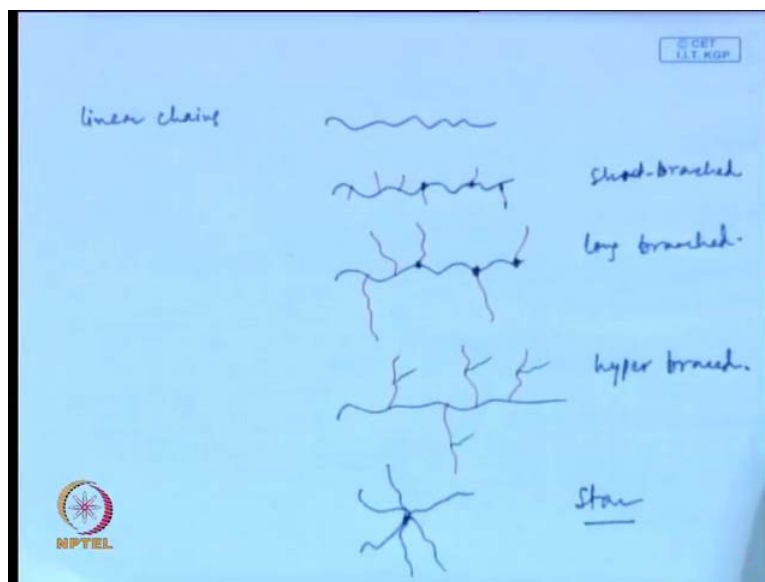
Synthetic polymers can be classified as homochain and hetrochain polymers as well. Homochain polymers mean a polymer which has a backbone of only carbon CCC. For example, polyethylene polypropylene, these are made of polymer. The polymer chain consists of only CCC backbone, whereas in heterogen, in case of heterogen, besides carbon, you might have nitrogen, oxygen and other hetero atoms. For example, nylon has nitrogen, oxygen along with carbon. Polycarbonate has carbon plus oxygen in the backbone.

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Polymers can be classified as according to the chain structure. It can have linear chains like this.

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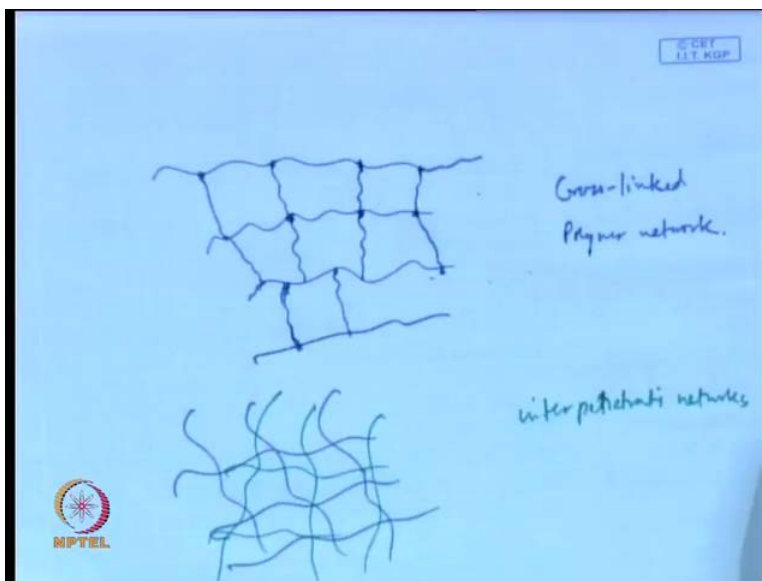


It can have branch chains, like you have this linear polymer plus you have these branches. You can have branches like this or you can have branches like this as well. Now, the main difference between these three branches chain in all are that all of these three are called branch chain

polymers. In this case, the length of the branches is much smaller compared to the length between two branching points, whereas in this case, the length of the individual branches is comparable to the length between two branching points and in this case, branches also have sub branches. So, in this case, we call this as short branched chain. Short branch and this is long branch and this is hyper branch.

Now, special type of branching if you have polymer like this where branches is coming from a single point, you get a star polymer.

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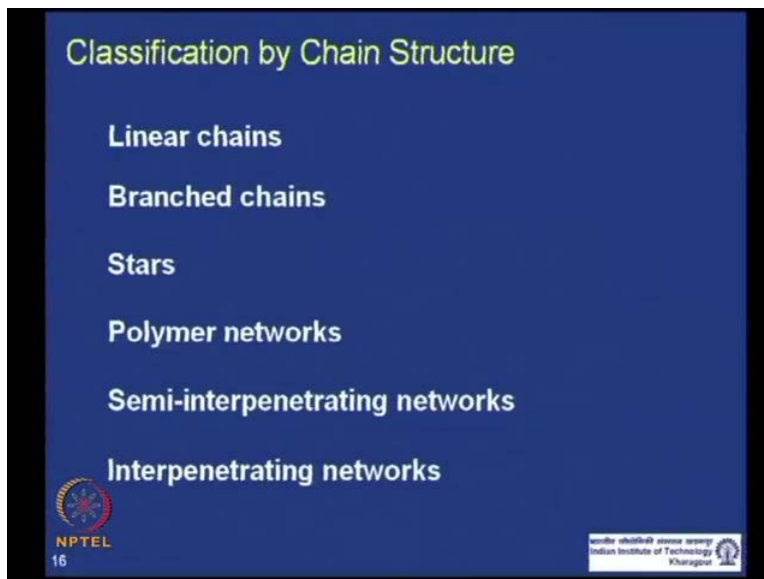


Now, you can also have network polymers. For example, if I have different chains in polymers which are connected, covalently connected like this and so on, then this entire polymer is cross linked, so that this individual chain does not exist. If you take, if you move one chain, the entire network will come along with it and this is called polymer network or network polymer.

Now, you can have a mixture of such networks. In a same sample, you have mixture of. If you have mixture of two networks, then this network will penetrate with each other and then, we call this as interpenetrating network. If I just show in some colors, different colors, you can have two networks inter twingled each other. So, you have interpenetrating network and in another case, you can have one of this network as link one of network along with long chain linear polymers.

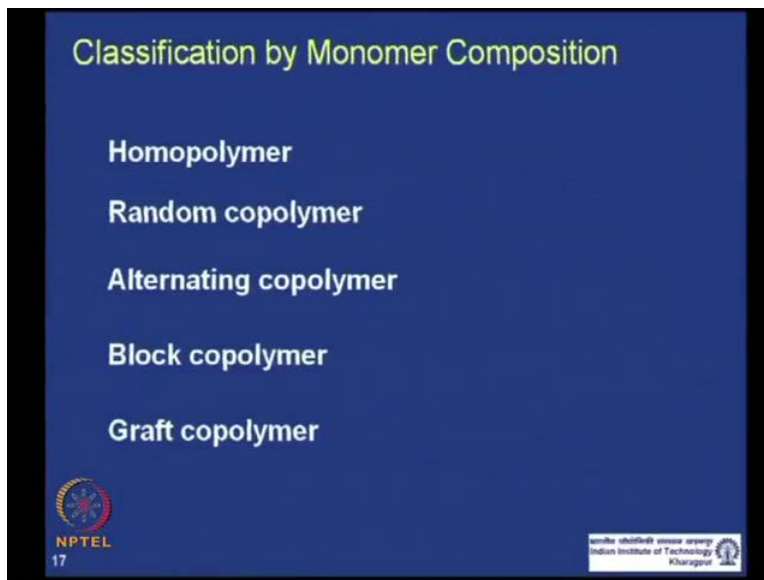
In that case, we call that system as a semi-interpenetrating network, where one of the constituents is linear chain polymer and another one is network polymers.

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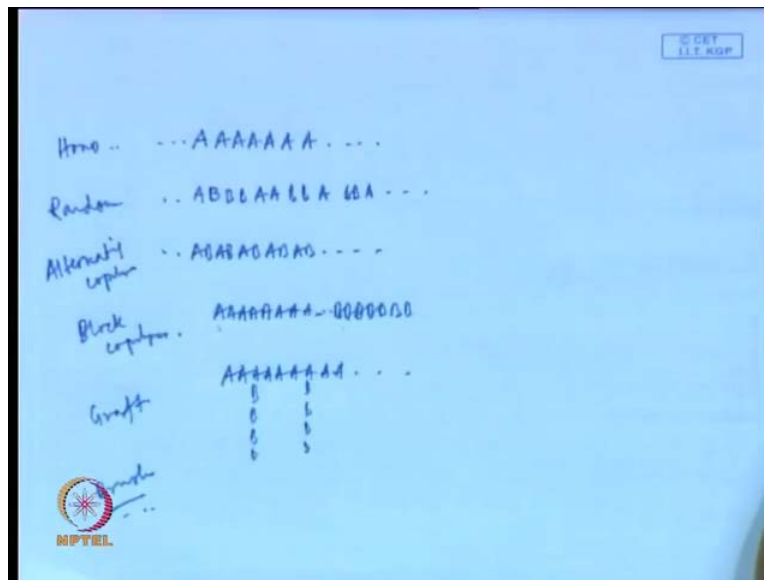
So, in that case, we call as a semi-interpenetrating and when both or more than one networks are inter twingled each other, then you call as interpenetrating network.

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Polymers can be classified according to the monomer compositions.

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Homopolymer, if you have a monomer represented by and linked with each other, then we call as a homopolymer. Homopolymer can have polymers made from two different monomers, say A and B as said in earlier classes, earlier class. Example given is polystyrene and you know polymer made up of styrene and MMA. Then, you can have copolymers.



Now, copolymers can be different molecular structures. They can be present in the polymer chain randomly with no order, something like that where you do not have any order of placement between any orders of placement of the monomers. They are present randomly. They may call random copolymers. If they are present alternatively, then we call alternating copolymer.

Now, if these two monomers are present like this where it is sort of combination of two small blocks of A and B, so it is like oligomer of A or polymer of A which is linked with oligomer or polymer of B. This is example of block copolymer and there is another version of the block copolymers, where you might have a backbone of homopolymer and so on and from which you may be hanging chains of another block, then we call this as a graft copolymers. You can extend this in 3-D and have this as a brass polymer where you have a backbone, two dimension and these brasses are hanging from the base. So, you can have brass polymers and so on.

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Classification by Chain Configuration

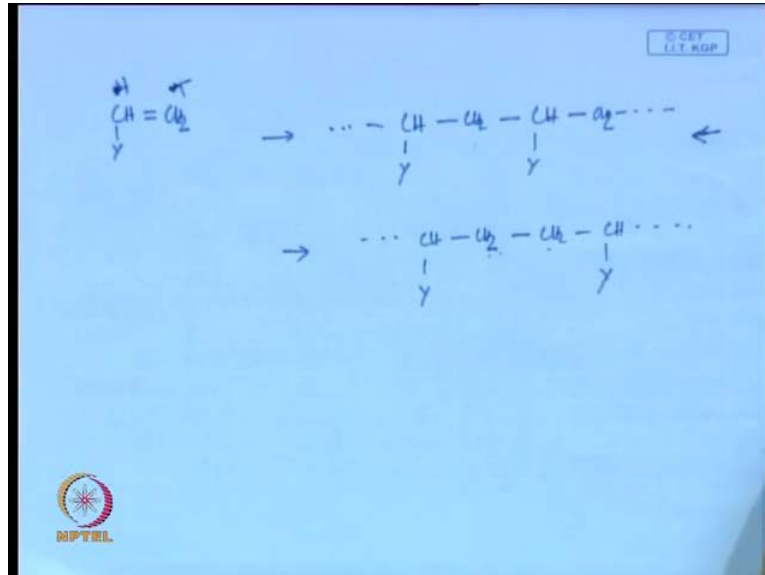
- **Monomer orientation**
 - Head-to-tail
 - Head-to-head



18

We can classify polymers as a chain configuration.

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For example, if I take a monomer like this, it can make polymers in two ways and so on, where if this is head and this is a tail, then polymer is formed by linking between head and tail and so on. So, it is a head and tail. Polymer or these polymers can be also imagined like this, where head

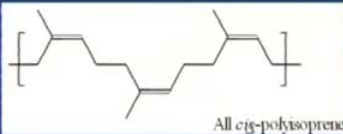
and head is linked and a tail and tail will be linked to next monomers. So, that is a head and head to head polymers.

Now, in practical sense, in most of the cases, you know exclusively almost every cases, when you synthesize a polymer, you get head or tail, head to tail polymers and you rarely get unless you make specific arrangement to make such a polymer, you don't get head to head polymers.

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Classification by Chain Configuration

- **Monomer orientation**
Head-to-tail
Head-to-head
- **Geometric or cis-trans isomerism**

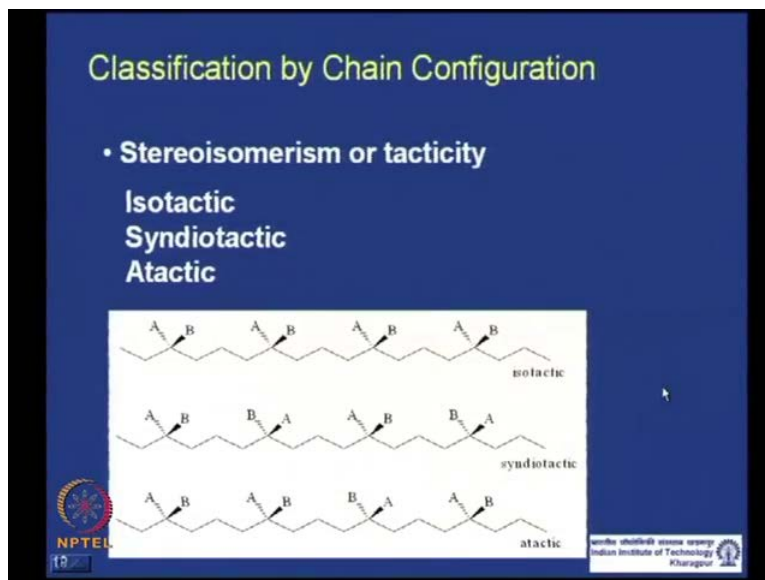


All cis-polyisoprene

The slide features a blue background with white and yellow text. It lists two categories of classification: 'Monomer orientation' (with sub-points 'Head-to-tail' and 'Head-to-head') and 'Geometric or cis-trans isomerism'. Below the text is a chemical structure of a polymer chain with three repeating units, all in a cis configuration. The structure is enclosed in brackets with bonds extending through them. The text 'All cis-polyisoprene' is written below the structure. In the bottom left corner, there is a logo for NPTEL (National Programme on Technology Enhanced Learning) and the text 'NPTEL'. In the bottom right corner, there is a logo for the Indian Institute of Technology Kharagpur and the text 'Indian Institute of Technology Kharagpur'.

You can have polymers as geometric isomers like in this case cis-iso, poly-iso from all the monomers are arranged in a polymer in a cis arrangement. Now, you can have them in trans arrangement or a cis-trans arrangement as well. So, that gives you geometric or cis-trans isomerism isomers.

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You can have stereoisomers or which you call in polymer term, different tacticity. If in this case, the (C) centers or this have similar geometries, all these monomers are linked with same geometries are stereo stereochemistry, then we call this as isotactic. If they have alternate stereochemistry next to next monomers or next to repeating units, then as call syndiotactic, and if the stereochemistry of the repeating units is randomly placed, there is no order and then, they are named as atactic.

So, if the repeating units have same stereochemistry, all the monomers, all the repeating units' chemistry called isotactic. If they are alternate one after one, then if you call syndiotactic and if there is no order, it is placed random and then, we call as atactic.

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Classification by Thermal Behavior

Thermoplastics - materials become fluid and processible upon heating, allowing them to be transformed into desired shapes that are hardened by cooling

Thermosets -
Begin as small molecules (low viscosity liquid)

React ("cures") by heat, catalysis, or other chemical means to form an infinite molecular network

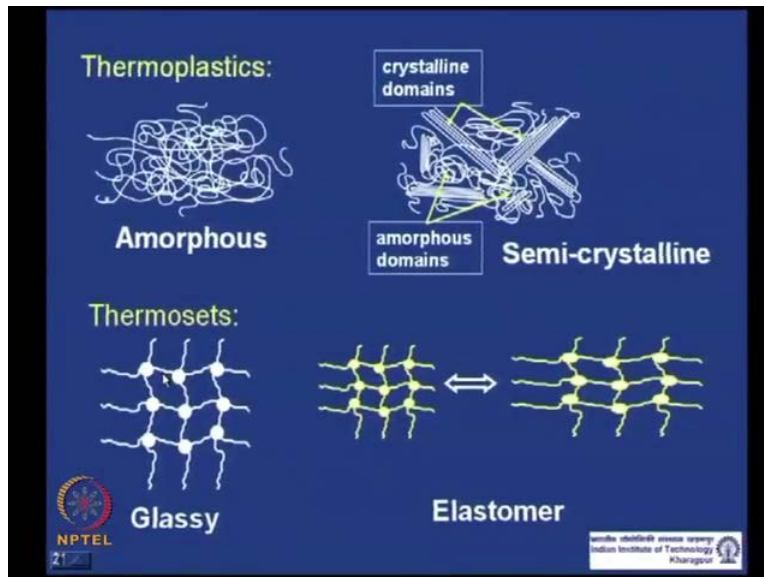
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Polymers can be classified as thermal behavior as well. Now, you commonly think polymer you know where you can take polymer that make polymeric material and then, heat it. On heating, it will become fluid and melt it and you give them a proper shape and cool them. It will harden and occupy or get the shape you are looking for, a similar like a wax where you melt it and when it cools; it takes up the shape of the container. You place the wax and these are called thermoplastics. Plastics is meaning formable. So, it is polymeric materials which can be formed or can be transferred into different shapes by heating and subsequent cooling and this cycle can be done several times. You can make a polymer of different shape and later on, if you melt it again by heating and again, you can reshape it, give it reshape, ok. So, that is this. These polymers are recyclable.

Another class is thermosets, where a polymer is made in C2. You start with small molecules monomers as a low viscous to liquid and then, put it in a container and then, cure it by heating or doing some chemical reaction by that doing this reaction are by heating. It forms a cross linked network. The terminologies I mentioned in last slide, last page where these polymer chains are networked. They are cross linked and frozen. So, once the polymer material has taken the shape of the container where we are doing the curing process, what happen is you cannot remelt it because they are cross linked. The polymers cannot be moved around with each other. So, they

cannot be molten, you know melted by heating. So, they are frozen. They are like having infinite molecular weight cross linked polymer network.

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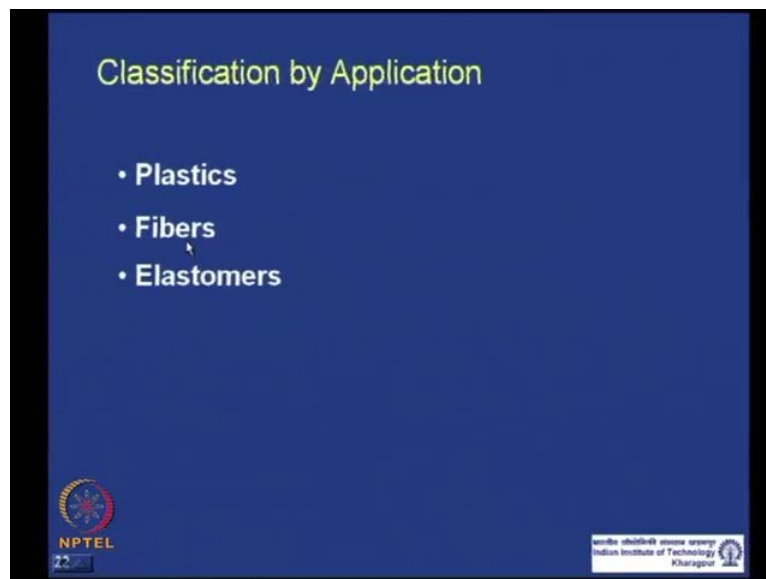
Thermoplastics can be amorphous or semi-crystalline. In case of amorphous polymers, where polymer chains, long polymer chains are placed randomly with no order and in case of crystalline polymers, you have the chains placed in like a crystal. You know they are having a definite order. We know the crystal; the molecules are arranged in a definite order. So, in a crystalline polymer, you have the polymer chains placed in definite order, but it is impossible or it is highly unlikely that you can make a perfectly crystalline 100 percent crystalline polymers because polymer chains are very large and they are flexible. It is almost impossible to align all the chains one after to make a 100 percent or perfect crystalline polymers.

So, we are going to talk about crystalline polymers. There is a mixture of a crystalline region and amorphous regions which do not have any order. So, in more technical sense, it is called a semi-crystalline polymer. Semi-crystalline polymer means a polymer having both crystalline regions and amorphous regions. Amorphous polymers are mostly clear and crystalline because this domain, crystalline domains will scatter light. They are depending upon the extent of crystalline and they can become translucent or opaque as well.

We will talk about this in little detail later. We will talk about the polymer properties, thermosets which we talked about in the last page. They can be glassy or elastomer. As I said, they are cross linked network and if these chains between networks, they have flexibility which happens if the temperature at which they are is above their glass transition temperature. I will talk about glass transition later in more detail but at present, just glass transition means temperature at which they becomes flexible, ok.

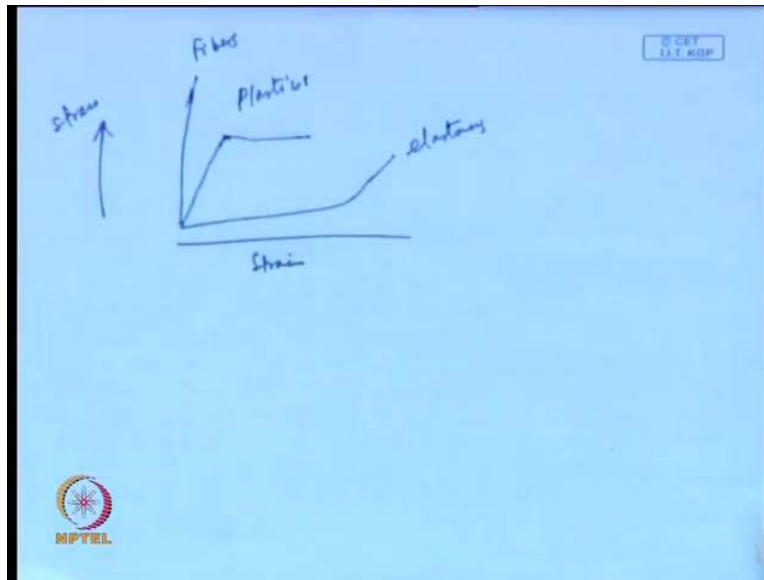
Now, if these chains are flexible in the temperature you are working, then they can be stretched and as soon as you remove the stress, they will come back to the original form. So, it is like rubber. So, you have a elastomer. Now, if these chains are below the glass transient temperature, that means they do not have any flexibility in the temperature operation, then you cannot stretch the polymer because they do not have any flexibility in the thermal motion you talking about. So, you cannot stress. So, they are like glassy thermosets.

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Polymer can be classified according to the applications. They can be plastics, fiber or elastomer.

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If they are defined more from a stress strain curve from the mechanical properties, if I plot strain versus stress or a polymer sample, then elastomers are like small strain, the small stress. You can strain the polymer samples much more. You know how the rubber works. With small pull, they stretch out longer time. So, this is like elastomer. With a small stress, you can strain the sample much more fibers is the extreme case. Other case, other side you take these fibers and strain it. That means to stretch it little bit, you have to apply very high stress.

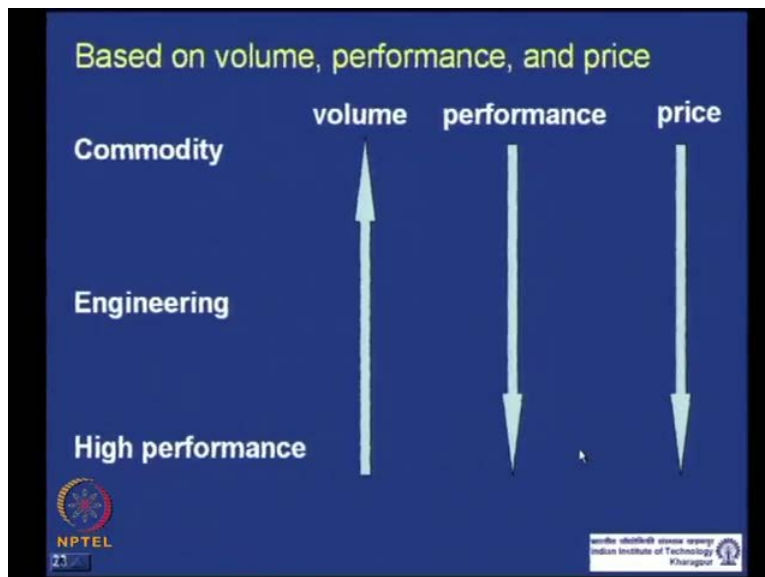
So, you have situation something like this. So, to strain a fiber, you have to apply a very high stress. For plastics are somehow in between this is fiber elastomers and this is plastic. Now, after sometime, plastics yields i will talk about more about this term and it becomes easy to strain if you have this. You know packaging films you have seen probably that when you stretch at the beginning, it takes a little difficult. You have to give a lot of force, but once it starts stretching, that means the samples yielded. Then, it becomes quite easy. So, that is an example of plastic which gives away this type of stress strain curve. We will talk about this more when we come back to the mechanical properties of the polymers.

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Polymers, according to the applications, they can be named or classified as coating gels and additives and so on. These are basically depending up on the applications where you are the polymers is find the application.

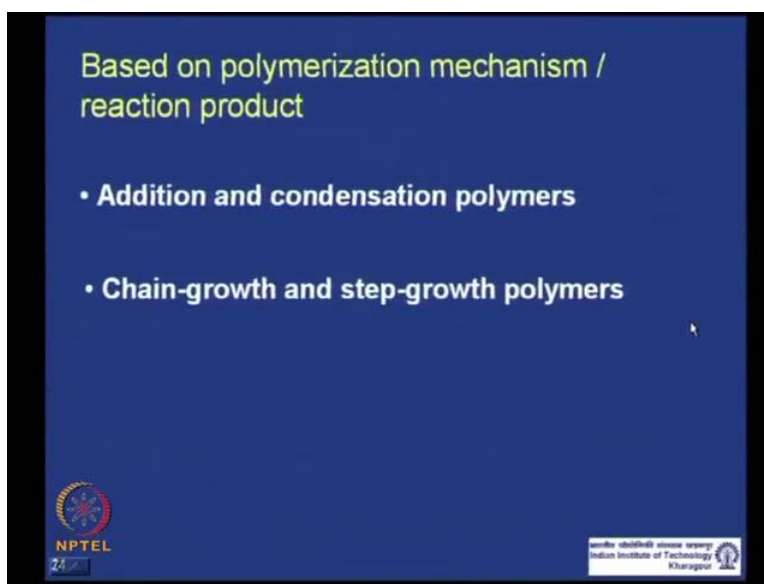
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Based volume, performance and price polymers can be also categorized in two class, three classes. Commodity polymers you know the polymers which you see in a real life in all the times, the bottles, buckets, shoes, clothes and all these things, they are having much volume used heavily and so, the prices are low and performance is also not so good compared to the others classes of polymers.

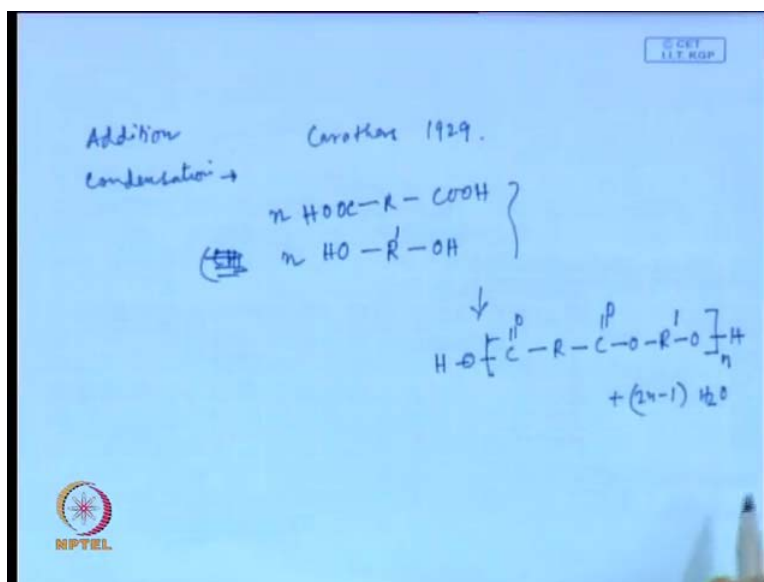
Other two is engineering polymers and high performance polymers and if the price in these three, the volume goes up like this. More volume for commodity polymers, performance goes up in this direction. The high performance polymers are having the highest performance and so does the price. You know nothing comes cheap. So, as you get more performance from a polymer, you have to pay for more. So, prices also go up.

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Now, I will come to the most important classification of polymers. This is last and most important. It is based on the polymerization mechanism and the reaction product. Depending upon the reaction product, you can classify polymers as addition polymers or condensation polymers and depending upon mechanism of the polymerization, the process by which polymers are synthesized; it can be classified as chain step polymers or chain-growth and step-growth polymers.

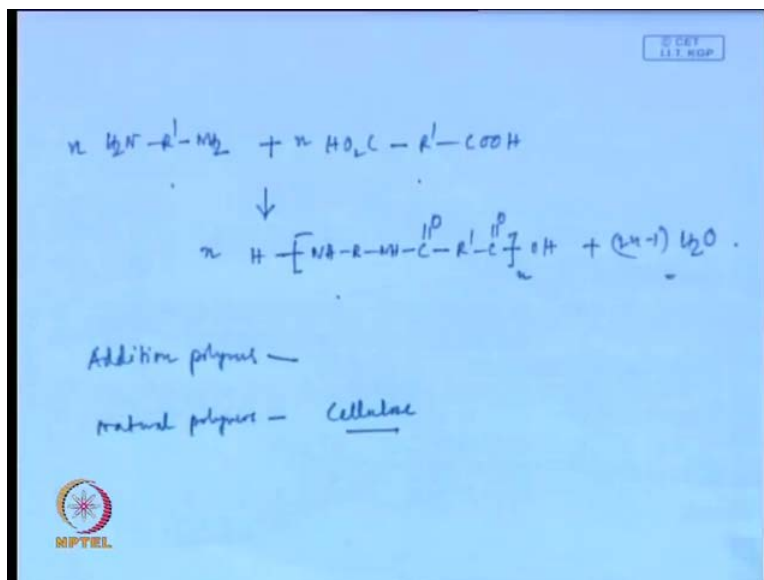
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This term addition and condensation, this classification is originally proposed by Carothers in 1929 and as name suggests, the condensation polymers are synthesized by condensation reactions of the monomers, you know condensation in organic chemistry. Condensation reaction means a reaction between two molecules and subsequent elimination of small molecules. We are talking about making ester between acid and alcohol. You make ester, a removal of a water molecule.

So, the condensation polymers are the polymers where you make or the polymers are synthesized by condensation reaction between the monomers. I will give you a specific example. For example, if I take, I will just give you a write a general way. Now, so if I have plus these two reacts, n molecules of this and n combination of this, it will give you polyesters. To give you more example, I take, I want to make polyamides.

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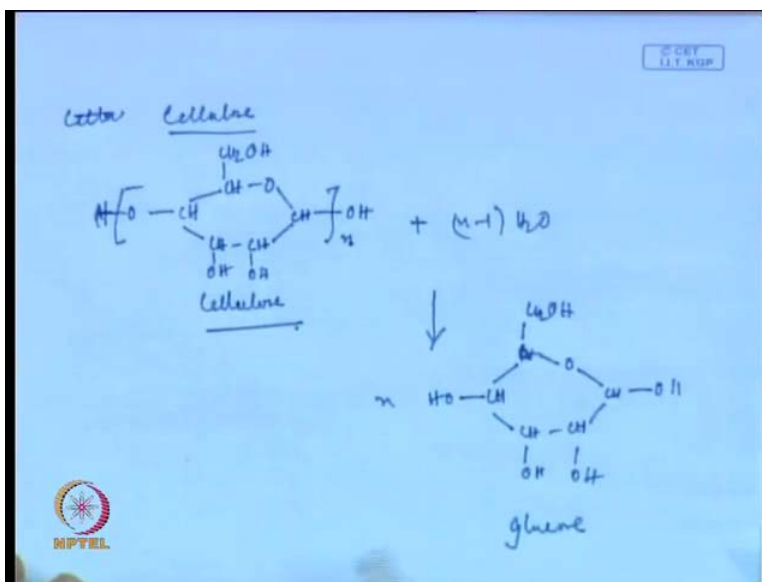


So, I take this molecule and n molecules of this which gives (n) . See, in both the examples, in the last case when we made polyester or in this case we are making polyamides, we have this elimination of this small molecule in this case water. Now, we can extend these examples. Remember the last class we talked about synthesis of polycarbonate from phosgene and based (n) , where the compound or the small molecules which eliminated what HCl . So, all these are examples of condensation polymers, where the polymer is made from condensation reaction of the monomers.

Now, in this particular case, forming polyamides you can make this from diamine and diacids. This can also be made from another variation of these monomers like diamines and diacyl chloride. You can land up in same polymer along with different small molecules or it can be, these polyamides can be synthesized by self condensation amino acids which will make polypeptides. So, same type of polymers. In this case, polyamides can be synthesized by different set of monomers or self condensation of amino acids. Now, what in addition? Polymers, they are defined as the polymers which are synthesized by addition reaction. You know additional reaction means where monomers are just adding with each other and making polymers without elimination of small molecules.

Now, this nature polymers, say like cellulose, how do you define which class they belong? Whether this addition polymers or a condensation polymers because they are not synthesized in the lab, so we do not know the constituent from or the monomers from which are the type of reaction is condensation reaction on a addition reaction by which they are synthesized, but looking at the structure, what we can anticipate or we can imagine or we can hypothesize, monomers form which they have been synthesized, they can be synthesized in the lab or in other words, the polymers can be degraded to some other small monomers, monomeric molecules, hypothetical monomeric molecules from which this can be synthesized.

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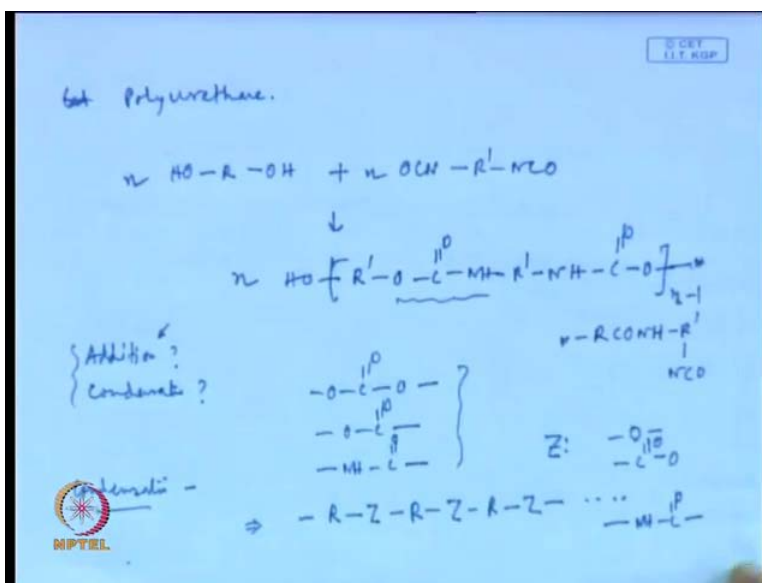
Now, I will give a proper structure, so that you get (()). Now, this is cellulose. Now, it can be degraded easily to this poly molecule which is nothing, but glucose. So, though this is a natural polymer, but if we imagine monomers like this from which they are formed and in this case because you imagine or you hypothesized that these are formed to a condensation reaction, most of this natural polymers are classified as a condensation polymer.

Now, these two polymers condensation and addition polymers, they are often used synonymously with chain growth and step-growth polymers because most of the condensation polymers are synthesized by chain growth polymer mechanism, and addition polymers are made through a chain polymerization mechanism, but this is not always the case. Students should not

confuse, should not equate the terms with addition polymers with chain polymers or condensation polymers with step-polymers.

Now, next example of polyurethane.

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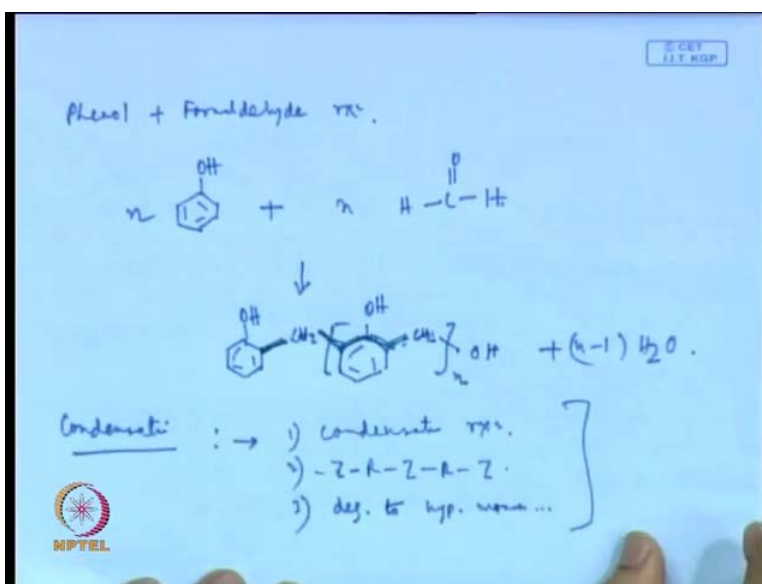
Polyurethane can be synthesized from diol and di isocyanate. Continue this here. So, this is a polyurethane which is synthesized from diol and di isocyanate. Now, what do you call this as addition polymer or a condensation polymer? According to a organic chemistry definition, this is addition reaction. This is not a condensation reaction, but if you compare this polymer along with another condensation polymers, they have similar backbone structure, like if you compare with polycarbonate, this has this structure. If you talk about polyester, we have this. You talk about amide, you have this.

So, this structure, the functionality in the backbone, they are much more similar with your condensation polymers rather than the addition polymers. Most addition polymer have a backbone of carbon, so according to the definition of addition polymers, it should be addition polymers and not the original definition of addition polymers. It should be addition polymers, not a condensation polymers, but you can itself justify it being a condensation polymers, rather than a addition polymer. So, the original definition of addition and condition polymers are modified and now, the condensation polymers are polymers where you have a functional group like this z,

where z could be any of this. It could be oxygen, ether, it could be ester, it could be amide or it would be any of these things, ok.

So, the original definition of addition and condensation polymers where addition was polymers which are made from addition reaction. Condensation polymers were the polymers which were synthesized from the monomers by condensation reaction got modified and now, condensation reaction is where the polymer contain or a functional group at the backbone. You can have a general representation of the backbone structure like this, where z represents any of the functional groups we talked about and any polymer which does not have this structure, we call them as addition reaction. Now, that did not solve the entire problem. If we give next example, then that will be clear.

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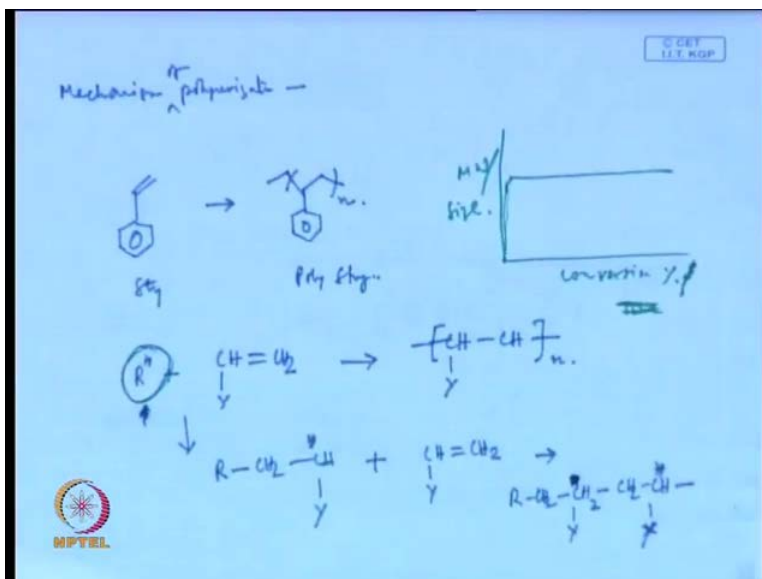


We talked about very old phenol plus formaldehyde reaction. This gives a polymer like this, ok. Now, with the original definition of addition and condensation polymers, you will definitely classify as a condensation reaction because in this reaction, small molecules are coming out. So, this polymer is formed by condensation reaction, but the definition we came up in the last few minutes back where condensation polymers at this represented by this anything else are called addition polymers. We talked about the backbone of these polymers. This is the back bone.

So, this is the backbone. In this case, what do you see here? There is no functional group in the backbone. These are all carbon. So, according to the definition, just now it should be an addition polymer and not a condensation polymer, but you can clearly see that given a choice, you will probably classify this as more of a condensation polymer rather than addition polymers.

So, now the definition is the classification is done by summation with conditions. For example, condensation polymers are polymers which fulfill any of these criteria. One made for condensation reaction or it has a functional group in the backbone or it can be degraded to hypothetical monomers from which they can be synthesized. At least imagine that they are formed by condensation reaction or by elimination of some small molecules, and if any of the polymers does not fulfill any of these criteria, then we call them as addition polymers. So, once again at present, you should classify condensation polymers. If it fulfills any of the conditions, it is synthesized by condensation reaction or it has a function group in the backbone or you can imagine that it has been synthesized from monomers by elimination of small molecules, and if any of the polymers which does not fulfill any of these criteria, we classify that as addition polymers.

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Now, we will come to the mechanism of polymerization. These two types of polymer, this classification chain growth and step-growth polymers, you take an example like I took in the

class. Styrene, you get polystyrene. I can write a general structure like this. $\text{CH}_2=\text{CH}$ gives polymers.

Now, how do you think that these polymers are formed? In this case, these polymers cannot react with each other just by itself. So, you need an initiator, whether the initiator is radical or cation or an anion, it has to initiate the chain. So, if you react with say this is initiator, you get an active centre here and on which the second monomer gets added and you have this. Don't consider this dot.

So, how these polymers are getting formed? Either the active centre on which next monomer is getting added and third monomer will be added in there. So, you have this type of polymers are getting formed in a chain reaction. Now, in a normal case, in general case, the formation of this active species, they are much lower compared to this step which basically is the propagation step of the polymers by which the chain is formed which means as soon this active species initiates, this is formed, it initiates and the chain formation is completed. I will come to more detail how this gets terminated and all these things, but for time being, we should understand that as soon as this in more often as soon as this active centre is generated, it reacts initiate the chain and the chain is formed.

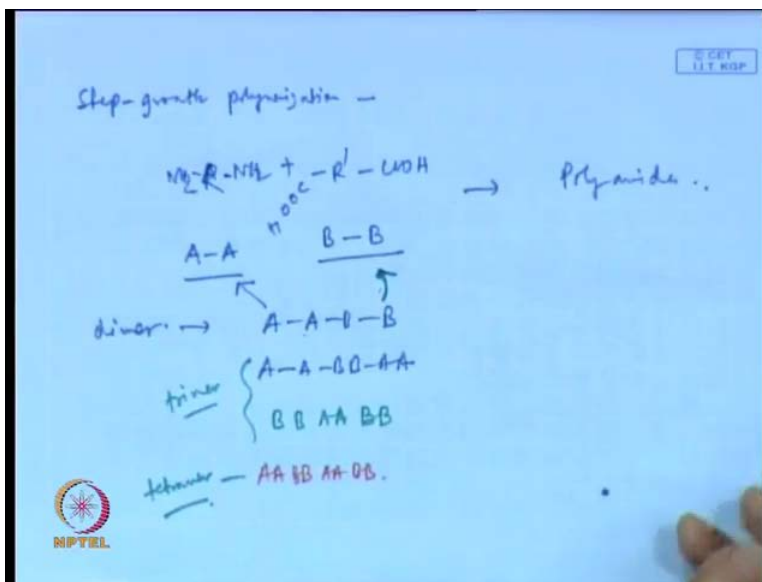
So, the more and more active centers, more and more initiator gets generated in a system, more and more chain form, so if I plot conversion, say percentage conversion means the fraction of monomers is reacted or this appeared from the reaction medium with the molecular weight or the size of the chain or a size. What do we expect with time conversion is, also you can write time, you know with more time. Let us talk about conversion now.

So, at the beginning when this initiator is formed, in most cases they said that it immediately start the activation and initiation and then, complete the chain. So, you have large molecule at the beginning itself. You have a large molecular weight. The more and more this initiator generates in the system, active species more and more chain gets. So, at very beginning itself, you get a high polymer, very high molecular weight polymer in the system and more and more active species get generated, more and more monomers reacts. So, more and more polymer chains are formed. So, what is happening here? At the very beginning itself, the polymers, large polymer chains are forming and as time goes, the conversion happens. More and more reactor you get

such the number of such polymer chains increases with conversion. The more conversion means more number of chains. Polymer chains are getting formed; it is not the molecular weight increases.

So, with conversion, more and more polymers chains are getting formed. So, if I stop, say the reactions somewhere here after 10 percent conversion or 5 percent conversion, what do you see? What do we expect in the system mixture? 5 percent conversion, that means 90 monomers are left in the system. So, you get plenty of monomers, 95 percent monomers. What about the fate of that 5 percent monomers which got converted, no which got reacted? This is all most all of them as formed belong chain polymers. So, along with that 95 of monomer present in the system, we get the other part as a long chain polymer molecules. So, even if you stopped at the very beginning with a very low conversion at say 5 percent, you see high molecular weight, polymers, monomers and the initiator in the medium. If you stop here as a 95 percent level, then you see lot of polymer, large chain polymers and the small amount of monomers and the left over initiators, ok.

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Now, I go to the step growth polymers, and then come back later to compare between these two. Now, say I take a monomer NH_2 , say RNH_2 R dash COH CO OH forming polyamides. I write this as AA and this as BB . This is diamines and this is diacids. These two monomers can react by

itself. It does not need any external initiator like chain polymers. As a matter of fact that you need catalyst to accelerate the reaction, but you do not need in true sense, you do not need an external initiator like in the case of chain polymers.

Now, how this will react? How do you form polymers? First, this will react. Two monomers will react and form like this, species like this. So, this is dimer. Now, this dimer, the choice of reacting with itself or has a choice of reacting with any of the two monomers, if it reacted with this, so you get a BB, again AA. If it reacts with this, if it reacts with this, then you get BB AA and BB, ok.

Now, if it reacts with itself, then you get BB AA BB. So, you form these trimers. This is a trimer consists of monomer molecules and this is tetramer consists of four monomer units or structural units. Now, once you form the trimer, the options increases. It can react with monomer. It can react with any of the dimers or it can react with the trimer itself making the possibilities more and more. If it reacts with monomer, it will form tetramer. If reacts with dimer, it will form pentamer. If it reacts with itself, it will form hexamer.

Imagine, once you form the tetramer, what will happen? It reacts with monomer, dimer, trimer and itself forming dimer, forming pentamer, hexamer, heptamer and so on. So, in the chain reaction, you have the long polymer chain at the beginning itself. In this case, you are not getting long polymer chain at the beginning. What you are getting is the polymer chains are forming in steps, dimer, trimer and tetramer and because these monomers can react this function group, so they will react immediately. So, the conversion of polymer, conversion of monomers will be very high, even at the beginning forming dimer, tetramer or these small oligomers. So, what happen is only at the last, at the end of the polymerization, you will see a long polymer chain are forming, unlike the chain polymers where you have even a small conversion, you get a larger polymer. So, if you stop the reaction in the beginning, you will see a lot of these high conformation conversion, but a lot of these small oligomers.

So, in the next class, I will continue with this condensation polymers, and talk about the, compare between or the difference between chain polymers and chain growth polymers and step growth polymers. Then, it will become more clear the difference in the mechanism of these polymers to polymerization medium. In next class, also I will talk about, continue with the

introduction, more talk about the, we will talk about the nomenclature. How polymers are you know named and also I will talk about give you a prospective of the molecular weight of polymers. You have learned that the polymers have larger molecular weight and invariably, either of these synthetic processes you land up in distribution of molecular. Not all the polymer chains are of same size or same molecular weight. They will be of different molecular size and I will talk about the molecular weight; why you need more definition of molecular weight and so on. So, we will come back to the next class with this.