Polymer Chemistry
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Lecture - 5
Step-growth Polymerization (Cond.)

Welcome back to this course on polymer chemistry. We will continue our discussion on step-growth polymerization which we were having in last lecture. Now, let us look at what we have learnt so far in terms of step-growth polymerization.

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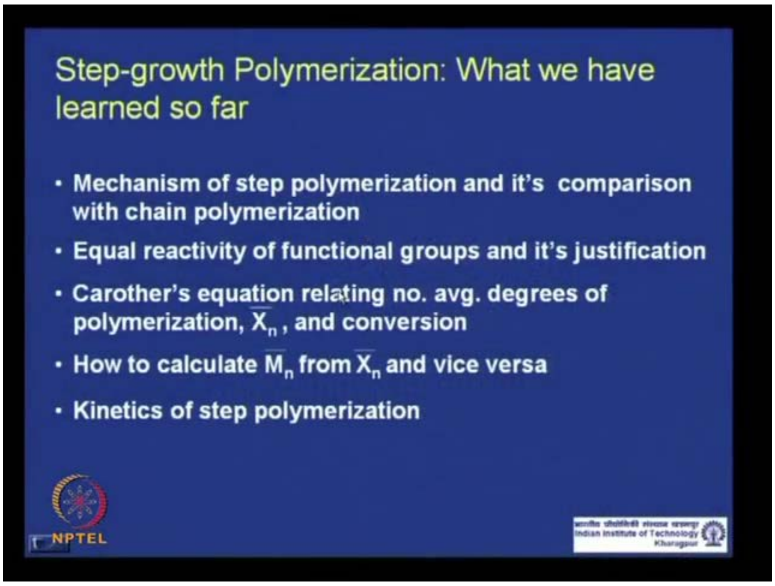

Step-growth Polymerization: What we have learned so far

- Mechanism of step polymerization and it's comparison with chain polymerization
- Equal reactivity of functional groups and it's justification
- Carother's equation relating no. avg. degrees of polymerization, $\overline{X}_n$, and conversion
- How to calculate $\overline{M}_n$ from $\overline{X}_n$ and vice versa
- Kinetics of step polymerization

We have learnt the mechanism of step-growth polymerization and its comparison over chain polymers, and we also learnt how and what is the effect of equal reactivity of functional group, and we also understood the justification of why the functional group of reacting molecules including the intermediate species should have same reactivity irrespective of their size and irrespective of whether the functional group present in the other direction is already reacted or not.

Also, we have seen that this is experimentally proven that once the length of the chain goes beyond 3 (()), then the reactivity actually becomes independent of the chain length of the oligomeric species. We also learnt the Carothers equation relating to the average degrees of polymers, polymerization and the conversion p, and we also same time learnt how to get the number of average molecular weight from the degree, average degrees of polymerization and I give more time in this because as I said that sometimes, there are confusion among students how to get m n from x n. It is actually m n is x n multiplied by the average molecular weight of the structural unit, not the repeat unit and we also discussed the kinetics of step polymerization.

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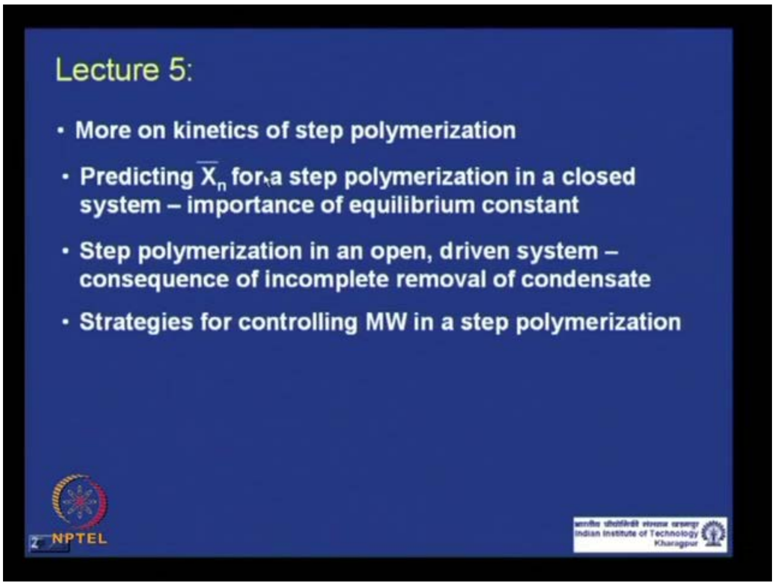

Lecture 5:

- More on kinetics of step polymerization
- Predicting $\overline{X}_n$ for a step polymerization in a closed system – importance of equilibrium constant
- Step polymerization in an open, driven system – consequence of incomplete removal of condensate
- Strategies for controlling MW in a step polymerization

In this class, in this lecture, what we will do is we will continue the discussion on kinetics of step polymerization and then, go for predicting the number average degrees of polymerization for a step-polymerization which is happening in a close system, and that will give us the importance of equilibrium constant of a step polymerization reaction. We then move to a step polymerization in a open and driven system, where it is not possible to completely remove the condensate out of the system. That means there will be some condensate remaining in the system, polymerization system. In that case, what is the consequence of that presence of the condensate on the molecular weight of the polymer and then, we will move to the different strategies of how to control the molecular weight in the polymerization. Now, let us go back and see what we have learnt in the last class in terms of kinetics of poly step polymerization.

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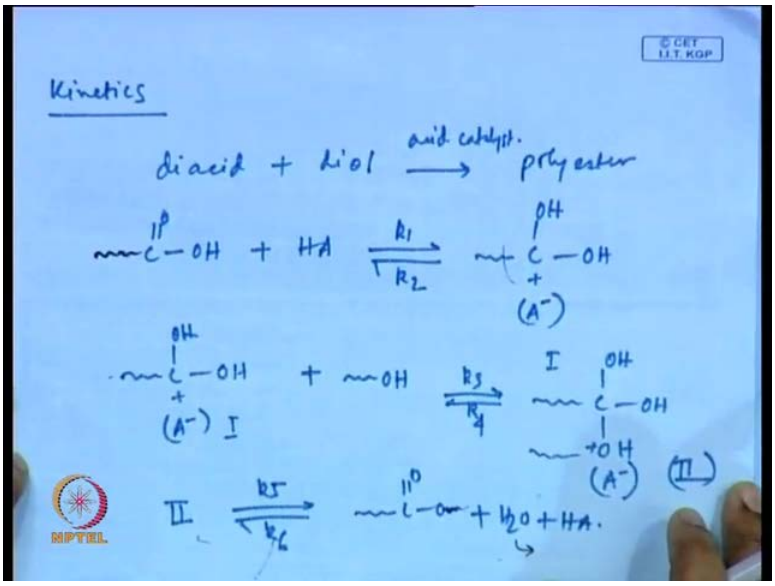

Now, this is the reaction. We took as our model the polyesterification reaction and this is the reaction we followed and finally, what we arrived at is as follows.

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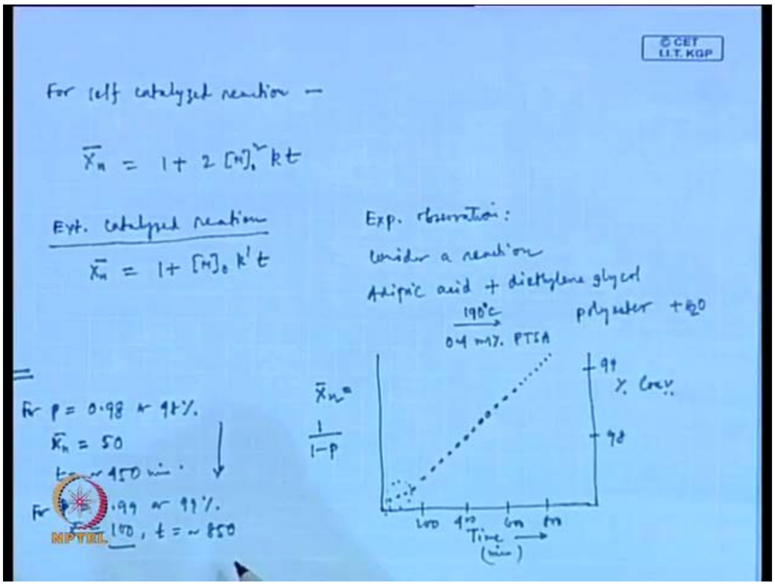
For self catalyzed reaction –

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

Ext. catalyzed reaction

$\bar{X}_n = 1 + [M]_0 k' t$

For $p = 0.98$ or 98%.

$\bar{X}_n = 50$

$t = \sim 450$ min.

For $p = 0.99$ or 99%.

$\bar{X}_n = 100$, $t = \sim 850$

Exp. observation:

Consider a reaction

Adipic acid + diethylene glycol $\xrightarrow[\text{0.4 mol\% PTSA}]{190^\circ C}$ polyester $+ H_2O$

That for self catalyzed reaction x n bar is 1 plus 2 n square k t, where n 0 is the concentration of the monomeric species at beginning, whereas for external catalyzed reaction, we got x n is 1 plus n 0 k dash t. Now, from these two equations, we have seen in the last class itself that and it is very difficult to build a high molecular weight, high value of x n bar for a self catalyzed reaction and that is the reason in most cases, in a most industrial polymerization has taken place in presence of a catalyst which is added from outside the system. So, most of the reactions in industrial setup are carried out in external catalyzed reaction. So, our discussion in our discussion, we will be mainly focusing on this external catalyzed reaction and we will not discuss too much about the self catalyzed reaction.

Now, let us take an experimental observation of an external catalyzed system. One, experimental observation. Let us consider reaction adipic acid plus diethylene glycol at 190 degree centigrade in presence of 0.4 mol percent of para toluene sulphonic acid as a catalyst and the product is polyester plus h 2 o. So, this is what is observed experimentally in this axis. We have time, say it minutes, 200,400, 600, 800 and so on and this axis, we have percentage conversion. This is 99, this is somewhere 98 and in this side, we have x n bar which is equals to 1 by 1 by p and experimental, it has been found to the following something like this.

Now, what do we see here in this experimental observation? We see that except this initial part, the entire region for the entire conversional region, you have a linear relationship of degrees, average degrees of polymerization with time which is predicted by your reaction mechanism. Now, what does it mean? Now, remember the reaction. How do the go about the reaction? Now, in during that deduction of that kinetic equation expression, we have used functional group like this which means we have considered the reactivity of functional group independent of the size of the molecules and here, it found to be that expression is valid for almost entire range of conversion region, which means that this assumption what we have considered here, that equal reactivity of the functional group is valid even experimentally.

So, even if at high conversion, the length of the polymer chain or the oligomer chains are quite high. The reactivity of the concern group at the end of that residing, at the end of the chain are same as when the conversion was smaller. That means the sizes of the polymer chains are smaller. Now, remember what are the other conditions we have assumed or imposed during the derivation of this expression was that there is one is to one stoichiometric composition of two monomers or two functional groups. In this case, carboxylic acid and OH and also, we were taking out this condensate, this small molecule, so that practically the reaction is irreversible. We are taking out the condensate small molecules h 2 o in this case to make sure that the reaction happened. This equilibrium reaction actually happens almost irreversibly.

So, what are the other observation we can make here, say at for a conversion of p? For p is 0.98 or 98 percent which correspondence to x n bar of 50 t is say, around 450 minutes. Now, for p, 0.99 or 99 percent x n corresponding to 100 and t is almost 85. So, we see here that from reaching up to 98 percent conversion, it takes about 450 minutes and build a average degree of polymerization of 50. If the average molecular of the structural units is 200, then the molecular weight will be above 10,000.

Now, that may not be sufficient for our purpose. We are looking for building high molecular weight for all practical purpose. We need high molecular weight, so this 98 percent conversion may not be sufficient for our, it will not serve our purpose. So, we must push the conversion higher, so that the molecular weight we get is high enough for which will serve our purpose. So, from 98, conversion going to 99 percent conversion, we have to almost double the reaction type, some 450 to 850. So, for a organic chemist which is doing a stratification reaction for small molecules, a 98 percent conversion may be quite satisfactory which means that at 450 minutes time, he can stop the reaction and take the product which is 98 percent conversion which is quite sufficient and quite satisfactory, but for a polymer chemist, that 90 percent conversion is not sufficient. You know there is no choice for a polymer chemist other than continues the reaction for almost similar time to get a high enough molecular weight.

In this case, x n bar degrees of polymerization of 100 and if this molecular is not sufficient enough, then you have to keep the reaction even longer to high the conversion and hence, higher the molecular weight of the polymers. Now, because you have to keep this reaction for longer time, sometimes that actually posses some difficulties in terms or stability of the ingredients, the chemical species which is present and as you have seen that this is typically done at higher temperature, which means that if you keep this for a longer time, there is the possibility of the polymer x species might degrade and form colour species which is not desired.

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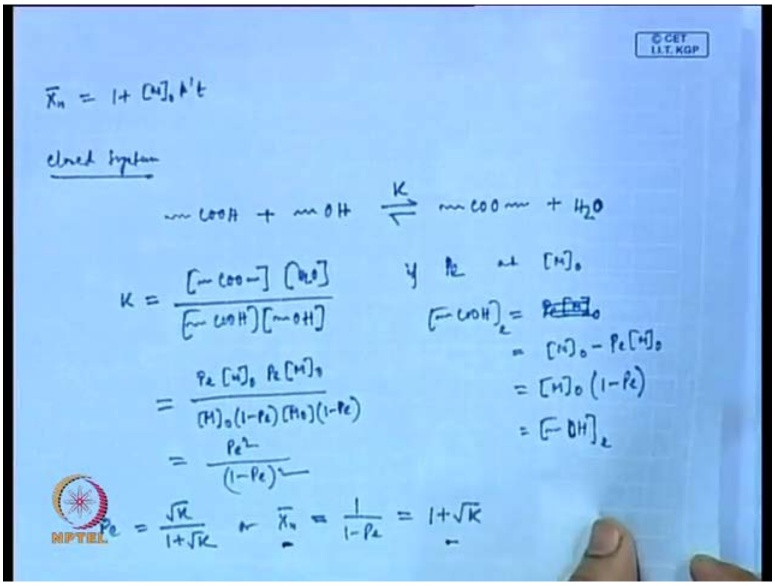

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$\bar{X}_n = 1 + [M]_0 k' t$

closed system

$$\sim COOH + \sim OH \underset{}{\overset{K}{\rightleftharpoons}} \sim COO \sim + H_2O$$

$$K = \frac{[\sim COO \sim][H_2O]}{[\sim COOH][\sim OH]}$$

if P_e at $[M]_0$

$$[\sim COOH]_e = \cancel{P_e [M]_0}$$
$$= [M]_0 - P_e [M]_0$$
$$= [M]_0 (1 - P_e)$$
$$= [\sim OH]_e$$

$$= \frac{P_e [M]_0 \, P_e [M]_0}{[M]_0 (1-P_e) [M_0] (1-P_e)}$$

$$= \frac{P_e^2}{(1-P_e)^2}$$

$$P_e = \frac{\sqrt{K}}{1+\sqrt{K}} \quad \text{or} \quad \bar{X}_n = \frac{1}{1-P_e} = 1 + \sqrt{K}$$

What we also have seen this from this equation that the x n bar is linearly dependent on the initial monomer concentration as well, which means that to increase for a given rate constant, it is always referred to use a high concentration of monomer and that is why, typically this reaction are done at very high concentration in solution or in some cases, they are done in a bulk. That means you take the monomers as such which ensures the maximum possible concentration of the monomeric unit.

So, we now move to that. This again, this was deduced for such a way that we are taking out the condensate, in this case H 2 molecules, so that reaction was almost irreversible reaction. Now, let us consider a close system and take that we will write this reaction and reaction is constant. So, equilibrium constant can be written as now, if the conversion is P, if the conversion at equilibrium is say P e in this case and m 0 is the monomer concentration at the beginning at t is equal to 0, then at the equilibrium what is the concentration of COH is P m 0. Initially, it was n 0. Now, P e m 0 has reacted. So, at equilibrium, the concentration of COH group is given by 1 minus P e and because we are talking about one is to one stoichiometric ratio here as well, this is same as the concentration of OH at equilibrium. What is the concentration of CO group and H 2 O at equilibrium? That is P e m 0. So, P e m 0, so in case of that rearranging, we get P e as root k 1 plus root k or x n bar is 1 by 1 over P e. It gives you 1 plus root k.

Now, remember the difference between the earlier case and this case. In this case, we are doing or we are carrying out the reaction in a close system which means none of the reactants or the products are taken out from the system, and reaction is allowed to reach a equilibrium and from this reaction, we now can say that this is the formula which relates an average degree of polymerization with the equilibrium constant. So, how this translates to the real number, let us look at this following data.

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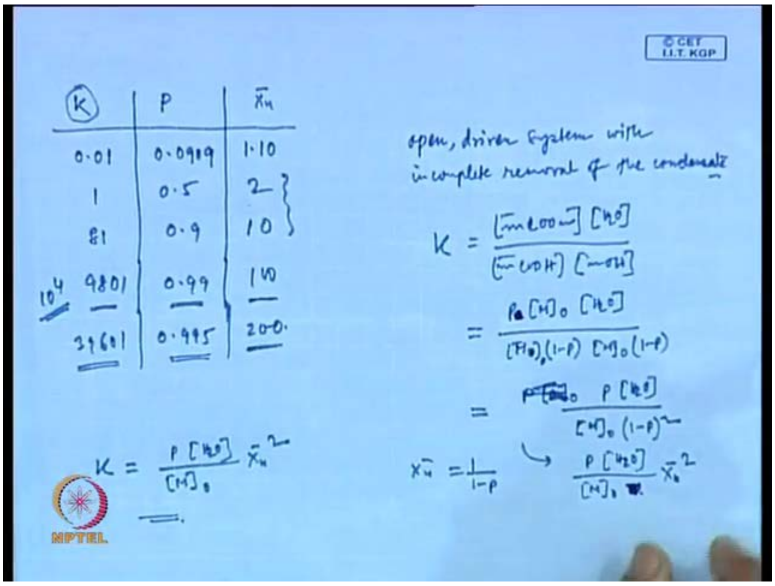

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K	P	$\bar{X}_n$
0.01	0.0909	1.10
1	0.5	2
81	0.9	10
10^4 9801	0.99	100
39601	0.995	200

$$K = \frac{p[H_2O]}{[M]_0}\bar{X}_n^2$$

open, driven system with incomplete removal of the condensate

$$K = \frac{[\sim COO \sim][H_2O]}{[\sim COOH][\sim OH]}$$

$$= \frac{p[M]_0[H_2O]}{[M]_0(1-p)[M]_0(1-p)}$$

$$= \frac{\cancel{p[M]_0}\ p[H_2O]}{[M]_0(1-p)^2}$$

$$\bar{X}_n = \frac{1}{1-p} \quad \hookrightarrow \frac{p[H_2O]}{[M]_0}\bar{X}_n^2$$

These are all calculated data from this expression. I will try to explain what it means in a minute. Now, if we carry out this reaction in a close system, if the equilibrium constant k you say 1, then the equilibrium conversion would be 0.5 and which will lead to degrees of polymerization, average degrees of polymer of 2. That means, if our reaction is such a way that your equilibrium constant is the value of equilibrium constant is 1, then at the end of the reaction that mean at the equilibrium, you are only going to get dimers. If you want to build a molecular weight that means, if you want to build say a degree of polymerization of 100 in a close system, then your equilibrium conversion has to be 0.9 which means your key has to be almost in the order of 10 to the power of 4. That means by itself your reaction has to be very highly reactive, so that by itself without removing the byproduct, you can get the product.

If you talk about a degree of polymerization 200, say this is probably the number we look for. When you make a high molecular weight polymer, then your equilibrium conversion has to be 0.995 which means you have to look at the number of k, value of k which is at the order of 10 to 5. That means your reaction has to be very much towards the product side, reactivity has to be very high, which is seldom the case, which is not the common case normally. Typically, polyesterification, they have the order of a 0.1 to 10 poly aberration of the order of which probably is the highest among the known reacts. Typical, common reaction is about the 10 to the power of 2 transesterification reaction of the order of 1 to 10. That means, typically these hang around between this and if you do not remove your condensate or the polymer, if you wish, then your reaction will end up at oligomer stage, may be dimer, trimer or tetramer. It will be mixture of that, but average will be say, a dimer for an equilibrium constant of 1 and for an equilibrium constant of 10 to the power 2 order. It will be at the stage of x n above 10.

So, that gives the importance of the equilibrium constant in a reaction in a step polymerization reaction that you always prefer. You always have a better reaction on your hand which is having a high equilibrium constant. So, this convinces that we have to, there is no other way. We have to do a reaction where we always continuously take out the condensate from the system.

Now, what happened if we take out the products is it will be moved towards right hand side. So, polymer will build, but it is not always possible or it is almost impossible for engineering design to take out every possible condensate, you know all the 100 percent with condensate. In this case, H 2 O for a polyesterification reaction, it is not possible to take out all the 100 percent H 2 O which is evolved. See because of so many reasons. Because of the high of in the molecular when it build up, there are high molecular weight. Then, the viscosity of the medium goes, you know increases quite a lot and when the viscosity goes up, this small molecular condensate diffusion of the condensate becomes very slow.

Now, to take out that H 2 molecule or any other condensate from the reaction, it has to first come to the surface. Then only, they can suck out that molecule from the system, but if it is forming inside the reaction in first, it has to defuse out to the surface of your reaction medium and then only, it will go up of the system. So, it becomes you know lot of cases. If the molecular weight is quite high and viscosity is very high which is you know more often the case. In case of bulk polymerization that melts when you are talking about no solvent, only the monomer molecules, it becomes very difficult. That means reaction almost becomes diffusion control.

So, what we now know that it is almost difficult to take out entirely the small condensate. So, we should consider a open and driven system where there is a incomplete removal of our condensate material. So, we will consider the same reaction here in this reaction and in this case, which will come the H 2. We will take out. It is taken out, but not all of them have been taken out of system. It will be part of it or trace of which will be remaining.

So, how we write the equilibrium constant in that case? So, for a open driven system with incomplete removal of the condensate k, again CO concentration H 2 O COH. So, same thing P e m 0. Now, in this case, we do not know what is the concentration of H 0 H2O. So, we are writing like this and again, m 0 1 minus P m 0 1 minus p which makes this.

Now, we know x n is 1 by 1 minus P. So, this can be written as let me write once again. So, what is finally, k comes p. Here, we are choosing to write P instead of P equilibrium because the two equilibriums have not been reached because we are taking out the system. So, instead of P equilibrium, in last case we are writing P as the conversion.

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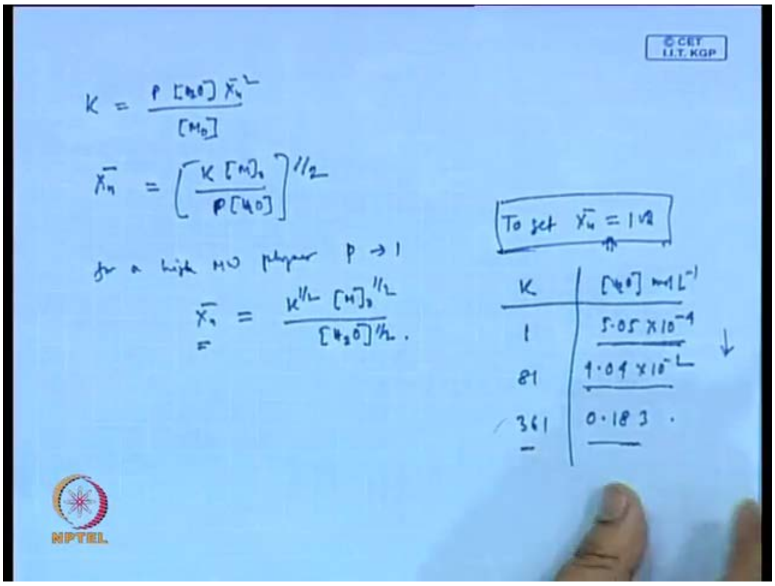

$$K = \frac{p\,[H_2O]\,\bar{X}_n^2}{[M_0]}$$

$$\bar{X}_n = \left[\frac{K\,[M]_0}{p\,[H_2O]}\right]^{1/2}$$

for a high MW polymer $p \to 1$

$$\bar{X}_n = \frac{K^{1/2}\,[M]_0^{1/2}}{[H_2O]^{1/2}}.$$

To get $\bar{X}_n = 100$

K	$[H_2O]$ mol L^{-1}
1	5.05×10^{-4}
81	4.04×10^{-2}
361	0.183 .

So, let us continue with the next page which means x n. Now, most cases as we learned by now that for a high molecular weight polymer, P is close to 1. So, we can ignore this for time being for if the molecular weight is high enough, so we can write. So, what does it mean? This means that the x n, the number wise molecular weight is inversely proportional to the square root of the amount of condensate present.

If I make a table with the corresponding numbers, how does it look? Now, to get it, we are trying to get x n bar of 100. How this k and H2 is related? What does this table means? The table means that if you have a reaction with high k to build same molecular weight, in this case average degrees of polymerization of 100 we are considering average degrees of polymers as 100 to reach that level, to reach that molecular weight. If your k is higher, then you can afford to keep some of the water molecules in the system. If your k is low, then you have to make sure that you takeout the water molecules as much as possible. So, to reach at level of 100 degrees of polymers, you have to reach a concentration level of water molecules as low as these, 10 to the minus 4 order whereas, if you have 10 to the 2 order of k, you can leave with 10 to the power of minus 2 level of H 2 in the system.

So, again this is meaning, this means that if you want to build a high molecular weight, always better to take out the condensate out from the system. Now, as I said that it is not possible always to take out the entire amount of condensate through the system. So, in that case, what happened is the next alternate way. You can build high molecular weight. The alternative way is to design reactions, where k will be high because if k is high, then you can afford to keep some of the condensate molecule in the system and still build a high enough molecular weight.

Now, as I said before that for engineer, it is not always very easy to build a reactor where you know you can take out the condensate molecules to the level, where you want for the building of molecular weight. So, in that case, there is a limitation, there is a limit at which you can take out the condensate from a system. So, what happened if there is a limit up to which you can go down in H2O level? You have to increase. The chemist would have to design a reaction which will be inherently having high equilibrium constant. Let us take an example. It will clarify more.

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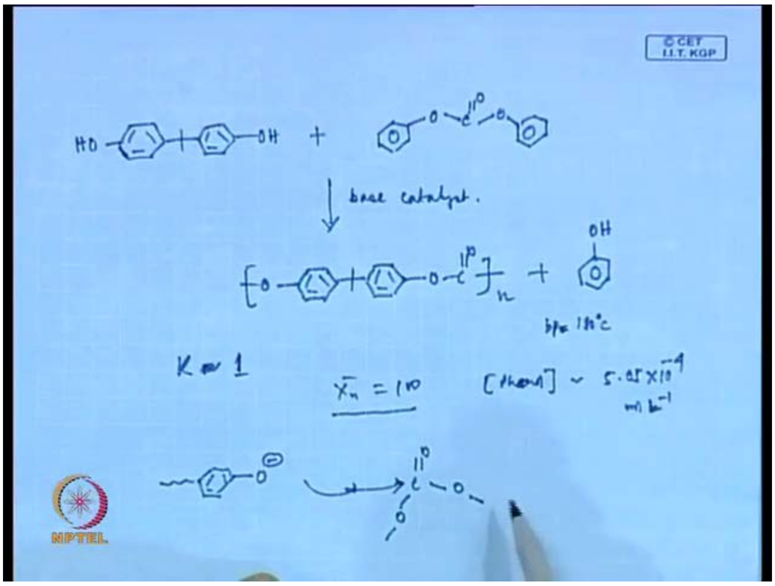

In one of the last lectures or previous lectures, so in the synthesis of polycarbonate form, this phenol, a using phosgene. Now, there is another way of synthesizing polycarbonate is by transesterification of this phenol with a diphenol carbonate in presence of base catalyst, base as a catalyst that gives us phenol as by product.

Now, in this reaction, the phenol boiling point is 180 degrees centigrade, bp of phenol is 180 degree centigrade. So, you can imagine that you have to at least have a reaction temperature of 180, so that you can take out the phenol vapor from the system. Now, the key of this reaction, equilibrium reaction if you are around close to one which means that if you do this reaction in a close system without taking out phenol from the system, you land up in an average degrees of polymer of two. It will land up in a, demerit will land up in a diametric state. So, naturally its reaction is done such a way that phenol is taking out from the system and reaction is done at very high temperature. So, the viscosity is lower and lower, so that you can take out the phenol molecule.

Now, you have to increase the temperature slowly because as you build up the molecular weight as the reaction goes, the viscosity of the medium builds. So, to take out the mineral molecule, you have to make the viscosity lower. So, you increase the temperature again and when you increase the temperature, again the time goes up; again the molecular weight builds up. So, it is a serial process. It is a consequence of a process.

So, here to build a molecular weight, if I consider this same as H 2 O, case in last line in the last page, this k is 1. So, to build a x n of 100, the phenol concentration should be of 5.05 into 10 to the power minus 4 mol per liter to understand because the equilibrium consent of this reaction is roughly one to build a molecular having a degrees of polymers of 100. You have to bring down the phenol level in the system to such a low level, but as I said that sometimes, it is limited by the design of the reactor, it is not possible.

So, the chemical engineer will come to a chemist that you design a reaction by which you can increase the key. Now, how can you do that? What is the mechanism of the reaction? Mechanism of the reaction is that you have a base catalyst reaction, so you have this molecule addicting to this carbonate group nucleophilic attack and the reaction starts from there. So, how do you increase the reactivity of this reaction? Let us see one of the strategies in the next page.

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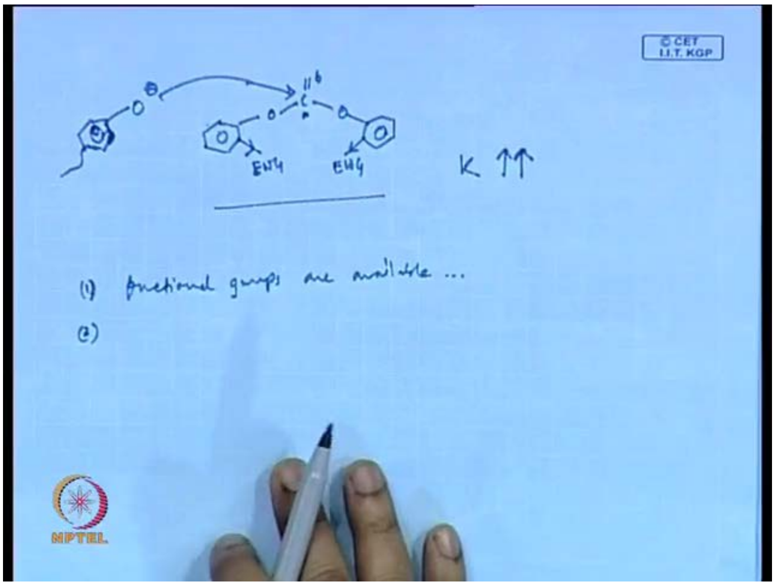

(1) functional groups are available ...

(2)

Now, if this is the lipophilic center, if we increase the electrophilicity of this carbon, then the attack of that phenolate coming from this phenolate group will be more feasible. So, equilibrium constant how it is achieved? If you increase photo electron withdrawing group, then the attack of this, the nucleophilic attack of this phenolate ion becomes much more feasible which will increase the k much higher compared to a di phenol carbonate, where there was no electron withdrawing group.

So, in this case, you can afford to keep this condensate at a much higher level compared to just phenol which we shown that that reaction equilibrium constant was 1. So, this one example where chemical engineers is restricted by the limitation of the reactor design, where the condensate can be taken out to a limited level, but still that will be not be sufficient to build up the molecular weight, enough molecular weight. So, in that case, chemist has to design the monomers such a way that the reaction, equilibrium reaction or equilibrium constant is higher. I just showed one example in this page.

Now, one thing you have to also remember is to build high molecular weight. You have to make sure of some other conditions. For example, you have to make sure that the functional groups are available during the entire reaction, so that some cases what happen you know these are exceptional case, where when you build a molecular weight after some size, it might feasibly turn the solution or from the melt of the reaction. So, you have to make sure that all the functional groups that mean all the monomeric species are the oligomeric species. They stay in the solution or in the reaction medium all the time during the reaction and here also, there are some exceptional cases that this equal reactivity or the functional group does not apply, but we are not talking about those cases in this course because they are exceptional cases and most of you know all those common reactions and the reactions we come across always follow this rule of a equal reactivity of the functional group.

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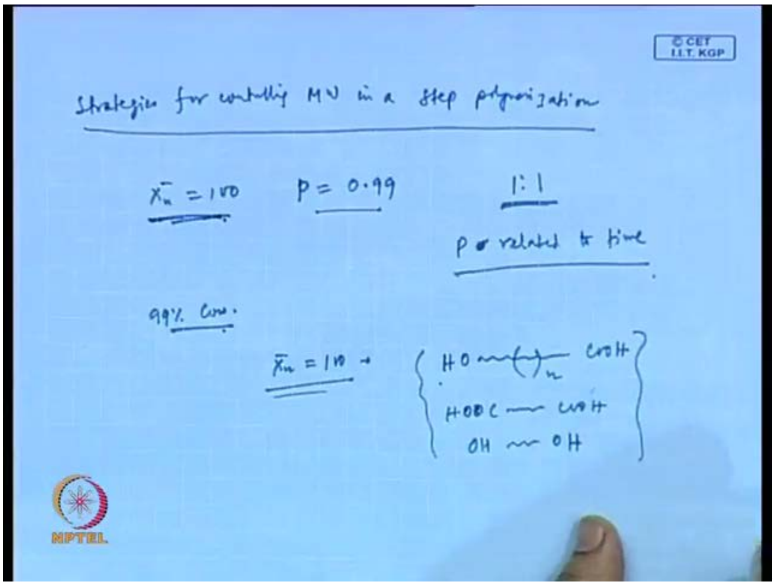

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Strategies for controlling MW in a step polymerization

$\bar{X}_n = 100$ $P = 0.99$ 1:1

P is related to time

99% conv.

$\bar{X}_n = 100$ → $\left\{ \begin{array}{l} HO \sim\sim (\;\;)_n \sim COOH \\ HOOC \sim\sim COOH \\ OH \sim\sim OH \end{array} \right\}$

So, we move to the next topic. How do you control the molecular weight? So, strategy is for controlling in a step polymerization. Now, why do we need to control a molecular weight of a step polymer? Now, if you see I am targeting a molecular weight of something which correspondence to an average degrees of polymerization of 100. Now, if we land up at the end of the reactions something higher than 100, then also problem. If we land up a number which is lower than 100, then also a problem. If it is lower than the polymer, it will not be serving our purpose and if it is higher, then it will pose a lot of other problems like taking the polymer and processing for the application will be difficult because the main viscosity of this polymer is higher. So, handling will be difficult. This is one example of the difficulties if you have higher molecular weight than the targeted one.

So, it is always desirable to have your reaction stopped or at the end of the reaction, you get whatever you target it for. So, you target for 100 is always desirable that at the end of the reaction, you should get an average degrees of polymerization of 100. Now, how do you do that? Now, we have seen that x n of 100 corresponds to a p of 0.99 in one is to one case, one is to isometric ratio of the functional group. So, you can say that if I stop the reaction and we have this reaction kinetics, how the p varies with time. We also know how p is related to time. We have seen in the previous pages. So, you can always say that if we stop the reaction, such a time which correspondence to a p of 0.99, then you will get a molecular weight corresponding to degrees of polymerization of 100. So, as simple as that.

Now, what is the problem in that if you stop reaction as a level of say, 0.99 or 90 percent conversion? What do we get in hand? So, if you are talking about a polyesterification reaction, what do you get at 99 percent conversion level? You get an average of 100 and what you have both the sides and you also may have some monomer present. So, at the level of 100 degrees of polymer, what do you have in this reaction medium? You have the hydroxyl acids which correspond to some size and you may also have, we will also have some unreacted monomers as well. So, you stop the reaction in this level. What you have? You have till the possibility of these molecules participating in the further reaction. So, when you take this polymer at this stage and mix with the other additives and fillers and do a compounding which is a further process which you do in a melt state, as I said in the first lecture, then these functional groups are free to react at there. So, they might do react and build molecular weight or they might bide in between and degrade the molecular weight.

So, if you stop your reaction to build a molecular weight or target a molecular rate of 100 degrees of polymers correspond to 100, if you stop the reaction at 99 percent conversion level starting from one is to one, so isometric ratio you get this, but this will pose lot of difficulties in the next step when you do processing steps like compounding or molding because this has presence of active functional group. So, this can react with each other or a polymer backbone and degrade the polymer or build the molecular. So, you know at the end of your molding step, the molecular weight might be different than what you target it for. So, your properties what you targeted will be different.

So, it is not advisable that you do a reaction and stop in between at the level what you target it for. So, how can we achieve that? What are the strategies we can achieve what we targeted one is to one of the monomers in excess?

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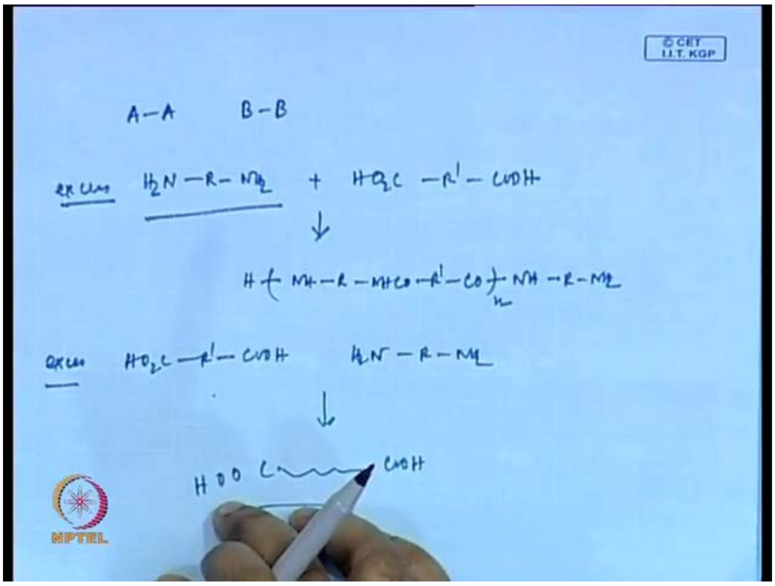

For example, say you have a monomer AA and BB. Now, take a concrete example of a polyamide formation. If I take this as excess, now this will react with this acid functionality as along they are present because they are present in a smaller amount. At the end, all these carbolic liquid will be consumed and you will land up a polymer or oligomer chain with both sides amine groups. So, you will land up something like this.

So, in this case, both sides are amine group. Now, this cannot react by themselves. So, if you stop the reaction in that level, you are ensuring that there is no left over swage group, carboxylic group in the medium, so that they cannot take the amines by itself, cannot take part in the reaction themselves. If I take the axis, the carboxylic group, what will land up in? You land up in something where both side are COH group, right? If you have excess, this diamine has an excess quantity, then we will land up in a polymeric or oligomeric chain, where both sides are capped with amine group. If you have excess di carboxylic acids, then you will land up in the polymeric or oligomeric chain have in di carboxylic acids. Carboxylic acids have both the ends which will ensure that this cannot react by themselves, so that your polymers are virtually dead.

Now, unless you have something in the reaction medium, further when you take these polymers out and do the compounding and molding step, unless you have something in your adding from outside which will be able to react with either of this left over functional group. Then, it will stay as it is. It will not react with the functional group present in the polymers formed itself.

So, that is one of the strategies of making or controlling the polymer. As we will see what is the quantification or how much excess we have to take to target a sudden molecular weight. We will come to that quantification level.

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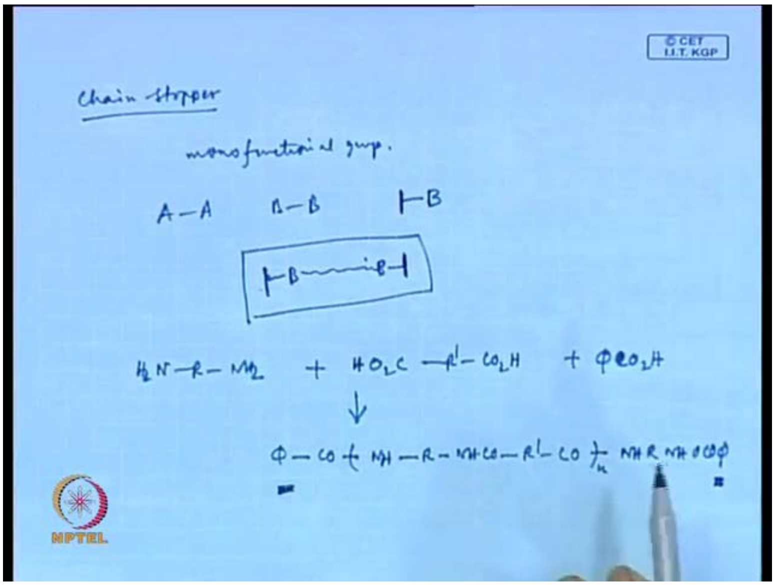

In next page, another strategy is to take chains topper. Chains topper molecules are molecules having mono functional group. So, instead of taking AA plus BB, you take just B in excess. Then, the chain in which the ends are capped with B, the other ends are dead. This is dead end. So, if you have some chain like this B with dead end here and again B with dead end here, then you are forming a chain which does not have a reactive group or either of the sides. That means this reaction this monomer cannot or this chain cannot take further reactions which will allow you to control the molecular rate.

Let us take example. If I take again go back to same polyamide formation. If I add a benzoic acid, you are going to get a molecule something like. So, this end does not have any reactive functional group. So, by this way, if you have all the chains are capped with a long functional entity, not reactive group, then will these molecules will not take part in further reactions. So, if you take this out, this polymer out and do further in a molding and compounding, go to the compounding step, then because these chains are capped with a known reactive group, they will not take part in further reaction which means the polymers are practically dead polymers.

So, your molecular weight has no change. So, whatever at the end of your processing steps, you will get the same polymer in the property which was related to the molecular weight, of your target molecular weight. So, you will get that same property, but in the first case, if you stop the reaction in between at some conversional level, then what happened in after step you go through the compounding and processing step. In the final article, final application, the molecular rate will vary from your target molecular rate. That means the properties also will vary.

So, it is advisable is always done in industrially. Also, it is done by either by taking one of the bi functional or poly functional monomers in excess or mono functional monomer which is termed as chains topper added externally, so that we can control the chain length you know target. Now, what is the, how we can relate to the amount of excess or amount of this mono functional chains topper? How does it is related with the target degrees of polymerization.

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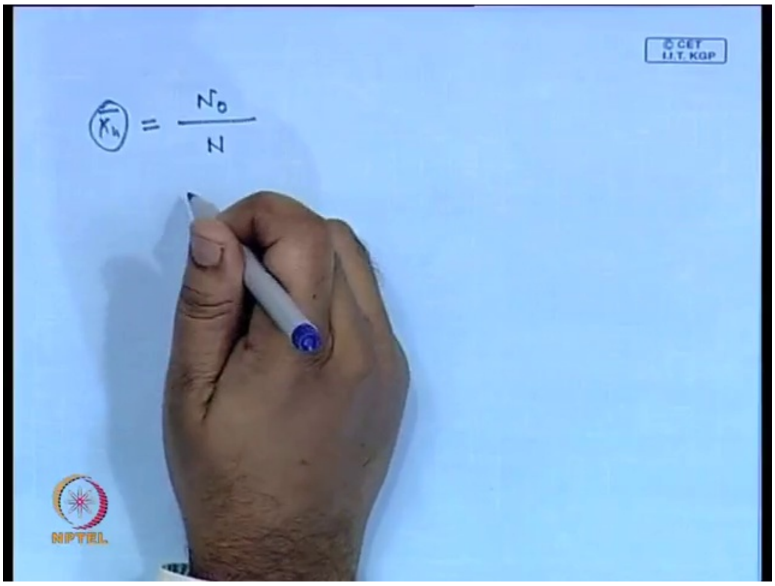

$$\bar{X}_n = \frac{N_0}{N}$$

We will come to the next class, next lecture, but in detail, but just before we go to that quantification, what was, how did we get the x n bar or any polymer mixture. Remember, it is the number of molecules at the beginning, and number of molecules at the end, which will give you the average degrees of polymerization. So, what will we do? We will take from this, from this and continue in the next lecture, the quantification. That means, we know that there are two strategies, we can follow taking one of the bi functional monomer in excess or we can add some amount of chains topper which are nothing but mono functional groups.

How much excess will I take? What is the relation between conversion and excess in the molecular weight? How much should I take, because if we take too much excess, then ultimately you will not land up in the target molecular weight, you know the molecular weights will be very, could be very low. So, you should know a priori what is the relation between a molecular weight and the ratio between the monomers by a function or if we add, what is the effect of molecular weight if we add some mono functional group from outside. We will come back in the next lecture with that.