# Polymer Process Engineering

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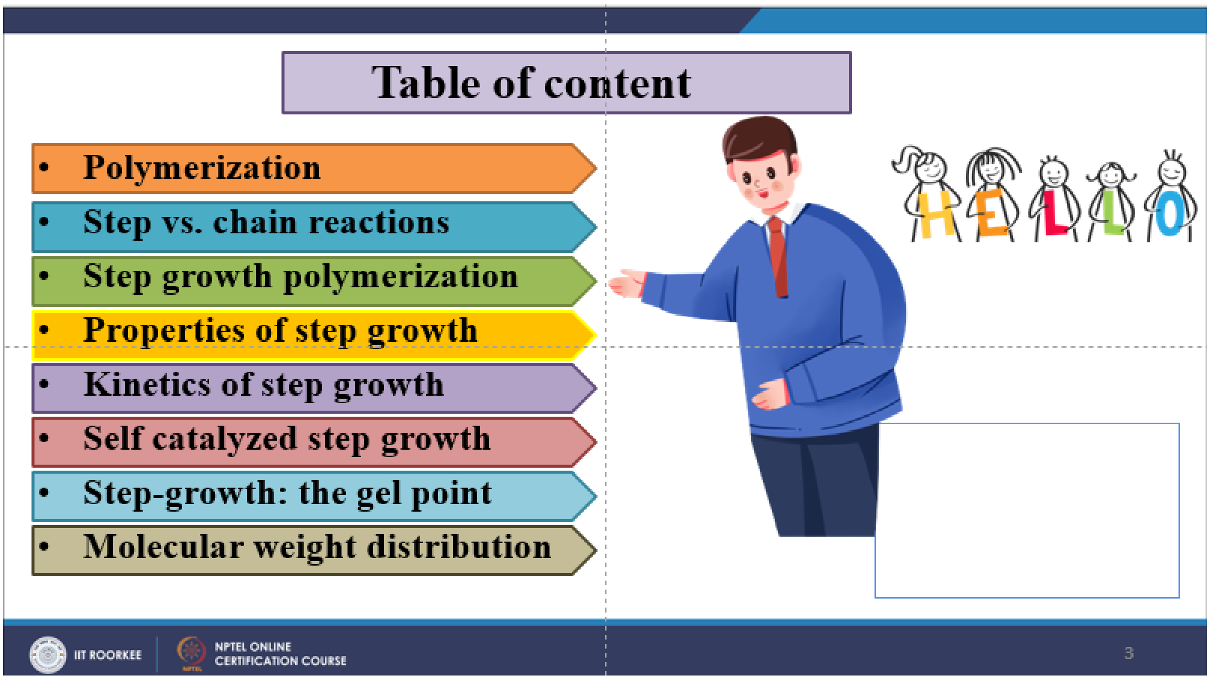
## Lecture 27

## Chemical reaction engineering in polymers: Condensation (Step-growth) polymerization

Hello friends, welcome to another segment of Chemical Reaction Engineering, the Polymer System. Here we are going to discuss about condensation which is the step of growth polymerization under the edge of polymer process engineering. Now, the topic we have covered previously, we discussed about chemical kinetics, we discussed about reaction rates, we discussed about the rate log, samples, molecularity, order of the reaction, temperature reaction rate, collision theory, and transition state theory. All those things we discussed a lot.



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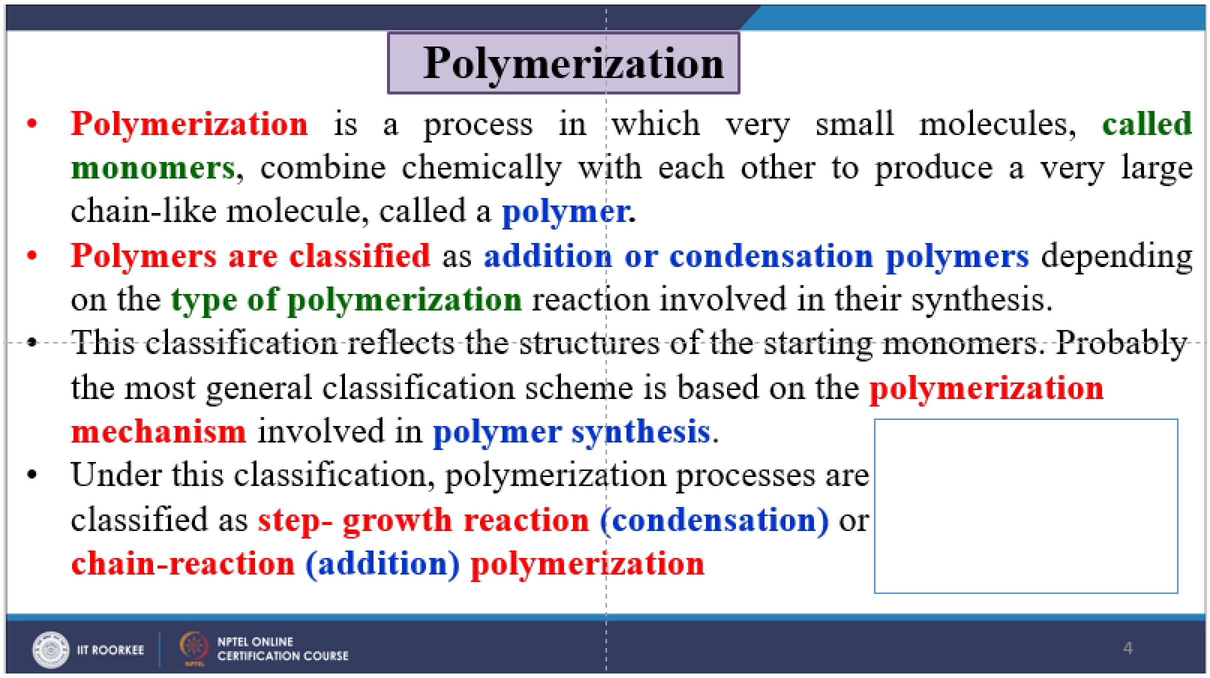
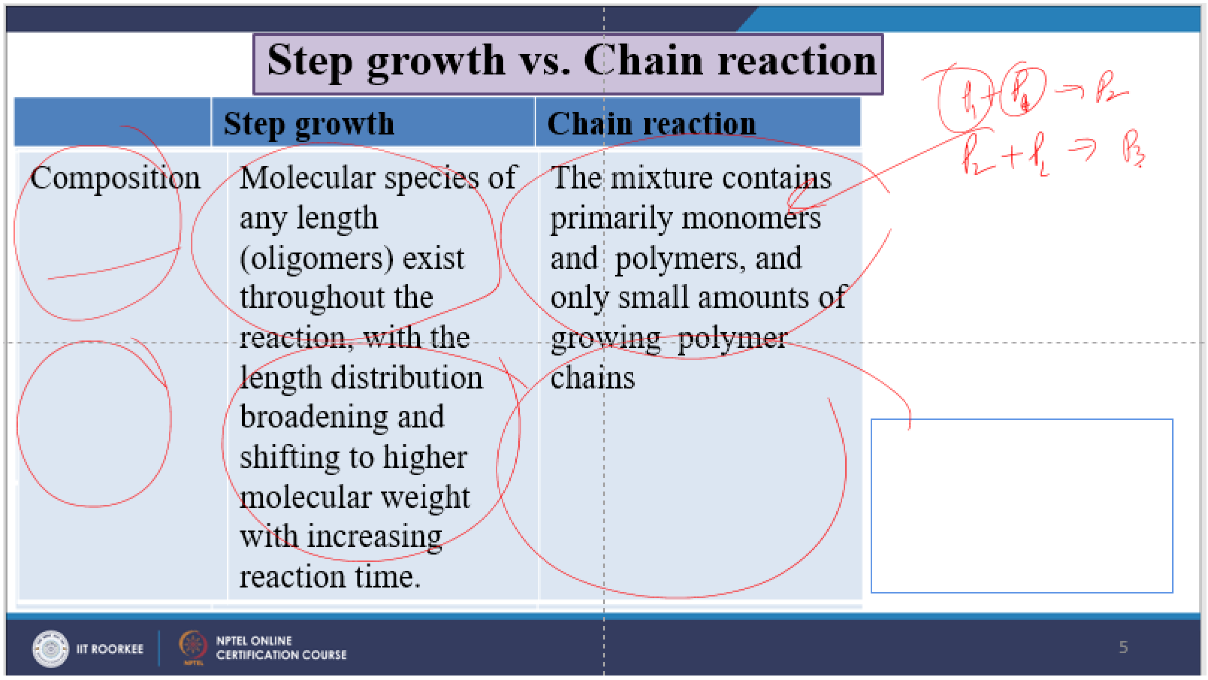
In this particular segment we are going to discuss polymerization, step growth versus the chain growth reactions, then step growth polymerization we are going to discuss with the various properties of step growth. Then we will discuss the kinetics of step-growth polymerization and, apart from this the self-catalyzed step growth. Then we will discuss the gel point and the molecular weight distribution.



## Polymerization

- **Polymerization** is a process in which very small molecules, **called monomers**, combine chemically with each other to produce a very large chain-like molecule, called a **polymer**.
- **Polymers are classified** as **addition or condensation polymers** depending on the **type of polymerization** reaction involved in their synthesis.
- This classification reflects the structures of the starting monomers. Probably the most general classification scheme is based on the **polymerization mechanism** involved in **polymer synthesis**.
- Under this classification, polymerization processes are classified as **step- growth reaction (condensation)** or **chain-reaction (addition) polymerization**

As we know molecular weight distribution plays a very vital role in deciding the properties of the polymer. Now, let us have a brief overview about polymerization. Now polymerization is the process by which very small molecules they are called monomers, they combine chemically with each other to produce a very large chain-like molecules they are called the polymers. So, the polymer is composed of chains, composed of various monomers.



## Step growth vs. Chain reaction

| | Step growth | Chain reaction |
|---|---|---|
| Composition | Molecular species of any length (oligomers) exist throughout the reaction, with the length distribution broadening and shifting to higher molecular weight with increasing reaction time. | The mixture contains primarily monomers and polymers, and only small amounts of growing polymer chains |

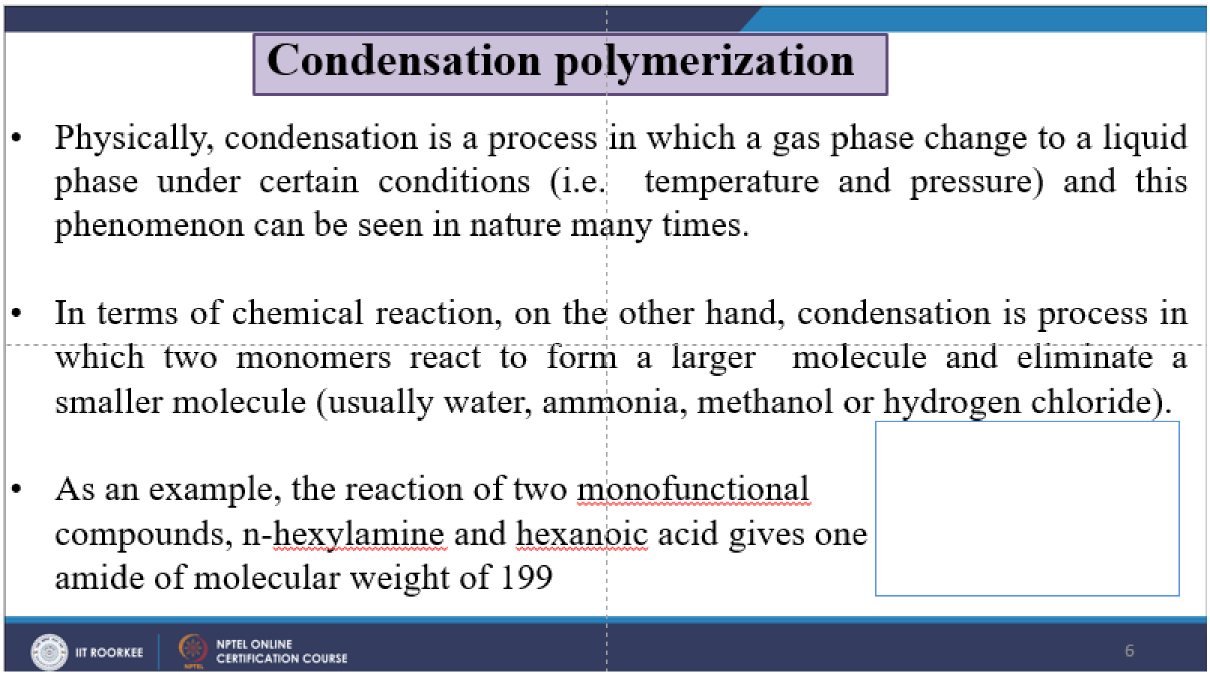
$P_1 + P_1 \rightarrow P_2$

$P_2 + P_1 \rightarrow P_3$

Now based on the reaction of all those monomers or all those monomer and polymeric chains, then there is a basic classification of the polymers. Polymers are basically classified as addition or condensation polymer, polymers depending upon the type of polymerization reactions they involved in their synthesis. In this particular class of classification this reflects the structure of starting monomers, probably the most general classification scheme is based on the polymerization mechanism, this involved in the polymer synthesis. So, under this classification the polymerization process they are classified like step growth reaction or step growth polymerization that is called a condensation polymerization and the chain growth polymerization or the chain reaction polymerization which is called as the addition polymerization. Now here is a comparison between the step growth and a chain reaction.

In the reaction mechanism, in step growth one reaction is responsible for the polymer formation, whereas in the chain reaction the initiation, propagation and the termination this reaction they have the different rates and the mechanism. Then if we talk about the polymer growth, so any two molecule or any two molecular species present this can react slowly or randomly and then the growth takes place. In the chain growth, the growth reaction takes place by the addition of one unit at a time to the active end of the polymer chain. And if we talk about the polymer molecular weight, the step growth molecular weight rises steadily, high conversion requires the high molecular weight and in the chain growth the high molecular weight polymer is formed immediately. If we talk about the monomer concentration, so monomer disappears in early stages of the polymerization so that the say like P1 is the monomer then P1 may react with the P1 it gives to P2 and this takes the disappearance and then P2 may react with P1 to form the P3 likewise.

In chain reaction, the monomer concentration decreases steadily throughout the reaction. Now if we talk about the composition in step growth polymerization, the molecular species of any length referred as a oligomer exist throughout the reaction with the length distribution broadening and shifting to higher molecular weight with increasing reaction time. Whereas in the chain reaction, the mixture contains primarily the monomers and polymers and only small amount of growing polymer chains.

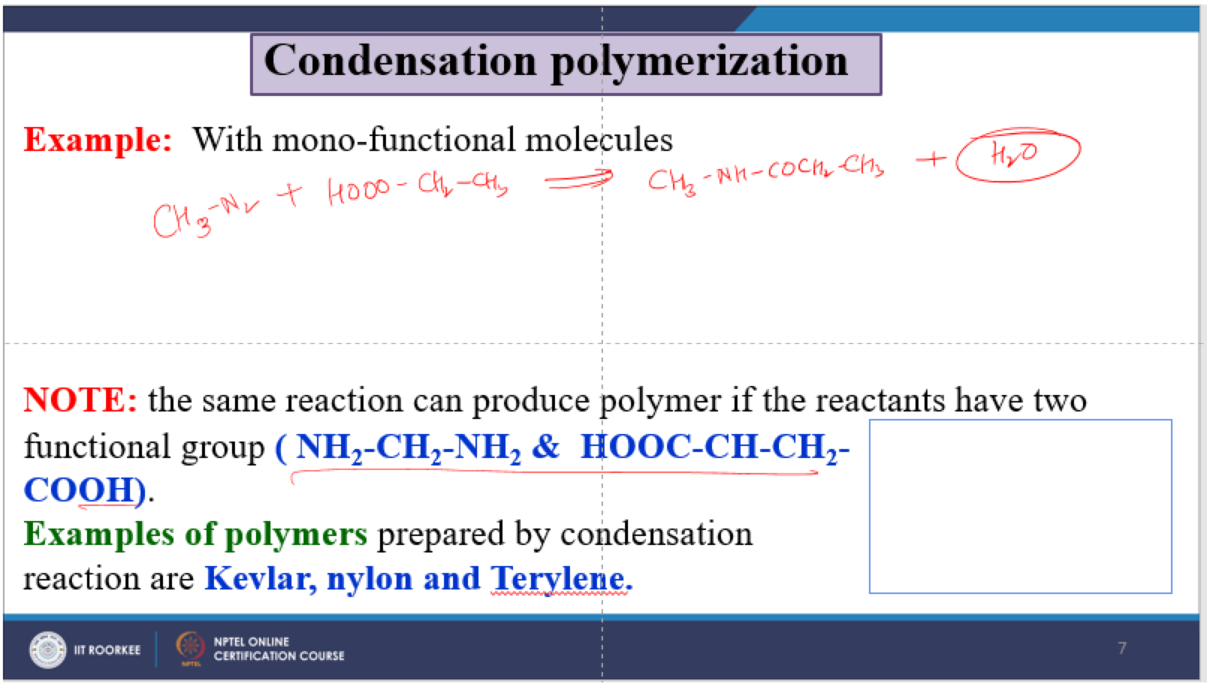


## Condensation polymerization

- Physically, condensation is a process in which a gas phase change to a liquid phase under certain conditions (i.e. temperature and pressure) and this phenomenon can be seen in nature many times.
- In terms of chemical reaction, on the other hand, condensation is process in which two monomers react to form a larger molecule and eliminate a smaller molecule (usually water, ammonia, methanol or hydrogen chloride).
- As an example, the reaction of two monofunctional compounds, n-hexylamine and hexanoic acid gives one amide of molecular weight of 199

Now let us talk about the condensation polymerization. Now physically the condensation is a process in which a gas phase changes to a liquid phase under the certain conditions that is a temperature and pressure and these phenomena can be seen in nature many times.

In chemical reaction on the other hand the condensation is a process which two monomers react to form a larger molecule and eliminates a smaller molecule sometimes water, ammonia, methanol or hydrogen chloride. As an example of the reaction of the two mono functional compounds, N-hexyl amine and hexonic acid this gives amide of molecular weight of 199. Let us take this mono functional molecule here CH3N2 this is amine then H the acid this gives the amide and this water is being eliminated. Now the same reaction can produce the polymer if reactant have two functional groups. These are the two functional groups.



## Condensation polymerization

**Example:** With mono-functional molecules

$CH_3-N_2 + HOOC-CH_2-CH_3 \Rightarrow CH_3-NH-COCH_2-CH_3 + \boxed{H_2O}$

**NOTE:** the same reaction can produce polymer if the reactants have two functional group **( $NH_2$-$CH_2$-$NH_2$ & HOOC-CH-$CH_2$-COOH)**.

**Examples of polymers** prepared by condensation reaction are **Kevlar, nylon and Terylene.**

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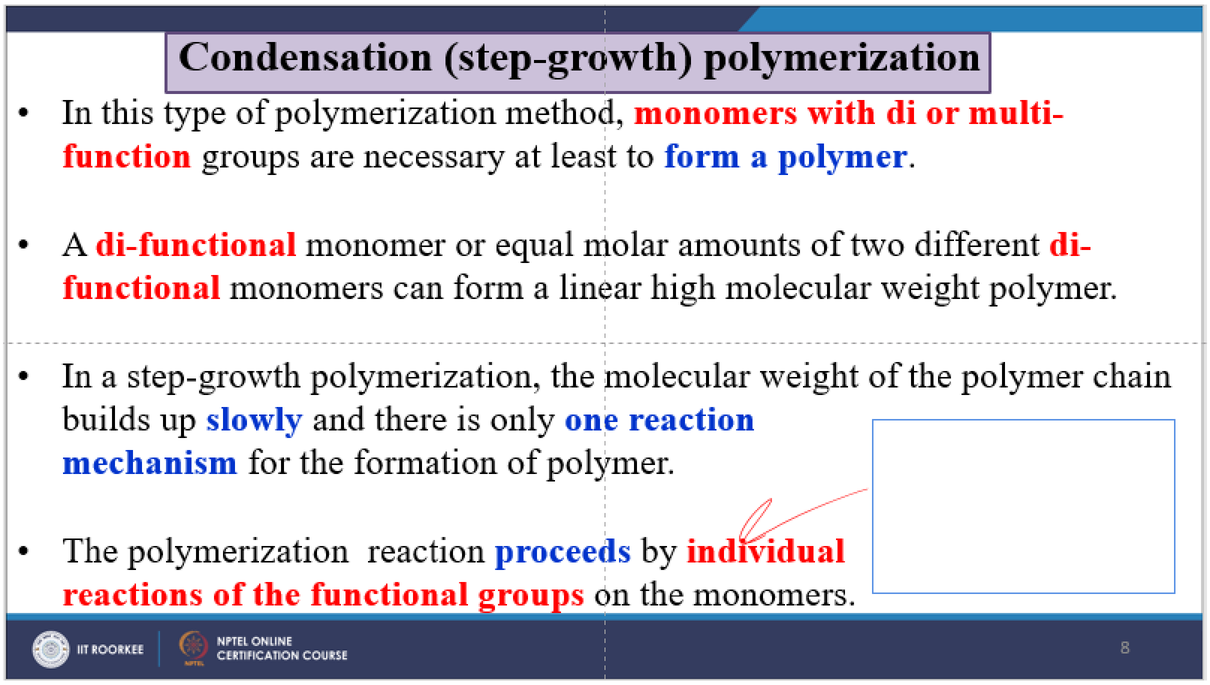
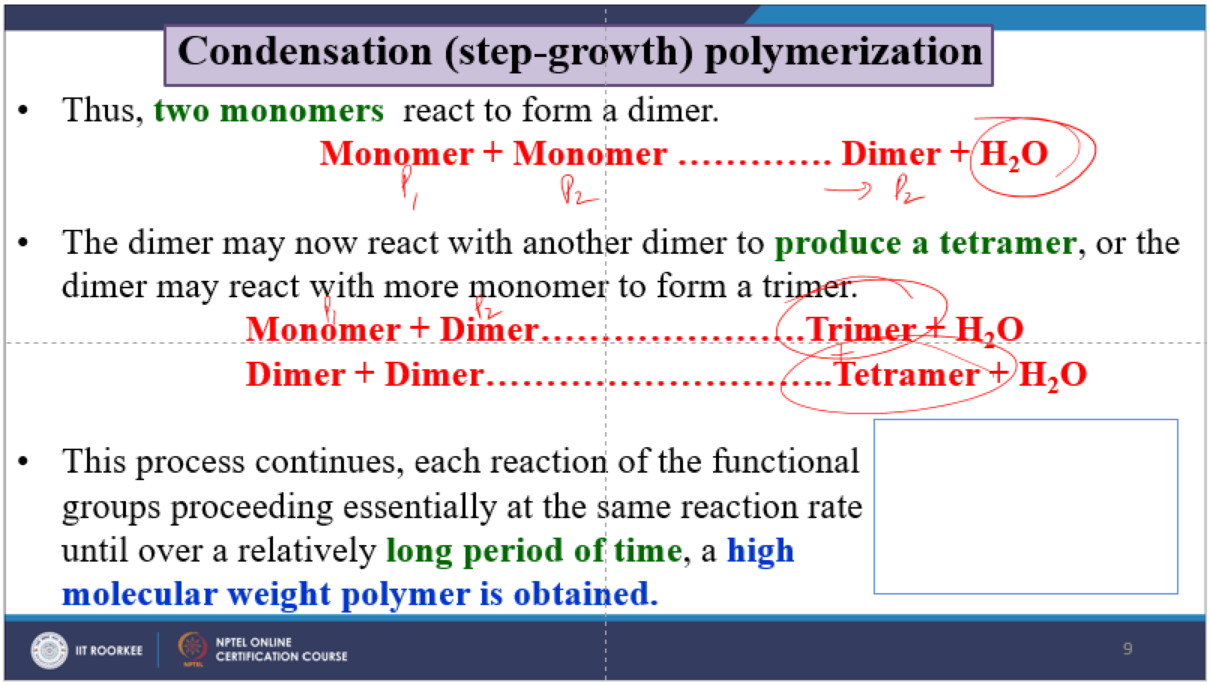
For example, the polymers they prepared for the condensation reaction are Kevlar, nylon, Tereline, etc. Now in this type of like if we talk about the step growth in detail that in this type of polymerization methods monomer with a dye or multifunction groups they are necessarily at least to form a polymer. Now a dye functional monomer or an equal molar amount of two different dye functional monomer this can be formed a linear high molecular weight polymer. Now in a step growth polymerization the molecular weight of polymer chain they built up slowly and there is only one reaction mechanism for the formation of polymer. Now the polymerization reaction proceeds by an individual reaction or of the functional group.



### Condensation (step-growth) polymerization

- In this type of polymerization method, **monomers with di or multi-function** groups are necessary at least to **form a polymer**.
- A **di-functional** monomer or equal molar amounts of two different **di-functional** monomers can form a linear high molecular weight polymer.
- In a step-growth polymerization, the molecular weight of the polymer chain builds up **slowly** and there is only **one reaction mechanism** for the formation of polymer.
- The polymerization reaction **proceeds** by **individual reactions of the functional groups** on the monomers.

Obviously, when we need to proceed for the polymerization reaction there must be some functional group. Now there are for the two monomers they react to form a dimer like here P1 and P2 they form the P2 and this is the reaction product and the dimer may now react with either dimer dimer or dimer monomer or sometimes if the trimer is formed then it can react with the trimer. So, the monomer plus dimer they form the trimer and dimer plus dimer they form the tetramer likewise and these can react all together. Now this process continues and each reaction of a functional group proceeding essentially at a same reaction rate until over a relatively long period of time a high molecular weight polymer is obtained. Now here you see this is a systematic illustration of a fundamental difference in the reaction mechanism.



### Condensation (step-growth) polymerization

- Thus, **two monomers** react to form a dimer.

**Monomer + Monomer ............ Dimer + $H_2O$**

$P_1$ $P_2$ → $P_2$

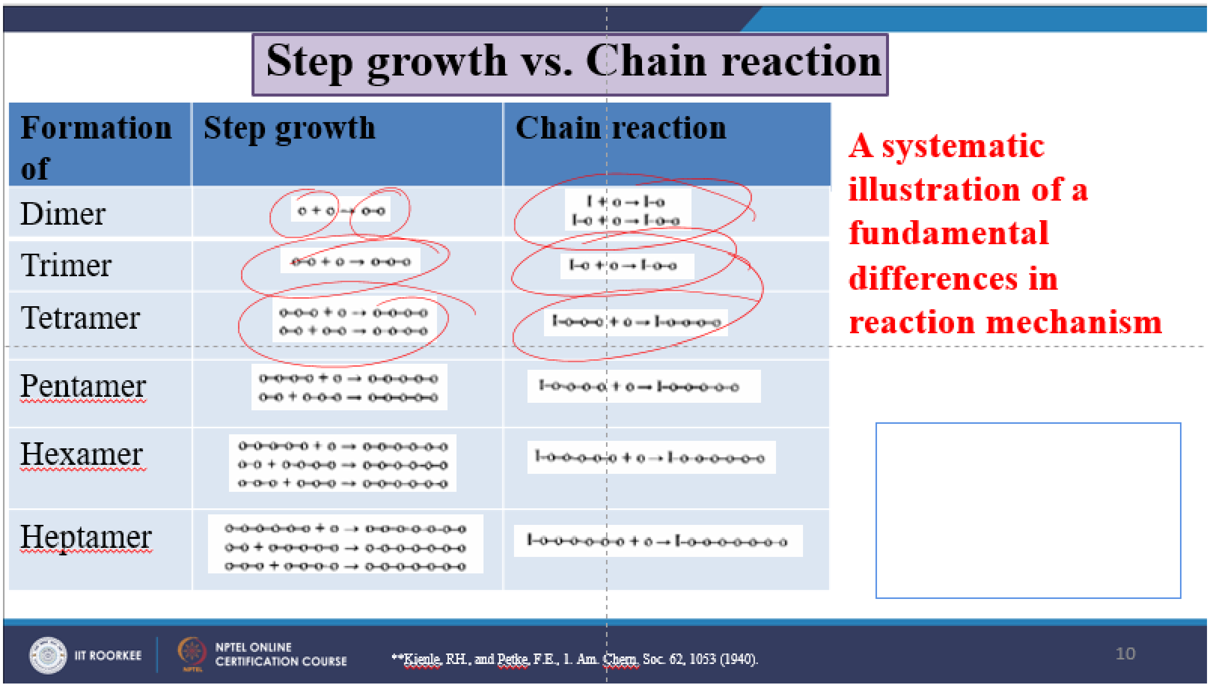
- The dimer may now react with another dimer to **produce a tetramer**, or the dimer may react with more monomer to form a trimer.

**Monomer + Dimer.......................Trimer + $H_2O$**

**Dimer + Dimer...................................Tetramer + $H_2O$**

- This process continues, each reaction of the functional groups proceeding essentially at the same reaction rate until over a relatively **long period of time**, a **high molecular weight polymer is obtained.**

Here you see that dimers are formed in the chain reaction it is quite different. Similarly, the trimer, tetramer and all these things are formed. Now let us talk about the mono functional versus difunctional condensation polymerization. The mono functional condensation reaction in this type of a reaction making an ester requires a carboxylic acid and alcohol and acid catalyst. So, you see that here this is the reaction mechanism.



## Step growth vs. Chain reaction

| Formation of | Step growth | Chain reaction |
|---|---|---|
| Dimer | o + o → o-o | I + o → I-o<br>I-o + o → I-o-o |
| Trimer | o-o + o → o-o-o | I-o + o → I-o-o |
| Tetramer | o-o-o + o → o-o-o-o<br>o-o + o-o → o-o-o-o | I-o-o-o + o → I-o-o-o-o |
| Pentamer | o-o-o-o + o → o-o-o-o-o<br>o-o + o-o-o → o-o-o-o-o | I-o-o-o-o + o → I-o-o-o-o-o |
| Hexamer | o-o-o-o-o + o → o-o-o-o-o-o<br>o-o + o-o-o-o → o-o-o-o-o-o<br>o-o-o + o-o-o → o-o-o-o-o-o | I-o-o-o-o-o + o → I-o-o-o-o-o-o |
| Heptamer | o-o-o-o-o-o + o → o-o-o-o-o-o-o<br>o-o + o-o-o-o-o → o-o-o-o-o-o-o<br>o-o-o + o-o-o-o → o-o-o-o-o-o-o | I-o-o-o-o-o-o + o → I-o-o-o-o-o-o-o |

**A systematic illustration of a fundamental differences in reaction mechanism**

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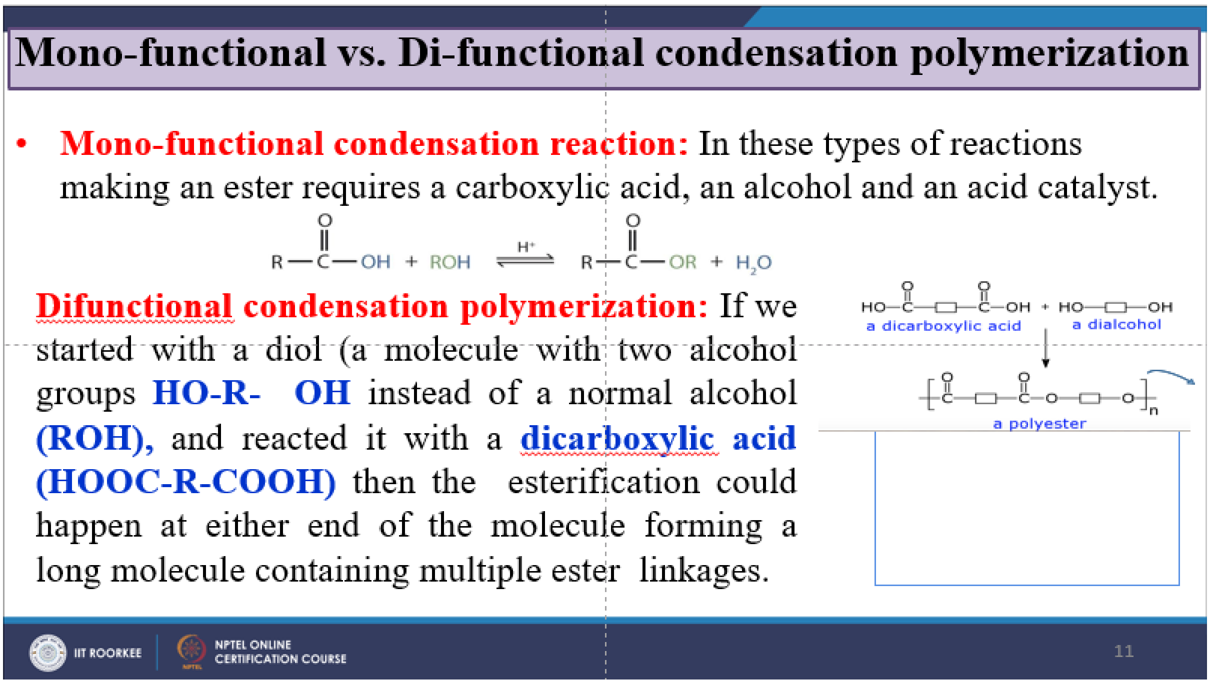
**Kienle, RH., and Petke, F.E., J. Am. Chem. Soc. 62, 1053 (1940).

Now difunctional condensation polymerization if we start with the diol that is a molecule with the two alcohol groups instead of a normal alcohol which we used previously they reacted with the dicarboxylic acid and therefore the esterification can happen at either end of the and the molecule forming a long molecule containing the multiple ester linkage. You see over here that this is a dicarboxylic acid reacts with the di-alcohol and it gives the polyester this is the structural unit. Now let us talk about the mono functional versus difunctional condensation polymerization. The formation of the polyester, polyamide or polyurethane represent typical condensation polymerization. Now these reactions can be written as like polyester this is for the polyamide and this is for the polyurethane and you see that this is the broad spectrum of this particular representation.



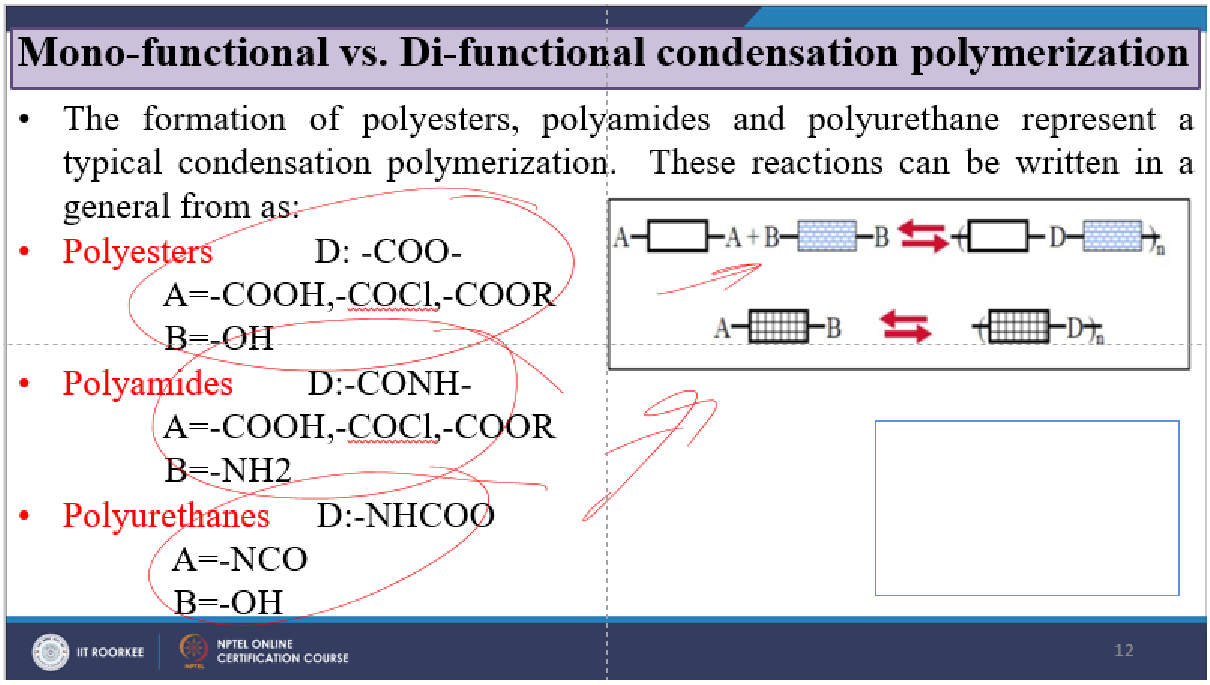
## Mono-functional vs. Di-functional condensation polymerization

- **Mono-functional condensation reaction:** In these types of reactions making an ester requires a carboxylic acid, an alcohol and an acid catalyst.

$$R-\overset{O}{\overset{\|}{C}}-OH + ROH \xrightleftharpoons{H^+} R-\overset{O}{\overset{\|}{C}}-OR + H_2O$$

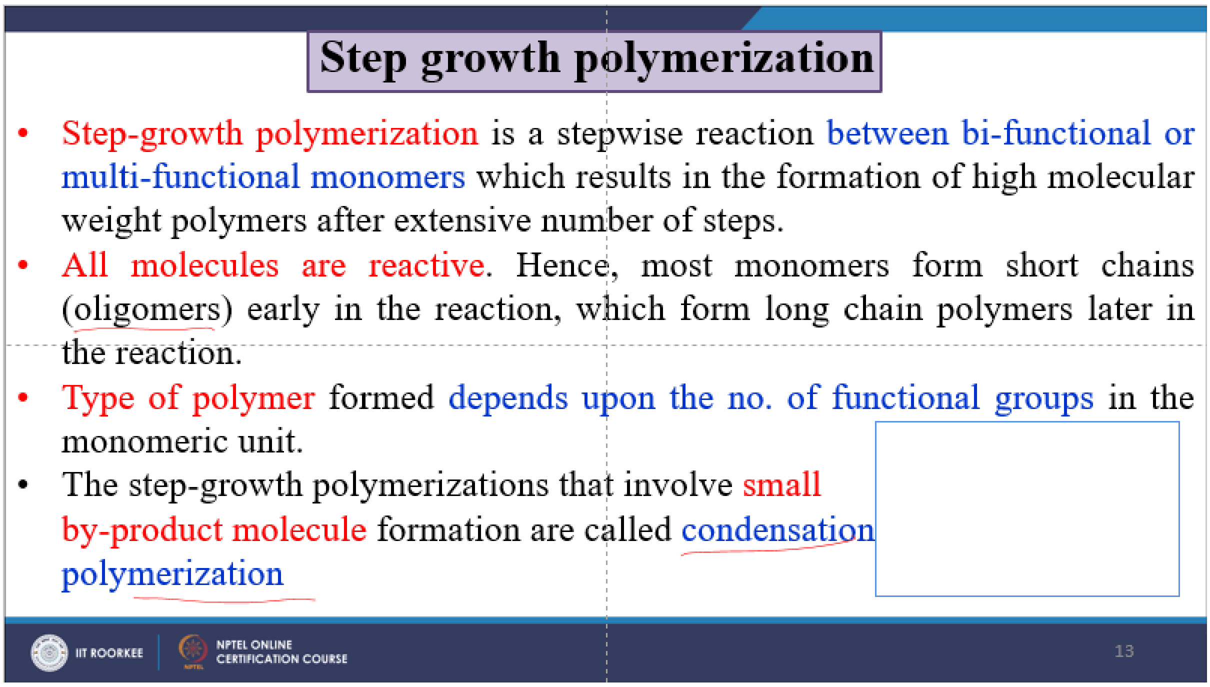
**Difunctional condensation polymerization:** If we started with a diol (a molecule with two alcohol groups **HO-R- OH** instead of a normal alcohol **(ROH),** and reacted it with a **dicarboxylic acid (HOOC-R-COOH)** then the esterification could happen at either end of the molecule forming a long molecule containing multiple ester linkages.

Let us talk about the step growth polymerization. Step growth polymerization is a stepwise reaction between a bifunctional or a multifunctional monomer which results in the formation of high molecular weight after extensive number of steps. So, the all molecules are reactive hence most monomers have a short chain that is called oligomers in early stages and these chains may combine over the period of time to form a longer chain. Now type of polymer this form depends upon the functional group in the monomeric unit. The step of growth polymerization usually that involves the small byproduct molecule formation and that is called condensation polymerization.



## Mono-functional vs. Di-functional condensation polymerization

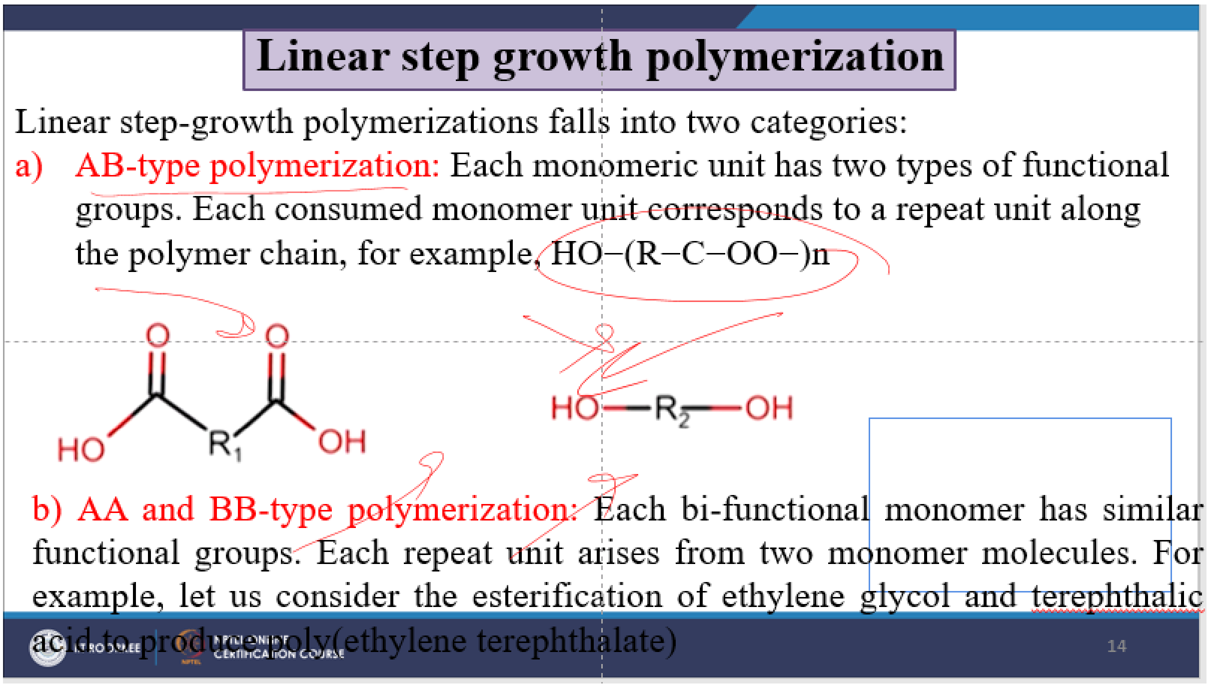
- The formation of polyesters, polyamides and polyurethane represent a typical condensation polymerization. These reactions can be written in a general from as:
- Polyesters D: -COO-
  A=-COOH,-COCl,-COOR
  B=-OH
- Polyamides D:-CONH-
  A=-COOH,-COCl,-COOR
  B=-NH2
- Polyurethanes D:-NHCOO
  A=-NCO
  B=-OH



## Step growth polymerization

- Step-growth polymerization is a stepwise reaction between bi-functional or multi-functional monomers which results in the formation of high molecular weight polymers after extensive number of steps.
- All molecules are reactive. Hence, most monomers form short chains (oligomers) early in the reaction, which form long chain polymers later in the reaction.
- Type of polymer formed depends upon the no. of functional groups in the monomeric unit.
- The step-growth polymerizations that involve small by-product molecule formation are called condensation polymerization

Now let us talk about linear step polymerization or linear step growth polymerization. This falls into two categories a b type of polymerization. Now each monomeric unit has two types of functional group each consumed monomer unit corresponds to a repeat unit along the polymer chain. Now let us take this particular example. Now a a and b b type of polymerization each bifunctional monomer has similar functional groups and each repeat unit arises from two monomer molecules.



## Linear step growth polymerization

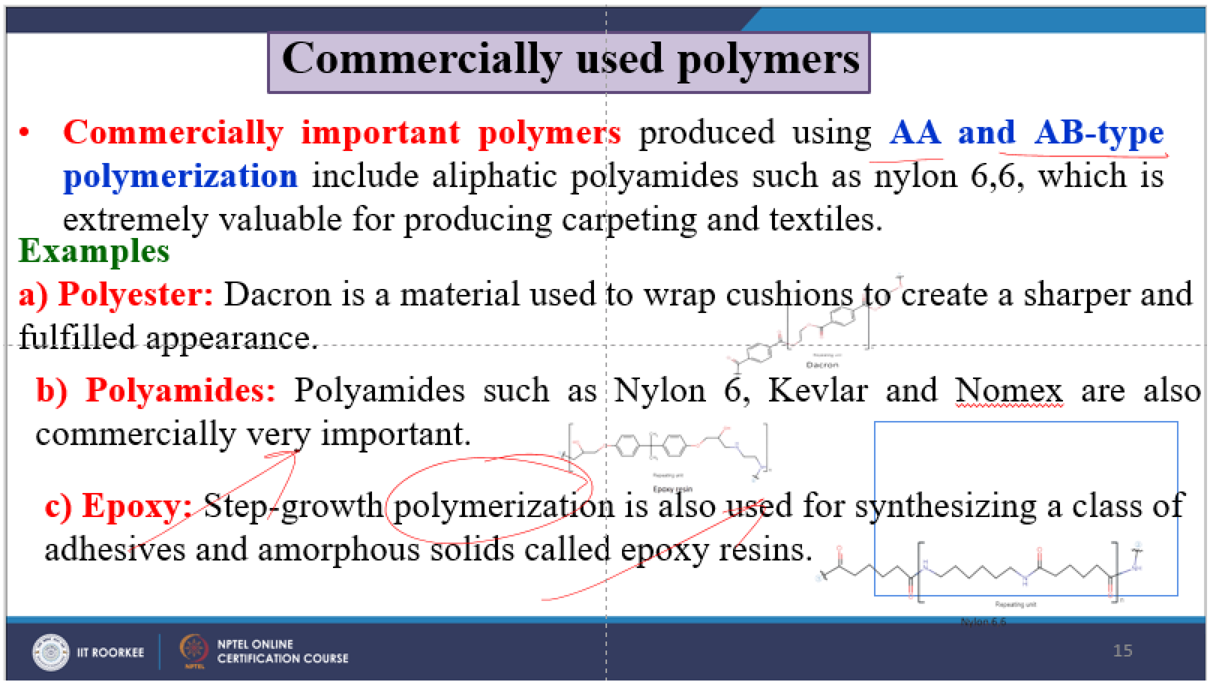
Linear step-growth polymerizations falls into two categories:

a) AB-type polymerization: Each monomeric unit has two types of functional groups. Each consumed monomer unit corresponds to a repeat unit along the polymer chain, for example, $HO-(R-C-OO-)_n$

b) AA and BB-type polymerization: Each bi-functional monomer has similar functional groups. Each repeat unit arises from two monomer molecules. For example, let us consider the esterification of ethylene glycol and terephthalic acid to produce poly(ethylene terephthalate)

For example, let us consider the esterification of ethylene glycol and terathenic acid to produce the PET. Now this is the example. There are several polymers which are commercially important. So, the commercially important polymer they produce aa and ab type of polymerization or a polymers. This includes the aliphatic polyamides like nylon-6,6 which is extremely valuable for producing carpet, textile, cloths all these things.

Now another example is the polyester. This is the dekron. Now dekron is the material used to wrap the cushions to create the sharper and fulfilled appearance. And polyamides this is the nylon 6 6. The polyamide nylon 6 6 Kevlar, Nomex these are also the the very important commercially available polymers.



## Commercially used polymers

- **Commercially important polymers** produced using **AA and AB-type polymerization** include aliphatic polyamides such as nylon 6,6, which is extremely valuable for producing carpeting and textiles.

**Examples**

**a) Polyester:** Dacron is a material used to wrap cushions to create a sharper and fulfilled appearance.

**b) Polyamides:** Polyamides such as Nylon 6, Kevlar and Nomex are also commercially very important.

**c) Epoxy:** Step-growth polymerization is also used for synthesizing a class of adhesives and amorphous solids called epoxy resins.

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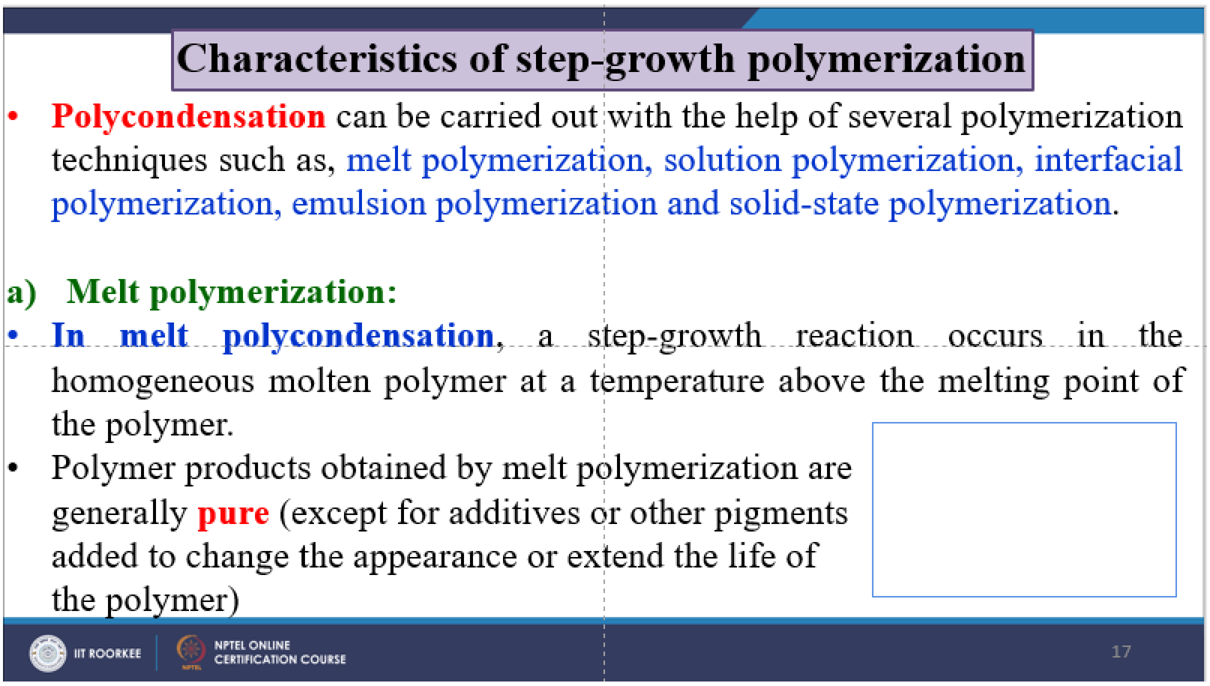
Epoxy, the step growth polymerization is also used for synthesizing a class of adhesive and amorphous solids and they are called the epoxy. This is the epoxy resins you see. Now let us talk about the characteristics of step growth polymerization. The equilibrium functional group because we are discussing the reaction engineering so the formation of the equilibrium functional group is very important. So functional group, this equilibrium functional group concentrations are affected by the concentration of eliminated compound.

Another more important aspect is that the removing of byproducts from the reaction medium reduces its concentration and thereby reducing the rate of reverse reaction and therefore promoting the use of functional group and the production of high-density polymer. Now there are several reactors of polycondensation that the large surface area that is used for the condensation byproduct from the polymer phase. In some process high vacuum this may also be applied. Polycondensation this can be carried out with the help of several polymerization techniques like melt polymerization, solution polymerization, interfacial polymerization, emulsion polymerization, solid state polymerizations. So, let us talk one by one melt polymerization.



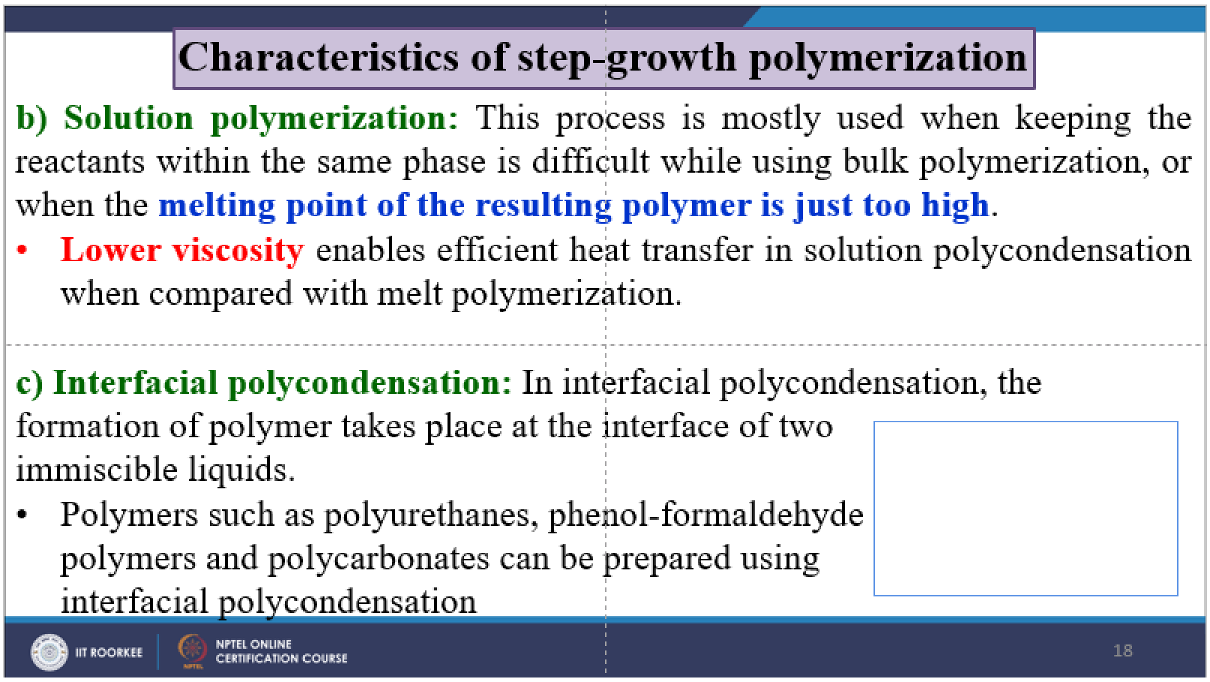
## Characteristics of step-growth polymerization

- **Polycondensation** can be carried out with the help of several polymerization techniques such as, melt polymerization, solution polymerization, interfacial polymerization, emulsion polymerization and solid-state polymerization.

**a) Melt polymerization:**

- **In melt polycondensation**, a step-growth reaction occurs in the homogeneous molten polymer at a temperature above the melting point of the polymer.
- Polymer products obtained by melt polymerization are generally **pure** (except for additives or other pigments added to change the appearance or extend the life of the polymer)

In melt polycondensation step growth reaction this occurs in homogeneous molten polymer at a temperature above the melting point of the polymer. So, it is in the molten stage. The polymer products obtained by the melt polymerization are generally pure except for additives or other pigments added to change the appearance or extent of the life of the poly. Now solution polymerization, this process is mostly used when keeping the reactant within the same phase which is very difficult while using the bulk polymerization or when the melting point of a resulting polymer is just too high. Lower viscosity sometimes this enables efficient heat transfer in solution polycondensation when if we compare with the melt polymerization.



## Characteristics of step-growth polymerization

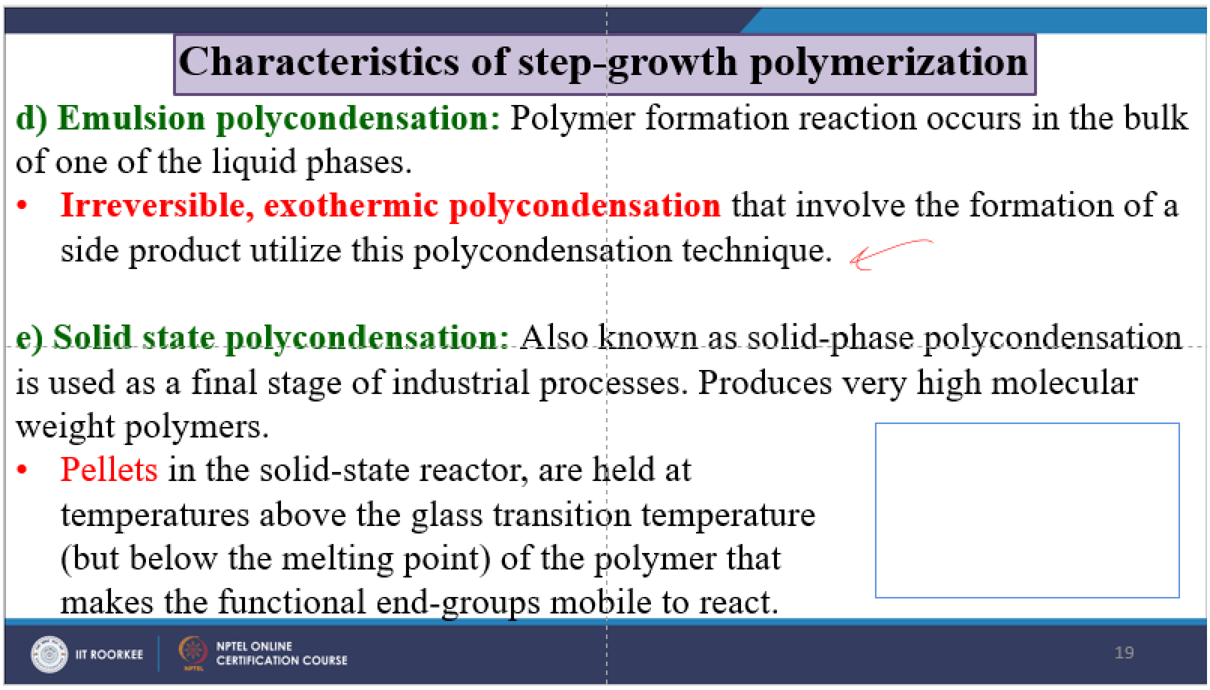
**b) Solution polymerization:** This process is mostly used when keeping the reactants within the same phase is difficult while using bulk polymerization, or when the **melting point of the resulting polymer is just too high**.

- **Lower viscosity** enables efficient heat transfer in solution polycondensation when compared with melt polymerization.

**c) Interfacial polycondensation:** In interfacial polycondensation, the formation of polymer takes place at the interface of two immiscible liquids.

- Polymers such as polyurethanes, phenol-formaldehyde polymers and polycarbonates can be prepared using interfacial polycondensation

The interfacial polycondensation is a formation of the polymer that take place in the interface of two immiscible liquids. So, a polymer like polyurethanes, phenol formaldehyde polymers, polycarbonate these can be prepared using the interfacial polycondensation. In solution polymerization or emulsion polycondensation usually the polymer formation reaction occurs in a bulk of one of the liquid phase. Irreversible exothermic polycondensation involve the formation of a side product this utilize this polycondensation technique. Solid-state polycondensation is also known as the solid-state polycondensation which is used as a final stage of industrial processes and this produces a very high molecular weight polymer.



## Characteristics of step-growth polymerization

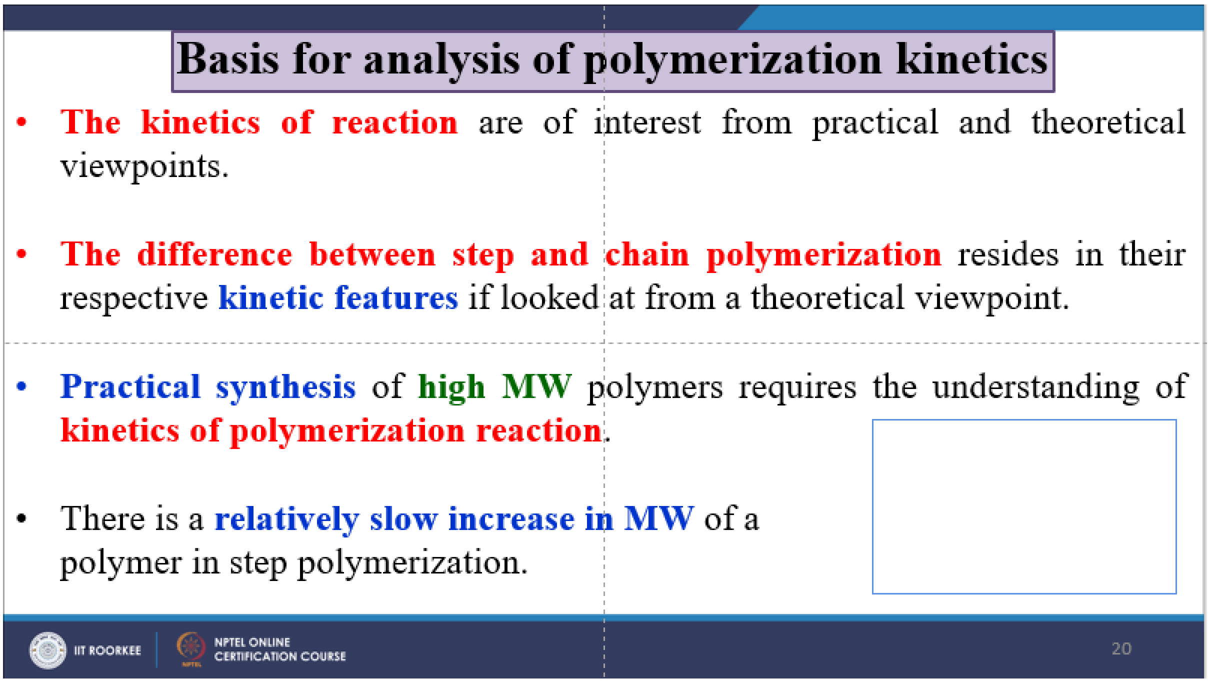
**d) Emulsion polycondensation:** Polymer formation reaction occurs in the bulk of one of the liquid phases.

- **Irreversible, exothermic polycondensation** that involve the formation of a side product utilize this polycondensation technique.

**e) Solid state polycondensation:** Also known as solid-phase polycondensation is used as a final stage of industrial processes. Produces very high molecular weight polymers.

- Pellets in the solid-state reactor, are held at temperatures above the glass transition temperature (but below the melting point) of the polymer that makes the functional end-groups mobile to react.

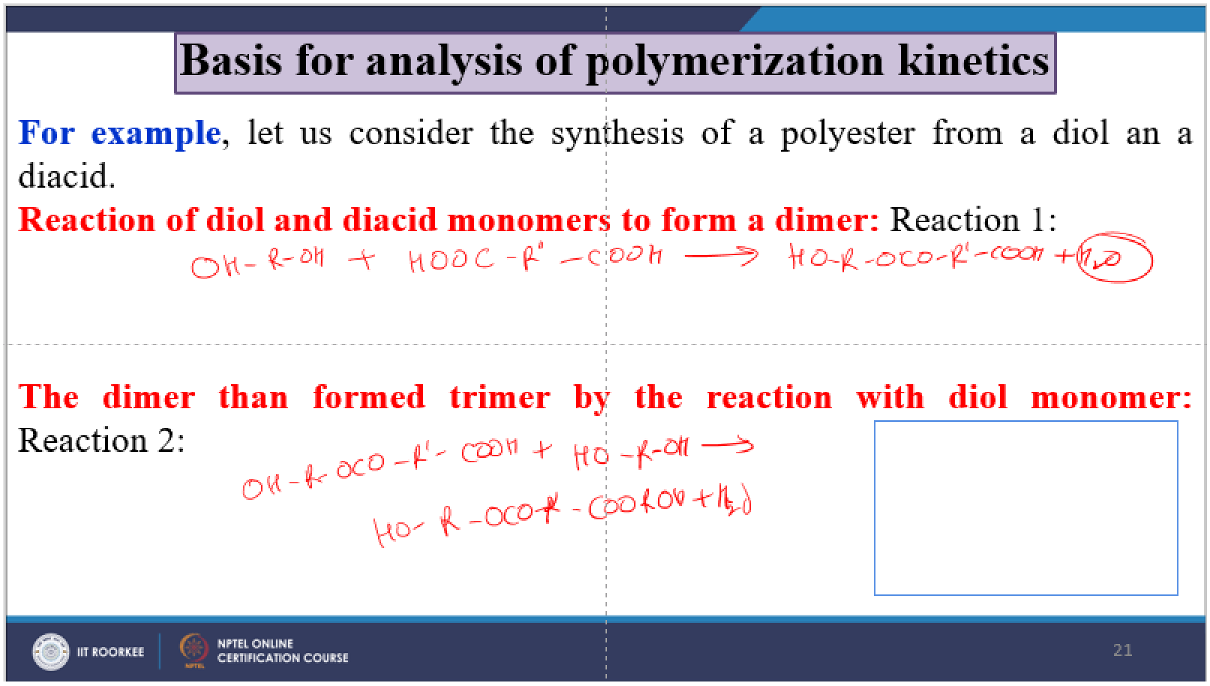
Pallets like in the solid-state reactor they are held at a temperature above the glass transition temperature but below the melting point usually occurs. Now if the polymer that makes the functional group and functional end group mobile to react. Now since we are here for the discussion of the reaction engineering aspect of the polymerization then what is the basis for the analysis of polymerization kinetics. The kinetic of reaction of or of interest from practical as well as the theoretical viewpoint. The difference between the step and chain polymerization this resides in their respective kinetic features.



## Basis for analysis of polymerization kinetics

- **The kinetics of reaction** are of interest from practical and theoretical viewpoints.
- **The difference between step and chain polymerization** resides in their respective **kinetic features** if looked at from a theoretical viewpoint.
- **Practical synthesis** of **high MW** polymers requires the understanding of **kinetics of polymerization reaction**.
- There is a **relatively slow increase in MW** of a polymer in step polymerization.

Now if you look from the theoretical viewpoint for the practical synthesis of high molecular weight polymers this require the understanding of the kinetics of the polymerization reaction. Now there is a relatively slow increase in molecular weight of a polymer in step polymerization. For example, let us take the synthesis of polyester from a diol and a diacid. Now reaction of diol and diacid monomer into formed dimer. So, the this is OHR plus this can be represented like this.



## Basis for analysis of polymerization kinetics

**For example**, let us consider the synthesis of a polyester from a diol an a diacid.

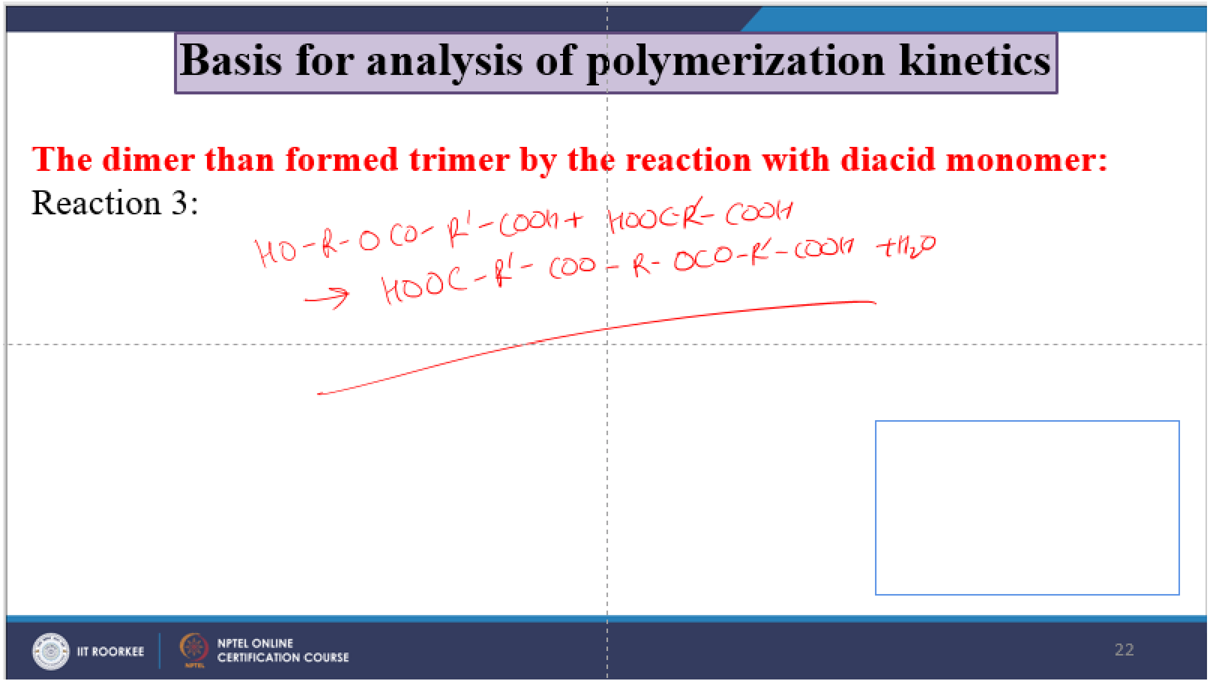
**Reaction of diol and diacid monomers to form a dimer:** Reaction 1:

$$OH-R-OH + HOOC-R'-COOH \longrightarrow HO-R-OCO-R'-COOH + \boxed{H_2O}$$

**The dimer than formed trimer by the reaction with diol monomer:** Reaction 2:

$$OH-R-OCO-R'-COOH + HO-R-OH \longrightarrow$$
$$HO-R-OCO-R'-COOROH + H_2O$$

Now another reaction that is a dimer that then formed trimer by the reaction with diol and this can be plus H2O. Now the dimer then formed trimer by the reaction with the diacid monomer. This can be represented as HOR OCO COOH. This is HOOC. Now the polymerization as the polymerization proceeds in a stepwise fashion with the molecular weight of the polymer increasing with over the period of time.



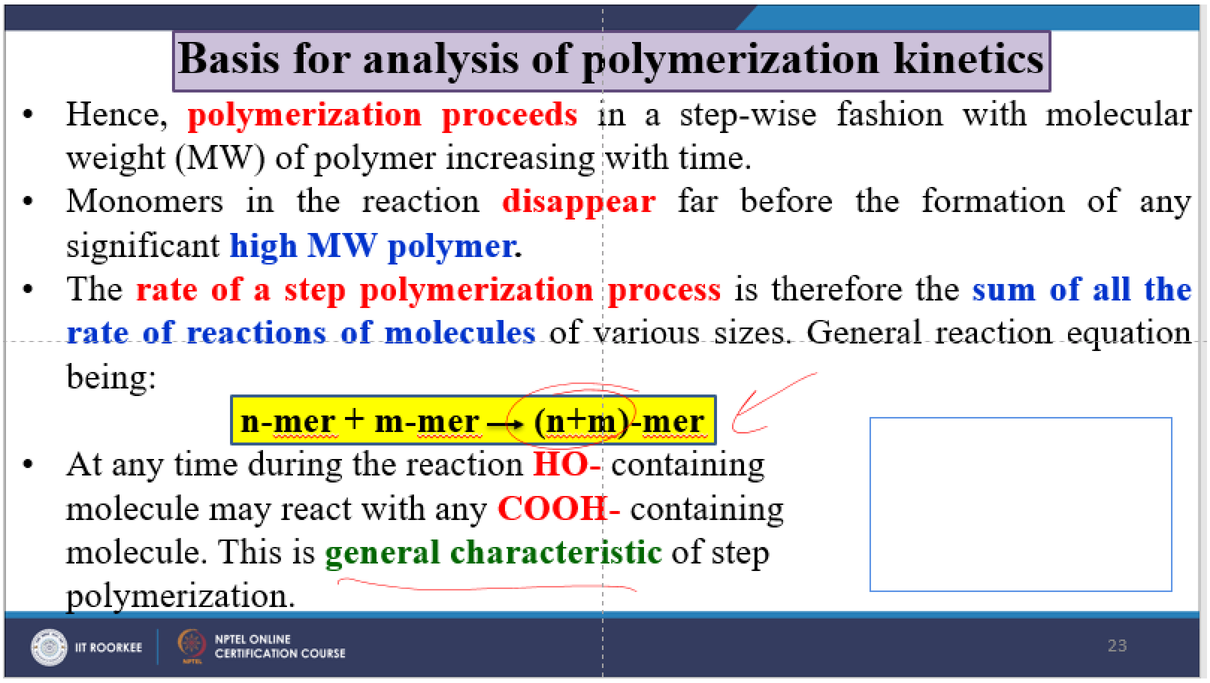
## Basis for analysis of polymerization kinetics

**The dimer than formed trimer by the reaction with diacid monomer:**

Reaction 3:

$$HO-R-OCO-R'-COOH + HOOC-R-COOH$$
$$\rightarrow HOOC-R'-COO-R-OCO-R-COOH + H_2O$$

So, the monomer in the reaction this disappear far before the formation of any significant high molecular weight polymer. The rate of step polymerization process is just therefore the sum of all the reactions of molecule of various sizes. Now general reaction equation this can be represented as Nmer plus Mmer that is N plus Mmer. At any time during the reaction like HO containing molecule may be react with the COOH containing molecules and this is a general characteristics of step polymerization. Now usually when talk about the experimental evidence the reaction rate constant for several polymerization they are seen in the independent of the reaction time or polymer molecular rate.



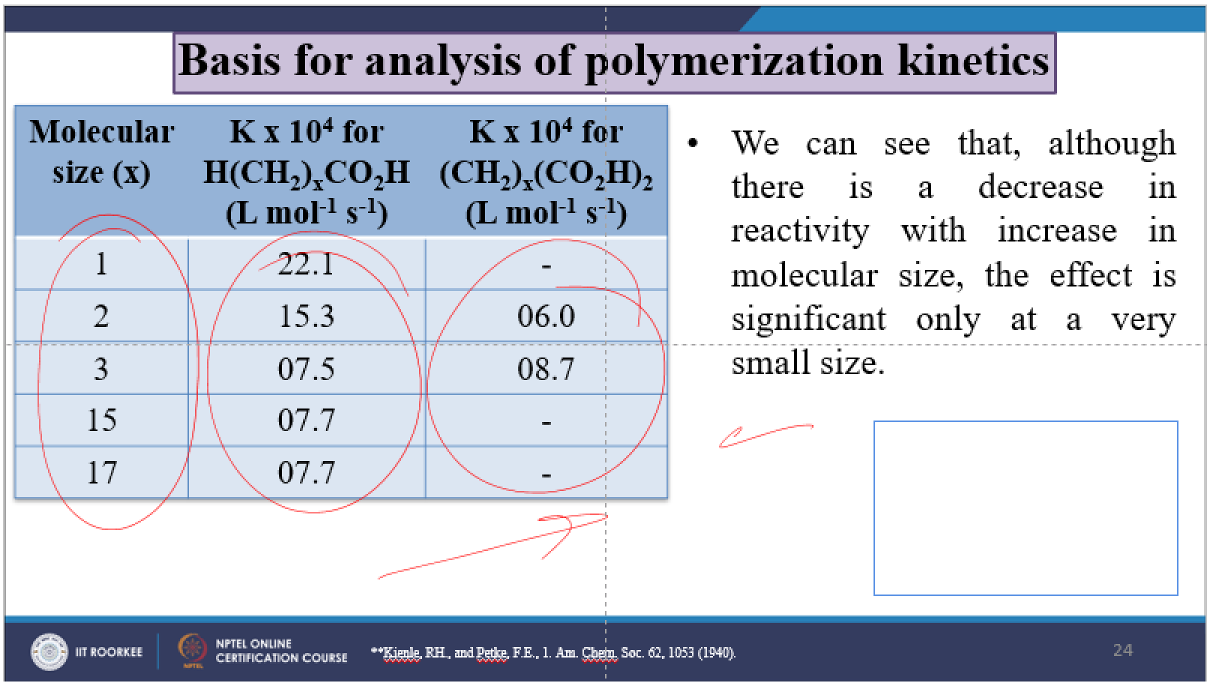
## Basis for analysis of polymerization kinetics

- Hence, **polymerization proceeds** in a step-wise fashion with molecular weight (MW) of polymer increasing with time.
- Monomers in the reaction **disappear** far before the formation of any significant **high MW polymer.**
- The **rate of a step polymerization process** is therefore the **sum of all the rate of reactions of molecules** of various sizes. General reaction equation being:

**n-mer + m-mer → (n+m)-mer**

- At any time during the reaction **HO-** containing molecule may react with any **COOH-** containing molecule. This is **general characteristic** of step polymerization.

Thus, justifying the above-mentioned assumption what we have discussed earlier. Now studies of reaction of certain non-polymeric molecules come in handy to examine the polymerization kinetics. Now let us consider the classification of the homologous carboxylic acid. Now here we see that the homologous carbonyl molecular size can be represented and the reaction rate constant and all those things. So, we can see that although there is a decrease in the reactivity with increase in the molecular size the effect is significant only at a very small size.



## Basis for analysis of polymerization kinetics

| Molecular size (x) | K x $10^4$ for $H(CH_2)_xCO_2H$ (L $mol^{-1}$ $s^{-1}$) | K x $10^4$ for $(CH_2)_x(CO_2H)_2$ (L $mol^{-1}$ $s^{-1}$) |
|---|---|---|
| 1 | 22.1 | - |
| 2 | 15.3 | 06.0 |
| 3 | 07.5 | 08.7 |
| 15 | 07.7 | - |
| 17 | 07.7 | - |

- We can see that, although there is a decrease in reactivity with increase in molecular size, the effect is significant only at a very small size.

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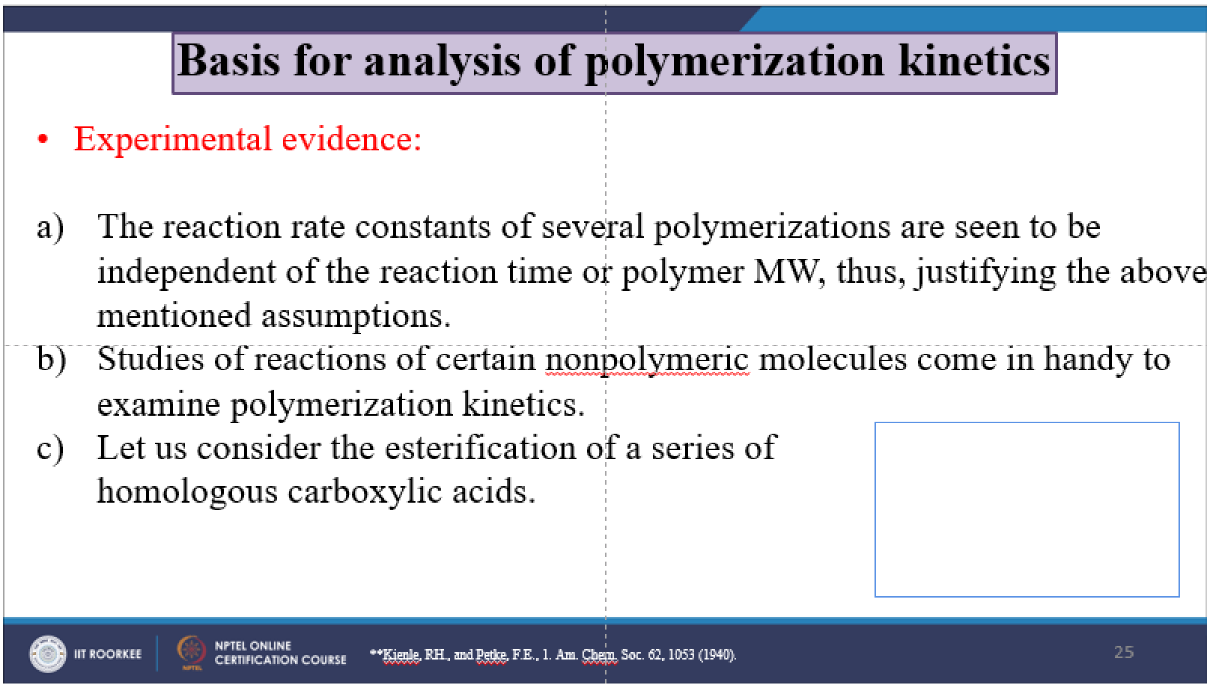
Now the reaction rate constant they very quickly reach a limiting value and remains constant and independent of molecular size. Some sort of results found by for the polyesterification of sibicoyl chloride with alpha omega LK in diols and the thought that reactivity decreases with increase in the molecular size is just a misconception. The difficult solubility of high molecular weight molecules in homogeneous series is a pitfall which is to be avoided. Now the kinetics of step growth polymerization it is imperative to understand how reaction proceeds over time. Now this information can tell us about the time it takes for a polymer to reach an optimum length.



## Basis for analysis of polymerization kinetics

- Experimental evidence:

a) The reaction rate constants of several polymerizations are seen to be independent of the reaction time or polymer MW, thus, justifying the above mentioned assumptions.

b) Studies of reactions of certain nonpolymeric molecules come in handy to examine polymerization kinetics.

c) Let us consider the esterification of a series of homologous carboxylic acids.

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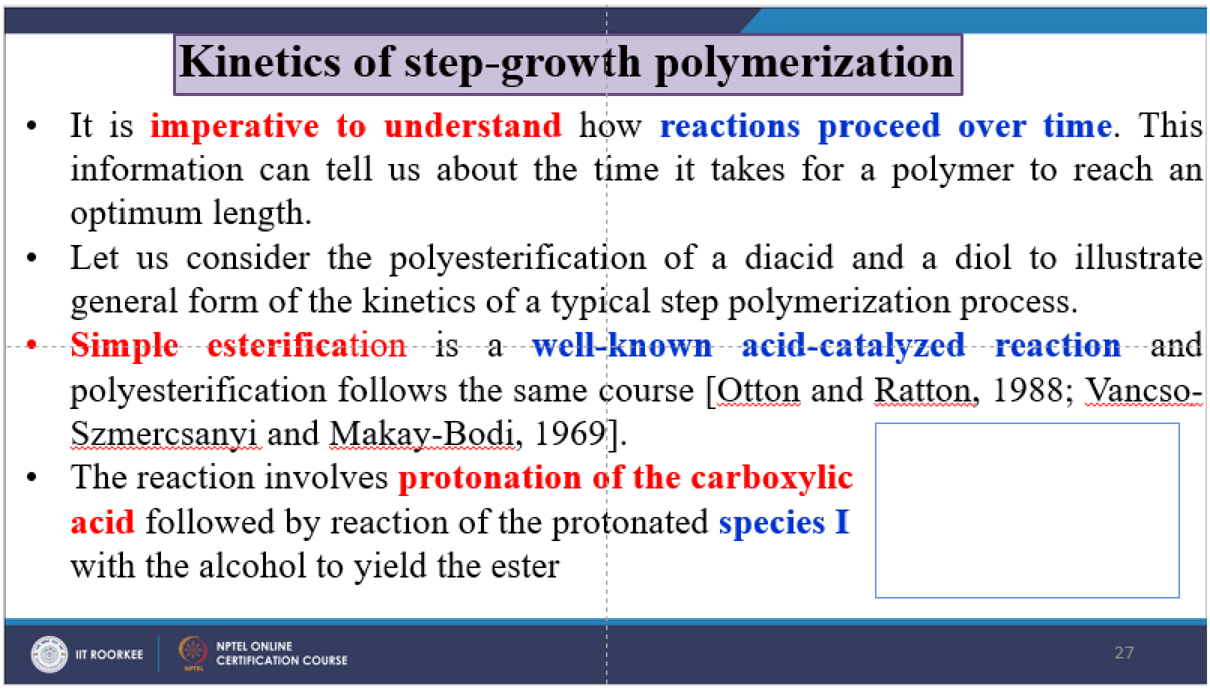
Let us consider the polyesterification of a diacid and diol to illustrate the general form of the kinetics of a typical step polymerization process. Now simple esterification is a well-known acid catalyzed reaction and polyesterification follows the same occurs. Now the reaction involves the protonation of a carboxylic acid followed by the reaction of the protonated species one with the alcohol to yield the ester. Now here you see that we have we are going to discuss the reaction mechanism plus HA reaction. This is the first one and then this is further this further reacts with.

So, the chain formation takes place, and this. So, this is given by like this plus H2. This is our equation 3. Now if from this reaction all acid or alcohol species that are monomer or dimer up to say enmer this the reaction mixture is indicated by 1 or 2 like here we discussed. Now since polymerization often take place in organic media of low polarity species 1 and 2 they are shown in the form of their associated ion pairs. Now A negative is counter ion derived from the acid HA here.



## Kinetics of step-growth polymerization

- It is **imperative to understand** how **reactions proceed over time**. This information can tell us about the time it takes for a polymer to reach an optimum length.
- Let us consider the polyesterification of a diacid and a diol to illustrate general form of the kinetics of a typical step polymerization process.
- **Simple esterification** is a **well-known acid-catalyzed reaction** and polyesterification follows the same course [Otton and Ratton, 1988; Vancso-Szmercsanyi and Makay-Bodi, 1969].
- The reaction involves **protonation of the carboxylic acid** followed by reaction of the protonated **species I** with the alcohol to yield the ester

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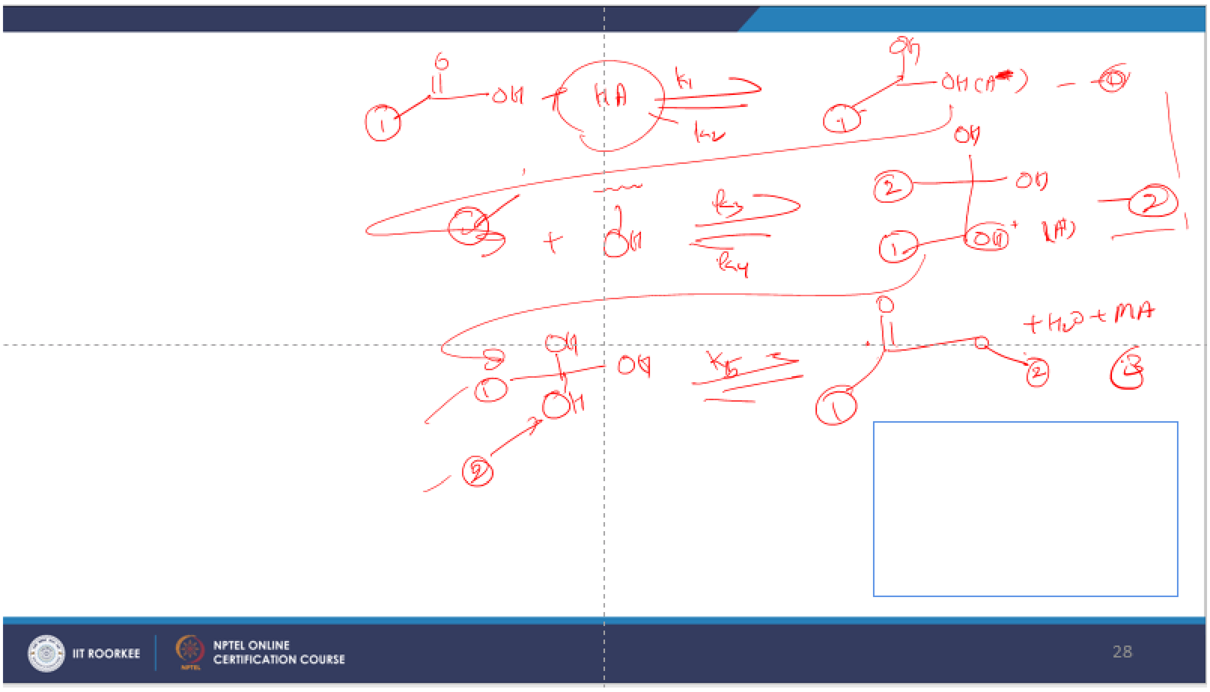
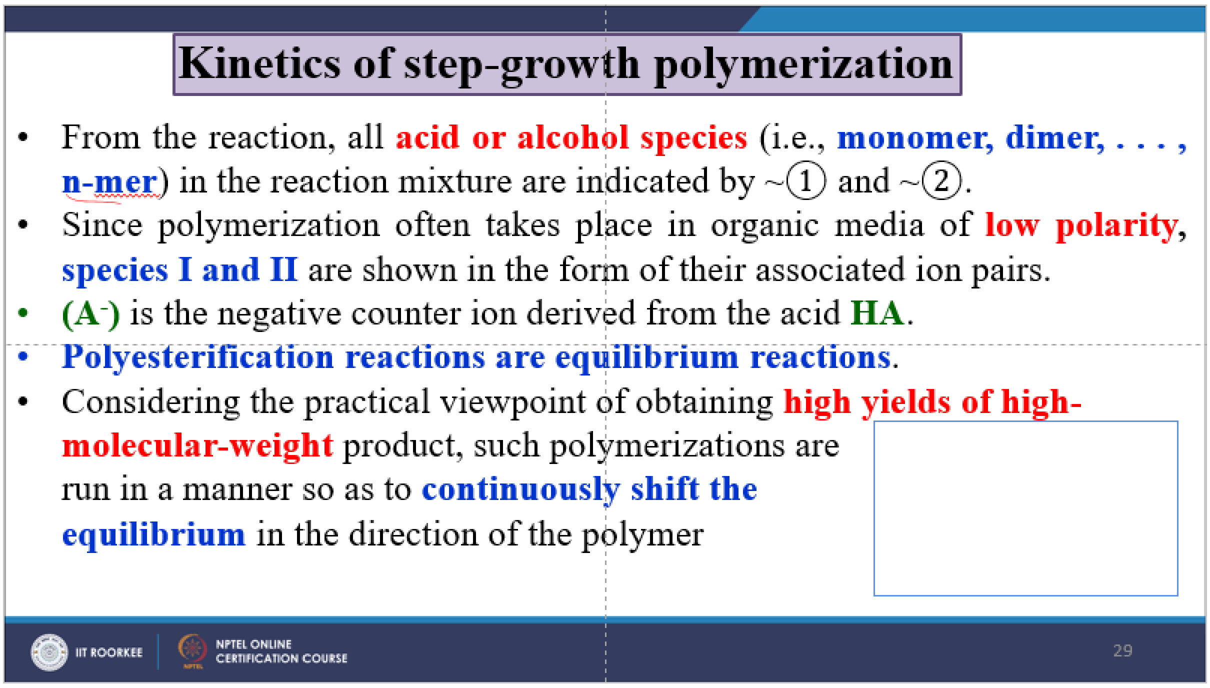
This is the A negative. Now, polyesterification reactions are equilibrium reaction and considering the practical viewpoint to obtain the high yields of high molecular weight product such polymerization is usually run in a manner so as to shift the equilibrium in the direction of the polymer continuously. Now the rate of step polymerization this can be conventionally expressed in terms of the concentration of the reacting functional groups. Therefore, the polyesterification can be experimentally followed by the titrating the unreacted carboxyl group with base. Therefore, the rate of polymerization that is RP this can now be expressed as a rate of disappearance of carboxyl group that is minus dCOH over dt over the period of time t. For usual polyesterification the polymerization rate is synonymous with the rate of formation of species 2 and that is K4 this is vanishingly small in since the reaction is run under the condition that derived.



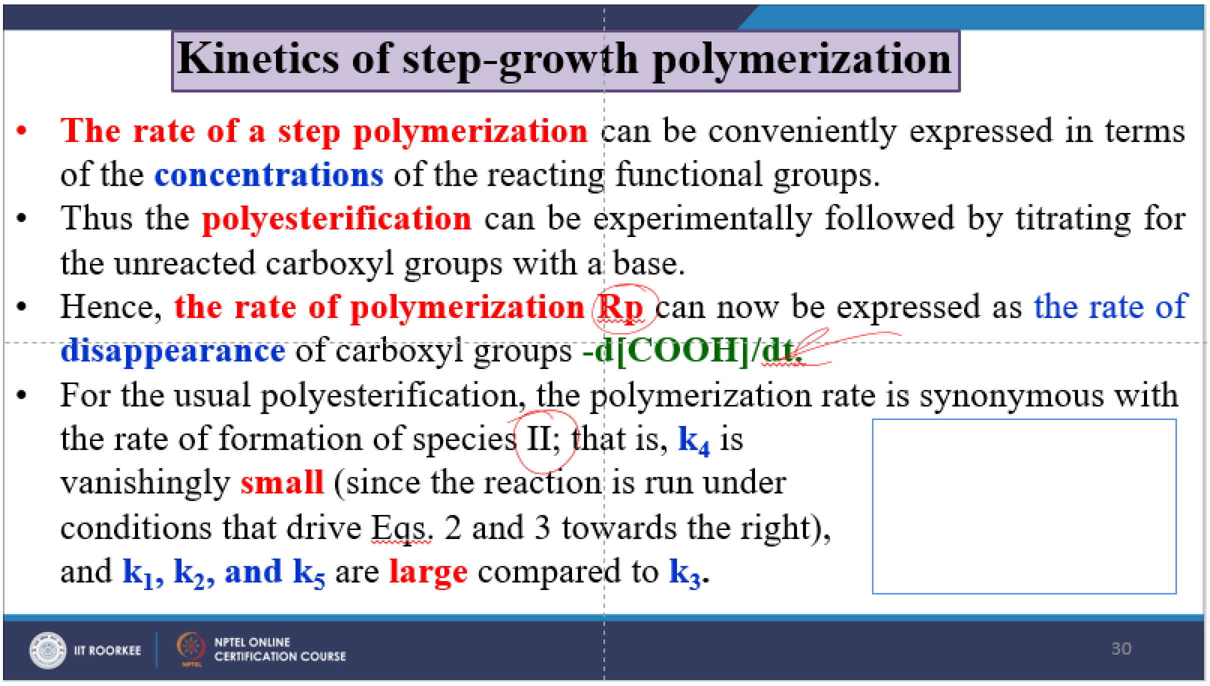
So, equation 2 here and 3 towards the right and K1, K2 and K5 are large compared to K3. So, the rate of polymerization reaction is given by RP is equal to minus d because it is being consumed over the period of time this is equal to K3C ion OH2 OH and this is equation number 4. Now here this is the concentration COH, OH and this one is present the concentration of carboxylic, hydroxyl and protonated carboxylic group respectively. The concentration terms are in unit of moles of the particular functional group per liter of solution. Now this particular equation is inconvenient as the concentration of protonated carboxylic group is not easily determined experimentally.



## Kinetics of step-growth polymerization

- From the reaction, all **acid or alcohol species** (i.e., **monomer, dimer, . . . , n-mer**) in the reaction mixture are indicated by ~① and ~②.
- Since polymerization often takes place in organic media of **low polarity**, **species I and II** are shown in the form of their associated ion pairs.
- **($A^-$)** is the negative counter ion derived from the acid **HA**.
- **Polyesterification reactions are equilibrium reactions**.
- Considering the practical viewpoint of obtaining **high yields of high-molecular-weight** product, such polymerizations are run in a manner so as to **continuously shift the equilibrium** in the direction of the polymer

So, one can obtain more convenient expression for this RP by substituting this group from this equilibrium expression for a protonation reaction. Now let us talk about this equation K1 over K2 this is equal to concentration of C ion OH this is our equation number 5. Now if we combine the equation 4 and equation 5 then we get this dt K3 K and this is equation number 6. Now in stuck group polymerization it is common to use this P symbol rather than X to refer the conversion of limiting functional groups. Now as the conversion is equal to the probability that the particular functional group say that is OH group in the original reaction mixture has reacted with another functional group say this C OH group.



### Kinetics of step-growth polymerization

- **The rate of a step polymerization** can be conveniently expressed in terms of the **concentrations** of the reacting functional groups.
- Thus the **polyesterification** can be experimentally followed by titrating for the unreacted carboxyl groups with a base.
- Hence, **the rate of polymerization Rp** can now be expressed as the rate of **disappearance** of carboxyl groups **-d[COOH]/dt**.
- For the usual polyesterification, the polymerization rate is synonymous with the rate of formation of species II; that is, $\mathbf{k_4}$ is vanishingly **small** (since the reaction is run under conditions that drive Eqs. 2 and 3 towards the right), and $\mathbf{k_1}$, $\mathbf{k_2}$, **and** $\mathbf{k_5}$ are **large** compared to $\mathbf{k_3}$.

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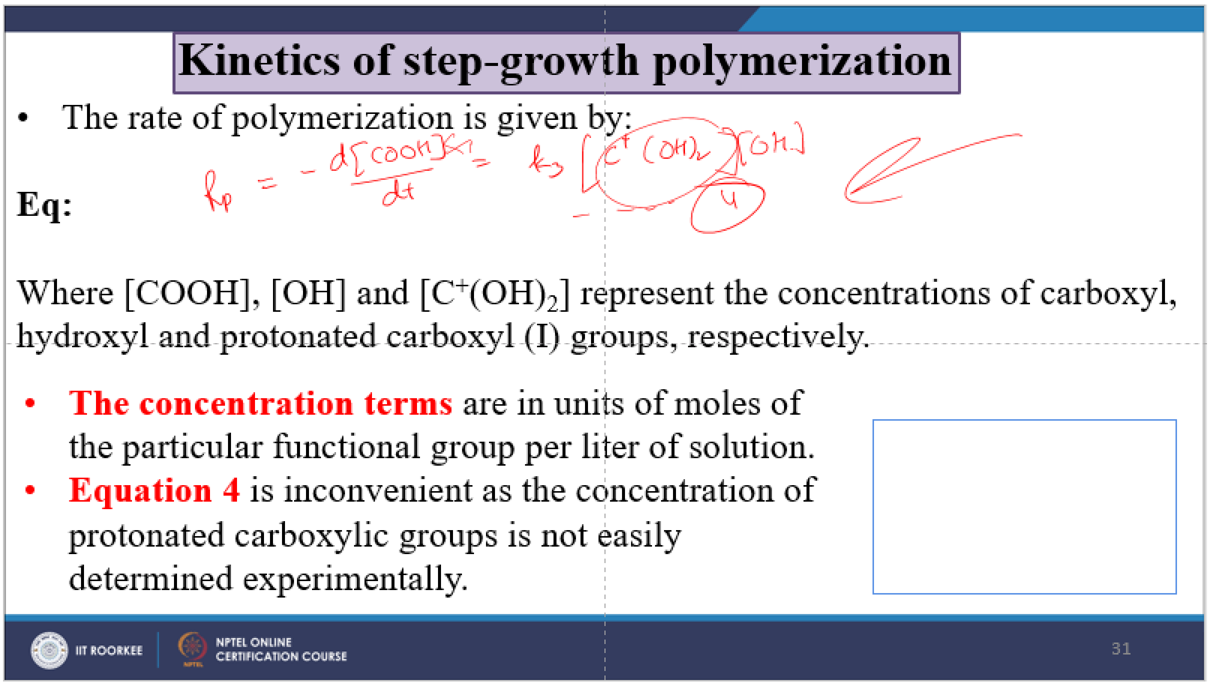
Therefore, the probability that a random molecule will have the length say n which is given by Pn is equal to P to the power n minus 1, 1 minus P which is represented as equation number 7. So, the consumption of exactly n monomer to form this polymer chain requires n minus 1 independent chain linking reaction each with the probability P and also that one hydroxyl group and that is one at the end of the resulting molecule has not been consumed which has the probability of 1 minus P. So, this distribution equation is called the most probable distribution or MPD or Schur's Flory distribution. Now as the conversion is equal to the probability and a particular functional group like OH group in the original reaction mixture has reacted with another functional group like C OH. Therefore, the probability that a random molecule will have a chain length n is given by Pn is equal to P to the power n into 1 minus P.



## Kinetics of step-growth polymerization

- The rate of polymerization is given by:

**Eq:** $R_p = -\frac{d[COOH]}{dt} = k_3 [C^+(OH)_2][OH]$ ④

Where [COOH], [OH] and $[C^+(OH)_2]$ represent the concentrations of carboxyl, hydroxyl and protonated carboxyl (I) groups, respectively.

- **The concentration terms** are in units of moles of the particular functional group per liter of solution.
- **Equation 4** is inconvenient as the concentration of protonated carboxylic groups is not easily determined experimentally.

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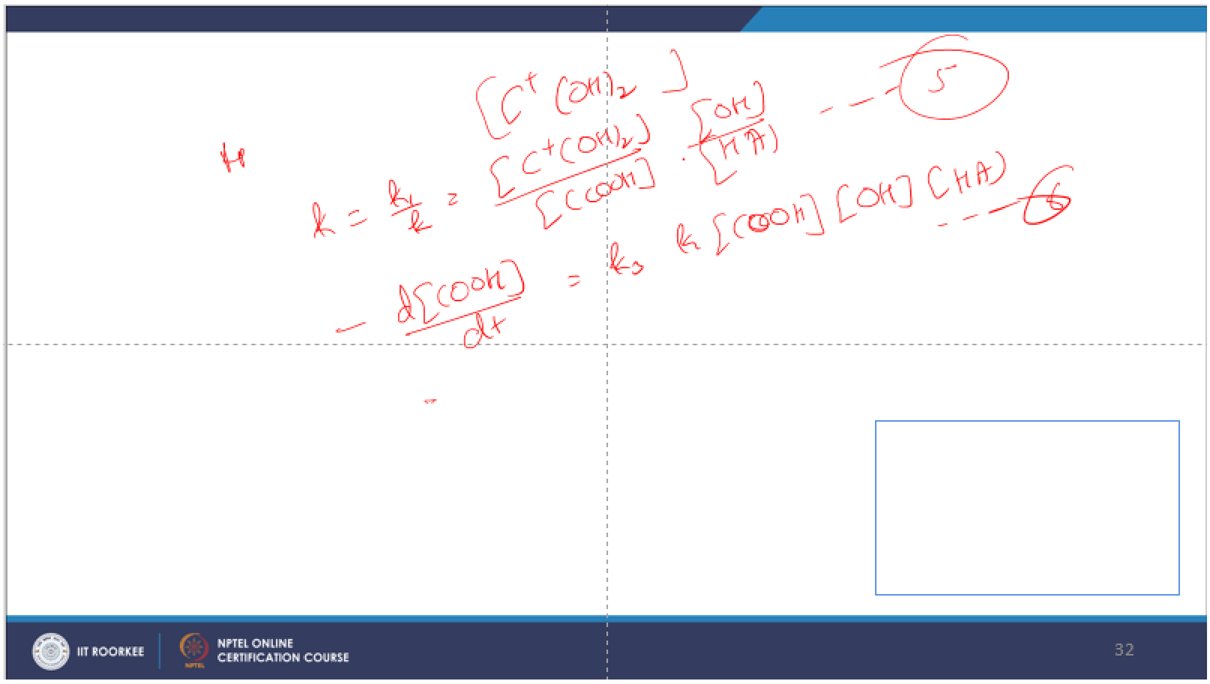
Now consumption of n monomer to form the polymer chain requires n minus 1 independent chain linking and each with the probability of a P. So, this Pn corresponds to the mole fraction of n mer. Now as conversion increases that is P tends to 1, the mole fraction of a small molecule decreases and mole fraction of large molecule increases. But the species with the largest concentration is always the monomer so that the chain length distribution or equation 7 is a decreasing function of chain length. So, if you use the equation 7 to develop an expression for the weight say CLD this is the AB polymeric system.



$[C^+(OH)_2]$

$R_p$

$K = \frac{k_1}{k_2} = \frac{[C^+(OH)_2]}{[COOH][HA]}$ ⑤

$-\frac{d[COOH]}{dt} = k_3 K [COOH][OH][HA]$ ⑥

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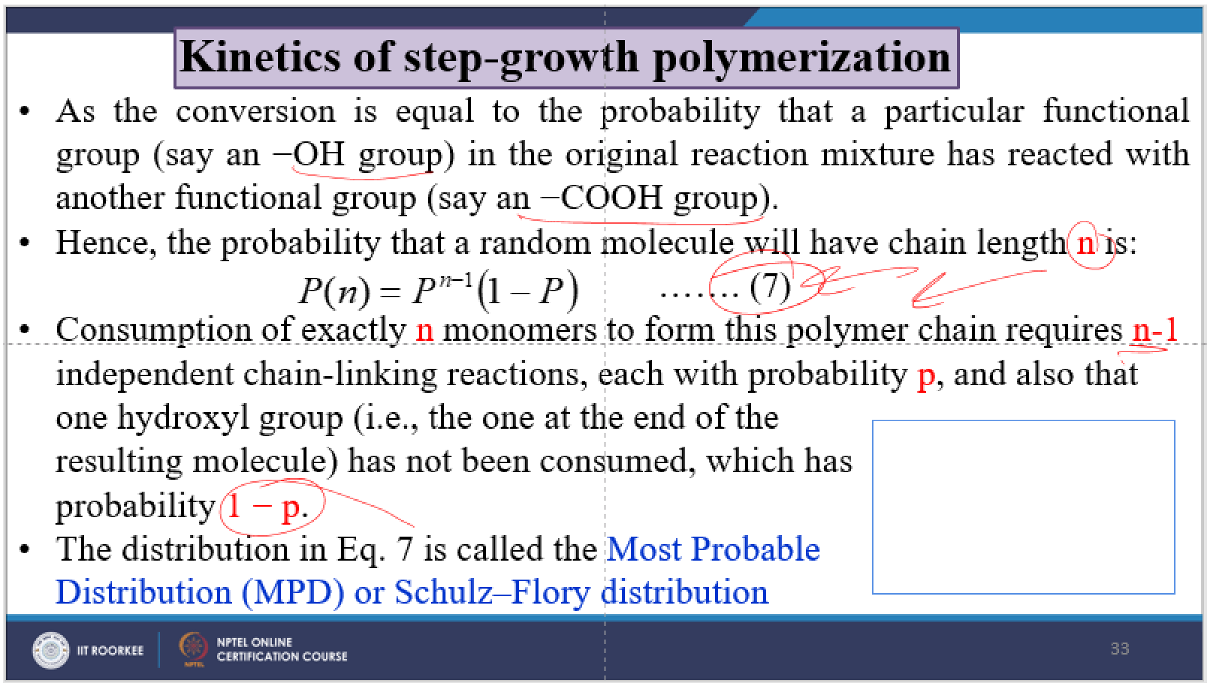
Now let n be the total number of molecules remaining in the conversation and n naught be the initial number of monomer molecules. So, this is n n is equal to n naught into 1 minus P it is quite obvious. So, the mole fraction of n mer is Xn is equal to n n over n naught 1 minus P and this is our equation number 8. Now since Xn is equal to Pn or Pn to the power Pn minus 1 1 minus P the number of moles of n mers are n n is equal to n naught Pn minus 1 into 1 minus P square this is equation number 9. So, the weight fraction of n mer is Wn is equal to n n n Wm over n naught Wm and n naught into 1 minus P square Pn minus 1 n over n naught which is equal to 1 minus P square P n minus 1 n this is equation number 10 where Wm this is the molecular weight of a repeat unit.



## Kinetics of step-growth polymerization

- As the conversion is equal to the probability that a particular functional group (say an −OH group) in the original reaction mixture has reacted with another functional group (say an −COOH group).
- Hence, the probability that a random molecule will have chain length n is:

$$P(n) = P^{n-1}(1-P) \qquad \ldots\ldots (7)$$

- Consumption of exactly n monomers to form this polymer chain requires n-1 independent chain-linking reactions, each with probability p, and also that one hydroxyl group (i.e., the one at the end of the resulting molecule) has not been consumed, which has probability 1 − p.
- The distribution in Eq. 7 is called the Most Probable Distribution (MPD) or Schulz–Flory distribution

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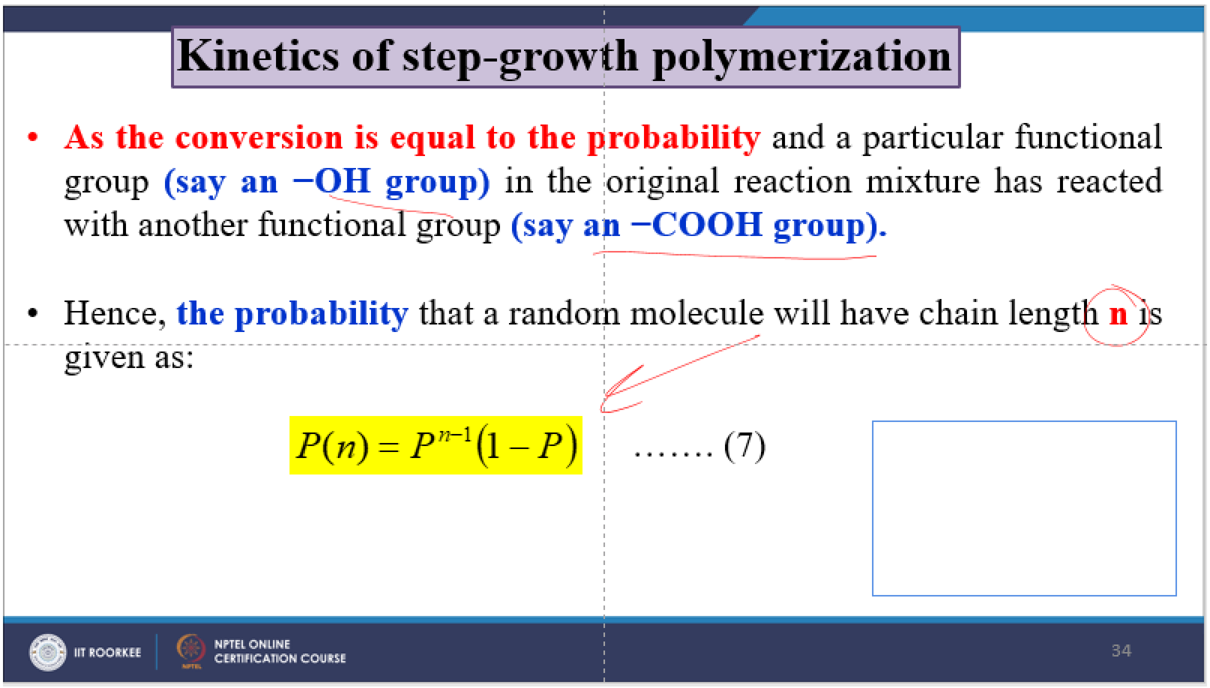

## Kinetics of step-growth polymerization

- **As the conversion is equal to the probability** and a particular functional group **(say an −OH group)** in the original reaction mixture has reacted with another functional group **(say an −COOH group).**
- Hence, **the probability** that a random molecule will have chain length **n** is given as:

$$P(n) = P^{n-1}(1-P) \qquad \ldots\ldots (7)$$

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## Kinetics of step-growth polymerization

- **Consumption of exactly n** monomers to form this polymer chain requires **n-1** independent chain-linking reactions, each with probability **p**.
- Also that one hydroxyl group (i.e., the one at the end of the resulting molecule) has not been consumed, which has **probability 1 − p.**
- The distribution in eq. 7 is called the **Most Probable Distribution (MPD) or Schulz–Flory distribution**

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## Kinetics of step-growth polymerization

- The **probability P(n)** corresponds to the mole fraction of **n-mer, x(n)**
- **As conversion increases (p → 1)**, the **mole fractions** of small molecules **decrease**, and the **mole fractions** of **larger molecules increase**, but the species with the largest concentration is always the monomer, so that the number **CLD (Chain Length Distribution)** or eq. 7 is a decreasing function of chain length.
- Now we use eq. 7 to develop an expression for the weight CLD for this **AB polymer system**

# Kinetics of step-growth polymerization

- **Let N** be the **total number of molecules remaining at conversion p** and **$N_0$** be the **initial number of monomer molecules**. Then, **$N = N_0(1 - p)$** and the mole fraction of n-mer is:

$$x(n) = \frac{N_n}{N_0(1-P)} \quad \text{………} (8)$$

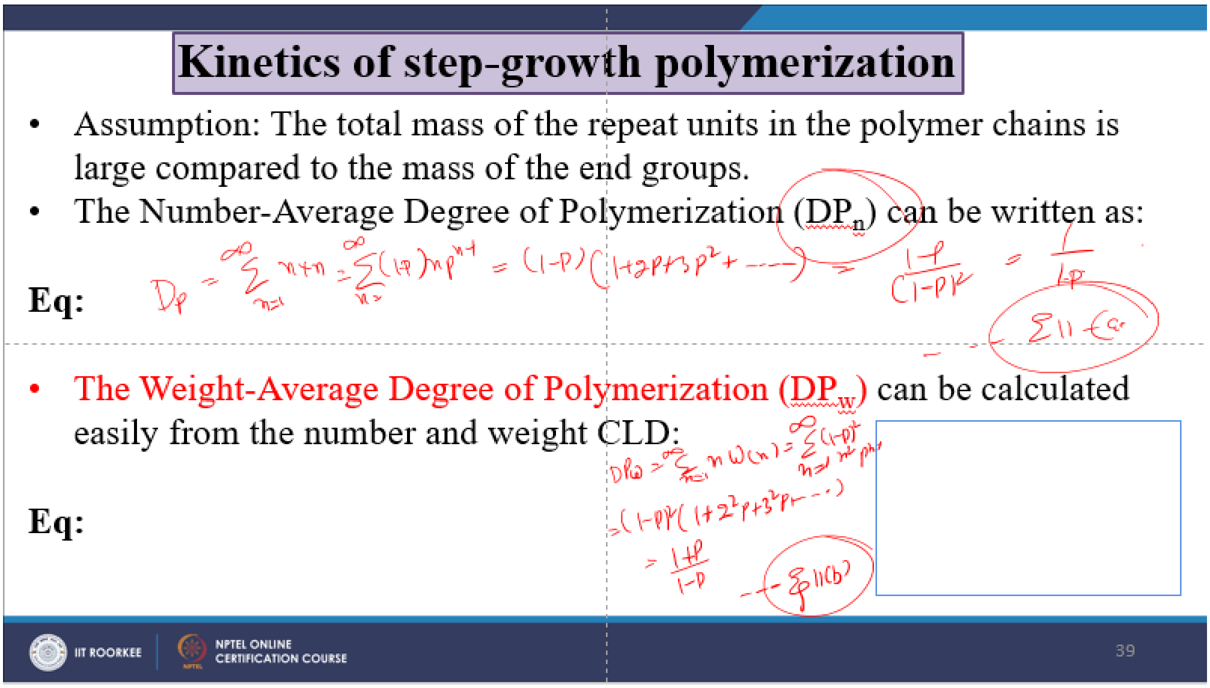
- Since **$x(n) = P(n) = p^{n-1}(1 - p)$**, the number of moles of n-mer is:

$$N_n = N_0 P^{n-1}(1-P)^2 \quad \text{……} (9)$$

---

$$W(n) = \frac{N_n(nW_m)}{N_0 W_m} = \frac{N_0 (1-p)^2 p^{n-1} n}{N_0}$$

$$= (1-p)^2 p^{n-1} n \quad ⑩$$



## Kinetics of step-growth polymerization

- Assumption: The total mass of the repeat units in the polymer chains is large compared to the mass of the end groups.
- The Number-Average Degree of Polymerization ($DP_n$) can be written as:

**Eq:** $D_P = \sum_{n=1}^{\infty} n f n = \sum_{n=1}^{\infty} (1-P) n P^{n-1} = (1-P)(1+2P+3P^2+\cdots) = \frac{1-P}{(1-P)^2} = \frac{1}{1-P}$ --- Eq 11a

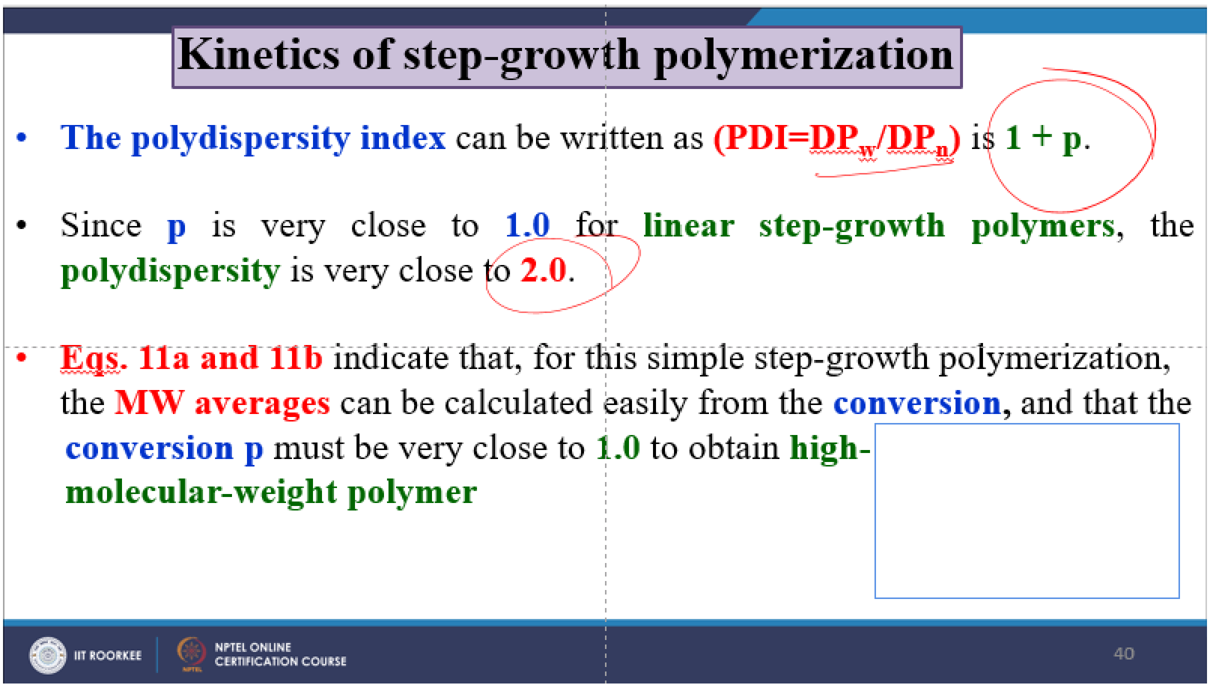
- The Weight-Average Degree of Polymerization ($DP_w$) can be calculated easily from the number and weight CLD:

**Eq:** $DP_w = \sum_{n=1}^{\infty} n W(n) = \sum_{n=1}^{\infty} (1-P)^2 n^2 P^{n-1}$

$= (1-P)^2(1+2^2P+3^2P^2+\cdots)$

$= \frac{1+P}{1-P}$ --- Eq 11(b)

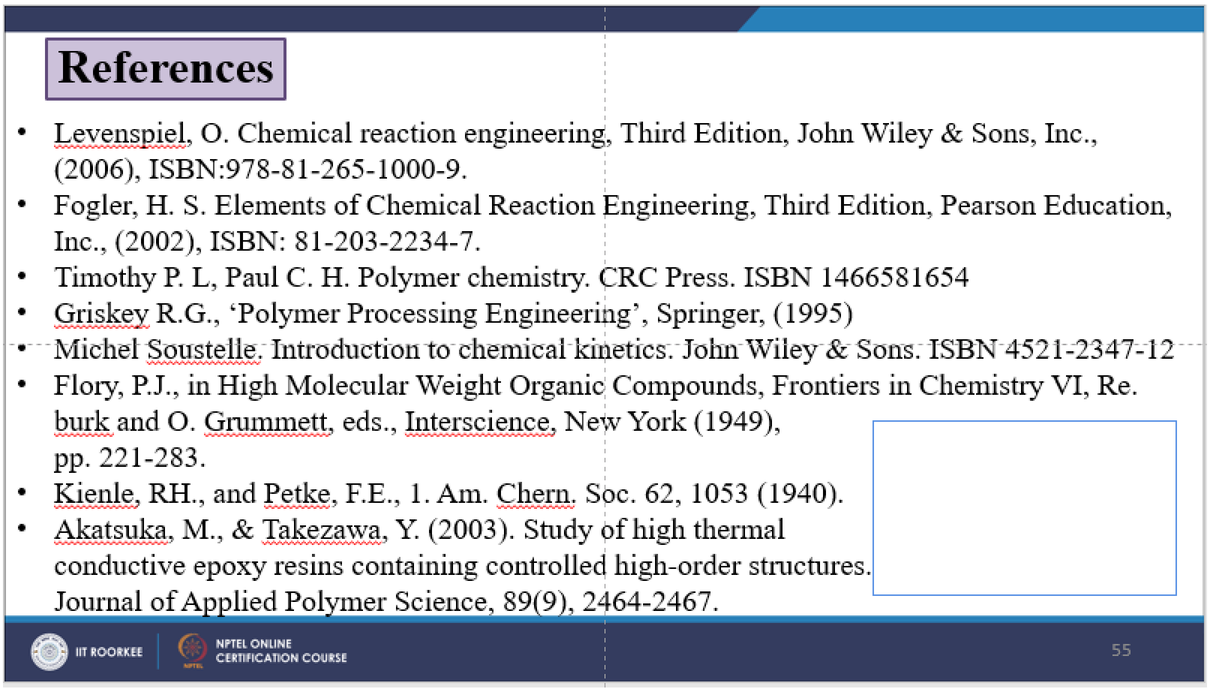
Now let us talk about one assumption that is the total mass of the repeat unit in the polymer chain is large compared to the mass of n group. So the number average degree of polymerization dP this can be written as dP is equal to summation n is equal to 1 to infinity n into n and that is equal to infinity 1 minus P and P to the power n minus 1 into 1 minus P 1 plus 2 P plus 3 P square plus and so on and this is equal to 1 minus P over into 1 minus P over 1 over 1 minus P this is equation let us say 11a. Now if we slightly modified this particular equation this becomes the dP W summation n with respect to weight this will become summation n is equal to 1 to infinity 1 minus P square n square P n minus 1 and this is equal to 1 minus P square into 1 plus 2 square P plus 3 square P plus and so on and that is equal to 1 plus P 1 minus P this is let us say equation 11b. Now the polydispersity index this can be written as Pdi is equal to dP W over dP n which is equal to 1 plus P since P is very close to 1 for a linear step growth polymerization the polydispersity is very close to 2. So, if we consider these equation 11a and equation 11b this indicate the simple step growth polymerization and the molecular weight averages can be calculated easily from the conversion and that the conversion P must be very close to 1.



## Kinetics of step-growth polymerization

- **The polydispersity index** can be written as **(PDI=$DP_w/DP_n$)** is **1 + p**.
- Since **p** is very close to **1.0** for **linear step-growth polymers**, the **polydispersity** is very close to **2.0**.
- **Eqs. 11a and 11b** indicate that, for this simple step-growth polymerization, the **MW averages** can be calculated easily from the **conversion**, and that the **conversion p** must be very close to **1.0** to obtain **high-molecular-weight polymer**

0 to obtain the high molecular weight polymer. So, dear friends in this particular lecture we discussed the kinetic aspects of chain growth and step growth polymerization we discussed about the basic nitty-gritty of the chain growth and step growth polymerization apart from the differentiation and we start the discussion about the kinetics of various polymerization steps.



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For your convenience we have enlisted different references which you can utilize over the period of time when as and when required. Thank you very much.