# Principles of Polymer Synthesis
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## Lecture - 45
## Synthesis of Industrial Polymers (Contd.)

Welcome back. We have been talking about the synthesis of polycarbonate in the previous class and we are going to continue on the same topic today. So, just to recap what we did in the previous class was to discuss 3 main synthetic routes to poly carbonates. One of them is inter facial poly condensation, and then there is melt trans esterification, and then the third process is solution polymerization. We talked about the relative advantages and disadvantages of different processes.

So, today we are going to talk about the 4th route towards polycarbonate and that is oxirane or epoxide route to polycarbonates.

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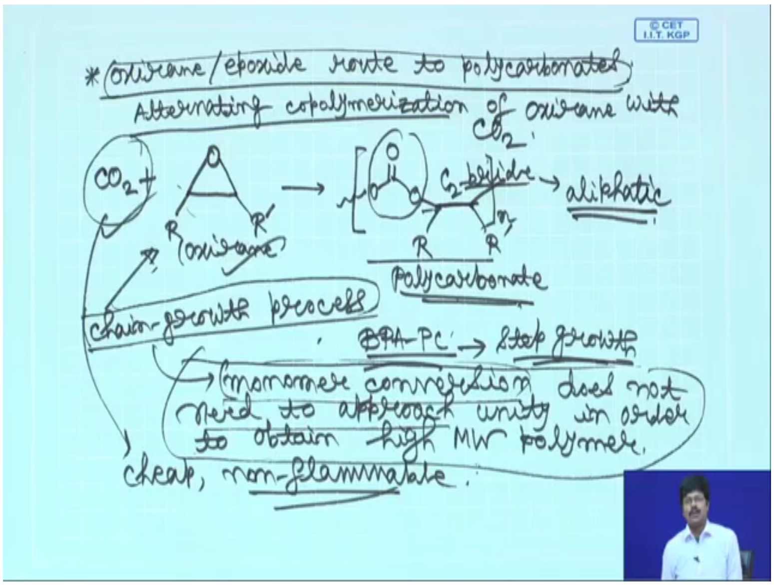

* Oxirane/epoxide route to polycarbonates

Alternating copolymerization of oxirane with $CO_2$.

Monomer conversion does not need to approach unity in order to obtain high MW polymer.

cheap, non-flammable.

So, basically this is an alternating copolymerization an alternating copolymerization of an epoxide or an oxirane the same thing basically of oxirane with carbon dioxide.

So, typically the process is something like this. So, you have carbon dioxide, you are reacting with an epoxide. I am not showing there are two bonds they are basically hydrogens ok. This is one hydrogen have one hydrogen here. So, this is your oxirane or epoxide we have talked about epoxirenes before. So, this linkage we talked about before. So, the product will be something like this ok. So, this is this is your polycarbonate and typically this particular route is not going to give you aromatic polycarbonates remember for bisphenol A polycarbonate we have aromatic rings that are coming from bisphenol A itself. Now, this particular process is for aliphatic polycarbonates as you can see R and R prime they actually denote your aliphatic units.

So, alternating copolymerization you are reacting oxirane with carbon dioxide and they will introduce themselves alternatingly carbon dioxide then oxidant carbon dioxide then oxygen like that and you have this polycarbonate that is produced.

Now, this process has advantages over the other industrial processes that we have talked about preparation of polycarbonates how the v p a, the the bisphenol A polycarbonate has prepared there basically step growth mechanisms that you are applying. So, this particular process is a chain growth process, this is a chain growth process. So, when you talked about this bisphenol A polycarbonate preparations those processes were step growth processes.

So, typically for a chain growth process as we have discussed before that in theory the monomer conversion does not need to approach unity in order to obtain high molecular weight polymer. So, this means that in the past phases of the reaction itself you already start to get higher molecular weight typical of your chain growth polymers.

Typically in your step growth polymers you need to go to very high conversion in order for your high molecular polymer to be produced I mean other than your typical interfacial condensations where we have argued before that in interfacial poly condensations you will have high molecular weight quality early in the in the reaction.

But typically in your step growth polymerization say if you are looking at melt poly condensation or solution polymerization route towards, towards poly carbonates then in molecular it will develop slowly. But in this case the molecular develops quite fast and your monomer conversion does not need to be close to you know 100 percent and still you will get higher molecular weight product.

And also this monomer carbon dioxide is readily available and this is cheap and this is not flammable non flammable. So, this process also then avoids hazardous phosgene.

However the nature of this particular process, so typically here if you are looking at this unit here, you basically have a C 2 bridge, two carbons here. Now, and this is an aliphatic C 2 bridge. So, the nature of the copolymerization the way you are doing this copolymerization it limits the type of backbone that you are going to get the type of backbone to an aliphatic C 2 bridge. So, basically then you get poly carbonates which have aliphatic backbone.

Now, what is the importance of considering this particular point as a disadvantage for this route? I am telling you that this is a disadvantage that you have an aliphatic backbone that is because if you compare these with the polycarbonate that are prepared from, Bisphenol A which are aromatic backbone I told you before that when you have aromatic backbone typically that gives you rigidity into the system because these are rigid units.

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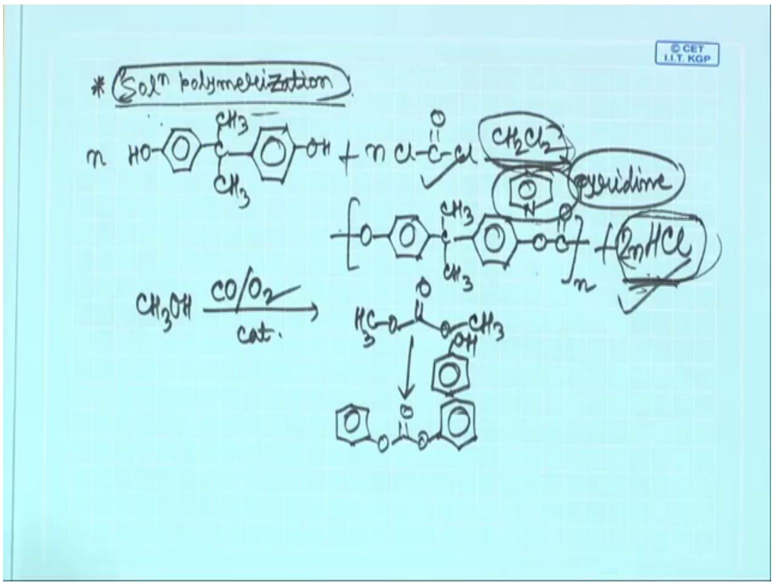

So, that means, it gives you higher stiffness and when it gives you higher stiffness it gives you higher glass transition temperature because glass transition temperature is a temperature beyond with your all the chains a large portion of the polymer change they start to you know have motions and those motions are basically not there at a temperature which is lower than glass transition temperature.

So, above that temperature then you start to lose the properties like your mechanical strength, your stiffness those properties you tend to lose. So, typically if your glass transition temperature is higher for a material then your properties can be maintained up to that much high temperature which is an advantage. So, if you have an aromatic ring because of the rigidity of the system basically your properties can be maintained up to your higher temperature that is because the glass transition temperature becomes higher and also if you have aromatic rings in the system that gives if you compare with the aliphatic rings that gives you a higher impact strength of the material.

And also we told about the heat resistance because that is another way of saying that the you know the preservation of properties that that we are persevere up to a higher temperature; that means, the heat resistance is quite higher if you have a higher T g or the glass transition temperature. And also if you have this bisphenol A based polycarbonate they have a they have typically very good transparency because amorphous their amorphous materials and they have good transparency.

So, we will come to this after, but let us talk about the epoxide route in somewhat more detail we. Now, already know then this process has a disadvantage that you have an aliphatic backbone rather than an aromatic one. So, the glass transition temperature will be lower the properties will be preserved up to a lower temple lower temperature if you compare with respect to the corresponding aromatic backbone based poly carbonates for example, BPA bisphenol A polycarbonates. And secondly, the mechanical strength also should be lower because instead of an aromatic rigid unit you are having these aliphatic units

So, this particular reaction this oxirane route this was first attempted to way back in 1968, 1968. And that reaction was done with an equimolar mixture with an equimolar mixture of diethyl zinc and water.

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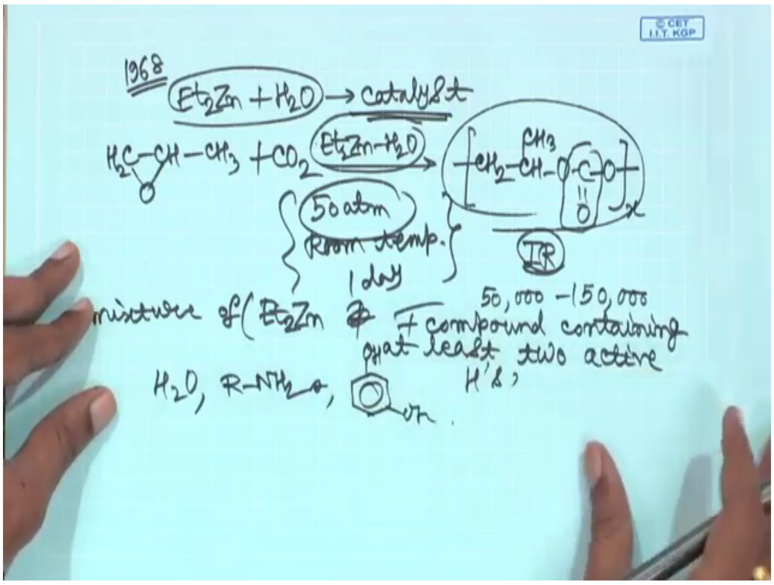

So, diethyl zinc and water this equimolar mixture was used as a as a catalyst and the, so you have two reactants one is carbon dioxide one is an epoxide and this epoxide that was used basically that epoxide was propylene oxide. So, the propylene oxide that reacts with carbon dioxide in presence of a catalyst more about that later diethyl zinc water equimolar mixture and then you get your aliphatic backbone based polycarbonate. So, this is your polycarbonate that you will get and typically these reactions they are done at a high pressure in this case the pressure was 50 atmosphere reaction was of course, at room temperature.

I mean in this case not high temperature room temperature and it was done for one day these are some experimental details just I thought might be useful for you. And of course, after the reaction is over the characterization involves checking infrared spectrum and when you check by infrared what you observe is that there is a strong carbonyl peak that corresponds to the to the carbonate. And the product contains almost equimolar quantity of both this component as well as this component which confirms this is an alternating copolymer and the molecular weight was somewhat around 50000 to 150000.

Now, the catalysts that you are using here they typically will have one common principle going for them and that is that contains a mixture the catalyst contains a mixture of diethyl zinc and a compound and a compound which contains containing at least two active hydrogens. So, if you have water you could use water it has two active hydrogens you could use an amine in combination with diethyl zinc or you could use these kind of phenols this or cineol so on and so forth.

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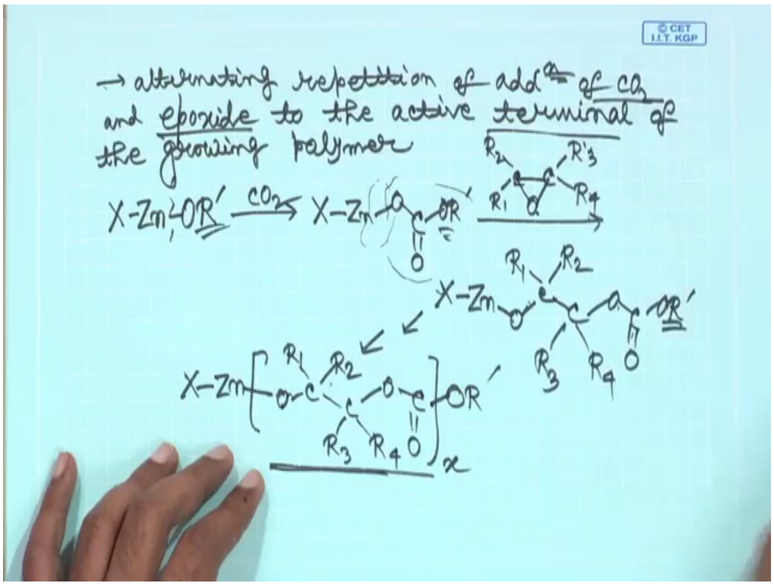

Now, this alternating copolymerization is considered to proceed via alternating repetition of addition of carbon dioxide and epoxide to the active terminal of the growing polymer. So, the growing polymer has an active terminal and to which alternatingly your carbon dioxide and epoxide they are adding. So, a typical process will look like that. So, you have this is your polymer it is growing and then you are adding carbon dioxide. And this carbon dioxide is basically adding here. So, you will have X zinc and then your carbon dioxide has come into the place and then you have O R prime.

And then in the next stage you will have the epoxide that will add to this epoxide it has two carbons here and let us say I am putting R 1, R 2, R 3, R 4. So, this epoxide now, will add here. So, somewhere here and what will happen is. So, you have the this part and then the epoxide will come here. So, you will have X zinc. So, it will open up of course, C and then this is that this carbon depends on the substitution. Of course, in this case I am just assuming it is this carbon R 1, R 2 and then the other two carbons to R units R 3 and R 4 and this oxygen has come here and then this unit is there O CO O R prime.

So, like this it can grow and ultimately the repeat unit will be consisting of something like this. So, this will be a repeat unit. So, you will have C R 1 and then you will have R

2 there and then C R 3, R 4 all right and then your O CO because this is going to repeat and this over prime is at the end from the start itself. So, that just goes outside here say X units. So, this is your repeating unit I mean in fact, this oxygen instead of putting here you could put this oxygen here also inside then also the repeat unit is correct. So, this is how the reaction will go.

So, this completes more or less our discussion of the synthesis of bisphenol A polycarbonate we have talked about 4 different routes to polycarbonate. And we have also told the last route that was the epoxide route that has certain advantages over the other routes because it is chain polymerization and typically you will have high molecular weight of the polymer without going to the very high conversion of the of the reaction also it is a phosphine free. But some of the other routes also have this kind of advantages.

For example, melt trans esterification is phosphine free and interfacial poly condensation typically you will have high molecular weight of the product produced unlike your typical your general step polymerization that we have talked about before.

So, some of the advantages are also there in the other processes. Now, a big disadvantage of epoxide route is that it only entertains aliphatic backbones and if you have aliphatic backbones typically you will route or lose rigidity of the material and you will also lose the heat resistance. And as I told that the significance of heat resistance lies in the fact that higher heat resistance typically will mean it has a higher glass transition temperature. So, the properties can be preserved up the higher temperature and that is something that is true for bisphenol A based polycarbonate because they have all these aromatic units that are in the repeating repeat structure ok.

So, now, that we have finished discussing the synthesis part it is time to talk about the structure property relationship in somewhat detail for these poly carbonates. Now, if you remember just a while back we were talking about some favorable properties of poly carbonates. So, we talked about if you have aromatic rings inside you have high heat resistance you have high impact strength you have high transparency.

So, these troika of properties they are very important for poly carbonates. So, much so that you would do different you would research into different ways to enhance some of these properties. And of course, because if you want to increase if you if you can increase the thermal stability of the material. In other ways if you can increase the glass transition temperature then you have a greater range of temperature to play with in which you can use the material for different purposes because a mechanical property is not lost up until a sufficiently high temperature.

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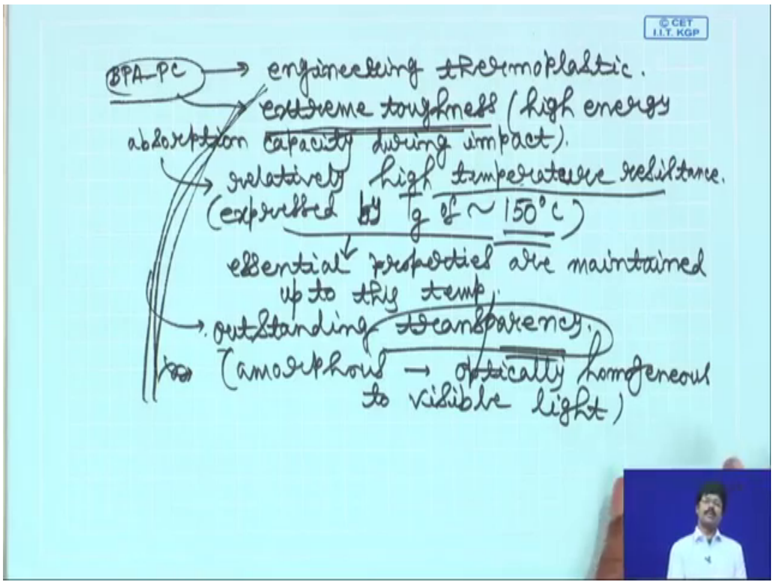

BPA-PC → engineering thermoplastic.

extreme toughness (high energy absorption capacity during impact).

relatively high temperature resistance.
(expressed by $T_g$ of ~ 150°C)

essential properties are maintained up to this temp.

outstanding transparency.
(amorphous → optically homogeneous to visible light)

So, we will talk about those things now. So, bisphenol A polycarbonate it is an engineering thermoplastic, and it has a unique combination of key properties which I have already told before. So, this has extreme, now, I am going to write it down. So, that you have some time to ponder over the importance of some of these particular points, extreme toughness.

So, it means basically high energy absorption so capacity during impact and also relatively high temperature temperature resistance which is expressed by plus transition temperature of around 150 degree Celsius. Typically a bisphenol A based polycarbonate unless modified by other means they will have a glass transition temperature of around 150 degree Celsius. So, that would mean that the essential properties are maintained up to this temperature, and they have these materials have outstanding transparency because they are typically amorphous materials and they are optically homogeneous to visible light.

So, these properties very good transparency and then high temperature resistance extreme impact strength; these are very important properties that signify your polycarbonates. So, some of these properties may be compromised when you go to aliphatic backbone which is a big disadvantage for your epoxide route towards polycarbonates.

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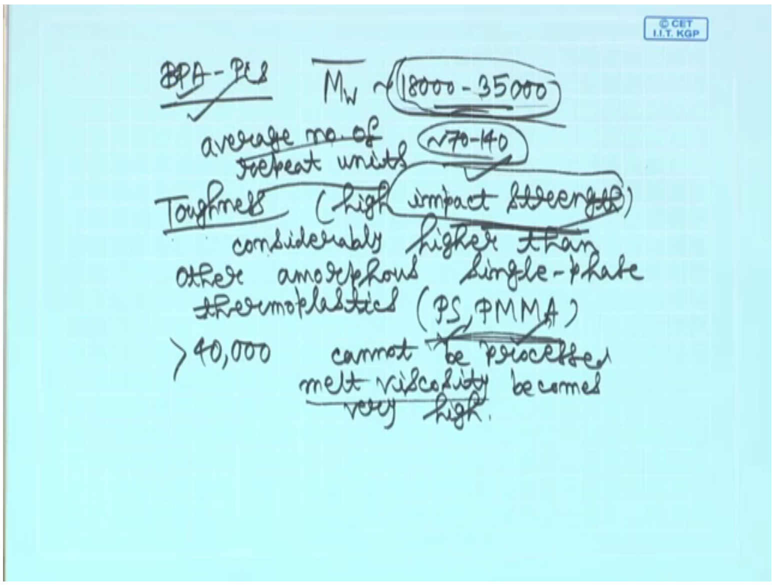

BPA - PCs $\overline{M_w} \sim$ 18000 - 35000

average no. of repeat units ~70-140

Toughness (high impact strength)

considerably higher than other amorphous single-phase thermoplastics (PS, PMMA)

> 40,000 cannot be processed

melt viscosity becomes very high.

Now, industrial, industrially used bisphenol A polycarbonates that are prepared the molecular weight I mean in this case the weight average molecular weight I am talking about that is in the range of 18000 to 35000 which is not very high. So, the degree of polymerization is relatively low and the number of repeating units in commercial products will be around 70 to 140. So, this is I mean average number of repeat units in the commercial polycarbonate bisphenol A based polycarbonate

Now, this number of repeating units although it is not very high it is good enough to have extraordinary toughness for the material and high heat resistance of the material; and the toughness if you are looking at the toughness of this material or the high impact strength of the material high impact strength of the material. So, they are considerably higher.

So, this is considerably the impact strength of this material considerably higher than other amorphous single phase thermoplastics example polystyrene or polymethyl methacrylate. So, the impact strength of bisphenol A polycarbonate is significantly higher than some of these other amorphous thermo thermoplastic materials because you are bisphenol A polycarbonate is also an amorphous thermoplastic material. So, it helps to compare these materials with their counterparts which are of the similar category ok.

Now, the of course, this is not very high and of course, as you understand the mechanical properties will continue to increase or continue to be enhanced or continue to get better as you go to higher and higher molecular weight. Then the question is why do not we go beyond this molecular weight the first thing is that we already will have enough of the properties good enough properties for industrial purpose at this kind of molecular weight in this range. And the second thing is that when you go to higher and higher molecular weight beyond 35000.

So, what will happen is that when the molecular weight reaches higher than 40000 the material cannot be processed the material cannot be processed. Why? Because the melt viscosity will become extremely high melt viscosity becomes very high.

So, you remember all these concepts are interconnected because we talked about melt viscosity when we are talking about melt trans esterification process. And there we argued that towards the end of the reaction you have increased the temperature to almost 300 degree Celsius not only to facilitate the removal of your by product phenol in order to take the reaction forward. But also you know to have sufficient melt viscosity or melt flow characteristics at that temperature because you know when you have a viscous product or a viscous melt the viscosity drops when you increase the temperature.

So, this melt viscosity is a problem for polycarbonate and this is also one of the reasons why you do not go to very high molecular because otherwise it becomes not easily processable because the viscosity becomes too high that is why you do not go beyond 30 to 35000 molecular weight 70 to 140 repeating units that is good enough to give you good properties all right.

Now, let us look at the properties in somewhat more detail. So, you have a combination playing a role here you have benzene ring present in the system.

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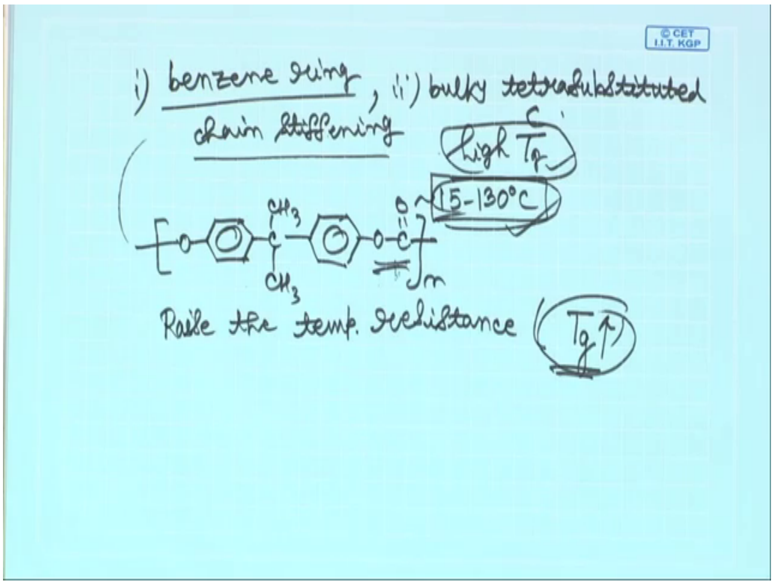

And you have bulky tetrasubstituted carbons that are also present in the system. So, you see here. So, this is your bisphenol A based polycarbonate. So, you have bulky tetrasubstituted carbons that are present you have these rigid aromatic units that are also present. So, all these things will lead to C N stiffening we talked about this. So, this leads to chain stiffening because of the presence of the benzene ring and secondly, because of the presence of bulky tetra substituted carbon in the backbone. So, you will have high T g.

So, you will have a good combination of properties over a considerable temperature range typically from 15 to 130, 135 degree Celsius close to your glass transition temperature. So, a properties are preserved all right. So, one more thing you need to keep in mind is that these let me draw the bisphenol A carbonate for my convenience. So, that I do not need to go back to the old script time and again to explain to you different properties related to the structure ok. So, this is your bisphenol A polycarbonate bisphenol A, carbonate bisphenol A polycarbonate.

Now, we already explained why it will have high T g and this is the range of temperature in which the properties preserve one more thing I would like to tell you here is that this carbonate of course, this carbonate can be can be hydrolyzed this is an ester group, but compared to typical polyester materials these are shielded from hydrolysis somewhat more I mean these are more resistant to hydrolysis and that is because you know these carbonate groups they are basically shielded by these hydrophobic aromatic units on both sides. So, they are less accessible to water for hydrolysis. So, if you compare with a typical polyesters these are more resistant to hydrolysis this is important to keep in mind and your b p a p c or bisphenol A polycarbonate resins and that this is the reason why the your bisphenol A polycarbonate resins will show some resistance to dilute mineral acids which can hydrolyze your ester group ok.

Now, the question the million dollar question is how do we improve the properties of bisphenol A polycarbonate. So, this is your basic polycarbonate structure we are going to only discuss bisphenol A based polycarbonate. Now, because a it is the most industrially prevalent polycarbonate and b it has all the good properties combination of properties over a good range of temperature. So, the question then is how do we improve the properties of these materials.

So, first thing that comes to mind is that we would like to raise the temperature resistance which means we would like to raise the glass transition temperature. So, that would mean that over a higher range of temperature your thermal your properties will be preserved. But also we need to keep in mind that your material should have good impact strength and transparency in this new situation.

So, we will talk about some of these things in more detail in the in the next class. In continuation of our discussion of the structure property relationship in an intimate way as far as the poly carbonates are concerned.

So, today we will stop them and till the next class thank you and goodbye.