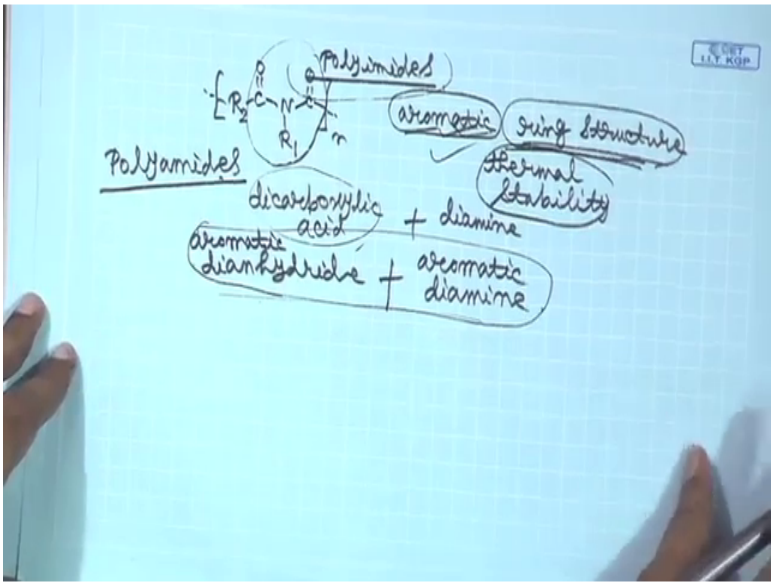
Principles of Polymer Synthesis
Prof. Rajat K Das
Department of Material Science Centre
Indian Institute of Technology, Kharagpur

Lecture - 39
Synthesis of Industrial Polymers (Contd.)

Welcome back. We have been talking about synthesis of industrial polymers over the past several lectures. So, the topic is going to continue in the same vein.

Today we are going to talk about the synthesis of polyimides which is a specialty polymer. We will start right with the structure of this polyimides.

(Refer Slide Time: 00:40)

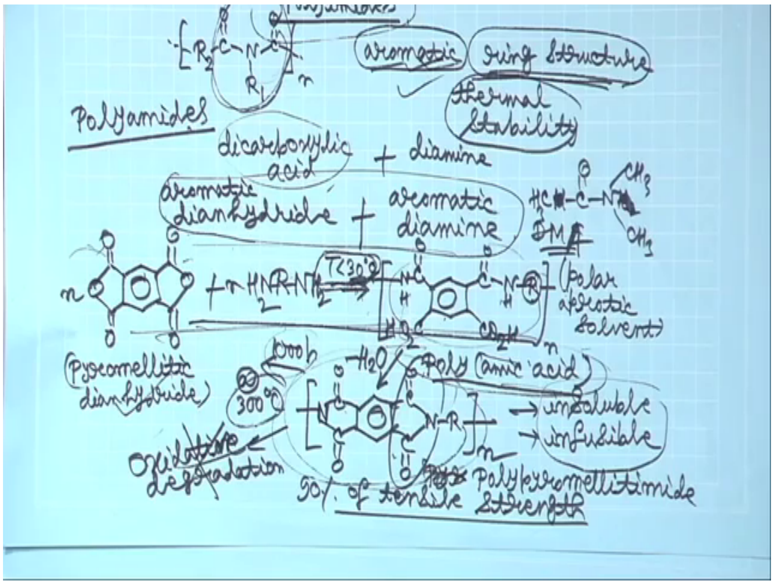


Now, this polyimides they have the characteristic functional group which looks like this in R 1 then you have. So, this is basically your imide functionality.

The most important polyimides are aromatic polyimides, because they have predominantly ring structure in the backbone and they are of exceptional high level the exhibit exceptional high level of thermal stability if you have all these aromatic units in the system. And that is why they are used for special applications even though the preparation cost is high they used for demanding applications. Now, when we talked about poly amides, polyamides we could prepare from a dicarboxylic acid and the diamine for polyimides what you do is instead of dicarboxylic acid you start with a dianhydrade of course, in this case it will be an aromatic dianhydride because you are talking about aromatic polyamides because those are the most important polyimides.

So, you start with an aromatic dianhydride, you react that with an aromatic diamine and typically this process is a two stage process. So, let us take an example here.

(Refer Slide Time: 02:54)



Let us take an aromatic dianhydride which is something like this, aromatic di dianhydride. This is called pyro mellitic dianhydride because the corresponding acid which is CO 2 H, CO 2 H, CO 2 H, CO 2 H that is pyromellitic acid. So, this is pyro mellitic dianhydride because here one one molecule of water is gone and then you can have this ring here also one molecule of water is gone and then you can have this ring.

So, you react this aromatic dianhydride with some aromatic diamine just putting an R because the general structure is very important you have to able to draw the general structure. Once you know the structure you can try to on start to try to understand the structure property relationship. So, you are reacting with the diamine then what you get is the following compound.

So, basically here you have an amide formation, so CO NH R. So, this side it will be CO NH because this is the repeating unit and here you have CO 2 H CO 2 H. So, basically it can attack here or it can attack here and then it just opens up these two CO 2 H groups can stay.

This is called poly amic acid. This is not your polyimide this is an intermediate that is why I told that this is a two stage process in the first stage you prepare what you call as poly amic acid then what you can do is that you can heat it up and that will induce a cyclization on both sides and you will get the final product which is your emide. So, this is nitrogen, this is your poly polyimide. In this case this is your pyro, so this is your poly pyro mellitimide because you have this emide linkage CO N CO this is your amide linkage that is present here this is your amide linkage.

So, this is a two stage process in the first stage you get polyamic acid on further heating it can cyclize and it gives you the polyimide in this case you started with the specific anhydride which is your pyromellitic dianhydride. So, you got what you called as polypyromellitimide. Now, you might ask me this question why we do not go directly to polyimide why do we need to synthesize polyamic acid first and then we go to the polyamide. The answer to this is this polyimides typically the final products the polyamides they are typically insoluble they are not soluble in most of the solvents and they are also infusible infusible means you cannot melt them you do not melt. So, if it is that situation how do you process these materials? You cannot process.

So, what you basically get if you are directly going this is one problem you have a you have a processability problem. Second thing is that if you directly try to go to this particular product what will happen is that before a high molecular weight is reached the polymer chains will start to precipitate out from the reaction medium polymerization will stop why they will start precipitate because they are insoluble once the amide is forming that is insoluble.

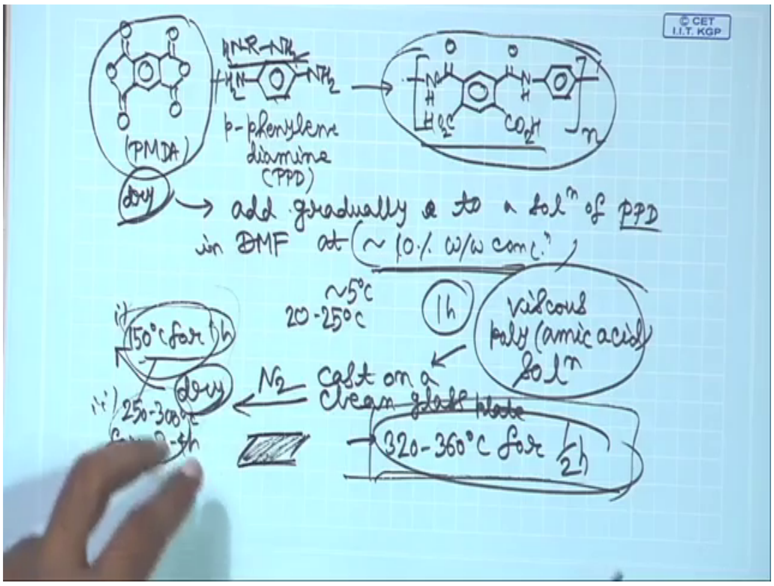
So, before a long chain could form they might precipitate out this is one thing. Second thing is that if you go directly there the processibility issue is there how do you circumferent that thing by two steps we will come to that but of course, one reason you now, understand that you initially want to go to the desired molecular weight and then you cyclize. Because if you start to prepare emide from the start from the starting point of the reaction you if you start to target that then the problem is it will become insoluble it will just come out before it can form a long chain that is the problem.

So, this first step that you are doing the preparation of polyamic acid basically this first step is carried out in a polar aprotic solvent. We will explain why we are doing these things, why a polar aprotic solvent. We already got introduced to polar aprotic solvents before polar aprotic solvents are polar which cannot donate a proton unlike water. So, in this case you can use dimethyl formamide. So, this is formamide. So, instead of these two hydrogens if you have two methyl groups that is dimethyl formamide d m f that you can use as a solvent for these reaction for the preparation of polyamic acid or you could use dimethyl acetamide. So, for acetamide it will have a CH 3 unit. So, that will be dimethyl acetamide. Those you can use as the solvent.

And these reaction the preparation of polyamic acid the first step here this reaction is carried out at a moderate temperature usually the temperature used here is lower than 30 degree Celsius because you do not want to start the reaction at high temperature since that can lead to cyclization cyclization happens at high temperature. So, until you get your polyamic acid you do not want the cyclization to start. So, this reaction you are doing at a lower temperature.

Now, an example of polyamic acid (Refer Time: 09:26) of course, we have already discussed one example. Another example could be, you start with pyromellitic dianhydride and you take a specific diamine ok.

(Refer Slide Time: 09:37)



So, let us say you start with your pyromellitic dianhydride its PMDA and the diamine that you are taking let us say this is para phenylene diamine, para phenylene diamine it is a PPD I am just putting like that. And when you prepare the polyamic acid what is the structure of this polyamic acid? It will be something like this, so instead of R here you will have this aromatic ring.

So, if you remember the general structure it is not difficult to find out what is the product. I am not drawing the carbons here, but carbons are there you could put also. So, that will be CO NH R and that R is an aromatic unit this is your R. So, this is basically R NH 2, NH 2 ok. So, that is your unit and you have a CO 2 H here, and CO 2 H here and then whole n alright. So, this is your product this is your polyamic acid.

So, in order to accomplish this reaction what you do, you take solid powder of pyromellitic dianhydride high purity solid powder dry pyromellitic dianhydride and you add this. The solid powder you add gradually to a solution a solution of para phenylene diamine PPD para phenylene diamine in DMF dimethyl formamide already we had shown the structure of dimethyl formamide at around 10 percent weight by weight concentration you have started say PPD is at around 10 percent weight by weight concentration and you add this gradually and temperature is around 5 degree Celsius. So, see the temperature is low temperature not very high temperature and then you are studying and keep in mind that when you are adding this dry powder you add this in exact stoichiometry.

So, you are add, so you weight out in exact stoichiometry with respect to a solution of para phenylene diamine in DMF that solution concentration is 10 percent say weight by weight and then you weight out maintaining the exact stoichiometry with this reactant and then you add it gradually to your solution in DMF and the temperature is low temperature and you start it.

So, the viscosity of the solution will gradually rise and that will indicate the formation of this polyamic acid first thing. Second thing is that when the addition of pyromellitic dianhydride is complete you increase the temperature to around 20 to 25 degree Celsius and you allow it to run for another hour or so, and then you are done your polyamic acid is produced.

Now, when you go to the second stage you have to prepare the corresponding polyamide by heating. So, what you do is that you have a viscous poly. So, you have now, a viscous poly amic acid solution right after this process you have a viscous polyamic acid solution viscosity has increased it has been produced. So, you take this solution, you cast on a clean glass plate maybe a clean glass plate you are casting onto that and then you allow it to dry under a nitrogen. So, what you will get you will get a film of the polyamic acid on the glass and then you heat it up further specifics are there of course, initially you heat at 150 degree Celsius for 1 hour and then you are heating at 250 to 300 degree Celsius for 3 to 4 hours as far as I am concerned remembering these specific things are not important what is important is the whole process.

So, you start with, so you see here it will cyclize and it will form the polyamide. So, you, so what I am telling you is how you get to your polyamide and how do you avoid this problem of processability. So, basically your polyamic acid is in a solution and you shape it into the desired physical form of the final product in this case let us say you want a film of your final product which is your final product what is a final product you are final product is your polyamide.

So, what you do you just make a film of polyamic acid on the glass plate, if you do not want to film if you want something else you can also take it in that physical form that kind of shape you can just put it. And after you have put it you remove the solvent and then you heat it up further when you heat it up it will add the cyclization and in this case for example, you started with a film and you end up with a dry film of polyamide.

So, your processing is done instead if you had produced polyamide directly and tried to start a processing it is difficult because first of all you will not reach high molecular weight because before high molecular it starts to precipitate out because of solubility problem in the solvent. Secondly, even if you could get high molecular weight it is now, insoluble and it is not you cannot melt this material also.

So, what will happen? You cannot process it. So, that is why you start with a material polyamic acid which is steel soluble you start with a material polyamic acid which is steel which steel can be melted and then you take into desired shape you remove your solvent you heat it up cyclize you get your final product in the process condition that is the idea.

So, what you have here then is your glass plate on which you have this film of polyamide. Now, you cool it down because the process has been done at high temperature cyclization has occurred you cool it down and then you emerge this glass plate in a water bath and then this film will just detach and take out this film with the tweezer maybe and then you dry it in air or heat it further and further.

So, you take it out you dry it in air. So, the exact thing is that after drying you heat it to 320 to 360 degree Celsius for a further half an hour and then you have a complete completion of cyclization ok. This is partially cyclized you take it out you dry it you heat it up further take it out in water heat it up further and you will get your product which is completely cyclized product and the and this kind of materials this poly pyromellitimides because you start with pyromellitic dianhydride here.

So, these materials their outstanding properties, they are very good flame resistance, they have exceptional heat resistance and they have exceptional resistance to oxidative degradation they do not degrade very easily oxidative degradation does not happen.

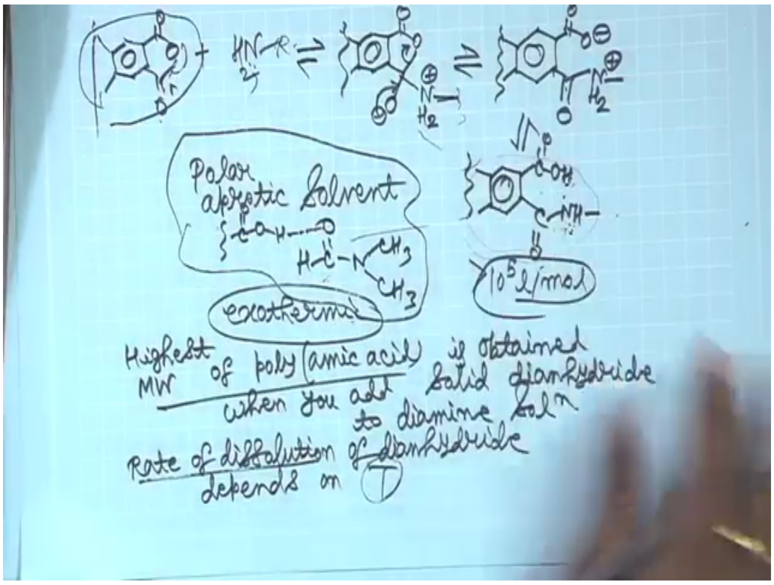
Now, I mean. Now, something I am going to tell you is an experimental fact that if you that it has been shown that if we expose these materials for 1000 hours to air at 300 degree Celsius. It is an extreme condition in which you are exposing this material to air the polymer even after the exposure to air at 300 degree Celsius per 1000 hours it retains 90 percent of its tensile strength, I mean this family of polyamides 90 percent of tensile strength is retained.

So, you see that it has exceptional thermal stability mechanical property is not degraded even at high temperature for long time not only that the oxidative degradation does not occur because you are exposing it to air at high temperature. Many of these reactions will be accelerated at high temperature and polymers might degrade not polyamides that is a reason why these are specialty polymers.

Now, let us look at this synthesis of here it has become lot congested. So, we will take a face page. So, let us look at this synthesis of polyamic acid in little bit more detail. We talked about we promised you that we will explain all the nitty gritties of this particular reaction why use polar aprotic solvents, why use less temperature and also I want to tell you why you are going to gradually add this pyro you know pyromellitic, dianhydride to a solution of diamine and not otherwise so on and so forth.

So, those things we are going to discuss now. Let us have a then a closer look of the pyro of the of the polyamic acid synthesis.

(Refer Slide Time: 19:02)



Highest MW of poly(amic acid) is obtained when you add solid dianhydride to diamine soln

Rate of dissolution of dianhydride depends on T

So, just I will draw genetically one site of the ring because it was a pyromellitic dianhydride. So, this side also dianhydride is there anhydride is there I am not drawing that. So, you have a anhydride here and even amine I mean one amine from the diamine I am just showing. So, let us look at the mechanism in a little bit more detail. So, the first step is basically this amine will attack here and this ring will open. So, what will be the product that will form? The product will be something like this, in the positive this is the product it has attacked here these negative charges move to oxygen nitrogen is positive charge these are all reversible steps.

Now, in the second step what will happen this negative charge comes back here this ring opens. So, what is your product that you are getting, you are getting something like this again I am not drawing the carbon here and then in the final step there is a simple proton exchange this proton goes here. So, it takes care of these charges. So, what you will have here basically? CO OH and CO NH 2, actually NH this, so you have the long chain. So, this is your polyamic acid I mean on this side also you will have a carboxylic acid like this and you have a chain that is going on ok. So, this chain is going on here R NH 2 is there. So, this chain is going on. So, this is your polyamic acid synthesis in a nutshell a mechanistic aspects.

Now, looking at this remember one thing the reactants and the products they are in equilibrium here. Now, if you look at this product here and if you want to go in the reverse direction the first step in the reverse direction is basically a transfer of this carboxyl proton to the adjacent carboxamide nitrogen, then only from here you can go to this particular species this proton will be transferred to this nitrogen. So, if you can stop that from happening then you can actually take the reaction forward so that means, you are decreasing the rate of the reverse reaction.

So, that would mean effectively you can pull the equilibrium to the right. How can you do that? You use a polar aprotic solvent. Now, polar aprotic solvents say you have you are using dimethyl formamide let us say you are using a dimethyl formamide this polar aprotic solvent they can form strongly hydrogen bonded complexes with this free carbonyl group. Meaning you have, so they can form strongly hydrogen bonded complexes with these 3 3 carboxyl groups. So, you have CO OH and they can have this kind of hydrogen bonding interactions.

So, this proton is no longer available to be transferred to this nitrogen. So, these kind of strong hydrogen bonding complexes the solvent forms with a free carboxyl group actually stops the proton from being transferred from carboxylic acid to the carboxamide. So, this reverse step is stopped. So, you shift equilibrium to the right. So much, so that the equilibrium constants for most of these isolation reactions at ambient or the room temperature are greater than 10 to the power 5 liters per mole.

So, you can actually obtain high molecular weight poly amic acid from many combinations of aromatic dianhydride and diamines. So, we just talked about pyromellitic dianhydride, you can have other combinations. We talked about pyromellitic dianhydride and para phenylene diamine you could have other combinations, you could have other aromatic diamines other dianhydride you will still get very high molecular weight poly amic acid if you are following this system you if you are using a polar aprotic solvent this is one thing.

Second thing is that this forward reaction is exothermic meaning that liberates heat. Since the forward reaction is exothermic if you do the reaction at a high temperature then the equilibrium will be shifting to the left; that means, the molecular weight of your polyamic acid will decrease that is what you do not want. That is why you want to do the reaction at a low temperature. If you do the reaction at a low temperature you have a high yield of high molecular weight poly amic acid, if you increase the temperature the equilibrium shifts to the left to the starting material. So, you compromise the molecular weight of polyamic acid that you have got that is why you have to do this reaction at a low temperature. And we also explained why you are going to use a polar aprotic solvent for this reaction.

Another thing is that highest molecular weight of polyamic acid is obtained when you add solid dianhydride to diamine solution. I already told this before that in order to do the reaction for this particular reaction we had we had explained you start with a solution of the diamine and you add the solid in this case pyromellitic dianhydride to the diamine gradually. So, if you do like this you will get very high molecular weight polymer. Why is that so? Because this dianhydride this aromatic dianhydrides are known to react with water of course, they will take water up and then they will just open this up. So, they can react with water what we want here is for them not to react with water, but rather to react with your diamine, so as to get your desired polyamic acid.

Now, one thing works in your favor that is the reaction with diamine the reaction of dianhydride with diamine is considerably faster than the reaction of dianhydride with water. So, if you add the dianhydride to a solution of diamine at any point of time you know you have a large amount of diamine that is present and you are adding some small amount of pyromellitic dianhydride. So, what will happen is that you can minimize these competing reactions like reaction with water and all, because before it can react with water it can immediately react with this because this reaction is faster and this amount is already lower because you are adding gradually to a solution of diamine this is one thing and of course, the solvent that you are using has to be dry.

Second thing is that this solid dianhydride that are that you are adding gradually you are using DM say dimethyl formamide DMF, as a solvent this solid does not dissolve immediately in the solvent. So, what can happen is that the rate of dissolution can be slower than the rate of polymerization, it can gradually slowly dissolve, but the rate of polymerization may be faster than the rate of dissolution. And we know if we have several rates involve the rate determining step is basically the step which is the slowest step.

So, what will happen is that if the rate of dissolution becomes lower than the rate of polymerization then the process will become diffusion controlled and in effect it will become a solid liquid interfacial poly polymerization reaction because it is a solid it has not dissolved yet. But it has started to react because this reaction is faster than the dissolution process, process becomes diffusion controlled interfacial polymerization and you know for interfacial polymerizations very high molecular well product will be formed almost immediately. We have talked about this before.

And you know long before all the dianhydride has dissolved you will get very high molecular rate of polymer and even before a stoichiometric balance has been achieved you will start to get very high molecular polymer. Even though finally, when everything has dissolved you have a stoichiometric balance because you have calculated this amount in such a way you do not need stoichiometric balance to get high molecular weight the property of interfacial polymerization and its becomes a ineffective solid liquid interfacial polymerization.

Lastly, you you want this to be dissolving very slowly. So, rate of dissolution of your dianhydride the rate of dissolution, the rate of dissolution of dianhydride it depends on temperature, rate of dissolution of dianhydride in the reaction medium depends on temperature. So, this rate goes up as you increase the temperature. This is one more reason why you want to do the reaction at a low temperature. So, not only because the reaction the equilibrium the reaction is basically exothermic, so the equilibrium will shift to the left. So, it will take the system to the left if you go to high temperature.

So, you want to be at lower temperature first thing second thing is that the rate of dissolution of your dianhydride also becomes lower at a lower temperature, and that will give it a higher chance to become diffusion control it will give it a higher chance rate in a situation where the rate of dissolution is actually lower than the rate at which it is reacting with the diamine. So, that it effectively becomes a diffusion controlled reaction.

It effectively becomes an interfacial polymerization solid liquid interfacial polymerization. And effectively it leads to getting higher molecular weight of polymer in this case polyamic acid even though the stoichiometry has not been reached, even though you have not reached a very high conversion a property of interfacial polymerization.

So, now, you understand I mean we have looked in a lot greater detail into this preparation of polyamic acid. And we have also talked about why we are going through polyamic acid in order to get a final polyimide because of the processability problem.

Polyamic acid is something that is soluble still soluble. So, that you take this solution you cast it in whatever kind of mold you want and then you simply heat it up and bingo it is cyclize and once it cyclizes you get your polyamide in the desired form clever indeed. So, that is why you do not want to go to the polyamide in a direct way you want to go in a two stage process.

So, we will come back in the next class. Stay right there we are still going on talking about.