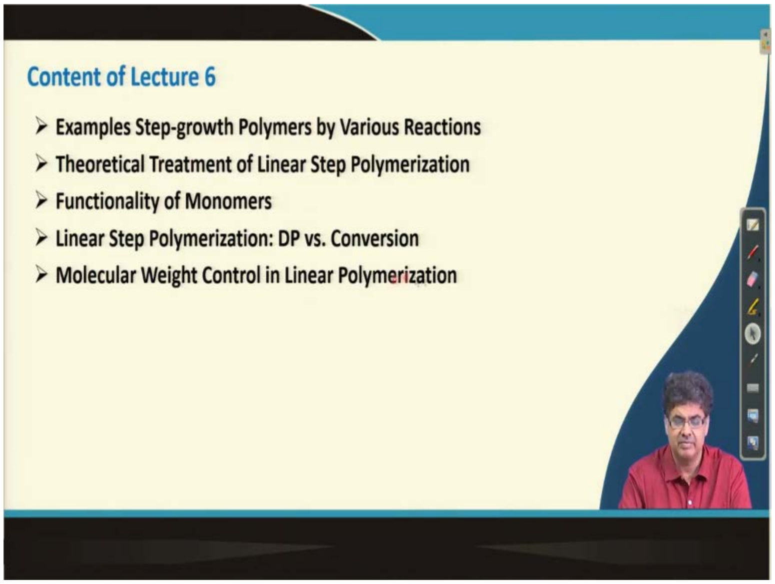
Introduction to Polymer Science
Prof. Dibakar Dhara
Department of Chemistry
Indian Institute of Technology – Kharagpur

Lecture - 06
Examples of Step Polymers Linear Step Polymerization

Welcome back; we will now move to our second module where we will start discussing different polymerization processes. Firstly, we will talk about the polymers which are synthesized by step-growth polymerization, which are sometimes also called step growth polymers or step polymers.

(Refer Slide Time: 00:52)

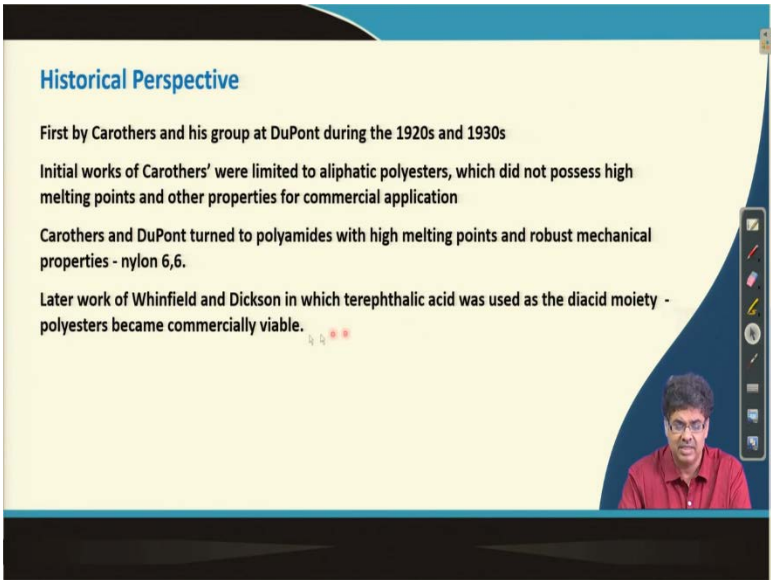


Content of Lecture 6

- Examples Step-growth Polymers by Various Reactions
- Theoretical Treatment of Linear Step Polymerization
- Functionality of Monomers
- Linear Step Polymerization: DP vs. Conversion
- Molecular Weight Control in Linear Polymerization

The polymers which are synthesized using step-growth polymerization are also called step-growth polymers, and sometimes they are just called step polymers.

(Refer Slide Time: 01:28)



Historical Perspective

First by Carothers and his group at DuPont during the 1920s and 1930s

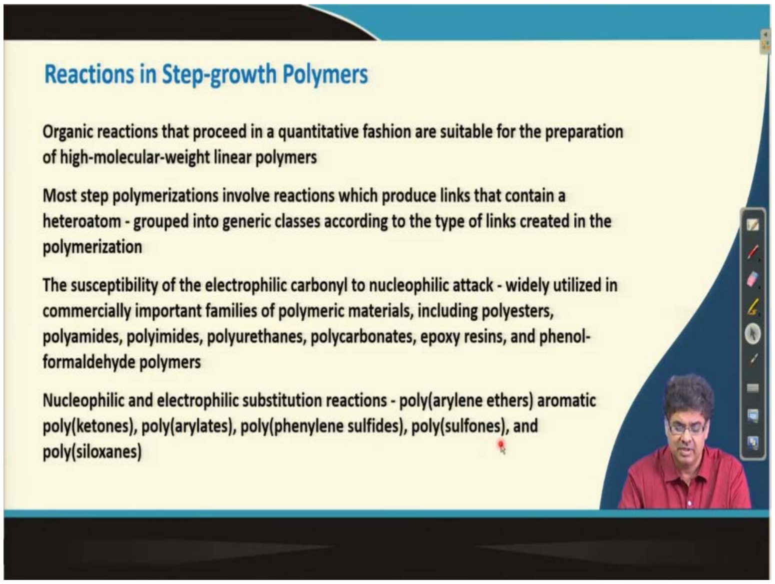
Initial works of Carothers' were limited to aliphatic polyesters, which did not possess high melting points and other properties for commercial application

Carothers and DuPont turned to polyamides with high melting points and robust mechanical properties - nylon 6,6.

Later work of Whinfield and Dickson in which terephthalic acid was used as the diacid moiety - polyesters became commercially viable.

To give you briefly a historical perspective, these step polymers were first synthesized by Carothers and his group at DuPont during the 1920s and 1930s. Carothers' initial work was limited to aliphatic polyesters that did not possess a high melting point and other properties for commercial applications. They also synthesized aromatic polyesters of isophthalic acid and ethylene glycol but that also did not have properties needed for commercial application. Hence Carother's team shifted towards synthesis of polyamides that had a high melting point and robust mechanical properties for the application. The first useful synthetic polyamide was nylon 66, which began the polymer age at that time. Later work by Whinfield and Dickson used terephthalic acid, instead of isophthalic acid, as a diacid moiety to synthesize PET, polyethylene terephthalate polyester which became commercially viable.

(Refer Slide Time: 02:55)



Reactions in Step-growth Polymers

Organic reactions that proceed in a quantitative fashion are suitable for the preparation of high-molecular-weight linear polymers

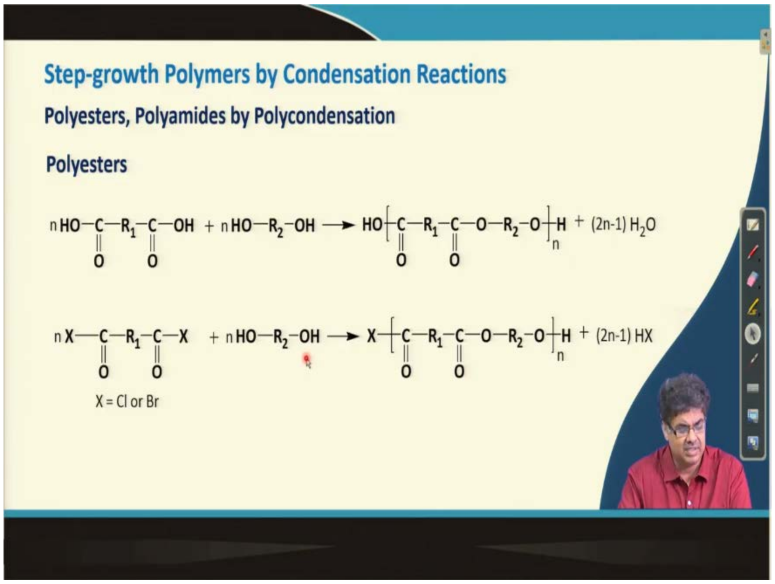
Most step polymerizations involve reactions which produce links that contain a heteroatom - grouped into generic classes according to the type of links created in the polymerization

The susceptibility of the electrophilic carbonyl to nucleophilic attack - widely utilized in commercially important families of polymeric materials, including polyesters, polyamides, polyimides, polyurethanes, polycarbonates, epoxy resins, and phenol-formaldehyde polymers

Nucleophilic and electrophilic substitution reactions - poly(arylene ethers) aromatic poly(ketones), poly(arylates), poly(phenylene sulfides), poly(sulfones), and poly(siloxanes)

Which are the reactions that are typically used for step-growth polymers? The organic reactions need to proceed almost in a quantitative fashion. Minimum 99% conversion yield has to be there in the organic reactions to produce high molecular linear polymers. Step polymerization involves reactions that produce links that containing heteroatoms like oxygen. That is why these polymers synthesized by step-growth polymerization are grouped into generic classes like polyesters, polycarbonates, polyamides, and so on. Many step polymers have a carbonyl group. Now carbonyl group, because of the δ^+ charge on the carbon, they are prone to nucleophilic attack. These are very useful for synthesizing commercially important families of polymeric materials like polyesters, polyamides, polyimides, polyurethane, polycarbonate, etc. Some nucleophilic and electrophilic substitution reactions are also used to synthesize step polymers like poly(arylene ethers), aromatic polyketones, polyacrylates, poly (phenylene sulfide)s, polysulfones, polysiloxanes, etc.

(Refer Slide Time: 04:33)



Step-growth Polymers by Condensation Reactions

Polyesters, Polyamides by Polycondensation

Polyesters

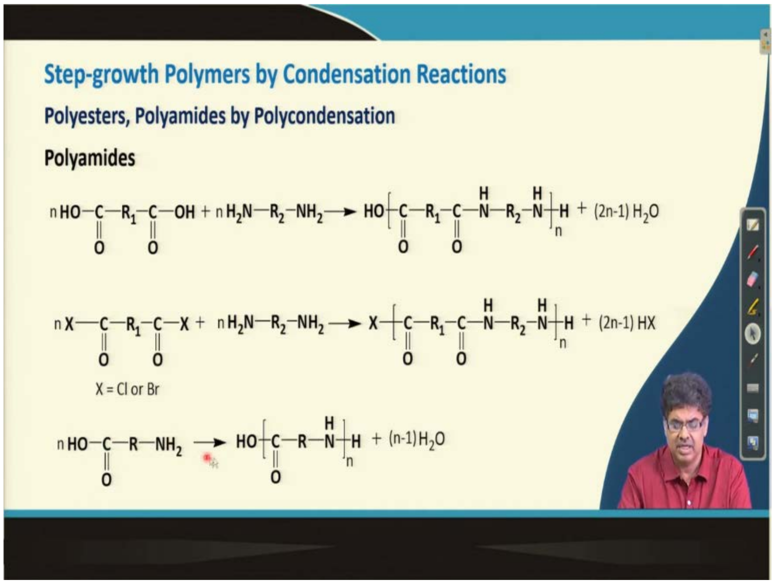
$$n\,HO-\underset{\underset{O}{\|}}{C}-R_1-\underset{\underset{O}{\|}}{C}-OH + n\,HO-R_2-OH \longrightarrow HO\left[\underset{\underset{O}{\|}}{C}-R_1-\underset{\underset{O}{\|}}{C}-O-R_2-O\right]_n H + (2n-1)\,H_2O$$

$$n\,X-\underset{\underset{O}{\|}}{C}-R_1-\underset{\underset{O}{\|}}{C}-X + n\,HO-R_2-OH \longrightarrow X\left[\underset{\underset{O}{\|}}{C}-R_1-\underset{\underset{O}{\|}}{C}-O-R_2-O\right]_n H + (2n-1)\,HX$$

X = Cl or Br

This is an example of polyester containing ester groups which is synthesized by condensation between diacid and dialcohol monomers. Similarly, we can make polyester using diacid halides reacting with dialcohol.

(Refer Slide Time: 05:02)



Step-growth Polymers by Condensation Reactions

Polyesters, Polyamides by Polycondensation

Polyamides

$$n\,HO-\underset{\underset{O}{\|}}{C}-R_1-\underset{\underset{O}{\|}}{C}-OH + n\,H_2N-R_2-NH_2 \longrightarrow HO\left[\underset{\underset{O}{\|}}{C}-R_1-\underset{\underset{O}{\|}}{C}-\overset{H}{N}-R_2-\overset{H}{N}\right]_n H + (2n-1)\,H_2O$$

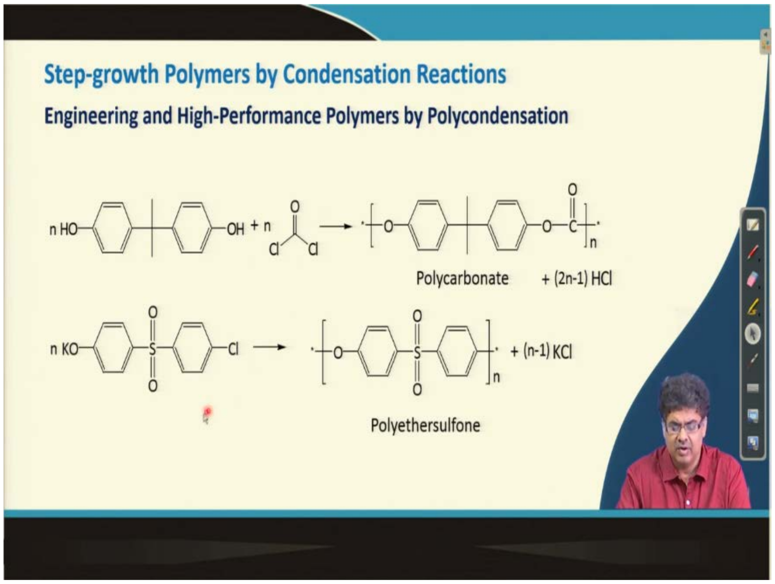
$$n\,X-\underset{\underset{O}{\|}}{C}-R_1-\underset{\underset{O}{\|}}{C}-X + n\,H_2N-R_2-NH_2 \longrightarrow X\left[\underset{\underset{O}{\|}}{C}-R_1-\underset{\underset{O}{\|}}{C}-\overset{H}{N}-R_2-\overset{H}{N}\right]_n H + (2n-1)\,HX$$

X = Cl or Br

$$n\,HO-\underset{\underset{O}{\|}}{C}-R-NH_2 \longrightarrow HO\left[\underset{\underset{O}{\|}}{C}-R-\overset{H}{N}\right]_n H + (n-1)\,H_2O$$

Polyamides can be synthesized using diacids and diamines or diacid halides or they can be synthesized by a monomer having amino acid where on one side there is an amino group and on another side there is an acid group such that monomers react with each other or self-condense to make a polycondensation product i.e. polyamides.

(Refer Slide Time: 05:39)

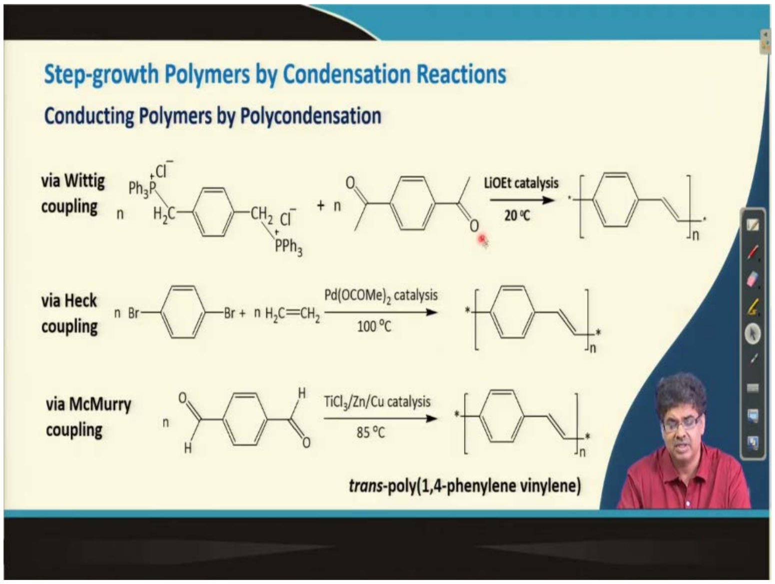


Step-growth Polymers by Condensation Reactions

Engineering and High-Performance Polymers by Polycondensation

Step-growth polymerization can be used to make high-performance polymers, like polycarbonate is synthesized using Bisphenol A and Phosgene. For example, we can also synthesize polyethersulfone.

(Refer Slide Time: 06:02)

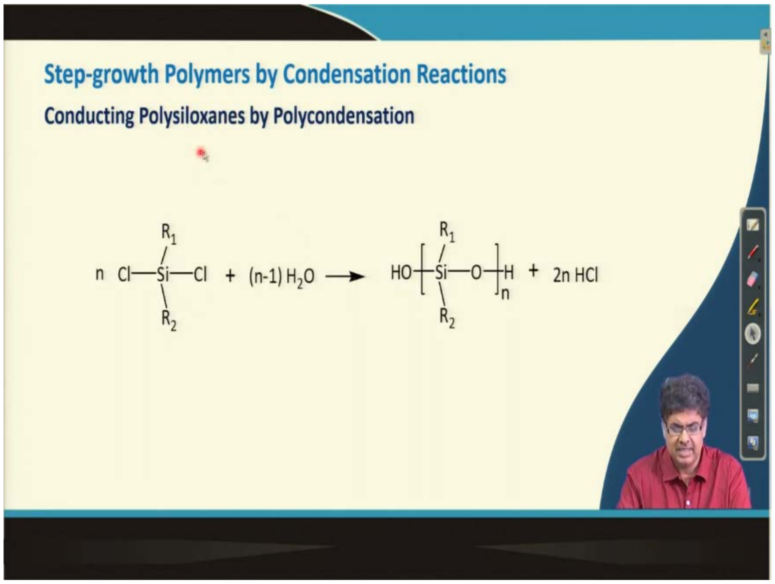


Step-growth Polymers by Condensation Reactions

Conducting Polymers by Polycondensation

Organic coupling reaction can also be used to synthesize this trans poly (1, 4-phenylene vinylene). Some examples are shown here, like Witting coupling, Heck coupling, McMurry coupling. These are common organic reactions utilized in these polymerization processes to make polymer products.

(Refer Slide Time: 06:42)



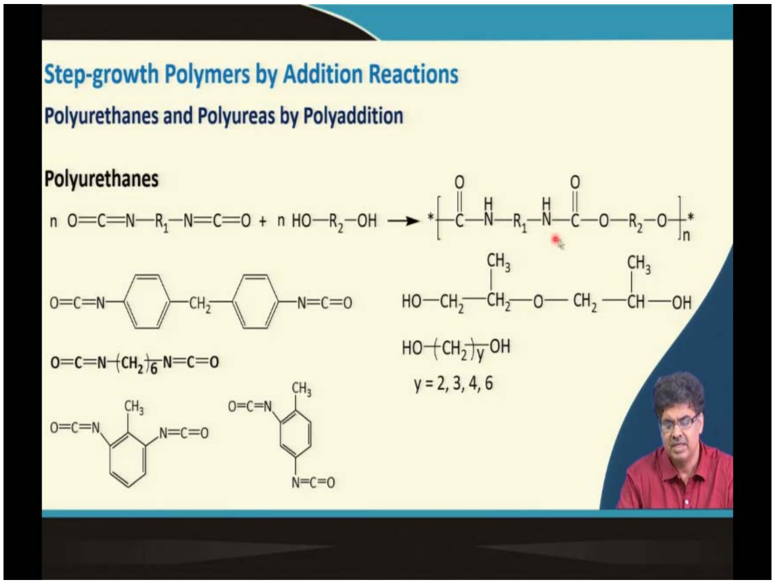
Step-growth Polymers by Condensation Reactions

Conducting Polysiloxanes by Polycondensation

$$n\ \mathrm{Cl}-\underset{R_2}{\overset{R_1}{\mathrm{Si}}}-\mathrm{Cl} + (n-1)\,H_2O \longrightarrow \mathrm{HO}\left[\underset{R_2}{\overset{R_1}{\mathrm{Si}}}-\mathrm{O}\right]_n\mathrm{H} + 2n\,\mathrm{HCl}$$

Other examples like polysiloxanes which contain silicone oxygen silicon bonds in the backbone.

(Refer Slide Time: 06:54)



Step-growth Polymers by Addition Reactions

Polyurethanes and Polyureas by Polyaddition

Polyurethanes

$$n\ O{=}C{=}N-R_1-N{=}C{=}O + n\ HO-R_2-OH \longrightarrow *\!\left[\overset{O}{\overset{\|}{C}}-\overset{H}{N}-R_1-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-O-R_2-O\right]_n\!*$$

$HO-CH_2-\overset{CH_3}{\overset{|}{CH_2}}-O-CH_2-\overset{CH_3}{\overset{|}{CH}}-OH$

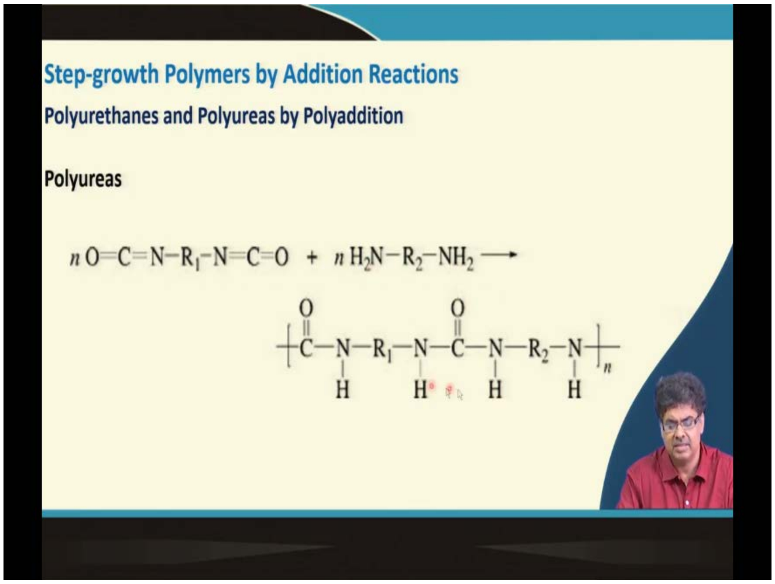
$O{=}C{=}N-(CH_2)_6-N{=}C{=}O$

$HO-(CH_2)_y-OH$

$y = 2, 3, 4, 6$

Polyurethane is synthesized by reacting an isocyanate with alcohol groups like di-isocyanate and dialcohol. They react with each other to form urethane linkage to synthesized polyurethanes.

(Refer Slide Time: 07:28)



Step-growth Polymers by Addition Reactions

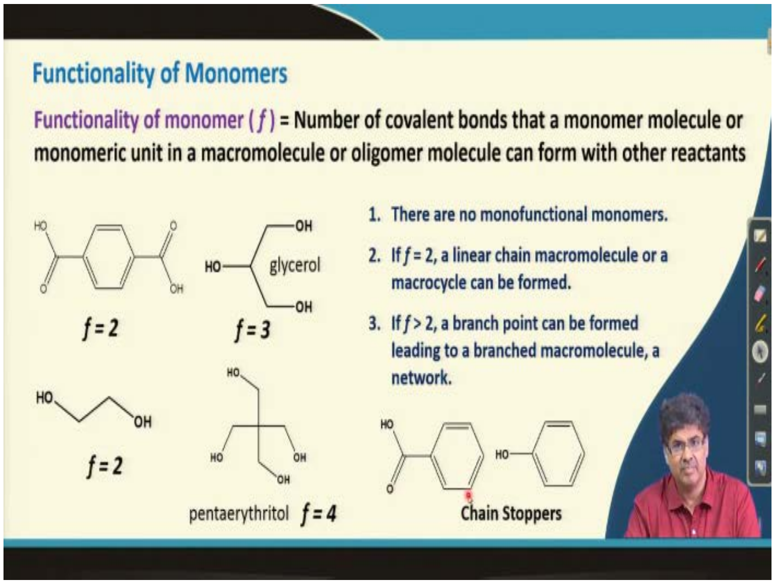
Polyurethanes and Polyureas by Polyaddition

Polyureas

$$n\,O{=}C{=}N{-}R_1{-}N{=}C{=}O + n\,H_2N{-}R_2{-}NH_2 \longrightarrow \left[\overset{\overset{O}{\|}}{C}{-}\underset{\underset{H}{|}}{N}{-}R_1{-}\underset{\underset{H}{|}}{N}{-}\overset{\overset{O}{\|}}{C}{-}\underset{\underset{H}{|}}{N}{-}R_2{-}\underset{\underset{H}{|}}{N}\right]_n$$

Polyureas can be synthesized by reacting these di-isocyanates with diamines forming urea linkage in the backbone. Now let us move to the theory of linear step polymerization.

(Refer Slide Time: 07:46)



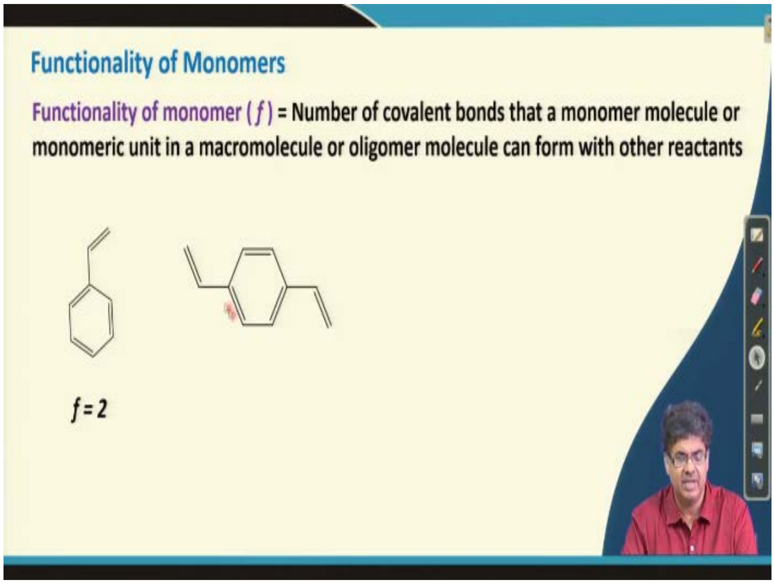
Functionality of Monomers

Functionality of monomer (f) = Number of covalent bonds that a monomer molecule or monomeric unit in a macromolecule or oligomer molecule can form with other reactants

1. There are no monofunctional monomers.
2. If $f = 2$, a linear chain macromolecule or a macrocycle can be formed.
3. If $f > 2$, a branch point can be formed leading to a branched macromolecule, a network.

Before that, we need to define the functionality of monomers, typically expressed as *f*. The functionality of monomers or *f* is defined as the number of covalent bonds that a monomer molecule or monomeric unit in a macromolecule or oligomer molecule can form with other reactants. So, as an example, tartaric acid can form 2 bonds that react with the alcohol groups or amine groups. So, the functionality is 2 because it can form 2 covalent bonds on 2 sides. Similarly, this dialcohol can react on 2 sides and form 2 covalent bonds, so this functionality is also 2. Glycerol has 3 hydroxy groups, which can react with 3 acid groups, to form 3 covalent bonds. So, *f* is 3, and this example pentaerythritol where we have 4 hydroxy groups, so it can make 4 bonds. So, in this case, *f* is 4. Now, let us learn few things about the functionality of monomers. There is no monofunctional monomer because if a monomer can only make 1 covalent bond, it cannot participate in the polymerization reaction. So, there are no monofunctional monomers that are useful in producing polymers. If *f* is 2 for all the monomers during a polymerization reaction, then we get a linear chain macromolecule. In some cases, we can get a macrocycle by reacting with 2 ends of a long polymer chain. And if *f* is greater than 2, that means we have at least 3 or 4 or even more functional groups in a monomer where it can lead to branching of a macromolecule, and in some cases, it can go up to forming network and gel. In some cases, deliberately or not deliberately, these monofunctional compounds may be present in the polymerization medium as an impurity, and then they react in the chain. No further reaction is possible in that particular chain. These are called chain-stoppers. These are not monomers, but sometimes they are used deliberately to control the molecular weight. Sometimes, if they are present unwantedly as an impurity, polymerization can become less useful because of this chain stopper.

(Refer Slide Time: 10:42)



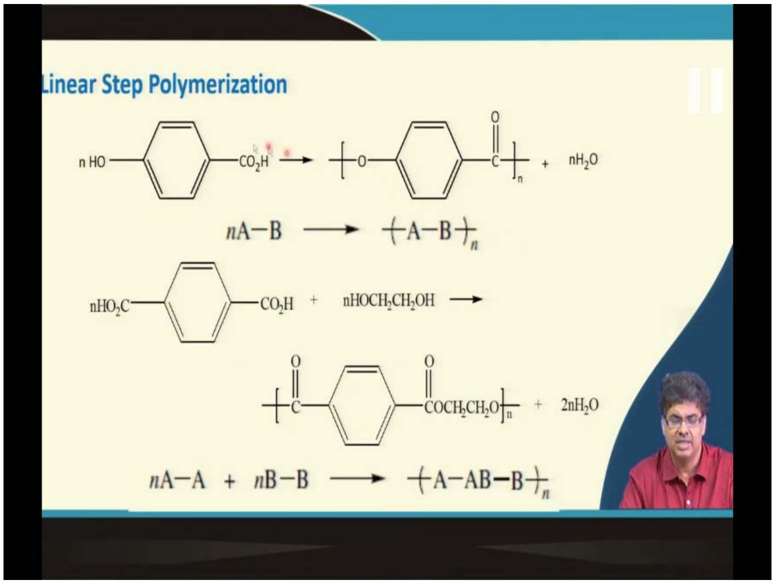
Functionality of Monomers

Functionality of monomer (*f*) = Number of covalent bonds that a monomer molecule or monomeric unit in a macromolecule or oligomer molecule can form with other reactants

$f = 2$

To conclude or summarize the story about functionality; if we have a monomer like styrene, it can form 2 bonds on both sides, so *f* is 2, and in the case of divinylbenzene, it can form 4 bonds to the side to the side. So, *f* is 4.

(Refer Slide Time: 11:08)



Linear Step Polymerization

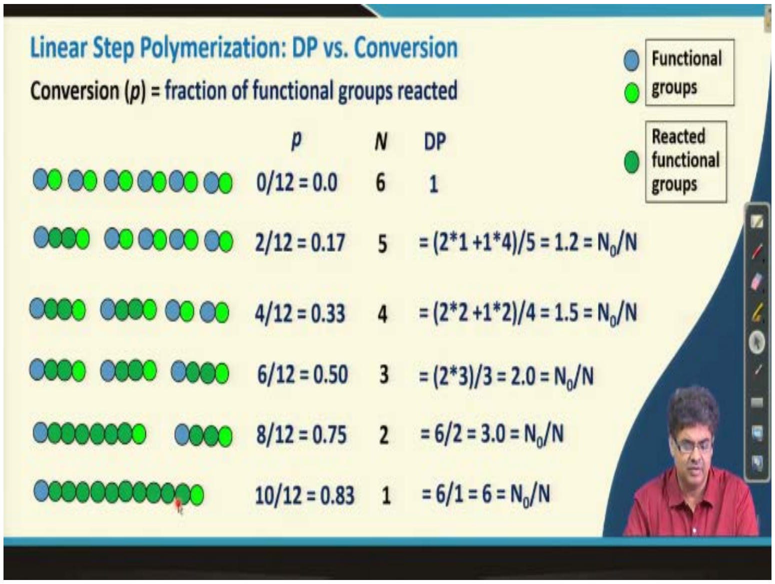
$$nA{-}B \longrightarrow {-}\!\!\left[A{-}B\right]\!\!{-}_n$$

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

We will move to the discussion of linear step-growth polymerization, which means the polymerization process where *f* is 2 for the monomers. Now *f* =2 can be obtained by a single monomer where monomer like 4-hydroxy benzoic acid, where we have 2 functional groups, can form a polymer from two sides. So, we call this AB-type monomer, or we can have 2 monomers AA type and BB type where a particular monomer having 2 similar functional groups and the other monomer having 2 different functional groups where the functional groups can react with each other. If we have this AB-type monomer, then the functional group ratio is always 1:1 but in this particular AA and BB type case, if we have the same number of monomers or the same molar ratio of these 2 monomers, we have the functional group ratio as 1: 1. We can also alter the molar ratio of the functional groups by varying the molar ratio of monomer in these particular cases, which is not possible in AB-type cases where the molar ratio of the functional groups is always 1: 1.

The importance of the molar ratio of the functional groups will be discussed when we discuss the molecular rate and calculate the molecular weight from the linear step polymerization.

(Refer Slide Time: 13:24)



Linear Step Polymerization: DP vs. Conversion

Conversion (*p*) = fraction of functional groups reacted

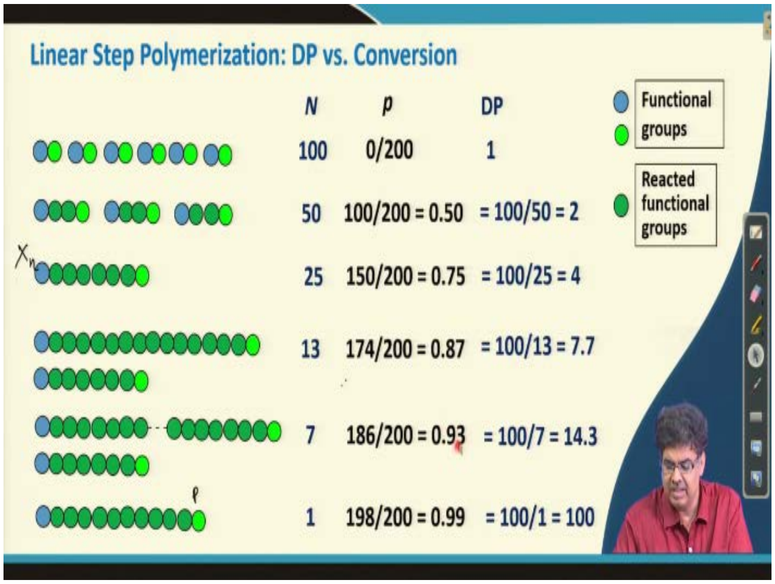
Functional groups

Reacted functional groups

p	*N*	DP
0/12 = 0.0	6	1
2/12 = 0.17	5	$= (2*1 + 1*4)/5 = 1.2 = N_0/N$
4/12 = 0.33	4	$= (2*2 + 1*2)/4 = 1.5 = N_0/N$
6/12 = 0.50	3	$= (2*3)/3 = 2.0 = N_0/N$
8/12 = 0.75	2	$= 6/2 = 3.0 = N_0/N$
10/12 = 0.83	1	$= 6/1 = 6 = N_0/N$

The term conversion was discussed earlier. The conversion in the case of linear step polymerization is the fraction of functional groups reacted. So, if there are 100 functional groups and 90 are reactive, then functional conversion is 90/100 or 0.9 or 90%. Let us take an example pictorially; we have 6 AB-type monomers. So, it has 12 functional groups at the beginning when there is no reaction happening and the number of monomers reacted, or the number of the functional groups reacted is 0, so conversion is 0. The number of molecules present at this moment is N= 6, and the degree of polymerization, in this case is 1 because there is only one structural unit in each molecule. If in this, 2 groups react or are coupled, then we now have 5 molecules, and 2 of the functional groups are now reacted, so *p* is 0.17, and the total number of molecules present is 5, and the degree of polymerization is 1.2. The total number of initial molecules is divided by the total number of present molecules or $N_0/N = 1.2$. Now, the number of molecules is 4 when 2 more groups react. So, the number of functional groups reacted is 4, *p* is (4 / 12) = 0.33, and we get the degree of polymerization of 1.5. The total number of molecules present initially divided by the total number of molecules present now, which is 6/4, which is 1.5. Similarly, if we can do this when all the molecules reacted, i.e. 10 functional groups reacted. So, the fractional conversion is 0.83, and the degree of polymerization is 6 because 6 molecules have joined in this case to make a polymer molecule.

(Refer Slide Time: 16:13)



Linear Step Polymerization: DP vs. Conversion

N	p	DP
100	0/200	1
50	100/200 = 0.50	= 100/50 = 2
25	150/200 = 0.75	= 100/25 = 4
13	174/200 = 0.87	= 100/13 = 7.7
7	186/200 = 0.93	= 100/7 = 14.3
1	198/200 = 0.99	= 100/1 = 100

● Functional groups

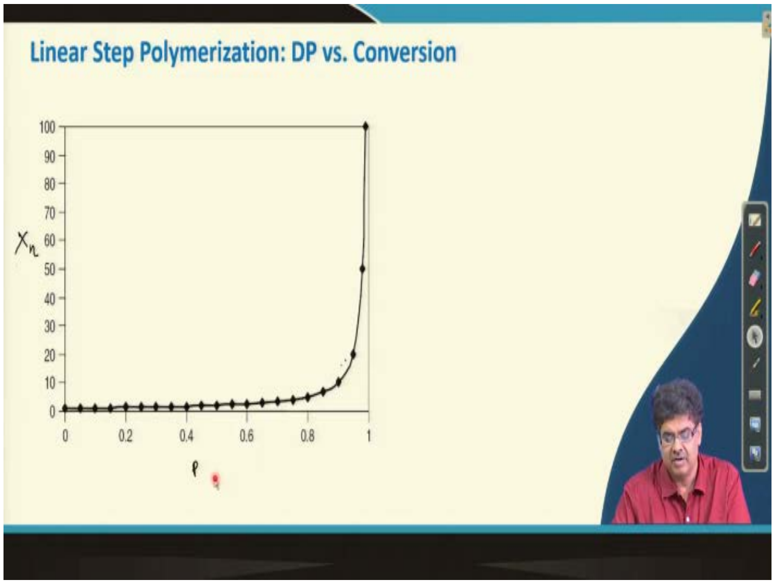
● Reacted functional groups

Moving to a little larger number say, 100 of these molecules. So, in the beginning, we have *p* is 0, so 100 molecules mean we have 200 functional groups. So, the degree of polymerization is 1.

If just hypothetically we think that each 2 of such molecules reacted, forming dimers, then now we have 50 molecules, and 100 functional groups react. So, *p* is 0.5, and the average degree of polymerization is 2. Similarly, if all these molecules reacted, i.e. dimers reacted to make tetramer. Now we have 25 molecules, and 50 functional groups are reacted. So, we get 0.75 as a conversion, and the degree of polymerization is 4. Similarly, if we proceed, when every molecule reacts with each other, we get a conversion of 0.99 and 2 functional groups remain unreacted. So basically, 198 functional groups reacted, so *p* is 0.99, and the number of structural units in this molecule is 100. So, the degree of polymerization is 100.

So, the degree of polymerization is, the number of molecules at the beginning divided by the number of molecules at present, and *p* is the fraction of molecules, the fraction of functional groups that are reacted.

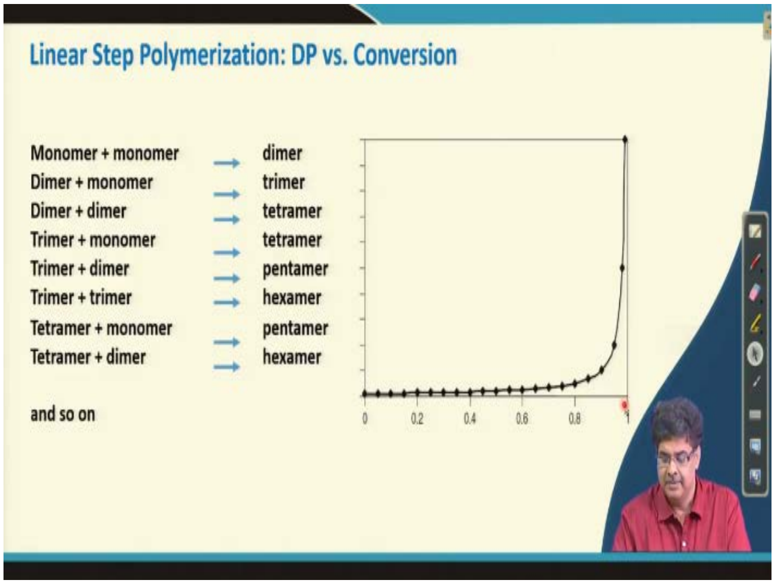
(Refer Slide Time: 18:21)



Linear Step Polymerization: DP vs. Conversion

If we plot the degree of polymerization (X_n) vs. conversion (*p*), then the graph will look like this. Unless we go to extremely high conversion, our molecular weight or degree of polymerization is not high. For example, if we go back and see that even when the conversion is 93% or 0.93, the degree of polymerization was 14.3. So, in this case, to get a high degree of polymerization, we must go to a very high conversion.

(Refer Slide Time: 19:20)



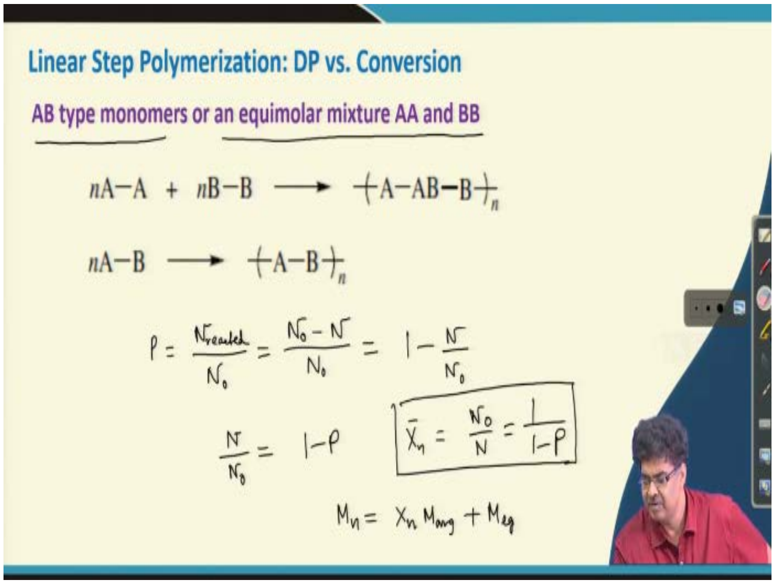
Linear Step Polymerization: DP vs. Conversion

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

In real cases, the sample will have all types of chain lengths. It means that to get a high molecular weight polymer, it should have a high degree of polymerization. For a high degree of polymerization, quantitative conversion of functional groups is needed. Thus, to make high molecular weight polymers in a step-growth polymerization, the reaction should have a high conversion value.

(Refer Slide Time: 20:19)



Linear Step Polymerization: DP vs. Conversion

AB type monomers or an equimolar mixture AA and BB

$$nA{-}A + nB{-}B \longrightarrow \left[A{-}AB{-}B \right]_n$$

$$nA{-}B \longrightarrow \left[A{-}B \right]_n$$

$$p = \frac{N_{reacted}}{N_0} = \frac{N_0 - N}{N_0} = 1 - \frac{N}{N_0}$$

$$\frac{N}{N_0} = 1 - p \qquad \boxed{\bar{X}_n = \frac{N_0}{N} = \frac{1}{1-p}}$$

$$M_n = X_n M_{avg} + M_{eg}$$

What is the relationship between the degree of polymerization and conversion? First, we will take the simplest case where we take the A and B monomers where the molar ratio of the A group and B group is always 1:1 or an equimolar mixture of AA and BB molecules. It ensures that the molar ratio of the A function group and B function group equals 1.

N_0 is the initial molecule, and the present number of molecules is N. So, (N_0 – N) is the functional groups that have reacted. So, conversion p is,

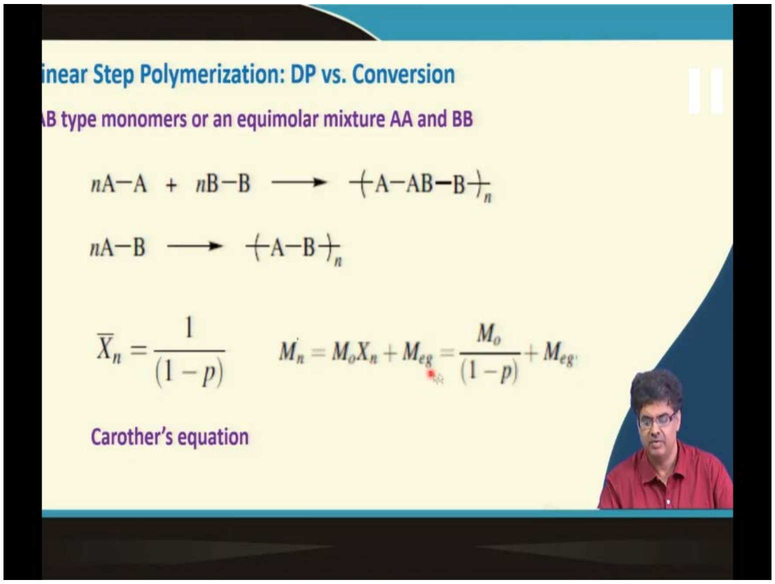
$$p = \frac{N_0 - N}{N_0} = 1 - \frac{N}{N_0}$$

$$\frac{N}{N_0} = 1 - p$$

$$\bar{X}_n = \frac{N_0}{N} = \frac{1}{1 - p}$$

So, the average degrees of polymerization ($\bar{X}_n$) is given by (1/1 – p). This is applicable for AB-type monomers or an equimolar mixture of AA and BB. And once we know the degree of polymerization, then the molecular weight (M_n) can also be known.

(Refer Slide Time: 23:01)



inear Step Polymerization: DP vs. Conversion

B type monomers or an equimolar mixture AA and BB

$$n\text{A}-\text{A} + n\text{B}-\text{B} \longrightarrow \left[\text{A}-\text{AB}-\text{B}\right]_n$$

$$n\text{A}-\text{B} \longrightarrow \left[\text{A}-\text{B}\right]_n$$

$$\bar{X}_n = \frac{1}{(1-p)} \qquad M_n = M_o X_n + M_{eg} = \frac{M_o}{(1-p)} + M_{eg}$$

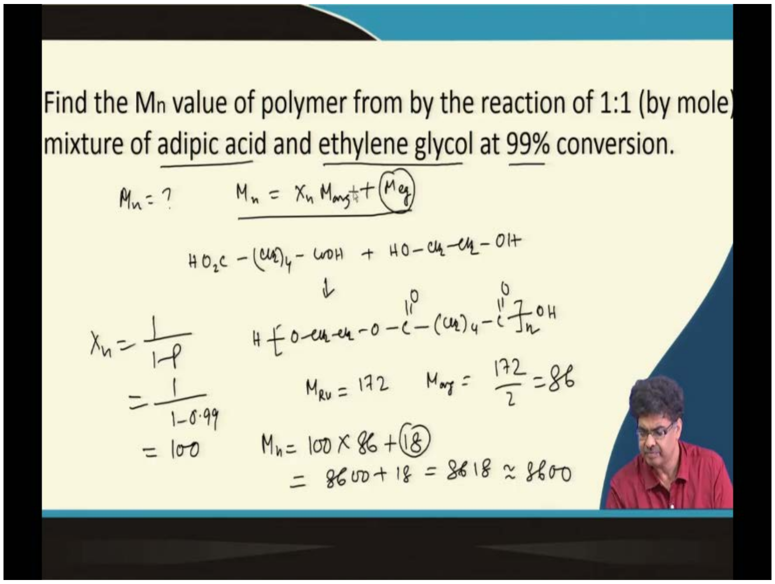
Carother's equation

Now, $\bar{X}_n$, the average degree of polymerization is given by (1/1 – p) where, p is the conversion, and this is called the Carothers equation, developed by Carothers. The molecular weight Mn is given by,

$$M_n = \frac{M_0}{1-p} + M_{eg}$$

Where, M_0, which is the average of the molecular weight and M_{eg} is the molecular weight of the end group.

(Refer Slide Time: 23:43)



Find the M_n value of polymer from by the reaction of 1:1 (by mole) mixture of adipic acid and ethylene glycol at 99% conversion.

$M_n = ?$

$M_n = X_n M_{avg} + \boxed{M_{eg}}$

$HO_2C-(CH_2)_4-COOH + HO-CH_2-CH_2-OH$

$\downarrow$

$H\left[O-CH_2-CH_2-O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right]_n OH$

$X_n = \frac{1}{1-p} = \frac{1}{1-0.99} = 100$

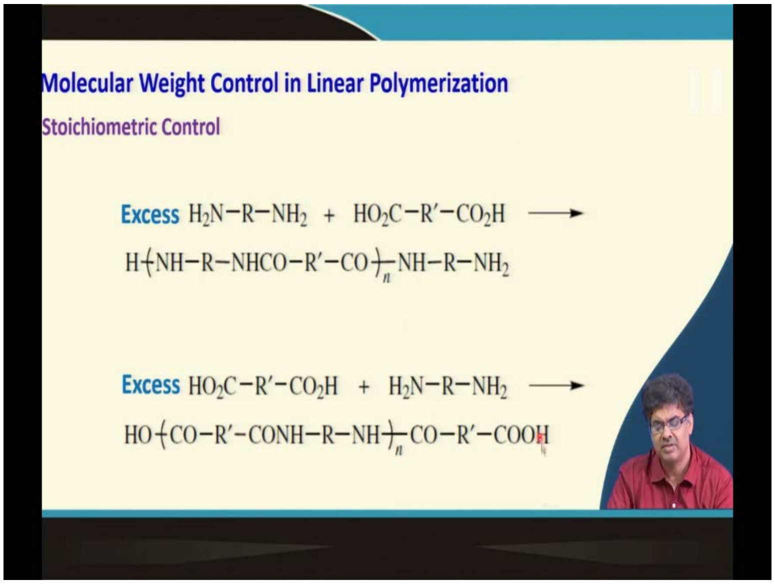
$M_{RU} = 172 \quad M_{avg} = \frac{172}{2} = 86$

$M_n = 100 \times 86 + \boxed{18}$

$= 8600 + 18 = 8618 \approx 8600$

Now, in the polymerization reaction of adipic acid and ethylene glycol, the molecular weight of these repeat units is given by 172. M_{avg}, which is the average of the structural unit, will be given by 172 / 2 is 86. So, X_n is given by $(1/1 - P)$, p is 99% or {1 / (1 - 0.99)}. So X_n is 100. So, M_n would be given by 100×86 + molecular of the end groups. The end groups are OH and H. So basically what 18. So, 8600 + 18 is 8618. In most cases, these molecular of the end groups are ignored.

(Refer Slide Time: 26:17)



Molecular Weight Control in Linear Polymerization

Stoichiometric Control

Excess $H_2N-R-NH_2 + HO_2C-R'-CO_2H \longrightarrow$

$H\{NH-R-NHCO-R'-CO\}_n NH-R-NH_2$

Excess $HO_2C-R'-CO_2H + H_2N-R-NH_2 \longrightarrow$

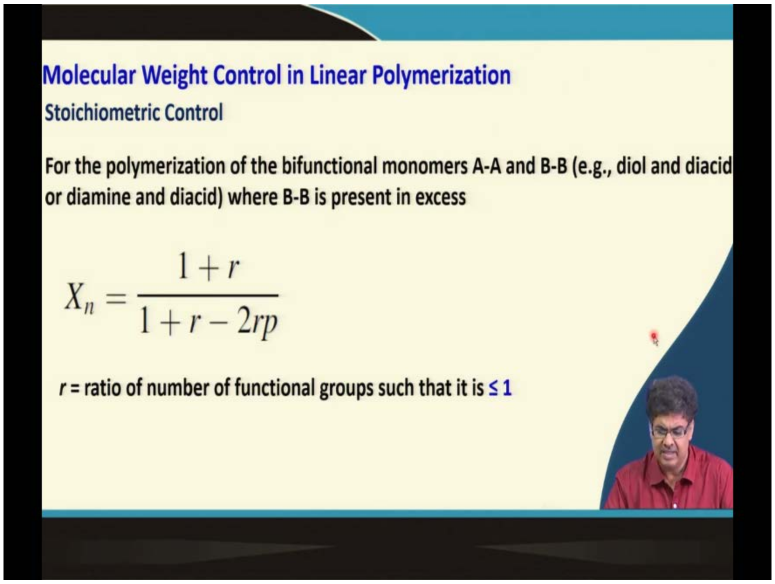
$HO\{CO-R'-CONH-R-NH\}_n CO-R'-COOH$

Now we will go to the next case where we have one of the molecules are present in excess. As we have seen in the last example, we can control the polymerization to control the molecular weight. If we control the *p*-value, we can control the molecular weight, but one problem in controlling the molecular weight by using just the value of *p* that at the end, we get the polymer having excess functional group present in the polymer.

Now, if we use that polymer in the product or during further processing, what happens is that the free functional groups which are present at the chain end can participate in the further reaction. As a result, there will be instability in the molecular weight of the polymers. So, we should have a strategy to control the polymer molecular weight without having the functional groups present at the end of the polymers.

One such strategy is by controlling the stoichiometry of two monomers. For example, for polyamide formation, if we take excess diamine, then we are likely to get amine groups at the end. If we have only amine groups at the end, no free carboxylic groups, then there is no further reaction possible between them, and so the molecular weight will be stabilized. Similarly, if we have an excess acid, we are likely to get acid groups at the end without amine groups, and so the volume of the molecule's weight would be stabilized.

(Refer Slide Time: 28:11)



Molecular Weight Control in Linear Polymerization

Stoichiometric Control

For the polymerization of the bifunctional monomers A-A and B-B (e.g., diol and diacid or diamine and diacid) where B-B is present in excess

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

r = ratio of number of functional groups such that it is ≤ 1

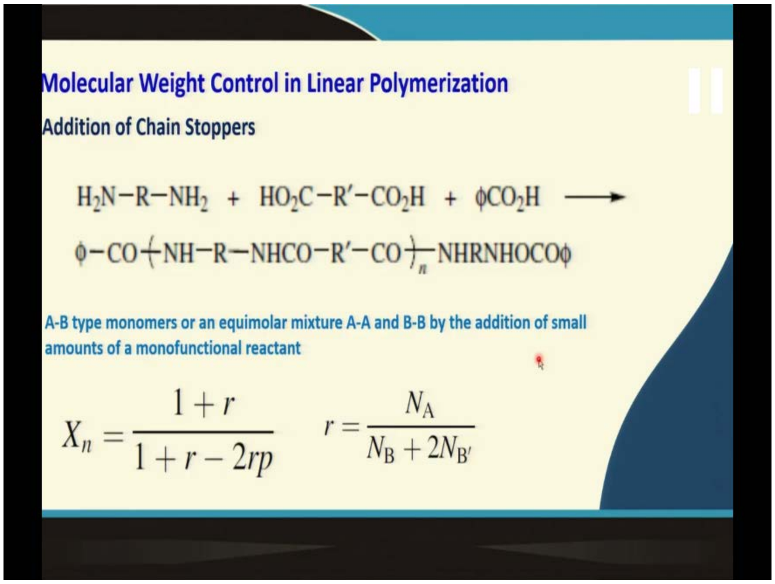
Now in case, we have 2 types of monomers of AA and BB functionalities and where the BB is excess, the average degree of polymerization is given by

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

This is not simple to derive. where r is the ratio of the functional groups present. It is always less than 1. The monomer which is present in excess, will be in the denominator. So, in this particular case, r would be given by the number of functional groups of A divided by the number of groups of B because we are talking about B in excess. So, r is always less than equals to 1.

Next, I give you another strategy by which we can control the molecular weight by adding a chain stopper.

(Refer Slide Time: 30:08)



Molecular Weight Control in Linear Polymerization

Addition of Chain Stoppers

$$H_2N-R-NH_2 + HO_2C-R'-CO_2H + \phi CO_2H \longrightarrow$$

$$\phi-CO\left(NH-R-NHCO-R'-CO\right)_n NHRNHOCO\phi$$

A-B type monomers or an equimolar mixture A-A and B-B by the addition of small amounts of a monofunctional reactant

$$X_n = \frac{1+r}{1+r-2rp} \qquad r = \frac{N_A}{N_B + 2N_{B'}}$$

For example, if we add a monofunctional acid in the reaction between diamine and diacid, then we get the polymer chains ended with these monofunctional groups. And we actually can use the same formula where we are defining the value of r like this.

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

Where $N_{B'}$ is the number of molecules of the monofunctional monomer.

This is applicable for the simplest case where we have AB type of monomer or a mixture of AA and BB, plus we have a small amount of monofunctional reactive monomer, number of which we are telling as $N_{B'}$. Then we use the same equation to finding out the average degree of polymerization. We have taken an equivalent mixture of A and B or taken AB-type monomer and $N_{B'}$ which is the number of monomers of this monofunctional reactant. To give an example of how this is used to control the molecular weight, we will continue for further discussion on step-growth polymerization in the next lecture.