Principles of Polymer Synthesis
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Lecture - 40
Synthesis of Industrial Polymers (Contd.)

Welcome back. We have been talking about the synthesis of polyamide in some poly imide in some detail and we continue to talk about that. In the last class the point where we left you is we are looking at the details of the polyamic acid synthesis, why we are using low temperature, why you we are using certain kind of solvents or polar aprotic solvent, why you are using one reactant as a solid form in this case dianhydride and adding gradually to a solution of a diamine while that gives you a high yield of polyamic acid, why at all go through polyamic acid and do not go directly to the poly amide those things we have discussed.

So, let us continue talking more about polyimides. So, let us say we will talk about one commercially important poly amide first up today. So, that is Kapton.

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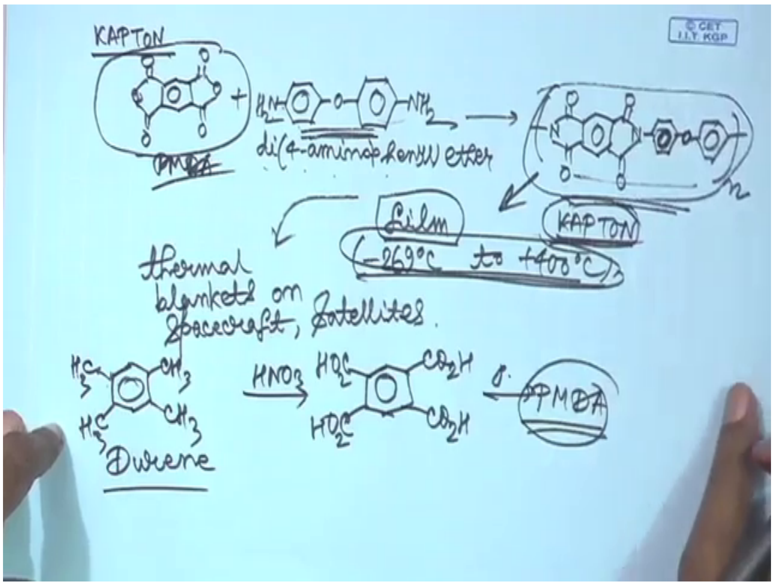

So, basically if you start with your pyromellitic dianhydride react this with a diamine which has an ether linkage a specific diamine we are using this case. So, basically this is di 4-aminophenyl ether. So, you an ether linkage and it is 1 2 3 4.

So, this is 4-aminophenyl and there are two of them. So, this is di 4-aminophenyl ether and this is a two step reaction of course, you go through the polyamic acid synthesis. And what will be a product? Your product will be after going through the polyamic acid path way of course, you will get your poly imide which is of this form oxygen and then you have this ok. So, this is your R group. So, this N R like this is the trade name of this particular polymer is kapton do not get confused between this circle and this circle this is your aromatic ring and this is your oxygen ok.

So, this particular kapton this material this particular material the kapton when you make a film out of this polyamide film is basically stable across a wide range of temperature from minus to 69 degree Celsius to plus 400 degree Celsius. And because of this kind of exceptional stability of this material this is especially used in some highly demanding applications. Say for example, as thermal blankets on spacecrafts satellites etcetera and they have very high I mean they are very costly in spite of their high price because of their exceptional heat resistance and good properties at high temperature we can use in such demanding applications.

And in fact, the reactant say for example, we are talking about this pyromellitic dianhydride, but we did not tell how it is prepared this reactant although it is quite costly it is still readily available how do you prepare this material. So, you start with of course, the corresponding methyl substituted benzene this is basically quite this a it is has a name. So, durene and durene and you oxidize with nitric acid.

So, liquid phase oxidation reaction and you get your pyromellitic acid as simple as that and this pyromellitic acid if you heat it up you cyclize and you get your pyromellitic dianhydride ok. Now, when we are looking at commercial polyimides commercial polyamides are not always prepared from you know a simple diamine and a dianhydride.

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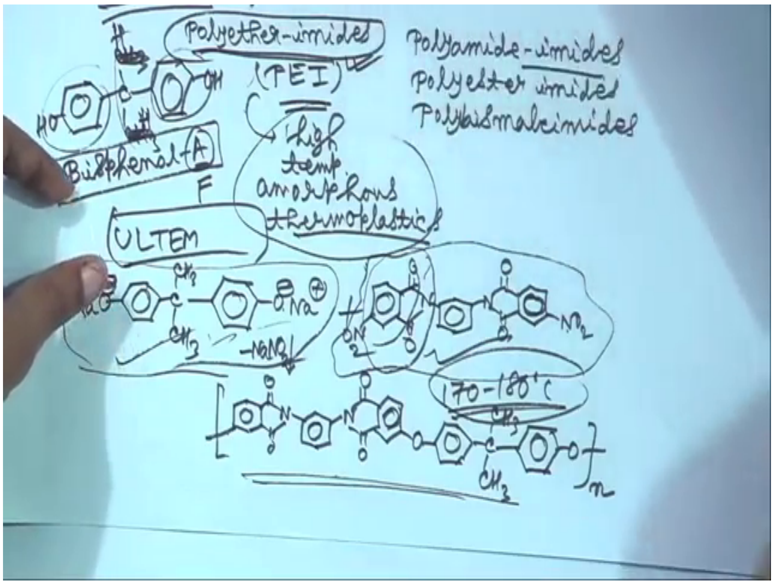

Because if you just look at yours these polyamides that we talked about I mean I am not talking about kapton because kapton is a slightly different. It has already and ether linkage here I am talking about just a diamine which does not have any other linkage say benzene ring NH 2, NH 2 and you are reacting with it dianhydride so on and so forth.

So, those kind of situations in those kind of situations polyimides that you are making although you can go through polyamic acid and all, but it does not change the fact that ultimately the final product that you have the applications are quite limited because they are infusible they cannot be molded by conventional thermoplastic technique. Because even though you have made the polyamic acid and you have removed the solvent and you get the shape you cannot more them by conventional thermoplastic techniques.

Because now, if you heat it up they do not they do not melt they do not simply melt if you can introduce some thermoplastic property for example, you are little bit flexibility at high temperature it will help. So, commercially modified polyimides are used. I mean lot of modified polyamides are there modification of polymer structure has been done. So, some of the important things for example, they are poly ether imides poly ether imides or polyamide imides or polyester imides or polybismaleimides which are better property than your conventional poly imides.

Let us say poly ether imides such as abbreviation as PEI. These typically are high temperature amorphous thermoplastics because they have not only repeating imide linkages which helps them to have high temperature stability I mean the material property can be retained, but not only that, but they are also thermoplastic materials because they have a regular repeating ether units in the system. So, the imide units they provide stiffness to the material and the ether linkages they will provide the flexibility to the material.

So, that will allow good melt flow characteristics of the material. So, that process ability I mean you know the process in the in the process ability it becomes easier the process ability becomes easier say injection molding or likewise extrusion those kind of things can be done.

Now, one example is ultem which is a commercially available poly ether imide and this basically is prepared by this process you start with this compound. So, this is a sodium salt of bisphenol A. So, this is sodium salt of bisphenol A. So, basically bisphenol A is this is bis phenol A. Now, bisphenol you know there are two phenol units why it is a basically it is produced by the reaction of acetone CH 3 C double bond oxygen CH 3 by the reaction of acetone with phenol and that is why this is called bisphenol A. So, and it could be bisphenol F for example, in that case it will be reaction with formaldehyde ok.

So, bisphenol A sodium salt of that and you react with this particular molecule. So, this is meta substituted molecule you have already have an imide linkage here this is aromatic ring on this meta position you have the same stuff that is here another aromatic ring and you have an N O 2 unit and if you react these two molecules sodium nitrite will go and the final products that you will have is this.

So, basically I am just drawing this part first. So, your imide linkage was already there to start with and so this was this part and then this in here this oxygen will be linked. So, you have oxygen and then you have the bisphenol A part this is your and here you had this N O 2. So, here will be the linkage. So, this is your ultem. So, this particular starting material can be obtained quite easily starting from phthali can hydrate. So, basically what you do is you start with phthali can hydrate. So, this is you know this is a phthalimide unit because if you are CO 2 are the CO 2 H here and only benzene ring that is called phthalic acid.

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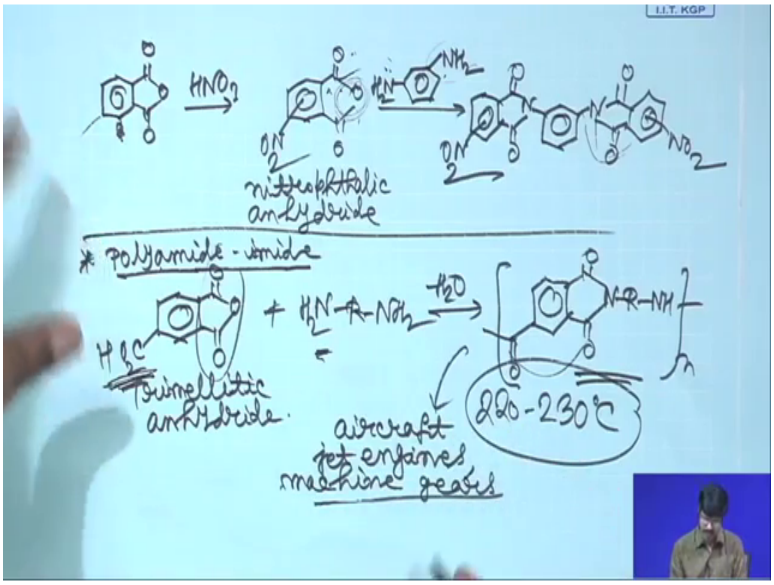

So, you start with phthalic anhydride and you oxidize this basically you react with nitric acid you nitration you nitrate this particular molecule. So, what will have is 2 position and 3 position, either 2 position or 3 position nitro group will be coming that scientists putting like this the nitro.

So, this is basically nitro phthalic anhydride nitro. So, this is your nitro phthalic anhydride ok. And then that you react with meta phenylene diamine. So, this is meta phenylenediamine this molecule has made its appearance before and then what you get is your bis imide monomer ok. So, your this nitrogen will come here. So, it is producing imide in the place of anhydride. So, basically it will be like this and your nitro group is here. So, this part is on this side.

Because here this can produce the imide linkage ok; It produces the amide and then it can cyclize by removing the water and you will get the imide linkage here the same way on this side also you can get the imide linkage. The structures sometimes might look complicated by as long as you are following the logic it is not that difficult and this is the starting material of this that you can react with the bisphenol, sodium bisphenol it salt and then sodium nitrate is evolved and you get what you called the commercial name is ultem.

So, basically in this step you are using a base in order to make it you know O minus and you can use again say a solvent which is polar aprotic solvent and you have to reflux this reaction and you get your product. Now, something that I need to tell you here; So, this particular product it is an amorphous product you know it has all these ether linkages here and the temperature at which you can use at around 170 to 180 degrees Celsius. So, still you know you can use at quite a high temperature and the solvent and chemical resistance are basically comparable to that of poly imides.

One thing that you have to keep in minds here when you are going to the second stage of the poly imide preparation on in the typical poly imide preparation process; Say for example, this process here you are going through polyamic acid synthesis.

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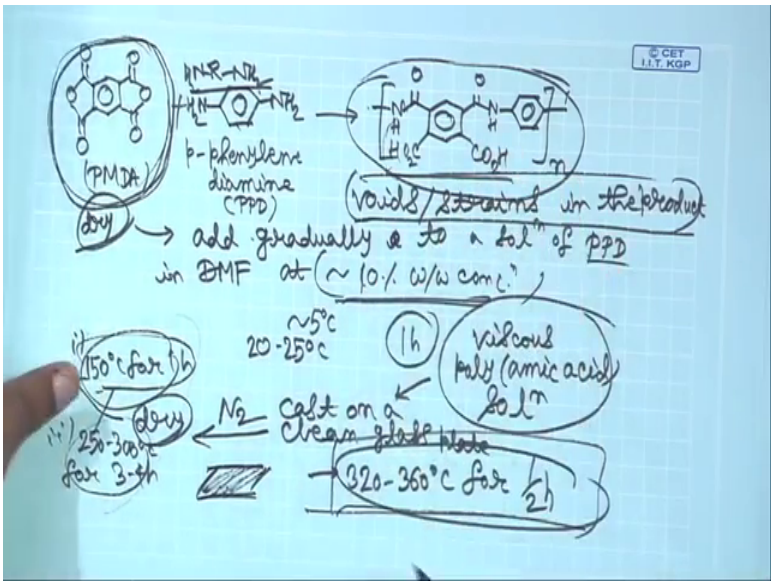

So, when you heat this up and you get your polyimide you are basically producing water because this is cyclizing. So, you are basically producing water which is volatile and which is going out and that can lead to the presence of voids or strains in the product in the in the product during the processing period. So, basically when you are going through polyamic acid ultimately or heating it up further once you have molded the material into the shape you want and then the poly amide is being produced this is releasing water from here and that is why the cyclisation is occurring.

So, you know that would mean the water has to go out. So, the material some voids some strains can be remaining because it is a volatile product that is going out and that kind of defect can be there and those defects will not be there or those kind of problems will not be there in this particular process because these does not involve you know production of any volatile component in this polyethyleimide preparation. So, this is also advantageous process ok.

Now, this is an example of poly ether imide an example of polyamide imide also I want to give you. So, you can simply start with again you have you need an anhydride and the reaction with a diamine in order to produce your amide linkage. Now, instead of another die another anhydride here which will be pyromellitic dianhydride you can have a CO 2 H here. This is basically you know when you have a CO 2 H, CO 2 H, CO 2 H, CO 2 it is paleomagnetic acid when you have a CO 2 H, CO 2 H, CO 2 H which in these 3 positions only that is trimellitic acid.

So, if you have this anhydride here this is called trimellitic and hydride ok. Now, if you react here after removal of water you know it will react and then you cyclize removing the water the product that you will get is something like this. Now, it should be easier for you to draw the product the imide linkage will be produced on this side and on this side your carboxylic acid that will react with this, I mean to produce amide linkage that is why you will have poly amide imide ok.

So, the product here will be something like this. So, this is your poly amide imide this also will have high strength high stiffness and these are amorphous polymers and the continuous use temperature is around 220 to 230 degrees Celsius. So, these do not fare too badly with respect to a typical polyimides I mean on conventional polyimides, but these are easier to you know handle some of these some of these materials.

Now, finally, what I want to talk about in this particular let us also talk about one of one or two uses of these kind of materials. So, the are they are used you know in aircraft jet engines, I mean when you see some of the uses it is important to try to rationalize on the basis of structures you know high temperature stability and you know say for example, kapton your using in spacecrafts there can be huge temperature fluctuations and all.

So, those things because it can which stand these kind of huge temperature fluctuations and still can maintain its mechanical strength; So, those kind of things will tell you why an application I mean can be envisaged from such materials depending on the structure that is why understanding the structure is very important correlation with properties comes after and designing of the structures.

So, as to obtain the polymer property that you want comes even after that. So, it is used for aircraft jet engines or engines or in industrial other industrial applications like you know in machine gears and other mechanical components so on and so forth ok. So, let us talk about another class of polyimides now, I mean commercially modified polyamides already we talked about polyamide imide, poly ether imide ultem is one of the poly ether imides. So, ultem we talked about ultem.

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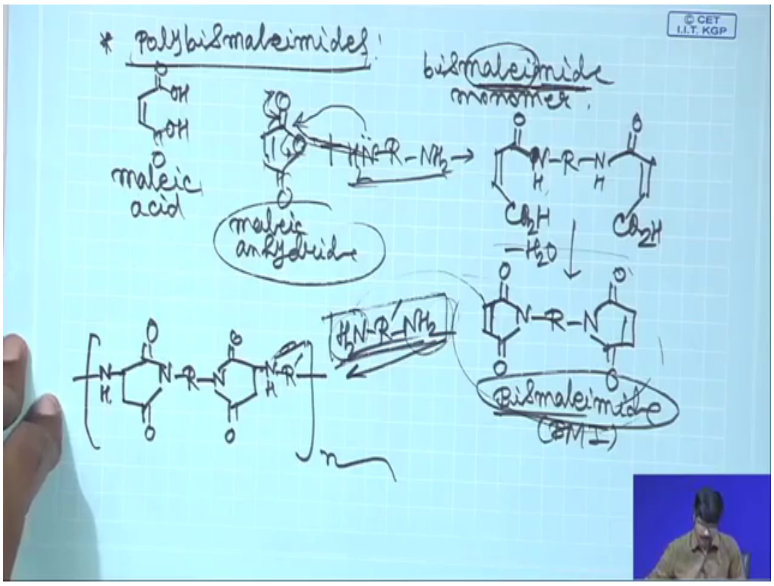

Now, let us talk about another kind of imides another class of imides which is called polybismaleimides. I will explain to you why it is called maleimides polybis maleimides etcetera. So, of course, this is polybismaleimides means you have to start with bismaleimide monomer whatever it is I will come to that in a moment.

So, maleimide basically this means an imide starting from maleic acid like pyromellitimide; that means, an imides starting from pyromellitic acid this is how you can link the things. So, your maleic acid is this is your maleic acid what you do in this case is you start with. Now, you can understand this is maleic anhydride you react an anhydride with a diamine I and what you will get you will get an amide linkage here and this will open up and produce the carboxylic acid and then if you heat it up they will get an imide linkage.

So, if you are reacting an anhydride with an amide you will get an imide after. First step you can get an amide linkage and a carboxylic acid and then I an heat it up they will come together to cyclize remove the water (Refer Time: 20:24) from the imide.

So, what you will get is this compound. So, sorry, CO NH R NH CO, CO 2 H, CO 2 H ok, so two of these molecules come together from both sides and this opens up because this will attack here and this will open up ok. So, you will get this compound and then when you heat this up water molecules will be removed from this side and from this side and you will get the cyclization and the corresponding production of imide. So, this will be your imide and this imide is produced from maleic acid. So, that is maleimide and there are two of them that is why this is your bismaleimide this is your starting material.

So, you are reacting maleic anhydride with a diamine and you get your bismaleimide. Now, what you do is that. So, this is BMI, bismaleimide, so this bismaleimides you react this bismaleimide with say another diamine that is why I am putting R prime. Now, since it has two functions here and this amine has two functions on both sides. So, basically it can form a polymer because this amine can attack here on this double bond. So, what will happen is that the product that you will get is a polymer which looks something like this. So, the basic skeleton is this and then instead of double bond you are actually reacting with this diamine.

So, you will have a diamine on both sides in this case here you are removing the R or R prime that R prime then should come on this side it will be NH R prime. Remember it should be able to draw the repeat unit in a correct fashion. If you do not put R prime here you can put R time here still the repeat unit is correct ok. You have to account for both of the molecules they will come into the repeat units. So, like this. So, this is your poly bismaleimide.

Now, let us say you carry out this polymerization with an excess of bismaleimide, then what will happen. From our previous discussion on step polymerization, so we know if you have an excess of one of the molecules that will end cap on both sides with the same functions. So, if you are using an excess of bismaleimide there in effect the product will have. So, this is a poly bismaleimide unit and on both sides you will have these maleimide linkages at the end because this is in excess. So, both sides they will end cap. So, ultimately the product that you will get the polymers that you will get they will be so, this is the polymer I am just not drawing the structure here in between. They will be end capped with this maleimide units because the bismaleimide has been used in excess. So, this is maleimide end capped polymer.

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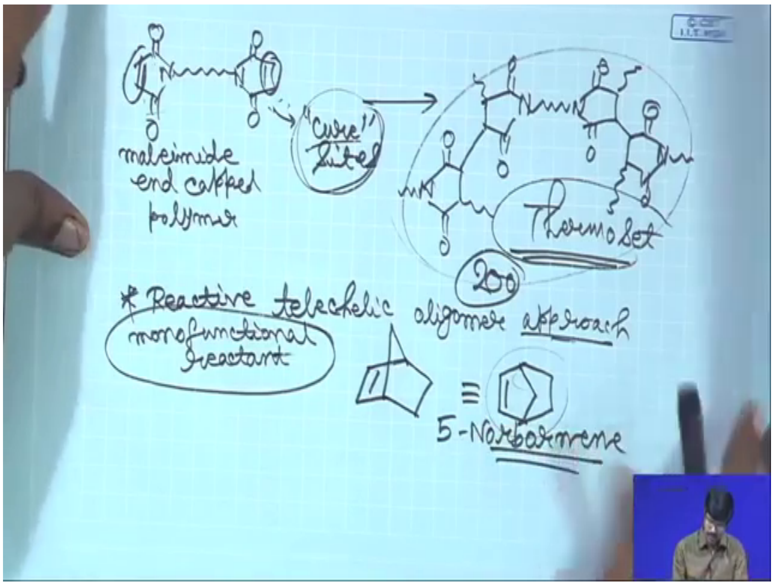

Now, here these terminal double bonds they are reactive double bonds. These double bonds can be further used they can actually serve as what you call as cure sites for the formation of cross linked material, you know this kind of material when you do what you call as a curing you basically add a cross linker that will cross linked the material and it will produce what you call as a thermo suede material. A 3-dimensional cross linked material will be produced and many times it. So, happens that you have a cross linker you have a functional group at the end in this case p maleimide end group end group this reaction is done at a higher temperature.

So, basically have to heat it up a little bit you put a cross linker you have your starting material which is a reactive functional end and it cross links. And then ultimately you get a material which is stable material which has a cross linking cross link structure covalent cross link structure and it is a thermo set material because you have set it into a particular structure by heating and it is a also a curing process then the curing agent being the cross linker.

So, once you have cross linked you get the thermo set product which is unlike your thermoplastic material because thermoplastic materials when in heat them up they become malleable, they become pliable, they become softer, you heat them up beyond their glass transition temperature they become softer and then if you cool them down. So, you heat it up you reshape it you cool it down it takes whatever shape you want ok.

So, that kind of thing is not possible when you are talking about thermo sets because you basically are adding a cross link or and then you are heating it up. So, it is actually setting the material into that particular structure which is covalently linked structure. Now, the only way you can do something is to break those bonds. So, you can destroy the material. So, it is not like you heat it up you can reprocess it. So, that is a thermo set material.

So, here so you have these kind of double bonds on both sides. So, you can do a cross linking and you can get thermo set products which will have these kind of structures. So, you have cross linking like these, like these here nitrogen and let us say. So, this was the actual polymer to start with and then so on and so forth.

So, this kind of cross linked materials this kind of thermo sets you can produce and the properties of this kind of cured polymers will be broadly similar to the polyamides or polyimides that we have talked about and the continuous use temperatures could be still as I had as high as 200 degree Celsius. So, you know again this can also be applied in aircraft spacecrafts and other kind of highly advanced applications.

So, finally, what I want to talk about is the is the following that basically, I mean since we are talking about these thermo set materials and we talked about these bismaleimide units. So, we already talked about the process in which you can create thermo set materials. So, basically there is a name for the for the approach it is it is called reactive telechelic I mean of course, whatever we have talked about it is different from this. I mean I am just trying to correlate in a way that we talked about thermo sets, we talked about maleimides. So, we are talking about another approach in which you can use these maleimides in order to create thermoset materials.

So, reactive telechelic aligomore approach, so in this approach what you basically do is that when you are polymerizing your system you include a mono functional reactant in the system. So, you basically add in a monofunctional reactant of course, this will end cap because it is monofunctional and this is how you can also control the molecular weight we talked about that before. So, this will limit the polymerization and. Secondly, it will end cap the oligomers with functional groups that are capable of further reaction, all right.

So, you can have cross linking you can obtain extension example, example being this cyclic material which you can also draw as this it is a highly strained system this is actually 5 norbornene ok. So, what you can do with this? You use this monofunctional material. So, you have an anhydride on this side and this is your norbornene unit.

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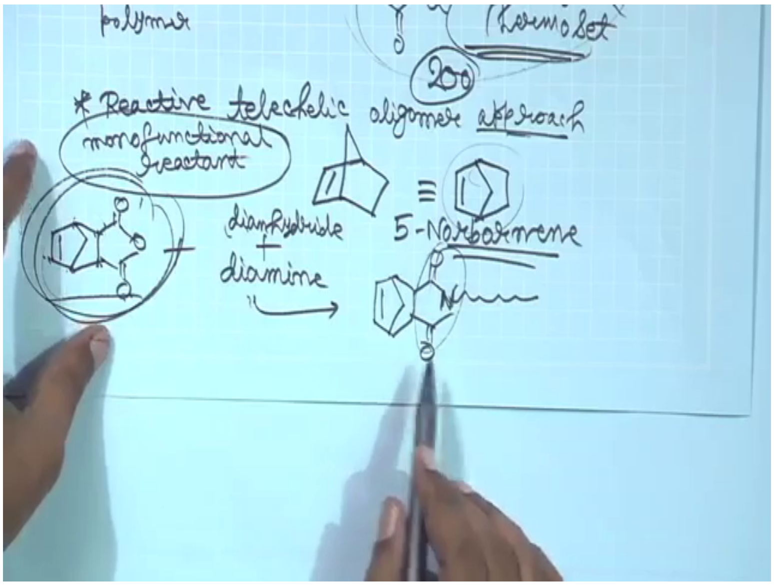

So, this is basically. So, this is 1 2 3 4 5, 1 2 3 4 5. So, this is 5 nor norbornene, 2 3 dicarboxylic anhydride unit. Now, this molecule if you include as a mono functional reactant in your polymerization reaction between a dianhydride and a diamine let us say you are making an imide polyimide. So, you are reacting a diamine with a dianhydride we have talked about it in detail before.

Along with these two reactants you add this particular monofunctional reactant monofunctional what is the function it is mono anhydride. So, basically it will add at the end it will not have another end to react further in with the diamine like that and at the end of this monofunctional unit one side is your diamine one side is your anhydride and another side is norbornene unit for post polymerization modification. So, what you will get? If you do the reaction, so you take a dianhydride and a diamine and you take this mono anhydride you add this also in this.

So, in the polymerization what we will get? We will obtain or let us say we have an oligomer or a polymer whatever. So, the at the end of the polymer chain we will have this unit because this anhydride has reacted amine to produce an imide linkage, but at the end this will stay because this is a monofunctional molecule.

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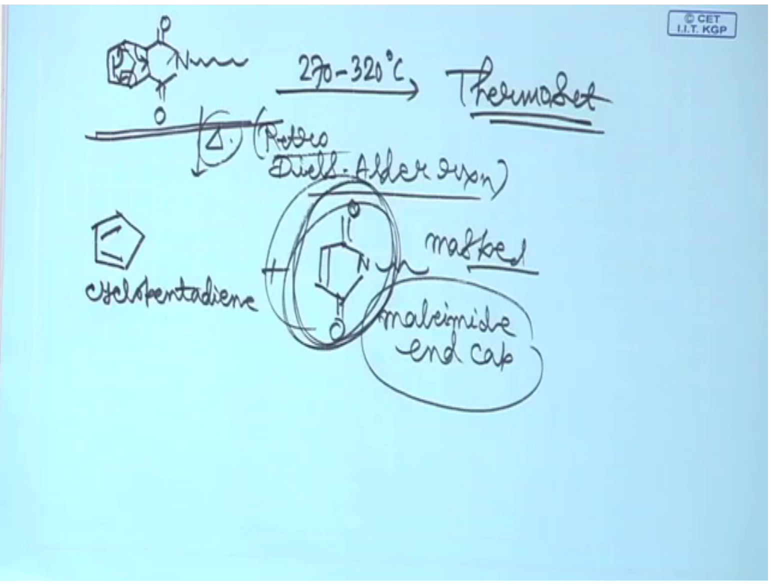

So, let me draw this again here. So, you have polymer chain at the end you have this. Now, if you heat this up around 270 to 320 degree Celsius if you heat this up you will get a thermoset product. How does that happen? This happens through what you call as retro diels alder reaction. So, basically it is a you know very cyclic reaction we will not go into the details of that class of reaction. But overall the ring opens up you know in a cyclic fashion the electrons will move like this and this comes here and this comes here. So, what will happen is that it will heat up and this molecule will come out and it will be this it will be cyclo pentadiene.

And what will be revealed on this side? Follow the arrows on this side you have a maleimide end cap. So, basically it was a masked it was a masked maliimide end cap unit to start with. So, you are in norbornene unit and you had a mono functional monomer in this case it is an anhydride that reacts with a amine and then and at the end of the polymer chain you will have this unit and imide unit because it is monofunctional.

So, it will end cap and then this will open up by a retro diels alder reaction revealing the maleimide unit here. And now, you know what is going to come next this can be cross linked. And we have already talked about these kind of cross linking reactions. So, you can get your thermo set material.

So, with this we will stop today because one thing the time is up and the second thing we are also done talking about poly imides. So, what we will do in the next class, we will start by talking about poly urethanes. The synthesis and the structure property relationship will again be at the heart of discussion.

Till then, thank you and see you then.