Polymer Chemistry
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Lecture - 06
Step-growth Polymerization (Contd.)

Let us continue our discussion on step growth polymerization. Now, before we come to this lectures topic, let us just recapitulate what we have learnt in last lecture.

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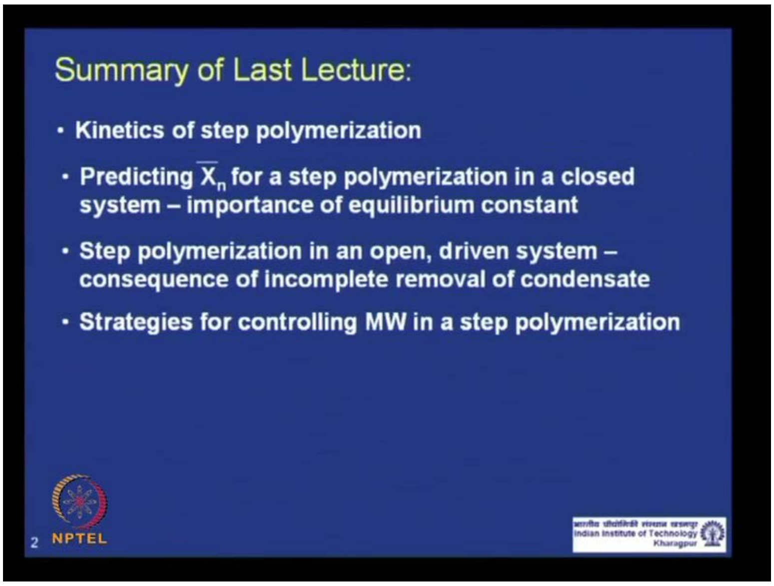

Summary of Last Lecture:

- 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 last lecture, we have completed the kinetics of step polymerization and we have seen what is after looking at the kinetic expression. We are convinced that in for polymer chemistry, this life is little difficult compared to organic chemistry. If we talk about the utility of conversion for an organic chemist which deals with the small molecules in 98 percent conversion may be good enough, but for a polymer chemist, 98 percent conversion might give you only a degree of polymerization of 50.

So, if you have to improve or increase their molecular weight, you have to take your reaction for longer and longer which makes it more difficult for a polymer chemist. We also in that kinetic polymerization proved the theory of equal reactivity of functional group. Then we went on and studied how the degrees of polymerization would vary with equilibrium constant in a closed system, and we found that the importance of equilibrium constant. In that case, if you want to build high molecular weight in a closed system without removing the condensate out of the polymerization medium, then your k value, the value of the equilibrium constant has to be quite high to build a descent enough molecular weight which is that is why, it is never practiced. The step polymerization is never practiced in a closed system is always done where you take out the condensate from the reaction medium and in continuation, we found that we understood that it is not always possible to take out 100 percent of the condensate which is produced, getting produced in the reaction.

So, we found the quantity of relations between the amount of condensate present at the end of the reaction with the degrees of polymerization in that along with its relational equilibrium constant, and we have seen that unless we have a quite high value of equilibrium constant, we have to go down the residual value of the condensate to a very low level to build a higher molecular weight. If we cannot take out the condensate from the reaction medium, such a way, such a high level, so that the residual level of the condensate in the polymerized medium is low, for whatever reason. Then we have to design the monomers such a way that the equilibrium constant is pushed up or the reactivity increases. In that case, we can afford to leave more amount of condensate molecules in the polymerization medium in order to build high enough molecular weight.

We also studied what are the strategies for controlling molecular weight in a step polymerization and two recommended strategies are either, one should use a slight excess of the one of the two bi-functional monomer or a slight amount of a chain stopper which is nothing but a mono-functional group.

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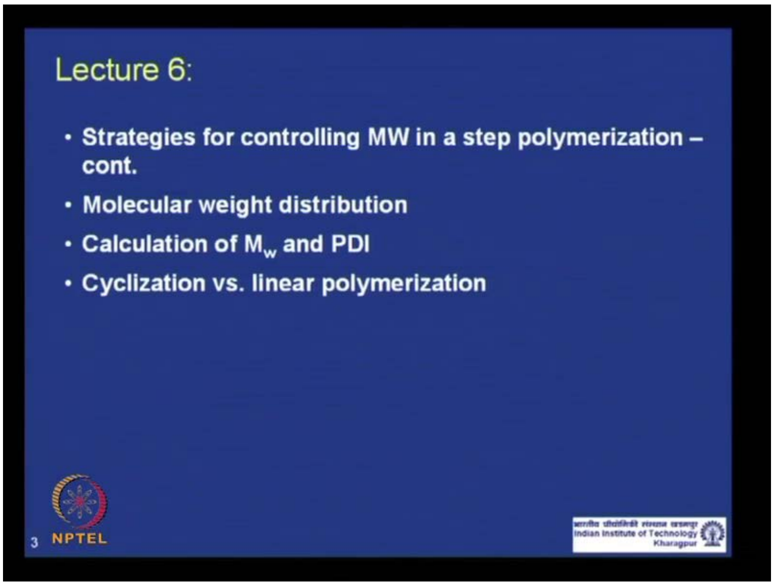

Lecture 6:

- Strategies for controlling MW in a step polymerization – cont.
- Molecular weight distribution
- Calculation of M_w and PDI
- Cyclization vs. linear polymerization

Now, what we planned to study in this lecture is continuation of the strategies and now, we in this lecture would quantify the relation. That means, how much excess we use, the term slight excess, so how much excess you should use for your target molecular weight or how much mono-functional monomer you should have for a target molecular weight. And then we also learnt molecular distribution among the chains which are formed in step polymerization, and then calculate MW and poly dispersed index and then at the end, we will compare between cyclization and linear polymerization. So, let us begin with where we left in the last lecture.

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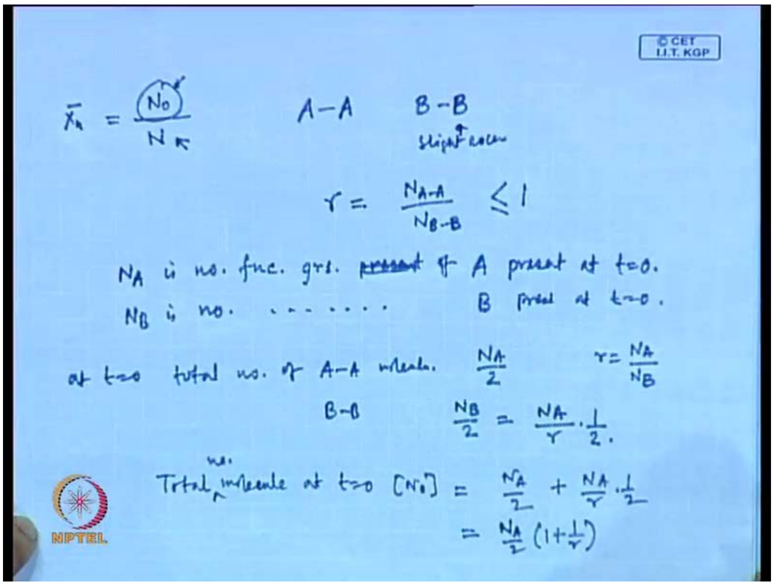

$\bar{X}_n = \frac{\boxed{N_0}}{N}$

A–A   B–B

slight excess

$r = \frac{N_{A-A}}{N_{B-B}} \leq 1$

N_A is no. func. grs. ~~present~~ of A present at t=0.

N_B is no. . . . . B present at t=0.

at t=0 total no. of A–A molecules. $\frac{N_A}{2}$ $r = \frac{N_A}{N_B}$

B–B $\frac{N_B}{2} = \frac{N_A}{r} \cdot \frac{1}{2}$.

Total no. molecule at t=0 $[N_0] = \frac{N_A}{2} + \frac{N_A}{r} \cdot \frac{1}{2}$

$= \frac{N_A}{2}\left(1 + \frac{1}{r}\right)$

Now, we know that degrees of polymerization, the first degrees of polymerization is given by the number of monomer group or functional groups at the beginning number of molecules at the beginning and by the number of groups at time t. Now, let us consider a case where we have this system AA and BB with slight excess of BBB. This is present in slight excess. So, define a ratio which is imbalanced ratio or which is the moles of AA number of BB. Now, r is defined in such a way that it is always less than equals to 1. It will never be more than 1. So, the monomer which is present, this should come as a denominator, so that r is always less than equals to 1.

So, what you need to find? The molecular weight or degrees of polymerization. We have to find N 0 and N. If N A is the number of functional group present at the beginning at t is equal to 0 and N B is a number of functional groups of B present at t is equal to 0, so what are the total number of a molecule at t is equal to 0? Total number of molecule is N A by 2 because each molecules has two functional groups and total number of BB molecules is given by N B by 2. Now, N B is r is N A by N B. So, N B is N A by r 1 over 2. So, total molecules at the beginning at t is equal to 0 or N 0 which is N 0 is N A by 2 number of AA molecules plus number of BB molecules N A bar r 1 by 2, which gives plus 1 by r. Clear? Now, we have to find out this. We know N 0. Now, we have to find out N which is the number of molecules at time t at some reaction if conversion is P.

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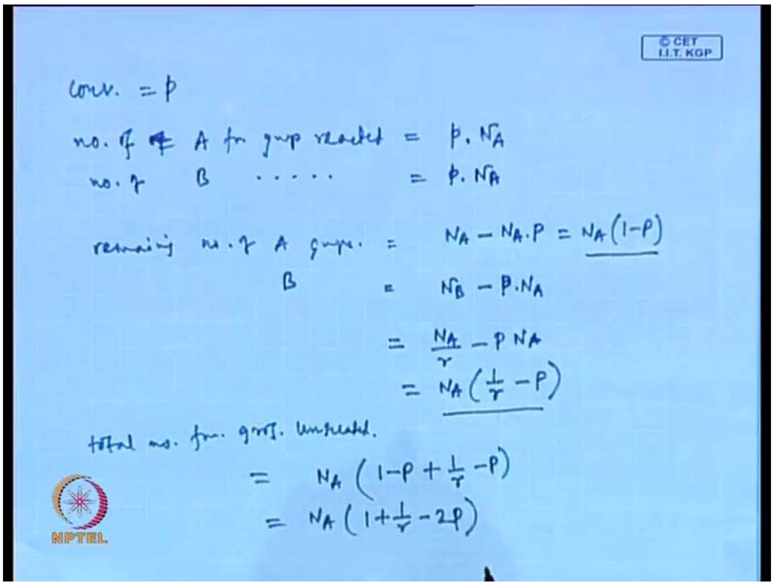

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conv. = p

no. of A fn grup reacted = $p . N_A$

no. of B ..... = $p . N_A$

remaining no. of A grps. = $N_A - N_A . P = \underline{N_A(1-P)}$

B = $N_B - P . N_A$

$= \frac{N_A}{r} - p N_A$

$= \underline{N_A\left(\frac{1}{r} - P\right)}$

total no. fn. grps. unreacted.

$= N_A\left(1 - P + \frac{1}{r} - P\right)$

$= N_A\left(1 + \frac{1}{r} - 2P\right)$

So, number of a molecules reacted a functional group reacted is P into N A. So, number of B group reacted again. Each A will react with one A will react with one B. So, number of BB group will react, will be same as number of A group. Is it clear? Because conversion is defined the fraction of functional group has reacted, in this case, A present in a small amount. So, we will consider AA number of A groups reacted is fraction in the total present, initially P into P multiplied by N A. Now, each A group will react with one B group. So, total number of B groups will react also this. So, how many of A is remaining? So, remaining number of A group is earlier what N A. Now, it is N A into P. It gives N A 1 minus P. How many B groups remaining? Earlier was N B minus P N A. Again, N B is N A by r P N A which gives us N A 1 by r minus P. So, this is the number of A groups remaining and this is the number of BB group, B group remaining. So, total number of functional groups remaining unreacted is sum of these two.

So, total number of functional groups unreacted is summation of these two. I can take both together 1 minus P plus 1 r minus P gives us N A 1 plus 1 by r minus 2 P. Now, each of these are the number of functional groups unreacted. So, how many molecules will be unreacted left over? Each molecule has two functional groups at two ends. So, how many of number of groups, number of molecules present now?

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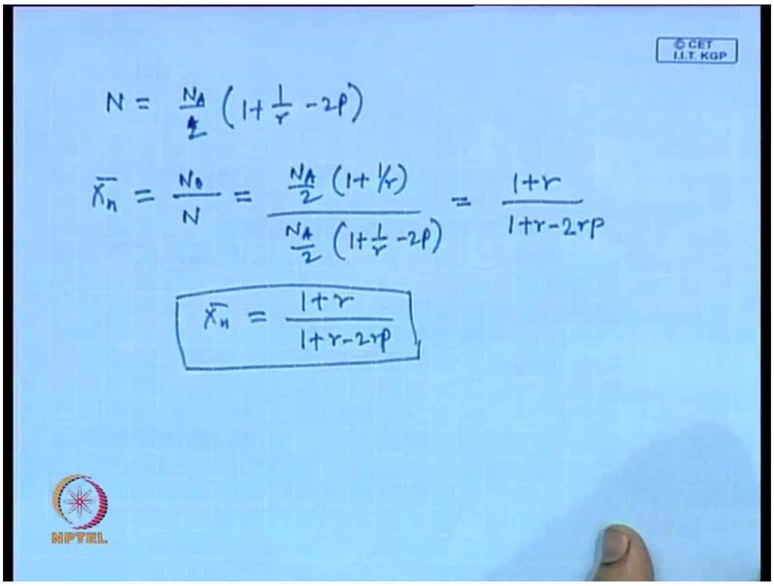

$$N = \frac{N_A}{2}\left(1+\frac{1}{r}-2p\right)$$

$$\bar{X}_n = \frac{N_0}{N} = \frac{\frac{N_A}{2}\left(1+1/r\right)}{\frac{N_A}{2}\left(1+\frac{1}{r}-2p\right)} = \frac{1+r}{1+r-2rp}$$

$$\boxed{\bar{X}_n = \frac{1+r}{1+r-2rp}}$$

So, N which is the number of molecules left over, each molecules which is left over now in the polymerization medium which have two functional groups. So, if you divide the total number of functional groups unreacted by 2, it will give you the number of molecules left. So, N is N A by 2, 1 plus 1 by r minus 2 p. So, x n bar is N 0 by N, which means N A by 2 1 plus 1 by r divided by N A by 2, 1 plus 1 r minus 2 P which leads to 1 plus r 1 plus r minus 2 r P.

So, that is the expression which relates the number of average molecular weight with r, which is ratio of the moles of two bi-functional monomers present in the system at the beginning, where r is defined such a way that it is always less than equals to 1 and P is the conversion which is defined as the fraction of the functional groups which is present in a smaller quantity as reacted. If in this case, A is the functional group present in a smaller quantity, the fraction of a group which has reacted is defined as the conversion. Now, if I plot this, how does it look?

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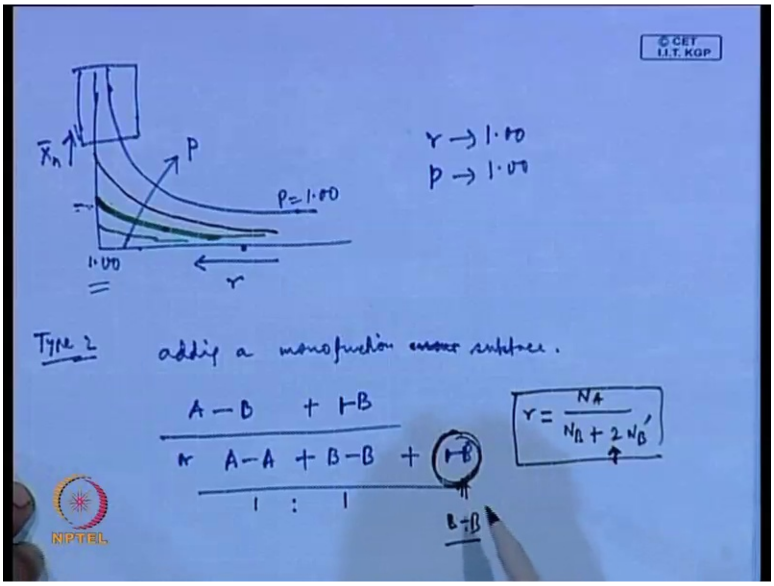

So, it will look something like this, where this is the direction of PP is 1 in this case, and the other curves are for lower P which means for a given r, you take any of the r here. As you increase P, molecular weight goes up which is expected and for a given P for any of this, if you consider any of this curve. As you increase r, if you go close to tri-symmetric, you will increase the molecular weight.

So, the ideal scenario of working is somewhere here, where your r is close to 1 and P is close to 1. That will give you the highest molecular you can achieve. If in any of these two factors, if r is somewhere here, then the matter what is a conversion level? You cannot reach high molecular weight. It will stop here same as if your P is low. So, like this curve, no matter what is your r, you can only reach up to this level.

So, to A for a successful step polymerization, successful by mean in A by successful, I mean to build a high molecular at you have to have a condition, where r is also close to 1. So, as P is 1, if you have some molecular weight in target, you can use this formula and you can complete the reaction in such a way, now r is the ratio of the functional group of the two bi-functional monomers. So, you need to know the concentration of each monomers very well.

Now, how do you know? You can only know the concentration of each other, the moles of each of the monomers and the functional groups if they are pure enough. If there are impurities present in your monomers, then you do not know, you are not sure what is the actual mole fraction or mole of the functional groups which restricts that you must have very pure monomer in order to get a successful step polymers and also at the same time, your reactor should be high enough, so that you can take out your condensate such extreme that you can push your conversion up to P. Now, sometimes it is difficult to quantify the P where you cannot take out the halicut giving the reaction and determine the functional group present. So, by which you can determine the conversion.

So, what is typically done? You do your reaction best possible way and that is your limitation. So, that is the maximum you can go and if your reactions system is good, your reactor is good, your vacuum system is good. Then you can hope that you will be, your P would be close to 1. Then you can control your molecular weight and you can target your molecular weight by adjusting the ratio between two monomer or the fixing the value of r.

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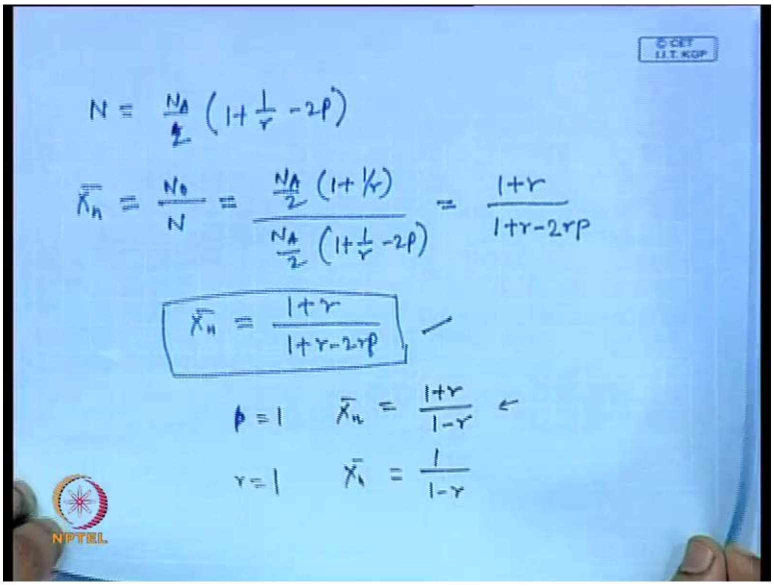

$$N = \frac{N_A}{2}\left(1+\frac{1}{r}-2p\right)$$

$$\bar{X}_n = \frac{N_0}{N} = \frac{\frac{N_A}{2}(1+1/r)}{\frac{N_A}{2}\left(1+\frac{1}{r}-2p\right)} = \frac{1+r}{1+r-2rp}$$

$$\boxed{\bar{X}_n = \frac{1+r}{1+r-2rp}} \checkmark$$

$$p=1 \quad \bar{X}_n = \frac{1+r}{1-r} \leftarrow$$

$$r=1 \quad \bar{X}_n = \frac{1}{1-r}$$

If you consider P as 1, if you make your P is 1, then x n would be 1 plus r, 1 minus r. This is typically done. You do your reaction best possible way as best you can do and hope that P is close to 1 and you can choose r in at the beginning, so that you can target x n accordingly and there is another case when r is 1 x n would give us back the original (( )) equation where we started with one is to one ratio of the two functional, two bi-functional groups. Now, there is a second strategy we discussed. Type 2 that was earlier was type 1. Type 2 where we said that we can control the molecular weight by adding a mono-functional group, mono-functional compound or monomer substance whatever.

Now, let us take A, as situation where we have saved AAAA B type molecules lose some excess B or a AA type BB type plus some excess B. You can use the expression which we will get it for the simple, any of this simple scenario where you have B or AA BB. One is to one plus these things plus some mono-functional monomer which is chain stopper. In that case also, you can use the same expression which we got in the last page. In that case also, you can use the same expression. Only difference is that in this case, r is defined as N A plus N B plus 2 N B dash. The same expression can be used for this scenario as well. What is scenario where you have either A or D or 1 is to 1 A B plus some excess d. In this case, the dash is the mole fact, number of moles of the molecular mono-functional group having B. You might question what is the origin of these two? That is because this has same effect as excess BB. These are same effect of a x is presence of a excess bi-functional monomer to equate these two is added compensate this.

So, now, with this formula, you can use, you can target a molecular weight. You can start with a one is to one A and B. These two monomers, A and B and then add slight amount of this mono functional group and target a certain molecular weight using this expression, where r is defined as this. What is the advantage of this mono functional group? If you remember, in this case using mono-functional group, the insert cap with non-functional group and when you use the other strategy, the type one where you have one of the groups excess is still has virtually date polymers, but there you have functional, same functional group present in both the sides.

When you use first strategy, you have same functional group present in both the sides, so that they do not interrupt with each other, react with each other, but you still have functional groups. So, in case there is in future, when you take this polymer for other reaction, if there are any impurities unlikely present which might react with this functional group, you might land up in a problem scenario whereas if you have a mono-functional (( )) or chain stopper, the insert cap with non-functional group. So, it will not react. That is only the advantage in this case, but in this advantage, you have two, have an extra molecule in the reaction. We will move to the next topic of molecular weight distribution.

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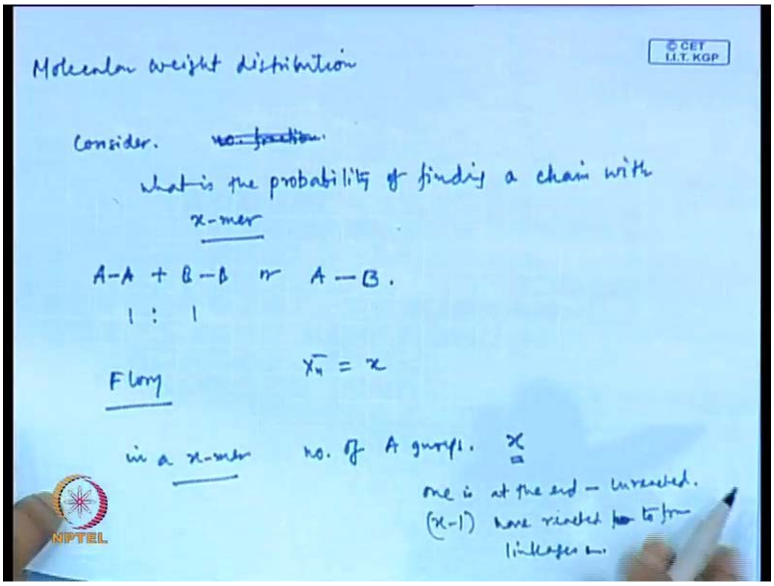

Molecular weight distribution

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Consider. ~~no. fraction.~~

what is the probability of finding a chain with x-mer

$A-A + B-B$ or $A-B$.

$1 : 1$

$\bar{X_n} = x$

Flory

in a x-mer no. of A groups. x

one is at the end – unreacted.

$(x-1)$ have reacted to form linkages

Now, you know that the product of a polymerization is a mixture of different chain links. So, in any polymerization reaction, you at the end of the reaction, you have a distribution which content similar molecular. Now, in the step molecular, how the distribution looks? We will try to get some information, some prediction from statistics. See whether we can estimate, we can predict what would be the molecular with distribution, both numbers average and weight average, weight fraction and distribution of the molecules present.

Now, let us, we have to consider or we have to find what the number of fraction is or say probability of finding a chain with x mar x structure units. If we can find the probability of all x or x mar, then we can surely get the distribution. So, to generalize, let us try to find what the probability of finding a chain in the reaction medium with the x bar is. Now, you consider a reaction of A plus BB type or say AB type and consider this is present in one is to one. This following statistics was first done by Flory. So, this distribution will guess is known as Flory distribution.

Now, how do you get this probability in x bar? X bar means x n is x x bar. If a chain which has x number of structure units which means, this is a polymer of this x. Now, how many molecules are there in x mar? In x mar, the number of groups, a structure, x structure, also number of groups will be x. X is the number of structure units. So, number of a group will be also x. Now, out of this x number of a groups, one is at the end unreacted, and x minus 1 have reacted to form linkages. See, if x mar at a, which one is the end which is free and x minus 1 is the number of a functional group as which is reacted. Now, what is the probability of finding one free A group?

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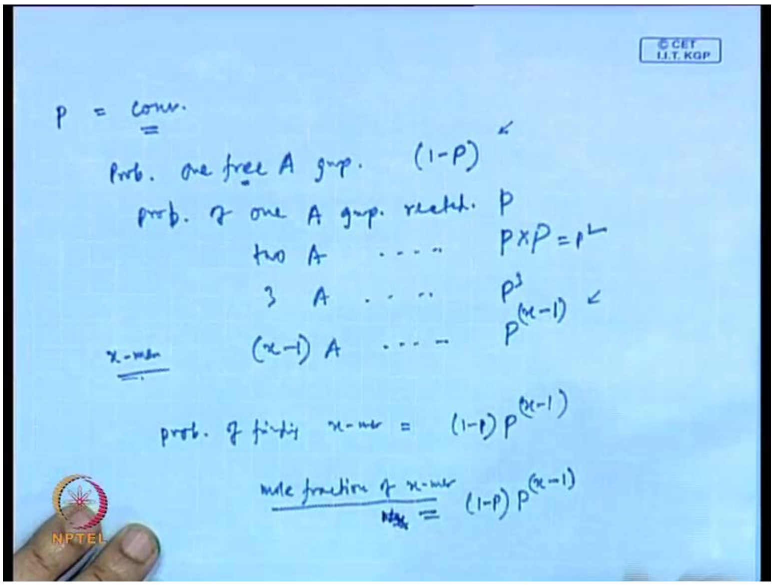

P = conv.

Prob. one free A grp. $(1-P)$

prob. of one A grp. reacted. P

two A .... $P \times P = P^2$

3 A .... P^3

x-mer $(x-1)$ A .... $P^{(x-1)}$

prob. of finding x-mer = $(1-P)\,P^{(x-1)}$

mole fraction of x-mer $N_x = (1-P)\,P^{(x-1)}$

If P is the conversion probability of one free A group is 1 minus P, means unreacted probability of one free A group. Reacted is P and P is the conversion. So, what is the property of two A group? Reactant P into P or P square. 3 A group reactant is P cube. So, in x mar, we have x minus 1 A group which is reactant. So, in x minus 1 x mar, a probability of x minus 1 A group reacted is P to the power x minus 1. So, in case of x mar which has one free one, free A group and x minus 1 A group which is reacted to probability of finding such x mar is given by 1 minus P. The product of these two probability is x minus 1. Now, what does it mean? The probability of finding a chain which has x structural unit which is nothing but the mole fraction, mole on number fraction of x mar which is say, N x 1 by P P to the power x minus 1. This is your mole fraction.

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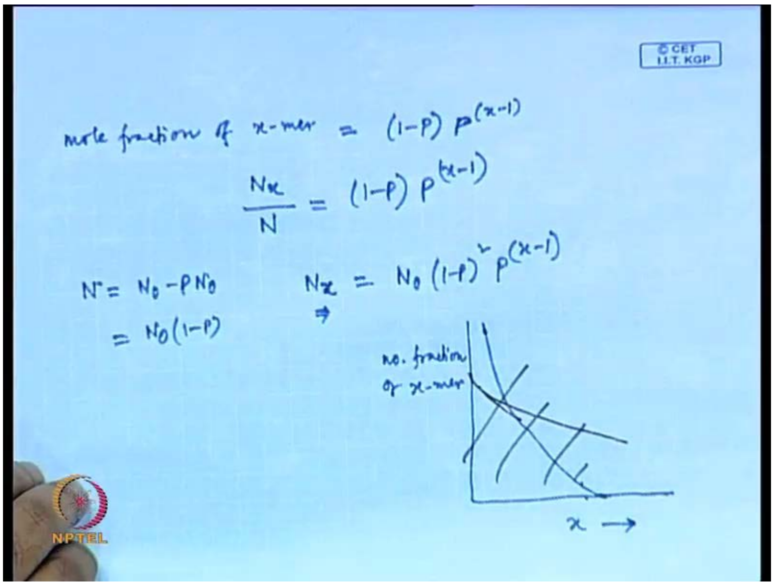

mole fraction of x-mer $= (1-P)\,P^{(x-1)}$

$$\frac{N_x}{N} = (1-P)\,P^{(x-1)}$$

$$N = N_0 - PN_0 = N_0(1-P)$$

$$\Rightarrow \quad N_x = N_0\,(1-P)^2\,P^{(x-1)}$$

So, again I write mole fraction of x mar is given by 1 minus P P to the power x minus 1. Now, what is this mole fraction? It is the number of molecules having in mar. So, N x is the number of molecules having in x mar in x structural units by total number of molecules present in that time is 1 minus P, so P to the power x minus 1. Now, what is N? N is the total number of molecules present at time t, which is given by the total number of molecule minus PN 0 has earlier, so N 0 1 minus P, where N 0 the number of monomers in the beginning.

So, N x will be given by N 0, 1 minus P square, P x minus 1. So, this is the number of molecules present which have x mar in x number of x mar, which means number of molecules or changes present at any time having x number of structural units. How does it look? This distribution let us draw it again in next page. This is of the order of p.

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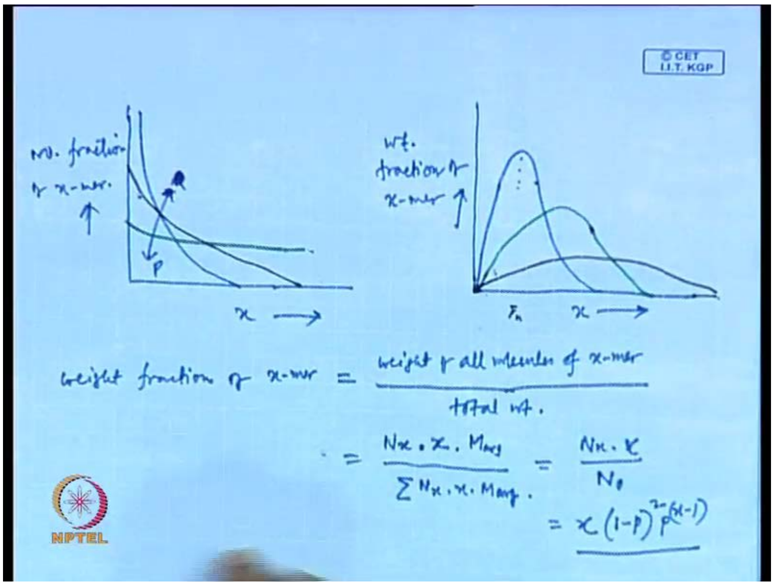

$$\text{weight fraction of } x\text{-mer} = \frac{\text{weight of all molecules of } x\text{-mer}}{\text{total wt.}}$$

$$= \frac{N_x \cdot x \cdot M_o}{\sum N_x \cdot x \cdot M_o} = \frac{N_x \cdot x}{N_0}$$

$$= \underline{x(1-p)^2 p^{(x-1)}}$$

So, if this is the duration of P which means at lower, this is the lowest P, this is the intermediate P and this is the highest P which means that at the lowest P, your polymer mixture has maximum number of molecules having low x. That means, low number of consol group, it has intermediate conversion. In that case also, the maximum number of group present or maximum number of molecules present is the molecules having lower number of structural units in the chain.

If we increase the conversion further, then also the maximum of the number of chains having small number of functional groups, small number of structural units and maximum, but this difference comes down as we increase p. So, what does it mean is that in any case of state polymerization, in any point of time whether you say small conversion or high conversion, what is the number of molecules which is present in maximum are the monomers because mono mass has the least number of structure units. Look at the distribution, the maximum mean on the left hand side which is the minimum of x. That means these are the monomers.

So, at any conversion region, whether it is a small low conversion, low conversion, medium conversion or high conversion, the reaction medium will have in number, fraction in number, not the width in number wise maximum number of monomer present. Now, the number of monomers will decrease as the conversion goes up, but even at very high concentration, there are significant numbers of monomers present in the reaction.

So, if you take a monomer, a polymerization mixture, the end of the things maximum number will be present at the monomers, then dinomers, then trinomers and so on. So, the real polymers would be in the smallest number present in the reaction medium in case of numbers, but the numbers are not always very significant. Weights are more significant than numbers.

So, how we will look at, how the weight fraction is distributed? How the weight fraction of this individual chain varies with x, which is the number of monomer present? So, weight fraction of x mar is the weight of all molecules of x mar divided by total weight of the mixture, if N x is the number of molecules having x structural units. So, N x is the number multiplied by x which is the number of structural unit present in one molecule. X is the number of molecule number of structural unit present in one molecule and n x is the number of such molecules. So, total in N x in x and in average is the molecular width of the structural units. So, this is the molecular structural units, this is the number of structural unit present in one chain and this is the number of such ends and you can sum total with it and sum up all such x mar, so all (( )) of x.

So, we can get in x by x N x total. This summation for all x s should give you N 0 total numbers of molecule and N x by N 0. We have seen earlier, we can put that value and we can get this expression. So, that is your weight fraction. So, weight fraction is given by this number, this expression whereas, number of fraction was given by this was N 0 here how a plot will look like if a plot here.

So, weight fraction of x mar, it will be something like this. This is the plot, the weight fraction as you can see from this distribution. Unlike in case of number of fraction, you have always the maximum number was the lowest x, the chains having lowest x and one more being the least x 1 x. In this case, there is distribution with the maximum. There is maximum and this maximum around comes above the x in bar number of average. This x is where the maximum comes. It is above the x in bar and this is again with increasing P. So, this is the least P and this is your intermediate P and this is your highest P.

So, as I expected with increasing P, you have x also increases, molecular poly molecular also increases, but if you plot with fraction, you can see this is not the monomer features. These are the timer dimer which is present in maximum number. What is present in maximum, it corresponds to the polymer chain which is having average degrees of polymers.

So, the weight, if you take all the chains and plot the weight fraction in five maximum, where x is equals to or (( )) to the average degrees of polymerization. When I increase number, if we talk about number fraction, it is the lower monomer, dimmer or trimmer. They are presenting the maximum number, but its weight reach matters most, not the number in terms of polymer property is. Their weight could be more because monomers, dimmers presents in not significantly contribute any polymer properties in the weight which will contribute more in terms of polymer properties. See if you want to get the M M bar and number wise molecular weight and weight of molecular form, this distribution, you will get it. We know the width number of fraction and weight fraction.

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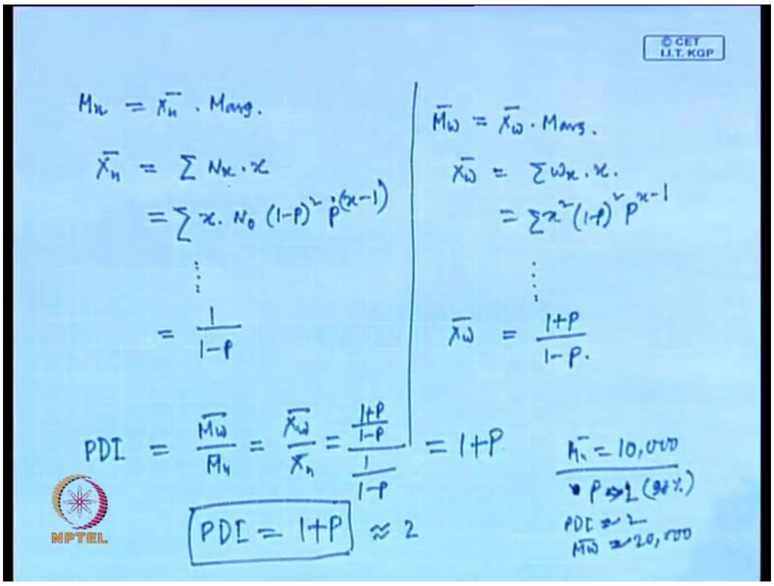

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$$M_n = \bar{X}_n \cdot M_{avg}.$$

$$\bar{X}_n = \sum N_x \cdot x$$

$$= \sum x \cdot N_0 (1-P)^2 P^{(x-1)}$$

$$\vdots$$

$$= \frac{1}{1-P}$$

$$\bar{M}_w = \bar{X}_w \cdot M_{avg}.$$

$$\bar{X}_w = \sum w_x \cdot x.$$

$$= \sum x^2 (1-P)^2 P^{x-1}$$

$$\vdots$$

$$\bar{X}_w = \frac{1+P}{1-P}.$$

$$\text{PDI} = \frac{\bar{M}_w}{\bar{M}_n} = \frac{\bar{X}_w}{\bar{X}_n} = \frac{\frac{1+P}{1-P}}{\frac{1}{1-P}} = 1+P$$

$$\boxed{\text{PDI} = 1+P} \approx 2$$

$\bar{M}_n = 10{,}000$

$P \to 1$ (99%)

PDI ≈ 2

$\bar{M}_w \approx 20{,}000$

We also know the expression of M n and M w M n. We know X n bar multiplied by average molecular of the structural units and X n bar is mole fraction multiplied by the number multiplied by the number which is given by X n 0 1 minus P square P to the power of x minus 1 sum over x, and if you do this math, you will land up 1 minus 1 minus P M w is X w bar m average X w bar is weight fraction multiplied. There is number of fraction. It is weight fraction. So, u X is square 1 minus P square P X minus 1 and if you solve this, you will get, we get X bar is 1 plus P 1 minus P. What is the (())

process index which is given by M w bar by M n bar, same as X w bar X n bar is 1 plus P 1 minus P divided by 1, 1 minus P which is given by 1 plus P. So, PDI is 1 plus P.

For step polymerization, this is very important because it will end up in most cases, PDI is 2. Why is it? So, as we have seen, I understood in last lectures, previous lectures that to make a high enough molecular weight which is useful for application P as to be very close to 1. If P is close to 1, PDI is almost in every case is close to 2. So, you cannot make a step polymerization of high molecular weight, where PDI is narrow. 1, 1.2, 1.3 that is not possible because do you remember what he have told that to make a high enough molecular width, you have to be having r is equal to 1 close to 1. So, as P is close to 1, if your half P to a lower level than no matter what is your r, no matter what is r, whether r is 1, still you get lower molecular widths.

So, if you have higher molecular width polymer, nobody can claim that he does not have narrow, very narrow distribution of 1.2, 1.3, 1.5. That is not possible. Whenever you make high molecular width by step polymerization, you are going to get poly dispersity of closed to 2. So, without knowing both the molecular wise M n bar M n, if you know only of them and you have given the structures, one structure, if know that this is made by step polymerization, if you are given only one of them. See if you have given M n has 10000 and a polymer is supplied to you, given you know the structure and from the structure you know that this is made by step polymers, then you even is 10000. This means you know also P which is close to 1. See in these cases say, 90 percentage or something and you also know PBI which is close to 2.

So, you know M w bar is close to 20000. So, from the single data of M n and the structure, you know all others P is close to 1. In this case, exactly is 98 percent, but for all purpose, we can consider P is 1 and PDI is close to 2 and MD is close to 20000.

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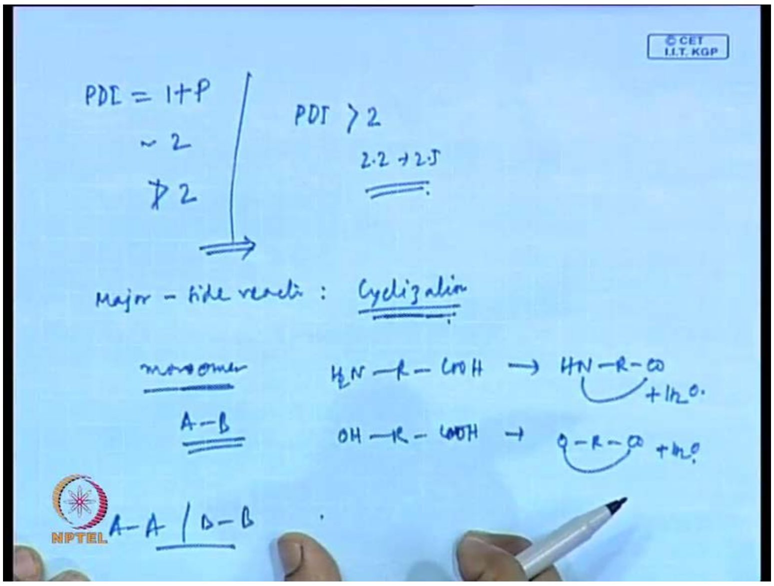

So, this should be clear now. We have seen in last page that PDI is 1 plus P which is always close to 2, or if the molecular weight is lower, it would be less than 2. It can never be more than 2 because P cannot be more than 1. Anytime, at any point, P cannot be more than 1. So, P is very close to 2, at most if your polymer molecular is low, it can be little lower than 2. It can never be more than 2. For in practice, most of the industrial polymers at the end of the polymers, if you measure the molecular weight distribution, you find, no it is found that PDI is slightly more than 2, not much say, 2.2, 2.5, something like that. So, theoretically, we have seen that it can never be 2 or more than 2, but in practice, we find that after end of the polymerization reaction, if you do explanatory finally what is polymerization distribution, you find that it is slightly over 2.

So, how this is possible? It can only be possible if there are side reactions which are producing smaller molecules in excess. Now, if any distributions have more smaller molecules than expected M w and M n, both will come down and as you know that smaller molecules effect more than M n than M w. So, drop the percentage, drop in M n because of presence of non-polymeric small molecules, the effect of M n will be more than M w

So, M n will be dropping more compared to M w. So, your PDI will go down. That means, it will be more broader. How can, what are the types of side reactions? We have one major side reaction is which is present in most of the polymerization step.

Polymerization side reaction is cyclization. Now, you understood why we are bringing this concept of cyclization.

As you have seen that most, as I said that most of the case, PDI of polymer after the reaction found to be little lower to in practice. That means, they are side product which are small molecular in nature which affect M M mode than M w, which means the N w by M n goes up. So, PDI goes up little lower. Now, how can cyclization product if you consider molecules, they are both functional in both the sides. So, if they can react inter molecularly and make a cyclic product, so if you talk about amino acid, it can form a cyclic product plus H 2 O.

If you have hydroxy acid, then it can form a cyclic product like the monomer. These are the intra molecular reactions in the monomers of AB type. If you have monomers like AA type or BB type, then you have the intra molecular reaction cyclization in monomers. It is not possible because both the sides, you have a di acid, di caboxly acid, both the side you have a two carboxyl acid or di-hydroxyl compound and both the side, two hydroxyl acid group. So, monomers, they cannot cyclize intra molecularly, but cannot they cyclize at all. They can in a (()) because in a (()), they have two defined functional group at both the sides. So, we are talking about reaction between di hydroxyl and di di-hydroxyl compound and Indus intermediare stages. Then you have hydroxy acids or hydroxy amine and then they can intra molecularly react and cyclize.

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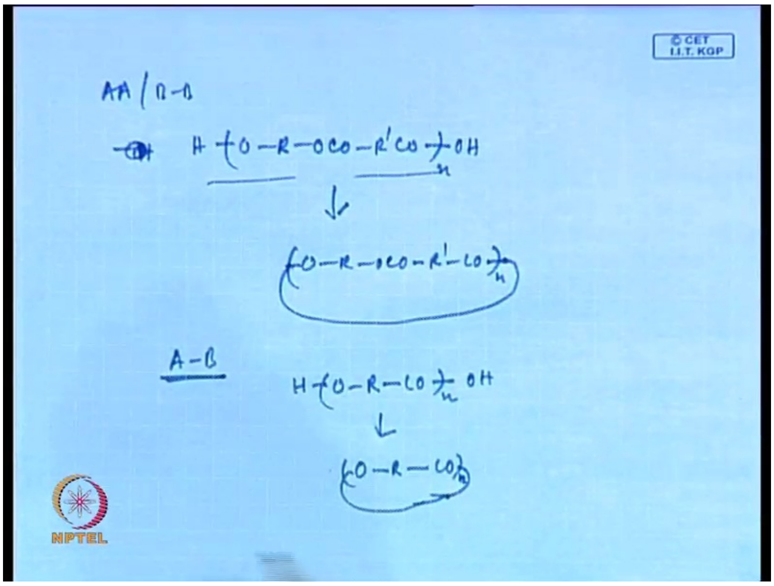

Let us see some example, generic example. See AA BB type structure, this can cyclize to give like this. Even in case of AB type of monomer also, you can also have cyclization at an intermediate step. So, these are showing the possibilities of cyclization.

If you have AB type monomers, then in monomeric stage also, it can intra molecularly cyclize. If you have BA or BB type monomer, it can only cyclize at (()) stage. Now, what is the tendency of a monomer to cyclize, participate in cyclization reaction compared to a linear reaction? If you have intermediate molecule like this, it can take part in a intra molecular cyclization reaction or it can also as usual, what you just learnt all the time, it can take out linear reactions to make high molecular polymer. Now, it is desirable fast, it is desirable that this take part in linear polymers and not in cyclization. If its cyclic form cycles, then it will form low molecular. It will come out from the reaction and those will contribute to the lower molecular fraction, and to increase your poly dispersity, you cannot avoid the cyclic formation. They are always present in the cyclic formation. That is the reason why your poly dispersity goes up little over because you cannot avoid completely. Formation of cyclic in a step polymerization is always present in little amount, so that its contribution to your PDI to be little lower.

Now, what is the comparison? If you compare a cyclization process and the linear polymerization process, what are the tendencies?

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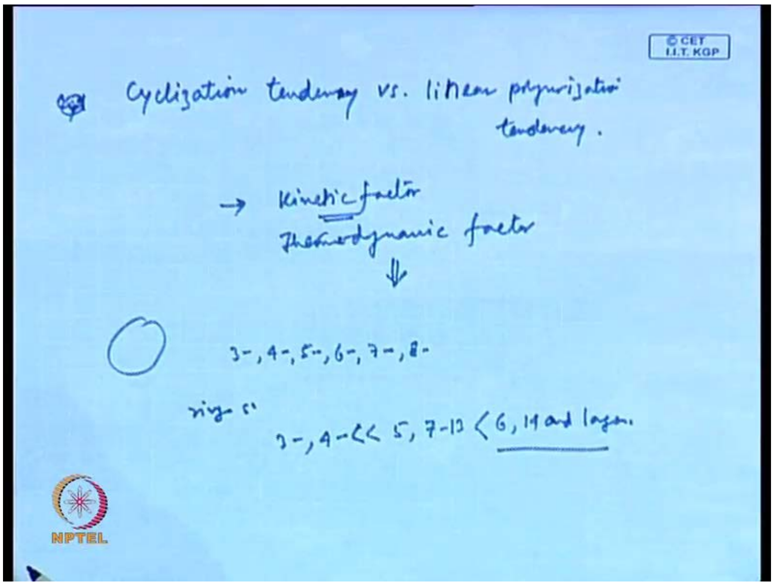

Cyclization tendency vs. linear polymerization tendency.

→ Kinetic factor
Thermodynamic factor
⇓

3-, 4-, 5-, 6-, 7-, 8-

ring size

3-, 4- << 5, 7-13 < 6, 14 and larger.

Now, if I compare between cyclization tendency verses linear polymerization tendency, now this depends upon both kinetic factor as well as thermodynamic factor. Thermodynamic factor comes from the stability of the ring size. Now, when they form cyclic, when this form cyclic, it is always forming a ring and the size of the ring determine whether it will form in thermodynamically, it will form the formation or not. Now, you know for organic chemistry knowledge, what is the stability of differing, what is the strain? If I go from a ring size to 3 to 4, strain comes down. Then 5 and again strain comes down. 6 is the least. If I go up again from 7 member ring, again it goes up 8, the strain goes up and then again it starts up to 13. It goes up and for instance after 13, it comes down in strain.

So, if you have ring stability order, then you have 3 member rings, 4 member ring. So, if you talk about the compare ring size, then 6, 14 and larger are the more stable rings. Then the 5 and 5 ring size within 7 to 13 and the least stable is the 3 to 4 ring size. This is applicable for methylene groups and also, this ether are the backbone, the cycling and ether other carboxylic groups, carbonic groups.

Now, what will be discussion in the next class is take this forward, this ring size and we know that what the thermilyn factor is. The ring size determines the stability, and of course guide the tendency of your formation. We will talk about kinetic factor in next class, in next lecture and then compare between what are the factors we should take care to reduce the cyclic formation as desire that this should have minimum amount of the cyclic in the polymer mixture, but as I said that we cannot have word cyclic formation.

So, that is the reason why you always get a (( )) a little lower to... So, we will come back and start with and repeat this thermionic factor and a little bit, and then start the kinetic factor, and also talk about reaction conditions which defers the cyclic formation which is responsible for cyclic formation. See you.