Polymer Process Engineering

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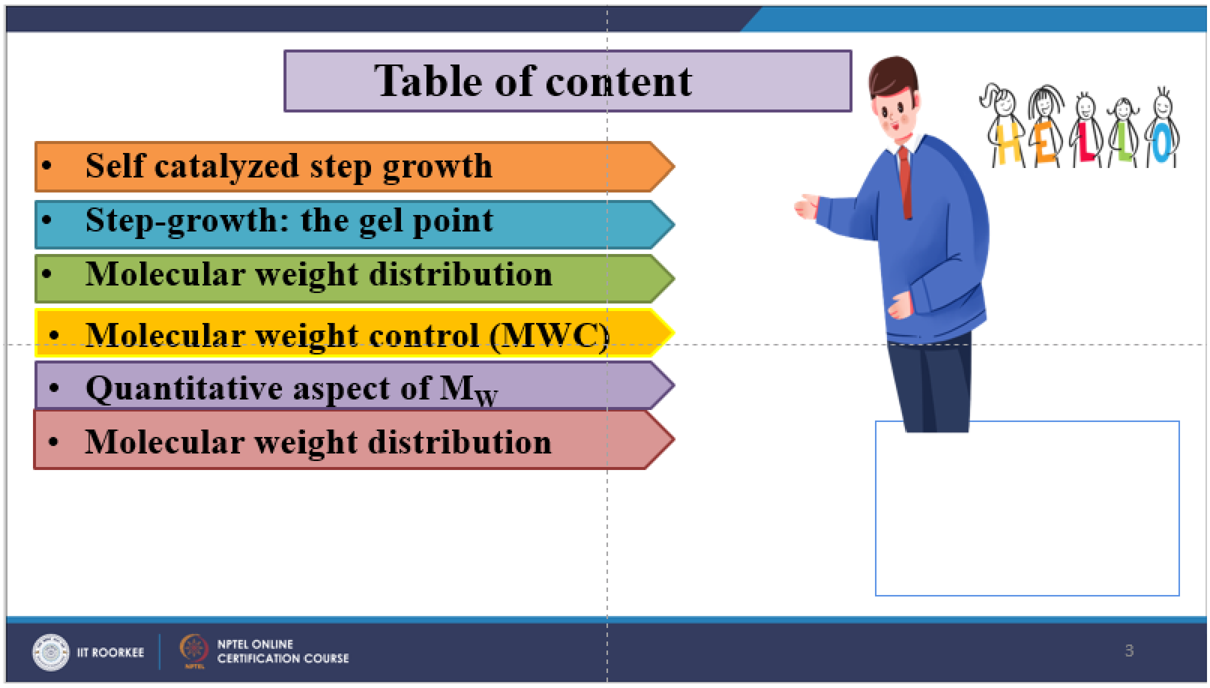
Lecture 28

Chemical reaction engineering in polymers: Addition (Chain-Growth) Polymerization-I

Hello friends, let us have a look about the molecular weight distribution and addition that is the chain reaction polymerization under the areas of chemical reaction engineering in polymeric systems. So, in the previous section we have covered the polymerization step versus chain reactions, step growth polymerization, we started the concept of step growth polymerization. Then we discussed about the various properties of the step growth polymerization and we started the kinetics of the step growth polymerization.



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In this particular segment we are going to discuss with the self-catalyzed step growth polymerization and step growth with respect to the gel point and molecular weight distribution, how we can control the molecular weight, we will have a quantitative aspects of molecular weight distribution, all these things we will discuss in this particular chapter. Let us start with the self-catalyzed step growth polymerization. Now you have to be sync with the previous lecture because the some of the equations we have discussed in the previous lecture.

$$\frac{-d[COOH]}{dt} = -k(COOH)^2(OH)$$

Self-catalyzed step growth polymerization

- In the absence of an **externally added strong acid** the diacid monomer acts as its **own catalyst** for the esterification reaction.
- For this case [HA] is replaced by [COOH] and eq. 6 can be written in the usual form.

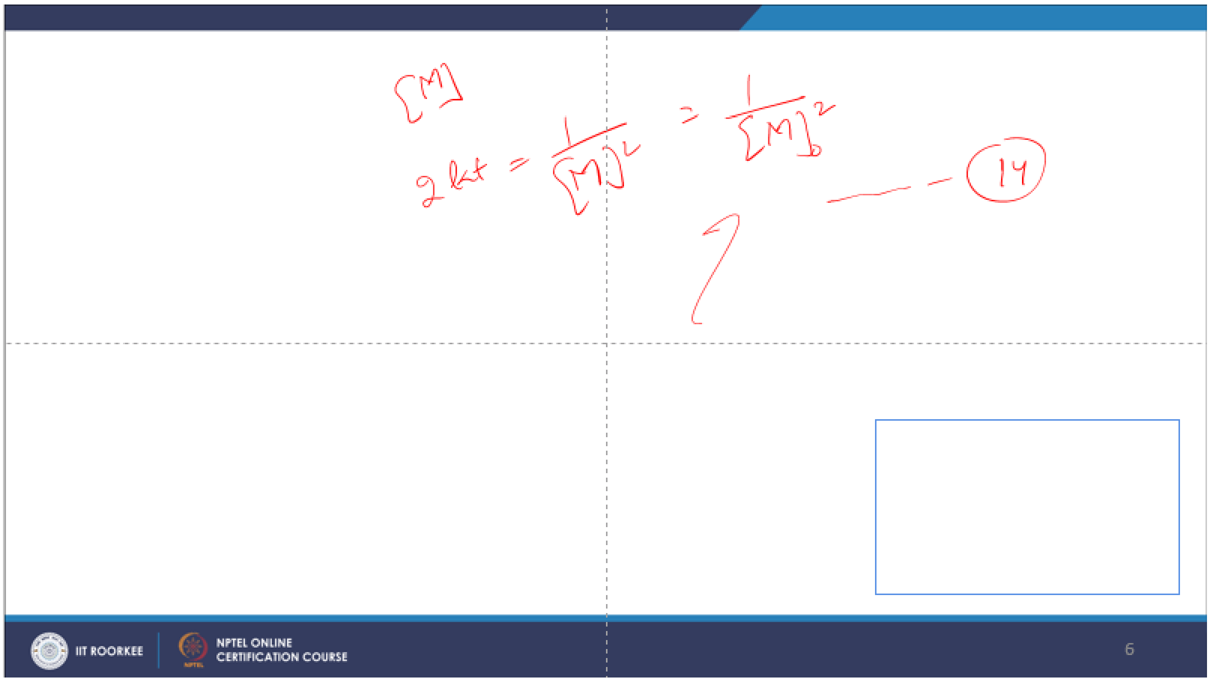
$$\frac{-d[COOH]}{dt} = -k(COOH)^2(OH) \quad \ldots\ldots (12)$$

- where **K and k3** have been combined into the experimentally determined **rate constant k**.
- Eq. 12 shows the important characteristic of the **self-catalyzed polymerization**.
- The **reaction is third-order** overall with a second-order dependence on the carboxyl concentration.

$$-\frac{d[M]}{dt} = k[M]^3 \quad \text{--- Eq (13a)}$$

or

$$-\frac{d[M]}{[M]^3} = k\,dt \quad \text{Eq (13b)}$$

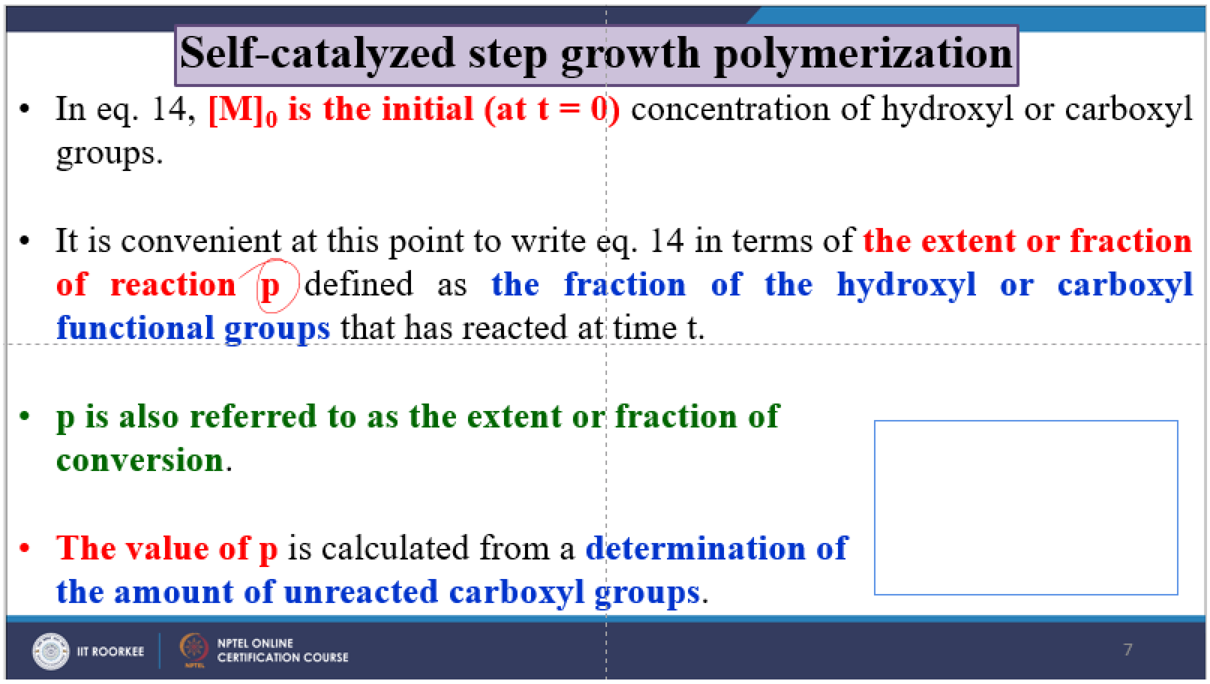


$[M]$

$$2kt = \frac{1}{[M]^2} = \frac{1}{[M]_0^2} \quad \text{---} \quad (14)$$

Now in the absence of you can say the externally added strong acid, the diacid monomer they acts as own catalyst for the esterification reaction. Now for this case this HA is replaced by COH and this equation 6 which you recall in the previous segment we discussed that can be rewritten as minus D concentration of the COH over DT is equal to minus k COH to the power 2 OH, this can be represented at equation number 12. Now here the k and k3 this has been combined in the experimentally determined rate constant k. So, this equation shows the important characteristics of the self-catalyzed polymerization and the reaction is third order overall with the second order dependence on the carboxyl concentration.

Now here for most polymerization the concentration of two functional groups they are very nearly stoichiometric and this particular equation can be written as minus D concentration of M over DT that is equal to k M to the power 3. This is let us say that equation number 13a or sometimes it can be referred as minus D M M to the power 3 that is equal to k DT that is equation 13b. So, where this M is the concentration of hydroxyl group or carboxyl group and if we integrate this equation then it becomes 2 kT is equal to 1 over M and that is equal to initially if the concentration of M is M naught then this is the equation number 14. Now this in this equation number 14 that we have already depicted that at this M naught concentration is at time t is equal to 0 that is at the start. It is convenient at this particular juncture to write this particular equation in terms of extent or a fraction of a reaction P which is defined as a fraction of hydroxyl or carboxyl function group that has reacted at time t.



Self-catalyzed step growth polymerization

- In eq. 14, **$[M]_0$ is the initial (at t = 0)** concentration of hydroxyl or carboxyl groups.
- It is convenient at this point to write eq. 14 in terms of **the extent or fraction of reaction p** defined as **the fraction of the hydroxyl or carboxyl functional groups** that has reacted at time t.
- **p is also referred to as the extent or fraction of conversion.**
- **The value of p** is calculated from a **determination of the amount of unreacted carboxyl groups.**

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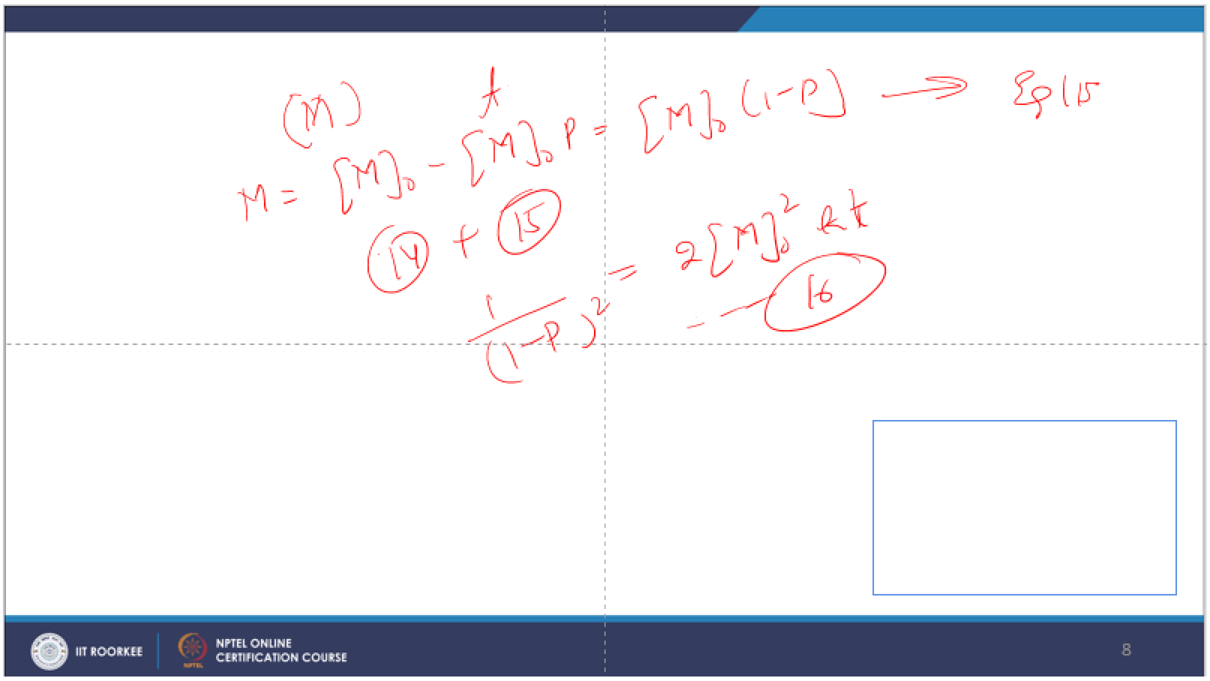
Now P is also referred to as the extent of or fraction of conversion. So, the value P is calculated from the determination of the amount of unreacted carboxyl group. Now here the concentration M at time t with either hydroxyl or carboxyl group is given by M is equal to M naught minus M naught P and that is M naught 1 minus P sometimes referred as equation 15. If we combine the equation 14 and 15, 14 and 15 if we combined then we get 1 over 1 minus P to the power 2 into 2 M naught to the power 2 kT and this is equation number 16. Now this indicates that a plot if we plot of 1 over 1 minus P to the power 2 versus t it should be linear in nature.



(M) t

$$M = [M]_0 - [M]_0 p = [M]_0 (1-p) \longrightarrow \text{Eq } 15$$

⑭ + ⑮

$$\frac{1}{(1-p)^2} = 2[M]_0^2 kt$$ ⑯

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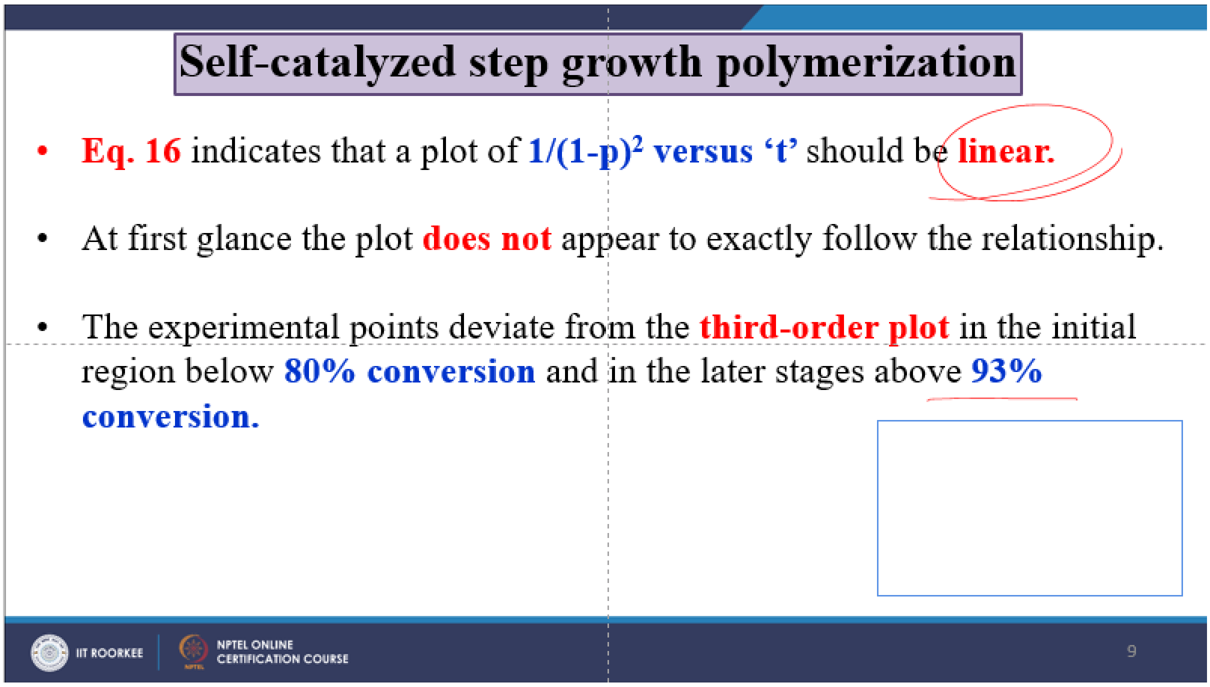
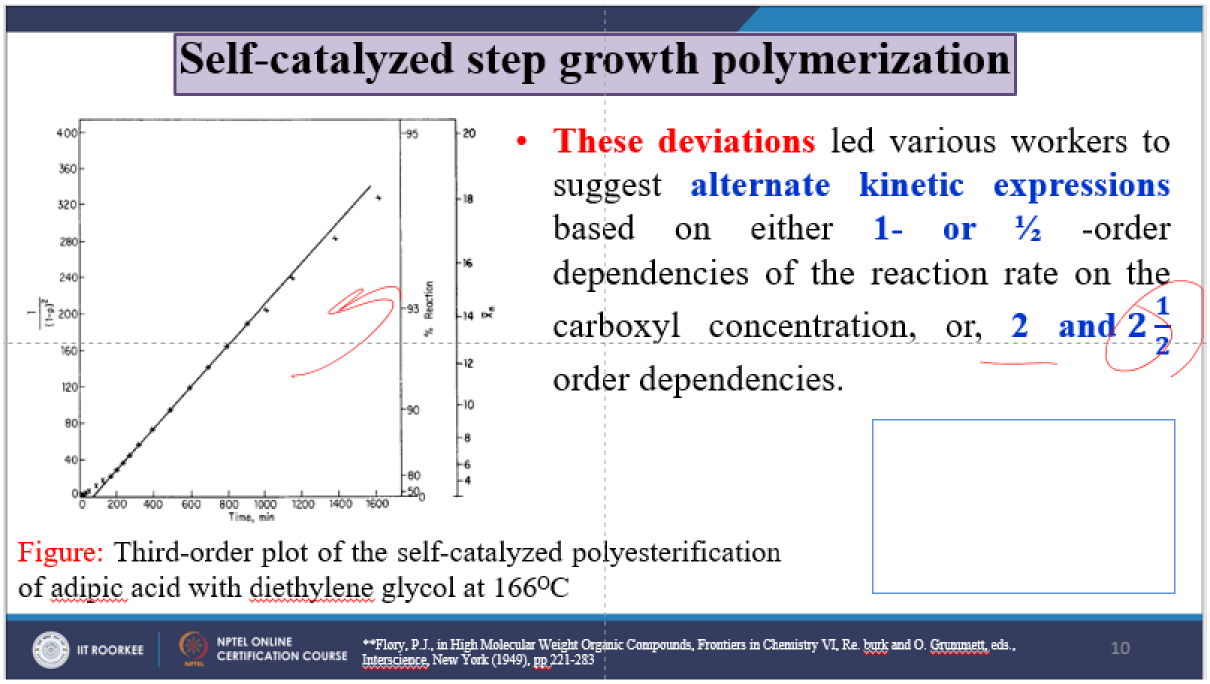
Now at a first glance the plot does not appear to exactly follow the relationship. The experimental point deviates from the third order plot in the initial region below 80 percent conversion and in the later stage say above 93 percent conversion. Now this is the plot, this deviation let various workers to suggest the alternate kinetic expression based on either one or half order dependencies on the reactions or rate and the carboxyl concentration or two and two and a half order dependencies. Now here you see that the rate equation can be given as minus d COOH over dt that is equal to k COOH OH this is equation 17a and minus d COOH over dt that is k COOH. This is equation number 17 can be referred as equation number 17b.



Self-catalyzed step growth polymerization

- **Eq. 16** indicates that a plot of **$1/(1-p)^2$ versus 't'** should be **linear.**
- At first glance the plot **does not** appear to exactly follow the relationship.
- The experimental points deviate from the **third-order plot** in the initial region below **80% conversion** and in the later stages above **93% conversion.**

Now the experimental rate data fits this particular equation which we discussed earlier that is 17a. Well only in the region between 50 and 86 percent conversion with an excessively poor fit above 86 percent conversion. On the other hand, if we talk about the plot according to this 17b equation reasonably well up to above say 80 percent conversion but deviates badly above that particular point. So, neither of the two alternate kinetic plots for based on equation 17a or 17b comes close to being as useful as a third order plot. Now the third order plot fits the experimental data much better than either of the higher conversion.

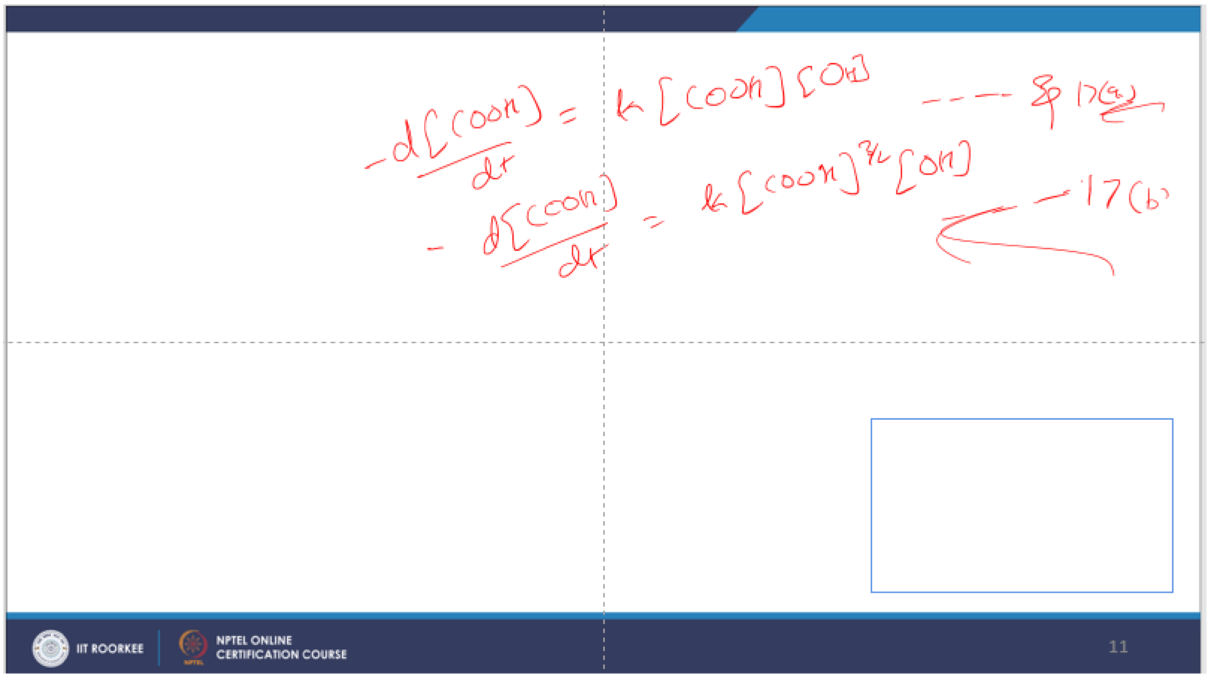


Self-catalyzed step growth polymerization

- **These deviations** led various workers to suggest **alternate kinetic expressions** based on either **1- or ½** -order dependencies of the reaction rate on the carboxyl concentration, or, **2 and $2\frac{1}{2}$** order dependencies.

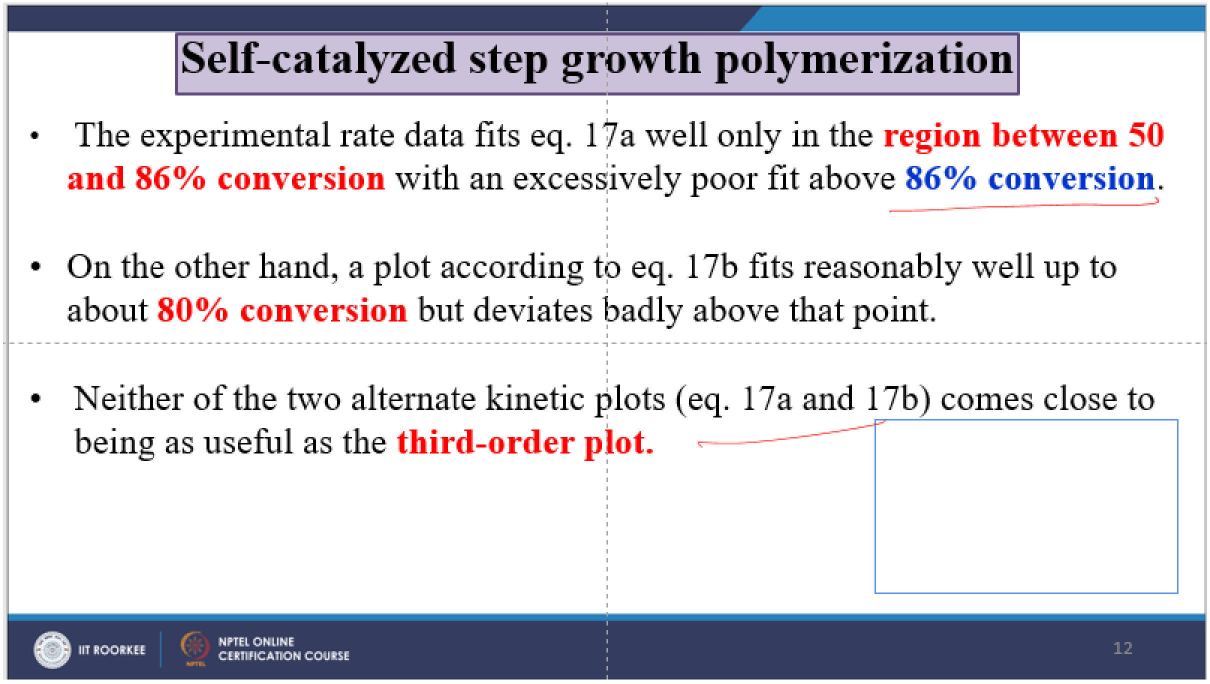
Figure: Third-order plot of the self-catalyzed polyesterification of adipic acid with diethylene glycol at 166°C

**Flory, P.J., in High Molecular Weight Organic Compounds, Frontiers in Chemistry VI, Re. burk and O. Grummett, eds., Interscience, New York (1949), pp 221-283



$$-\frac{d[COOH]}{dt} = k[COOH][OH] \quad \text{---- Eq 17(a)}$$

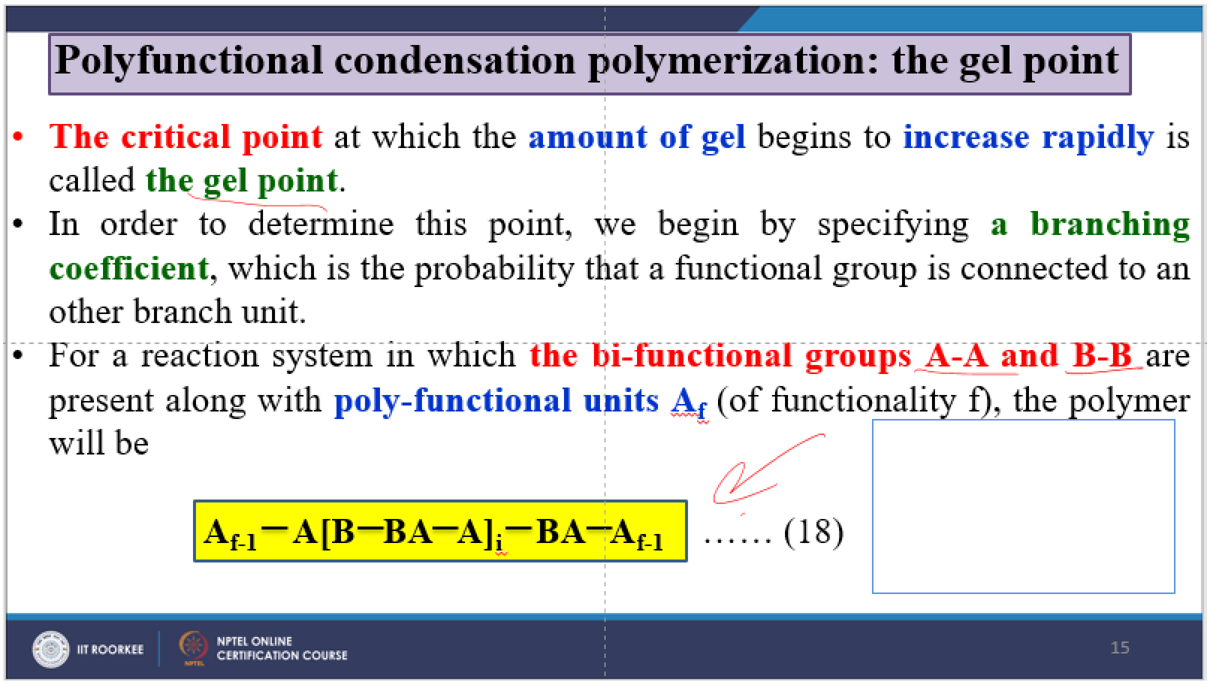
$$-\frac{d[COOH]}{dt} = k[COOH]^{3/2}[OH] \quad \leftarrow \text{--- 17(b)}$$



Self-catalyzed step growth polymerization

- The experimental rate data fits eq. 17a well only in the **region between 50 and 86% conversion** with an excessively poor fit above **86% conversion**.
- On the other hand, a plot according to eq. 17b fits reasonably well up to about **80% conversion** but deviates badly above that point.
- Neither of the two alternate kinetic plots (eq. 17a and 17b) comes close to being as useful as the **third-order plot.**

The fit of the data to the third order plot is reasonably good over much much greater range of higher conversion region. Now the region of higher conversion is of prime importance since high molecular weight polymer is obtained only at high conversion. So, the practical viewpoint the low conversion region of the kinetic plot is of little significant. Now when we talk about the gel point especially in case of poly function condensation polymerization the functionality higher than 2 introduce the possibility of branching or cross linking. In the latter case it is ultimately possible to attain the molecular weight that approaches infinity.

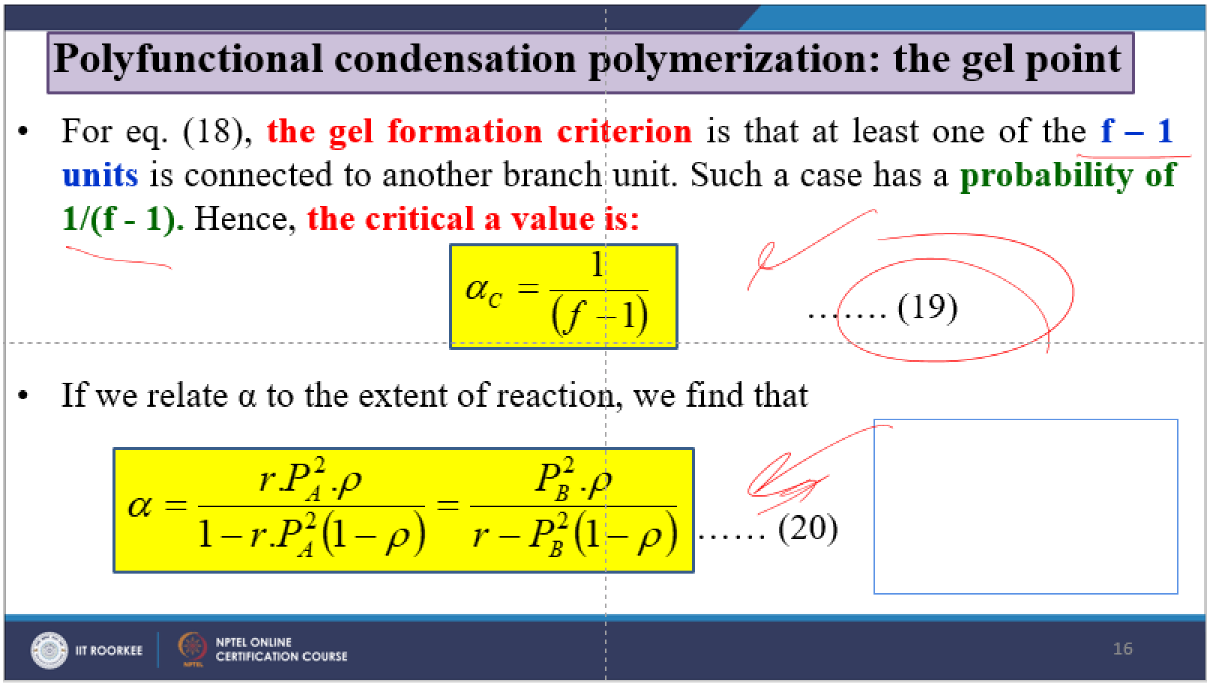


Polyfunctional condensation polymerization: the gel point

- **The critical point** at which the **amount of gel** begins to **increase rapidly** is called **the gel point**.
- In order to determine this point, we begin by specifying **a branching coefficient**, which is the probability that a functional group is connected to an other branch unit.
- For a reaction system in which **the bi-functional groups A-A and B-B** are present along with **poly-functional units A_f** (of functionality f), the polymer will be

$$\boxed{A_{f-1}—A[B—BA—A]_i—BA—A_{f-1}} \quad \ldots\ldots (18)$$

Now such materials they term as gel with the remainder of the reaction mixes with the sols the sol which is soluble that can be separated from the insoluble gel. This occurs because the viscous thermoplastic mass is transformed into the most elastic solid with a very high viscosity. Now the critical point at which the amount of gel begins to increase rapidly is called the gel point. In order to determine that this particular point we begin with the specifying the branching coefficient which is the probability that functional group is connected to another branch unit. For reaction system the bifunctional group like AA and BB they are present along with the poly functional units of the polymer that will be that can be represented by this particular equation 18.



Polyfunctional condensation polymerization: the gel point

- For eq. (18), **the gel formation criterion** is that at least one of the **f – 1 units** is connected to another branch unit. Such a case has a **probability of 1/(f - 1).** Hence, **the critical a value is:**

$$\boxed{\alpha_C = \frac{1}{(f-1)}} \quad \ldots\ldots (19)$$

- If we relate α to the extent of reaction, we find that

$$\boxed{\alpha = \frac{r.P_A^2.\rho}{1-r.P_A^2(1-\rho)} = \frac{P_B^2.\rho}{r-P_B^2(1-\rho)}} \ldots\ldots (20)$$

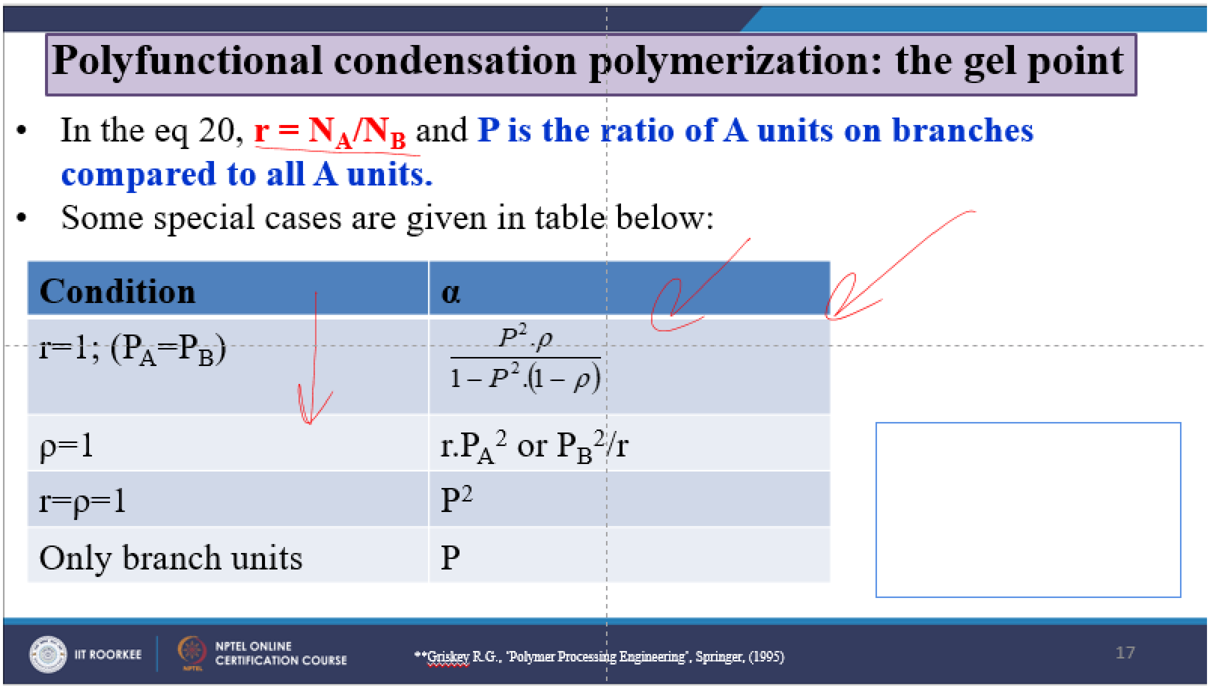
Critical value of a is

$$\alpha_C = \frac{1}{(f-1)}$$

If we relate alpha to the extent of reaction, we have

$$\alpha = \frac{r.P_A^2.\rho}{1 - r.P_A^2(1-\rho)} = \frac{P_B^2.\rho}{r - P_B^2(1-\rho)}$$

You see you can have a look of this particular equation 18. Now for this particular equation the gel formation criteria that is the least one of the F minus 1 unit is connected to another branch unit such case has a probability of 1 over F minus 1. Now the critical A value or sometimes referred as alpha, alpha c is represented as alpha c is equal to 1 over F minus 1 this is equation 19. Now if we relate alpha to the extent of reaction we can find the relationship of alpha in a more precise manner which is represented in this equation number 20. So, this based on this particular equation number 20 the r is equal to NA over NB and p is the ratio of a unit, on branches compared to all a units.



Polyfunctional condensation polymerization: the gel point

- In the eq 20, **$r = N_A/N_B$** and **P is the ratio of A units on branches compared to all A units.**
- Some special cases are given in table below:

Condition	α
r=1; (P_A=P_B)	$\frac{P^2.\rho}{1-P^2.(1-\rho)}$
ρ=1	$r.P_A^2$ or P_B^2/r
r=ρ=1	P^2
Only branch units	P

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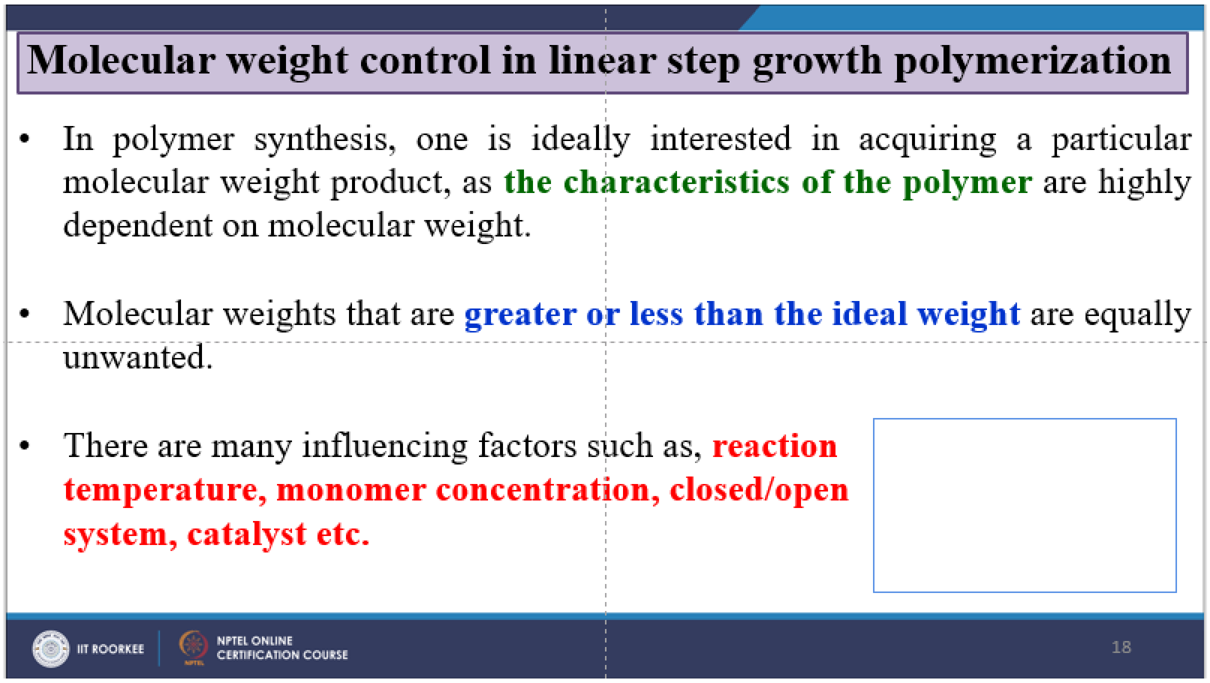
**Griskey R.G., 'Polymer Processing Engineering', Springer, (1995)

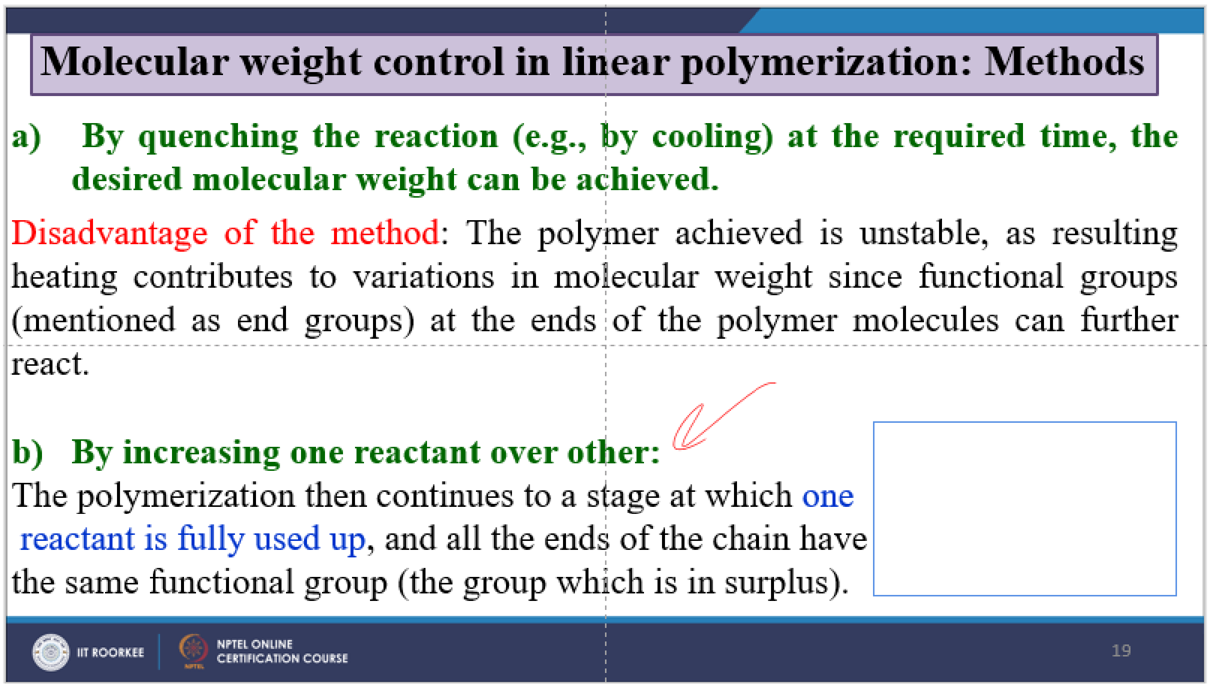
So, some of the special cases we have already enlisted some of the special cases or we have represented several conditions like r is equal to 1 and PA is equal to PB then what will be the nature of alpha. So, we have represented for the ease of convenience that you can roll out the different equations based on these conditions. Now let us talk about the molecular weight control in linear step growth polymerization. So, in the polymer synthesis one is ideally interested in acquiring a particular molecular weight product or molecular weight distribution product. So, the characteristics of the polymer they are highly dependent on the molecular weight.



Molecular weight control in linear step growth polymerization

- In polymer synthesis, one is ideally interested in acquiring a particular molecular weight product, as **the characteristics of the polymer** are highly dependent on molecular weight.
- Molecular weights that are **greater or less than the ideal weight** are equally unwanted.
- There are many influencing factors such as, **reaction temperature, monomer concentration, closed/open system, catalyst etc.**

So, the molecular weight that are greater or less than the ideal weight they are equally unwanted. Now there are many influencing factors like reaction temperature, monomer concentration, closed or open system, catalysed all these things are influencing factor in the system. Now there are various methods which are used for the molecular weight control in linear polymerization. One method is that by quenching the reaction by or by cooling at the required time and the desired molecular weight this can be achieved. Another the disadvantage of this particular method is that the polymer achieved whatever the polymer which is we are getting this is highly unstable in nature and resulting heating contributes to variation in molecular weight.



Molecular weight control in linear polymerization: Methods

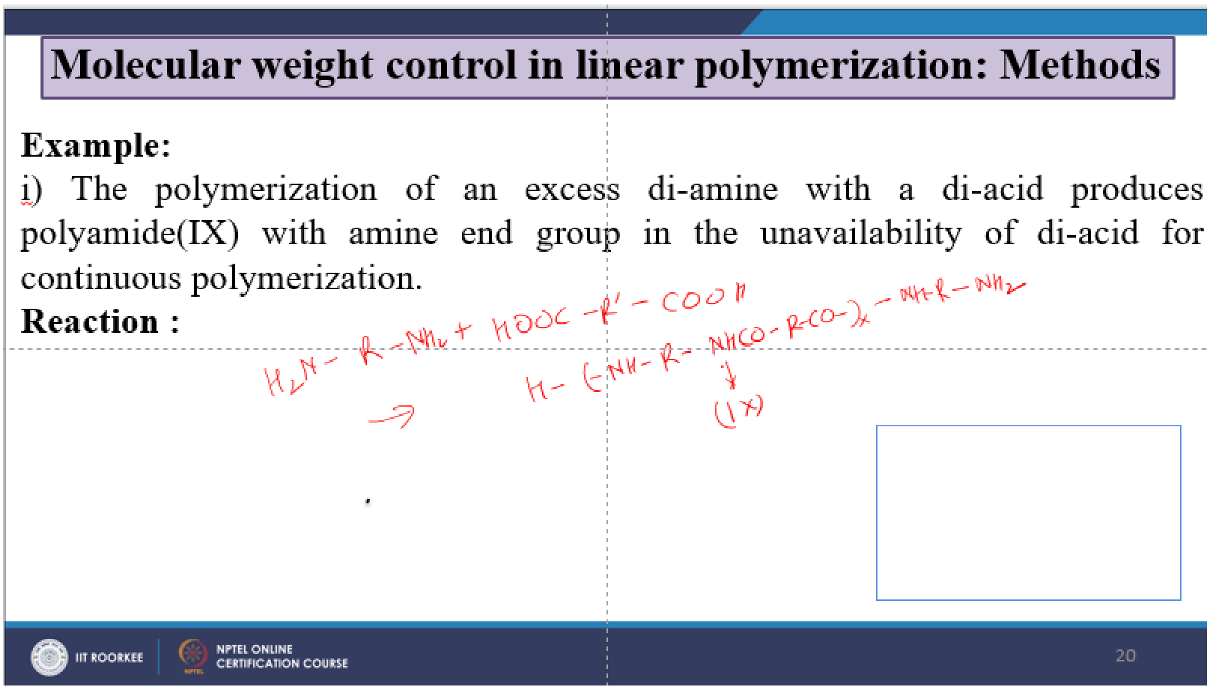
a) By quenching the reaction (e.g., by cooling) at the required time, the desired molecular weight can be achieved.

Disadvantage of the method: The polymer achieved is unstable, as resulting heating contributes to variations in molecular weight since functional groups (mentioned as end groups) at the ends of the polymer molecules can further react.

b) By increasing one reactant over other: ✓

The polymerization then continues to a stage at which one reactant is fully used up, and all the ends of the chain have the same functional group (the group which is in surplus).

So, that is the functional group or end groups at the end of the polymer molecule can further react. Another way is by increasing the one reactant over other. The polymerization then continues to a stage at which one reactant is fully used up and all the ends of the chain have the same functional group. So, the group which is in surplus. Let us take example, the polymerization of an excess diamine with the diacid produces polyamide with an amine and group in the unavailability of diacid for the continuous polymerization.



Molecular weight control in linear polymerization: Methods

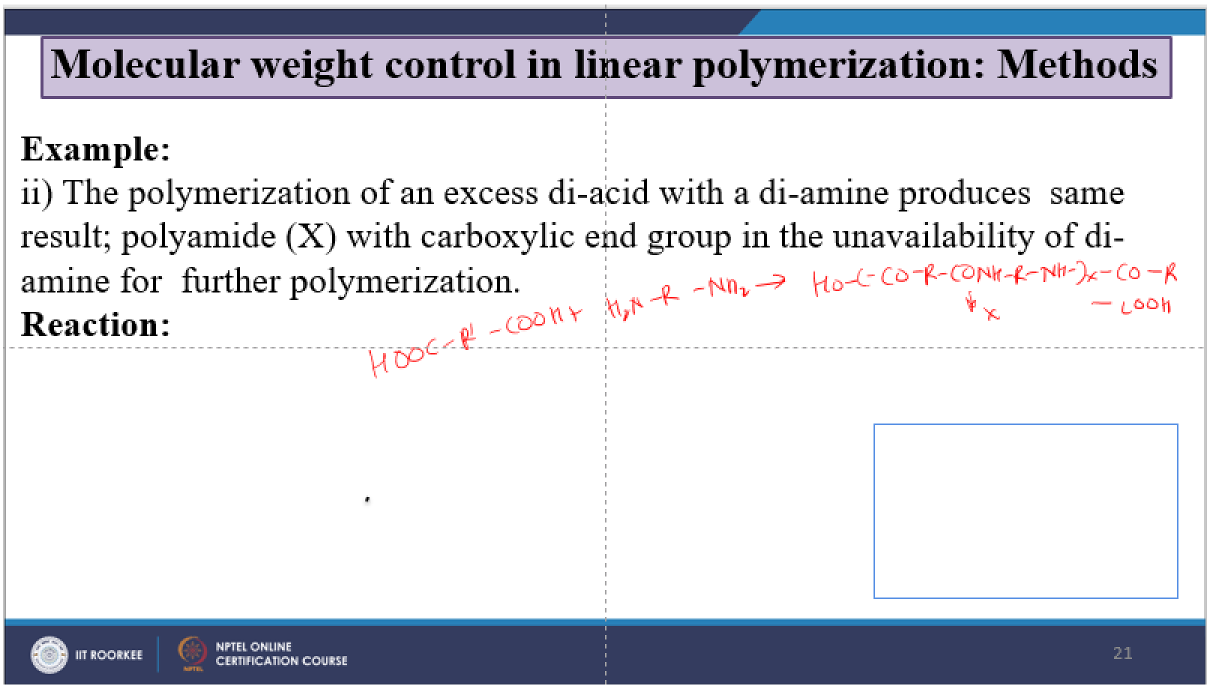
Example:

i) The polymerization of an excess di-amine with a di-acid produces polyamide(IX) with amine end group in the unavailability of di-acid for continuous polymerization.

Reaction :

$$H_2N-R-NH_2 + HOOC-R'-COOH \rightarrow H-(-NH-R-NHCO-R-CO-)_x-NH-R-NH_2$$

(IX)



Molecular weight control in linear polymerization: Methods

Example:

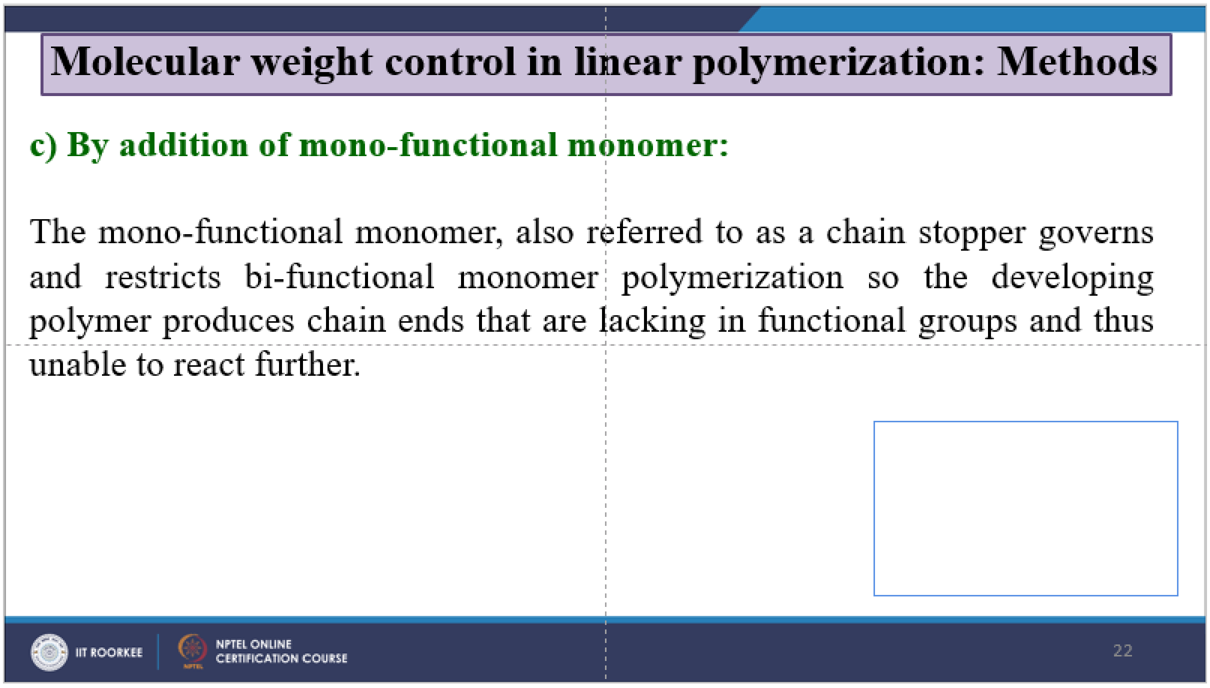
ii) The polymerization of an excess di-acid with a di-amine produces same result; polyamide (X) with carboxylic end group in the unavailability of di-amine for further polymerization.

Reaction:

$$HOOC-R'-COOH + H_2N-R-NH_2 \rightarrow HO-(-CO-R-CONH-R-NH-)_x-CO-R-COOH$$

(X)

So, the reaction can be represented as H 2 n R NH 2 plus H O O C R C O H which is H 2 n R NH 2. Another example that polymerization of excess diacid with the diamine produces the same result the polyamide with carboxylic end group in the availability of diamine for further polymerization. This can be represented as like H O O C R C O O H plus H 2 n R NH 2 H O C O R NH C O O H. Now another method is by addition of a monofunctional monomer. The monofunctional monomer also referred as a chain stopper governs and restricts the bifunctional monomer polymerization.

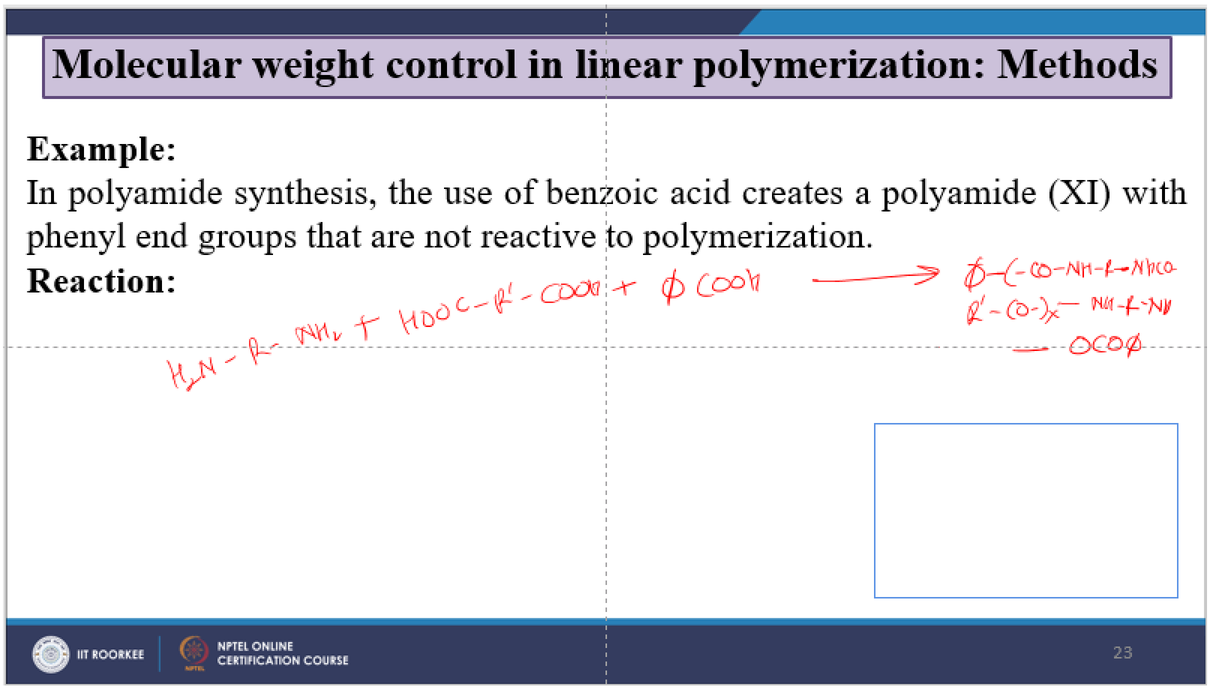


Molecular weight control in linear polymerization: Methods

c) By addition of mono-functional monomer:

The mono-functional monomer, also referred to as a chain stopper governs and restricts bi-functional monomer polymerization so the developing polymer produces chain ends that are lacking in functional groups and thus unable to react further.

So, the developing polymer produces the chain ends and that are lacking in the functional group and thus unable to react further. Let us take the example, polyamide synthesis the use of benzoic acid creates a polyamide X i which phenyl end group that that are not reactive to polymerization. So, this reaction is represented as H 2 n R NH 2 plus plus 5 C O O H this can be 5 C O NH R NH C O R dash NH R NH O C O 5. Now the quantitative aspect if we talk about the molecular weight control and to better regulate the polymers molecular weight the stoichiometric ratio of bifunctional monomer or monofunctional monomers must be precisely balanced. If the non-stoichiometry is too high the molecular weight of the polymer would be too small and this is essential in understanding every reactive contaminants quantitative effect that maybe initially exhibits in the reaction medium or is produced by involuntary side reactions.

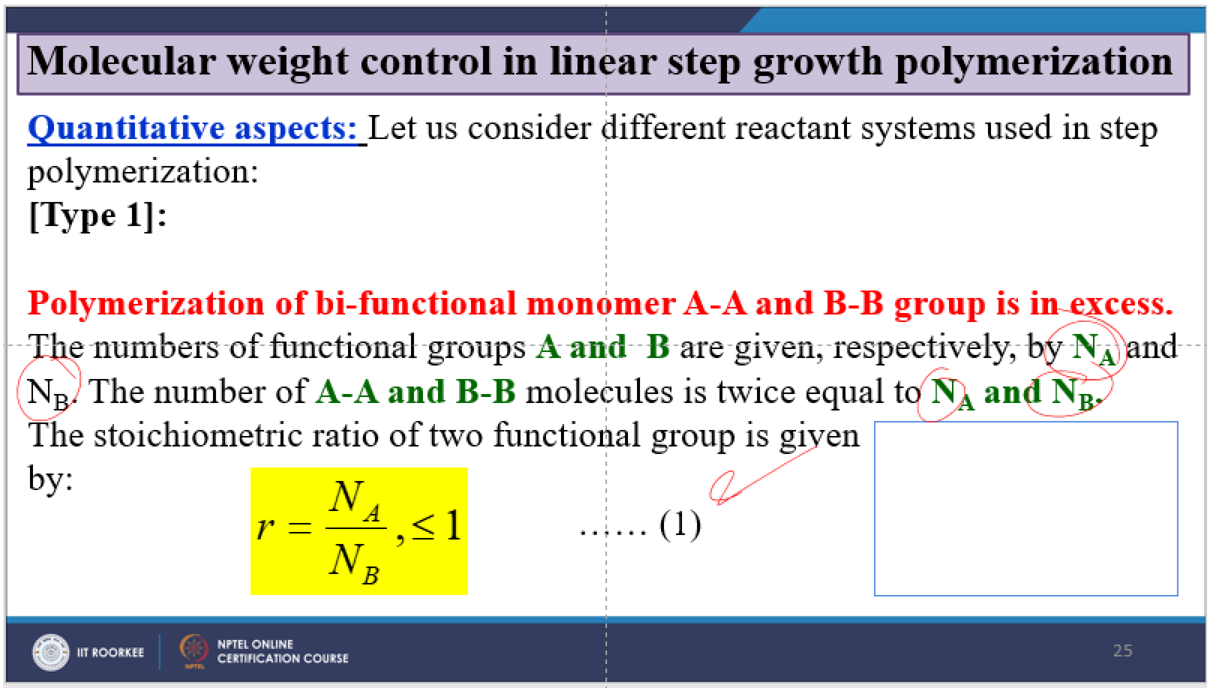


Molecular weight control in linear polymerization: Methods

Example:
In polyamide synthesis, the use of benzoic acid creates a polyamide (XI) with phenyl end groups that are not reactive to polymerization.
Reaction:

$H_2N-R-NH_2 + HOOC-R'-COOH + \phi COOH \longrightarrow \phi-(-CO-NH-R-NHCO-R'-CO-)_x-NH-R-NH-OCO\phi$

Let us take this quantitative aspect. Now let us consider the different reactor system used in the step polymerization that is type 1 we discussed earlier. Now the polymerization of a bifunctional monomer AA and BB group is in excess. So, the number of functional group A and B are given the respectively like say NA and NB. The number of AA and BB molecules is twice equal to NA and NB.



Molecular weight control in linear step growth polymerization

Quantitative aspects: Let us consider different reactant systems used in step polymerization:

[Type 1]:

Polymerization of bi-functional monomer A-A and B-B group is in excess.

The numbers of functional groups **A and B** are given, respectively, by **N_A** and N_B. The number of **A-A and B-B** molecules is twice equal to **N_A and N_B.**

The stoichiometric ratio of two functional group is given by:

$$r = \frac{N_A}{N_B}, \leq 1 \qquad \ldots\ldots (1)$$

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$$r = \frac{N_A}{N_B}, \leq 1$$

So, the stoichiometric equation can be given as R is equal to NA over NB which is less than equal to 1. Now the total amount of monomer molecule is determined by NA plus NB over 2 or NA 1 plus 1 upon R over 2. Now this is this we can say the equation number 2. Now the fraction of unreacted functional group is usually given by 1 minus p and 1 minus rp. So, the total number of unreacted functional group can be represented as NA into 1 minus p and NB into 1 minus rp.

$\frac{N_A+N_B}{2}$ or $\frac{N_A(1+\frac{1}{r})}{2}$ ---- ②

$(1-p)$ and $(1-rp)$

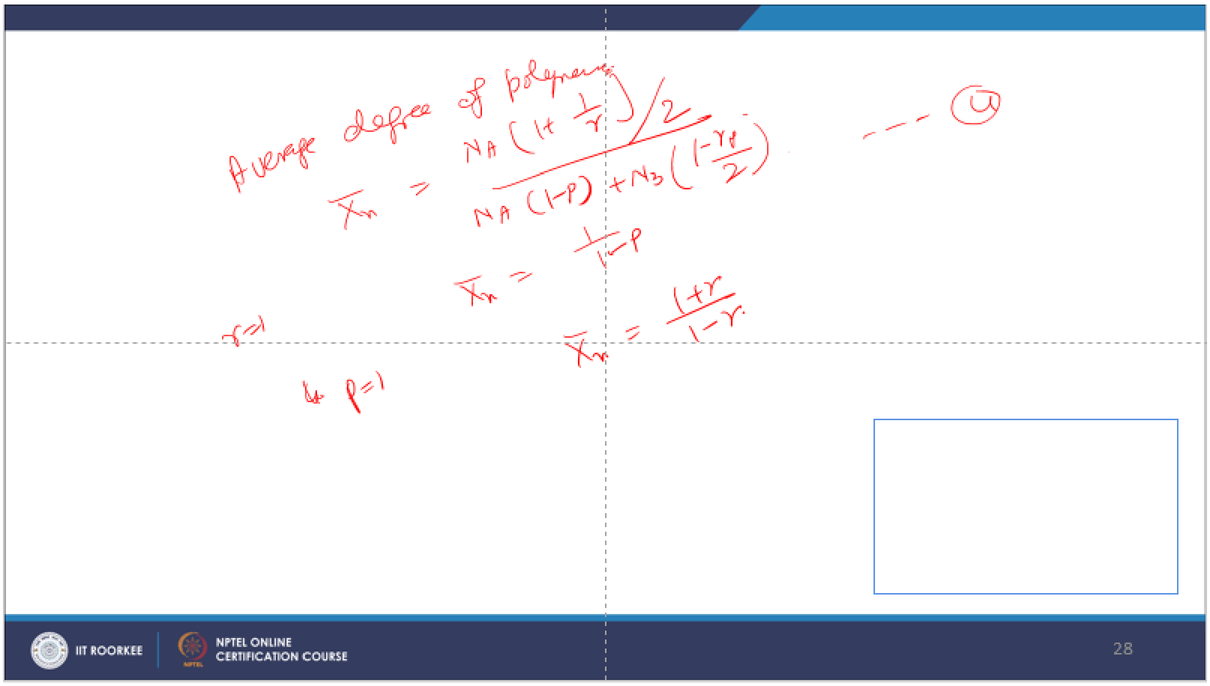
$N_A(1-p)$ & $N_B(1-rp)$

$\frac{N_A(1-p)+N_B(1-rp)}{2}$ ---- ③

So, the total amount of polymer molecules they are determined by NA into 1 minus p plus NB into 1 minus rp over 2. Let us say this is equation number 3. So, the total number of average degrees of polymerization dp and which is represented as Xn bar is given by the total number of molecules initially present over total number of polymer molecules. So, we can represent like average degree of polymerization polymerization. This is given by bar Xn is equal to NA into 1 plus 1 over R over 2 NA into 1 minus p plus NB into 1 minus rp over 2.

Molecular weight control in linear step growth polymerization

- **The total number of average degree of polymerization** (DP) ($\bar{X}_n$)is given by : **Total number of molecule initially present/Total number of polymer molecule**.



Average degree of polymeri

$$\bar{X}_n = \frac{N_A\left(1+\frac{1}{r}\right)/2}{N_A(1-p)+N_B\left(1-\frac{rp}{2}\right)} \quad --- \text{④}$$

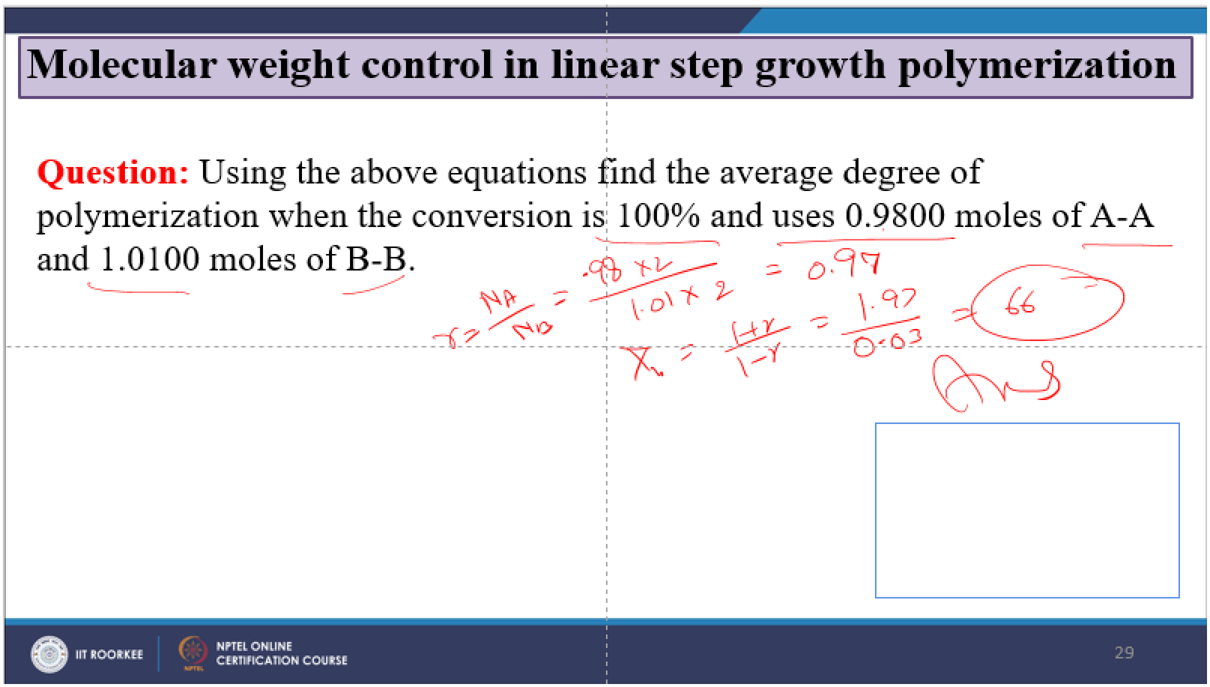
$r=1$

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

& $p=1$

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

This is let us say this is equation 4. So, when R is equal to 1 then bar Xn is equal to 1 over 1 minus p and when p is equal to 1 then bar Xn is equal to 1 plus R over 1 minus r. Let us take an example.



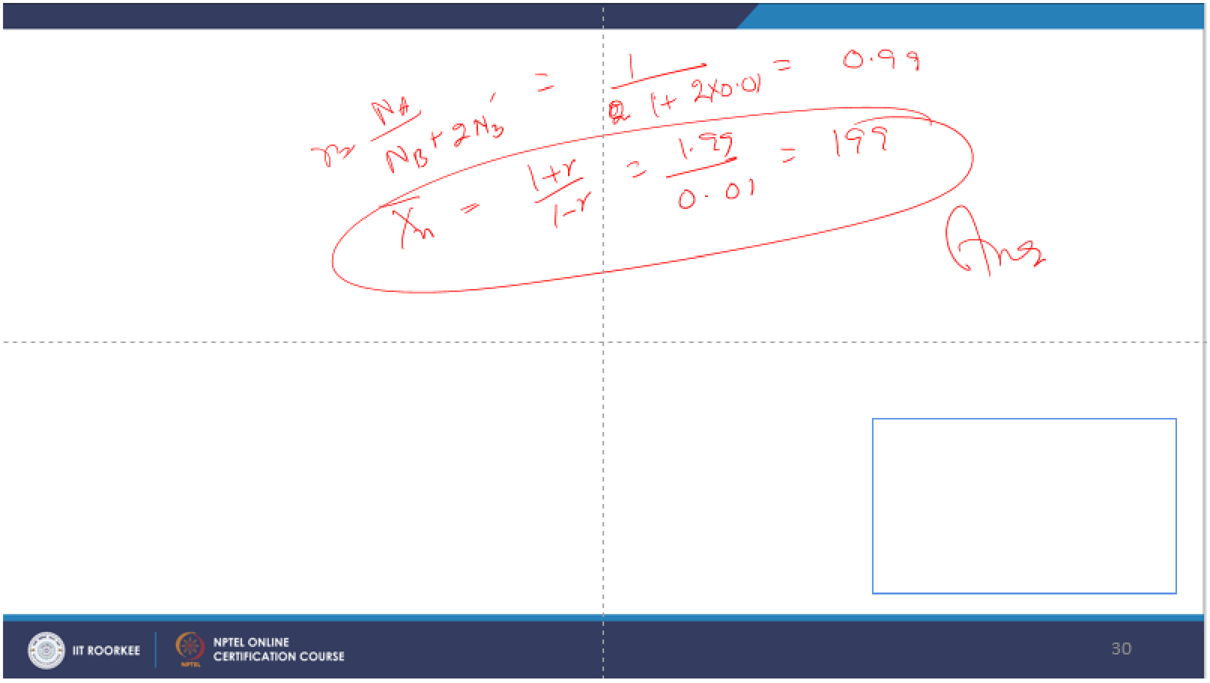
Molecular weight control in linear step growth polymerization

Question: Using the above equations find the average degree of polymerization when the conversion is 100% and uses 0.9800 moles of A-A and 1.0100 moles of B-B.

$r = \frac{N_A}{N_B} = \frac{.98\times2}{1.01\times2} = 0.97$

$X_n = \frac{1+r}{1-r} = \frac{1.97}{0.03} = \boxed{66}$

Ans



$r = \frac{N_A}{N_B + 2N_B'} = \frac{1}{1+2\times0.01} = 0.99$

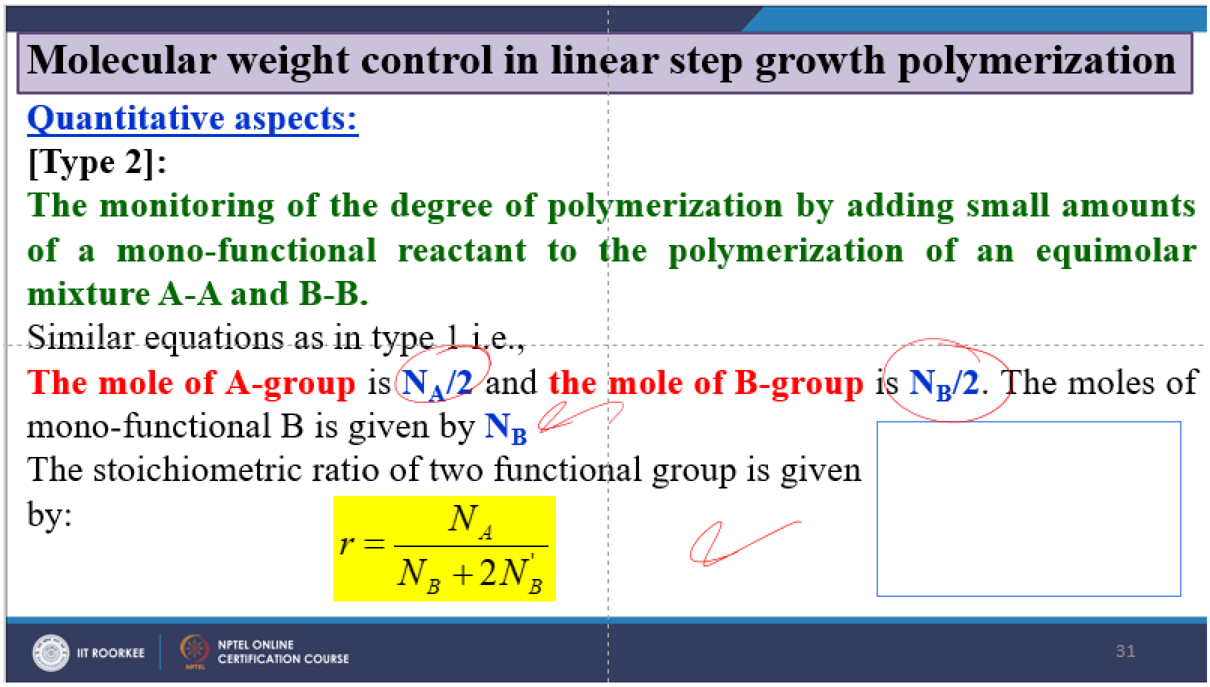
$X_n = \frac{1+r}{1-r} = \frac{1.99}{0.01} = 199$

Ans

$$r = \frac{N_A}{N_B} = \frac{0.98\times2}{1.01\times2} = 0.97$$

$$\overline{X_n} = \frac{1+r}{1-r} = \frac{1.97}{0.03} = 66 \text{ (answer)}$$

Now using this previous equation find the average degree of polymerization when the conversion is 100 percent and uses 0.98 moles of AA and 1.0100 moles of BB. So, it is quite simple like we derived this formula R is equal to NA over NB. Now here this is given as 0.98 this is for NA so 0.98 into 2 over 1.01 into 2 and this comes out to be 0.97. So, bar Xn is equal to 1 plus R plus over 1 minus R which is 1.97 over 0.03 which is 66 this is our answer. So, this is I mean you can say that typical example that how we can utilize this thing. Now another thing that which like to reflect and that is R is equal to NA over NB plus 2 dash NB 1 over 1 plus 2 into 0.01 this is comes out to be 0.99 and bar Xn is equal to 1 plus R over 1 minus R 1.99 into 0.01 that is 199 this is our answer.



Molecular weight control in linear step growth polymerization

Quantitative aspects:

[Type 2]:

The monitoring of the degree of polymerization by adding small amounts of a mono-functional reactant to the polymerization of an equimolar mixture A-A and B-B.

Similar equations as in type 1 i.e.,

The mole of A-group is $N_A/2$ and **the mole of B-group** is $N_B/2$. The moles of mono-functional B is given by N_B

The stoichiometric ratio of two functional group is given by:

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

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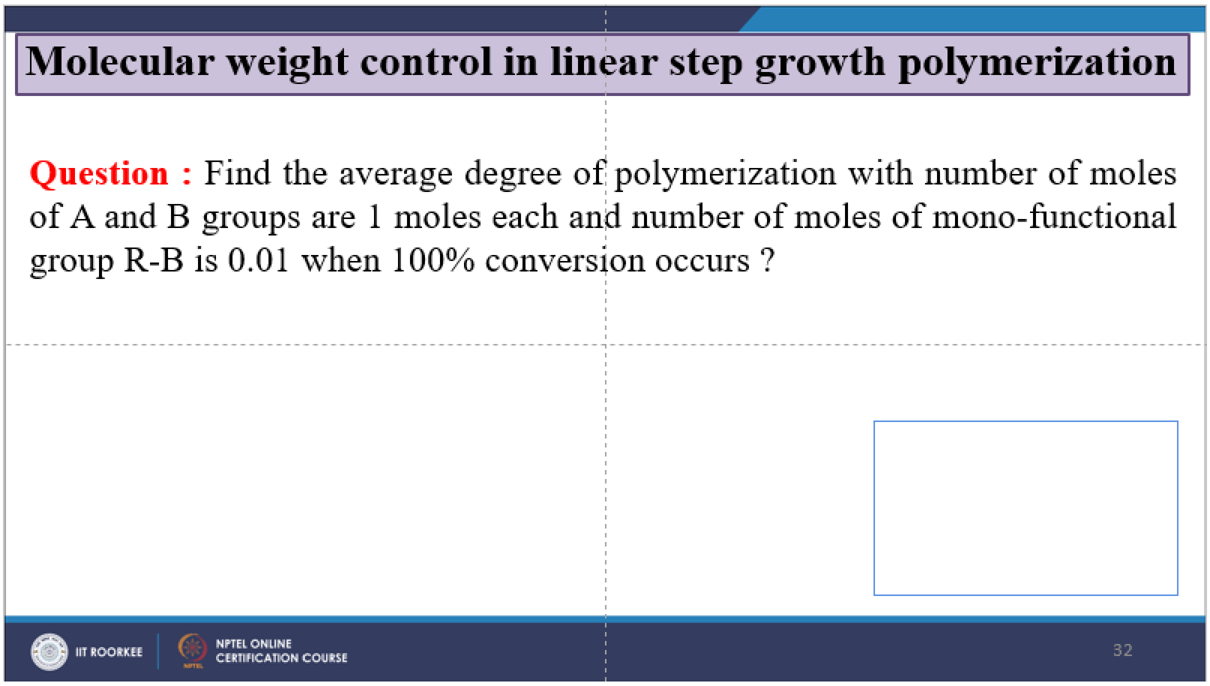
Now let us talk about the quantitative aspect that is type 2 the monitoring of the degree of polymerization by adding a small amount of mono functional reactant to the polymerization of an equimolar mixture AA and BB. So, this type of similar equation type 1 the mole of A group that is given by NA over 2 and the mole of B group that is NB over 2 the moles of mono functional B is given by NB. So, the stoichiometric ratio of 2 functional group can be given like R is equal to NA over NB plus 2 NB.

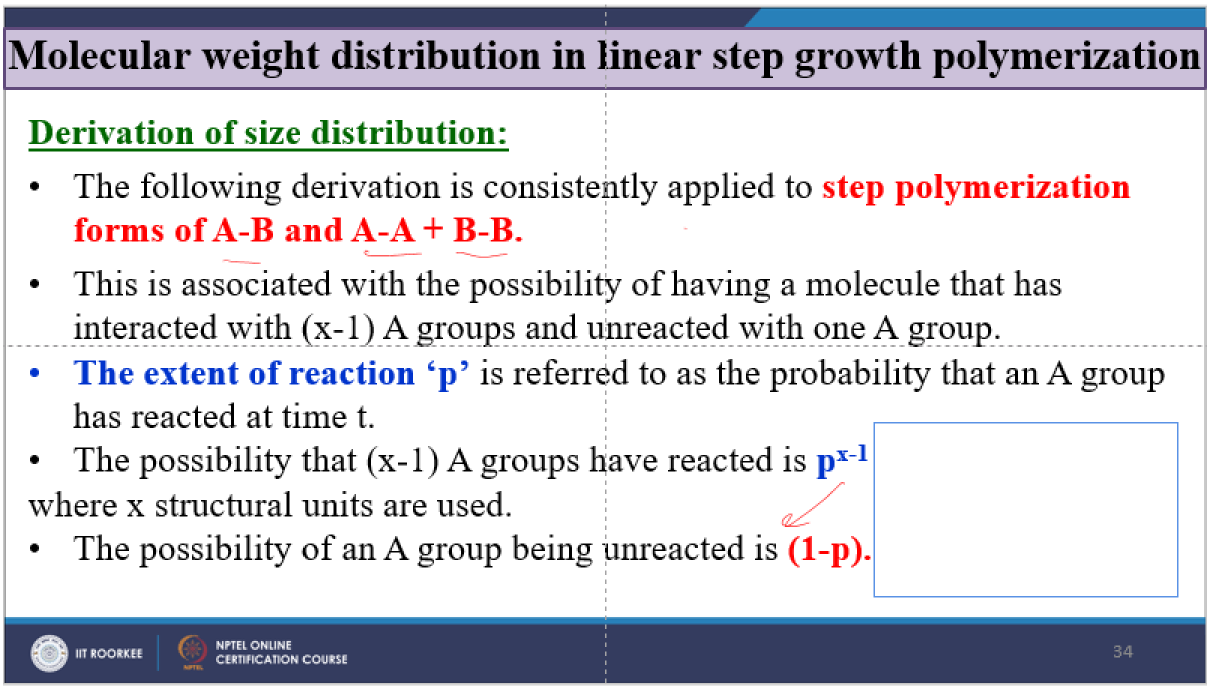


Molecular weight control in linear step growth polymerization

Question : Find the average degree of polymerization with number of moles of A and B groups are 1 moles each and number of moles of mono-functional group R-B is 0.01 when 100% conversion occurs ?

Now here you we need to calculate the average degree of polymerization with the number of moles of A and B are given and each of the number of the moles of mono functional group RB is 0.01 when a 100 percent conversion occurs. So, I am leaving this particular example this particular question for your as a tutorial form. Now the polymerization, polymerization is a combination of polymer molecule of varying molecular weight. Chains with the wide distribution of chain length they are found in a standard synthetic polymer sample. The distribution is rarely symmetric and involves the several high molecular weight molecules. So particularly polymerization parameters they are influenced the specific width of the distribution of molecular weight.

For instance, if it the polymerization of a certain olefins this can lead to a substantial molecular weight distribution. PJ Flory that he derived the molecular weight distribution through a statistical approach focus on equal reactivity of the functional groups. This particular derivation is consistently like if you derive the size distribution derivation this is consistently applied to the step polymerization of A, B and AA and BB. This is associated with the possibility of having a molecule that has interacted with X minus 1 A group and unreacted with 1 A group. The extent of reaction P is referred to as the probability that an A group has reacted at time t and the possibility that X minus 1 A group have reacted is P to the power X minus 1 where X is a structural unit.

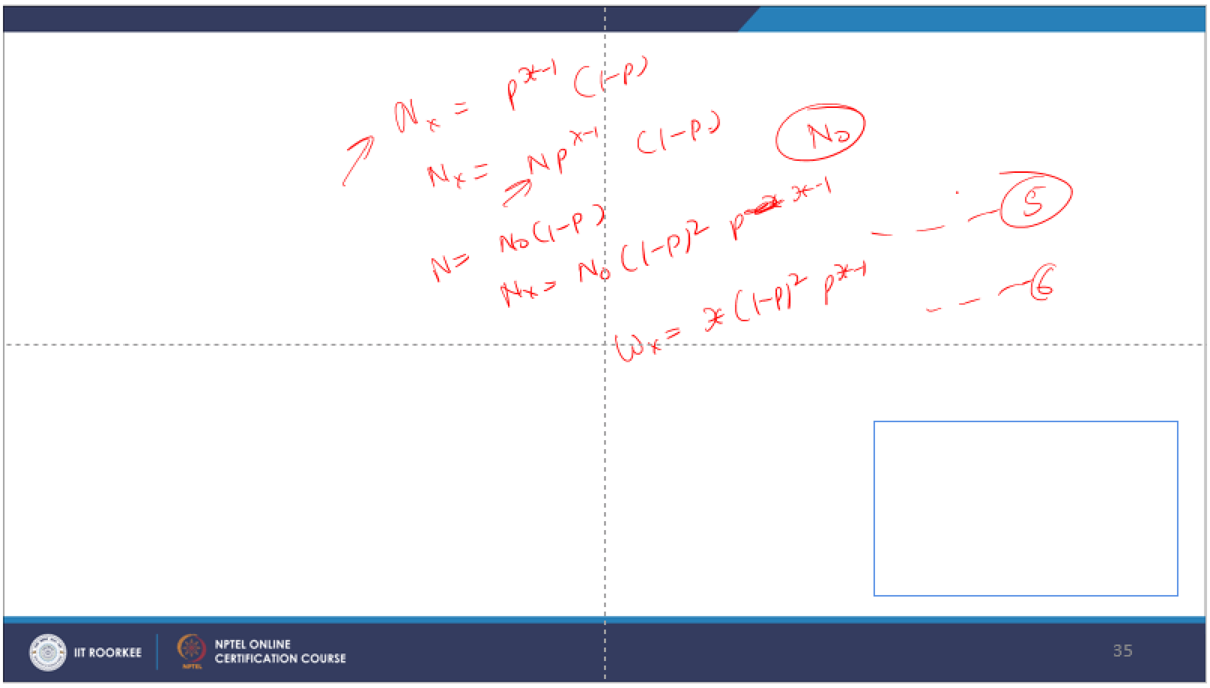


Molecular weight distribution in linear step growth polymerization

Derivation of size distribution:

- The following derivation is consistently applied to **step polymerization forms of A-B and A-A + B-B.**
- This is associated with the possibility of having a molecule that has interacted with (x-1) A groups and unreacted with one A group.
- **The extent of reaction 'p'** is referred to as the probability that an A group has reacted at time t.
- The possibility that (x-1) A groups have reacted is $\mathbf{p^{x-1}}$ where x structural units are used.
- The possibility of an A group being unreacted is **(1-p).**

Now the possibility of an A group being unreacted is 1 minus P. So, this can be represented as n X is equal to P to the power X minus 1 1 minus P and n X this is associated with the mole or a number fraction of X-mers in the polymeric mixture. So, n X is equal to n P X minus 1 into 1 minus P. Now this n is associated with the number of polymer molecules. So, the overall amount of structural unit initially present is n naught.



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

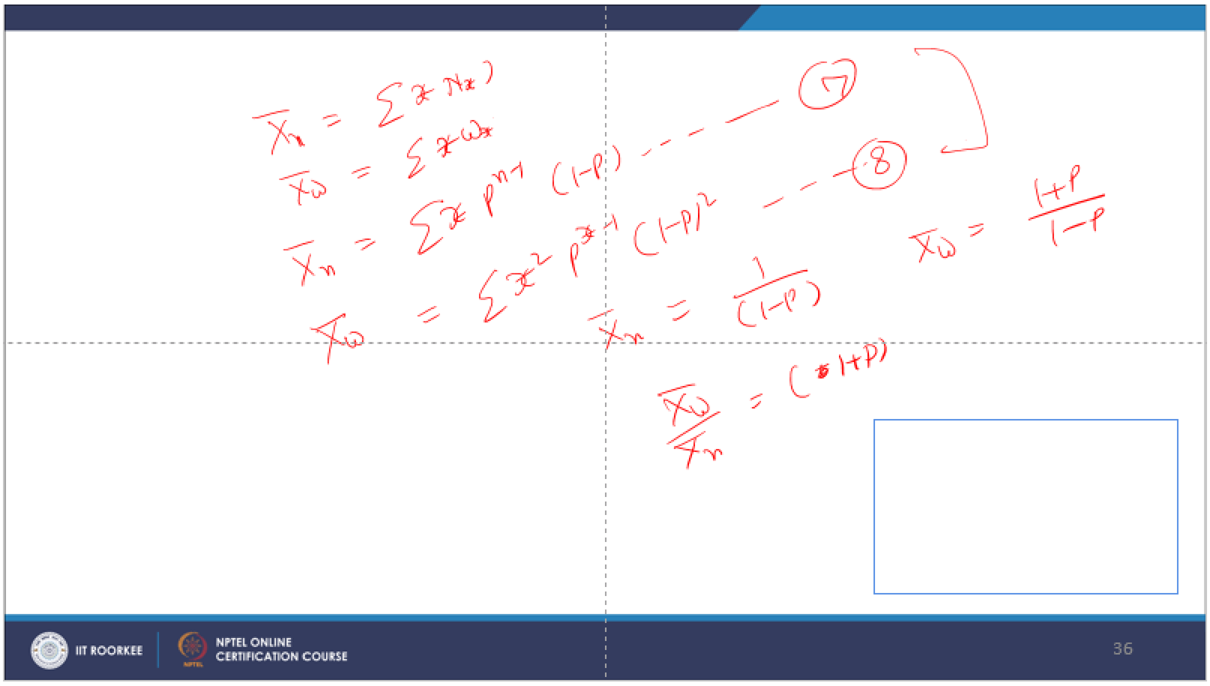
$N_x = N p^{x-1}(1-p)$ $\quad \boxed{N_0}$

$N = N_0(1-p)$

$N_x = N_0(1-p)^2 p^{\cancel{x}\,x-1}$ ---- ⑤

$W_x = x(1-p)^2 p^{x-1}$ ---- ⑥

So, n is equal to n naught into 1 minus P. Therefore, n X is equal to n naught into 1 minus P to the power 2 into P to the power X minus 1. This can be represented as equation number 5. Now the weight fraction W X of X-mers that is X structural unit can be given as W X is equal to X into 1 minus P to the power 2 P to the power X minus 1. This is equation number 6. Now the molecular weight of a number and weight average is given by bar X n is equal to summation X n X and bar X W is summation X W X.



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

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

$\bar{X}_n = \sum x p^{x-1} (1-p) \text{ - - - - } ⑦$

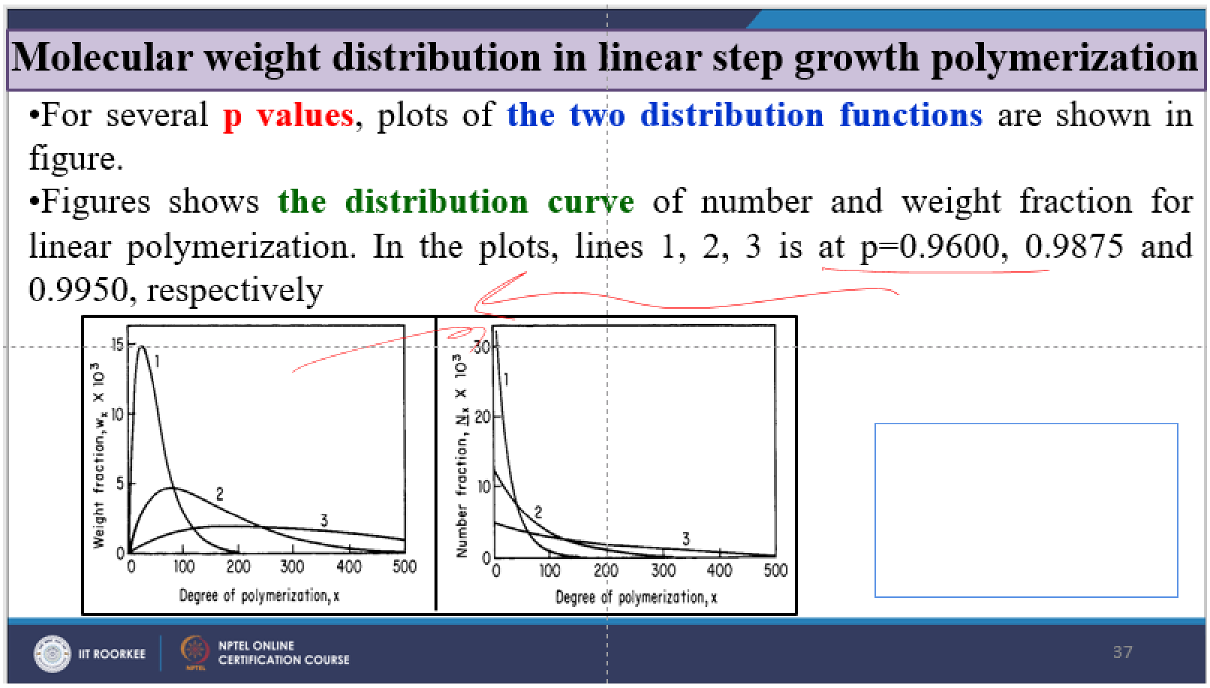
$\bar{X}_w = \sum x^2 p^{x-1} (1-p)^2 \text{ - - - } ⑧$

$\bar{X}_n = \frac{1}{(1-p)}$

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

$\frac{\bar{X}_w}{\bar{X}_n} = (1+p)$

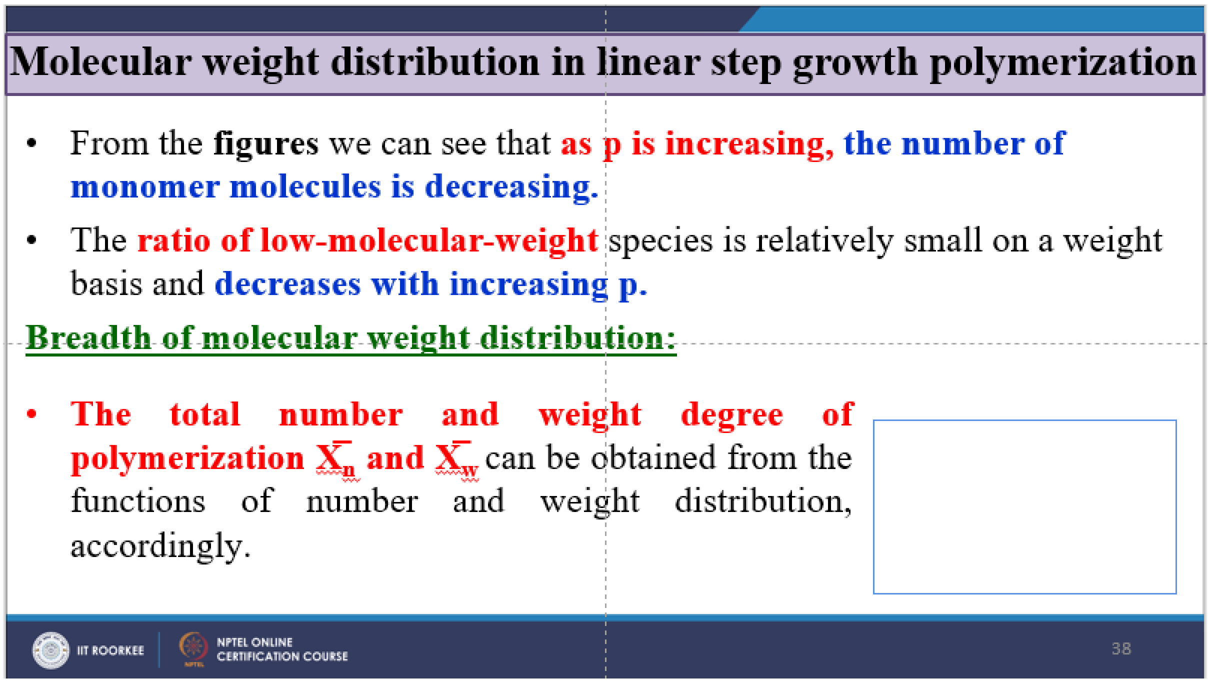
So, if you put the value of n X and W X from this the previous equation then the whole equation can become bar X n is equal to summation X 1 minus 1 into 1 minus P that can become the equation number 7 and bar X W is equal to summation X to the power 2 P to the power X minus 1 into 1 minus P square that is equation number 8. Now for several, now if we evaluate the equation 7 and 8 this can be X bar X n is equal to summation upon 1 minus P and bar X W is equal to 1 plus P plus 1 minus P. The breadth of the molecular weight distribution which is also referred as a polydispersity index or PDI this can be given as bar X W over bar X n equal to 1 plus P. Now for several P values of two distribution functions which are shown in these figures. These shows the distribution curve of number and weight fraction of linear polymerized polymers.



Molecular weight distribution in linear step growth polymerization

- For several **p values**, plots of **the two distribution functions** are shown in figure.
- Figures shows **the distribution curve** of number and weight fraction for linear polymerization. In the plots, lines 1, 2, 3 is at p=0.9600, 0.9875 and 0.9950, respectively

Now in these plots the line 1, 2, 3 here the P is equal to 0.96, 0.9875 and 0.9950 you can easily calculate. Now from this particular figure we can see that P as P is increasing the number of monomer molecule they are decreasing.



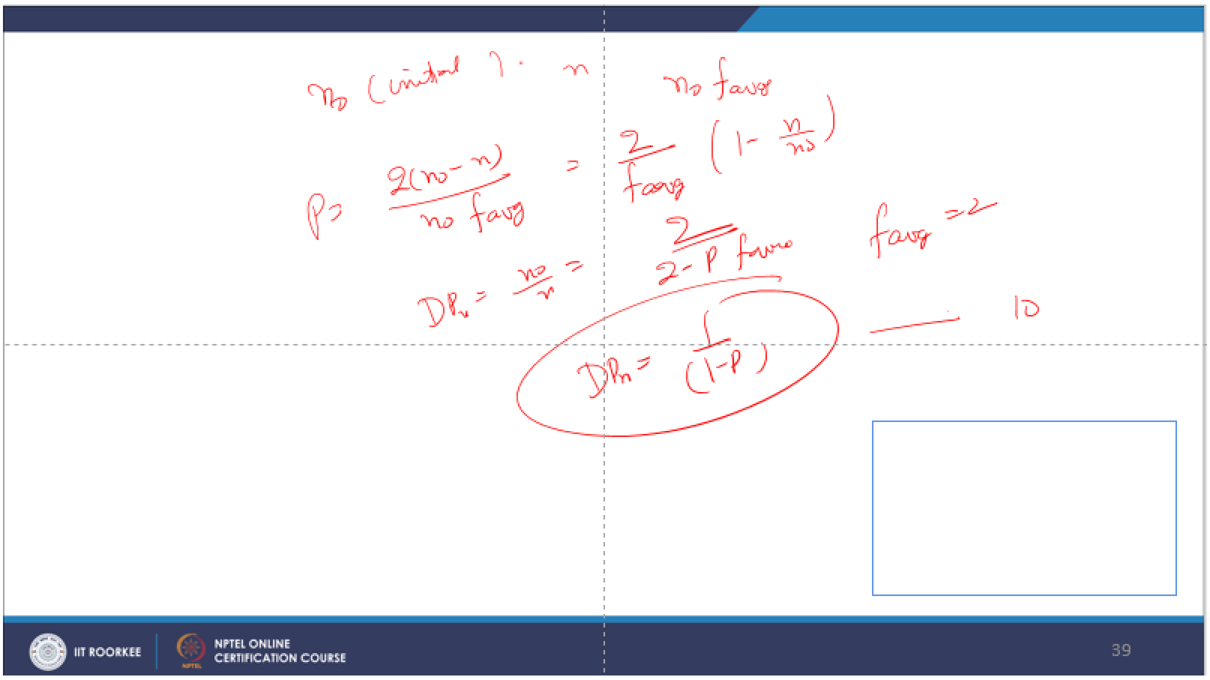
Molecular weight distribution in linear step growth polymerization

- From the **figures** we can see that **as p is increasing, the number of monomer molecules is decreasing.**
- The **ratio of low-molecular-weight** species is relatively small on a weight basis and **decreases with increasing p.**

Breadth of molecular weight distribution:

- **The total number and weight degree of polymerization $\bar{X}_n$ and $\bar{X}_w$** can be obtained from the functions of number and weight distribution, accordingly.

Now the ratio of the low molecular weight species is relatively small on the weight basis and decreases with increasing P. So, the breadth of molecular weight distribution the total number of total number and weight degree of polymerization bar X n and bar X W this can be obtained from the function of a number and weight distribution accordingly. Now if you see that the initial and total number of molecules is n naught and n this is the initial and n is after time t then n naught f average is the number of the initial function. Therefore, the fractional conversion is given by P is equal to 2 n naught minus n over n naught into f average and that is given by 2 1 minus n over n naught or d P naught is equal to n naught n which is 2 over 2 minus P f average. Now when f average is equal to 2 where there is a AB monomer then d P n is equal to 1 minus P this is our equation number 10.



n_0 (initial) . n $\quad n_0 f_{avg}$

$$P = \frac{2(n_0 - n)}{n_0 f_{avg}} = \frac{2}{f_{avg}}\left(1 - \frac{n}{n_0}\right)$$

$$DP_n = \frac{n_0}{n} = \frac{2}{2 - P f_{avg}}$$

$f_{avg} = 2$

$$\boxed{DP_n = \frac{1}{(1-P)}}$$

10

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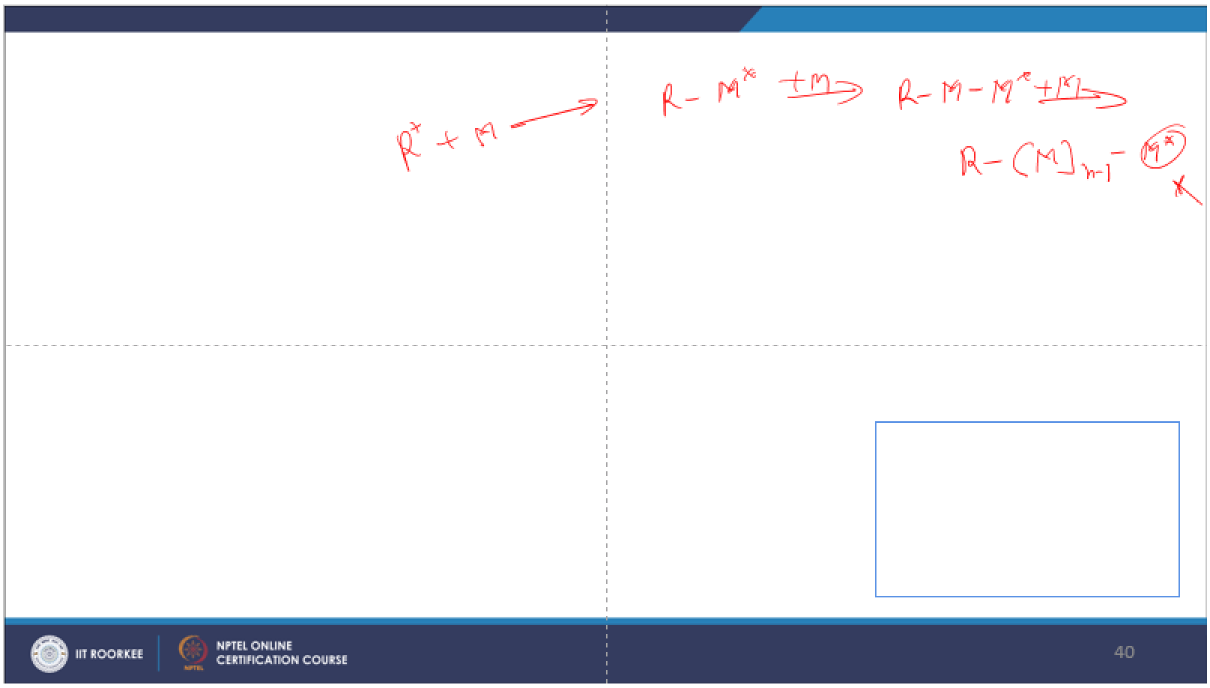

$$R^* + M \longrightarrow R-M^* \xrightarrow{+M} R-M-M^* \xrightarrow{+M} R-(M)_{n-1}-M^*$$

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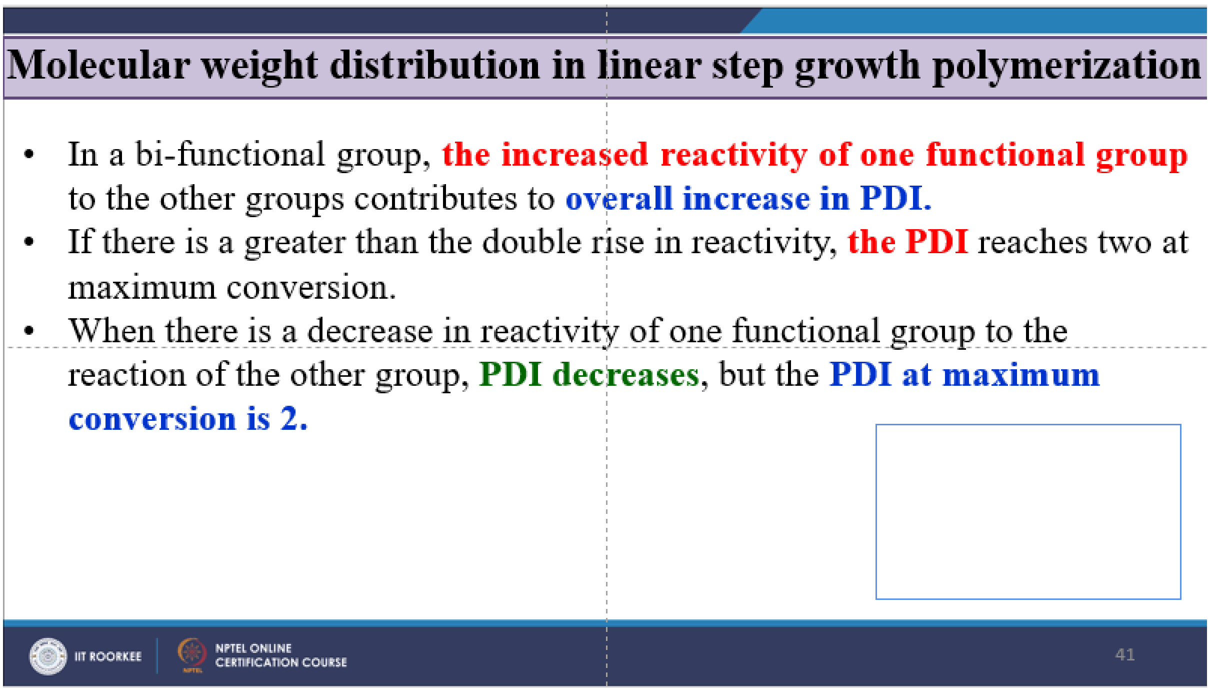
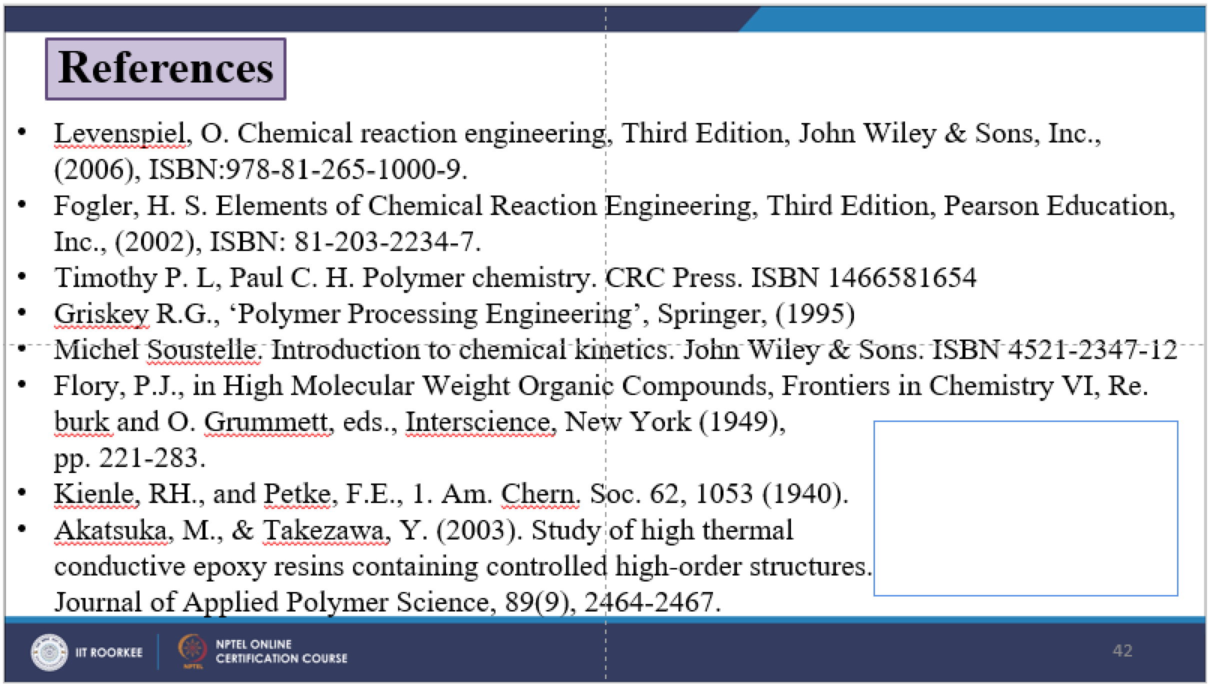
Now for sake of an example this can be given like this R m plus again monomer. So this the by this way the chain grows repeatedly. Now this is the chain again it can act as a proper functional group. So in bi-functional group the increased reactivity of one functional group to the other group contributes to overall increase in polydispersity index. If there is a greater than the double rise in the reactivity the PDI reaches 2 at maximum conversion.



Molecular weight distribution in linear step growth polymerization

- In a bi-functional group, **the increased reactivity of one functional group** to the other groups contributes to **overall increase in PDI.**
- If there is a greater than the double rise in reactivity, **the PDI** reaches two at maximum conversion.
- When there is a decrease in reactivity of one functional group to the reaction of the other group, **PDI decreases**, but the **PDI at maximum conversion is 2.**

When there is a decrease in the reactivity of one functional group to the reaction to the other group the polydispersity index increases but PDI at maximum conversion too. So dear friends in this particular aspect we discussed the PDI we discussed various reaction kinetics rate etc.



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For your convenience we have enlisted various references exhaustive list of references are here and you can go through if you need the further reading. Thank you very much. Thank you very much.