Polymer Reaction Engineering
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Lecture - 31
Step-Growth Polymerization – IV

Welcome to this lecture of Polymer Reaction Engineering. In this lecture, we will discuss about the molecular weight control in the linear polymerization system. Then we will discuss about the molecular weight distribution in linear and non-linear polymerization.

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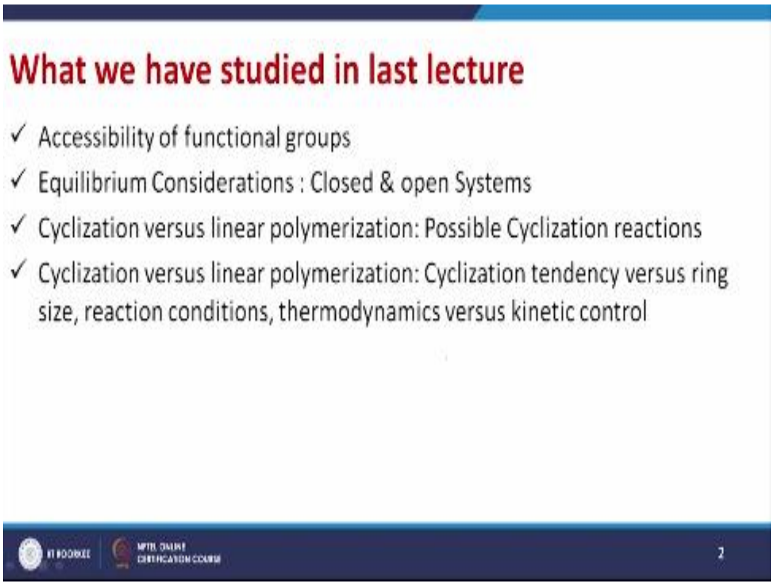

What we have studied in last lecture

- ✓ Accessibility of functional groups
- ✓ Equilibrium Considerations : Closed & open Systems
- ✓ Cyclization versus linear polymerization: Possible Cyclization reactions
- ✓ Cyclization versus linear polymerization: Cyclization tendency versus ring size, reaction conditions, thermodynamics versus kinetic control

Now, before we start the discussion, let us have a look at that what we have studied in the last lecture. We discussed about the accessibility of various functional groups. We had the equilibrium consideration under the edges of closed and open system. We discussed about the cyclization versus linear polymerization with the possible cyclization reactions.

We gave major emphasis towards the cyclization versus linear polymerization under the head of cyclization tendency versus ring size, reaction conditions, thermodynamic versus kinetic control.

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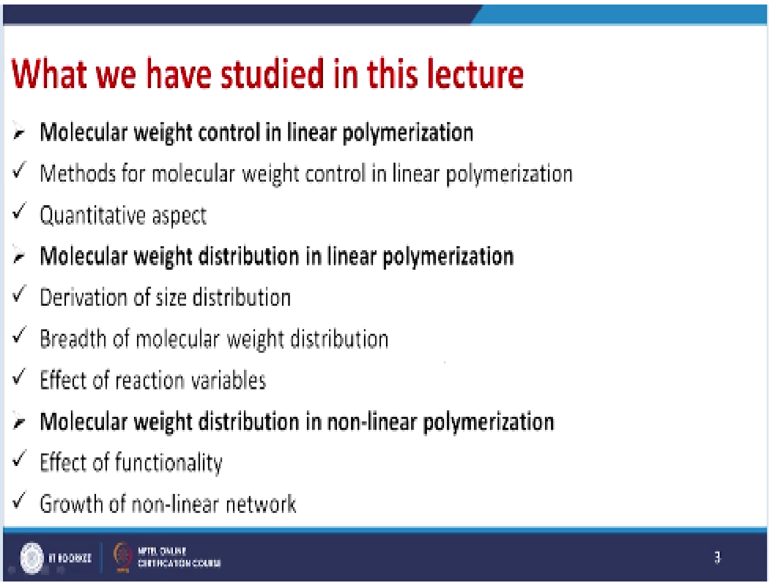

What we have studied in this lecture

- **Molecular weight control in linear polymerization**
  - ✓ Methods for molecular weight control in linear polymerization
  - ✓ Quantitative aspect
- **Molecular weight distribution in linear polymerization**
  - ✓ Derivation of size distribution
  - ✓ Breadth of molecular weight distribution
  - ✓ Effect of reaction variables
- **Molecular weight distribution in non-linear polymerization**
  - ✓ Effect of functionality
  - ✓ Growth of non-linear network

In this particular lecture, we are going to discuss the molecular weight control in linear polymerization methodology. And this particular head, we will discuss about the methods through which we can control the molecular weight in linear polymerization. We will give the quantitative aspect to those approaches, then we will have a discussion about the molecule of a distribution in linear polymerization with respect to the derivation in the size distribution.

Breadth of molecular weight distribution, then we will discuss about the effect of reaction variables. Apart from this, we will discuss about the molecular weight distribution in non-linear polymerization, especially under the head of effect of functionality and growth of non-linear network. Now, let us start with the concept of molecular weight control in linear polymerization.

So, usually in polymer synthesis, one is ideally interested in acquiring a particular molecular weight product as the characteristics of the polymer being developed. They are highly dependent on the molecular weight and that is why we always talk about the molecular weight distribution, number weight molecular weight, weight average molecular weight, etcetera. Then these molecular weights are great or less than the ideal weight; they are equally unwanted.

So, there are many influencing factors such as reaction temperature, monomer concentration, close type of system or open type of a system, effect of catalysts, etcetera. So, these are the various things those who are participating in the molecular weight control of those linear polymerization. Now, let us have a discussion about the methods for which the molecular weight can be controlled in linear polymerization.

Now, one way is that by quenching the reaction that is by the cooling at the required time, so, that the temperature maintained at the desired molecular weight you can achieve. Now, sometimes, this particular methodology offers a disadvantage. Now, the advantage is that the polymer achieved is unstable as the resulting heating contributes to the variation in molecular weight, since the functional group at the end of the polymer molecule can further react and this is sometimes a disadvantage.

And furthermore, another thing is that that whenever you quench the reaction mass in that case, the polymer molecule may not have sufficiently strong with respect to the mechanical approach and that type of thing is essentially required in the suspension polymerization type of thing. So, that is why this is a disadvantage. Now, another method is that by increasing one reactant over other, the polymerization, then continue to a stage at which one reactant is fully used up.

And all the end of the chain have the same functional group, the group of which is usually in surplus. The example of this particular type of thing is that the polymerization of an excess di-amine with di-acid produces the polyamide with amine end group in the unavailability of the di-acid for the continuous polymerization.

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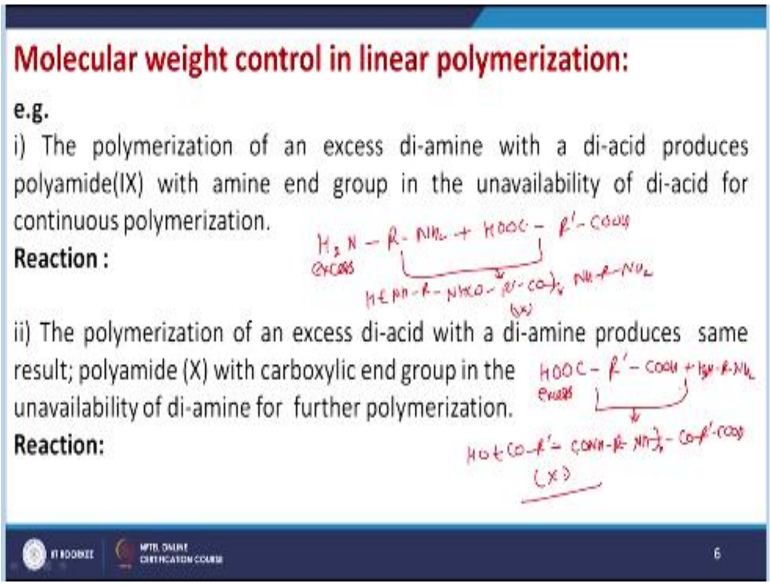

Molecular weight control in linear polymerization:

e.g.

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 :

$$\underset{excess}{H_2N} - R - NH_2 + HOOC - R' - COOH \rightarrow \underset{(IX)}{H\!-\![NH-R-NHCO-R'-CO]_n}-NH-R-NH_2$$

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:

$$\underset{excess}{HOOC} - R' - COOH + H_2N-R-NH_2 \rightarrow HO\!-\![CO-R'-CONH-R-NH]_n-CO-R'-COOH$$

(X)

Now, let us have a look about this one that is

$$\underset{excess}{H_2N} - R - NH_2 + HOOC - R' - COOH \longrightarrow$$

that is this one is in excess. So, this gives you the

$$H-(NH-R-NHCO-R'-CO)_x-NH-R-NH_2$$

Now, the polymerization of an excess di-acid with di-amine produces same result that is the polyamide with a carboxylic end group in the unavailability of di-amine for the further polymerization. Now, this can be represented like this at

$\underset{excess}{HOOC}-\ R'-COOH+\ H_2N-R-NH_2 \xrightarrow{\hspace{4em}}$ that is in excess of COO R

$$HO-(CO-R'-CONH-R-NH)_x-CO-R'-COOH$$

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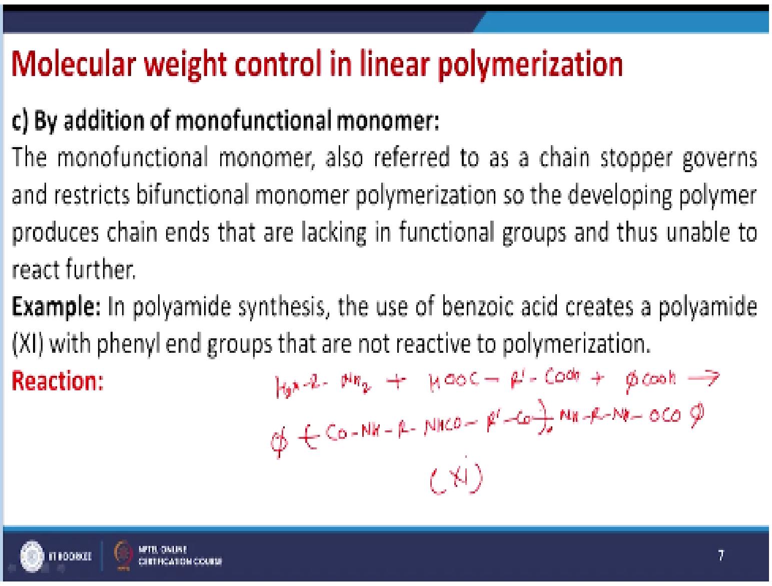

Molecular weight control in linear polymerization

c) By addition of monofunctional monomer:

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

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

Reaction: $H_2N-R-NH_2 + HOOC-R'-COOH + \phi COOH \rightarrow$

$\phi \left(CO-NH-R-NHCO-R'-CO \right)_x NH-R-NH-OCO\,\phi$

(XI)

Now, sometimes by addition of mono functional monomer, also referred to as a chain stopper governs and restricts bi-functional monomer polymerization. So, that developing polymer produces the chain and that are lacking in functional group and thus, unable to react further. Let us have an example like the polyamide synthesis, the use of benzoic acid creates a polyamide 11 with the phenyl end group that are not reactive to polymerization.

Now, it can be represented like this

$H_2N-R-NH_2+\ HOOC-R'-COOH+\ ph-COOH \xrightarrow{\hspace{4em}}$

$$ph-(CO-NH-R-NHCO-R'-CO)_x-NH-R-OCO-ph$$

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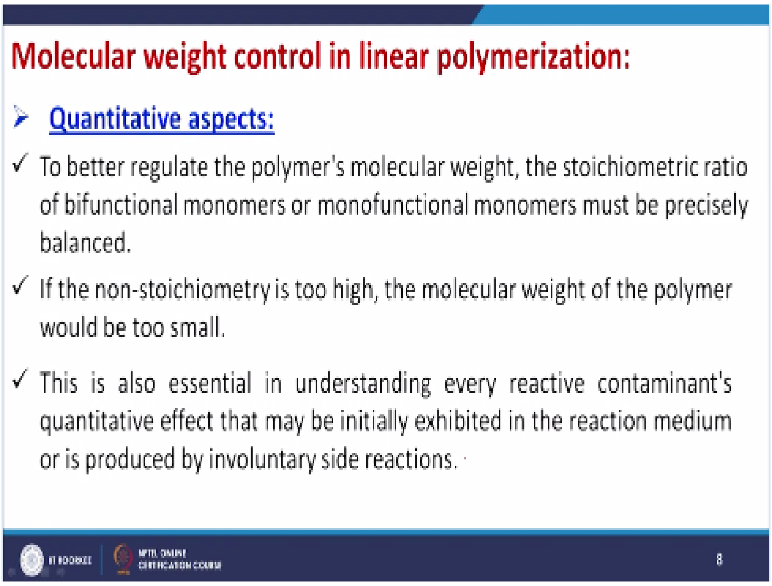

Molecular weight control in linear polymerization:

- **Quantitative aspects:**

✓ To better regulate the polymer's molecular weight, the stoichiometric ratio of bifunctional monomers or monofunctional monomers must be precisely balanced.

✓ If the non-stoichiometry is too high, the molecular weight of the polymer would be too small.

✓ This is also essential in understanding every reactive contaminant's quantitative effect that may be initially exhibited in the reaction medium or is produced by involuntary side reactions.

Now, another approach is based on the quantitative aspect. Now, to better regulate the polymers molecular weight, the stoichiometry ratio of bi-functional monomer or mono functional monomer must be precisely balanced. So, by this way, you can regulate the things. Now, if a non-stoichiometry is too high, the molecular weight of polymer would be too small.

Now, this is also essential in understanding every reactive contaminant’s quantitatively effects that may be initially exhibit in the reaction medium or is produced by involuntarily side reactions. Let us consider the different reaction system used in the polymerization. So, the first type of this one is that the polymerization of bi-functional monomer A-A and B-B. Where B-B group, is in excess.

So, the number of functional groups A and B usually, they are given and they are respectively given by the N_A and N_B. The number of A-A and B-B molecules is twice equal to N_A and N_B.

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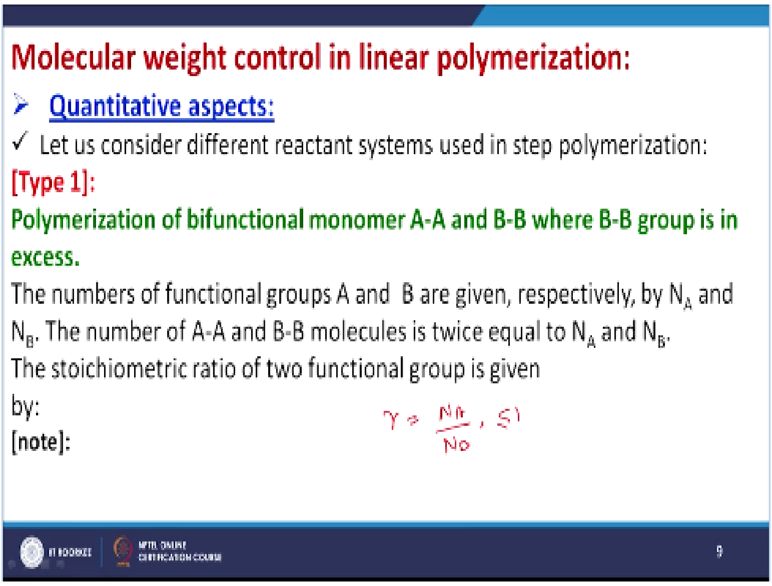

Molecular weight control in linear polymerization:

- **Quantitative aspects:**

✓ Let us consider different reactant systems used in step polymerization:

[Type 1]:

Polymerization of bifunctional monomer A-A and B-B where 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:

[note]:

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

So, the stoichiometry ratio of two functional group is given by

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

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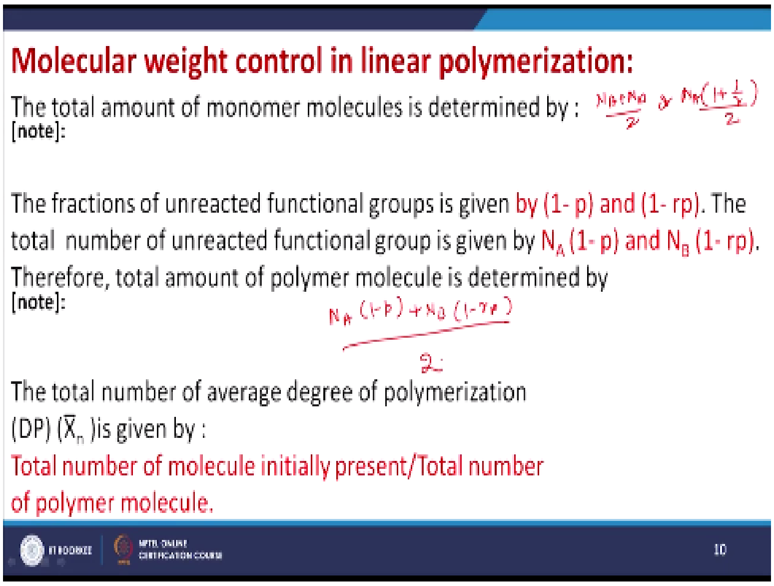

Molecular weight control in linear polymerization:

The total amount of monomer molecules is determined by : $\frac{N_A+N_B}{2}$ or $\frac{N_A(1+\frac{1}{r})}{2}$

[note]:

The fractions of unreacted functional groups is given by (1- p) and (1- rp). The total number of unreacted functional group is given by N_A (1- p) and N_B (1- rp).

Therefore, total amount of polymer molecule is determined by

[note]:

$$\frac{N_A(1-p)+N_B(1-rp)}{2}$$

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.

Now, the total amount of a monomer molecule is determined by $\frac{N_A + N_B}{2}$ or $\frac{N_A\left(1+\frac{1}{r}\right)}{2}$

So, the fraction of un-reacted functional group is given by 1 – p and 1 – rp, the total number of un-reacted functional group is usually given by $N_A(1 – p)$ and $N_B (1 – rp)$. So, therefore, the total amount of polymer molecule is determined by

$$\frac{N_A(1-p) + N_B(1-rp)}{2}$$

The total number of average degree of polymerization $(DP)\ \overline{Xn}$ action is usually given by the total number of molecules initially present divided by the total number of polymer molecule.

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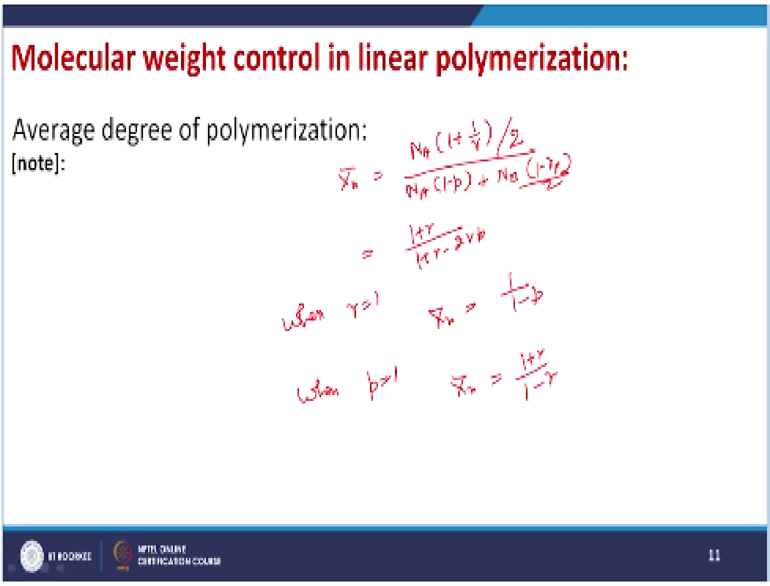

Molecular weight control in linear polymerization:

Average degree of polymerization:

[note]:

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

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

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

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

So, we can represent mathematically as by

$$\overline{X_n} = \frac{\frac{N_A\left(1+\frac{1}{r}\right)}{2}}{N_A(1-p) + \frac{N_B(1-rp)}{2}} = \frac{1+r}{1+r-2rp}$$

When; r = 1

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

When; p=1

$$\overline{X_n} = \frac{1+r}{1-r}$$

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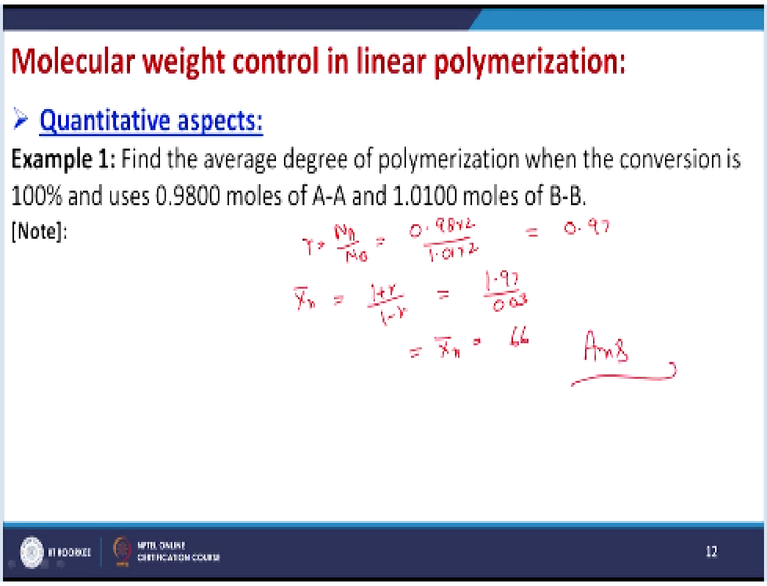

Molecular weight control in linear polymerization:

- **Quantitative aspects:**

Example 1: 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.

[Note]:

$$r = \frac{N_A}{N_B} = \frac{0.98 \times 2}{1.01 \times 2} = 0.97$$

$$\bar{X}_n = \frac{1+r}{1-r} = \frac{1.97}{0.03}$$

$$\Rightarrow \bar{X}_n = 66$$

Ans

Now, let us take one example that is here, you need to find the average degree of polymerization when the conversion is 100% and uses 0.98 moles of A-A and 1.0100 moles of B-B.

So, we know, let us solve this particular thing. So, you know that

$$r = \frac{N_A}{N_B} = \frac{0.98 \times 2}{1.01 \times 2} = 0.97$$

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

and that is the answer.

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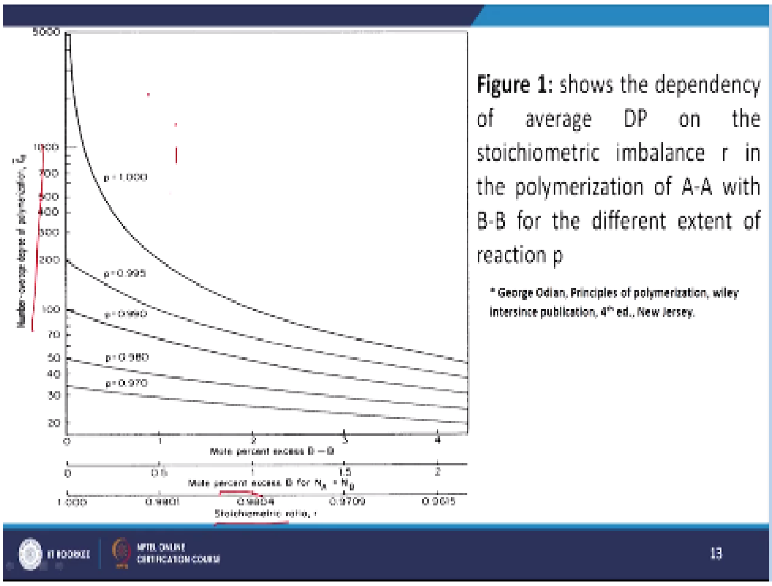

Figure 1: shows the dependency of average DP on the stoichiometric imbalance r in the polymerization of A-A with B-B for the different extent of reaction p

* George Odian, Principles of polymerization, wiley intersince publication, 4th ed., New Jersey.

So, you can see here that this particular figure shows the dependency of average degree of polymerization on the stiochiometry imbalance are in the polymerization of A-A and with the B-B for the different extent of a reaction. So, you can see here the stiochiometry ratio mole percent and then there is the number average degree of polymerization. So, you see that the variation of this p correspond to the different values.

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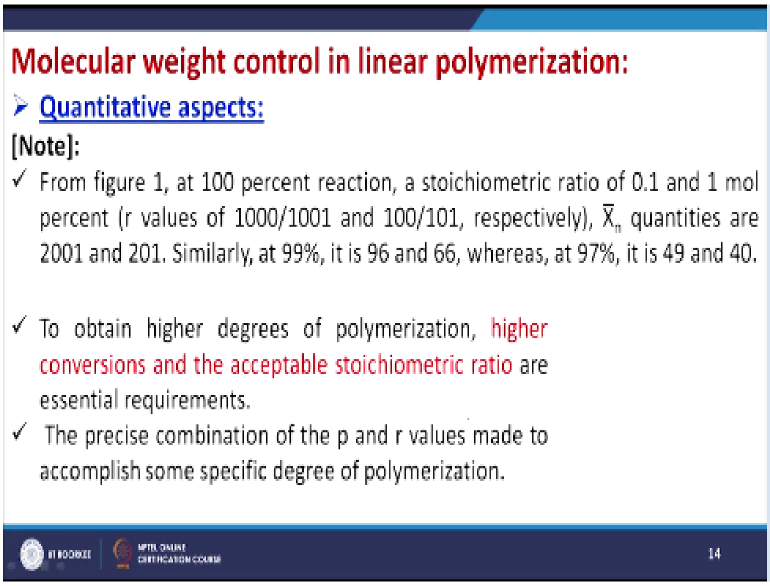

Molecular weight control in linear polymerization:

➢ Quantitative aspects:

[Note]:

✓ From figure 1, at 100 percent reaction, a stoichiometric ratio of 0.1 and 1 mol percent (r values of 1000/1001 and 100/101, respectively), $\bar{X}_n$ quantities are 2001 and 201. Similarly, at 99%, it is 96 and 66, whereas, at 97%, it is 49 and 40.

✓ To obtain higher degrees of polymerization, higher conversions and the acceptable stoichiometric ratio are essential requirements.

✓ The precise combination of the p and r values made to accomplish some specific degree of polymerization.

Let us have a look about the quantitative approach again. Now, if you see the figure 1 that is represented in the previous slide that 100% reaction, stiochiometry ratio of point 1 and 1 mole percent if r values of 1000 / 1001 and 100 / 101 respectively, the bar X n quantities are 2001 and 201. Similarly, at 99%, it is 96 and 66. Whereas at 97%, it is 49 and 40.

Now, to obtain the higher degree of polymerization, higher conversions and the acceptable stiochiometry ratios are always having an essential requirement. The precise combination of p and r values made to accomplish some specific degree of polymerization. Now, let us have a look about that type 2 type of quantitative aspect. Now, the monitoring of degree of polymerization by addition of a small amount of a mono function reactant to the polymerization of an equimolar mixture A-A and B-B.

So, similarly, if we talk about the equations, which we discussed in type 1 type of approach, the mole of A group is $N_A / 2$ and the mole of B group is $N_B / 2$

So, the moles of monofunctional B is given by N_B'. The stiochiometry ratio of two functional group is usually given by

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

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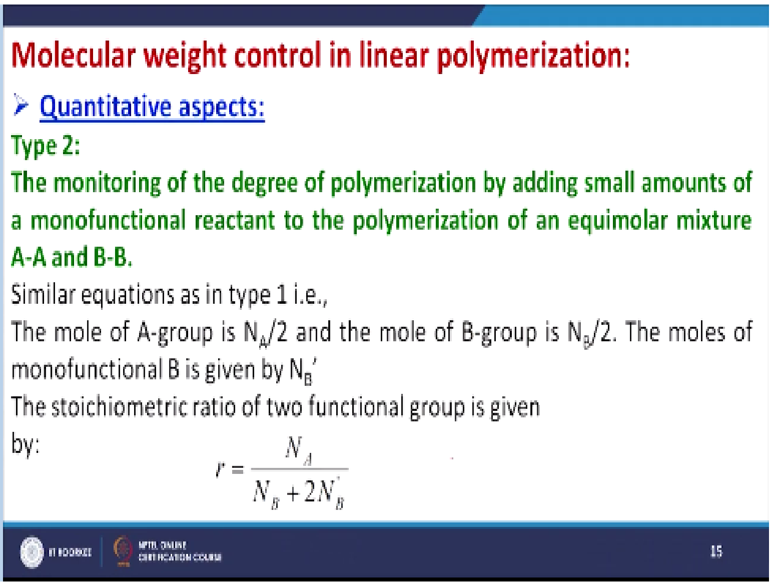

Molecular weight control in linear polymerization:

- **Quantitative aspects:**

Type 2:

The monitoring of the degree of polymerization by adding small amounts of a monofunctional 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 monofunctional 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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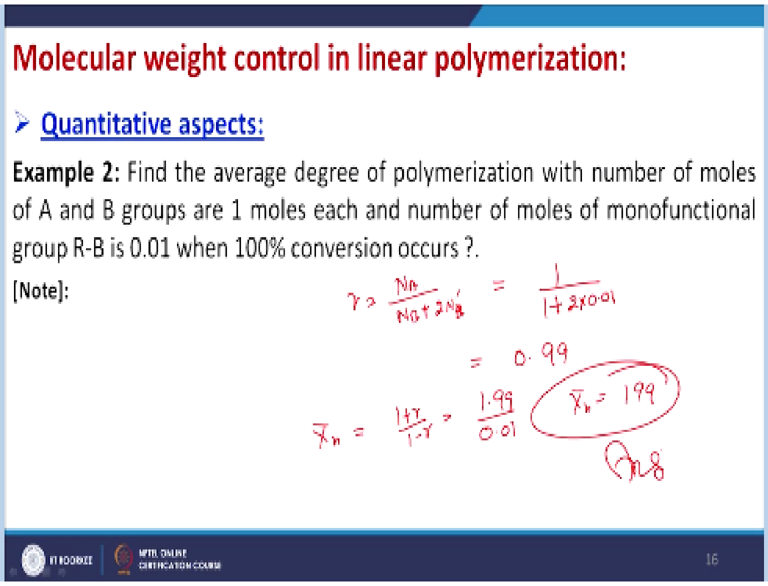

Molecular weight control in linear polymerization:

- **Quantitative aspects:**

Example 2: Find the average degree of polymerization with number of moles of A and B groups are 1 moles each and number of moles of monofunctional group R-B is 0.01 when 100% conversion occurs ?.

[Note]:

$$r = \frac{N_A}{N_B + 2N_B'} = \frac{1}{1+2\times 0.01}$$

$$= 0.99$$

$$\overline{X}_n = \frac{1+r}{1-r} = \frac{1.99}{0.01} \quad \boxed{\overline{X}_n = 199}$$

Ans

Now, let us have another example to cater the need of this type 2 system. Now, here, you need to find the average degree of polymerization with number of moles of A and B group. They are one mole in each number and the number of moles of mono functional group rp is 0.01 where 100% conversion occurs. So, you need to find the average degree of polymerization. Now, see here, we are having

$$r = \frac{N_A}{N_B + 2N_B'} = \frac{1}{1 + 2 \times 0.01} = 0.99$$

as per the previous equation which we discussed over here.

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

that is my answer.

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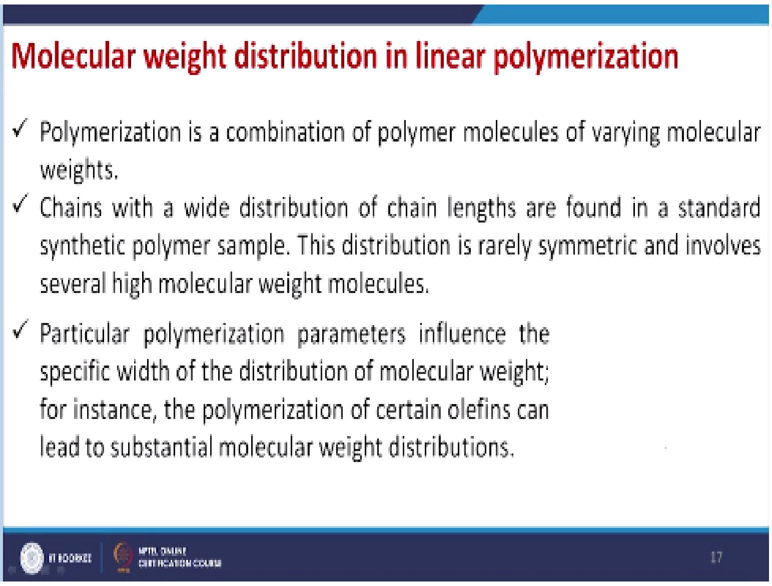

Molecular weight distribution in linear polymerization

- ✓ Polymerization is a combination of polymer molecules of varying molecular weights.
- ✓ Chains with a wide distribution of chain lengths are found in a standard synthetic polymer sample. This distribution is rarely symmetric and involves several high molecular weight molecules.
- ✓ Particular polymerization parameters influence the specific width of the distribution of molecular weight; for instance, the polymerization of certain olefins can lead to substantial molecular weight distributions.

Now, when we talk about the molecular weight distribution in linear polymerization, now, usually this polymerization, one major factor we need to address that polymerization is a combination of polymer molecules of varying molecular weights. Now, chains with a wide distribution of chains length, they are found in a standard synthesis synthetic polymer sample. Now, this distribution is rarely symmetric and involves several high molecular weight molecules.

So, particular polymerization parameters influence the specific width of the distribution of molecular weight. For instance, the polymerization of certain olefins can lead to the substantial molecular weight distribution. Now, Flory derived the molecular weight distribution through a statistical approach focused on equal reactivity of functional group. This is purely an assumption that he assumed that every functional group is having the equal reactivity.

So, all un-reacted functional group have equal opportunities at any point of polymerization to participate in the reaction regardless of the size of the molecule to which it is attached. The probability that a given functional group has reacted after the conversion is usually equal to the distribution of all functional groups. Now, when we talk about the derivation of the size distribution, in that case, this derivation is considerably applied to the step polymerization having the forms of A-A plus B-B and A-B.

Now, this is associated with the possibility of having a molecule that has interacted with the (x–1) A groups and un-reacted with one at least one A group. The extent of reaction “p” is referred to as the probability that an A group has reacted at time t. So, the possibility that (x – 1) A group have reacted is $p^{(x-1)}$ where x is the structural units. These are being used in that particular polymerization process. So, the possibility of a group being A group being un-reacted is (1 – p).

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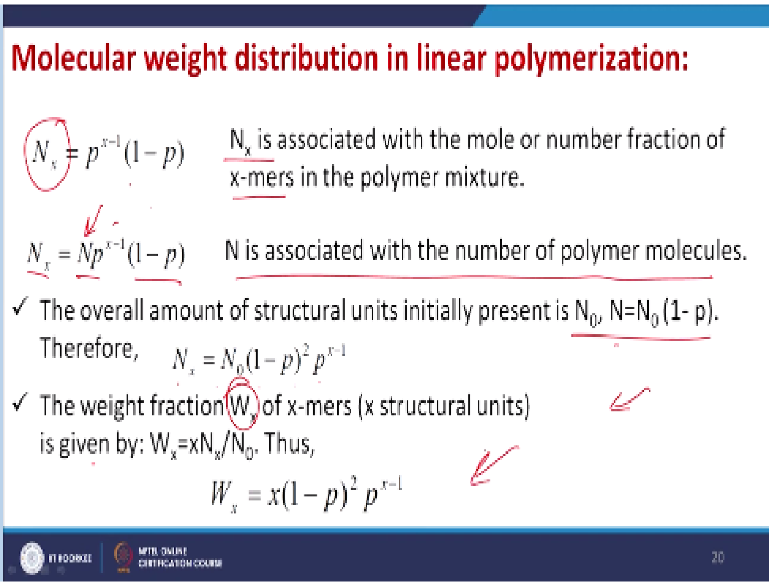

Molecular weight distribution in linear polymerization:

$N_x = p^{x-1}(1-p)$ N_x is associated with the mole or number fraction of x-mers in the polymer mixture.

$N_x = Np^{x-1}(1-p)$ N is associated with the number of polymer molecules.

✓ The overall amount of structural units initially present is N_0, $N=N_0(1-p)$.
Therefore, $N_x = N_0(1-p)^2 p^{x-1}$

✓ The weight fraction W_x of x-mers (x structural units) is given by: $W_x=xN_x/N_0$. Thus,

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

Now, here you see that

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

Now, N_x is associated with the moles or number fraction of x-mers in the polymer mixture. Similarly,

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

This N is associated with the number of polymer molecules. So, the overall amount of structural units initially present is N_0 that is $N = N_0(1-p)$

So, therefore, if we substitute the value of this N to this particular equation, then it is found that

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

So, the weight fraction W_x for x-mers is given by

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

Therefore, if we substitute all the values, the W x is equal to x into 1 – p square into p x – 1.

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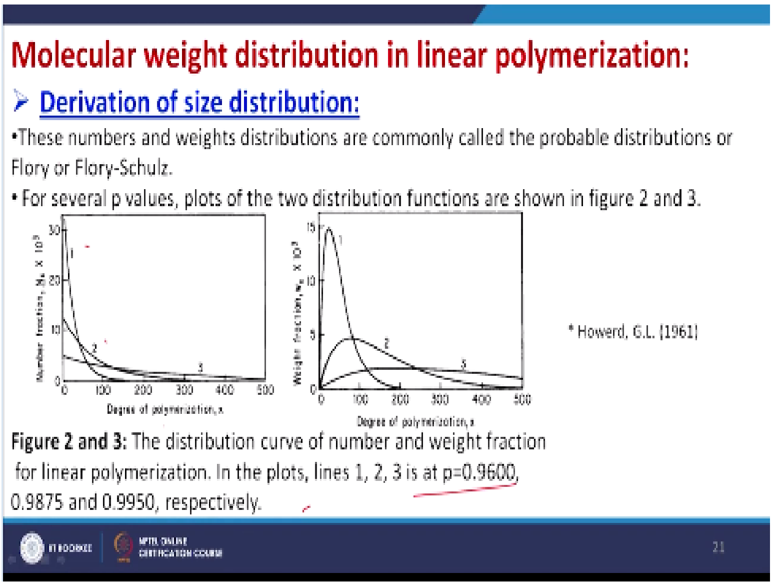

Molecular weight distribution in linear polymerization:

- **Derivation of size distribution:**

•These numbers and weights distributions are commonly called the probable distributions or Flory or Flory-Schulz.

• For several p values, plots of the two distribution functions are shown in figure 2 and 3.

* Howerd, G.L. (1961)

Figure 2 and 3: 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, to give the more pictorial view that derivation of various size the distribution can be expressed with the help of these 2 figures. Here, we have represented the distribution curve of number and weight fraction for linear polymerization. Now, in the plot, various lines like 1, 2, 3, this p is equal to 0.96, 0.9875 and 0.9950 respectively. So, these number and weight distribution are commonly called the probability distribution or Flory-Schulz distribution.

For several p values, the plots of these 2 things like polymerization versus the number of fractions and degree of polymerization versus the weight fraction. It is given over here.

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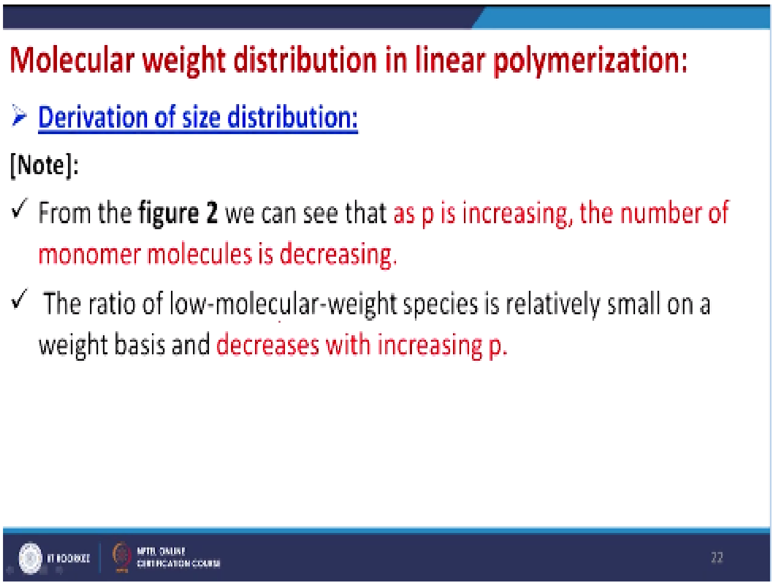

Molecular weight distribution in linear polymerization:

- **Derivation of size distribution:**

[Note]:

✓ From the **figure 2** 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.

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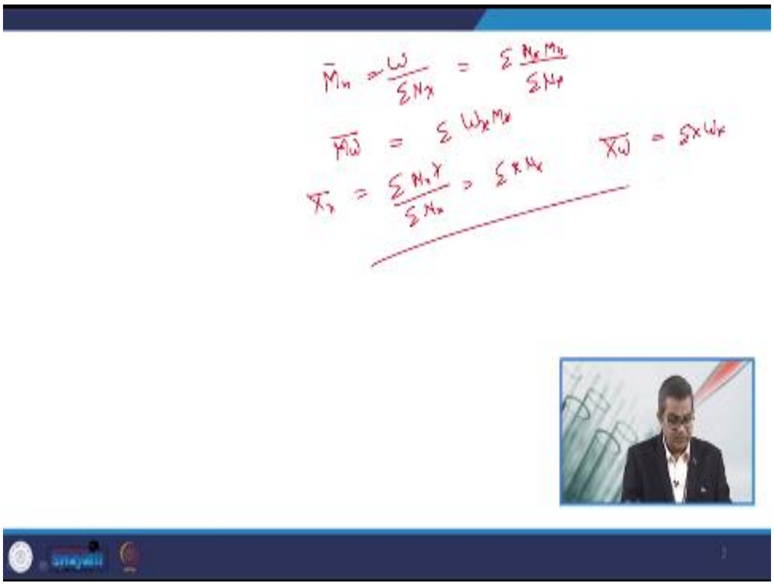

$$\bar{M}_n = \frac{W}{\Sigma N_x} = \frac{\Sigma N_x M_n}{\Sigma N_x}$$

$$\bar{M}_w = \Sigma W_x M_x$$

$$\bar{X}_n = \frac{\Sigma N_x X}{\Sigma N_x} = \Sigma x N_x \qquad \bar{X}_w = \Sigma x W_x$$

Now, when we talk about the molecular weight of number and weight average, it can be given as $\overline{M_n} = \frac{W}{\sum N_x} = \frac{\sum N_x M_n}{\sum N_x}$

$\overline{M_w} = \sum W_x M_x$

Now, if we divide both the equations with the M n, the M x, then it is

$\overline{X_n} = \frac{\sum N_x X}{\sum N_x} = \sum x N_x$ or

$\overline{X_w} = \sum x W_x$

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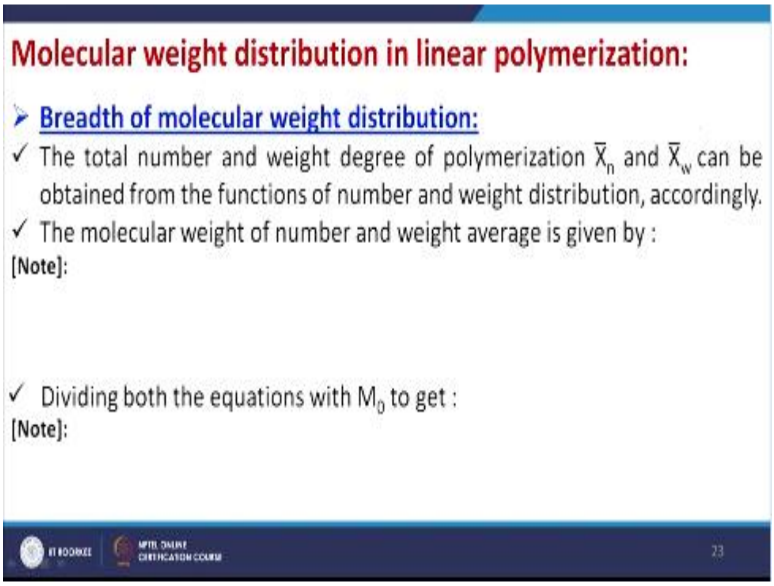

Molecular weight distribution in linear polymerization:

- **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.
- ✓ The molecular weight of number and weight average is given by :

[Note]:

- ✓ Dividing both the equations with M_0 to get :

[Note]:

Now, sometimes, it is quite significant that when we talk about these $\overline{X_n}$ *and* $\overline{X_w}$, which you obtained in the previous slide from the function of number and weight distribution.

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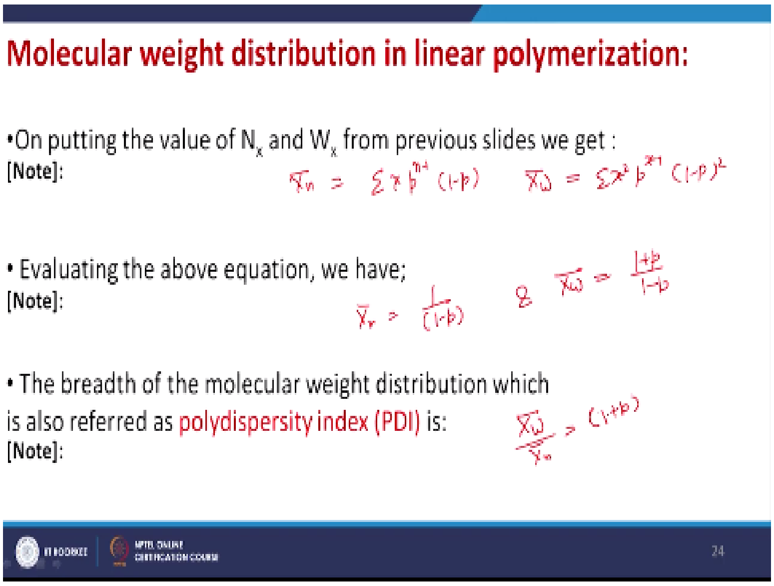

Molecular weight distribution in linear polymerization:

- On putting the value of N_x and W_x from previous slides we get :

[Note]: $\overline{X}_n = \sum x p^{x-1}(1-p)$ $\quad \overline{X}_w = \sum x^2 p^{x-1}(1-p)^2$

- Evaluating the above equation, we have;

[Note]: $\overline{X}_n = \frac{1}{(1-p)}$ & $\overline{X}_w = \frac{1+p}{1-p}$

- The breadth of the molecular weight distribution which is also referred as polydispersity index (PDI) is:

[Note]: $\frac{\overline{X}_w}{\overline{X}_n} = (1+p)$

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Now, in that case, if we have these two particular mathematical equation in question, now, if we put the values of N_x and W_x from this previous equation, we may have

$$\overline{X_n} = \sum x p^{-1}(1-p)$$
$$\overline{X_w} = \sum x^2 p^{x-1}(1-p)^2$$

So, on evaluating this particular equation, we may have

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

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

The breadth of the molecular weight distribution which is sometimes referred as polydispersity index (PDI), it can be given as

$$\frac{\overline{X_w}}{\overline{X_n}} = 1 + p$$

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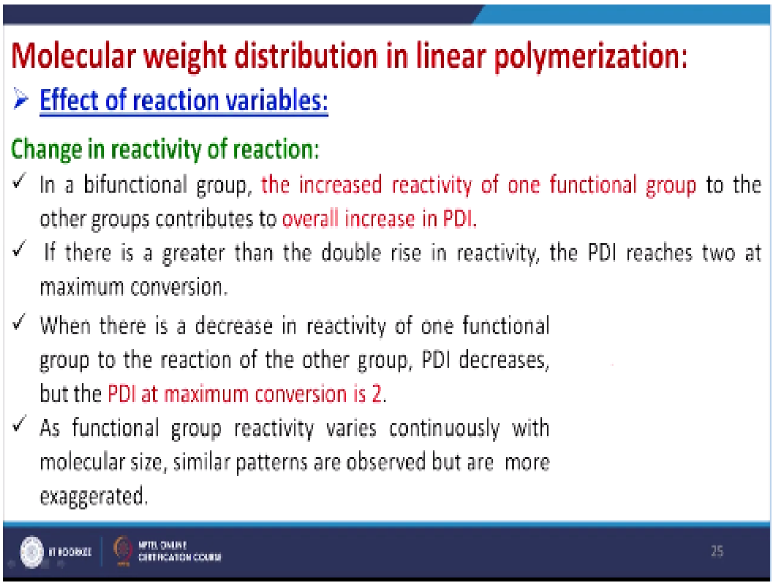

Molecular weight distribution in linear polymerization:

- **Effect of reaction variables:**

Change in reactivity of reaction:

- ✓ In a bifunctional 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.
- ✓ As functional group reactivity varies continuously with molecular size, similar patterns are observed but are more exaggerated.

Now, let us have a look about the effect of reaction variables. Now, sometimes changing the reactivity of reaction plays a very vital role. In a bi-functional group, the increased reactivity of one functional group to the other group contributes to overall increase in polydispersity index. Now, if there is a greater than a double rise in the reactivity, the polydispersity index reaches to maximum conversion.

Now, when there is a decrease in the reactivity of one functional group to the reaction to other group, the polydispersity index decreases, but PDI that is a polydispersity index at a maximum conversion is having too. So, as functional group reactivity varies continuously with molecule size, similar patterns are observed, but are more exaggerated. Now, let us talk about the molecular weight distribution in non-linear polymerization.

Now, using over 2 reactive and groups, such as tri sometimes tetra functional monomers were produced as a step polymerization of a non-linear polymer molecules, such as over branch or a cross link polymer and sometimes that dendrimers and denry grafts polymers.

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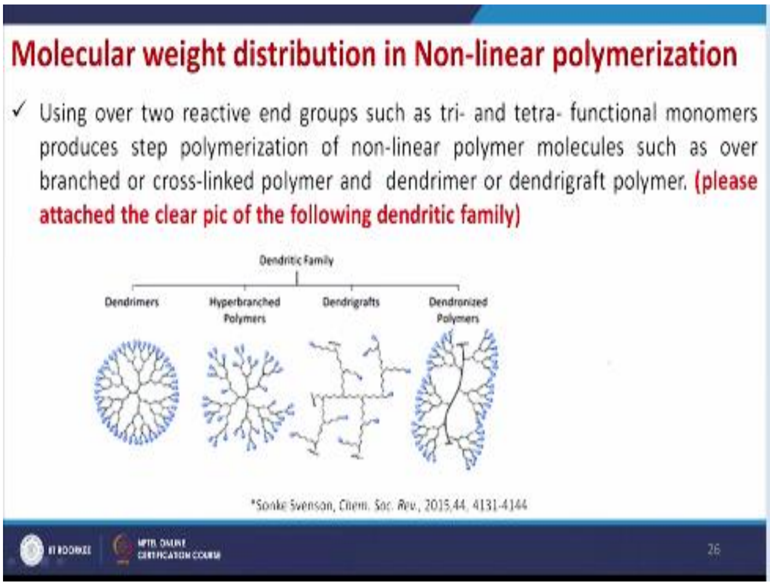
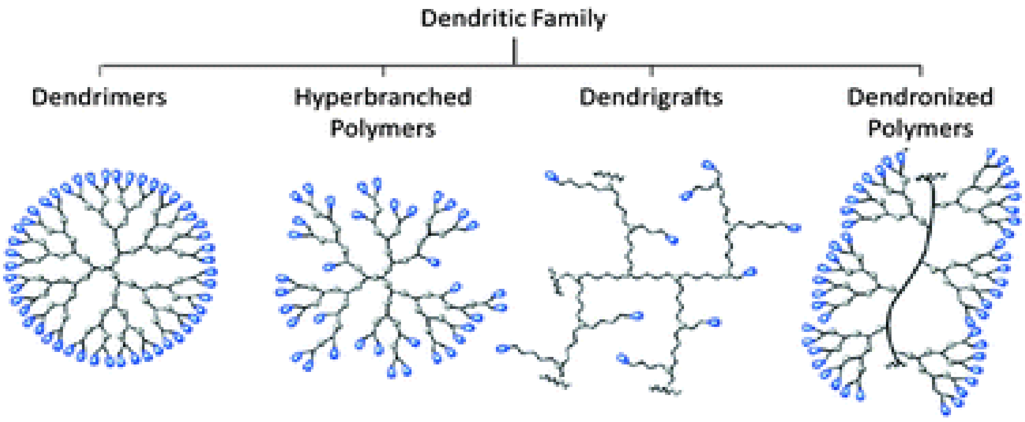


Molecular weight distribution in Non-linear polymerization

- ✓ Using over two reactive end groups such as tri- and tetra- functional monomers produces step polymerization of non-linear polymer molecules such as over branched or cross-linked polymer and dendrimer or dendrigraft polymer. **(please attached the clear pic of the following dendritic family)**

*Sonke Svenson, Chem. Soc. Rev., 2015,44, 4131-4144



Source: Sonke Svenson, *Chem. Soc. Rev.*, 2015,44, 4131-4144

So, this type of approach is important while considering the various issues related to the non-linear polymerization.

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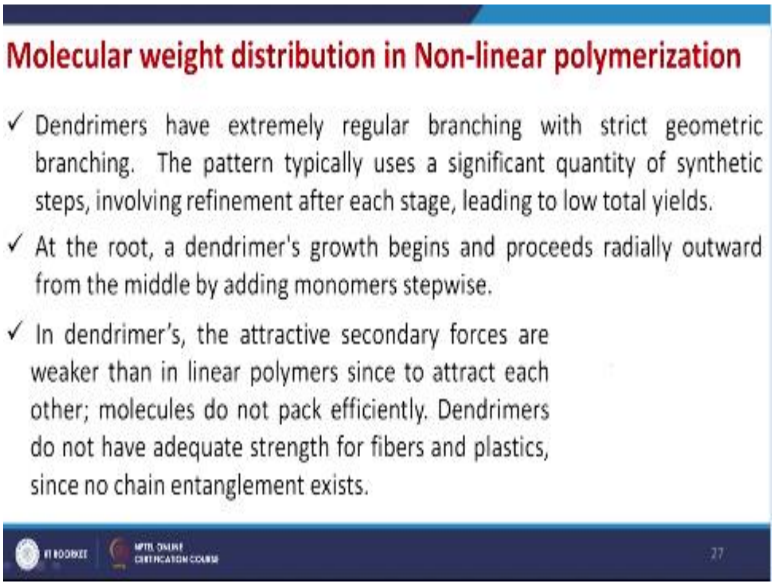

Molecular weight distribution in Non-linear polymerization

- ✓ Dendrimers have extremely regular branching with strict geometric branching. The pattern typically uses a significant quantity of synthetic steps, involving refinement after each stage, leading to low total yields.
- ✓ At the root, a dendrimer's growth begins and proceeds radially outward from the middle by adding monomers stepwise.
- ✓ In dendrimer's, the attractive secondary forces are weaker than in linear polymers since to attract each other; molecules do not pack efficiently. Dendrimers do not have adequate strength for fibers and plastics, since no chain entanglement exists.

Now, dendrimers have extremely regular branching with a strict geometric branching. The pattern typically uses a significant quantity of synthetic steps involving refinement after each stage, leading to low cost yield. Now, at a root dendrimer's growth begins and proceeds radially outward from the middle of by adding monomer steps wise. So, in dendrimers, the attractive secondary forces are weaker than in linear polymer, since to attract each other, the molecules do not pack efficiently.

So, that effects sometimes to the nature of these non-linear polymers. Now, dendrimers do not have adequate strength of fibres and plastic since no chain entanglement to exist in this type of dendrimers. Now, with the other materials that dendrimers have better solubility and miscibility making them suitable as viscous additives.

Now, synthesis of hyper-branched polymers with the structures that are less conventional than dendrimers; it can be performed using multifunctional type A-B and monomers and where you may have $N \geq 2$ or through merging linear multifunctional monomers such as A-A and B3. Now crystallisation, this can be prevented by branching in over branch to polymers. So, these can be used as a functional additives for crosslink polymers.

And now, the adhesives and coatings sometimes play a vital role in that linear polymerization system under the edges of molecular weight distribution system. Now, linear molecules like AB or a mixture of A-A and B-B and the tri-functional crosslink molecules like A-B2, A3, B3, they may be used to generate the cross-linked configuration. Now, let us talk about the functionality.

Now, multifunctional monomer molecules can have this specific type of functional groups like A3 or various forms of group like A B2. So, the average functionality of the analysis of polymerization kinetics for multifunctional monomer is usually defined as the average number of functional groups per monomer molecules.

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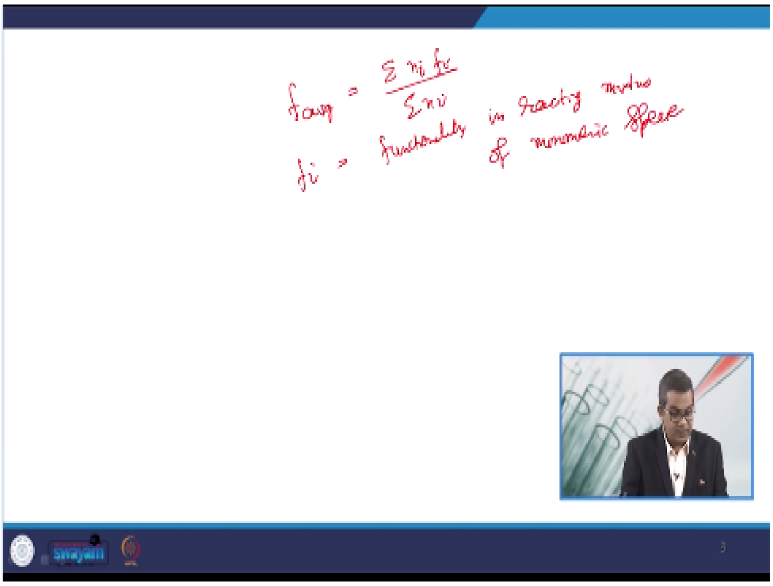

$$f_{avg} = \frac{\sum x_i f_i}{\sum x_i}$$

f_i = functionality in reacting mixture of monomeric species

So, it can be represented like

$$f_{avg} = \frac{\sum x_i f_i}{\sum x_i}$$

where f_i is the functionality in reacting mixture of monomeric species.

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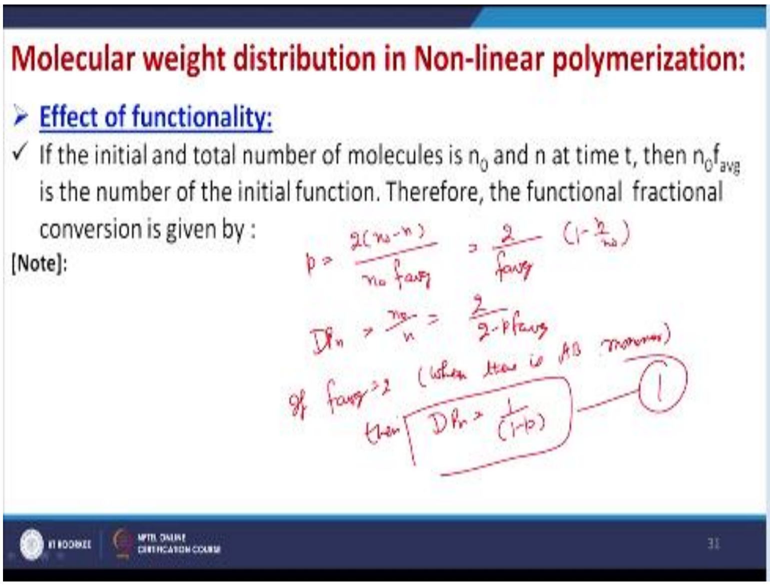


Molecular weight distribution in Non-linear polymerization:

- **Effect of functionality:**
- ✓ If the initial and total number of molecules is n_0 and n at time t, then $n_0 f_{avg}$ is the number of the initial function. Therefore, the functional fractional conversion is given by :

[Note]:

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

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

If $f_{avg} = 2$ (when there is AB monomer)

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

Now, if the initial and the total number of molecules is represented as n_0 and n at time t, then n_0 f_{avg} is the number of initial functions, therefore, the functional fractional conversion is given by

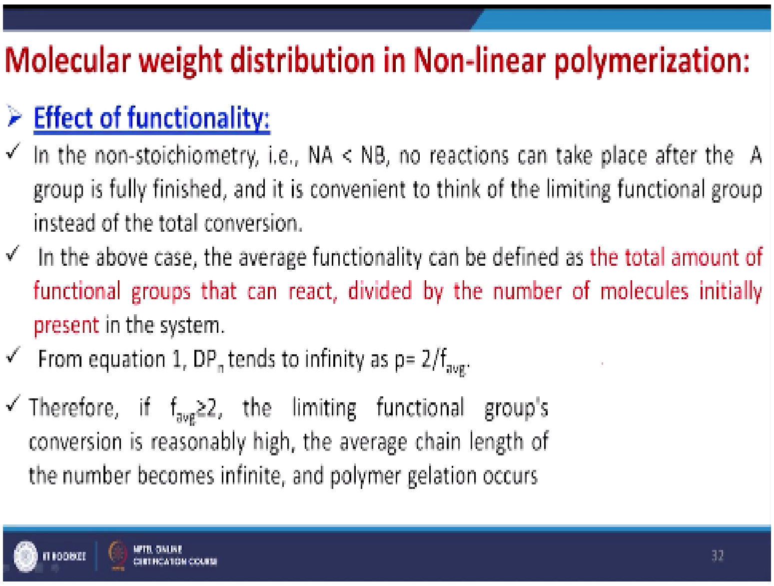
$$p = \frac{2(n_0 - n)}{n f_{avg}} = \frac{2}{f_{avg}}(1 - \frac{n}{n_0})$$

$$Dp_n = \frac{n_0}{n} = \frac{2}{2 - p f_{avg}}$$

Now, if f_{avg} is 2 (when there is A-B monomer), then

$$Dp_n = \frac{1}{1-p} \tag{1}$$

(Refer Slide Time: 28:47)



Molecular weight distribution in Non-linear polymerization:

- **Effect of functionality:**
- ✓ In the non-stoichiometry, i.e., NA < NB, no reactions can take place after the A group is fully finished, and it is convenient to think of the limiting functional group instead of the total conversion.
- ✓ In the above case, the average functionality can be defined as the total amount of functional groups that can react, divided by the number of molecules initially present in the system.
- ✓ From equation 1, DP_n tends to infinity as $p = 2/f_{avg}$.
- ✓ Therefore, if $f_{avg} \geq 2$, the limiting functional group's conversion is reasonably high, the average chain length of the number becomes infinite, and polymer gelation occurs

So, in the non-stiochiometry type of system that is $N_A < N_B$, no reaction can take place after the A group is fully finished and it is convenient to think of the limiting functional group instead of the total conversion. So, in this case, the average functionality can be defined as the total amount of functional group that can react divided by the number of molecules initially present in the system.

So, from the previous equation which we discussed over here, the degree of polymerization tends to infinity as $p = 2/f_{avg}$ .Therefore, if$f_{avg} \geq 2$, the limiting functional groups conversion is reasonably high, the average chain length of the number becomes infinite and the polymer gelation occurs. Now, let us talk about the growth of non-linear network because non-linear network development of non-linear network is again important aspect.

Now, considering the combination of 2 bi-functional groups A-A and B-B and tri-functional monomer that is A 3, to a further investigation of growth of branched polymer network and gel molecules development. So, PJ Flory, he identified a chain or a section of branch polymer as a segment of a molecule among 2 separate units or branch unit and an un-reacted terminal functional group.

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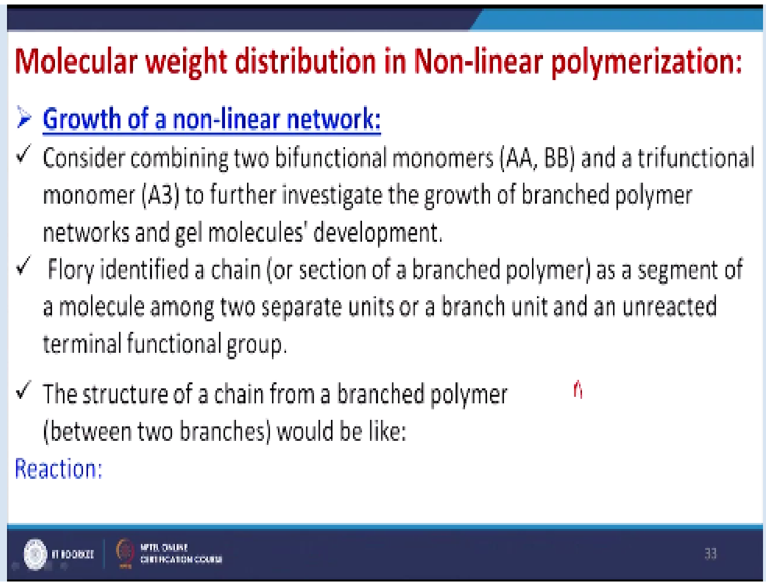

Molecular weight distribution in Non-linear polymerization:

- **Growth of a non-linear network:**
- ✓ Consider combining two bifunctional monomers (AA, BB) and a trifunctional monomer (A3) to further investigate the growth of branched polymer networks and gel molecules' development.
- ✓ Flory identified a chain (or section of a branched polymer) as a segment of a molecule among two separate units or a branch unit and an unreacted terminal functional group.
- ✓ The structure of a chain from a branched polymer (between two branches) would be like:

Reaction:

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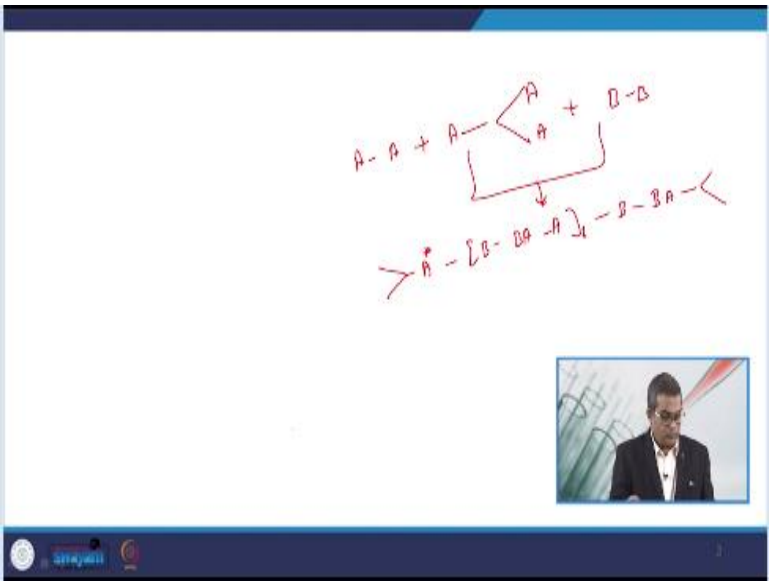
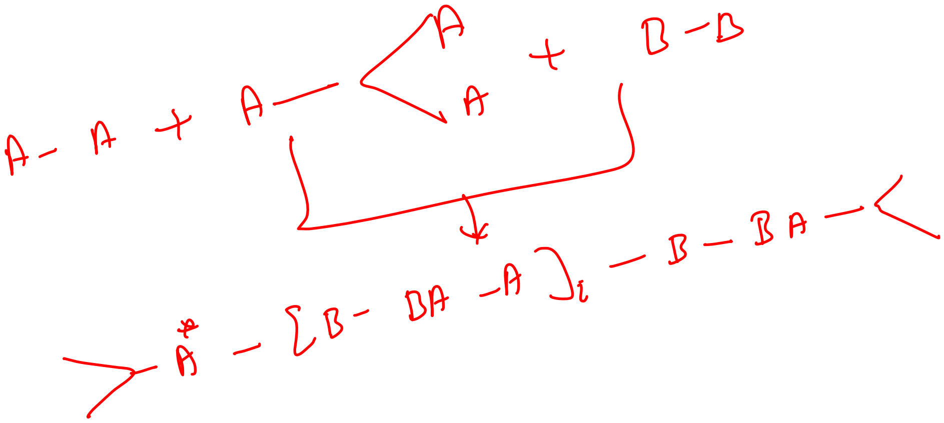


So, the structure of a chain from branched polymer between 2 branches, this can be represented as



Now, the probability sometimes, we may have to look into the probability, we will discuss sometime later in this particular approach.

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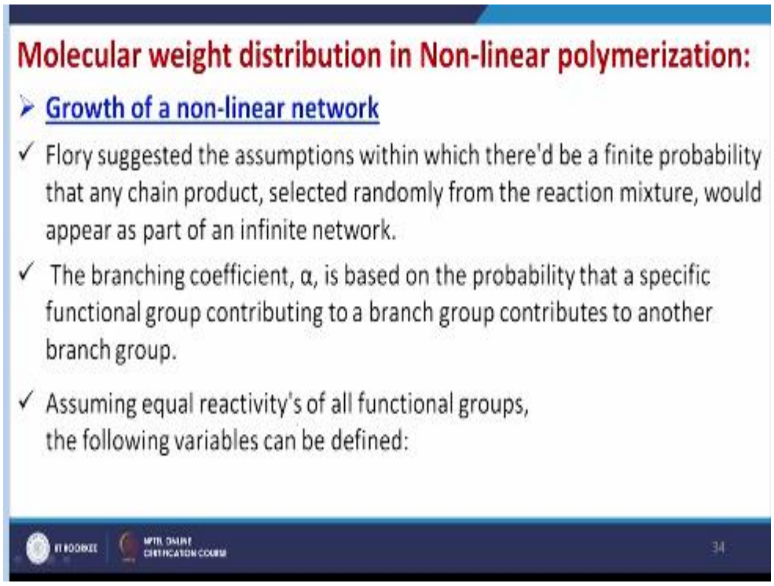

Molecular weight distribution in Non-linear polymerization:

- Growth of a non-linear network
  - ✓ Flory suggested the assumptions within which there'd be a finite probability that any chain product, selected randomly from the reaction mixture, would appear as part of an infinite network.
  - ✓ The branching coefficient, α, is based on the probability that a specific functional group contributing to a branch group contributes to another branch group.
  - ✓ Assuming equal reactivity's of all functional groups, the following variables can be defined:

Now, before we go into the probability approach, let us discuss that Flory is suggested the assumption within which there will be a finite probability that any chain product or selected randomly from the reaction mass would appear as a part of infinite network. The branching coefficient alpha usually is based on the probability that a specific functional group contributing to a branch group. Usually, it contributes to another branch group.

Now, assuming the equal reactivity of all functional group as we discussed previously, the following variables, you can define like p is a functional group of A has reacted along the chain.

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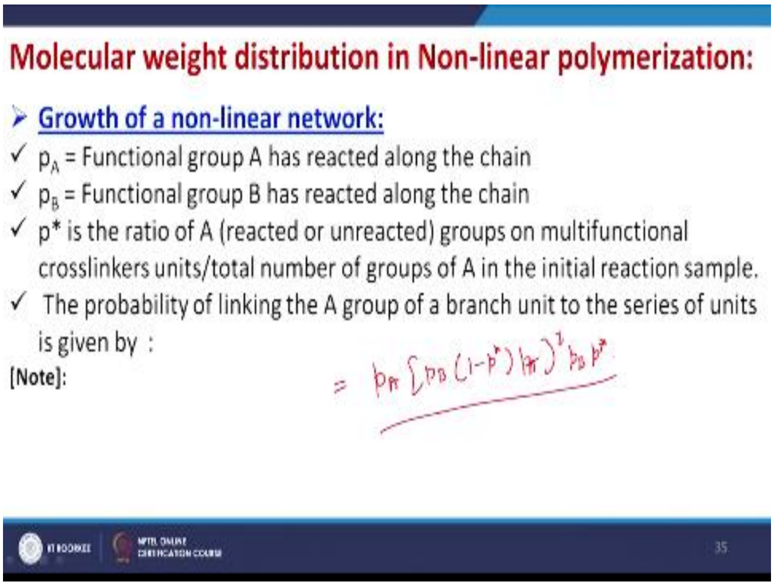

Molecular weight distribution in Non-linear polymerization:

- Growth of a non-linear network:
  - ✓ p_A = Functional group A has reacted along the chain
  - ✓ p_B = Functional group B has reacted along the chain
  - ✓ p* is the ratio of A (reacted or unreacted) groups on multifunctional crosslinkers units/total number of groups of A in the initial reaction sample.
  - ✓ The probability of linking the A group of a branch unit to the series of units is given by :

[Note]:

$$= p_A \{ p_B (1-p^*) p_A)^i p_B p^*$$

Let us see first that what the equation, we are proposing.

- ✓ p_A = Functional group A has reacted along the chain
- ✓ p_B = Functional group B has reacted along the chain
- ✓ p* is the ratio of A (reacted or unreacted) groups on multifunctional crosslinkers units/total number of groups of A in the initial reaction sample.
- ✓ The probability of linking the A group of a branch unit to the series of units is given by :

$$p_A\{P_B(1-p^*)p_A\}^2 p_B p^*$$

Now, here p A is the functional group A has reacted along the chain. p B is the functional group B has reacted along the chain. p star is that ratio of A that is reacted whether reacted or un-reacted group on multifunctional cross-linkers unit divided by the total number of groups of A in the initial reaction samples. So, these are the usual notations.

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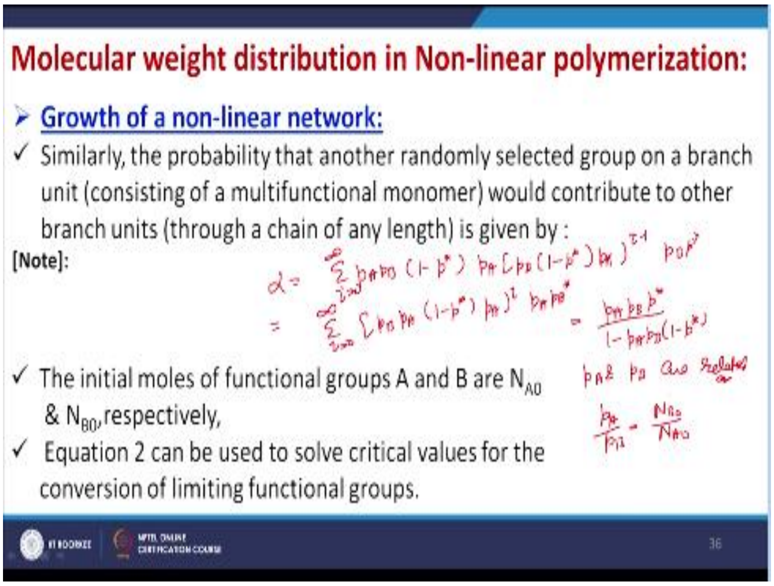

Molecular weight distribution in Non-linear polymerization:

- **Growth of a non-linear network:**
- ✓ Similarly, the probability that another randomly selected group on a branch unit (consisting of a multifunctional monomer) would contribute to other branch units (through a chain of any length) is given by :

[Note]:

$$\alpha = \sum_{i=0}^{\infty} p_A p_B (1-p^*)\, p_A \{p_B(1-p^*)p_A\}^{i-1}\, p_B p^*$$

$$= \sum_{i=0}^{\infty} \{p_B p_A (1-p^*) p_A)^i\, p_A p_B^* = \frac{p_A p_B p^*}{1-p_A p_B(1-p^*)}$$

- ✓ The initial moles of functional groups A and B are N_{A0} & N_{B0}, respectively,
- ✓ Equation 2 can be used to solve critical values for the conversion of limiting functional groups.

p_A & p_B are related

$$\frac{p_A}{p_B} = \frac{N_{B0}}{N_{A0}}$$

Now, similarly, the probability for another randomly selected group on a branch unit that may consist of a multifunctional monomer would contribute to other branch units through a chain or any length is usually given by

$$\alpha = \sum_{i=0}^{\infty} p_A p_B (1-p^*)\, p_A \{p_B(1-p^*)p_A\}^{i-1}\, p_B p^*$$

$$= \sum_{i=0}^{\infty} \{p_B p_A (1-p^*) p_A)^i\, p_A p_B^* = \frac{p_A p_B p^*}{1-p_A p_B(1-p^*)}$$

p_A & p_B are related

$$\frac{p_A}{p_B} = \frac{N_{B0}}{N_{A0}}$$

So, the initial modes of functional group A and B are N A 0 and N B 0 respectively. Now, these equation can be used to solve the critical values for the conversion of the limiting functional groups.

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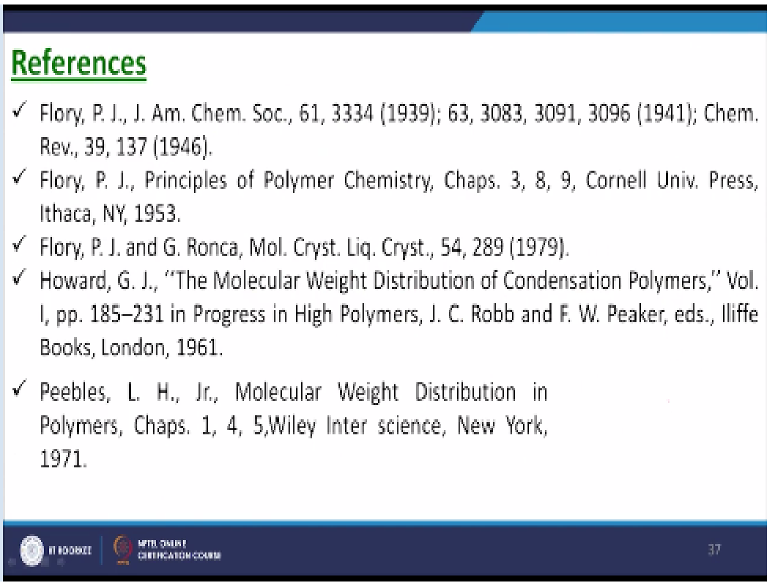

References

- ✓ Flory, P. J., J. Am. Chem. Soc., 61, 3334 (1939); 63, 3083, 3091, 3096 (1941); Chem. Rev., 39, 137 (1946).
- ✓ Flory, P. J., Principles of Polymer Chemistry, Chaps. 3, 8, 9, Cornell Univ. Press, Ithaca, NY, 1953.
- ✓ Flory, P. J. and G. Ronca, Mol. Cryst. Liq. Cryst., 54, 289 (1979).
- ✓ Howard, G. J., "The Molecular Weight Distribution of Condensation Polymers," Vol. I, pp. 185–231 in Progress in High Polymers, J. C. Robb and F. W. Peaker, eds., Iliffe Books, London, 1961.
- ✓ Peebles, L. H., Jr., Molecular Weight Distribution in Polymers, Chaps. 1, 4, 5,Wiley Inter science, New York, 1971.

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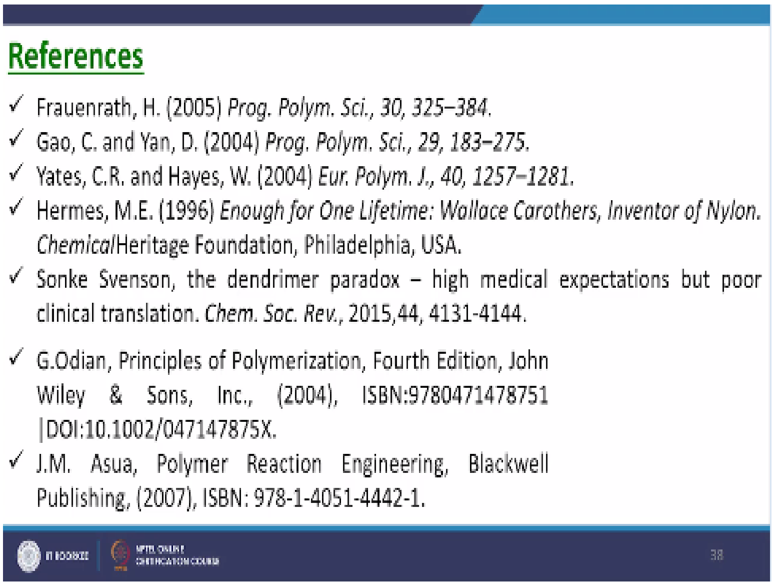

References

- ✓ Frauenrath, H. (2005) *Prog. Polym. Sci., 30, 325–384.*
- ✓ Gao, C. and Yan, D. (2004) *Prog. Polym. Sci., 29, 183–275.*
- ✓ Yates, C.R. and Hayes, W. (2004) *Eur. Polym. J., 40, 1257–1281.*
- ✓ Hermes, M.E. (1996) *Enough for One Lifetime: Wallace Carothers, Inventor of Nylon. Chemical*Heritage Foundation, Philadelphia, USA.
- ✓ Sonke Svenson, the dendrimer paradox – high medical expectations but poor clinical translation. *Chem. Soc. Rev.*, 2015,44, 4131-4144.
- ✓ G.Odian, Principles of Polymerization, Fourth Edition, John Wiley & Sons, Inc., (2004), ISBN:9780471478751 |DOI:10.1002/047147875X.
- ✓ J.M. Asua, Polymer Reaction Engineering, Blackwell Publishing, (2007), ISBN: 978-1-4051-4442-1.

Now, in this last, when we sum up that particular chapter, then at last in the conclusion that we say that the molecular weight distribution play a very vital role. And in this particular chapter, we determined both theoretically as well as mathematically, this molecular weight distribution pattern of both non-linear as well as linear polymer. For your convenience, we have listed some several research papers as well as several books.

You may look into all these references for your convenience and for further study. A lot of things are there in these references. By this way, thank you very much for paying your attention.