Principles and Polymer Synthesis
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Lecture - 41
Synthesis of Industrial Polymers (Contd.)

Welcome back. We have been talking about synthesis of a several commercially important polymers specifically the step growth polymers. In the last class we finished with the synthesis of a polyimides, and today we are going to start by talking about the synthesis of polyurethanes. So, the topic remains the same, it is in general the synthesis of industrial polymers.

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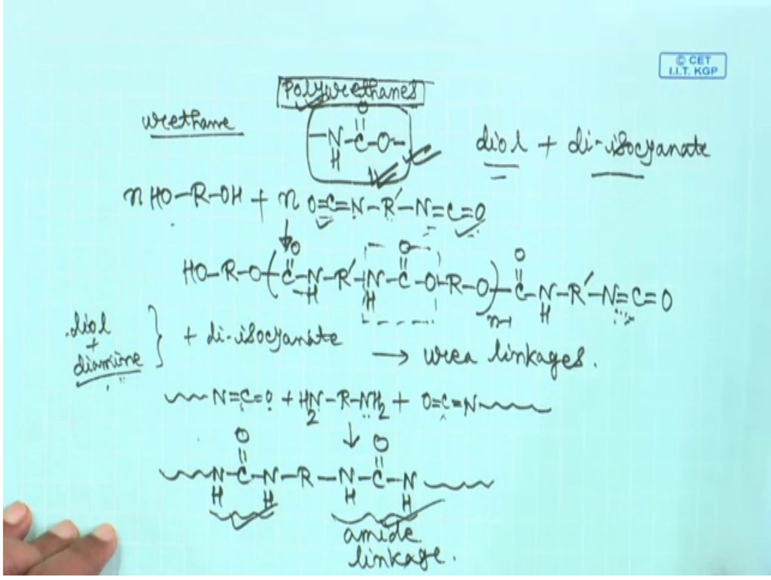

So, let us start the discussion. So, today we are going to talk about polyurethanes. These are also important engineering polymers and polyurethanes they contain this urethane functional group which is this. So, this group is content in this polyurethane molecules. So, this functional group is called urethane.

Now, you might already know from our discussion in the earlier classes that this kind of a linkages can be obtained by reacting an alcohol with a di isocyanate or just an alcohol with an isocyanate then you get the urethane, but if you react a diol with a di isocyanate. Then you will get the poly urethane because these are both are bi functional monomers. So, if you use stoichiometric amount of both. So, you are reacting your diol with di isocyanate. So, this is your isocyanate group N CO and R prime just to differentiate it from the R here and then you have N CO. So, you have di isocyanate if you are reacting stoichiometric amount of both then the product will be a polyurethane. So, on one end there will be alcohol and this is your urethane linkage CO NH and then R prime NH CO O R O ok. So, both size these there is you there is isocyanate moiety that reacts with a alcohols. So, this is in urethane linkage and then the alcohol also has to be in the repeat unit.

So, this N minus 1 units. So, this and then you have to end with another di isocyanate because this is stoichiometric amount one side it will end with isocyanate another side it will end with alcohol. So, this will be NH R prime N CO. So, this is your polyurethane with the urethane linkage. You can already see the this is your urethane linkage that I was talking about. Now, this is a simplistic way of depicting polyurethane synthesis just you take your alcohol diol and you react with the di isocyanate and you get your product.

Now, in actuality what is done is that the polyurethane during polyurethane synthesis diamine is also present in the system. So, basically you have a mixture of diol and diamine that is reacted with your di isocyanate. So, that what will happen is that you will also have urea linkages in your polyurethanes. So, what will happen is that you have diamine present now you also di isocyanate present. So, there will be polymer chains which will end with isocyanate linkage.

Now, let us say this is a polymer chain with isocyanate linkage this wavy line depicts a long chain may be I do not know the length of the chain just in general I am depicting here. And two of these molecules I am just writing down face to face drawing the structure of this, now two of these molecules can react with a diamine because you also added diamine along with a diol in the system and you know that when isocyanate reacts with amine you get an amide linkage.

So, basically in this case it will be urea linkage. So, what will happen is that this can attack here and also this lone pair can attack here. So, ultimately you will get this linkage on this side CO NH. So, we this is urea linkage R and this side also you will have the same urea linkage.

So, basically that in general you will have amide linkage in the system. So, you are doing the reaction of the diol with di isocynate in the presents of a diamine. So, this kind of urea linkages also will be produced in the system. Now something that you need to keep in mind is the fact that of course, when you are preparing polyurethanes you have this, your urethane functionality in the polymer and also when you are preparing polyurethane in presence of a diamine you will have this amide or the urea linkages in the polymer. So, basically in the system you have both urea linkage as well as your urethane linkage urethane linkage. So, both are present.

Now, you also have this isocyanate function that is present in a starting material as well as in your polymer when your one N group is there, now these isocyanate can react with both the amide linkage as well as the urethane linkage by itself. So, what I mean is that there can be side reactions because of course, during the synthesis of polyurethane as the name suggests you will have urethane linkage and since you are having the diamine you will have a amite amide linkage in this case the urea linkage.

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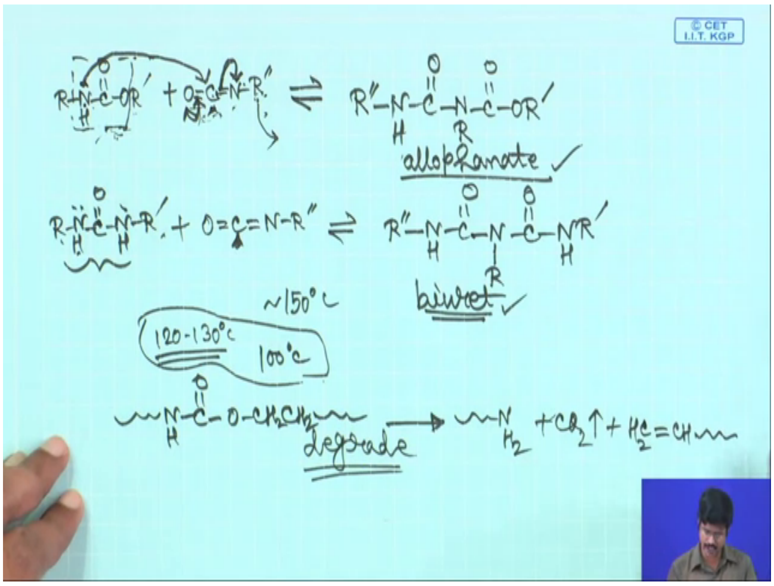

So, your isocyanate that is present in the system say this is your isocyanate I am just depicting it as R double prime the side of that isocyanate on one side, now that can actually react with your urethane linkage that has been produced. So, this could be a polymer you know this R prime a long chain this R can be a long chain in general because this is urethane linkage that is of course, print with there because the polymer is polyurethane an isocyanate isocyanate is also going to be present because this is a monomer this is one of the monomers or this could be also at the end of polymer chain.

That can react with your urethane linkage, so here you have a lone pair on the nitrogen of this urethane linkage that can attack on this carbon. This carbon is electron deficient oxygen is withdrawing nitrogen is it withdrawing electrons. So, it can attack here and it can produce a linkage.

Now, this reaction is reversible. So, I am just drawing from this site the molecule, now this attacks here on the carbon. So, and then this double bond will open up. So, that ultimately and then the proton will be transferred to this nitrogen. So, it will be R double prime NH and this C double bond oxygen will remain and then the linkage of this carbon will be with this nitrogen. So, you will have N R CO O R prime.

So, basically you can just say that this lone pair will attack here it is like that arrow goes this side on this side double bond remains intact and this will come here and ultimately this proton will be transferred here. So, this is your product. So, the linkage that you produce here is called an allophanate linkage. And if this R double prime contains another isocyanate group then it is not difficult to understand that on the side there will be another isocyanate and that can react with another polymer chain let us say this is a polymer chain in which you have been urethane functionality like this. So, this urethane functionality reacted with this isocyanate.

Now, this R double prime if it contains another isocyanate group then after this reaction you have been another dangling isocyanate from this side that can react with urethane linkage that is present in another polymer chain. So, this way there will be cross linking system you can have cross links if you have R double prime, if the R double prime contains an isocyanate.

Also this isocyanate that you have here that can react with your urea linkage that is that is produced in the system because you have a diamine also present during the polymerization. So, in general I am just drawing this urea linkage as this. So, you have urea linkage. Again when your think the reaction you have to be the same way now depending on R or R prime either this side will attack on this carbon or this nitrogen will attack on this carbon.

So, let us say this nitrogen attacks on this carbon this is also a reversible reaction. So, the product will be something like this R double prime NH C double bond oxygen now this nitrogen is attached to this carbon. So, that will be nitrogen directly attached this R will be here this side and then you have CO NH R prime this is called biuret linkage. In this way also you can cross link different polymer chains let us assume these are double prime contains an isocyanate unit in that case this is also a way in which you can cross link different polymer chains.

So, this kind the cross links then will be present in the system when your preparing polyurethane polymers considering the polyurethane. Of course, as I name suggest will continue urethane linkage and also it will continue urea linkage because your diamine is present and your isocyanate is there both in the polymer and the end of the polymer it could be are also in the monomer it is present.

So, this kind of cross links could be produced, but typically these are you see these are reversible reactions and if you heat it up say around 150 degree Celsius, if you heat it up then what happens is that the reaction goes backwards. So, even if this kind of cross links are producing the system that is not sentimental assuming you do not want this cross links. So, because you are doing at a slightly high temperature and then this reaction means reaction we actually go backwards and this cross links will no longer exist in the system we will talk about is sortable we do not want is kinds of cross links in the system ok.

Now, typically you will do the reaction at moderate temperature 120 to 130 degree Celsius. I mean typically greater than 100 degrees Celsius and I mean sometimes what we will do you will also go to lower than 100 degree Celsius not very high temperature. As a as a matter of fact many times you will do around 100 degree or slightly less than 100 degree maybe.

The reason being if you have reaction temperature set at quite a high value then your polyurethane let us draw the polyurethane like this is a polyurethane. If the temperature is high enough then this will degrade and this can produce NH 2 your amine and this carbon dioxide will be evolving as a gas and an alkene can be produced. So, this can degrade at high enough temperature.

So, normally you do not go beyond 120, 110 like that. So, of course, one of the one of the starting materials is a is a di isocyanate di isocyanate monomer and typically what it what you will do is you will put some aromatic rings in the system because you have aromatic rings provide stiffness and they will also provide higher temperature stability.

So, your di isocyanate monomer that you will use normally you will use an aromatic di isocyanate.

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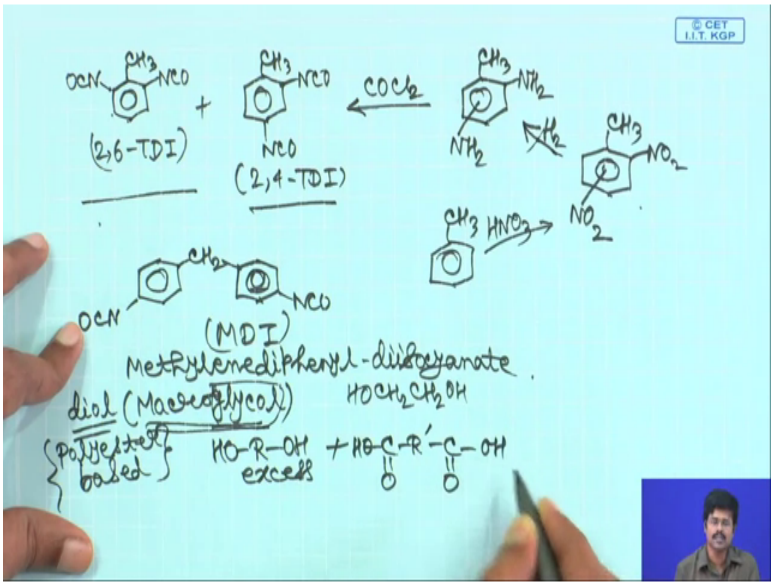

So, the commonly used di isocyanate are toluene di isocyanate. So, you have a toluene and the isocyanate groups could be at. So, this is 1 2 3 4 5 6, 2 and 6 position. So, this is 2 6 toluene di isocyanate or they could be at 2 and 4 position.

Now, the reason I am just drawing it like this is because I am going to show you the synthesis of this from the starting material. So, the basically both will be produced together. So, how can you get this if you go backwards it is coming like this reaction of this diamine I am just putting the other NH 2 like this because is NH 2 could be on this position and on this position it is the mixture of them. So, if you react this carbonyl chloride you will get a isocyanate. And how can you get this particular molecule basically? You reduce the corresponding nitro derivative.

So, we are actually working backwards just show you how the products are get obtained and this nitro units how do you get by simple nitration with nitric acid, simple nitration of toluene with nitric acid will give you this product. So, this is 1 2 3, 3 step and then you can get your toluene di isocyanate. Another di isocyanate is also used quite commonly and that is methylene diphenyl isocyanate. So, you have typical it is called MDI. So, this is methylene, so these are methylene group that is way it is methylene and there two phenyl units, so diphenyl ok, diphenyl diisocyanate all right.

Now, in actuality I already told that you are using a diol you are reacting with a di isocyanate if you see the first page of today that was the reaction that I talked about. Now, normally the diol that you are going to use this diol this will be some kind of and oligomeric system or maybe it is itself a polymer to start with. What I want to mean it will become clearer now.

So, I told you that you are going to use a diol and di isocyanate know this diol typically it is a macro glycol it is a macro glycol. So, how do you get? I mean this is called glycol because suppose you take this diol. What is this? This is ethylene glycol. So, that is why you are saying glycol and it is a macro glycol because it is a macromolecule it is not a small molecule there is there are there are a there are lot of units in between the two end alcohols that is why it is a macro glycol.

Now, there are two kinds of macro glycols that are used one is polyester based and another is polyether based. So, poly ester polyester based macro glycol that is produced by very simple reaction we already talked about that you use a diol and excess of that and you make a polyester out of it. So, you also use a diacid. So, if you react a diol with a diacid and if you have an excess of diol we have talked about this things it is a polyester that is produced and that will be on both sides at the end there will be alcohol because this is in excess.

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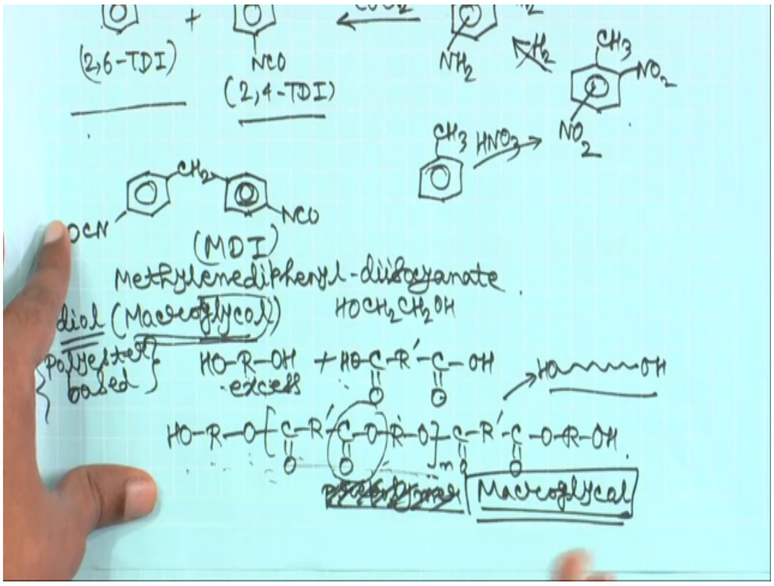

So, typically what you will have is this molecule. So, this is basically a diol that you can use as a starting what you can say is a prepolymer because this is a precursor to the polymer. So, this diol you react with a di isocyanate in order to produce your product.

Now, this diol is a macro glycol because this is obviously, not a small molecule you have a polymer unit here N number of units and this is also polyester based macro glycol because basically this reaction has produced a polyester linkage. So, at the ester linkage and this thing you have talked about before how to prepare polyesters reacted di dior diol with a diacid and you will get a polyester.

Now, this diol is used in excess. So, has to have alcohol at the end of the polymer chine and both sides. So, basically this you can draw up as a chain like this and both sides you have a alcohol. So, this is the kind of diol that you are going to use for your polyurethane synthesis and this is based on polyester.

Now, polyester if you have esters are thrown to hydrolyses. So, instead of polyester based macro glycol you could also use what you call as polyether based macro glycol.

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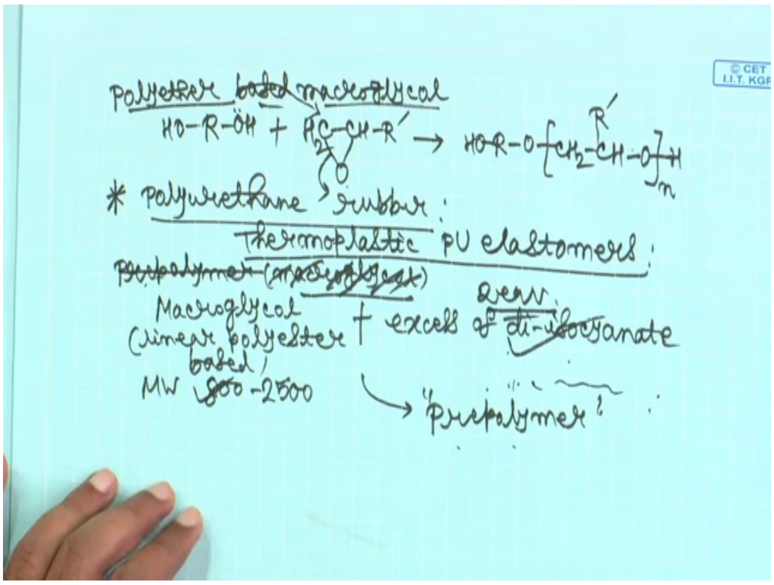

Now, polyether as the name suggests there will be multiple ether linkages what you do is just you react with diol istead of a diacid you react with an epoxide ester and 3 member ring containing your oxygen. So, what will happen? This will attack here this is the less hindered site and this will open up and that O minus can again attack on another molecular this and then the process can go on. So, ultimately the product that you will get is the following.

So, you have an oxygen here and this opened up. So, this oxygen is connected to a CH 2 and then you have CH R prime and this oxygen can again attack and ultimately what will happen at the end you will have a alcohol unit here. So, this is your polyether based polyether based macro glycol. So, we talked about two kinds of a starting diols, one is your polyester based diol another is polyether based diol and we call this diol as macro glycol because this is a macromolecule either it is a polyester or a polyether actually it is a polyether or polyester and both ends are alcohol that is why it is a macro glycol.

So, how to use this macro glycol in order to prepare your polyurethane? So, let us say we will talk about poly urethane rubber preparation. So, basically you are going to talk about the preparation of thermoplastic polyurethane elastomers and I will tell you what the properties of this materials and why there are called like this. So, what you do? So, you start by producing a prepolymer a prepolymer which is basically a macro glycol this you produce by by reacting by reacting a you know.

So in fact, what you can also say just to make sure that your nomenclature is correct let us not call this particular molecule as a prepolymer because that will be confusing. Let us just stick to telling that this is macro glycol we are going to use the term prepolymer in some other case and I am going to come to that let us say this is the macro glycol. So, again, so we will not say that macro glycol is a prepolymer.

Let us say you start with a macro glycol it will become clear in a minute what I want to mean and this macro glycol let us say it is a polyes polyester based macro glycols. So, linear linear polyester based macro glycol and you know this molecule will have a molecular weight in the range of not a very long molecule 800 to 2500. Now, this macro glycol you can react with an excess of di isocyanate and then what you will have is a polymer chain which will end on both sides with di isocyanate.

Of course this is diol. So, this is a alcohol react with isocyanate to produce urethane linkage, but this molecule to start with this is not a very long molecule only 800 to 2500 is the molecular weight and if you react with excess of di isocyanate this molecule will be having urethane linkage as well as at the at the end of the chain both sides you will have isocyanate. And this molecule is not a long molecule and that is the reason why you will call that as a prepolymer this is just to clarify the nomenclature.

So, you react with your your macro glycol with an excess of di isocyanate typically you take two equivalent of di isocyanate two equivalent. And normally you will use this diisocyanate methylenediphenyl di isocyanate MDI. And then after this reaction you get what you call as prepolymer. We will explain this further now in another page.

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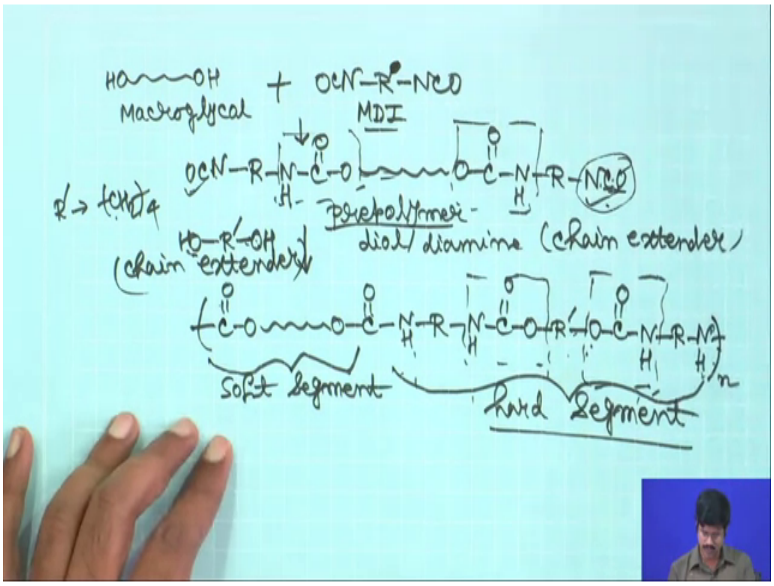

So, let us say you take your macro glycol this is your macro glycol of molecular weight 800 to 2500 and you react with excess typically two equivalent of di isocyanate let us say it is R N CO ok. And this is maybe methylenediphenyl diisocyanate MDI, so this two equivalent. So, if you do that then what you will get? You will get this particular product N CO on one side and then you have R NH CO O O CO NH R N CO. This is a product that you will get I mean I am just drawing it in a very general way this is what you call as your pre polymer ok. So, this is your prepolymer.

Of course, this is an urethane linkage as you can see and this is also an urethane linkage, inside you have this polyester. So, basically this is a polyester this is a polyester which aims on both sides with an alcohol because you are you are taken excess of alcohol when you reacted the di carbocyclic acid with the diol and this is a di isocyanate. So, ultimately what you will get on both sides you will have isocyanate linkage isocyanate that is ready to be reacted and you have this molecule this is your prepolymer if you have to go by the correct nomenclature.

Now, this you react with a small bifunctional molecule which is maybe either diol or a diamine a small molecule which can be called as a chain extender chain extender. If you if you remember here, so if you have a diamine and a it reacts with isocyanate. So, basically this can act as a chain extender because you had this chain and these chain now since it has come in between through coherent linkage a chain has the chain link has become close to double. So, this could be acting as a chain extender like that. So, what you do is that you have this prepolymer and you react with let us say one 4 butane diol or just a small diamine.

So, let us say you react with a small diol maybe this is one 4 butane diol it could be. So, the your R prime it could be CH 2 whole 4 ok. So, if you do that then what will happen this will produce urethane linkage and this will actually link the chains because this is your what you call as your chain extender. So, if you react with this diol which is your small diol which is your chain extender that then what will be the product.

So, let us first draw the macro glycol unit and from this end we will attach this and then try to complete the repeat unit. So, you have N CO which is isocyanate that reacts with your alcohol. So, if its reacts with your alcohol then what will be the product you will have an urethane linkage here urethane linkage that will be produced here which will be NH CO O and then this R prime will be there and then this alcohol you have to finish alright.

Now, this alcohol is acting as a chain extender. So, on the other side also it react with another isocyanate. So, on the other side have to again draw the isocyanate linkage which will be this and then you have to finish this molecule R NH of course, this will be again producing another isocyanate alright and that isocyanate could be this isocyanate because you started with this side.

So, that is why the linkage will finish like this. So, you have to able to draw the repeat unit, correctly. So, if you are reacting this di isocyanate with a diol then what will happen is that you start with this particular unit here this particular unit. So, this is your poly poly this is your macro glycol unit and then on this side you have an N CO isocyanate that can react with this alcohol to produce your urethane linkage.

Now, this alcohol has another O H and this is acting as chain extender. So, on this side it will react with another N C O. So, that is why you have another urethane linkage and then you have to complete the chain and that is why here it is ending at NH because here was also another N CO that has reacted with this alcohol of the at the end of this chain at the end of the macro glycol chain to produce the urethane linkage. So, this C double bond oxygen instead of putting here you could also put here.

So, ultimately what you have got? This polyester part this polyester segment that you have got in the repeat unit this is basically a soft segment because you have flexible polyester linkage in between. However, if you look at the urethane linkage that is lot of possibility of hydrogen bonding interactions between difference chains and that gives it a characteristic. So, this particular part this particular part will become movable or flexible at a higher temperature when you say soft block or hard block that would mean soft block it will the methyl the chains will become movable at a lower temperature.

So, another way of saying this is that is soft block has a lower glass transition temperature and the hard block has a higher glass transition temperature. So, to make a long story short in a repeat unit you have both hard block hard segment as well as soft segment.

Now, this part this kind of molecules that you are going to get here from this kind of structure if you are producing this is your thermoplastic elastomer. We will explain this further as we go along.

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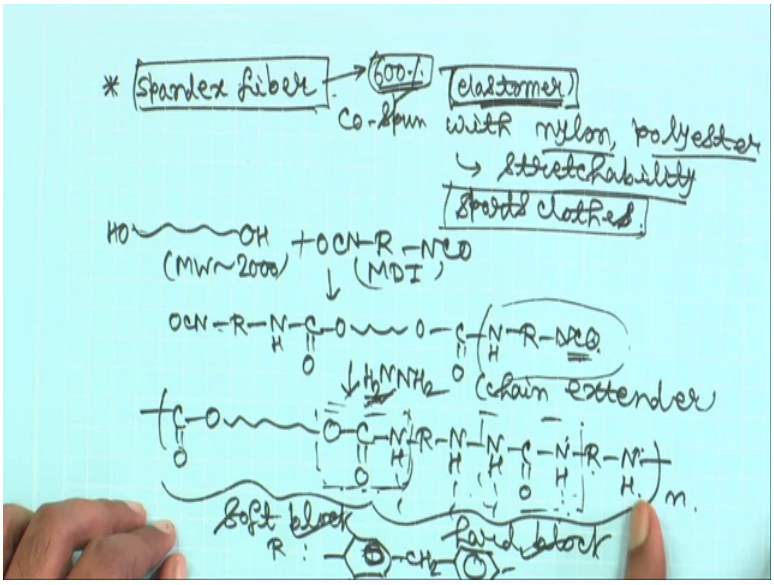

So, one of the kinds of thermoplastic elastomers thermoplastic polyurethane elastomers is your spandex fibre ok. So, which can be actually extended up to 600 percent strain and. So, it is quite high in this flexible it can be stretched to a high length. So, that the overall strain that could become 600 percent of original and afterwards when you remove the strain it can come back to with original length and also it can retain its tensile strength it does not break.

So, that is the property of an elastomer that basically if your applying force on the material it can be extended to quite a high length and afterwards if you remove the applied force it can come back with it is original dimension. I mean the stress versus strain curve will not be linear, but then it can still come back with original configuration. So, it will not break. So, it is quite highly quite stretchable to a very large strain ok.

So, one particular form of thermoplastic polyurethane elastomer is this spandex fiber and this fiber as I told you it can which stand up to 600 percent strain and these fibers they are co span with let us say nylons or polyester when you are making the fabric co span with this.

So, as to impart stretchable stretchability and flexibility to the clothes and typically there you know sports wears because they will have to undergo lot of you know those wears when you are playing sport they have to undergo lot of a forces. They have to experience lot of forces and stretching and also they should not tear. So, this is already you see one of the uses of this material all right.

So, how do you prepare this specific kind of molecule? You react your diol as I told you this is a this is molecular this is typically 2000, this is your macro glycol polyester based macro glycol you can react with your methylenediphenyl diisocyanate, so this is MDI and this reaction will produce already I have shown you before the product the structure. So, this is the prepolymer that you will get and in this particular situation instead of a diol you use a diamine is a hydrogen, hydrogen which is the chain extender in this case, and the structure of the repeat unit of spandex will be something like this all right.

So, further rule that I have told you about regarding drawing the structure of this. So, this side you finish NH R and then here this will produce the linkage in this case it will be a urea linkage. So, that will be NH NH CO NH. So, you see here in fact, you have this N CO.

So, on this side basically you have an urethane linkage that is produced by reacting of the amine of this and on this side you have a urea linkage that is produced all right because this is NH 2, NH 2 and that NH 2 on this side it can react with your this part of the molecule. So, then you have to extend this on this side. So, this will be NH R NH and then it will have at this amine here it has to react with. So, basically this is not amine this is you start with an N CO and that N CO reacts with the corresponding alcohol.

So, you will have an urethane linkage on this side all right. So, so you have an urethane linkage here you have an urea linkage here. So, ultimately this is having a lot of possibility of hydrogen bonding and so this is your hard block and this is your flexible unit which is your soft block. So, this will have a lower t g and this will have a higher t g I mean separately if you take and the R here as I told you this is your methylene unit flanked by to aromatic units, this methylene diphenyl diisocyanate.

So, this is your spandex the structure of your spandex it has both the hard block as well as the soft block in this material. So, what we will do is that in the next class we will start by explaining a little bit more how thus how the property that we talked about the stretchability of the material without breaking the material, you can stretch it non-linearly and it can come back to its original configuration when you remove the applied stress. Those things how they generate that we will talk about and then we will start talking about. So, we will finish the discussion on polyurethanes and we will start talking about other important polymers.

So, till then, thank you and good bye.