Introduction to Polymer Science
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Lecture - 07
Linear Step Polymerization: MW Control, MW Distribution, kinetics

Welcome back. In this lecture, we will talk about linear step polymerization and continue the discussion on molecular weight control and talk about molecular weight distribution, polymerization kinetics of linear step polymerization.

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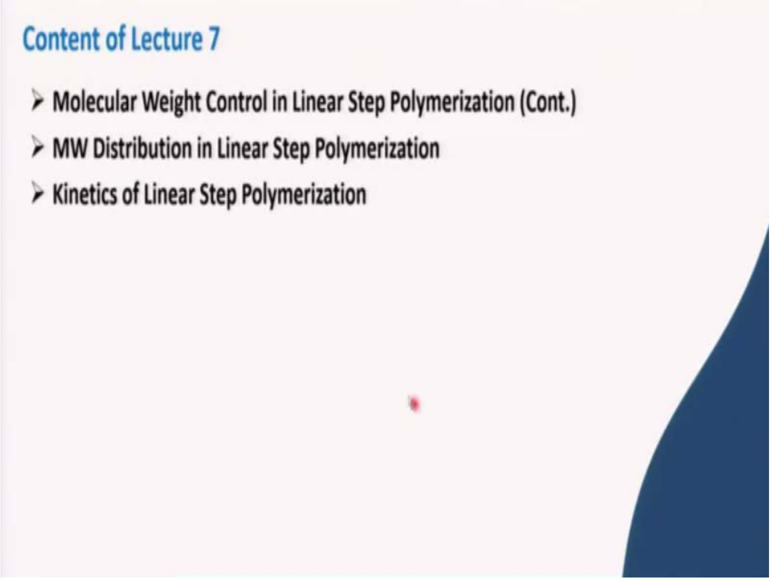

Content of Lecture 7

- Molecular Weight Control in Linear Step Polymerization (Cont.)
- MW Distribution in Linear Step Polymerization
- Kinetics of Linear Step Polymerization

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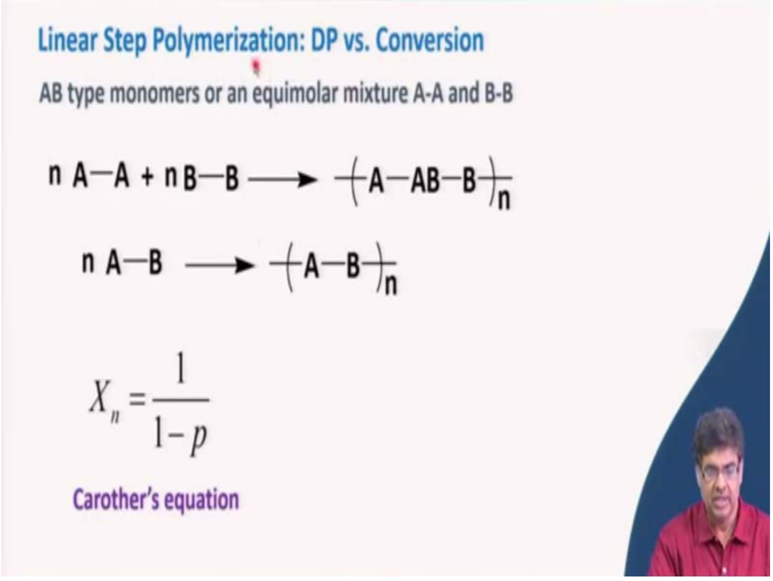

Linear Step Polymerization: DP vs. Conversion

AB type monomers or an equimolar mixture A-A and B-B

$$n\,A{-}A + n\,B{-}B \longrightarrow \left(A{-}AB{-}B \right)_n$$

$$n\,A{-}B \longrightarrow \left(A{-}B \right)_n$$

$$X_n = \frac{1}{1-p}$$

Carother's equation

Now, in the last lecture, we discussed how we could control the molecular weight with conversion or how the degree of polymerization is related to conversion. We started with a simple system where either we have taken an AB-type monomer, where the molar ratio of two functional groups are always 1: 1, or we have taken two monomers of AA type and BB type. We have taken this in an equimolar mixture. In that case, we have found that the degree of polymerization is related to the conversion by this equation.

$$X_n = \frac{N_0}{N} = \frac{1}{1-P}$$

And we call that equation Carother's equation. Now, we also said that controlling polymer molecular weight by controlling this conversion is not recommended because, then at the end of the polymerization, we are always left with the functional groups present at the end of the polymer chain, which can further react with themselves so that during processing we might get instability in molecular weights.

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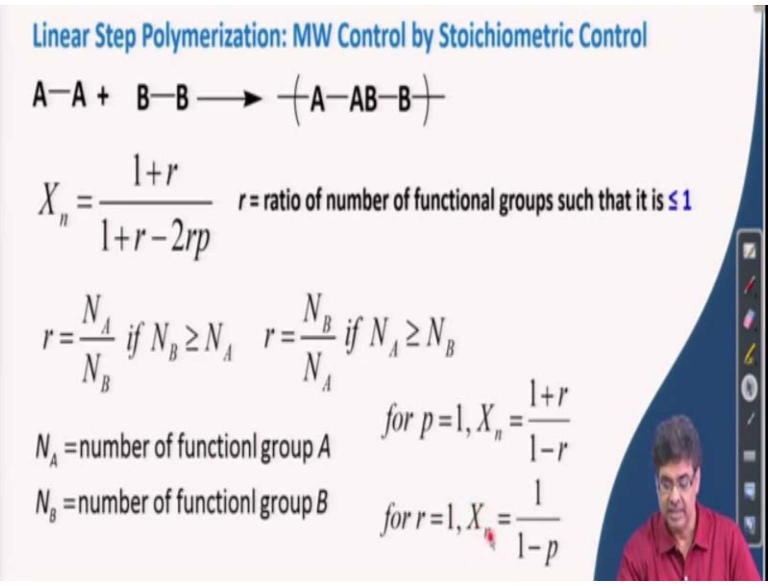

Linear Step Polymerization: MW Control by Stoichiometric Control

$$A{-}A + B{-}B \longrightarrow -\!\!\left[A{-}AB{-}B\right]\!\!-$$

$$X_n = \frac{1+r}{1+r-2rp}$$ r = ratio of number of functional groups such that it is ≤ 1

$$r = \frac{N_A}{N_B} \; if \; N_B \geq N_A \qquad r = \frac{N_B}{N_A} \; if \; N_A \geq N_B$$

N_A = number of functionl group A

N_B = number of functionl group B

$$for\ p = 1, X_n = \frac{1+r}{1-r}$$

$$for\ r = 1, X_n = \frac{1}{1-p}$$

Next, we discussed how we could control the molecular weight by controlling the stoichiometry of the functional groups. And we have taken AA and BB type monomer, and we have shown that the degree of polymerization is related to conversion and r,

$$X_n = \frac{1+r}{1+r-2rp}$$

'r' is the ratio of the functional groups so that is always ≤ 1, r is given by N_A/N_B, If $N_B \geq N_A$. N_A is the number of the functional group of A, and N_B is the number of the functional group of B. Now, if $N_A \geq N_B$, then r we should define as N_B/N_A; and in this case, if we can manage to push the reaction till completion or towards p = 1, then $X_n = \frac{1+r}{1-r}$ Or if r is 1, then $X_n = \frac{1}{1-p}$ and we get the Carother's equation which we talked in last slide.

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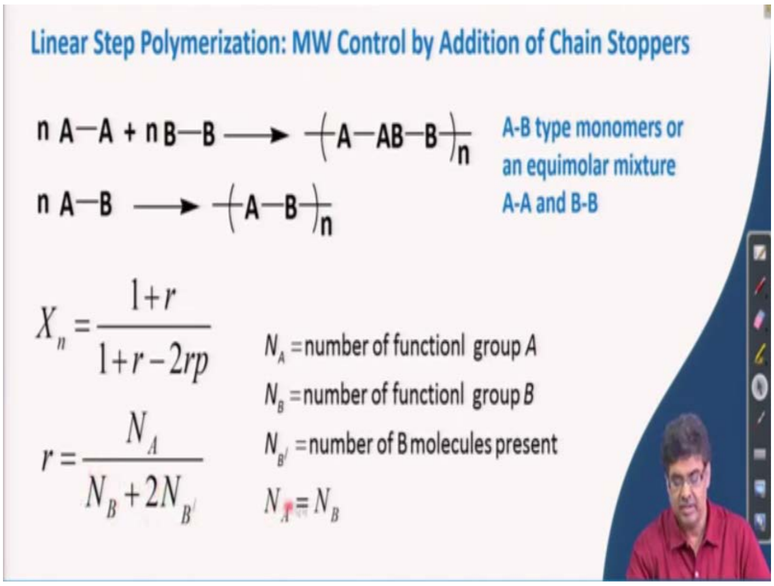

Linear Step Polymerization: MW Control by Addition of Chain Stoppers

$$n\,A{-}A + n\,B{-}B \longrightarrow \left(A{-}AB{-}B\right)_n$$

$$n\,A{-}B \longrightarrow \left(A{-}B\right)_n$$

A-B type monomers or an equimolar mixture A-A and B-B

$$X_n = \frac{1+r}{1+r-2rp}$$

$$r = \frac{N_A}{N_B + 2N_{B'}}$$

N_A = number of functionl group A

N_B = number of functionl group B

$N_{B'}$ = number of B molecules present

$N_A = N_B$

Now, there is another way we can control the molecular weight; by adding a chain stopper. We have discussed that this is the expression where we have considered 2 monomers in equal ratio, AB-type monomer or an equimolar mixture of AA and BB type monomer but in that case, r is defined a little differently

$$r = \frac{N_A}{N_B + 2N_{B`}}$$

Where $N_{B`}$ is the number of B monomer molecules present that are monofunctional one monofunctional monomer does a similar effect like excess of one difunctional monomer.

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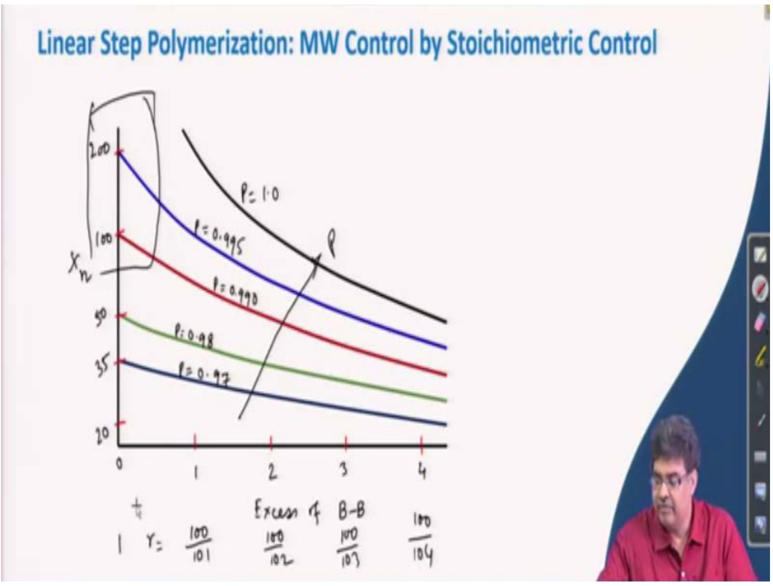

Linear Step Polymerization: MW Control by Stoichiometric Control

So, if we see this graph, how to control the molecular weight by stoichiometric control. Where there is an excess of one of the monomers say, for example, in this case BB, then the r-value would be 100 / 101, 100 / 102, 100 / 103, when there is 1,2,3 excess BB molecules present respectively. When the excess is 0, that means r is 1 in this. If we are plotting Xn vs degree of polymerization, from this, we can see that degree of polymerization depends on both ratio and the conversion. If we want to achieve a high molecular weight or high degree of polymerization, then the reaction must proceed to that extent so that p is very high and r should be as close to 1 as possible. Otherwise, if r is away from 1 and p is less, then we are bound to get a lower value of the degree of polymerization.

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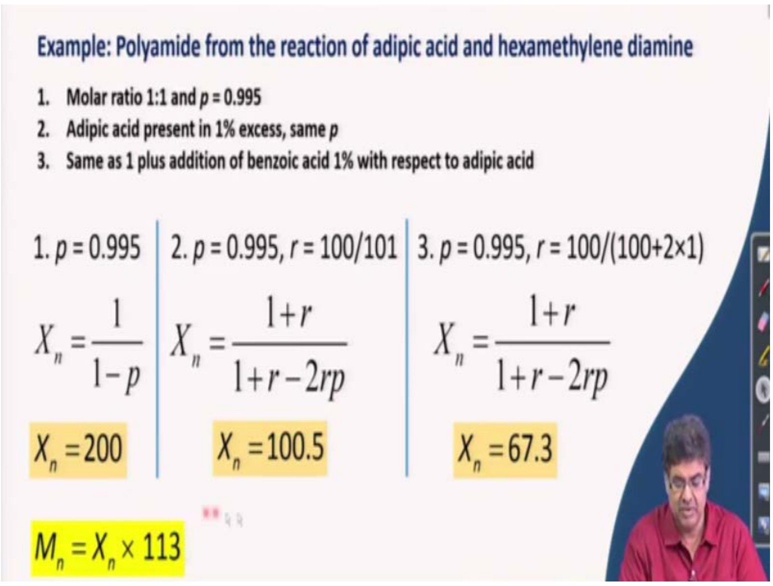

Example: Polyamide from the reaction of adipic acid and hexamethylene diamine

1. Molar ratio 1:1 and $p = 0.995$
2. Adipic acid present in 1% excess, same p
3. Same as 1 plus addition of benzoic acid 1% with respect to adipic acid

1. $p = 0.995$	2. $p = 0.995$, $r = 100/101$	3. $p = 0.995$, $r = 100/(100+2\times1)$
$X_n = \frac{1}{1-p}$	$X_n = \frac{1+r}{1+r-2rp}$	$X_n = \frac{1+r}{1+r-2rp}$
$X_n = 200$	$X_n = 100.5$	$X_n = 67.3$

$M_n = X_n \times 113$

As an example, if we talk about a polyamide from the reaction of adipic acid and hexamethylenediamine, and we have 3 scenarios in this case. First, if the molar ratio is 1:1 and p is 0.995, the second scenario where we have one of the monomers say adipic acid present in 1% excess and having same p 0.995, and third case where we have the same molar ratio, 1:1, and p = 0.995. Still, we have added benzoic acid, a monofunctional molecule, which is present as 1% excess with respect to the monomers like adipic acid. So, in the first case, p is 0.995, and the molar ratio is 1:1. So, we applied this to Carother's equation, to get X_n= 200. In the second case, p is 0.995, r is 1% excess monomer, i.e. r =100 / 101. So, we put this number here, and we get X_n = 100.5. In the third case, p is again 0.995, r = 100 / (100 + 2 × 1), which will turn out to be X_n = 67.3. Now you can see that adding 1% monofunctional reactants, which are chain stoppers, has more effect than adding 1% excess of one of the monomers. So that is why the reaction mixture must be devoid of any monofunctional monomers present in the system. If we want to reduce or want to control the molecular weight, we can always use this monofunctional monomer as a chain stopper to reduce the molecular weight. To say how to get the molecular weight, we have seen that $M_n = X_n \times 113$, the molecular weight of the repeating unit of this polymer is 226, so the molecular M_n would be X_n multiplied by 113.

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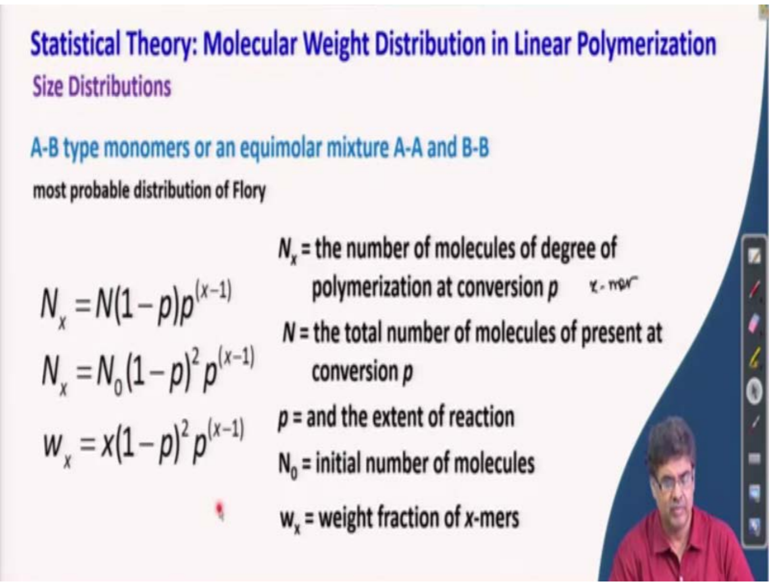

Statistical Theory: Molecular Weight Distribution in Linear Polymerization

Size Distributions

A-B type monomers or an equimolar mixture A-A and B-B

most probable distribution of Flory

$$N_x = N(1-p)p^{(x-1)}$$

$$N_x = N_0(1-p)^2 p^{(x-1)}$$

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

N_x = the number of molecules of degree of polymerization at conversion p x-mer

N = the total number of molecules of present at conversion p

p = and the extent of reaction

N_0 = initial number of molecules

w_x = weight fraction of x-mers

Next, we will go to a statistical theory of molecular weight distribution in linear polymerization. We will talk about size distribution and again consider the simplest situation where we have AB type monomer or an equal ratio of AA and BB. This distribution is provided by the most probable distribution, provided by Flory. This is the final expression

$$N_x = N(1-p)p^{(x-1)}$$

N_x is the number of molecules of the degree of polymerization of a particular value at conversion p, where N is the total number of molecules present at conversion p. So N_x is the number of molecules of the degree of polymerization, equivalent to x-mer. So, N_x is the number of molecules of x-mer.

Similarly, with N_0, we get this expression

$$N_x = N_0(1-p)^2 p^{(x-1)}$$

Where N_0 is the initial number of molecules and N is the total number of molecules present at that particular conversion p. W_x is the weight fraction of the x-mer. And the x is the value of x-mer. So, if we are talking about dimer, then x is 2. In case of octamer, x is 8, and so on. These expressions can be used to calculate the mole fraction of a particular mer or weight fraction of a particular mer in a reaction mixture.

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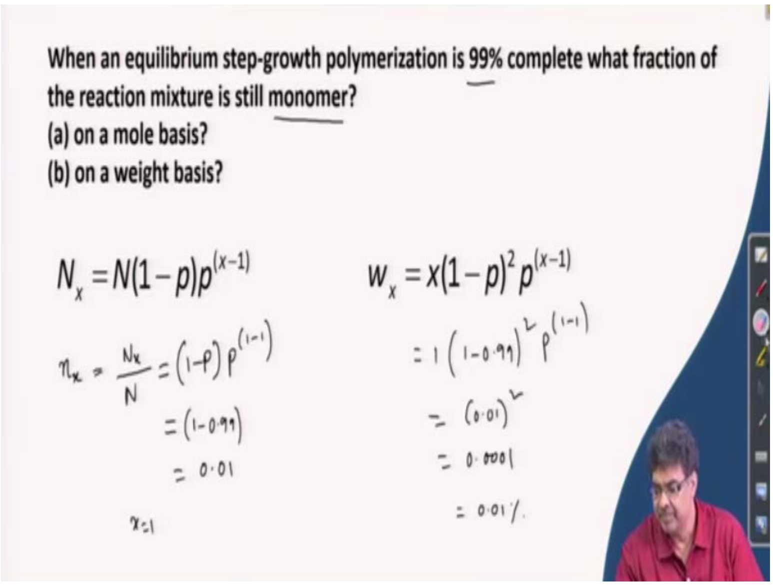

When an equilibrium step-growth polymerization is 99% complete what fraction of the reaction mixture is still monomer?

(a) on a mole basis?

(b) on a weight basis?

$N_x = N(1-p)p^{(x-1)}$

$n_x = \frac{N_x}{N} = (1-p)p^{(1-1)}$

$= (1-0.99)$

$= 0.01$

$x=1$

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

$= 1(1-0.99)^2 p^{(1-1)}$

$= (0.01)^2$

$= 0.0001$

$= 0.01\%$

For example, we can calculate the monomer percentage for an equilibrium step-growth polymerization. What are the fraction of monomer by mole present and weight present? So, this formula we should apply for the mole fraction. The mole fraction of x-mer, given by

$$N_x = N(1-p)p^{(x-1)}$$

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

$$= (1-0.99) = 0.01$$

We are talking about monomer, so x = 1. So monomer mole fraction is 0.01 or 1%, which means even after 99% conversion, we still have 1% of the molecules present as monomers. Whereas, if we want to get the value for the weight fraction, we should apply this expression. And in this case, x is 1.

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

$$= 1 \times (1-0.99)^2 \times p^{(1-1)}$$

$$= 0.01^2 = 0.0001 = 0.01\%$$

So, the weight fraction of the monomer is much lower, which is 0.01%, which means by weight, in the reaction mixture, the monomer is about 0.01%. The lower molecular weights or lower x-mers are present more in number than in weight.

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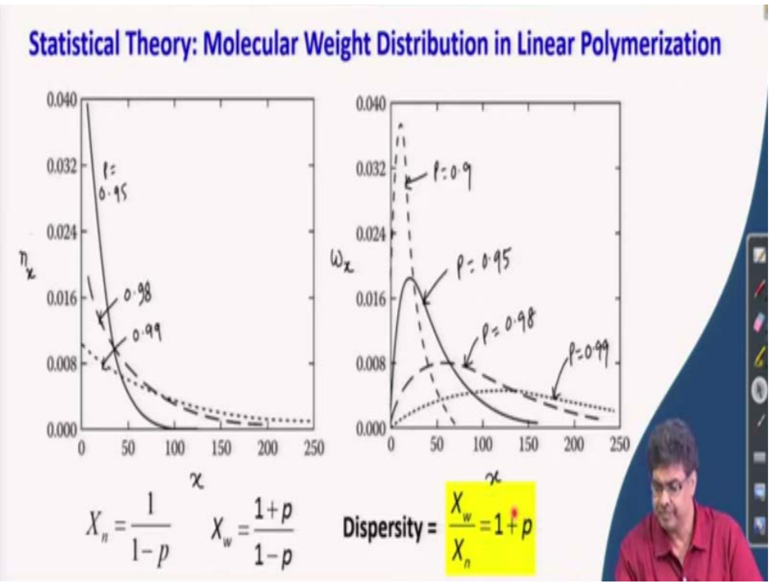

Statistical Theory: Molecular Weight Distribution in Linear Polymerization

$$X_n = \frac{1}{1-p} \qquad X_w = \frac{1+p}{1-p} \qquad \text{Dispersity} = \frac{X_w}{X_n} = 1+p$$

The first is the plot of the number fraction vs. X_n. Different lines are for a different p-value. So, as we can see, when there is lower conversion or lower amount of reaction, then the percentage of low molecular weights, in terms of number percentage, is much higher. As the reaction goes towards completion and more and more reactions happen, the monomer percentage goes down. However, even at 99% conversion, we can see that the percentage of lower mers is much higher in number. So in the case of number, a lower mer will always be present, always in a higher number than a mer with a higher x value, which means in any condition, if there is a greater number of tetramer present in a reaction mixture compared to say, a pentamer, the difference will come down as we increase the p value or proceed towards completing the reaction.

Now, this will be a little different when we talk about the weight fraction of this x mer. As we can see, always the mers that have intermediate values have the highest weight fraction. The mers that will have the highest weight fraction get shifted towards the right or higher x value as we increase the conversion or go towards the completion of the polymerization reaction. So, there is little difference between number fraction distribution and weight fraction distribution in a step-growth polymerization. So, when we take this is for simple 1 :1 molar ratio,

$$X_n = \frac{1}{1-p}$$

$$X_w = \frac{1+p}{1-p}$$

So, the dispersity value or polydispersity index is always given by 1 + p. This is the derived dispersity value for step-growth polymers. Now we can understand that for a high molecular weight step polymer, the p value would be close to 1. So the dispersity value should always be close to 2. Now in practice, we get a little above 2, and that happens because of two reasons.

One, when we isolate these polymers, say by precipitation mechanism or some other method, then some of these low molecular weights are stripped off from the polymer mixture. As a result, the X_w goes up, and also X_w goes up comparatively higher than X_n. And also, there is always a probability of forming cyclic molecules. Once the cyclic molecule forms, this dispersity goes a little above 2, like 2.2, 2.3, and so on. We cannot completely avoid this cyclic formation. Still, we can minimize by carrying out the reaction at higher monomer concentration. There are ways to minimize the formation of cyclics. So, from this slide, we should remember the number distribution and weight fraction distribution for a step polymer or a high molecular weight step polymer, where the dispersity value is always near 2, but in practice, we get a little above 2.

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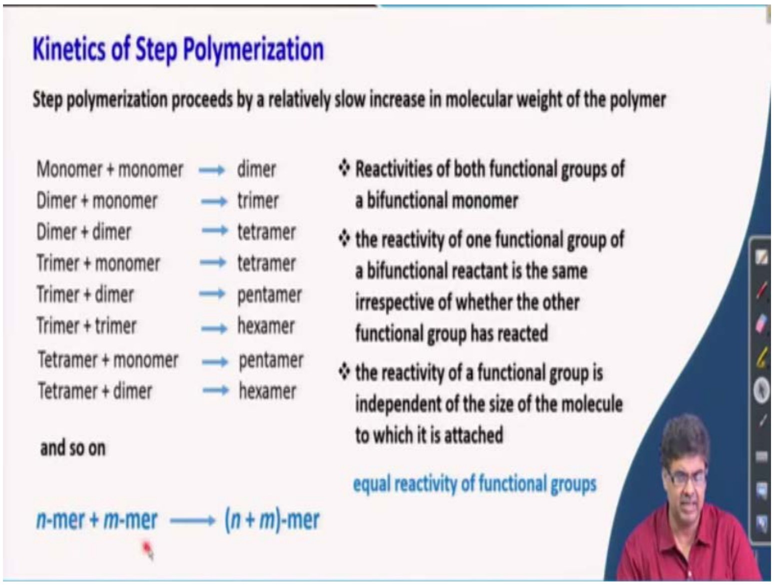

Kinetics of Step Polymerization

Step polymerization proceeds by a relatively slow increase in molecular weight of the polymer

Monomer + monomer → dimer
Dimer + monomer → trimer
Dimer + dimer → tetramer
Trimer + monomer → tetramer
Trimer + dimer → pentamer
Trimer + trimer → hexamer
Tetramer + monomer → pentamer
Tetramer + dimer → hexamer

and so on

n-mer + m-mer ⟶ $(n+m)$-mer

- Reactivities of both functional groups of a bifunctional monomer
- the reactivity of one functional group of a bifunctional reactant is the same irrespective of whether the other functional group has reacted
- the reactivity of a functional group is independent of the size of the molecule to which it is attached

equal reactivity of functional groups

We now move to the next topic of the kinetics of step polymers. Now we will go back and look at the mechanism once again, how the step-growth polymers are formed. There are many reactions possible in a reaction mixture, if we need to calculate the rate expression for each reaction, then it is almost impossible obtain the reaction kinetics for the polymerization reaction. So, there are a few assumptions, that the reactivity of both the functional groups of a bifunctional monomer is the same, i.e. in case of AB type monomer the reactivity of A and B group is the same. Next, the reactivity of one functional group of a bifunctional reactant is the same irrespective of whether the other functional group has reacted or not. This means that whether B has reacted or not reacted, the reactivity of A does not change. The third is that the reactivity of a functional group is independent of the size of the molecules to which this is attached. This means that if, we have a dimer or a trimer or a tetramer or even hexamer or pentamer the molecule, the functional group which is at the end, say for polyesterification, the acid group at the end of either of these mers have same reactivity irrespective of the size of the molecule to which it is attached, which means effectively the reaction kinetics of each of these reactions are same. We call this principle of equal reactivity of functional groups. These are not just an assumptions, these are established experimentally. So, if we assume all these things, we can write these as a general reaction of n-mer + m-mer giving (n + m)-mer.

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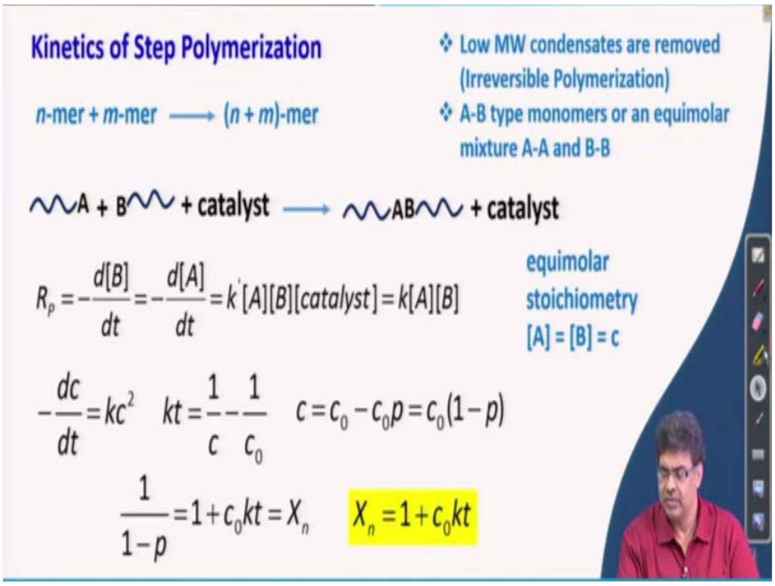

Kinetics of Step Polymerization

n-mer + m-mer $\longrightarrow$ $(n+m)$-mer

- Low MW condensates are removed (Irreversible Polymerization)
- A-B type monomers or an equimolar mixture A-A and B-B

$$\sim\sim A + B\sim\sim + \text{catalyst} \longrightarrow \sim\sim AB\sim\sim + \text{catalyst}$$

$$R_p = -\frac{d[B]}{dt} = -\frac{d[A]}{dt} = k'[A][B][catalyst] = k[A][B]$$

equimolar stoichiometry

$[A] = [B] = c$

$$-\frac{dc}{dt} = kc^2 \quad kt = \frac{1}{c} - \frac{1}{c_0} \quad c = c_0 - c_0 p = c_0(1-p)$$

$$\frac{1}{1-p} = 1 + c_0 kt = X_n \quad X_n = 1 + c_0 kt$$

The step polymerization is most cases is under the influence of a catalyst. In this particular case, we are assuming 3 things, that the low molecular weight condensates like water or HCl or whatever is coming out during this reaction, are being removed continuously. So, this reaction is irreversible. We are discussing the irreversible polymerization with AB monomer type in the simplest case or equimolar mixture of AA and BB. We know the rate of polymerization or rate of reaction is the rate of disappearance of a functional group. So, in this case, we can consider either A or B. As both are same, we can write rate = rate constant × concentration of A × concentration of B × the concentration of catalyst. Since catalyst concentration is constant, we put this within this new rate constant, giving [A] × [B]. Now we know that we have considered here equimolar stoichiometry. So, for the concentrations of A and B, considered as c, we can write the rate expression like this, and we do this integration,

$$-\frac{dc}{dt} = kc^2$$

$$kt = \frac{1}{c} - \frac{1}{c_0}$$

C_0 is the initial conc, at t = 0, or C_0 is the initial monomer concentration. We do some rearrangement, and where p is the conversion, the fraction of functional groups which reacted at time t, so we get this expression.

$$\frac{1}{1-p} = 1 + c_0\,kt = X_n$$

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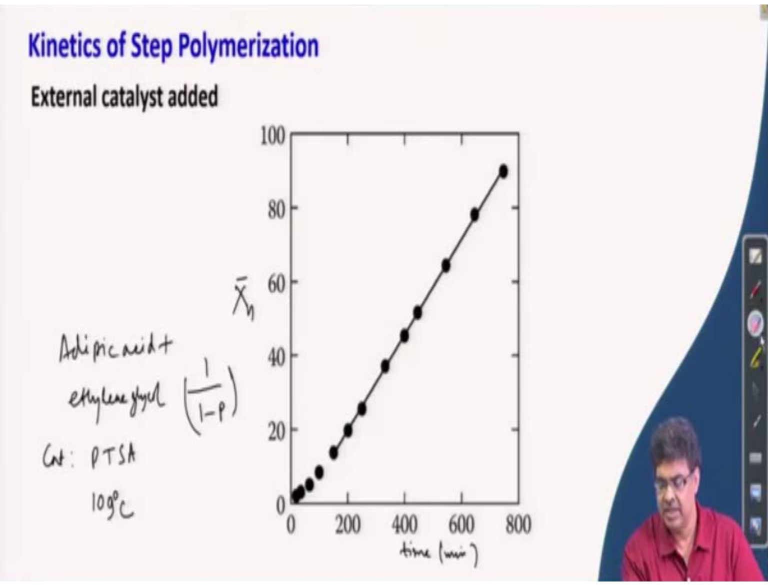

Kinetics of Step Polymerization

External catalyst added

So, this is experimentally verified that X_n, equals 1 / (1 – p). This is verified for the reaction between adipic acid + ethylene glycol catalyst by PTSA Para Toluene Sulfonic Acid at the temperature of 109 °C. So, whatever we have derived from that rate equation is experimentally verified.

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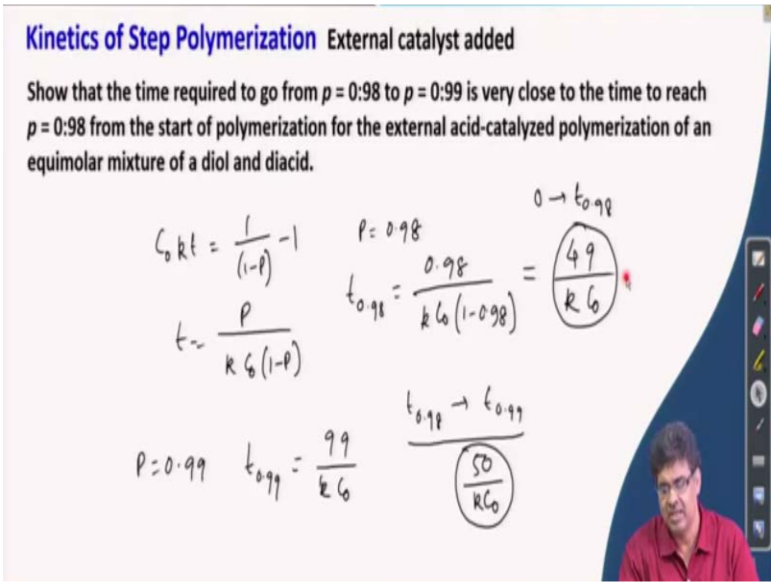

Kinetics of Step Polymerization External catalyst added

Show that the time required to go from p = 0:98 to p = 0:99 is very close to the time to reach p = 0:98 from the start of polymerization for the external acid-catalyzed polymerization of an equimolar mixture of a diol and diacid.

$$C_0 kt = \frac{1}{(1-p)} - 1$$

$$t = \frac{p}{kC_0(1-p)}$$

$0 \to t_{0.98}$

$p = 0.98$

$$t_{0.98} = \frac{0.98}{kC_0(1-0.98)} = \boxed{\frac{49}{kC_0}}$$

$p = 0.99$

$$t_{0.99} = \frac{99}{kC_0}$$

$$\frac{t_{0.98} \to t_{0.99}}{\boxed{\frac{50}{kC_0}}}$$

Now, there could be another possibility where we are not adding any external catalyst. This is the example; we need to show that the time required to go from p 0.98 to 0.99 is very close to the time to reach 0.98 from the start of the polymerization. So if we quickly try to show this, we know this expression

$$C_0kt = 1 / (1 – p) - 1.$$

$$t = \frac{p}{k \times C_0 \times (1 - p)}$$

now when p is 0.98, we write $t_{0.98} = 49 / k C_0$. So, the time required to go from 0 conversion to 0.98 conversions is given by this value. And the time from 0.98 to 0.99 is given by $50 / k C_0$. And this is the time for 0 to t 0.98 which means that completing the reaction up to 98% almost took us the same time from 98% conversion to 99% conversion. That happens because when we have converted 98%, 98% of functional groups have reacted. Now the effective concentration of functional groups is very low. That is the reason why the reaction rate comes down. So, which means for a step polymerization, we can achieve some value of conversion very fast. Still, to get a very high value of conversion, we need to run our reaction for a much longer time because that is very difficult to build or achieve the high conversion at a later part. So with this, we will stop for this lecture, and in the next lecture, we will start with another possibility of step polymerization, which is not very practically done. This externally catalyzed polymerization is the most frequently done step polymerization. Still, we, for completion of the record, will start with another possibility of a step polymerization, kinetic of step polymerization where we will not add any catalyst from outside. One of the reactants can be used as a catalyst. So that will start in the next lecture.