Principles of Polymer Synthesis

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Lecture – 07
Principles of Step Growth Polymerization (Contd.)

Welcome back to this course on Principles of Polymer Synthesis and today is the 7th class. And in this class, we are going to continue our discussion of principles of step polymerization. So, let us go back to the derivation that we were making as far as the kinetics of step polymerization is concerned we were talking about self catalyzed reactions; in this case we are taking for polyesterification as an example. So, let us go back to the derivation right where we left it.

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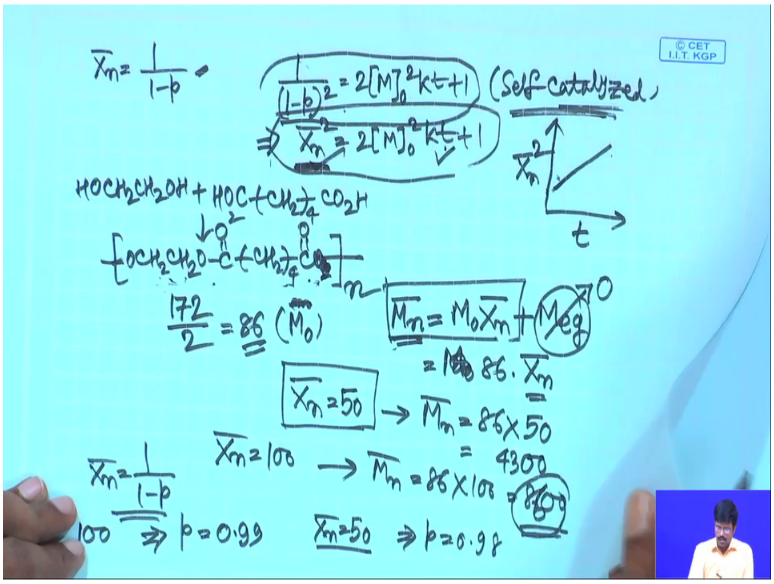

$\overline{X}_n = \frac{1}{1-p}$

$\frac{1}{(1-p)^2} = 2[M]_0^2kt+1$ (Self catalyzed)

$\Rightarrow \overline{X}_n^2 = 2[M]_0^2kt+1$

$HOCH_2CH_2OH + HO_2C(CH_2)_4CO_2H$

$\left[OCH_2CH_2O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right]_n$

$\frac{172}{2} = 86\ (\overline{M}_0)$

$\boxed{\overline{M}_n = M_0\overline{X}_n} + \cancel{M_{eg}} \to 0$

$= 86\cdot\overline{X}_n$

$\boxed{\overline{X}_n = 50} \to \overline{M}_n = 86\times 50 = 4300$

$\overline{X}_n = 100 \to \overline{M}_n = 86\times 100 = 8600$

$\overline{X}_n = \frac{1}{1-p}$

$100 \Rightarrow p = 0.99 \quad \overline{X}_n = 50 \Rightarrow p = 0.98$

So, we had actually derived an expression for X n bar which is the number average degree of polymerization and this number average degree of polymerization was equal to 1 divided by 1 minus p. Now this particular expression is valid when you have stoichiometric amount of starting materials. So, this is your Carothers equation. Now if we go back to the particular expression that we had got 1 divided by 1 minus p square equals to 2 M 0 square k t plus 1 that is for self catalyzed reactions, and if we use this particular expression here, then what we have is X n bar square equals to 2 M 0 square k t plus 1. So which means, that basically the number average degree of polymerization square of that is varying with t linearly.

Now this number average degree of polymerization by now you might know from our previous discuss discussion on degree of polymerization that is the average number of structural units per polymer chain. This has a direct relationship with the molecular weight of the compound.

So, before we go further on this, what I would like to do is to take a very simple example and tell you what is actually means here; this X n. So, again we will take this example of ethylene glycol and adipic acid. Let us draw the repeat unit here, OCH 2, CH 2 O and then you have COCH 2 whole 4 CO 2 H; in fact this will be CO like that. So, what is the molecular weight of this repeat unit if you just add things up it becomes 172. Now in this repeat unit you basically have 2 structural units. So, the average molecular weight per structural unit for this particular polymer then it is 172 by 2 and that will be equal to 86.

Now there are different convinces with regards to this. Sometimes what people will tell is that they will take the total of 172 itself, but the other convention which is generally more accepted is that if you have n number of structural units per repeat unit then you have to take the average molecular weight of the structural unit which means you have to divide by n. So, in this case you have to divide by 2. So, 86, you call it as M 0 that is the average molecular weight per structural unit.

Now M 0 bar let us say or M 0 you can put. So, what is the number average molecular weight for this particular polymer? That will be then, the average molecular weight per structural unit into the degree of polymerization. So, total number of structural units you are multiplying by the molecular weight per structural unit average of it. And you then add the molecular weight of the nth group then that becomes your number average molecular weight.

Now this molecular weight of the n group, it can be regarded as 0 for all practical purposes because if the polymer is of very long chain then the n group; the contribution to the total molecular weight becomes insignificance. Suppose you have 1000 units together in a polyester and you have an alcohol on one side that alcohol is how much it is oxygen 16 and hydrogen is 17 only. So, you can actually neglect or you may have may be 20000 units. So, that part you can neglect. So, for all practical purpose then M n equals to M 0 into X n.

So, in this case your M n equals to M 0 into; so, M 0 is 86 86 into X n. Now let us say your X n; X n bar is let us say your X n bar is 50, I mean you are actually targeting a particular number average degree of polymerization for your purpose; let us say you are targeting X n equals X n bar equals to 50, then what is the molecular weight; you will get your molecular weight will be 86 into 50. So, that will be 4300. What about X n bar equals to 100, if you are aiming for a higher molecular weight let say you are aiming for degree of polymerization 100 then what is your M n, M n becomes 86 into 100 M n bar becomes 8600.

So, you are beginning to get polymer of some practical significance. As I told in general at least, you know 5000 should be the polymer molecular weight. So, then the properties start to manifest say mechanical strength so on and so forth.

So, you see in general, if you are X n bar for a polymeric system is 100 then your number average molecular weight is round about 10000 in that range, it may not be 10000 depends on the structure and all it is in that range. So, what you are targeting for this kind of step polymerizations is your X n bar at least in that range say 100 then you get 8000, 9000 molecular weight. If you want a molecular weight of say 50000, then you need it is a correspondingly higher value of X n. Now in order to achieve this value of X n or X n bar whatever the degree of polymerization how much the reaction is to proceed this will be given by your Carothers equation.

So, you know your Carothers equation is X n bar equals to 1 divided by 1 minus p. So, in order to in order to get X n bar 100 if you put that value here what is the value of p; the conversion or the extent of reaction that is 0.99. So, you need 99 percent of the reaction. So, 99 percent of conversion is required in order to get an X n bar of 100 which will give you only a molecular weight of 8600 for this particular system, what about X n bar 50, if you put X n bar 50 here, then your p becomes 0.98 and X n bar 50 means your M n bar is 4300. So, you have molecular weight of only 4000 approximately, even if you have gone up to 98 percent of conversion. So, when you go to 99 percent conversion, then you have molecular weight of 8600. So, you have to go beyond 99 percent conversion, in order to get some molecular weight 2000 or something a 20000 or something.

So, even 98 percent of conversion is not sufficient for step polymerization and you know a 90 percent conversion in normal organic chemistry labs is regarded as excellent, but there is a disaster, then for step polymerizations, how much time is required and all. We will come to that. If you remember in this particular slide here in this particular page on the top if you if you see here this is the expression or this is the expression X n bar; how X n bar square is related to time for self-catalysed reaction that changes linearly with time, but that changes actually slowly because time is related to the to the second power of degree of polymerization.

So, with time it will increase, but it will increase whether slowly. So, what will happen if you consider a different scenario that is if you are using an external catalyst?

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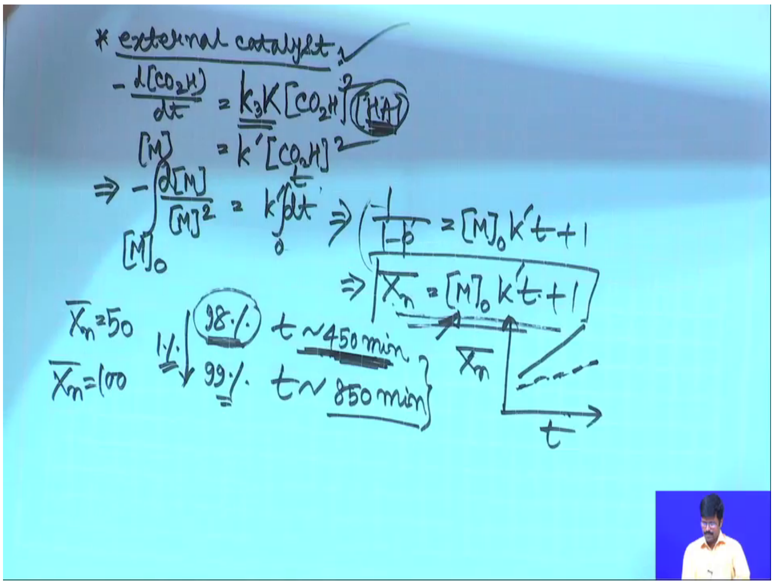

* external catalyst

$$-\frac{d[CO_2H]}{dt} = k_3K[CO_2H]^2[HA]$$

$$= k'[CO_2H]^2$$

$$\Rightarrow -\int_{[M]_0}^{[M]}\frac{d[M]}{[M]^2} = k'\int_0^t dt \Rightarrow \frac{1}{1-p} = [M]_0k't+1$$

$$\Rightarrow \boxed{\overline{X}_n = [M]_0k't+1}$$

$\overline{X}_n = 50$ 98% $t \sim 450$ min

1%

$\overline{X}_n = 100$ 99% $t \sim 850$ min

So, you know that X n bar is related to time and we have not yet told you this in order to go from 98 percent to 99 percent of reaction; how much time is necessary and all those we will tell you after discussing these things here.

So, let us now talk about the external catalyst, we talked about the self catalyst self catalyzed system now we are going to talk about the external catalyst system. Now I am not going to derive everything here. So, here I am going to start from this particular expression your minus d CO2 H d t that is the rate of the reaction is basically your k 3 k recall that particular expression there into CO2 H into OH into HA and both of CO2 H and OH; these concentrations of the same to same with because it is stoichiometric. So, this becomes square and we do not replace HA with your 2 H because we have added a mineral acid small amount of a mineral acid as an external catalyst.

So, this stays here, but since this is the catalyst this concentration is constant. So, basically this can be incorporated into this constant. So, you just remove this and you incorporate that into this is constant, again this is capital K this is small k. So, let us say small k prime and then it becomes CO2 H whole square now you do the same way in the same way what you do is you do an integration the CO2 H you can replace by m. So, minus d M by M square equals to k prime d t integral 0 to t integral M 0 to M and if you do the calculation here what you will get is 1 divided by 1 minus p equals to M 0 into k prime t plus 1 this 1 divided by 1 minus p from Carothers equation is X n bar that is equals to M 0 into k prime into t plus 1.

So, you see here your X n bar is linearly changing with time, but if you compare that with this particular graph here for self catalyzed reaction you can immediately see that the time is varying with the second power of X n bar square for self-catalysed reaction where as it is varying directly with X n bar in the external catalysed reaction which actually means that this slope of this particular curve is much stripper with respect to this. So, in effect your degree of polymerization will increase much faster with time or with conversion if you compare if you are using an externally catalysed reaction.

So, for all practical purposes, then yourself catalysed reaction you do not use because the reaction will take so much time in order to get to a X n which is acceptable to you it is actually inconceivable; inconceivable in industrial situations here within a reasonable amount of time you develop the X n bar. So, if you just plot them together. So, this is X n here and if you are plotting X n bar square that will be something like this. So, same time it will be developing the degree of polymerization of the molecular weight the polymerization, it will be going much slowly the molecular weight will be developing much slowly.

So, we will then say that external catalyst is the reasonable conclusion that is what you are going to do always for this kind of reactions, say especially for polyesterification reactions. Now one more thing, I would like to point out here in regards to a previous discussion that you know people thought some reactions where very slow they thought the size is very big for the polymer.

So, the functional groups are reacting slowly. So, the functional group reactivity has become lower in direct contradiction to the assumption that we had that the functional group reactivity does not change. So, one of the reasons was also this that when people used self-catalysed reactions the reaction was very slow. So, they thought when the size is very high for the polymer maybe the functional group reactivity has dropped, but later on when they realise that this is the kind of analysis that you can do; you can add little bit of mineral acid and the reaction will go very fast because your X n bar or the degree of polymerization directly varies with t rather than the square of that.

So, now if you take this particular expression here you will see that I mean if you do a calculation if you do the maths here and if you compare with the previous page here if you are having an X n bar say 50 and X n bar say 100 we told this is for 98 percent reaction this is for 99 percent reaction, if you compute the t correspondingly, the t basically will become for this for this particular reaction approximately say that t will be say 450 minutes as a matter of fact I mean you can put in this particular equation also, but if you look at the exact experiment that was done in order to derive this; it is not ethylene glycol that they used they used diethylene glycol in that case.

So, the point is the time that it takes in order for the 98 percent of the reaction to be completed the time that the time that it takes for 99 percent of the reaction to be completed towards 850 minutes.

So, from 98 to 99 percent for this one percent of the reaction you had to weight double the amount of time that you had to actually weight for the first 98 percent of the reaction. So, you know how difficult it is, but you have to actually wait for this extra time because if you stop at 98 percent, you get only 50 degree of polymerization your molecular weight is only around 4000, if you want more than 8000-9000, you have to wait for this double amount of time. Now this kind of problem is therefore, step polymerization towards the end each percent of conversion will take almost like double the time say from 98 percent to 99 percent.

So, I hope that this particular small calculation has given you the idea of the importance of this kind of analysis of kinetics because if you did not do this kind of analysis you would not know; what are the things that you need to do to achieve high molecular weight. So, these equations then show you need to go at least 99 percent of conversion in order to get a reasonable molecular weight for your polymer.

So, now let us move on with this particular discussion to something else. Now we have talked about these reactions as equilibrium reactions.

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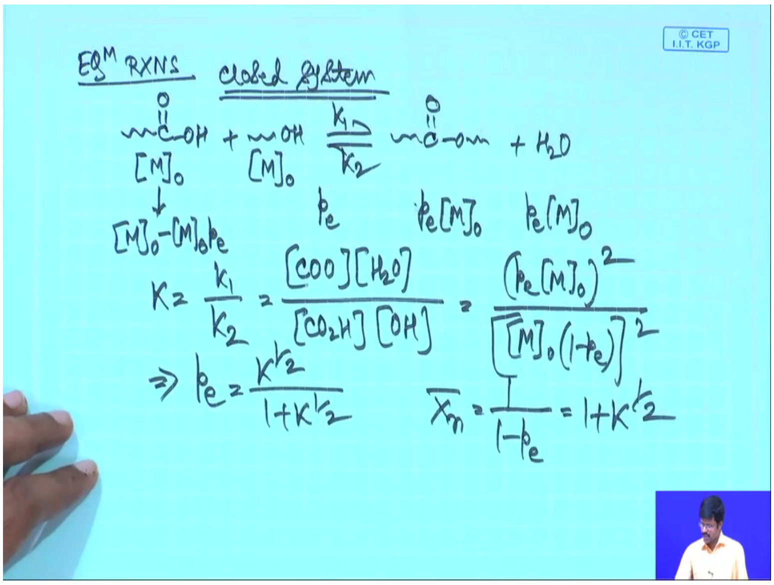

EQ^M RXNS closed system

$$\sim\!\!\overset{O}{\overset{\|}{C}}-OH + \sim\!OH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \sim\!\!\overset{O}{\overset{\|}{C}}-O\!\sim + H_2O$$

$[M]_0 \quad [M]_0$

$\downarrow$

$[M]_0 - [M]_0 p_e \qquad p_e \qquad p_e[M]_0 \qquad p_e[M]_0$

$$K = \frac{k_1}{k_2} = \frac{[COO][H_2O]}{[CO_2H][OH]} = \frac{(p_e[M]_0)^2}{[[M]_0(1-p_e)]^2}$$

$$\Rightarrow p_e = \frac{K^{1/2}}{1+K^{1/2}} \qquad \overline{X_n} = \frac{1}{1-p_e} = 1+K^{1/2}$$

These are equilibrium reactions which needs no further explanation that you have to remove the water from the system; what happens if you do not remove water, what happens if you do the reaction in a closed system; you do not remove any of the products after sometime when enough amount of the product has developed, then the backward reaction will be first enough and the depolymerisation will take place. So, equilibrium will be reached. So, you have to find out if you can at all do this reaction in a closed system if it is acceptable at all in terms of the yield.

So, if you are looking for a closed system here. So, let us say you have a closed system here and you consider the same reaction of the external catalyst. So, you have a acid you have an alcohol. Now I will draw the full reaction in one go, you have your product here ester and you have water. So, this is in equilibrium, it has reached equilibrium, it is a closed system.

Now, in this particular situation; let us say you started with a concentration of M 0 for both when the equilibrium has been reached, let us say the conversion; I mean the extent of reaction is p e stands for equilibrium situation. So, at equilibrium what is the concentration of this M 0, it will become M 0 minus M 0 into p e same concentration will be for this what will be the concentration of the products. It will be p e into M 0 and this will also be p e into M 0. So, if you write down the expression of equilibrium constant which is nothing but small k 1 divided by small k 2 which is equal to say this product. We write as the ester we write as COO and water is water here concentration and this is CO2H starting material and this is OH.

So, this will be then p e M 0 square on the up and on the bottom it will be M 0 into 1 minus p e square. So, this M 0 will go and if you do the final calculation what you can find out is small p e which is your extent of reaction it will be equal to k to the power half divided by 1 plus k to the power half and your X n bar which is nothing but one divided by 1 minus p e Carothers equation that will be equal to 1 plus k to the power half.

So, the point that we want to find out here is can we have acceptable degree of polymerization at very high conversion very high conversion is not at your hand because conversion is limited by the fact that equilibrium has been reached. So, conversion has stopped that is your p e. So, in that equilibrium condition can you have high enough value of x n. So, that this reaction is acceptable to you that will depend on the equilibrium constant if the equilibrium constant is high. Then you can get a very high value of X n because X n will be equal to this it cannot go higher than this value in equilibrium situation. Now let us have some data here in order to consolidate this idea.

In fact, this data can be derived you put the value of k some values of k corresponding we can calculate the value of p e and X n and you can have some kind of realisation of what is the situation here.

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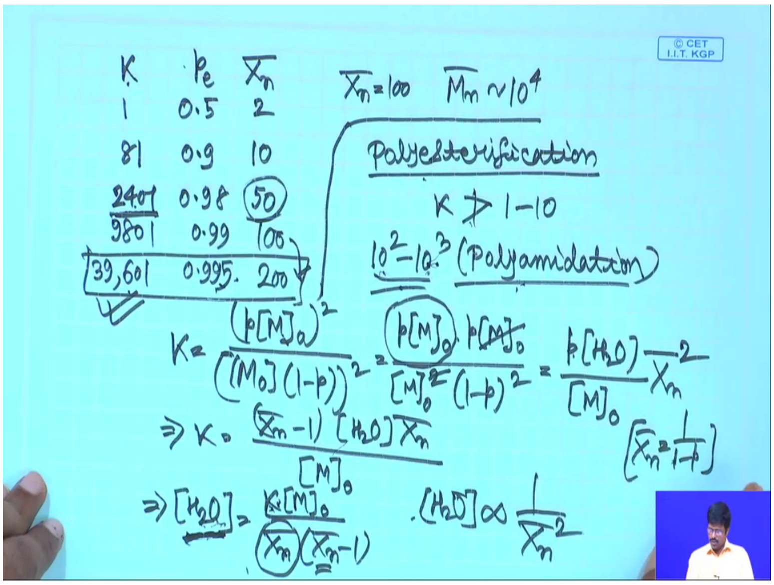

K	p_e	$\bar{X}_n$
1	0.5	2
81	0.9	10
2401	0.98	50
9801	0.99	100
39,601	0.995	200

$\bar{X}_n = 100$ $\quad \bar{M}_n \sim 10^4$

Polyesterification

$K \not> 1-10$

10^2-10^3 (Polyamidation)

$$K = \frac{(p[M]_0)^2}{([M_0](1-p))^2} = \frac{p[M]_0 \cdot p[M]_0}{[M]_0^2 (1-p)^2} = \frac{p[H_2O]}{[M]_0}\bar{X}_n^2$$

$$\left[\bar{X}_n = \frac{1}{1-p}\right]$$

$$\Rightarrow K = \frac{(\bar{X}_n - 1)[H_2O]\bar{X}_n}{[M]_0}$$

$$\Rightarrow [H_2O] = \frac{K[M]_0}{\bar{X}_n(\bar{X}_n - 1)} \qquad [H_2O] \propto \frac{1}{\bar{X}_n^2}$$

So, K and then you have p e and then you have X n; X n bar. So, if your k is 1; only 50 percent of reaction occurs, if the equilibrium constant is 1 and your X n bar is 2, it is like a oligomer if your k is say 81, then 90 percent of reaction is occurred your X n bar is only 10. So, 90 percent of reaction is not acceptable to you molecular weight will be very low if your k is 2401, then 98 percent of the reaction will occur at equilibrium X n bar will be only 59801; 99 percent of reaction X n bar is 100, it is becoming reasonable 39601.995 X n bar is 200.

Now, as I told in general for your typical step polymers when X n bar is 100, your molecular weight becomes around 10 to the power 4. So, you have to go beyond that. So, you need this kind of situation. So, your equilibrium constant has to be as high as this in order to get this kind of reaction extent of reaction will be the 99.5 percent and your X n bar will be 200 reasonable maybe.

So, for a reaction to be successful in a closed situation your equilibrium constant has to be very high at least in this range it cannot be even say you have 3000 4000 your X n bar is not good enough. So, let us look at what are the typical k values or equilibrium constant values for your typical step polymerisation reactions say if you are looking at polyesterifications; polyesterification reactions your typical k values are of the order of 10, they do not normally go beyond 10, I am just putting one to 10. So, if the k values is a 10; you are getting X n value very very low, this reaction cannot work if you are looking for polyesterification, you cannot do in closed system you cannot simply get high enough degree polymerization which will lead to high enough molecular weight of the product.

Even for polyamidation your k value is ten square to ten cube in the range of 1000 for polyamidation. So, how much you can get you see you need at least around 2400 to get X n value of 50 which for the reaction of adipic acid and an ethylene glycol it came to around 4000 the molecular weight still quite low. So, even polyamidation will not work. So, the conclusion is that you cannot do this reactions in closed system, you simply do not have high enough degree of polymerization simply cannot have high enough molecular weight for industrial application. So, you need an open system and where you were doing an open system in principle, it will ultimately reach an equilibrium.

So, you are removing water. So, how much of water you have to remove in order to get an X n bar of the degree of polymerization that you want that becomes a question that is why this kind of analysis is necessary you want to have a target of molecular weight this range I want to get. So, correspondingly what is the X n bar degree of polymerization and correspondingly to what extend the reaction has to progress. So, that will tell you how much of equilibrium concentration of water has to be there in order to shift the equilibrium towards the product so that you can get that kind of molecular weight.

So, if you do the same analysis for an open system, then your expression is something like this your equilibrium constant the same equilibrium constant expression. Until now, I am not modify anything it is like this M 0 into 1 minus p whole square now here your p M 0 is basically. So, you have p M 0 into p M 0 divided by M 0 square into 1 minus p square. Now one of the M 0s you can remove. Now p n 0 it is the concentration of water as well as the concentration of the ester at conversion p. So, you can just replace this p n 0 by water and p into concentration of water this p stays there and then you have M 0 at the bottom and 1 divided by 1 minus p whole square is nothing but X n bar square Carothers equation you only derived that.

Now, you know your X n bar is equal to 1 divided by 1 minus p. So, you can correspondingly you can derive the expression of p in terms of X n bar. So, which is nothing but X n bar minus one divided by X n bar. So, you replace p with that and then what you will get is your k will become equal to X n bar minus one into concentration of water into X n bar divided by M 0. So, ultimately the concentration of water that you will be having at equilibrium is nothing but k into M 0 divided by X n bar into X n bar minus 1.

So, it shows that in order to get a higher value of degree of polymerization you need to remove water more. So, to the lower is the concentration of water at equilibrium the higher is the value of this degree of polymerization. So, basically this X n bar you want very high. So, X n bar minus one is close to X n bar. So, typically your water then concentration of water is proportional to 1 divided by X n bar square. So, what it tells you also this equilibrium constant if your equilibrium constant is higher you can have you can remove actually lower amount of water to obtain the same high value of X n bar because this water this concentration here is the equilibrium concentration.

So, if you remove. So, this k and water they are actually varying in a similar way. So, if your equilibrium constant is higher in order to get the same value of X n bar you have to remove water less which becomes easier for you. So, actually you would like to have a reaction with high equilibrium constant. So, that you have to remove less amount of water to obtain the same degree of polymerization if you are comparing those things. So, that way if you are looking for say for example, polyamides; I already told you polyamides have a higher equilibrium constant of 2 orders or 3 orders of magnitude then polyesterification.

So, polyamide reactions will be easier to do in open condition then polyesterification close condition forget open reactions polyamidation will be easier reactions for you why is that. So, because you are k value is very high very high in comparison to your polyesterification. So, if k value is high. So, correspondingly you have to actually take out less amount of water. So, if I show you a table like this.

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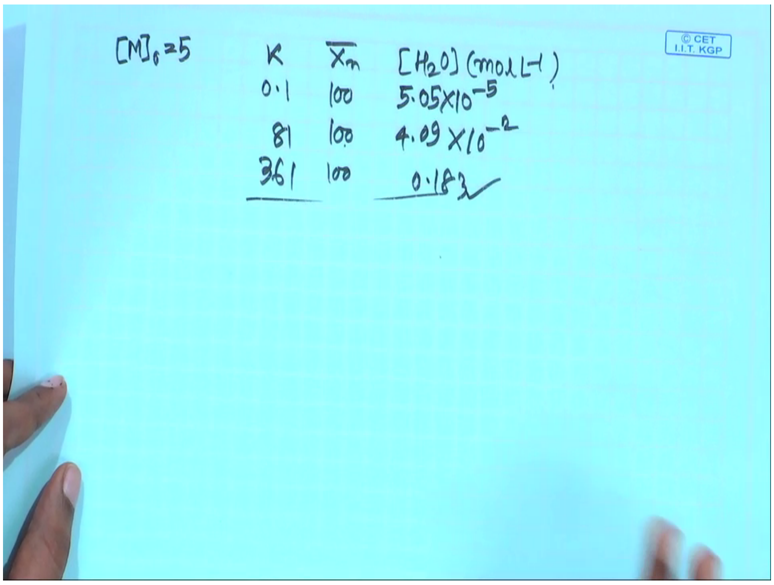

$[M]_0 = 5$

K	$\overline{X}_n$	$[H_2O]$ (mol L^{-1})
0.1	100	5.05×10^{-5}
81	100	4.09×10^{-2}
361	100	0.183

So, let us say your concentration of your starting monomers is around 5 molar and then this is the k value and you are putting your X n bar here and water; water is moles per litre. So, k value of 0.1 X n bar. So, X n bar you are always looking for 100 say. So, if k is 0.1, the equilibrium concentration of water that you have to achieve is this; that means, you have to remove water until you have this much low concentration the lowered is this value the more is the difficulty for you. That means, you have to actually remove more water. So, if k value is say 81 in order to achieve the same degree of polymerization your equilibrium; equilibrium concentration of water has to be in this range much more manageable if the k value is 361, then interest with 0.183 moles per litre.

So, if you have to remove water in order to target this concentration final concentration of water and if you have to remove water in order to target this concentration you would better do this because this is easier for you and that can only happen when the equilibrium constant for that reaction is high enough that helps you in this respect all of them you want the same molecular weight which is designated by X n bar corresponding to M n bar. So, that is why the polyamides polyamidation is basically easier under this kind of situations.

So, the kinetic analysis for the moment is complete as far as I thought is required for this develop the course. So, what we will next start is molecular weight control of the reactions and as I am telling you here when I am talking about molecular weight control

I am really saying that you want a precise range of molecular weight I mean you want to be as much as precise as possible of course, you want to decrease the polydispersity as I was telling before in the previous week M w by M n; you want to have lower distribution of the molecular weight. So, for that you are looking for special techniques and all, but the aspect here I am going to tell for this for this kind of reaction; say you want a particular X n bar suppose you want 100, then you have to release the water to a particular value concentration final equilibrium concentration corresponding to the equilibrium constant value of that particular reaction.

Now you might say I would like to reduce the concentration of water even further you can if you reduce the concentration of water you can further probably, you can go to higher molecular weight, but that is not desirable for you; you want a specific molecular weight you do not even want to go higher than that because certain properties may become undesirable as I am telling you the processability may become difficult for that. So, that is why what we will do next is we will have a discussion on the how you can control the molecular weight for this kind of step polymerization we have a few minutes left in this particular class.

So, we will just give you an introduction to that for the moment and then we will continue in the next class. So, when you are trying to control the molecular weight say again you are reacting a diamine with a dicarboxylic acid. So, what will happen if you are using stoichiometric amount of both the final product will have an amine on one side and carboxylic acid on another side. And typically, what you do is that at a particular time you want to stop that particular reaction, because the time is related to your X n bar degree of polymerization which is related to a molecular weight.

So, when you are stopping essentially what you are doing is you quench the reaction many times you decrease the temperature and then you quench the reaction that is all well and good except for the fact that later on the reaction has to come back to room temperature of slightly higher temperature when you are trying to take it out or whatever.

Then what can happen is that your potential reacting groups at the end of polymer chains let us say each polymer chain one end is amine one end is carboxylic acid. So, that polymer chain has a potential to react with another polymer chain the amine of that polymer chain can now further react with the carboxylic acid of another polymer chain this is something that can happen and that can actually now play havoc with your molecular weight. So, that does not that is not a good control. So, one of the ways will be to use a slight excess of one of the starting monomers. So, that that excess monomer at the end will be will be shown as the functional group at the end of the polymer chains.

So, if you have a diamine and a dicarboxylic acid reacting and if you take a slight excess of the diamine at the end of the reaction what you will have is a polymer chain on sides of that there are amine, because the acid reactant it was in lower quantity, so it has been completely used up still there where amines left so that reacted. Now both ends are amine; though a amine cannot react with itself that way. So, then the polymer chain becomes unreactive. So, we will discuss this and more in the next class.

Till then, thank you for your attention.