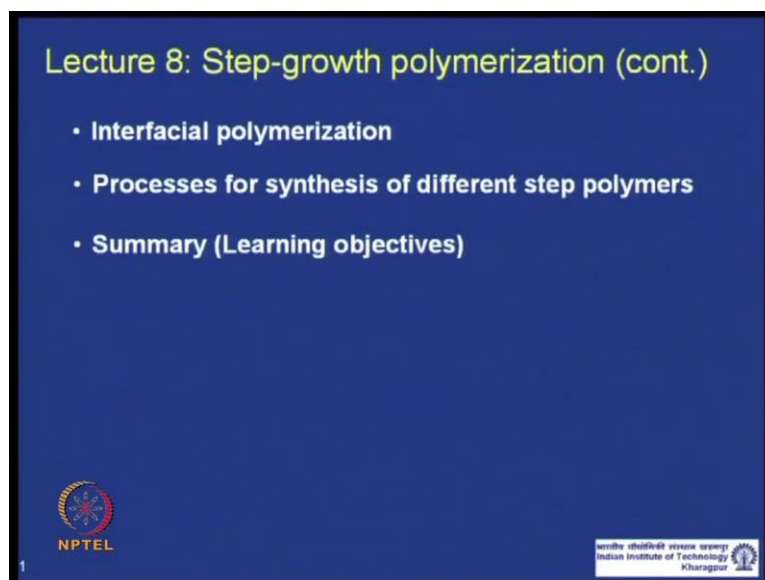


**Polymer Chemistry**  
**Prof. Dibakar Dhara**  
**Department of Chemistry**  
**Indian Institute of Technology, Kharagpur**

**Lecture - 8**  
**Step-growth Polymerization (Contd.)**

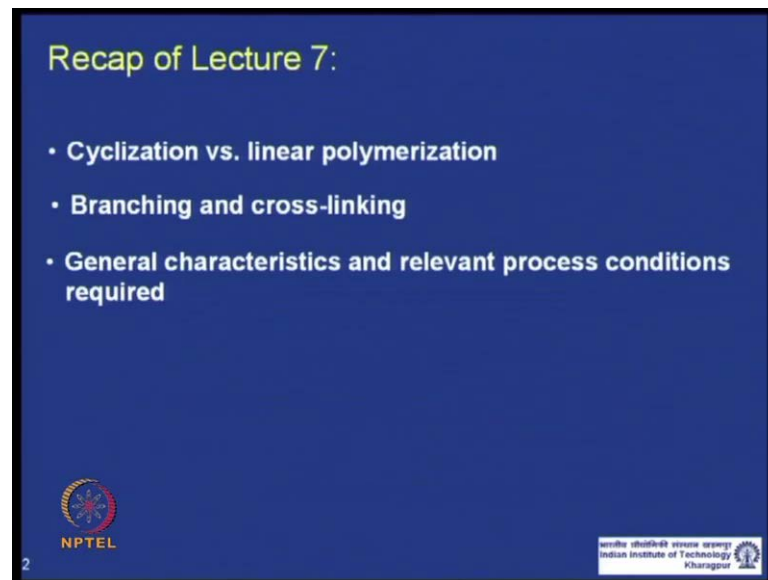
Welcome back to this 8 th lecture of this course in Polymer Chemistry. In today's lecture we planned to cover interfacial polymerization, and we also will be talking about different synthesis of different step polymers in very brief briefly. And at the end, I planned to just give a summary of this module on step growth polymerization.

(Refer Slide Time: 00:49)



And I will be telling you what is my expectation at the end of this module. Now, let us look at the whatever topic we covered in the last lecture. In the last lecture we have covered the cyclization verses linear polymerization, what are the conditions which prefer linear polymerization, which are different the preferred ones. We also discussed various way of making branched and cross linked polymers.

(Refer Slide Time: 01:37)



The slide is titled "Recap of Lecture 7:" and lists three bullet points: "Cyclization vs. linear polymerization", "Branching and cross-linking", and "General characteristics and relevant process conditions required". It features the NPTEL logo and the Indian Institute of Technology Kharagpur logo at the bottom.

**Recap of Lecture 7:**

- Cyclization vs. linear polymerization
- Branching and cross-linking
- General characteristics and relevant process conditions required

NPTEL

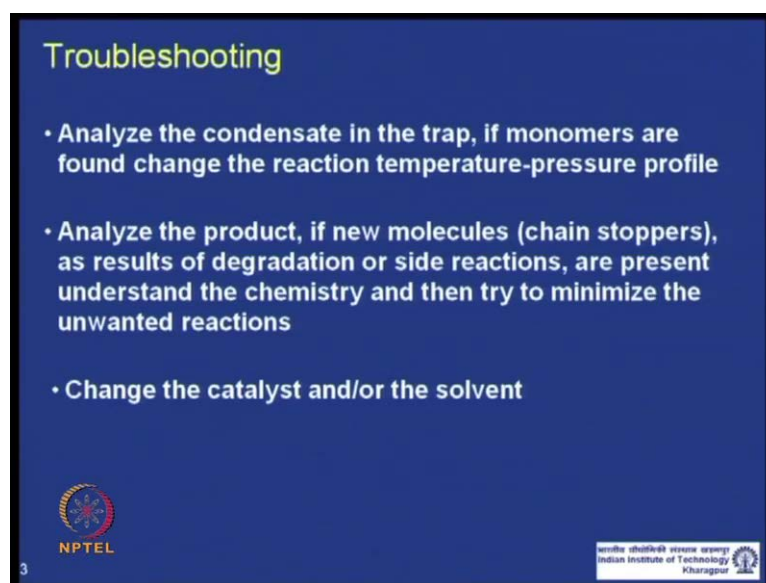
Indian Institute of Technology Kharagpur

And we also studied in that context that in case of branching reaction going on the molecular build up is higher for a given conversion in comparison to a linear polymerization. And at the end we discussed the complete list of conditions or the criteria, which one must be maintaining during the polymerization or at the beginning of the polymerization to have a successful step polymerization. I mean by successful, I mean a building of the molecular weight of the polymer, which is targeted and in most cases it is a high molecular weight polymers.

Now, suppose you have done everything right, whatever instruction is given to you in the this course or in any text book, you have followed everything right. You have taken monomers in a ratio very close to  $r$  is equal to 1 and you have done the reaction at high temperature for longer time, try to take out the condensate for you know as much as possible. And you have done whatever I have been instructed to you have done that.

In spite of doing that you found that at the end of the reaction your desired polymer has not formed. That means, you must be expecting a high molecular weight you have got a low molecular weight polymers. Now, what does it mean it does not mean it all the instruction given to you are incorrect, you have to deep you know look into deep what might have happened. And I just I will give you few guide line in the deep something goes wrong in spite of doing your best possible way; now what are the things to look for and let us look one by one.

(Refer Slide Time: 03:39)



The slide is titled "Troubleshooting" in yellow text on a dark blue background. It contains three bullet points in white text. At the bottom left is the NPTEL logo, and at the bottom right is the Indian Institute of Technology Kharagpur logo. A small number '3' is visible in the bottom left corner of the slide area.

**Troubleshooting**

- Analyze the condensate in the trap, if monomers are found change the reaction temperature-pressure profile
- Analyze the product, if new molecules (chain stoppers), as results of degradation or side reactions, are present understand the chemistry and then try to minimize the unwanted reactions
- Change the catalyst and/or the solvent

NPTEL

Indian Institute of Technology Kharagpur

3

So, there is a guide line for trouble shooting, now you must be capturing the condensate in a trap will distilling of the condensate byproduct you must be you know must be collecting that in a trap. Now, you analyze the end of the reaction, you analyze that that material in the trap and see whether you found any monomers in there.

Now, if we find any monomer there, which means that during the polymerization one or more than one monomers has escaped by volatilization. And that is going to imbalance your monomer ratio, you must have you might have taken one is one ratio or whatever very close to one what is your target molecular weight. But still, because one of the monomers might have volatile in excess than other, which will imbalance your stoichiometric ratio and which will definitely going to decrease your final molecular weight.

Now, what are the ways you can tackle this, one thing you can do if you find that their monomers are getting volatilized during the reaction. You can start slowly, which means that you take a you take the reaction and carry out the reaction for some time at a lower temperature and at atmospheric pressure. And when a reaction has progressed some for some duration and then duration there is a chance that monomers might form dimer or small molecular weight, oligomers.

Then their volatility tendency of volatility would come down as their molecule weight increases increased by this time. Now, if you apply the vacuum or reduce the pressure,

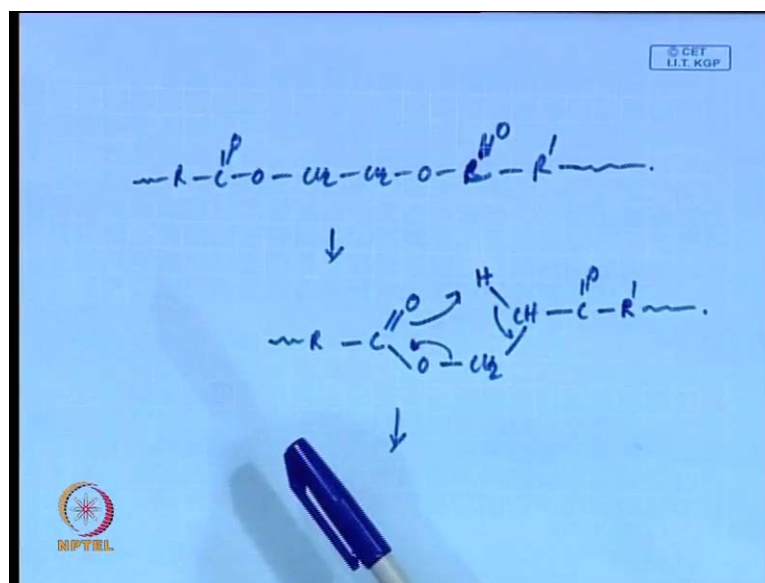
then chances of you know volatilization of the monomers comes down. So, what you can do in reaction you can do in the steps, you can do the first step in a lower temperature and at higher pressure and then slowly increase the temperature and reduce the pressure. And at the finally, when your molecular weight the conversion is you know quite high, there are less amount of monomer present in the reaction medium, you ramp the temperature as high as possible, you know and then you reduce the pressure as much as possible.

So, that is the one way you can reduce and the volatility of the volatilization of the monomers. Second thing you can analyze the product, if the product is colored or if you by analyzing the reaction mixture of the end of the product at the end of the reaction we find there are new molecules. And specially look for the chain stoppers which are mono functional molecules, if you find them which means it is as a result of degradation or a side reaction there would be either imbalance in the stoichiometry.

Or there would be generation of this mono functional chain stopper, which will which will stop your polymer chains to progress further. So, that will again reduce the molecular weight build up. And what you have to do to tackle this you will understand what is going on and understand the chemistry behind this side reaction and then do whatever now your best way to minimize this side reaction unwanted reactions.

And sometimes the catalyst, which you are using in the reaction that might be one source, which might be catalyzing the side reactions as well. So, you might consider chancing the catalyst or even reducing catalyst amount in the reaction. So, that your side reactions comes down as low as possible, one side reactions we can consider during polyester formations.

(Refer Slide Time: 08:05)

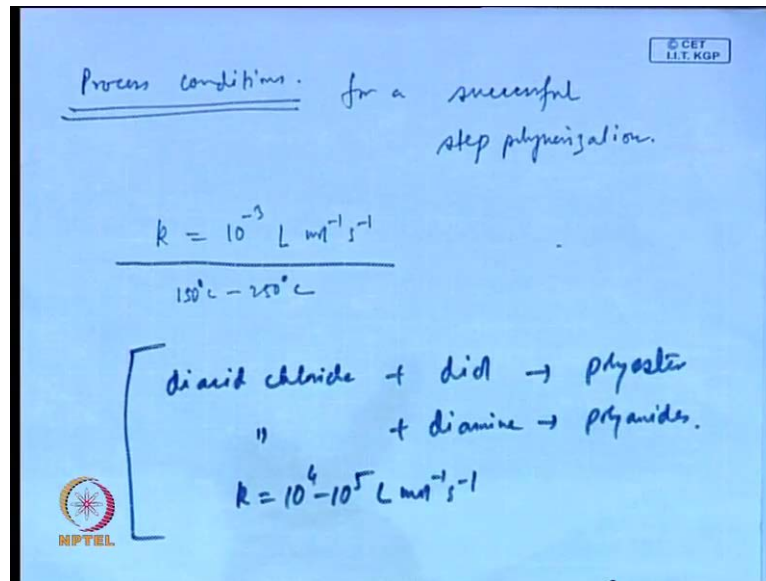


For example, if you have say during a polyester formation, if you have something like this, there is one more very common side reaction is happens is by beta elimination reaction. So, with this you can generate free acid group and a alkene group here, at this is very common by if you have a beta hydrogen present then by doing a 6 membered considered reaction, it might do a side reaction.

And you can end up getting new functional group or new products, which might give you color in the at the end of the reaction, so that is one example. So, third thing you can do as I was mentioning is that you change the catalyst or sometimes catalyst a I said might accelerate the side reactions as well. And if you are doing in a solution, you are doing this poly step polymerization reaction solution, then you can also try and change the solvent.

Now, so these are the things you can try out, if your reaction goes wrong and of course, if this nothing else work with this you might have to consider changing your reaction monomer, you are changing your monomers all together.

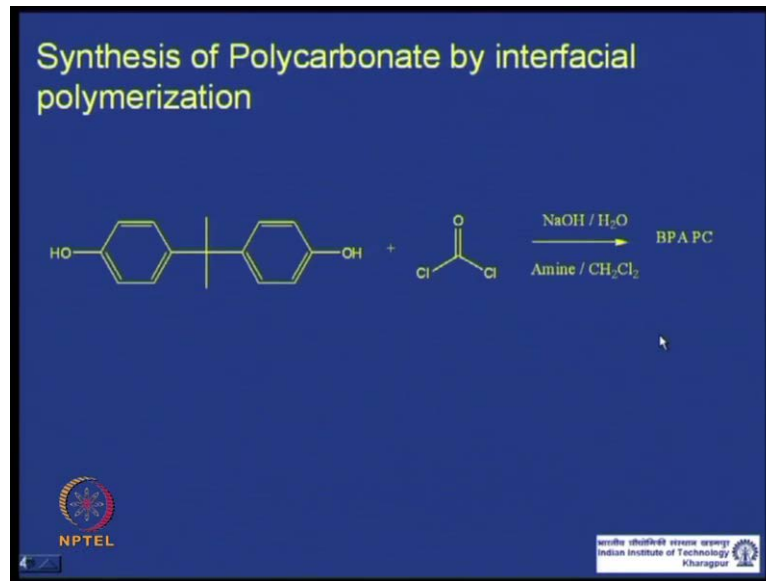
(Refer Slide Time: 10:25)



Now, let us go back to the last lecture, we talked about that the  $k$  rate constant for step polymerization is quite low  $10$  to the minus  $3$  liter per mole per second. Now, there are few exceptions, there are actually very few exception, one example is the reactions with diacid chlorides. For example, if you have diacid chloride, chloride plus diol forming polyester polyester, say diacid chloride plus diamine polyamide.

Now, these diacid chloride reactions with dial or diamine there are very fast and  $k$  r of the order of  $10$  to the power  $4$  to  $10$  to the power of  $5$  L in term of per second inverse, which means they are much fast reaction compared to the normal step polymerization reactions. And this first reaction are you know the has been taken that, this the fastness of these reactions has been taken. And it has been used in making polymers by interfacial polymerization.

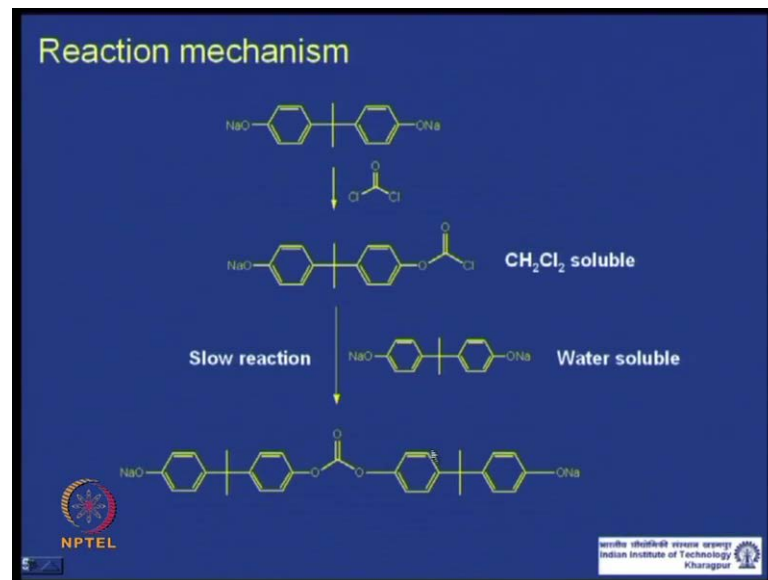
(Refer Slide Time: 12:01)



And I will come to the example of interfacial and polymerization. Interfacial polymerization reactions are happened in the interface between 2 liquid phase, 2 monomers are taken in two different liquid phase and the reaction happen in the interface. For example the polycarbonate, most of the polycarbonate major rate of the polycarbonates are synthesized by this interfacial polymerization bisphenol this is the monomer bisphenola.

And this is phosgene bisphenola is taken in the aqua sodium hydroxide solution and phosgene is passed through a organic solvent, in this case say methylene chloride forming BPA PC or bisphenola poly carbonate.

(Refer Slide Time: 12:48)



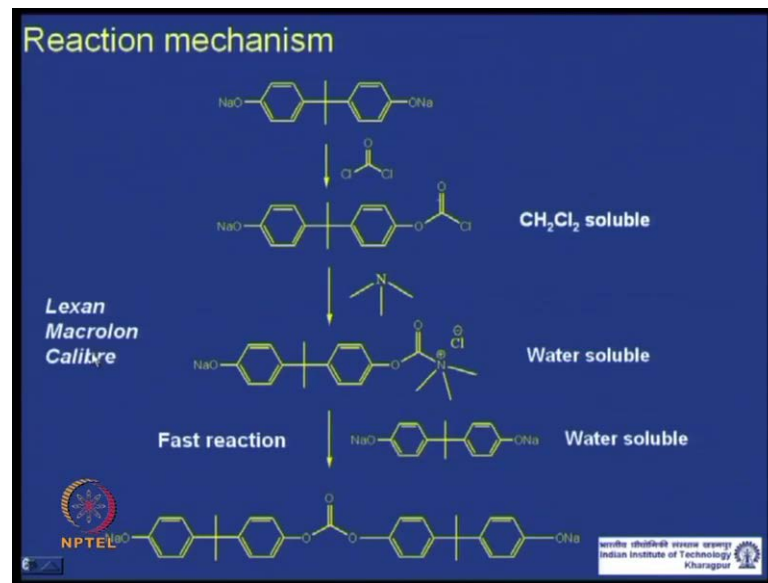
Now, what is the mechanism, you have BPA bisphenol a present in the aqueous solutions of sodium hydroxide, so you have phenolate salt. Now, this at the interface reacts with phosgene forming this monomer which again with reaction with this phenolate salt will form a dimer in this case and reaction will proceed further in this way.

Now, what is the problem here the only one thing to consider that this is a water soluble monomer, this bisphenol in a sodium hydroxide solution and this phosgene is formed through the organic medium in this case methylene chloride. So, when this is formed this is a methylene chloride soluble species, so this will stay in the methylene chloride solution.

To react, now if you want to react with the bisphenol phenolate ion to form a polycarbonate species, this has to migrate to the interface, this is currently now in the organic phase and this is in the aqueous phase. So, the chances of reacting of these two species is low, the chances of this species reacting with this species is low. So, this is a very slow reaction, if you do the reaction in this way this will give you a very slow reaction.



(Refer Slide Time: 14:47)

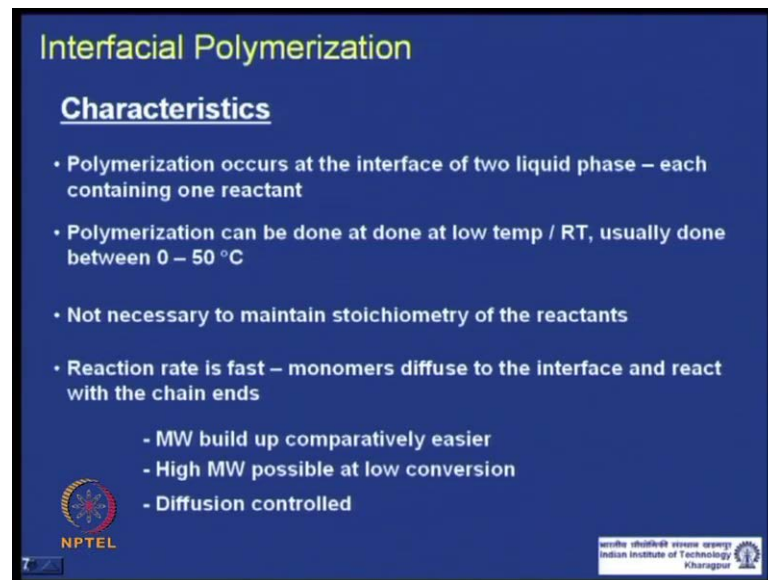


So, what is done to tackle this problem a tri a amine is added in the organic medium, say triethylamine or trimethylamine and when this reacts with this species it is form a salt now this is water soluble. So, now, you have a water soluble species, again this is water soluble. So, now, they can do reaction in the water side of the interface, so the reaction become faster. So, you have to add this amine catalyst to facilitate the reaction and have the reaction happening in first way, no first space.

The same thing you can do if you what to keep this in the organic medium you can add a phase transfer catalyst in the water side, which will then complex with this bisphenol a salt and bring it closer to the organic medium. So, then the reaction of this two reacting species will be happening in the organic side of the interface. So, either you can add trimethylamine to bring this species to closer to water side or you can add a phase transfer catalyst to bring this bisphenol a ion to the organic side to make the reaction faster.

Bisphenol a poly carbonate is having this commercial trade names, I will be giving all this you know some of the trade names of this polymers in the next few slides as well.

(Refer Slide Time: 16:47)



**Interfacial Polymerization**

**Characteristics**

- Polymerization occurs at the interface of two liquid phase – each containing one reactant
- Polymerization can be done at low temp / RT, usually done between 0 – 50 °C
- Not necessary to maintain stoichiometry of the reactants
- Reaction rate is fast – monomers diffuse to the interface and react with the chain ends
  - MW build up comparatively easier
  - High MW possible at low conversion
  - Diffusion controlled

NPTEL

Indian Institute of Technology  
Kharagpur

So, what are the characteristics for the characteristic for the interfacial polymerization we just discussed one that polymerization occurs the interfacial of two liquids and each of the liquid phase contains one reactant. Now, because reaction is very fast you saw the rate constant of the reaction is very high. So, the reaction is very fast, so you can do it at low temperature in room temperature and it is usually done at a temperature between 0 to 50 degree centigrade.

Now, because the reaction is happening in the interface and at interface one one reactant is reacting with one of the other reactant. So, you do not need not to maintain a stoichiometry of say very close to one is to one like the other linear poly condensation reaction here. Because, the stoichiometry are the interface is always maintained at one is to one, because reaction is not happening in the volume phase of the two monomers it is happening only at the interface and because reaction happening one is to one.

So, the stoichiometry at the reaction side, which is the interface is always maintained at one is to one. So, you do not need make a effort to maintain the stoichiometry of the two monomers close to one is to one. Now, the reaction is fast, so the when the monomer diffuse to the interface immediately it find a chain end reactive chain end and in reacts before even can approach to the other monomer, which means that this unlike this linear poly condensation reaction, which talked about it happens in a kinetic control way and it is very fast.

So, what is the outcome that molecular build up is much easier, because the as soon as the monomers diffuse from the bulk to interface it reacts with the chain end and the chain grows one after one. And in other case normal linear poly condensation case you have dimer, trimer, tetramer and it go slowly one after one, but in this case the monomers comes by diffusion to the interface reacts with the chain end. So, the chain grows in size, so it is very you know it is comparatively much easier to build molecular weight.

And as the reactions are happening or the monomers is getting added at the end of the chain, high molecular weight even possible at low conversion. Unlike the normal poly condensation or step polymerization process. And because the diffusion is slower compared to the actual reaction, polymerization reaction this reaction this polymerization reaction are often diffusion controlled.

(Refer Slide Time: 19:59)

**Interfacial Polymerization**

**Requirements**

- Inorganic base is required to neutralize HCl
- Minimize acid chloride hydrolysis
- Proper choice of solvent
- Proper stirring

**Disadvantages**

- High cost of acid chloride
- Use of lots of organic solvents
- Polymer need to be taken out by precipitation, chances of more impurities
- Batch process
- More cyclics

NPTEL  
Indian Institute of Technology  
Kharagpur

So, what are the requirements for a successful inter polymerization interfacial polymerization you need to have a inorganic base, which you require to neutralize the produce HCl otherwise HCl with go back and hydrolyze the salt. In this case the example I showed you polycarbonate the sodium hydroxide was present to neutralize the HCl byproduct. And the other way also you should restrict or minimize the acid chloride hydrolysis, because if it hydrolyze and form a plane alcohol, then it will just acid chloride if it hydrolyze to form simple acid carboxylic acid.

Then the reactivity will come down the reaction rate will be much lower and it will not

happen it will not take place in the temperature we are working. Proper choice of solvent, you must be taken and you need, because this reaction is happening interface. So, if you start well you can generate more and more interface and by doing by generating more and more interface you can make the reaction the polymerization reaction faster. So, product might will form much faster rate, if you are not starting the reaction.

So, what are the disadvantage in spite of all this advantages, this is not this interfacial polymerization are not practiced very frequently commercially, so there must be some disadvantages. And the main disadvantages are that the acid chloride acid chlorides are very costly. So, it is is not very economic in true sense and as you as you saw that we have to use wider lot of organic solvent and handling that large amount of organic solvent recycling them, and storing them and is a environmental hazard as well storing and handling them this organic solvent.

So, you know increasingly people are trying to avoid this root simply to avoid this use of large amount of organic solvent, which are not environmentally friendly. Now, also polymers if you with it is presented in a solution most and most commonly in the organic solvent. So, you need to take out the polymerization by precipitation for example, in poly carbonate case the poly carbonate are solvable in the methylene chloride phase. So, you have to at the end of the polymerization you have to take out the poly carbonate by steam precipitation if you steam precipitation.

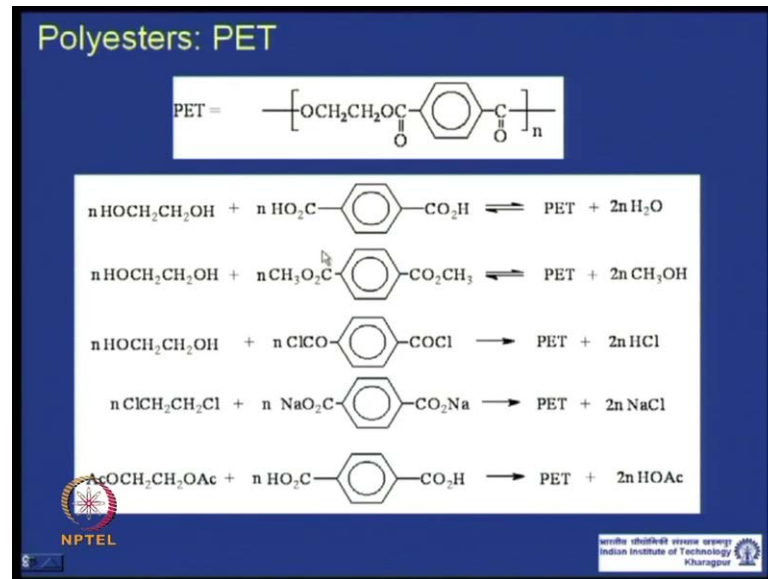
So, there are always chances of having more impurities, compared to if you are doing in a bulk condition or a in a solution pure solution and also it is a batch process it is very difficult to do it continuously and as this reaction is kinetically controlled. So, this byproduct as the byproduct HCl is not taking part in the reverse reaction, so this reaction is kinetically controlled. The chances of forming cyclics are much more, because cyclics are not reacting with the byproduct and forming the linear product once again, which means once cyclics forms it will remain in the final product. So, chances of having more cyclics are more in this interfacial polymerization.

So, now we move to the different polymers, in coming few slides I just wanted to give you the standard synthetic process of the common commercial step polymers. Starting from polyester this is not exclusive least of polymers or it is not the detailed synthetic process or all the processes, which are utilized commercially. I just wanted to give you a

brief idea of different types of step polymers and how they are synthesized commercially, just in a very brief.

We will start with polyester and just example we will take is the most important and most used polyester poly ethylene terephthalate.

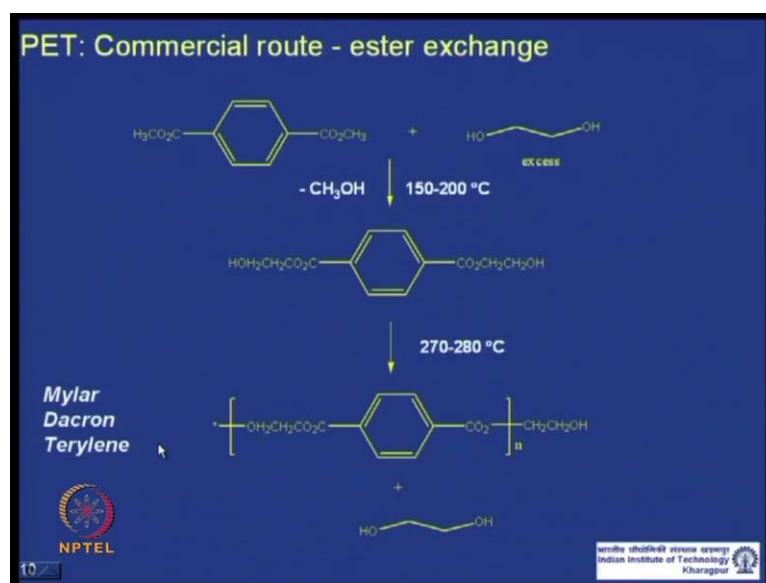
(Refer Slide Time: 24:24)



This is the structure we have been showing you many times, these are several ways you can see synthesis PET Poly Esters Terephthalate, you can do take a ethylene ethylene glycol and diacid terephthalate acid. And direct reaction you can take instead of terephthalate acid you can take dimethyl ester of terephthalate acid you can take acid chloride and acid an hydride and so on an hydride and so on.

But, this reactions we know this direct esterification of alcohol and acids or say ester an acid groups are very slow reactions. So, you may require high temperature, so this are typical not used commercially this two reactions are not used commercially.

(Refer Slide Time: 25:24)

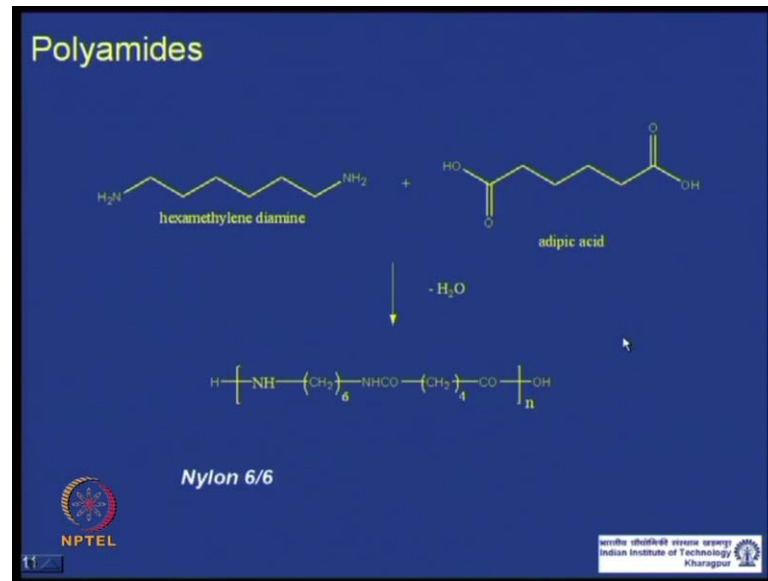


What did the commercial way of synthesis or the most practiced the synthetic process of making polyester or poly ethylene terephthalic. This case is by ester exchange it can be done either starting from dimethyl ester of terephthalic acid or from terephthalic acid itself. It is a two stage ester exchange process, first stage dimethyl terephthalic M T is reacted with excess of ethylene glycol at say around moderate temperature and methanol is distilled out to form this compound.

And then these are now heated to a much higher temperature and the ethylene glycol is distilled out from the reaction. So, between two of this molecules exchange ester exchange happen and as you take out this ethylene glycol from the system polymerization medium the polymer start growing slowly this is the. And another way of making the PET is instead of taking dimethyl terephthalate, you can start with terephthalic acid and make first this an then follow the same process.

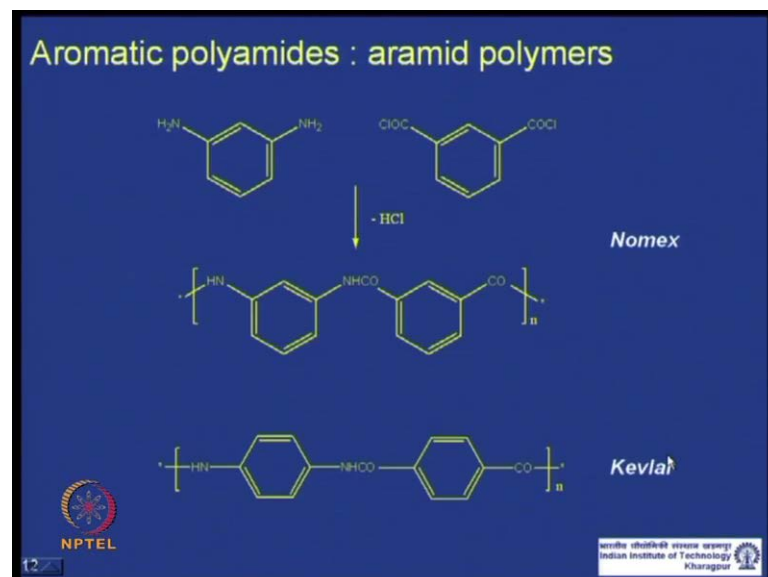
So, this is the most this is the commercial root of synthesis poly and these are the names trade names, which under which under which this poly ethylene terephthalate are sold in the market.

(Refer Slide Time: 27:11)



We will move to the next class of polymers step polymers polyamides and we have this is linear poly polymerization reactions this is aliphatic diamine with aliphatic diacid you can directly under go reaction to form linear polyamide. And this is you know it is known as nylon 6 6 and this is very common polymers starting from hexamethylene diamine and adipic acids.

(Refer Slide Time: 27:54)



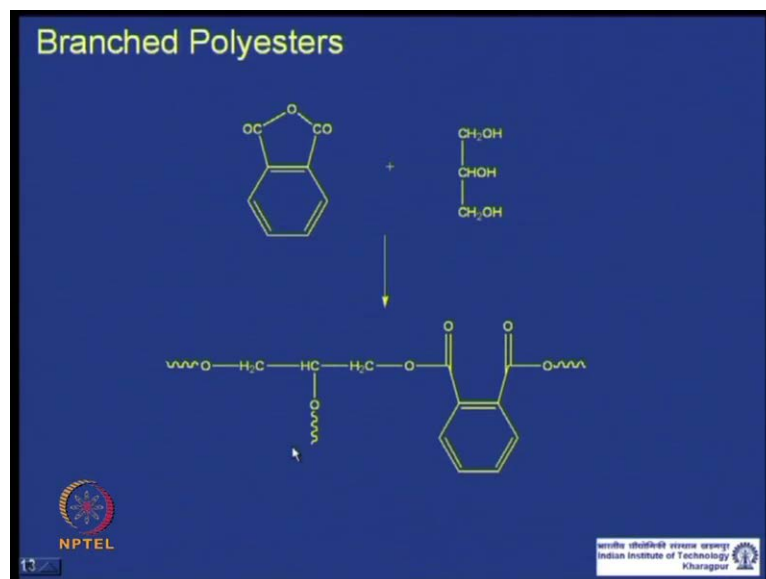
Now, in last slide we saw aliphatic diamine and aliphatic diacids, now we want to move to the aliphatic diamines and aliphatic diester or diacid chloride in this case. And these

this polyamides are completely formed from aromatic groups containing aromatic groups. So, these are aromatic polyamides and commonly known as aramid polymers and because the reactivity of this nitrogen attach to the aromatic ring is much less compared to if it as a simple aliphatic aliphatic aliphatic group.

In this case we cannot simply do the polymerization reaction with diamine and diacids you require much reactive component functional group. So, typically in case of aromatic polyamide synthesis, aromatic diamines are reacted with aromatic diacid chloride and you get this completely aromatic polyamides. Instead of you can use the para substituted diamine with para substitute diacids to form this linear polyamides aromatic polyamides.

And this is known as kepler as a trade name and this is nomex and these are both nomex and kepler have very high melting points. You know they are used for very high in the application where you require very high temperature to sustain even kepler has a melting point which is higher than 500 centigrade, sometimes it even burn before it melt.

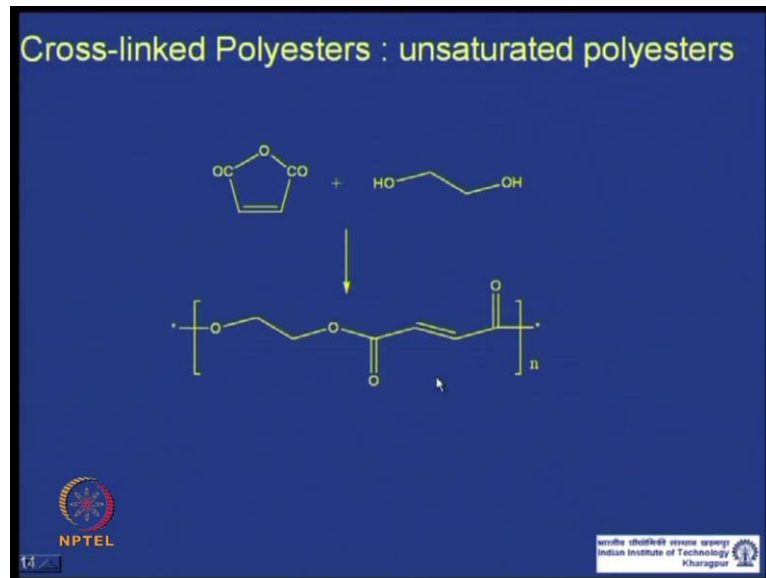
(Refer Slide Time: 30:08)



So, these are very high polymers which are high very high performance polymers we move to next say we have just given generic example of branching and cross linking in last lecture. Here, we I show you a definite examples you have ethyl an hydride here and we have a glycerol, when it reacts in this to reacts it form a linear chain along with a branch coming from this hydroxyl group. So, this is how you can carry out a there is a one example of forming bunch you know synthesis bunch polyester.



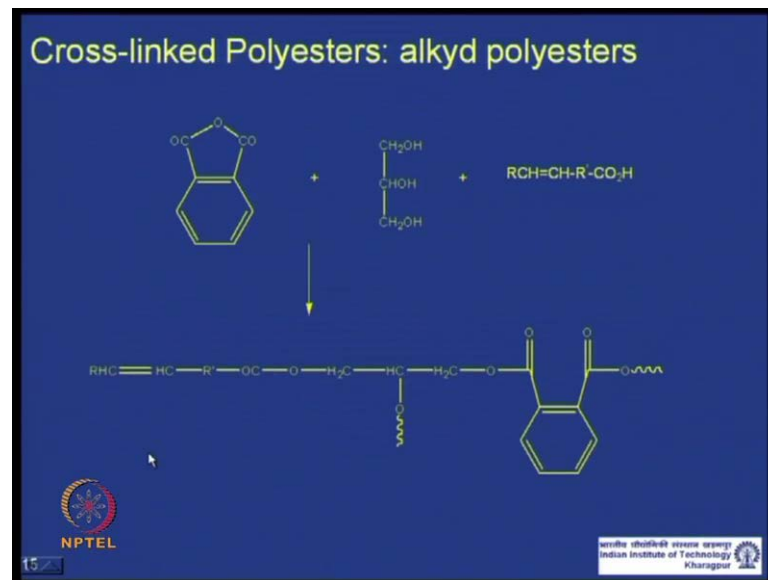
(Refer Slide Time: 30:50)



Move to the next one which is cross link polyester in this case one example can be taken is a maleic anhydride reaction with ethylene glycol; and once it forms the polymerization is complete at the end you have a double bond in the polyester back bone. So, you have synthesized in this way a unsaturated polyester. Now, this double bond are available to react radically or some other chain polymerization mechanism by itself alone, are you can add a another monomers like styrene or MMA methyl methacrylate and then copolymerized with and form a cross link.

So, here you first make a step polymers, by step polymerization mechanism you make a unsaturated polyester, and then by doing a chain reaction you can do a cross linking reaction to form a cross linking reaction.

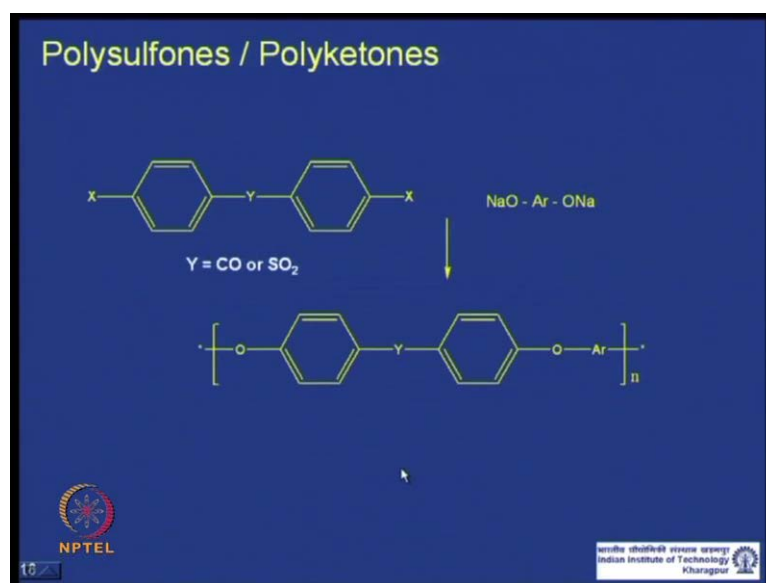
(Refer Slide Time: 32:00)



If this unsaturation is at the end of the polyester, which you formed then these are known as alkyd polyesters, how do you do that, the same reaction like in this case phthalic anhydride glycerol there you are hiding one mono functional acids, which has a alkene group a double bond at the other end. These are typically you know, these are available in the fatty acid there are lots of fatty acid which are which can be unsaturated available where you have a unsaturation or double bond in a other side not necessary end, but other side.

Now, this double bond is free to undergo chain polymerization. So, you can first stage you do a step polymerize to syntheses this and then you can take this and do a second step of chain polymerization either by oxidizing this or no using the other methods. So, you can cross link this polyester unsaturated polyester chains, so by doing this we can make a cross linked network.

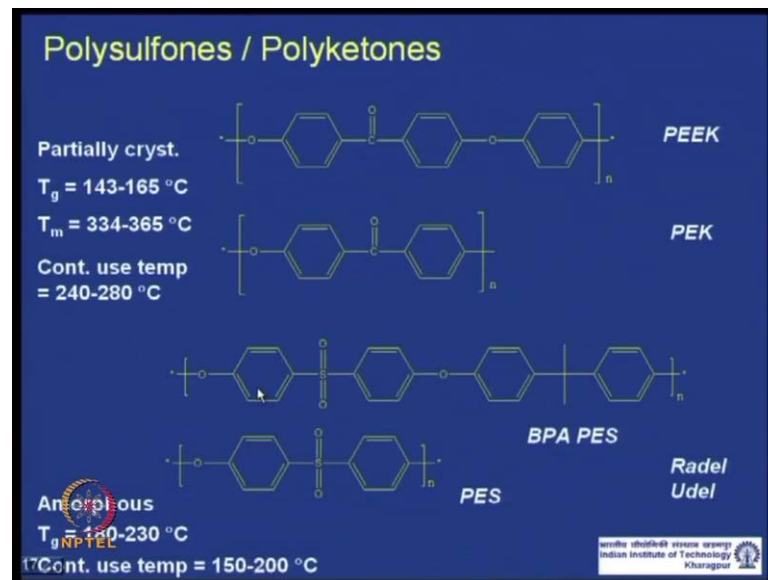
(Refer Slide Time: 33:23)



Next set of polymers we go is polysulfones and polyketones the generic structure is this its similar to the bisphenol astructure is polycarbonate X is, but in this case X is allied instead of H and Y is either a carbonyl or SO<sub>2</sub> group. Now, typically this aromatic halides are not very reactive towards a nucleophilic substitution reaction, but because you have a strong electron withdrawing group present here CO or CO<sub>2</sub>, CO or SO<sub>2</sub> this becomes more reactive towards nucleophilic substitution.

So, you can carry out the reaction with this the salt of phenolate phenolate ion and you can make a polymers like linked this.

(Refer Slide Time: 34:32)

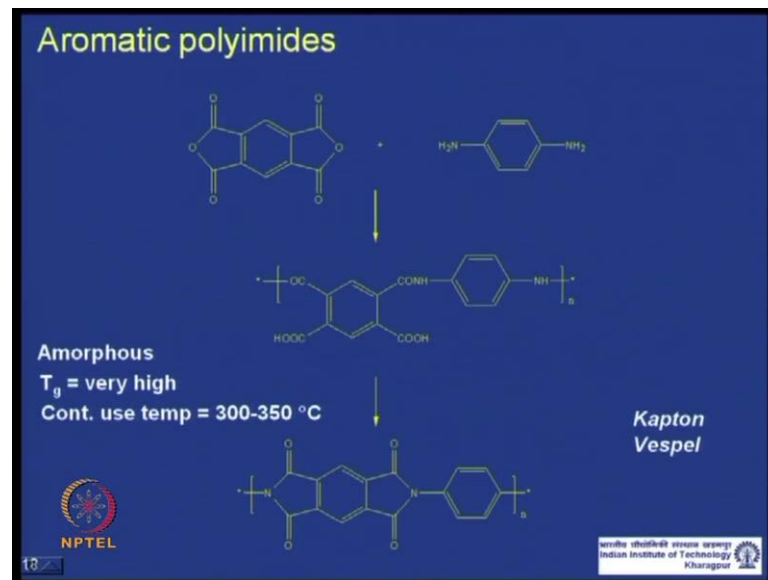


And the commonly these are called I will show you the example in the next slide, if you have CO these are called polyketones and specifically this structure is called poly ether ether ketones and simple this called polyether ketone, you have if you have a sulfone group  $\text{SO}_2$  group in here then these are polysulfones. So, this is poly ether ether ketone (Refer Slide Time: 34:59), this is polyether ketone, this is poly bisphenol a polyether sulfone and this is simply called polyether sulfone. And this is these are the trade names of this polymers in this trade name they are sold Radel and Udel.

They are partially crystalline this PEEK and PEK poly ether ether ketone and polyether ketone they are partially crystalline polymers they have a  $T_g$  around this range and they have a very high melting point. So, they are they are again very high performance high performing polymers, which are used at very high temperature applications; and they can be used in a applications where the constant temperature is say around as high as 240 to 280 degree.

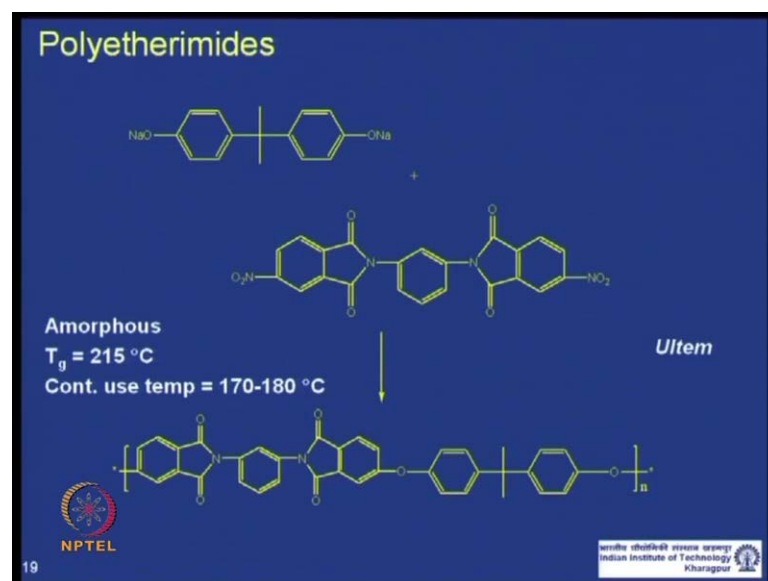
So, they are very you know high performing polymers this poly sulfones or polyether sulfones, they are amorphous in nature the  $T_g$  is around one they are also very high  $T_g$  180 to 230 and they have continuous use temperature is between 150 to 200. So, they also used in applications where string and link requirement for high temperature.

(Refer Slide Time: 36:24)



Next set we move to poly aromatic polyimides, these are formed by reaction with diamine with dianhydride, an aromatic dianhydride so aromatic diamines are reacted with aromatic dianhydrides, And first this is formed then one cyclization this is this imides are formed these are again very high performing polymers they are used for applications requiring very high temperature and they are known in under the trade name of captain and ( ). There are also amorphous  $T_g$  is very high and their continuous use temperature is 300 to 350 degree centigrade temperature.

(Refer Slide Time: 37:17)

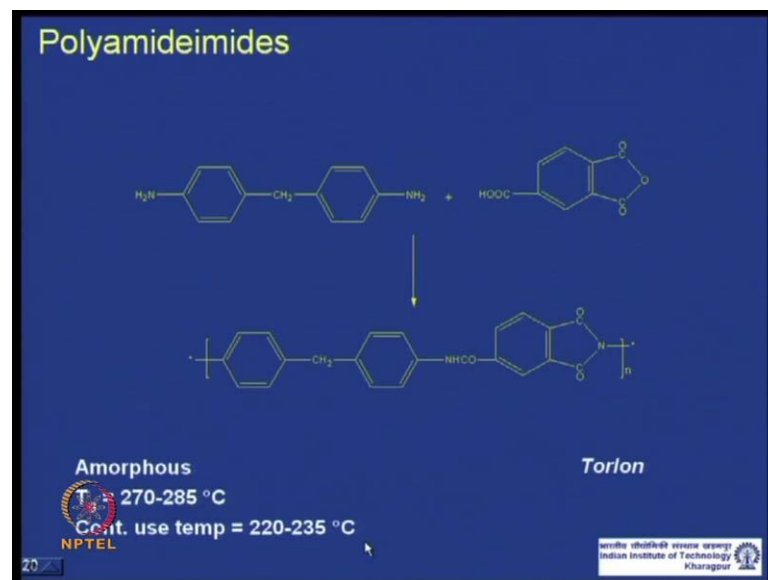


I am just moving it fast, because this just information I my aim is to just give you the generic synthetic procedure for this class of step polymers. Now, you can always go through any detailed publications or in a detailed text book where you will find out the detail you know detail method of making this polymers. But just for this course I am just giving you a over view of this different step polymer and just generic method of synthesizing this.

So, we move to polyether imides again this is the process of making polyether imides and these are again very high heat polymers; that means, this having very capability of you know they can be used in very high temperature. They are known in the trade name of ultem, there amorphous T g is as high as 215 degree centigrade and there are constant use temperature is between 18 170 to 180. So, in the if the application required that you the polymer will should be present at this high temperature.

So, you can use ultem as your material; obviously, these polymers are costly, because they have, so high performance and they are also difficult to synthesize there are the same time much costlier then the common polymers.

(Refer Slide Time: 38:58)





This is another example another set of polymers is polyamide imides you take this aromatic diamines with one side poly anhydride and the carbo oxalic acid silica acids to form this amide polyamide imides. And this is sold as a trade name as turlon, this is also very high heat polymer, this is also amorphous T g having 270 to 285 and the constant

use temperature is 220 to 235.

(Refer Slide Time: 39:38)

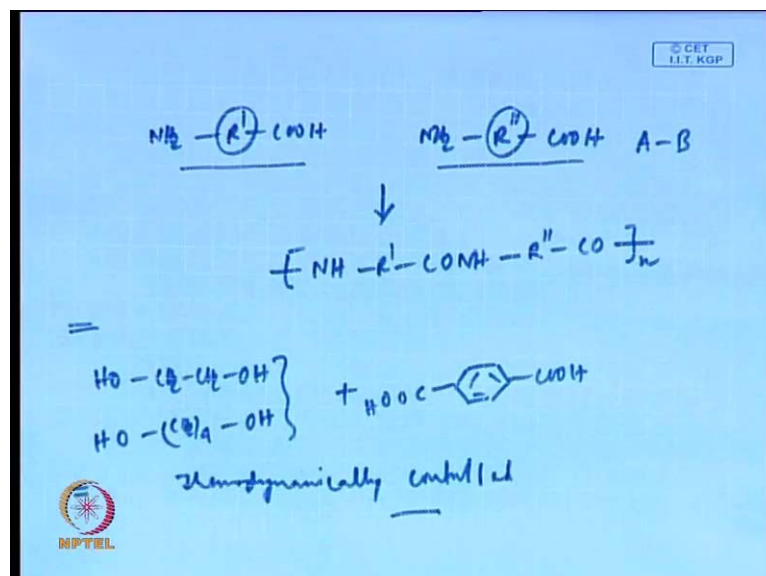
**Other step polymers**

- Polyurethanes
- Polysiloxanes
- Polysulphides
- Phenolics
- Amino plastics
- Epoxy resins



Now, there are other step there are several other step polymers, which you know because of time or this course of this polymers is not to go through the detailed synthesis procedure of this polymers. So, there are this is just a to mention that there are other step polymers as well listed in this slide. And which you can go through any text book or any standard publications to find out, if you are interested how they are synthesized and what are their property you know basic property.

(Refer Slide Time: 40:29)



So, what I wanted to do next to just give you idea about step copolymers, now if you have say a amino acid  $R-CO-NH_2$  and  $NS_2-R-CO$ . Now, obviously it will form, now why do we put the bracket will be always next to each other should I put the bracket here and put N like this, it may not be it could be somewhere here and there could be another bracket here. So, these is one example of making copolymers in step by step polymerization method you take say a by functional monomers A B type.

And if you have two different group in side then you can make a copolymer, but this has not very regularly used method from making copolymer, if you the practiced methods are normally if you say, if you are making a polyester, if you have say  $CH_2-CH_2-OH$  ethylene glycol. Now, if you have this along with plus if you have say terephthalic acid in the other side. Now, you have to make the total of these total of this diol with the ratio of this thing is close to one is to one. So, total number of functional group of OH group is almost close to the number of groups of COH group, so that the polymers take place.

Now, in this case you make a copolymer, which have this poly ethylene terephthalic unit and also have a polybutylene terephthalate unit. So, this a example of copolymers of PET and PBT polyethylene terephthalate copolybutylene terephthalate depending upon the ratio of these two you know which in which one will be higher or not. Now, what do you expect when you make this copolymer will there be alternative copolymer, that mean will you have this ethylene glycol group.

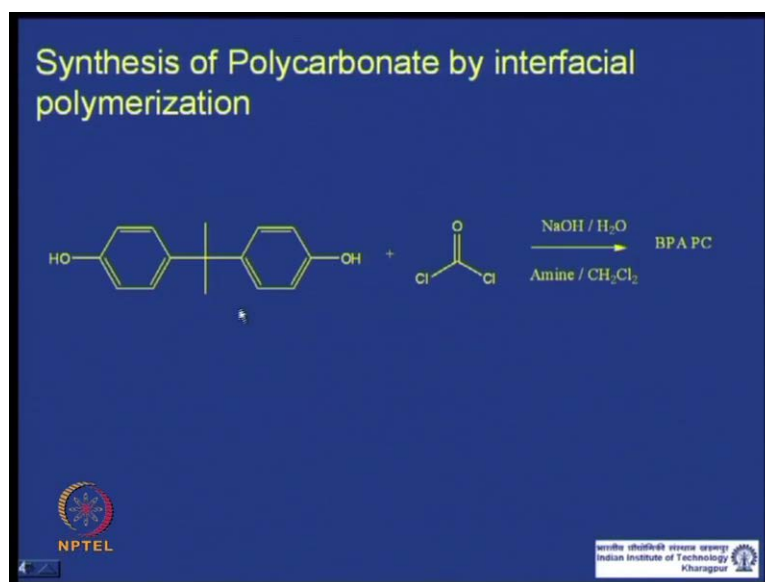
And butylene glycol group butylene glycol group always next to each other will we expect that or will you expect that there be will random copolymers. Now, if you normal in the normal step polymerization reaction, because this goes through a thermodynamically control process. That means, the byproducts also take part in the reverse reaction and the chains intermediate chains also take part reactions with exchange reaction between them.

So, they reshuffle all the time you know during entire reaction there always reshuffling happening between the chains. So, there is a transfer happening between the extraction is happening between two groups, which means that if the reaction proceed through thermo dynamical control, if the reaction is thermodynamically control controlled. Then you will always land up in a completely random copolymer, you understand why, because this reaction when they are happening there is slow reaction.



So, during the reaction time the byproducts also taking part in the reverse reaction and also the intermediate chains they are also reacting with each other by exchange ester exchange. And by doing, so they are always reshuffling between them self at the end you always have a completely random copolymer.

(Refer Slide Time: 45:13)



Now, if you are doing the other reaction say for example, if I go back to the polycarbonate example in this case, if I instead of taking this BPA. If I take this BPA and bisphenol a and also some other di hydroxyl group say something else some substituted group here, instead of methyl we have ethyl group or some other group. And you have taken that is one is to one and you are heating with phosgene.

Now, in this case reaction is kinetically controlled, which means once the polymer all as a matter of cyclics we just talked about few minutes back. Once they are formed they are not taking part in the reshuffling reaction or reaction with the byproduct reverse reaction with the byproduct. Because, they very fast reaction once the product is formed the byproduct HCl is getting neutralized with sodium hydroxide, which means there is one reaction is formed.

They are not taking part in the reshuffling reactions which means the nature of the copolymer would depend upon the reactivity of this group. Unlike the earlier case say butylene glycol and ethylene glycol even if there are were any differences in the activity between two hydroxide groups. Ultimately at the beginning even if they are making

blocky copolymers at the end by doing reshuffling finally, you would land up in a random copolymer.

But in this case, the nature of the copolymer would depend upon the reactivity of the functional group if this functional group is same having same reactivity with the other functional group then it will form a random copolymer. If they are different, then the most react in a more reactive group would react faster forming a block, then the second monomer would react forming a another block.

So, in this case because it is a kinetically controlled fast reaction reactivity of the reacting monomers would determine, whether its form a random copolymer or a or a block a copolymer. If there are significant differences in the reactivity of the two diols then there will be a blocky nature in the copolymers. So, you understand the terminally controlled polymers would give always a statistically random copolymer whereas, in kinetically controlled polymerization reaction.

The nature of the copolymer would depend upon the reactivity of the functional groups of the monomers, if there are significant difference in the reactivity of the functional groups among the comonomers. Then there will be blocky nature, in the copolymer resulting copolymers, if there is no reactivity difference then there is no. And you have to consider what is the diffusivity? You know reactivity coupled with the reactivity if some monomers is diffusing first at the interface it will react faster.

So, when I talking about the reactivity it would also include the diffusivity diffusivity aspect of the monomers is well. So, if the if the reaction between the one monomer with the phosgene is faster, then it will be a blocky copolymer. So, we have come to the end of this module and what we will do now, I want to tell my expectation you know what are the learning objective in this module in the step growth polymerization; now what I expect from a student after going through this module.

(Refer Slide Time: 49:13)

**What is expected from a student  
(Learning objectives)**

- Understand the mechanistic differences between step and chain polymerization.
- Given structure of a synthetic polymer a student should be able to identify by which process the polymer is synthesized.
- Know the relationship between  $\bar{X}_n$  with  $r$  and  $p$ ; appreciate the fact that to make high MW polymer reaction should be pushed as close to the completion and  $r$  should be close to 1.
- Should be able calculate  $M_n$  from  $\bar{X}_n$
- Know the strategies / conditions one need to follow to synthesize a polymer of a pre-defined MW

NPTEL  
23  
सर्वोच्च शिक्षण समूह  
Indian Institute of Technology  
Kharagpur

Let us, go one by one I expect that a student after going through this module should understand the mechanistic differences between step and chain copolymers, chain polymerization should which polymerization, so it should be polymerization. So, I expect that a student should understand the mechanistic difference between chain and step polymerization, if I stop a reaction after some conversion, what you expect in the polymerization medium, how the molecular weight build up with time and so on. What are the functional groups you require for a step polymers or a chain polymers, so on.

If I give you a structure of the of the polymer synthetic polymer, then you should be able to identify by which process it has been synthesized, whether it is a step polymers polymerization process or a chain polymerization process. Just by looking at the structure you should be able to tell or you should be able to identify, what is the difference you know in which method by which method it has been synthesized.

You should know the relationship between  $\bar{X}_n$  the number average degree of polymerization with  $r$  the stoichiometry ratio and  $p$  the conversion in a normal step polymerization process. And you know by then this car others equation and you also should appreciate that the fact to make high polymer high molecular weight polymer you should have  $p$  value close to one. So, you should push the reaction as much as possible and also if you want to build a high molecular weight polymer your  $r$  should be close to 1.

And I have given few example during my lectures you should be able to calculate the  $M_n$  there the number average molecular weight from  $X_n$  the degree number average degrees of polymers. And so as  $M_w$  from  $X_w$  you know number average with weight average molecular weight from, weight average degree of polymerization. If you want to control the molecular weight, if have want some reason you want to target some molecular weight with both the ends having some particular functional group or no functional group.

Then you should know the strategies if you want to have some functional group at the end of the polymers both side, then you should use the monomers containing that functional groups in higher amount and the ratio should be according to your target. And if you at the end to the polymer if you do not want to have any reactive functional group, then you should use mono functional chain stoppers and your molecular weight, when you use a chain stoppers, what is your target molecular weight you know the calculation hence you should be knowing the calculation.

(Refer Slide Time: 52:33)

**What is expected from a student  
(Learning objectives)**

From the kinetics of step polymerization, understand that to achieve a high conversion (and as a result high MW) preferred conditions – ext. catalyzed, open driven system with ability to take out condensate molecule as much as possible, long reaction time, and high K.

Know the expected MWD and PDI in a step polymerization. Also know that for a high MW step polymer PDI should be close to 2;

Also know why in reality PDI is found to be always slightly greater than 2, possibility of cyclic formation, condition to minimize cyclic formation.

Condition and utility for branching, cross-linking, gelation

NPTEL

24

संस्कृत विश्वविद्यालय  
Indian Institute of Technology  
Kharagpur

From the kinetics of step polymerization you should understand that you know to achieve high conversion and as a result high molecular weight. The what are the preferred conditions you know it should be external catalyzed it should be open driven system where you your systems should have ability to take out the small molecular byproduct as much as possible from the system.

And you must continue the reaction for long time, because the kinetics is lower and also is always preferred is always preferable to have a high equilibrium constant, which will depend upon the reactive. So, if you design you can design highly reactive monomers, then they will have naturally high equilibrium constant. So, it will be easier for you to make high molecular even if you cannot remove the small molecular weight byproduct completely or quantity from the reaction medium.

A student should know are expected to know the molecular distribution and polydispersity index in a step polymerization and we should also know that the for any high molecular step polymer the PDI should be close to 2 or as a matter of close to 2. And he also should know that why in reality PDI always end up being slightly higher than two because of side reaction cyclization. And the same time he should or she should know, what are the ways you can minimize the cycling formation in a step polymerization.

And a student should know the condition and you know what are the what are the conditions you know what are the monomers to be used if you what a branching or cross linking. And if you do not what are the monomers you should not use for branching and you should also know the utility, if you what sometimes it is undesired to have branching in the polymer.

And sometimes it is deliberately you know wanted it is deliberate somebody, who will deliberately want to include want the branching or cross linking in the polymers. So, what are the ways you can do that or what are the ways you can have avoid that and what are the utilities or the problem if a student being.

(Refer Slide Time: 55:31)

**What is expected from a student  
(Learning objectives)**

- Understand complete list of criteria to carry a successful step polymerization, should also know the common troubleshooting.
- Know processes of making different step polymers including interfacial polymerization
- Different commercial step-polymers, their utility, how they can be synthesized, and they are commercially synthesized.

NPTEL

25

Indian Institute of Technology  
Kharagpur

So, if you want to work in the lab or if you join in the industry you should be able to know what are the complete list of criteria, you know we have gone in last lecture to carry out a successful step polymerization. And in case following all the normal process normal directions, if you do not build high molecule weight what are the first things to look for, what are the common trouble shooting? You should first look for that also you should by know and have a graphs in by this time.

And in also know different what are the common step polymers, what are their property and what are the different ways of making step polymers, same polymers can be making different ways. And one including what is the fundamental differences in interfacial polymerization they utilize the very first reaction of diacylchloride or diacylchloride. And what are the mechanism and what are the problem in interfacial polymerization.

And finally, different commercial polymers you know student have a idea at least you should not I do not expect that a master of all the polymers, step polymers there as many step polymers. At least I have some idea that these are the polymers are made by synthesized by step polymerization mechanism and one the most common ways of synthesized I have given examples in today's lecture for quite a few. And I also did not I could not include several others.

So, I would expect that which are not covered in this in this lecture you please read the book or any other text to go through the common synthetic method for those polymers as

well. And you should be knowing the polymers, which I have covered in today's lecture. So, with this I conclude this module on step growth polymers and polymers and polymerization step growth polymerization mechanism. And next lecture onwards I will start the chain polymers and chain polymerization with starting with radical chain polymerization.