Principles of Polymer Synthesis

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Lecture – 10
Principles of Step Growth Polymerization (Contd.)

Welcome back this is a lecture number 10 of the NPTEL course principles of polymer synthesis. And as has been the theme throughout this week we continue to discuss and emphasise on the principles of step polymerization for the last class of this week also. So, in the previous class we have discussed about the number fraction distribution, and the weight fraction distribution. These 2 things as a function of the number of structural units. And there we also emphasized on how the averaging is done. So, for example, if you are looking at number average molecular weight.

So, basically then so, average means you have many different species present they have different molecular weights, that is why you are taking average. So, when you are taking number average molecular weight. So, you are actually taking the molecular weights of all the species, and then you are weighing them with the number fraction. Or the mole fraction so, when you are doing likewise when you are taking the number average degree of polymerization you are taking degree of polymerization of all the different species.

And x mer has a degree of polymerization of x and y mer has a degree of polymerization of y. So, all these different species you are taking and when you are taking the number average of that which is termed as the number average degree of polymerization. Then you are weighing up those number, then you are weighing up those degrees of polymerization of different species with a number fraction of the mole fraction when you go for weight average you weigh up for a weight fraction.

So, likewise and this analysis ultimately gave a very important conclusion, that the polydispersity index has to be closer to 2 in order for having a successful step polymerization reaction. Successful means to have high molecular weight, because high molecular weight means your conversion has to be close to 100 percent, and since your polydispersity index as per the statistical approach is equals to 1 plus p there is no chance that you can be close to one if you are at one and you are happy with all the chains vary mono disperse, or whatever your polymer is of no practical utility.

So, as promised in the last class we will now talk about one of the major side reactions that can create problems for step polymerization and that is cyclization. It is not difficult to understand that way. That if you have a monomer which has both the functionalities present say, if you have an amino acid amino acid has both the amine and carboxylic acid. So, if you are making a polyamide from an amino acid like this.

So, you have the molecule which can do a self amidation 2 of this molecule come together, this is one scenario. And in this particular scenario instead of doing this kind of polymerization the molecule can decide to react it is 2 ends together, because on both ends you have functions that can react one end carboxylic acid one end, you have amine it can form amide and it can rein closed if it rein closes that is detrimental for the molecular weight because the polymer the chain does not proceed now it could rein close in a monomer stage or it could rein close in the oligomer stage. Still you will have the problem.

So now let us go into some details of this particular topic.

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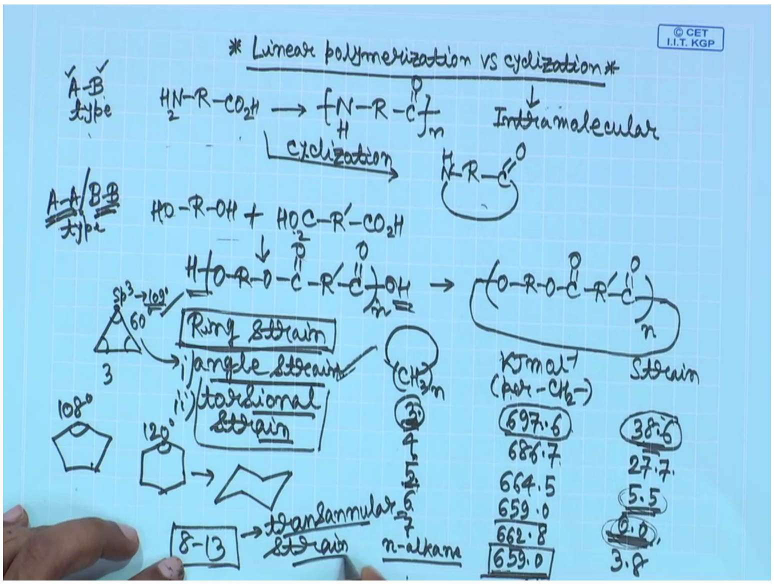

So, the problem here is linear polymerization verses cyclization. So, suppose you have A B type monomer; that means, the same monomer has 2 different functions. In that case say you have as I was telling an amino acid. So, you are looking for a polymer like this; however, there is also a possibility that there could be a rein closer. So, you could have cyclization and what you will have then is something like this.

So, this is you know this is an intramolecular process, or what you could have is a system which is A A and B B type. The kind of systems that we have discussed a lot. So, suppose you have a diol you are reacting with diacid. Now when you have a diol or a diacid they typically would not do cyclise intramolecularly, I mean in a way if you have an a and B B type of monomer in the monomer stage they may not cyclise instead if you have A A B type of monomer in the monomer stage they could cyclise like this in the monomer stage itself. Now here suppose it does not cyclise here in the monomer stage, but it has formed say some oligomer say like this some oligomer n has certain value.

Now, this oligomer also has reactive end groups, instead of reacting continuing to react linearly with other monomers. It could cyclise like this and it could produce something like this. So, there also it is detrimental. So, the question that needs to be asked is how do we avoid this cyclization. In order to find an answer to this question, what we need to know is what are the factors that will favour cyclization of a linear polymerization, and what are the factors that we have to control in order to gain a preferential linear polymerization over cyclization. In certain cases it is not possible in other situations it is possible. We will explain this towards the end of this particular discussion what we mean by this statement.

Now, when the ring is forming, there has to be a driving force for this ring formation. So, when you are trying to analyse this question about this linear polymerization versus cyclization you have to look for 2 things. What are the thermodynamic what is the thermodynamic factor what is the kinetic factor. Thermodynamic factor relates directly to the stability of the particular ring being formed. And kinetic factor what does that mean you have a chain both ends have different functional groups, they will come together and for a cycle cyclic cyclization. Now in order for them to come together they have to come sufficiently close. So, that is the kinetic factor and sometimes they will act opposite to each other.

So, let us talk about first the ring stability factor. So, you know for example, if a ring is very stable thermodynamically. Then there might be a propensity. So, let me rephrase this sentence like this. Say, for example, 6-member drinks are very stable. Now let me qualify the statement that I had made before that some of the reactions you may not be able to control the linear polymerization over cyclic polymerization. Suppose you have an oligomer or for example, you have a monomer you have a monomer say with 2 functional groups. And this monomer if it cyclises it can form a 6-membered ring. In many, many cases you cannot actually avoid formation of this 6 memeberd ring, why because this 6-membered ring is thermodynamically one of the most stable rings.

So, thermodynamics then governs this situation. So, like that. So, when we say thermodynamic stability ring stability, how do we actually know what do we mean by this thermodynamics stability? How do we actually measure this thing? This is measured by the heat of combustion. So, if you have a cycle cyclic system, it has some strain and that strain will determine it is stability.

It might be having an angle strain, suppose you have a triangle. So, if you have something like this, say a ring size of 3. Then each angle is 60 degrees. Now if you have s p 3 hybridization there, it has to be close to 109 degrees, that is what it dictates. So, if you have a saturated ring system, say alkyne ring system which is a 3-membered ring then you have an enormous angle strain so, the stability. So, what is the thermodynamic stability actually relates to the ring strain, if you have a higher strain you have a lower stability.

So, here the ring strain is arising from what you call as angle strain. We will come back to this and compare the other things, but first let us look at some of the experimental details of how it is found out that some of the rings are more stable, some of the rings are less stable. So, it turns out you can actually find out the heats of combustion of cycloalkanes. So, per methylene unit per CH 2 unit you can find out the heat of combustion. And then you compare that with the heat of combustion per CH 2 of the linear alkane linear alkanes do not have that strain. This subtraction will give you the corresponding stability or instability by that amount of energy. So, what we mean by that?

So, let us say you are you have a ring like this CH 2 and you have whole n. So, you have a ring and in kilo joules per mole per C H 2, you will show here the heats of combustion. And corresponding strain also you calculate in kilo joules per mole. So, if you have a 3-membered ring, then the heat of combustion per CH 2 unit is 697.6 kilo joules per mole. 4 membered unit 4 membered ring 686.7 5 membered ring, 664.5 5 membered ring, 6 membered ring 659.0 7 membered ring, 662.8.

Finally let me write down for an n alkane; that means, linear alkane per CH 2 unit, what is the heat of combustion per CH 2 unit, it is 659. So, how do you calculate how do you find out the strain per CH 2 unit in a 3-membered ring. So, this is the heat of combustion. Now n alkane is a reference this is the heat of combustion. So, this is unstable I mean this has strain by this this much of higher energy. So, this so, you subtract this value from this value. So, this difference will give you. So, 38.6 kilo joules per mole strain per CH 2 unit is there for 3 membered ring. So, the reference is n alkane. So, correspondingly for 4 the strain is little bit lower because this heat of combustion is lower. So, that will be 27.7, and for 5 5 membered ring it is 5.5, 6 membered ring it is 0, 7 membered ring it is 3.8 so on and so forth.

Now so, you will see for example, the 3-membered ring is one of the most strained rings. So, strain is the highest 4 membered ring, the strain is lower 5 membered ring it is much lower 6 membered ring there is no strain at all because your comparing with the n alkane. And then again, the strain increases little bit. So, this ring strain basically arises from it can arise from different factors, one factor is angle strain, the second factor is conformational or torsional strain. So, this is easy to understand for 3 membered ring, you know there is a lot of angle strain there. For 4 memberd ring also there is a lot of angle strain angles are 90 degree much away from 109 degrees.

So, for 5 membered ring this angle is 108 degrees very close to tetrahedral angle. For 6 membered ring the angle is 120 degrees. So, basically 5 membered ring the angle is basically closer to tetrahedral angle than for 6 membered ring. So, it is then suppose to be more stable in terms of angle strain, if you are looking at angle strain is lower than this; however, you will see that say for 5 memberd ring it is 5.5 the strain energy per CH 2 unit and 6 membered ring it is 0. So, 5 membered ring is slightly less stable with respect to the 6-membered ring.

Because this something called torsional strain also. 6 membered ring can actually take a chair form. And so, these are torsional conformational strain. So, if you are looking at 5 membered ring or some other rings for example. So, those rings will basically have different confirmations in which the hydrogens may come over each other. So, that eclipsing conformation will actually lead to higher strain energy. That is not exactly angle strain that is called torsional strain. So, that kind of strain is absent in cyclohexane because of that chair conformation. So, it can assume other conformations also, but here conformation will have the lowest energy highest stability. So, that explains some of these things.

So, basically the rings strain decreases. So, ring strain can arise from angle strain as well as torsional strain. So, the ring strain decreases from. So, from 3 to 4 it decreases from 4 to 5 it decreases a lot, and when you go to 6 there is no ring strain. And when you are looking for the higher rings say ring number 8 to 13, again the ring strain will increase. That is because of what you call as trans annular strain. So, what will happen is that this big rings will have some of the atoms that are directed towards inside. And those atoms can actually come very close, and then there will be some strain energy. So, that is a transannular strain.

And again, where you are going to higher ring say 14, 15 etcetera, that will be absent. Because those bigger rings that can that can actually adapt different conformations in which this hydrogens that we are pointed inverse they do not have to come that close in order to I mean, have that stable conformation. So, it can have different confirmations in which they are not that close. So, the transannular strain is absent. So, again 14 15 16 onwards the chains the rings are stable. So, this would mean of course, that for 6 membered ring it is having most propensity to form. If the chain can close to 6 membered ring may be the polymerization will be very difficult to do linear polymerization.

But that may also mean that when you are going to very large rings they will be even more easier to form at least thermodynamically, but the point here is you have to also consider kinetic factor. When you are considering a linear chain of a very big size, and if you can form the ring that ring is of course, thermodynamically stable. So, thermodynamics helps it; however, the kinetic does not help it because if it is a very long chain it can have many more confirmations in which the 2 ends are not in close approximately compared to much less number of confirmations in which the 2 ends are closer where the rings can form. So, that would mean kinetically then the ring formation will be discovered for very long chains.

So, this is the thermodynamic and kinetic stability factor that I wanted to discuss here.

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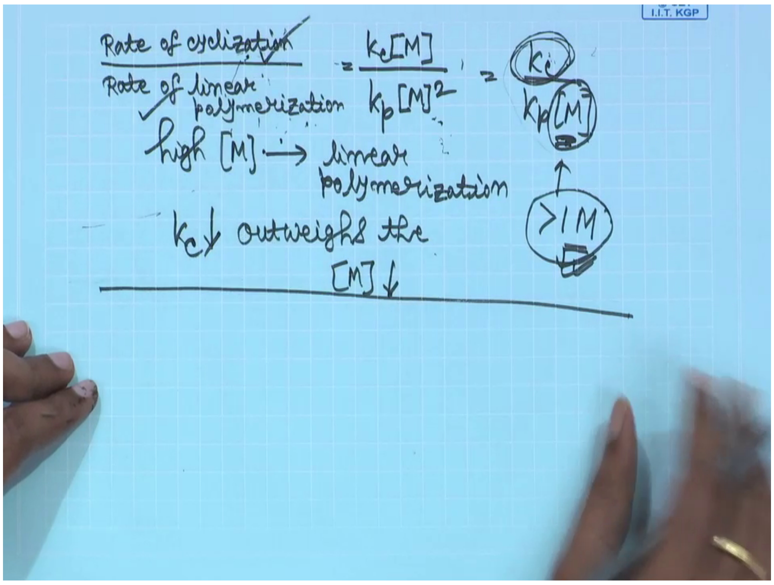

$$\frac{\text{Rate of cyclization}}{\text{Rate of linear polymerization}} = \frac{k_c[M]}{k_p[M]^2} = \frac{k_c}{k_p[M]}$$

high $[M] \longrightarrow$ linear polymerization

$>1\,M$

$k_c\downarrow$ outweighs the $[M]\downarrow$

now something else so if you are looking at the rate of cyclization, the ratio of the rate of cyclization and the rate of linear polymerization, if you are looking at this particular thing. So, that will be something like this. So, rate of cyclization let us say the rate constant is k c c stands for cyclization into M, M is the concentration of monomer, divided by rate of linear polymerization let us say k p is the rate constant for linear polymerization into M square.

Now, this is because when you are looking at cyclization that is basically an intramolecular process. And when you are looking at linear polymerization that is intermolecular process. So, if in effect if you go to high concentration then linear polymerization will be favoured. If you go to dilute system your cyclization will be favoured because the different chains will be far from each other. And they can cyclise easier intuitively. So, higher if you have high concentration that favours linear polymerization.

So, this means here k c divided by k p into M. So, typically when your concentration is. So, this M is more than one molar, you will have linear polymerization that will be favoured. So, there is a kind of crossover point here. And something else that also I wanted to mention is that as the reaction progresses, your monomer concentration will crop. So, when the monomer concentration drops this particular expression tells you that the cyclization maybe favoured over linear polymerization; however, as the reaction progresses, the chain becomes longer and longer. So, the kinetic factor becomes important and cyclization may be disfavoured. So, in that case the k c will also decrease.

So, the situation is like this as you go to higher and higher extent of reaction your M decreases. So, that in effect will disfavour, the I mean will favour the cyclization more over the linear polymerization; however, your k c also decreases because of the kinetic effect. So, your rate of cyclization will also drop. So, this 2 opposing effects are there, but typically as the linear polymer increases in size your drop in k c will be out weighing this out weighs the dropping monomer concentration. So, typically then as the linear polymer increases in size there will be more chance that linear polymerization will be favoured then the cyclization. So, that is all I wanted to discuss about cyclization, and linear polymerization to the last topic for this class will be interfacial polymerization.

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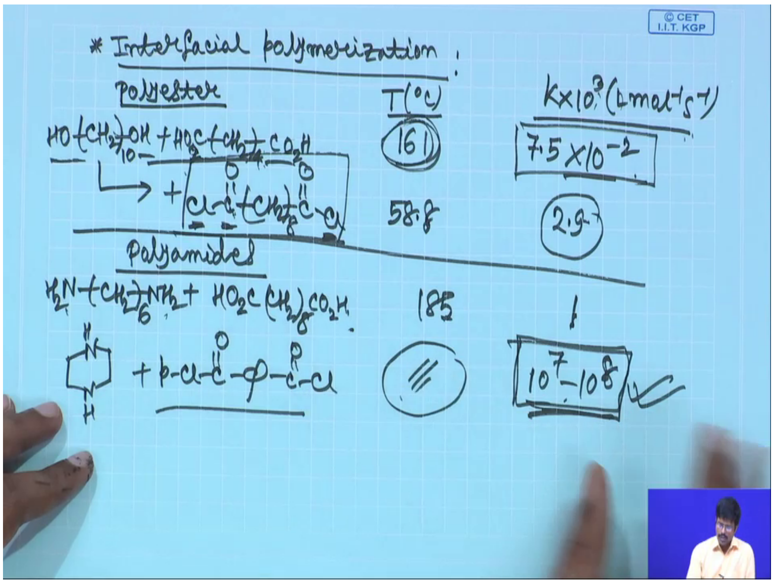

And then we will finish our discussion for the moment on step polymerization, we will come back to it when we talk about individual industrial polymer preparations, interfacial polymerization.

So, let us say I have a table something like this. Let us say if you are looking at polyester formation. This is the rate constant litre per mole per second say. So, these are some of the experimental data say you have an alcohol like this CH 2 whole 10 OH, and you have an adipic acid CO 2 H CH 2 whole 4 CO 2H. This reaction is done at 161 degree celsius.

And the rate constant is let this 10 to the power minus 2 you have actually multiplied by 10 to the power 3. So, this rate constant is quite low.

However same alcohol if you react with an acid chloride, I mean the data is not available data are not available for CH 2 whole 4 is available for CH 2 whole 8, but the principle remains the same, and I will tell you why. You can do the reaction at a much lower temperature, and the rate constant is at least 2 orders of magnitude higher. Same situation if you are looking at polyamides. So, you have a diamine like this, and a diacid like this. 185-degree celsius. So, this is 1.

So, already you see if you have an amine an acid reaction, rate constant is at least 2 orders of magnitude higher, than if you have an alcohol and acid reaction. Of course, if you activate this acid by introducing a chlorine here, the rate constant goes up, at least 2 orders of magnitude. So, you need an activated acid. So, the electrophilicity of this carbon increases. So, what happens for polyamides. Again, the data are available for this polyamide the corresponding polyamide for this particular monomers. So, piperazine and this is benzene ring of course. So, again you have acid chloride, temperature I do not have here I do not have the data here temperature is not the data is not there important thing is that you see here the rate constant is so high.

So, what I wanted to tell you here is that for some of these reactions the temperature that you are using is quite high, even then the rate constant is low; however, if the dicarboxylic acid say you are reacting dicarboxylic acid with the diol, or a dicarboxilic acid with a diamine, if you can activate the dicarboxilic acid by using an acid chloride then the reaction rate goes up manifold rate constant goes up manifold.

All though the data is not there for the temperature here you will see that many of this reactions can be done between 30, 40-degree celsius even close to 0-degree celsius. So, that is the effect. So, if you can reduce the temperature and you can increase the rate constant, even at lower temperature you can do the reaction at a high rate that is very good. So, the idea then is that you can use acid chloride instead of acid if you if you want. So, your rate constant becomes higher you can do the reaction at lower temperature.

Interfacial polymerization is a class of polymerization in which you can use this kind of activated acids for example, they are one of the reactants, say and you can use say this diamine this polyamide formation reaction you can do the reaction in a interfacial way. That name suggests it this polymerization works at the interface. Interface of what interface of 2 solvents?

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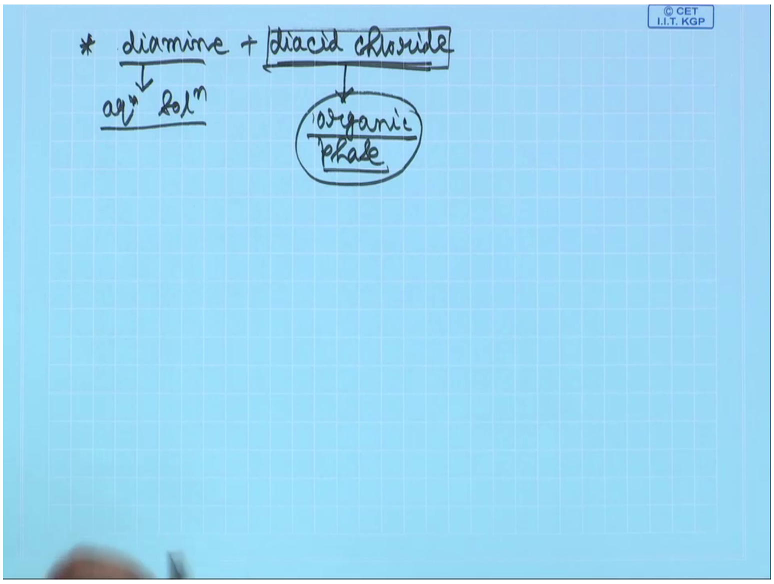

So, I will give you a generic example. So, typically the temperature is lower 40, 50-degree celsius or even lower than that and the rate constant is quite high with respect to a normal reactions, because you are using acid chloride. And so, let us say you are reacting diamine with a diacid chloride. So, you are making a an amide polyamide.

So, what you will do is that you take an aqua solution, aqua solution of diamine and you take this diacid chloride in an organic solvent. So, basically you will have 2 phases one is aquas phase in which your diamine is there, and one is your organic phase in which your diacid chloride is there. So, that 2 reactants will diffuse towards the interface your organic phase and the aquas phase that do not mix. So, they will form an interface the 2 reactants diffuse towards interface and the reaction occurs at the interface.

Now, and at the interface what will happen is the polymer will precipitate not always it might precipitate, but in general the polymer will precipitate at the interface, and these polymer then can be drawn out from the interface by using some glass rod or whatever. I say continuous filament because if you do not draw that out what will happen is that the reactants are defusing and that diffusion rate will drop because of the presence of a thick layer of polymer. And that kind of problem can occur with the polymer formed is mechanically week.

So, that you cannot draw it out and you keep it there. So, several important features need little bit more consideration here. So, when you are doing this kind of reaction you have a formation of acid. So, you are using acid chloride, and diamine diacid chloride and diamine. So, the bi product is an a mineral acid HCl there is a bi product. Now this HCl what will happen is that this HCl you have to remove somehow. Because the diamine that is there in the aquas phase it can react with the HCl and it can it can form an ammonium salt. Once it forms an ammonium salt the lone pair of the amine is no longer available to react with the acid chloride.

So, the reactivity goes down a reactant is gone that way. So, this acid that is produced has to be taken out. So, there has to be an acid scavenger. So, what you do you use an inorganic base that you put in the aquas medium that will take care of this by product hydrochloric acid, but again that base concentration also has to be carefully controlled because if the base concentration is too high. Then it can hydrolyze your acid chloride because acid chloride is in contact acid chloride will defuse towards the water layer. So, acid chloride maybe hydrolyzed.

Before the reaction has proceeded to a large extent if the acid chloride is hydrolyzed what you will get is an acid and you are not doing the reaction at high temperature. So, the acid will now have to react with the amine. So, it is basically your simple reaction of diacid with a diamine and your temperature is not very high, because you are doing interfacial polymerization you are actually using activated acid, but no longer activated acid is available. So, this is detrimental.

So, your you have to control the base concentration also. And the final thing here is that this rate constant of the reaction of diacid chloride with the diamine has to be appreciably high to start with if it is not, then the reaction will be slow, and if the reaction is slow the acid chloride has more chance to get hydrolyzed because it is exposed to water more and if it is getting hydrolyzed again that will be further detrimental to the rate of the reaction.

So, that is why when you are doing a polyesterification reaction the rate constant is orders of magnitude lower than the polyamidation reaction. So, typically for polyesterification reaction interfacial polymerization cannot be used because, the acid chloride reacts with the amine with a rate constant which is orders of magnitude sorry the acid chloride reacts with the alcohol with a rate constant, which is orders of magnitude lower than the corresponding amidation reaction where the acid chloride reacts with the amine diacid chloride reacts with the diamine. So, the diacid chloride has more chance to get hydrolyzed in the polyesterification reaction. So, typically it will be mostly hydrolyzed before the reaction can progress to a certain extent. So, polyamidation you can use interfacial polymerization, but typically for polyesterificain you do not use that.

And one more thing I would like to mention here you do not needs stoichiometric control. That way because the stoichiometric control will be maintained at the interface. That is the first thing. And the second thing is that high molecular weight product will be forming even at low conversion.

You do not need to go to very high conversion like your traditional step polymerization reactions. And the reason being when the polymer has formed the 2 ends are now available for the incoming monomers and the other species could not form because the incoming monomers can just now add to the 2 ends. In order to produce the other smaller species, they have to go in they have to diffuse into the layer. So, before that they will react with the end of the polymer.

So, high molecular weight species will be very quickly formed. So, whenever possible you could use this kind of interfacial polymerizations say for polyamidation reaction you can do at a lower temperature, and also you could you know that do the reaction quick fast. So, that is all that I wanted to discuss about the interfacial polymerization technique, and you will see when we discuss about different individual industrial polymerizations, this some of these principles will come back again and we will validate this principles by showing you the real examples of the preparation of those industrial polymers.

So, this is the conclusion of our discussion on step polymerization. So, next week we will start with chain polymerization reactions chain growth polymerization reactions till then.

Thank you.