Principles of Polymer Synthesis
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Lecture - 44
Synthesis of Industrial Polymers (Contd.)

Welcome back to this NPTEL course on principles of polymer synthesis for the last several classes, we have been talking about the synthetic aspects of the preparation of different industrial polymers, we mainly emphasize on the chemistry part of the synthesis and secondly, we also talked about the wherever applicable the structure property relationships in as much detail as possible. So, today we are going to talk about polycarbonates.

Polycarbonates; they are also prepared by step growth polymerization and typically these poly carbonates that we are going to talk about they are also engineering polymers and mainly, you will see that they have the aromatic backbone they could be also prepared from aliphatic precursors, but mainly there are prepared from aliphatic aromatic backbones. So, we will start with that we will explain to you why that is so also in a detailed fashion as we go along in the class.

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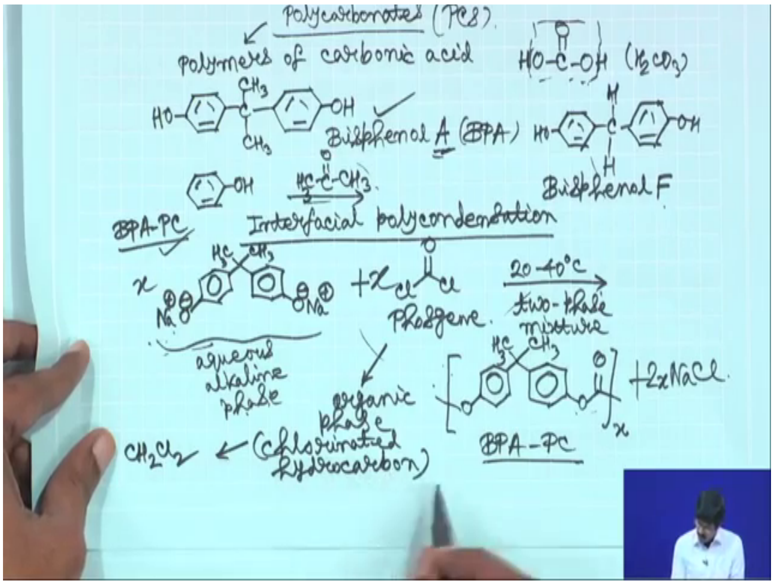

So, we will start with polycarbonates ok. So, basically these are polymers of carbonic acid. So, basically you have this carbonate linkage that will be there present in the polymer. So, that is why they are poly carbonates and the most important commercial poly carbonate is based on Bisphenol A we have talked about Bisphenol A before.

So, the most important poly carbonates are prepared from this starting material. So, this is your Bisphenol A or BPA, you can also tell. So, basically this is prepared from the reaction of phenol with acetone. So, this A comes from acetone. So, if you are instead reacting formaldehyde with phenol, then what you will get is this compound and that is Bisphenol F. So, going by what component you are using. So, it is formaldehyde it is F, it is if it is acetone it is A so on and so forth.

So, one molecule of acetone will react with two molecules of phenol to produce your Bisphenol A now. So, we are going to talk about Bisphenol A based polycarbonates. So, BPA p c and one of the main ways to prepare Bisphenol A based polycarbonate which is mainly you will see mainly these poly carbonates are the industrial important polycarbonates so, one of the main ways to prepare that is interfacial polycondensation. So, you see now that we have discussed the principle of interfacial polycondensation when we are talking about the principles of polymer synthesis in the in the first part of this course so.

Now, you will see the application of those principles here when we are talking about specific synthesis of different polymers. So, interfacial poly condensation this is currently widely used for the industrial production of poly carbonates. So, what you do briefly is you start with Bisphenol A. In fact, it will be the Bisphenolate ion that will be used and you react that with phosgene ok.

Now, this particular reaction that you do the temperature is from 20 to 40 degree Celsius and it is a basically a two phase mixture, if you remember, the principle of interfacial poly condensation, it is basically there are two solvents which do not mix and the reaction occurs at the interface one is typically an aqueous solvent and another is an organic solvent. So, here also; so, you are using a two phase mixture.

Now, it consists of an aqueous alkaline phase. So, basically you have an aqueous alkaline phase. Now this phase is alkaline. So, when you add Bisphenol A to this system, it forms the phenolate salt and then this phosgene is in your organic phase and this aqueous phase and organic phase they are two immiscible solvents. So, basically it produces a two phase system. So, schematically say x molecules of these and x molecules of this and then the product will be your Bisphenol A carbonate. So, you see O C double bond oxygen O that is the linkage that you have that is the carbonate.

So, this is Bisphenol A BPA PC polycarbonate and 2 x molecules of sodium chloride will be produced. So, what is done here is. Firstly, you take your Bisphenol A.

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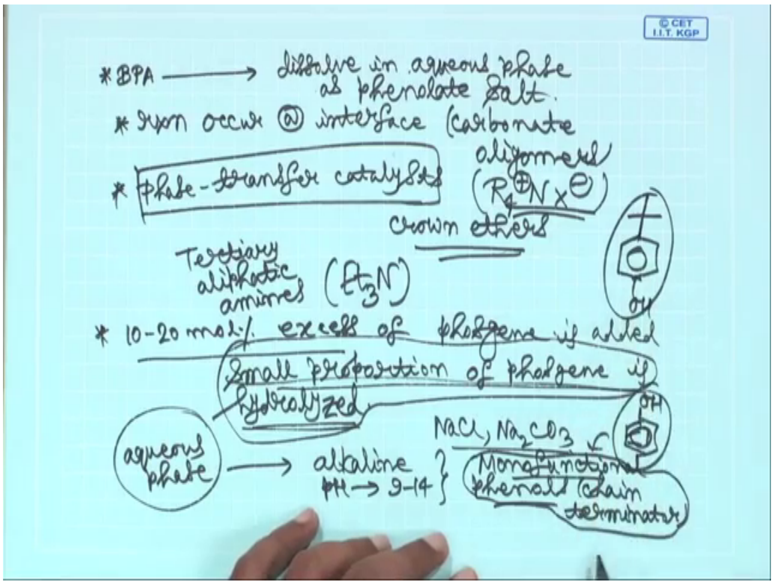

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* BPA → dissolve in aqueous phase as phenolate salt.

* rxn occur @ interface (carbonate oligomers)

* phase-transfer catalysts ($R_4^{\oplus}NX^{\ominus}$)

crown ethers

Tertiary aliphatic amines (Et_3N)

* 10-20 mol% excess of phosgene is added

small proportion of phosgene is hydrolyzed

NaCl, Na_2CO_3

aqueous phase → alkaline pH → 9-14

Monofunctional phenols (chain terminator)

And this Bisphenol A; you dissolve in aqueous phase as phenolate salt. So, there will be sodium hydroxide present in the aqueous layer. So, ultimately means Bisphenol A will dissolve as a phenolate salt. This is to aid the solubility of this system that you are using, this salt in it is in the salt form and the phosgene you take in organic phase.

Now, typically this organic phase will consist of chlorinated hydrocarbon that will be the solvent that you are using say it could be dichloromethane ok. So, you have then two phase mixture your B Spinnel S is present as a phenolic salt in the aqueous phase and your phosgene is present in the organic phase and the organic phase is at the bottom if it is halogenated solvents it is heavier than water. So, it is at the bottom.

Now, the reaction will occur at the interface as the name suggests interfacial polymerization at the interface of the two solvents and it will produce carbonate oligomers carbonate oligomers. Now typically you will use phase transfer catalyst, say for example, a quaternary ammonium salt or you can use also crown ethers, the reason why you will use these phase transfer catalyst is because these catalysts will enhance the transfer of the phenolate salt across the interface into the organic layer.

So, the reaction may not occur exactly at the interface, it will occur either slightly towards the organic site or slightly towards the aqueous site in this case, it will occur slightly towards the organic site. So, the phenolate salt that is there dissolved in water that has to be brought to the organic layer. So, this salt does not have very large very high solubility in organic layer. So, this anion that phenolate anion this big anion that can pair very well with this tetra alkyl carbon tetra alkyl ammonium salt. So, this tetra alkyl ammonium salt which is a big which has a big cation that can pair with this big anion which is a phenolate ion and bring it towards the organic layer.

or if you are using say crown ether crown ether has a lot of oxygens and it has the cavity and this can actually these oxygens they can interact with a corresponding cation in this case you have the sodium ion which is the counter ion for the Bisphenolate anion. So, it can actually interact with the sodium ion and bring that along with the ion which is the anion the Bisphenolate a along with that it can bring to the organic layer.

So, this crown ether that will interact with the counter ion of Bisphenolate A which is your sodium ion n a plus and it will bring it towards the organic layer and along with that n a plus your big phenolate ion also will come towards the organic layer. So, this is how the phase transfer catalyst will work. So, you can also use. So, this is phase transfer catalyst and typically to catalyze the reaction itself you could use tertiary aliphatic amines.

For example, triethylamine, you could use to catalyze the polycondensation reaction. So, initially oligomers will form, but as the reaction progresses you will get high molecular weight Bisphenol A polycarbonates and typically 10 to 20 mole percent excess of phosgene. So, this is your phosgene 10 to 20 mole percent excess of phosgene is added to the system, it is not exactly one is to one 10 to 20 mole percent is excess with respect to your Bisphenol A because that is because a small proportion a small proportion of phosgene is hydrolyzed during the reaction.

So, as you see that if the phosgene hydrolysis during the reaction of this is a kind of activated form of the acid because this chlorine withdraws electron and this carbonyl carbon becomes much more electron deficient and we have talked about this during the discussion of the principle of interfacial polycondensation, there we specifically talked about the reaction of a diamine with a diacid to prepare the polyamide and instead of using diacid we used diacid chloride because that actually enhances the electrophilicity of that acid. So, the reactivity goes up a notch.

Now, if that hydrolyzes, then the corresponding acid will be produced and the reaction rate will become lower remember, you are not using a very high temperature, since, this is these are a this is an activated starting material or reagent you are using quite a low temperature which is also an advantage on interfacial polycondensation. So, now, if this gets hydrolyzed and if it forms the corresponding acid I mean in general if you are having an acid chloride, it is prone to getting hydrolyzed and if it forms the corresponding acid, then at this temperature at the rate constant of the reaction will be quite small. So, the reaction will proceed very slowly and in some cases not at a rate which is practical for industrial purposes.

So, small proportion of phosgene will be hydrolyzed. So, in order for enough amount of phosgene to remain to react with your Bisphenolate ion you use 10 to 20 mole percent of excess and of course, the hydrolysis products are sodium chloride sodium carbonate these are dissolved in the aqueous phase and during the poly condensation reaction this aqueous phase, it is kept alkaline, just to ensure that Bisphenol A stays as Bisphenolate sodium Bisphenolate salt because otherwise its solubility in water will be affected because Bisphenol A solubility is low in water in order to dissolve that in water and let the reaction happen, you used sodium hydroxide in the first place to make the solution alkaline and dissolve it as the phenolate salt and of course, to bring it towards the organic layer you used phase transfer catalyst either tetra alkyl ammonium salt or a crown ether.

So, you make sure that the aqueous phase remains alkaline. So, that the p h is in the range of 9 to 14 during the course of the reaction and mono functional mono functional phenols can be used as chain terminators to control the molecular weights we have discussed this principle before chains terminator, we have told that if you have a mono functional monomer present, then that can actually end cap the growing polymer and there will be no further functionality available to react.

And the polymer will stop growing and depending on how much you are adding you can limit your molecular weight. So, these mono functional phenols, they could be what could be the compound that you are using I mean this class of phenols you are using you can use phenol itself or you could use say 4 tert butylphenol. So, those kinds of mono functional molecules you could use to limit the or the control the molecular weights ok.

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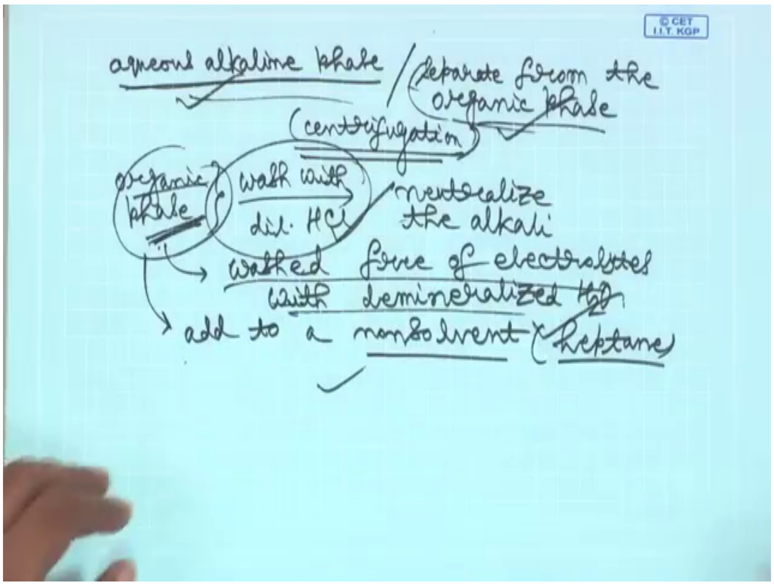

aqueous alkaline phase / separate from the organic phase

(centrifugation)

organic phase

wash with dil. HCl

neutralize the alkali

washed free of electrolytes with demineralized H_2O

add to a nonsolvent (heptane)

So, once the reaction is complete what you have you have the aqueous alkaline phase now these aqueous alkaline phase you separate this separate from the organic phase there will be two layers produced. So, you separate this aqueous layer from the organic layer your product will be in the organic layer and this separation could be done for example, by centrifugation, all right. So, you will have a bottom layer which is organic and you carefully take out until the interface is reached. So, the organic phase is collected out now. So, centrifugation once you have collected the organic phase which now contains your product you have the organic phase.

Now, this organic phase you wash that with dilute acid wash with dilute acid in this case HCl this will neutralize the alkali, it was in contact with the alkaline aqueous layer. So, it will have some alkali. So, you have to neutralize this neutralize the alkali. So, you wash with dilute HCl dilute hydrochloric acid dilute mineral acid and then you washed free washed free of electrolytes washed free of electrolytes with demineralized water. So, first you wash with dilute HCl.

Then you wash with water salts and all those things will go whatever has come into this organic phase whatever liquid has come. So, this organic phase, now contains your product which is your polycarbonate. So, what you do is that you add you, you add this solution. So, what you can do is you add this solution to a particular solvent in which your polycarbonate is not soluble. So, you add to a non solvent.

So, polycarbonate is typically they will not be soluble in say heptane. So, you add the solution to heptane and then the polycarbonate will precipitate out or what you can do is that you can introduce the solution into hot water and subsequently you can evaporate and then you will get your product. So, this is how then you can use interfacial poly condensation to get your polycarbonate and all the telltale science of interfacial polymerization is there we have already discussed before. So, you have you an interface you have two solvents one is aqueous layer one is organic layer and you are using a phase transfer catalyst to bring your Bisphenol A which is not in Bisphenol A form, but which is in its salt form Bisphenol it, it is a salt form in the aqueous layer.

So, it is dissolved in aqueous layer and then you are bringing it towards the organic you are using a phase transfer catalyst and the organic layer itself contains the activated acid which is in this case the phosgene and then the reaction happens somewhere close to the interface to it in slightly towards the organic site and in order to control the molecular weight of the product, you are using mono functional monomers, in this case, the mono functional phenols also the derivatives of mono functional phenols and then once the reaction is complete you just separate them out by centrifugation when the two distinct layers are formed.

So, our top layer is water the bottom layer is the top later is aqueous layer the bottom layer is organic layer and then you take it out and then you can wash it with dilute HCl to remove the residual alkali or and then the residual salt is removed by washing with water and then you can precipitate your polycarbonate by adding this solution to a solvent in which the polycarbonate is not soluble in this case say heptane and then you get a solid.

And you can dry it and you can use it. So, this is all about the synthesis of polycarbonate through interfacial poly condensation there are other processes also that we are going to discuss now that are used to synthesize polycarbonate.

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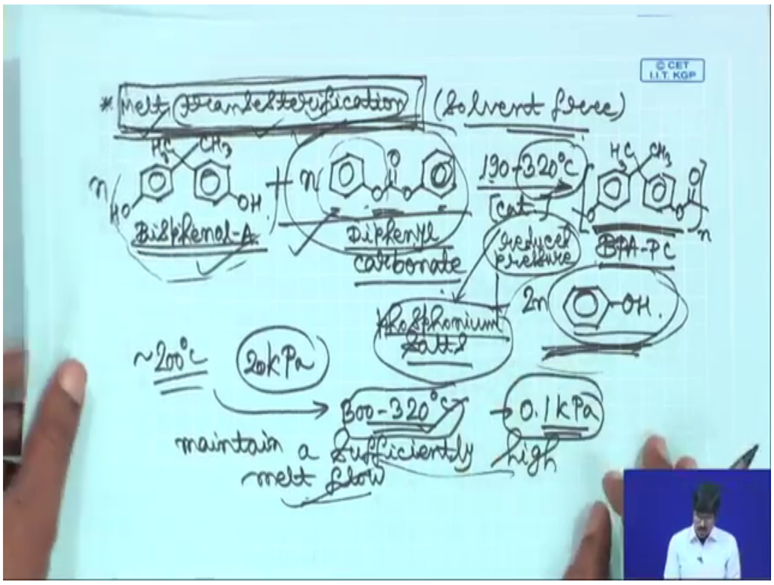

So, one of them is melt transesterification. So, basically this is a solvent free process and as the name suggests this is transesterification. So, again you start with a Bisphenol A this in this case you are not using a Bisphenolate salt because you are not using a solvent in which it has to be dissolved. So, you can just use the parent Bisphenol A

So, this is your Bisphenol A; now Bisphenol A you can react with this molecule. So, this is a carbonate linkage and there are two phenyls. So, this is basically your diphenyl carbonate. So, this is an ester here this is a acid and this is the alcohol part. So, there will be a transesterification. So, basically what you will have is that this alcohol part will be removed and this alcohol will be added to this. So, this will be a transesterification process. So, the bi product will be phenol.

So, this reaction is done at temperature quite high. So, this is a range means you start with a lower temperature and then you go to higher temperature. So, that is why this range is there and you are using some catalyst and you will get your Bisphenol A polycarbonates which is having this repeat unit. So, you see that this alcohol here has been replaced by these alcohols that is why it is a transesterification process.

So, this is BPA PC Bisphenol a polycarbonate that is the abbreviation and you will have. So, if you have n number of molecules here n number of molecules here then you will have two n number of phenol molecules that is that are produced and this phenol has to be removed through distillation in order to drive this reaction forward.

Now, this reaction is usually catalyzed by very small amounts of phosphonium salts and this reaction of course, is done at a high temperature and it is done under reduced pressure in order to facilitate the removal of phenol through distillation. So, initially the temperature is not very high, initially, it is around 200 degrees you see you start at 190 degrees and the pressure is slightly reduced.

So, the pressure is around 20 kilo Pascal and during the course of the reaction you raise the temperature towards 300 degree 300 to 320 degree Celsius, gradually, you raise the temperature and the pressure is reduced further up to 0.1 kilo Pascal. So, towards the end of the reaction, you have to use quite high temperature because you need to maintain you need to maintain a sufficiently high melt flow.

Now, the reaction is done in molten condition these two they will be in molten state that is why it is a melt transesterification because this is a process of transesterification as you can see this alcohol is replaced by this alcohol. So, maintain a sufficiently high melt flow because the melt viscosity will go up as the temperature is going down. So, if you go up in temperature. So, the viscosity will go down. So, unless you go to this much temperature at the melt will become very thick.

So, in order to have a sufficiently high melt flow you go to high temperature and the pressure must be as low as possible towards the end of the reaction; so, as to eliminate the phenol from this viscous melts and the in fact, this melt transesterification process was the first industrial process for the production of polycarbonates. Now of course, we use also interfacial polycondensation, but melt transesterification was the first industrial process that was used for the production of polycarbonates.

So, the other; so, this is your second technique then second process one is interfacial poly condensation and the other one is melt transesterification.

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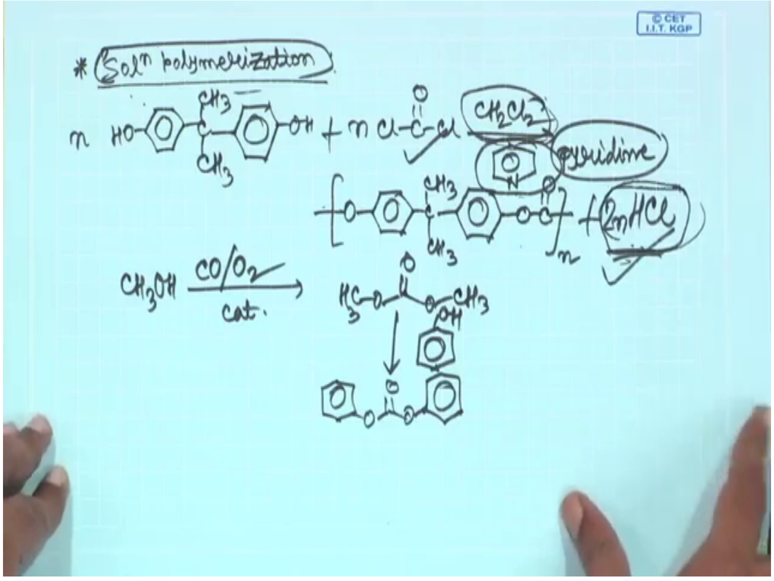

The third process through which you can prepare polycarbonate is solution polymerization basically this is very similar to your interfacial polycondensation, but here you are not using two solvents you are basically using only one solvent which is your organic solvent. So, it is done in one phase not like in two phase.

So,. So, what you do is that you start with your Bisphenol A and of course, in this case it is Bisphenol A because you are not using an water an aqueous solvent in which the solubility is a problem this dissolves well in the organic solvent. So, you react this with what else phosgene chloride in dichloromethane. So, you have this halogenated solvent and you use pyridine also i will tell you why. So, in presence of pyridine you are doing the reaction.

So, this is your product you see that we are drawing the structures differently all of the structures they will actually tell you the same product I mean I you can either draw it like this or you can draw like this. So, as long as your you understand it you can draw whichever way you would like as long as the structure is correct. So, this is your product along with that HCl will be produced now where do you have a interfacial ploycondensation what happened is instead of HCl sodium chloride was produced because it was a sodium salt. Now in this case it is not sodium salt. So, you are having an HCl; HCl production and in order to scavenge this HCl in order to remove this HCl you have to use a base that is why you are using pyridine. So, you have to remove this CHl.

So, you are using pyridine because then it will form a salt with HCl pyridinium chloride it will form now the difference with interfacial polycondensation, apart from the obvious point that the reaction is not at interface, but it is in one phase is that in the interfacial polycondensation sodium hydroxide is your acid acceptor because you are using alkaline medium and in solution poly condensation or polymerization you have pyridine as the acid acceptor. So, some general comments I would like to make when you are comparing your solution polymerization with interfacial polycondensation. So, industrially the interfacial polymerization is more prevalent because it is also economic and you have an easier control of molecular weight.

However this melt transesterification has. So, either you have say solution polymerization which is very similar to your interfacial polycondensation we have talked about or we have melt transesterification. So, basically we are going to compare melt transesterification with interfacial because there is not much of difference between solution polycondensation and interfacial polycondensation, you are using both in both the cases phosgene and in one case, you are using a sodium salt in other case you are not using sodium salt, but you are using an halogenated solvent nevertheless.

But the difference with a melt transesterification is more stark as you can see that in melt transesterification you are not using phosgene phosgene is a very poisonous substance. So, it hazardous material and in fact, other than phosgene, you are also using say dichloromethane I mean both in solution polymerization as well as your interfacial polycondensation. So, this is also suspected carcinogen. So, these reactions then either your solution poly polycondensation or interfacial polycondensation, they are not in the environmentally friendly. So, that way your melt transesterification offers you a distinct advantage.

And also as I told you this is a phosgene free process and when you are preparing diphenyl carbonate it is also fairly straightforward process to prepare diphenyl carbonate. So, basically you start with methanol and you react with carbon monoxide and oxygen mixture in presence of some catalysts and then what you have is dimethyl carbonate now these dimethyl carbonate if you react with phenol what you will have is a transesterification reaction and you will get diphenyl carbonate this is how you prepare your starting material for the melt transesterification reaction and Bisphenol A, already we talked about how it is prepared, but one disadvantage of melt transesterification is that it requires high temperature in order to remove phenol.

So, you have to go upwards of around 300 degree Celsius, but if you compare with interfacial polycondensation for example, you just need to use 20 to 30 degree Celsius. So, that is a big disadvantage for melt transesterification reaction. So, I think that that completes our discussion on these more or less these first three techniques say melt transesterification indust industrial preparation of polycarbonate either melt transesterification or interfacial polycondensation or solution polymerization.

So, today we will stop here and in the next class we are going to talk about another process to synthesize polycarbonate. So, in total we will talk about four different processes that can be used to synthesize polycarbonates so.

Thank you for your attention and see you in the next class.