Introduction to Polymer Science

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Lecture-09

Linear Step Polymerization: Summary-General Requirement, Non Linear Step Polymerization

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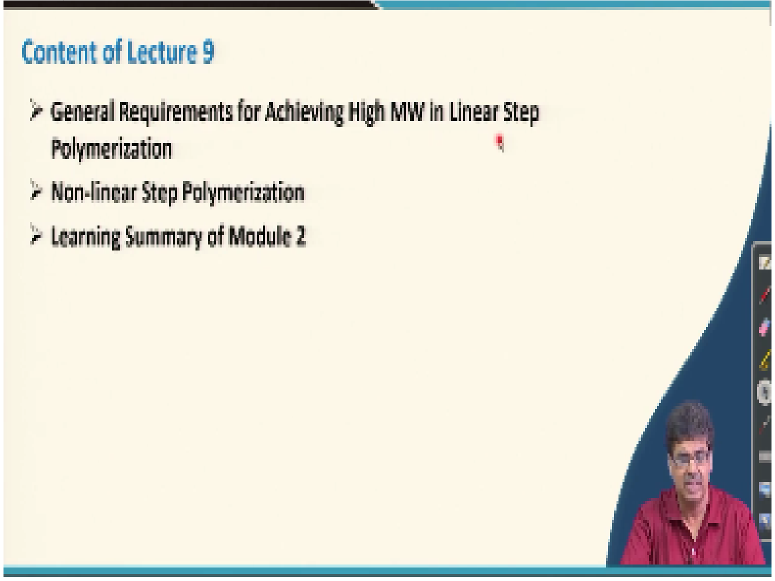

Content of Lecture 9

- General Requirements for Achieving High MW in Linear Step Polymerization
- Non-linear Step Polymerization
- Learning Summary of Module 2

Welcome back, in this lecture, we will sum up the learnings from step linear step polymerization and then move to nonlinear step polymerization. These are the topics will be covered in this lecture. We have discussed different aspects of step-growth polymerization, linear step-growth polymerization and understood how to control the molecular weight, what are the kinetics associated with this linear step polymerization, and what are the limitations.

Our target is to increase the molecular weight or to achieve the target molecular weight during synthesis. We have learned about the requirements for achieving high molecular weight during this linear step growth polymerization.

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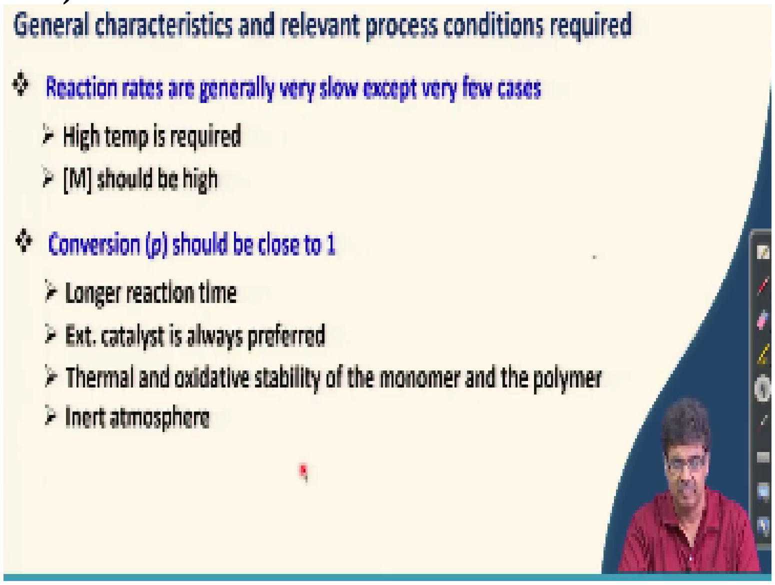

General characteristics and relevant process conditions required

- Reaction rates are generally very slow except very few cases
  - High temp is required
  - [M] should be high
- Conversion (p) should be close to 1
  - Longer reaction time
  - Ext. catalyst is always preferred
  - Thermal and oxidative stability of the monomer and the polymer
  - Inert atmosphere

The reaction rates are generally very slow except few cases. The reaction rate for polycarbonate, a step polymerization, the rate constant is of the order of 10^{-3} L mol^{-1} s^{-1} in the temperature range of 150 °C to 250 °C So, this is quite a slow reaction process. There are a few examples like the reaction between acid chlorides with alcohol or with amines which are quite fast, but in general, the reaction rates are slow.

We need to do a reaction at a high temperature and the concentration of monomers or the functional groups should be high. From Carother's equation, we know, the conversion should be close to 1 and it is better to have an external catalyzed reaction rather than self catalyzed reaction. Because the reaction takes a longer time, we must choose monomers properly. The chemical structure of the polymers should be such that they can sustain or survive in high-temperature conditions. It should have enough thermal and oxidative stability. We should ensure that the reactions are carried out in an inert atmosphere to avoid any thermal and oxidative degradation of the polymers.

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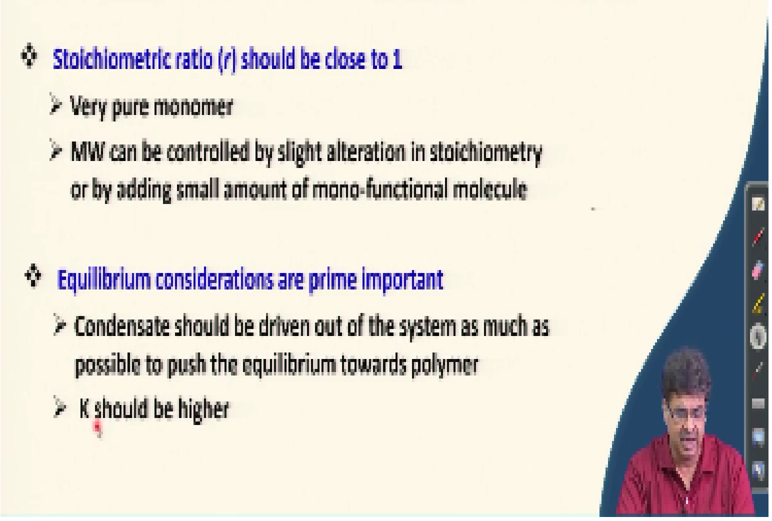

General characteristics and relevant process conditions required

- Stoichiometric ratio (r) should be close to 1
  - Very pure monomer
  - MW can be controlled by slight alteration in stoichiometry or by adding small amount of mono-functional molecule
- Equilibrium considerations are prime important
  - Condensate should be driven out of the system as much as possible to push the equilibrium towards polymer
  - K should be higher

To build a high molecular weight, the reaction stoichiometric ratio should be at close to 1 as possible. Hence, we need to have very high pure monomers. Otherwise, if the monomers are impure, then, the actual molar ratio of functional groups is not known. Additionally, if the monomers are not pure, then it is not known whether the impurities actually can act as chain stoppers or not. If they act as chain stoppers then synthesizing high moleculear weight polymers would be difficult. To control the molecular weight, we can change the stoichiometry of functional groups or the monomers, or deliberately add small molecular weight monofunctional molecules. Equilibrium considerations are also of prime importance. To have a decent or acceptable molecular weight, we must remove the small molecular condensates out of the reaction as much as possible. To push the equilibrium towards polymerization, we should design monomers such that the reaction between the functional groups is of high feasibility so that the equilibrium constant for the reactions becomes higher.

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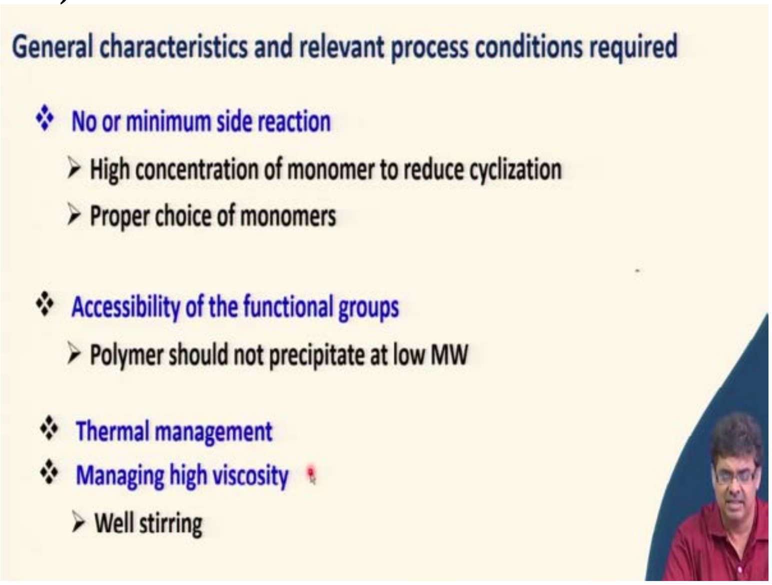

General characteristics and relevant process conditions required

- No or minimum side reaction
  - High concentration of monomer to reduce cyclization
  - Proper choice of monomers
- Accessibility of the functional groups
  - Polymer should not precipitate at low MW
- Thermal management
- Managing high viscosity
  - Well stirring

It must be ensured that there is no or minimum side reaction occurs because, if the side reaction take place, then the stoichiometry can be different from the targeted stoichiometry, or it might be generating some monofunctional chain stoppers or some chemicals which might degrade or accelerate the oxidative or thermal instability of the polymers. It is also preferred to do the reaction with high concentration of monomer to reduce the cyclization process and proper choice the monomers need to be also taken care of.

One more important aspect is the accessibility of functional groups. The polymers which are synthesized during the polymerization, should not precipitate. They should be soluble in the medium or the reaction mixture, especially at the low molecular weight region. If the polymers which are getting synthesized, come out or precipitated from the reaction mixture at a lower molecular weight, then it is not possible to build a high molecular weight.

All the polymerization processes are exothermic because, in the polymerization process, new bonds are created and any bond creation is an exothermic process. During the polymerization process, heat is generated and as a result, the local temperature of the mixture becomes high. So managing the heat during polymerization is a very important aspect. It is done by proper stirring so that no local hotspots are created. If it is done in a solution phase then obviously viscosity problems are much lower. Hence, the reaction mixture must be stirred well to manage viscosity as well as to manage the heat generated in the system.

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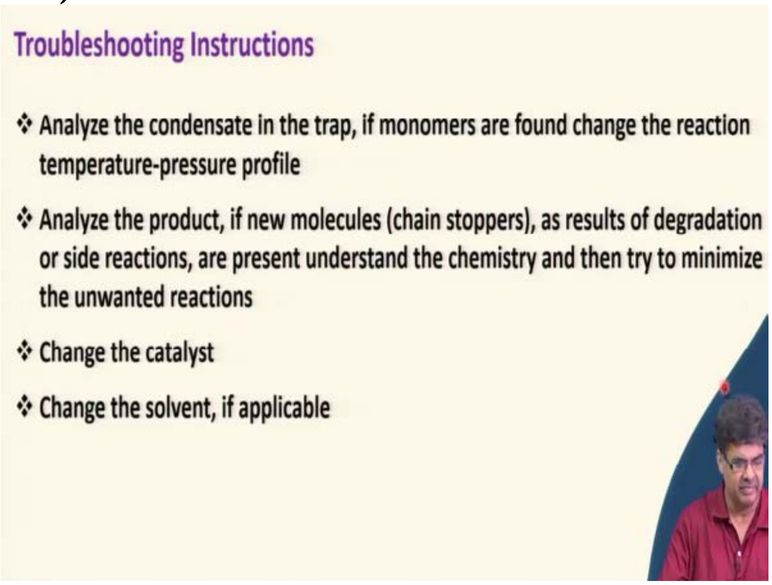

Troubleshooting Instructions

- Analyze the condensate in the trap, if monomers are found change the reaction temperature-pressure profile
- Analyze the product, if new molecules (chain stoppers), as results of degradation or side reactions, are present understand the chemistry and then try to minimize the unwanted reactions
- Change the catalyst
- Change the solvent, if applicable

Even though taking care of all these aspects, if anyone finds that he/she is not able to synthesize the target molecular weight, then there are a few troubleshooting instructions that must be analyzed. The trap where the the small molecular condensates are collected need to be analyzed to check weather monomers are escaping from the reaction medium and getting trapped. Because high vacuum and high temperature are applied, there is a possibility that some monomers may also vaporize and come out at that low pressure. So, the trap should be checked to find out if the monomers have deposited or not. If the monomer comes, then the loss of monomer needs to compensated by changing the molar ratio of the functional groups. Also, the temperature and pressure profile can be changed to reduce the monomer loss from the system. The products should be analyzed to find out whether the chains are stopped by a different molecule than what is expected. In that case, there is a possibility that chain stoppers were produced during the reaction as a result of degradation or side reactions. So, one should understand the chemistry of those possible side reactions and try to minimize them. And of course, there are other ways to try, by changing the catalyst, and changing the solvent if the reaction is done in the solution. So, these are some troubleshooting instructions one should follow during linear step polymerization when the targeting molecular weight is not achieved.

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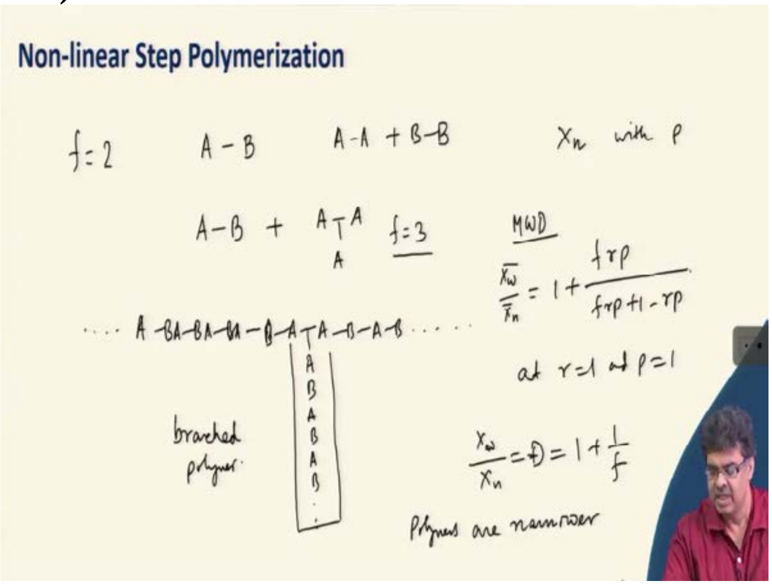

Non-linear Step Polymerization

$f=2$ A - B A-A + B-B X_n with p

A-B + $\mathrm{A}\underset{\mathrm{A}}{\top}\mathrm{A}$ $\underline{f=3}$

$\underline{\text{MWD}}$

$$\frac{\bar{X}_w}{\bar{X}_n} = 1 + \frac{frp}{frp+1-rp}$$

.... A-BA-BA-BA-B-A-A-B-A-B .....

A B A B A B . .

branched polymer.

at r=1 and p=1

$$\frac{X_w}{X_n} = Đ = 1 + \frac{1}{f}$$

Polymers are narrower

Nonlinear step polymerization. Till now we have been discussing the case of linear step polymerization, where the monomer functionality is 2, we are either using A-B type monomer or mixture of A-A and B-B type monomers. Now, in case we have the value of monomer functionality *f* > 2, for example, if we take the mixture of monomer A-B and a monomer having *f* = 3, in this case, what type of polymer we will get? For single monomer A-B, we get a polymer like A-B A-BA-BA-B ---. If we have functionality a monomer with *f* = 3, then we will get a branch structure. The branches are shown in the figure. Now, in this case, the reaction rate is faster compared to linear step polymerization and also the more increase in the degrees of polymerization with conversion. The relation between X_n with p is, in the case of nonlinear polymerization, X_n goes up the higher rate compared to a linear polymerization with respect to p. The molecular weight distribution in this case, without deriving the formula, can be written,

$$\frac{X_w}{X_n} = 1 + \frac{frp}{frp + 1 - rp}$$

So, at *r* = 1, *p* = 1 we get,

$$\frac{X_w}{X_n} = Đ = 1 + \frac{1}{f}$$

In this case, the polymers produced are narrow or have narrower distribution compared to a linear step-growth polymerization.

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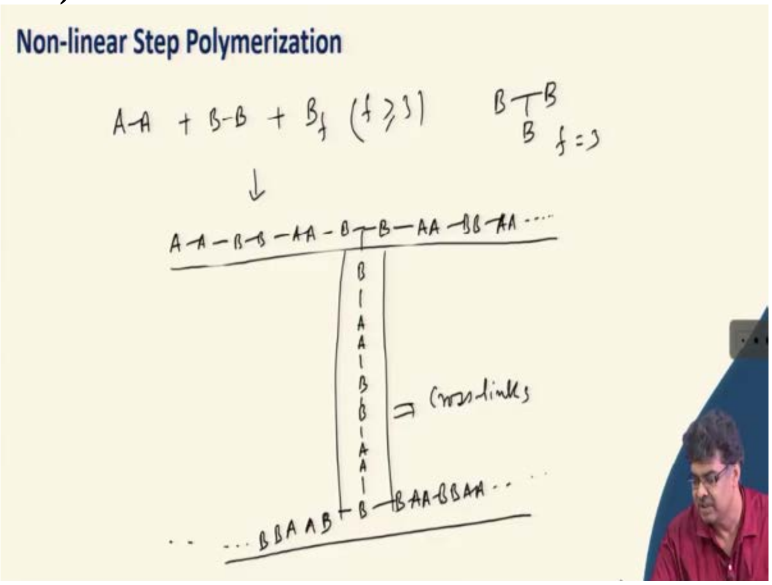

Non-linear Step Polymerization

Now, to the second case, instead of A-B type monomer we have A-A + B-B type monomer, and we are adding a multifunctional monomer with $f \geq 3$ as shown in the figure. Now, if we write the structure then we get this polymer like in the figure. Now if there is a monomer B_3 for which $f = 3$, then it will get into the chain and can react in three directions. In this case, two chains are connected with a bridge, which is called a cross-link. Cross-linked polymers are produced in this particular case. If the monomer ratio is such that or the reaction continues till high conversion, it might happen that all the polymer chains are tied up with each other through cross-links and we get a network polymer with infinite molecule weight.

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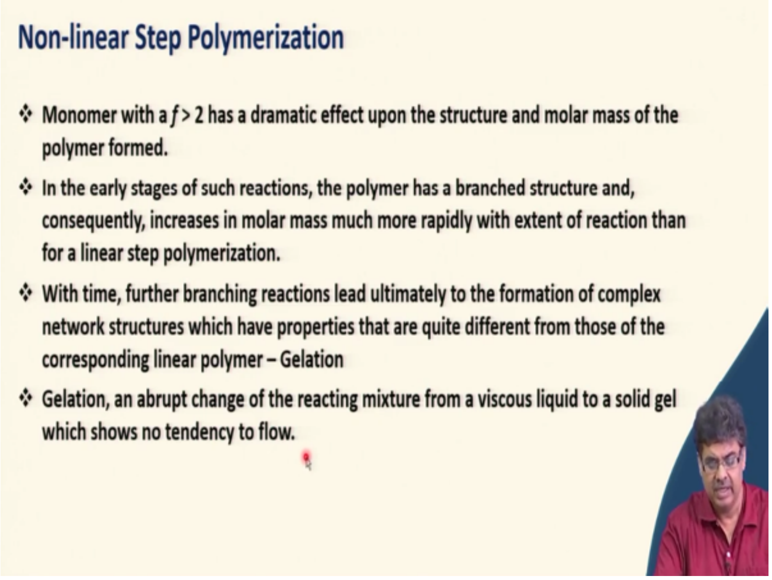

Non-linear Step Polymerization

- Monomer with a $f > 2$ has a dramatic effect upon the structure and molar mass of the polymer formed.
- In the early stages of such reactions, the polymer has a branched structure and, consequently, increases in molar mass much more rapidly with extent of reaction than for a linear step polymerization.
- With time, further branching reactions lead ultimately to the formation of complex network structures which have properties that are quite different from those of the corresponding linear polymer – Gelation
- Gelation, an abrupt change of the reacting mixture from a viscous liquid to a solid gel which shows no tendency to flow.

In the non-linear step polymerization monomers with f > 2 has a dramatic effect on the structure and molar mass of the polymer formed. In the early stage of the reaction, the polymers have branch structure, as we just discussed, and with time, because of the branched structure, the molecular weight or the molar mass increases more rapidly with the extent of a reaction than in a linear step polymerization. And with time further branching reactions leads ultimately to the formation of a complex network structure that has properties that are quite different from those of the linear polymerization. Once these entire polymer chains present get linked to each other, and there is enough concentration of such polymers in the solvent, we get a gelation or gel formation. What is gel? Gelation is a step where the reaction mixture forms a viscous liquid with solid mass and solid mass shows no tendency to flow, gelation is an abrupt change of the reaction mixture from a viscous liquid to a solid gel, which has no tendency to flow. The concentration or the time when this gelation happens, we call this point as a gel point.

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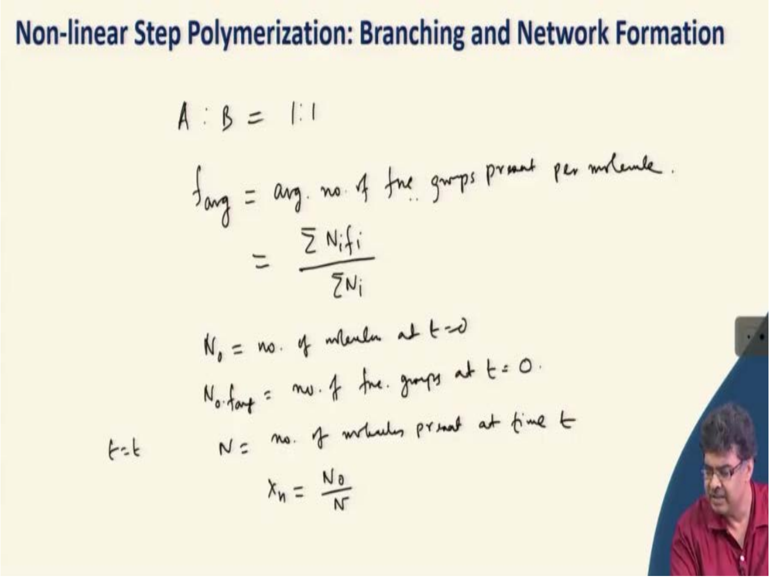

Non-linear Step Polymerization: Branching and Network Formation

$A : B = 1:1$

f_{avg} = avg. no. of fnc. groups present per molecule.

$$= \frac{\Sigma N_i f_i}{\Sigma N_i}$$

N_0 = no. of molecules at $t=0$

$N_0 \cdot f_{avg}$ = no. of fnc. groups at $t=0$.

$t=t$ N = no. of molecules present at time t

$$X_n = \frac{N_0}{N}$$

Now, during gel formation, we get a kind of different polymer, all the polymer chains in the system are connected to each other and have a network formation. This polymer sample does not flow at all, form a gel and the molecular weight or the degrees of polymerization, in this case, would be infinity because all the polymers are linked to each other. Now, to use Carother's equations to find out the conversion when we get this value of $X_n = \propto$, we will consider the simplest situation. We will consider monomer mixture with A:B functional group in 1:1 ratio, and we define f_{avg} as the average number of functional groups present per molecule,

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

where N_i is the number of molecules with functionality of f_i. In the beginning, N_0 is the number of molecules at t = 0. So $N_0.f_{avg}$ would be the number of functional groups at t = 0. If N is the number of molecules present at time t then,

$$X_n = \frac{N_0}{N}$$

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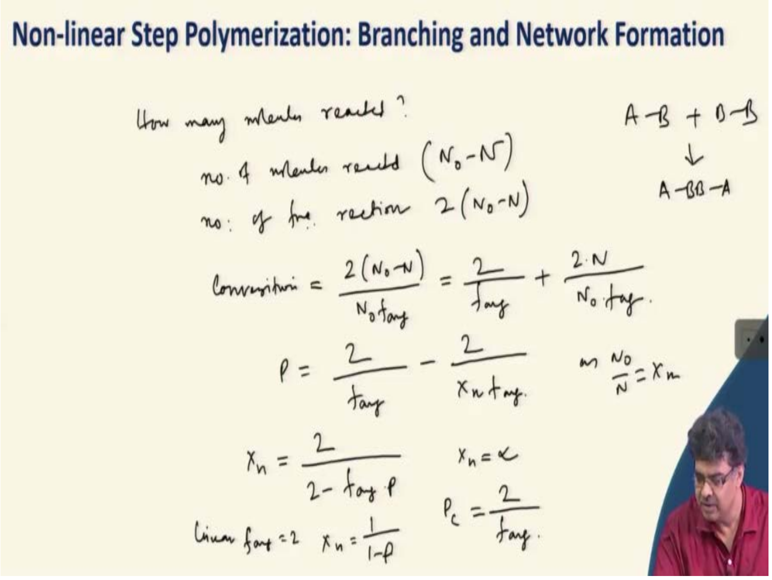

Non-linear Step Polymerization: Branching and Network Formation

How many molecules reacted?

no. of molecules reacted $(N_0 - N)$

no. of fn. reaction $2(N_0 - N)$

$A-B + B-B \rightarrow A-BB-A$

$$\text{Conversion} = \frac{2(N_0-N)}{N_0 f_{avg}} = \frac{2}{f_{avg}} + \frac{2 \cdot N}{N_0 f_{avg}}.$$

$$p = \frac{2}{f_{avg}} - \frac{2}{X_n f_{avg}}. \quad \text{as } \frac{N_0}{N} = X_n$$

$$X_n = \frac{2}{2 - f_{avg} p} \quad X_n = \infty$$

$$P_c = \frac{2}{f_{avg}}.$$

Linear $f_{avg} = 2$ $X_n = \frac{1}{1-p}$

So, the number of molecules reacted is given by $(N_0\text{-}N)$. The number of functional groups reacted is $2(N_0 – N)$. Each molecule's disappearance is equivalent to the reaction of 2 functional groups. So, the total number of functional groups reacted is $2(N_0 – N)$. So, the conversion is –

$$p = \frac{\text{no of functional groups reacted}}{\text{total number of fuctional groups present at t} = 0} = \frac{2(N_0 - N)}{N_0 f_{avg}} = \frac{2}{f_{avg}} + \frac{2N}{N_0 f_{avg}}$$

So, p is given by,

$$p = \frac{2}{f_{avg}} - \frac{2}{X_n f_{avg}}$$

As N_0/N is X_n,

So, we can rearrange it to,

$$X_n = \frac{2}{2 - f_{avg} p}$$

Now for a linear polymerization, f_{avg} is 2 which means, in this case,

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

that leads to the original Carother's equation. Now for gel formation, X_n is infinity. So in that case, p_c, which is the critical conversion where gel formation takes place, is given by just placing $Xn = \propto$, and we get,

$$p_c = \frac{2}{f_{avg}}$$

p_c is where the molecular weight becomes infinity. As we increase the average value of functionality, we get gelation at a much lower concentration of the reaction.

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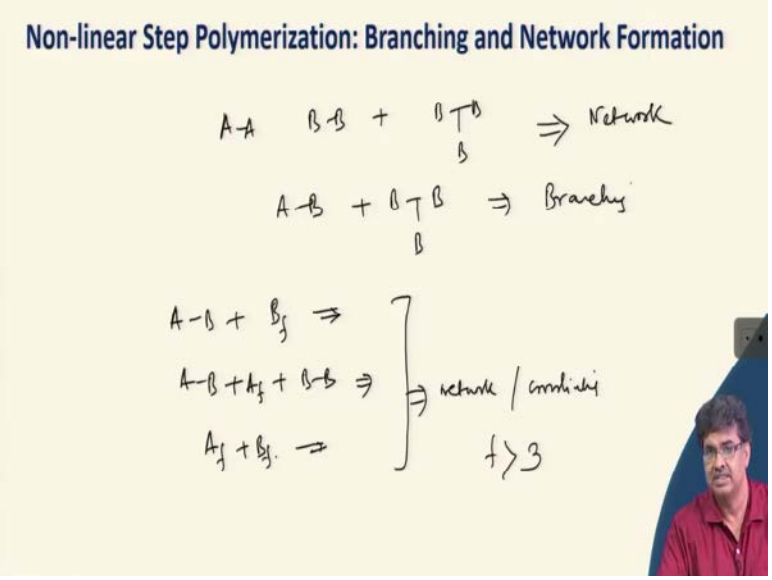

Non-linear Step Polymerization: Branching and Network Formation

$A-A \quad B-B + B\text{-}\underset{B}{T}\text{-}B \Rightarrow$ Network

$A-B + B\text{-}\underset{B}{T}\text{-}B \Rightarrow$ Branching

$A-B + B_f \Rightarrow$

$A-B + A_f + B-B \Rightarrow$

$A_f + B_f. \Rightarrow$

$\Rightarrow$ network / crosslinking

$f > 3$

Earlier, we gave an example of a network formation, and in another case branching formation took place when $f > 3$. So, these are some of the systems that can be designed if one wants to get gel formation or network formation. If the f_{avg} is higher, then the gel formation can be achieved at lower conversion.

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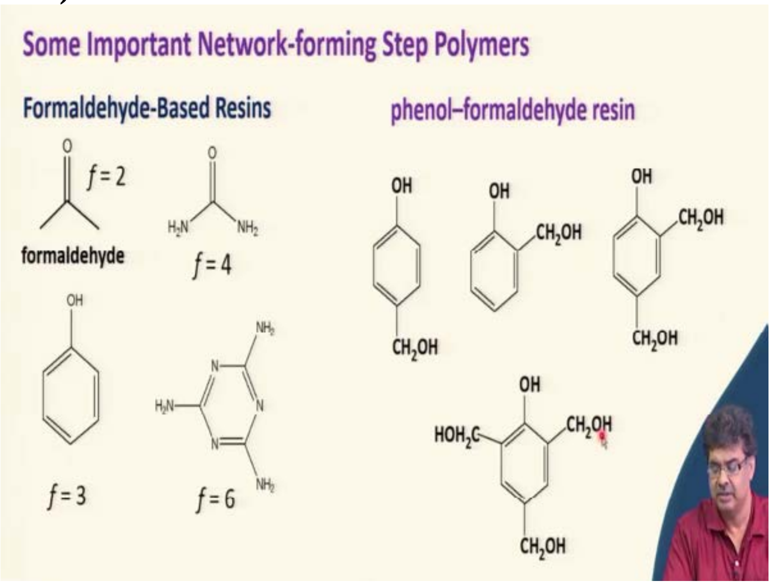

Some Important Network-forming Step Polymers

Formaldehyde-Based Resins

phenol–formaldehyde resin

There are some important examples of network polymers synthesized by step polymerization and one very important such example is phenol formaldehyde resin and this network product of step polymers is generally termed resins. For this reaction, *f* I for formaldehyde is 2 whereas, a phenol has 3 places to react so, it has *f* = 3. Similarly, for urea *f* = 4 and for melamine *f* = 3. In the case of phenol formaldehyde reaction, we get 3 to 4 possible different products that react to each other and formaldehyde to produce network structure.

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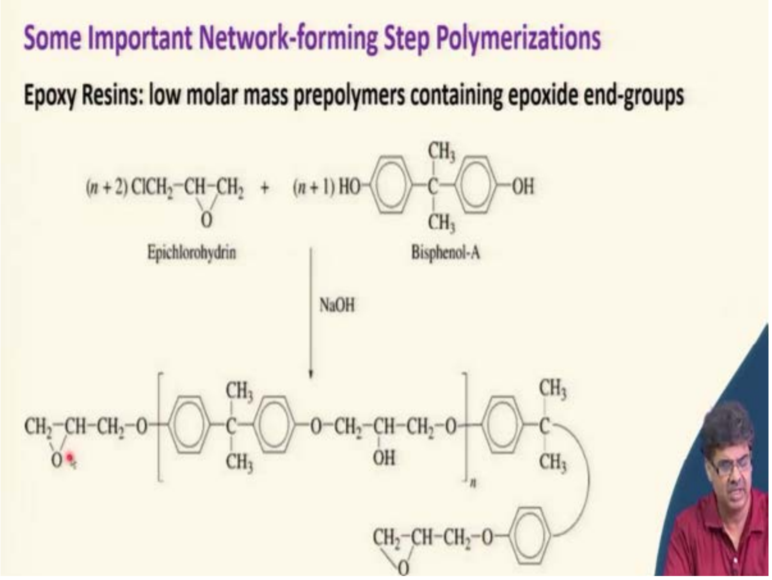

Some Important Network-forming Step Polymerizations

Epoxy Resins: low molar mass prepolymers containing epoxide end-groups

Similarly, another important network polymer is epoxy resin. In this case, at the beginning low molecular weight prepolymer containing the epoxide groups are synthesized by reacting epichlorohydrin with the sodium salt of Bisphenol-A. It forms prepolymer, a small molecular weight polymer with epoxide end groups.

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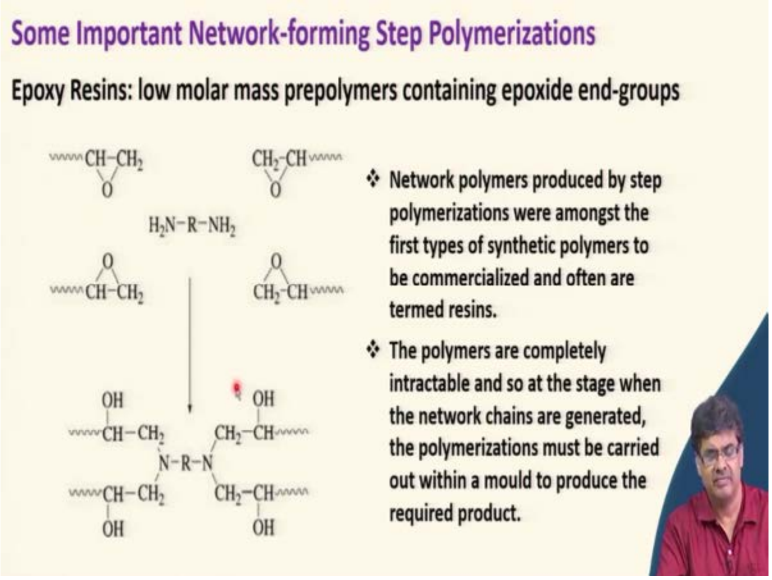

Some Important Network-forming Step Polymerizations

Epoxy Resins: low molar mass prepolymers containing epoxide end-groups

- Network polymers produced by step polymerizations were amongst the first types of synthetic polymers to be commercialized and often are termed resins.
- The polymers are completely intractable and so at the stage when the network chains are generated, the polymerizations must be carried out within a mould to produce the required product.

Using functionality more than 3, we can crosslink these epoxy prepolymers to make network polymer. Because amine can react with epoxide to form 2 covalent bonds, the diamine has functionality, 2 + 2 = 4. It can form a network as it is shown in the scheme. Now, as we can understand that once network formation happens, it is difficult to handle because you cannot take out or reprocess these polymers. So, typically the final reaction is done in the mold to give the final shape. First, the prepolymers are made in a liquid form and the prepolymers are added to the mold and then for the cross-linking reaction to happen, the crosslinker is added. Network polymers were the first production of step polymers. Ther were the first type of synthetic polymers to be commercially used or commercialized, and often termed resins. The polymers are completely intractable. So, at the stage when the networks are generated, the polymerization must be carried out within a mold to produce the final cross-linked product.

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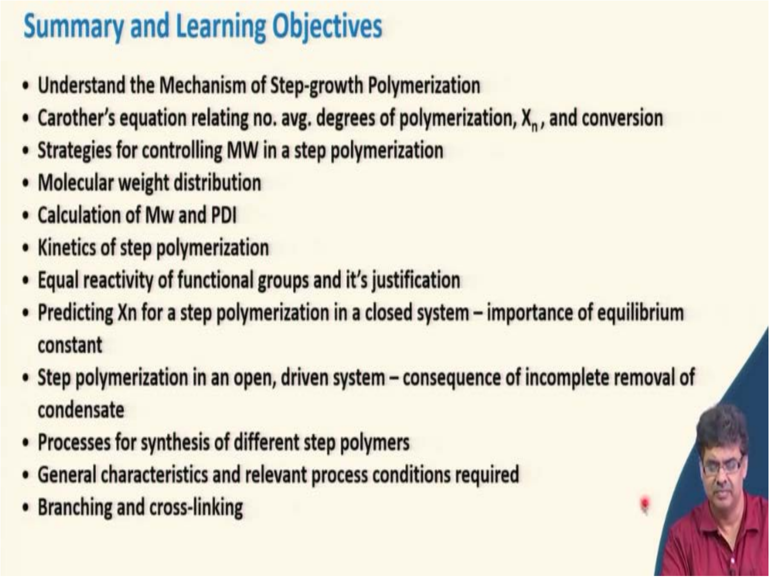

Summary and Learning Objectives

- Understand the Mechanism of Step-growth Polymerization
- Carother's equation relating no. avg. degrees of polymerization, X_n, and conversion
- Strategies for controlling MW in a step polymerization
- Molecular weight distribution
- Calculation of Mw and PDI
- Kinetics of step polymerization
- Equal reactivity of functional groups and it's justification
- Predicting Xn for a step polymerization in a closed system – importance of equilibrium constant
- Step polymerization in an open, driven system – consequence of incomplete removal of condensate
- Processes for synthesis of different step polymers
- General characteristics and relevant process conditions required
- Branching and cross-linking

With this, we come to the end of this module. One should be able to understand the mechanism of step-growth polymerization and should be able to relate the number average degrees of polymerization with conversion. One should also know how the molecular weight or degree of polymerization in a linear step polymerization can be the control using symmetric imbalance or using chain stopper, the molecular wight distribution expression in case of liner step polymerization, how to calculate molecular weight and PDI, polydispersity index or dispersity.

The externally catalyzed reactions are faster than internally catalyzed or self catalyzed reactions. In that respect, one should understand the principal of equal reactivity of functional groups and its justification. One should be able to predict the degrees of polymerization for step polymerization in case of a closed system, and an open and driven system. One should realize that for a step polymerization to happen, it is always preferable to remove the small molecular condensates to the maximum extent possible. Some examples of different synthetic processes are given. With this, we come to the end of this module.