Polymer Reaction Engineering
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Lecture - 30
Step-Growth Polymerization-III

Welcome to the lecture having the information about the accessibility of functional group equilibrium consideration cyclization versus linear polymerization under the head of polymer reaction engineering. Now, have a look about that what we studied in the last lecture.

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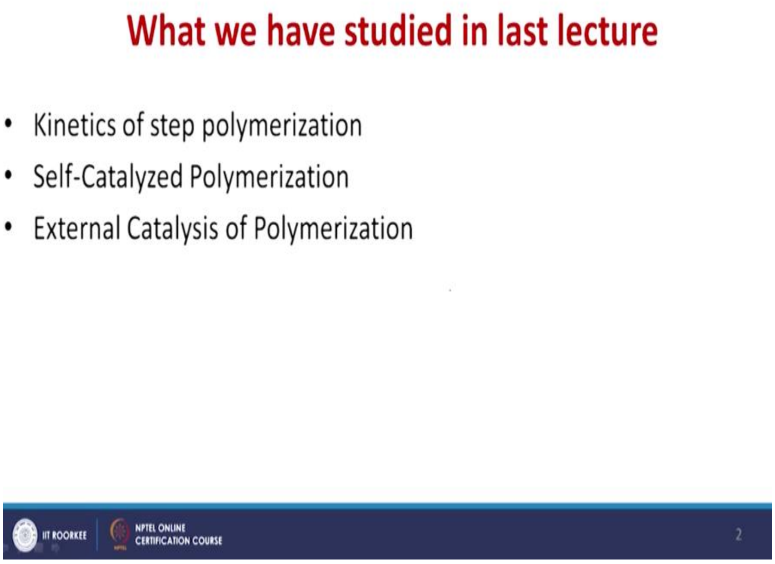

What we have studied in last lecture

- Kinetics of step polymerization
- Self-Catalyzed Polymerization
- External Catalysis of Polymerization

We discussed about the kinetic problems of step growth polymerization under the head of self-catalyzed polymerization and external catalysis of step growth polymerization.

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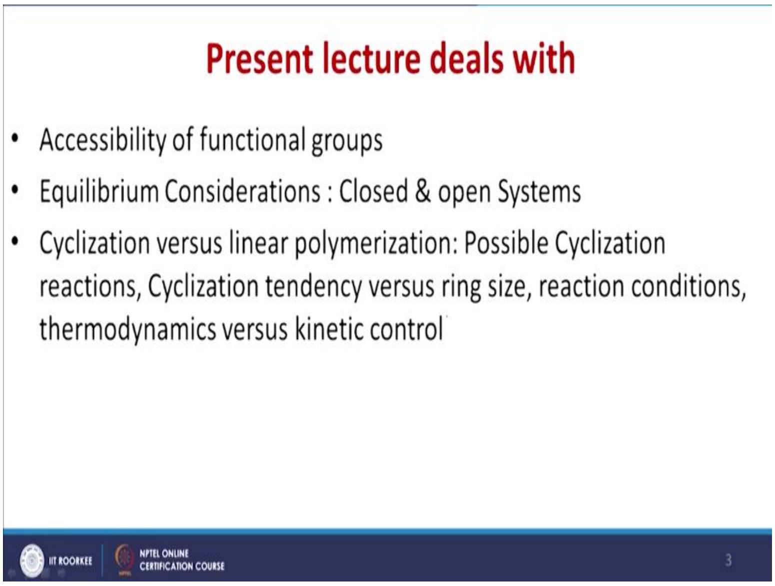

Present lecture deals with

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

Now, in this particular lecture, we will discuss about the accessibility of functional groups. We will have the equilibrium consideration with respect to the closed and open type of system. We will discuss about the cyclization versus linear polymerization and possible cyclization reactions, cyclization tendency versus ring size, reaction conditions. We will give the major emphasis to the thermodynamic versus kinetic control differences etcetera.

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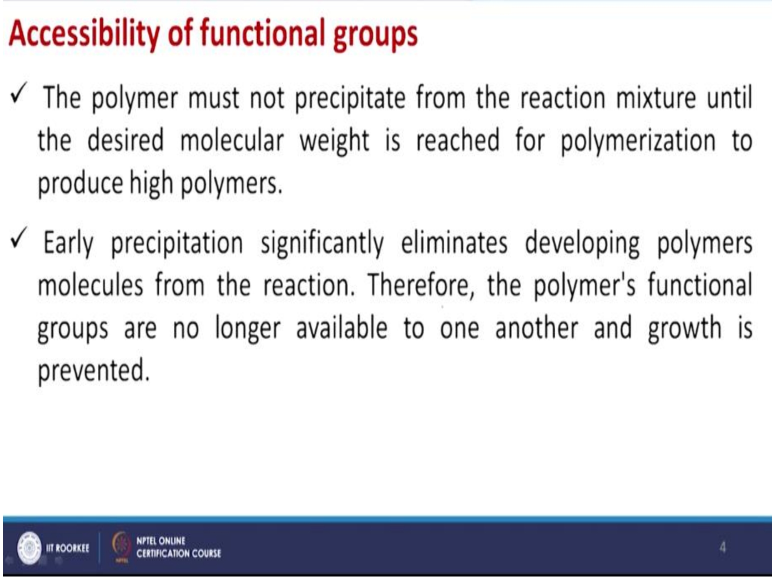

Accessibility of functional groups

- ✓ The polymer must not precipitate from the reaction mixture until the desired molecular weight is reached for polymerization to produce high polymers.
- ✓ Early precipitation significantly eliminates developing polymers molecules from the reaction. Therefore, the polymer's functional groups are no longer available to one another and growth is prevented.

Now let us have a look about the accessibility of the functional group concept. The polymer must not precipitate from the reaction mixture until the desired molecular weight is reached for the polymerization to produce the high polymer. Now, this is the desired effect for any kind of a reaction mechanism that you should not stop the reaction until you reach the desired effect or desired product profile.

So, that is why this particular approach is having the prime importance. Now, early precipitation significantly eliminates the development of polymer molecules from the reaction. And therefore, the polymers functional groups are no longer available to another and the growth is prevented. So, that is sometimes a good candidate of disadvantage of the polymerization process.

Therefore, one has to look into this particular approach that the whatever functional group because the functional groups are sometimes heart of the polymerization reaction. So, the functional group should be readily available to carry out the desired polymerization. And they must be accessible for all the reacting mass as long as you need to carry out the polymerization process.

Now, the polymer molecular weight it can be determined through the inherent viscosity and sometimes referred as eta inherent. Now, high molecular weights are indicated by greater value of this eta. The result of solvent on molecular weight in the polymerization of sometimes say this 4 iso cyano cyanatophenyl methane, now, with ethylene glycol this can be seen in this particular figure.

Now, the polymer molecular weight this can be determined through the inherent viscosity nu inh. Now, the high higher molecular weights they are indicated by the greater value of this eta. Now, sometimes we need to address with the help of some practical example that the result of a solvent (()) (03:42) molecular weight in the polymerization of this bis 4 isocyanatophenyl methane with ethylene glycol this can be seen in the table which is presented in the next slide.

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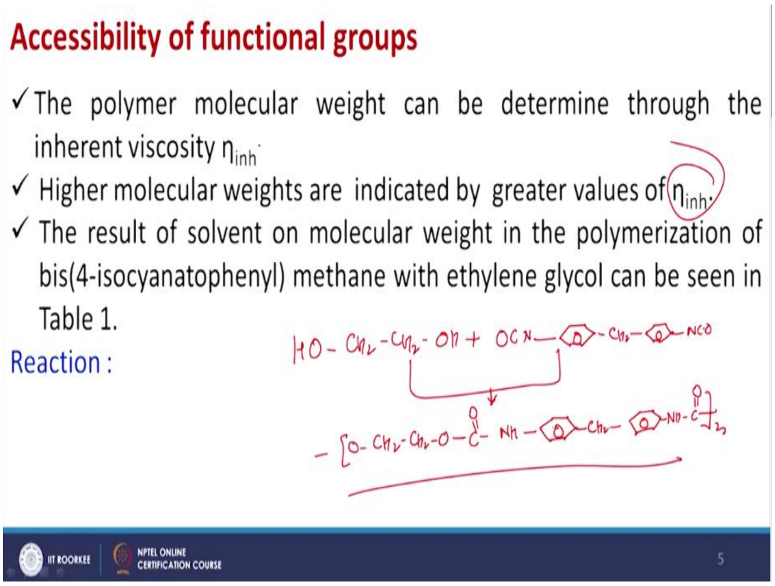

Accessibility of functional groups

- ✓ The polymer molecular weight can be determine through the inherent viscosity η_{inh}.
- ✓ Higher molecular weights are indicated by greater values of η_{inh}.
- ✓ The result of solvent on molecular weight in the polymerization of bis(4-isocyanatophenyl) methane with ethylene glycol can be seen in Table 1.

Reaction :

But, before we go for the reaction, now, here the reaction is HO CH_2 CH_2 OH plus OC N CH_2 NCO, now, here, C double bond O NH CH_2. Now, this is my reaction.

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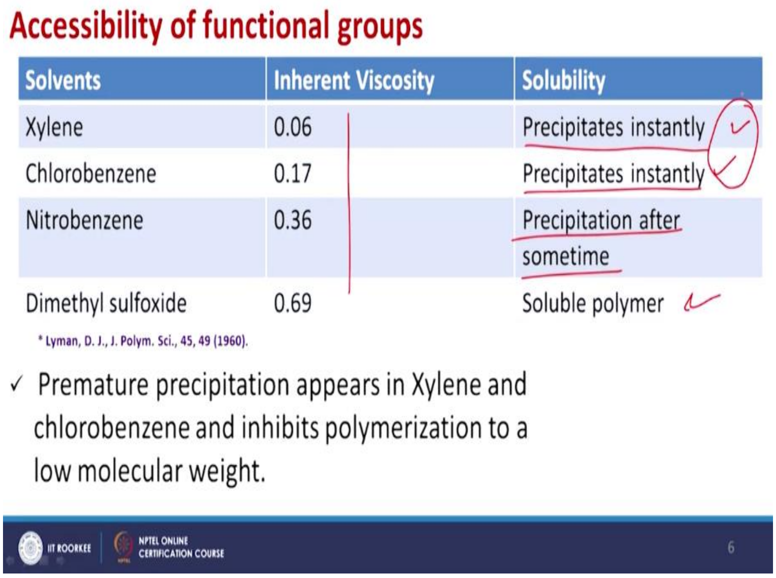

Accessibility of functional groups

Solvents	Inherent Viscosity	Solubility
Xylene	0.06	Precipitates instantly
Chlorobenzene	0.17	Precipitates instantly
Nitrobenzene	0.36	Precipitation after sometime
Dimethyl sulfoxide	0.69	Soluble polymer

* Lyman, D. J., J. Polym. Sci., 45, 49 (1960).

- ✓ Premature precipitation appears in Xylene and chlorobenzene and inhibits polymerization to a low molecular weight.

Now, if you see the table this talks about the solvent, inherent viscosity and solubility. Now, you see they are the various solvents being used and they the inherent whereas viscosity is enlisted over here. And what is the impact with respect to the solubility that it precipitated instantly. And here this the precipitation effect that is it is precipitated instantaneously. Then if we use the nitrobenzene then the precipitation may take place after sometimes and dimethyl sulfoxide it is the it soluble the entire polymer.

So, premature precipitation appears in the xylene and chlorobenzene and inhibits the polymerization to a low molecular weight. So, that is why say the basic phenomena in the under this category is that initially when we use the xylene and chlorobenzene they precipitated or they facilitate the precipitation instantaneously. In that case they inhibit the further polymerization and thus this may lead to the low molecular weight.

Because if you keep on polymerizing the things then you may experience or you may have the higher molecular weight polymers. So, when the solvent for the reaction becomes more potent solvent higher molecular weights are usually obtained for the polymers. So, the higher molecular weight of the polymer is obtained in the strongly polar aprotic solvent like DMSO dimethyl sulfoxide in which the polyurethane is fully soluble during the polymerization process.

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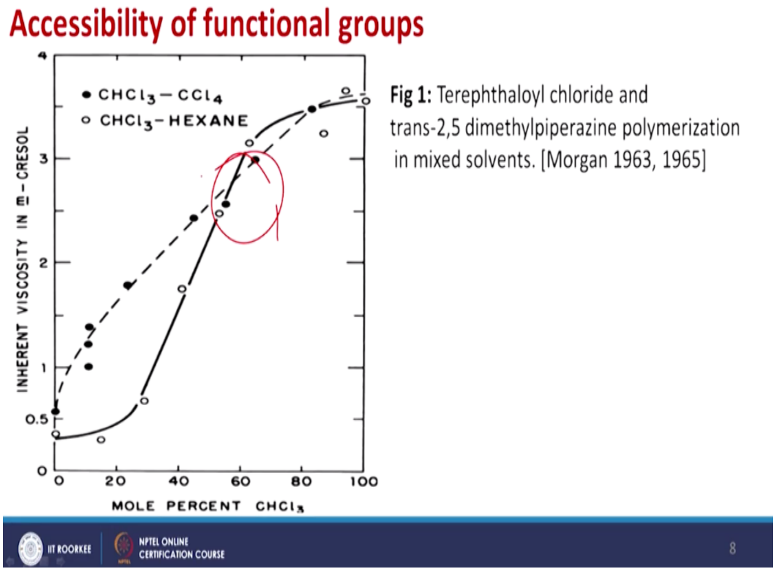

Accessibility of functional groups

Fig 1: Terephthaloyl chloride and trans-2,5 dimethylpiperazine polymerization in mixed solvents. [Morgan 1963, 1965]

Now, here you can see the terephthaloyl chloride and trans 2 dimethylpiperazine polymerization in the mixed solvent. You can see that where your critical point is achieved.

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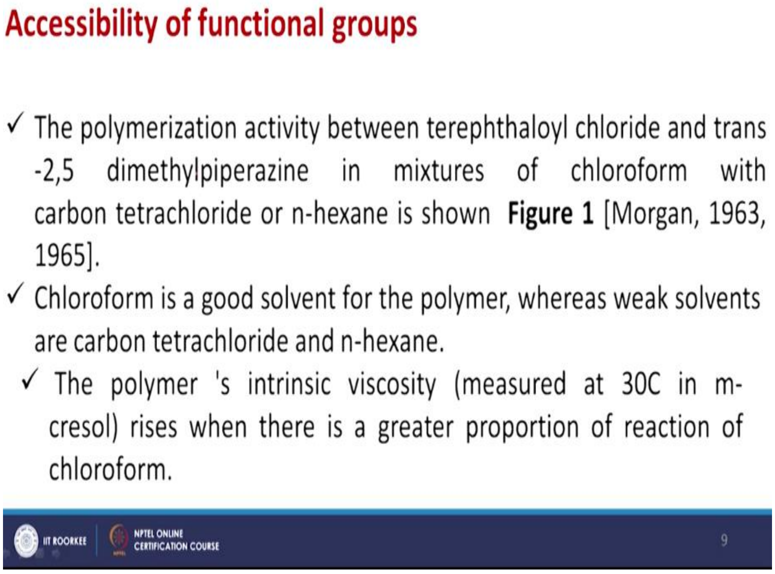

Accessibility of functional groups

- ✓ The polymerization activity between terephthaloyl chloride and trans -2,5 dimethylpiperazine in mixtures of chloroform with carbon tetrachloride or n-hexane is shown **Figure 1** [Morgan, 1963, 1965].
- ✓ Chloroform is a good solvent for the polymer, whereas weak solvents are carbon tetrachloride and n-hexane.
  - ✓ The polymer 's intrinsic viscosity (measured at 30C in m-cresol) rises when there is a greater proportion of reaction of chloroform.

Now, the polymerization activity if you recall this particular plot the polymerization activity between the terephthaloyl chloride and trans 2,5 dimethylpiperazine in mixtures of chloroform with carbon tetrachloride or n benzene which is shown in this particular figure. Now, chloroform is a good solvent for the polymer whereas weak solvent are carbon tetrachloride and n hexane.

That is why the property and the quality of the solvent also play a very vital role in this type of polymerization. So, the polymers intrinsic viscosity usually measured at 30 degree Celsius in say m cresol. This rises when there is a great proportion of reaction of chloroform. So, the stronger the reaction medium for the polymer as a solvent the longer the polymer remains in solution and the greater is the molecular weight of the polymer.

So, with the solvent medium which is a weak polymer solvent precipitation limits the molecular weight. Solvent sometimes influences since the rates of polymerization and the molecular weight due to the preferential solvation and other unique relationship with either the reactants or the reactions transition state or sometimes both. Now, with a transition state more polar than the reactants, the polar solvent increases the rate of polymerization.

So, for reaction involving transition state that are less polar than the reactants, polar solvent are usually not termed as an ideal one. So, specific interaction of solvent with the reactants functional group many significantly affect the path of polymerization. So, this particular point is again very crucial while discussing these accessibilities of the functional group. Now, specific interaction with the solvent can alter the reactivity of a functional group.

Now, sometimes when we talk about the equilibrium consideration there are 2 type of a system closed system and open system. So, let us have a look about the closed system first. Now, equilibrium reactions are involved in step polymerization. And it is important to examine how the balance affects the degree of conversion and more specially the molecular weight of polymer.

So, the polymerization is referred to as the equilibrium polymerization or reversible polymerization where the monomers and polymer are in equilibrium. So, that is again important for the stability of the product. So, a closed system is supposed to mean one where none of the forward reaction products are removed. The product concentration usually the polymer and typically small molecules such as water etcetera they the product concentration usually built up until the reverse reaction rate is equal to the rate of polymerization. That is the foremost requirement.

Now, the reverse rate is commonly referred to as a reaction of a depolymerization. And sometimes in other words such as the if you take the example that is the glycolysis or hydrolysis. The molecular weight of polymer is usually measured by the degree to which when the equilibrium is achieved the forward reaction has proceed. The reason is that whenever you achieve this particular juncture the equilibrium juncture in that case your system would be pseudo stabilized.

And in that case, you can say the molecular weight of polymer is usually stable in the range of the desired one. Now, let us take consider the external polyesterification of acid catalyzed reaction.

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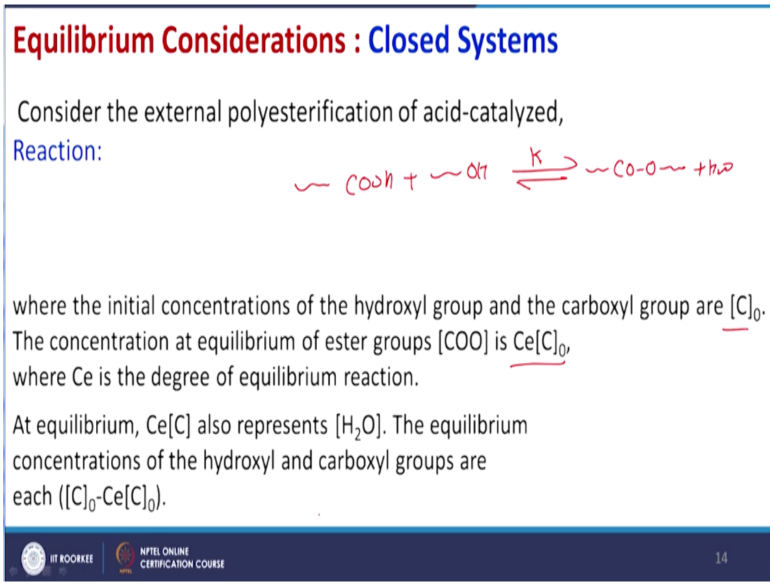

Equilibrium Considerations : Closed Systems

Consider the external polyesterification of acid-catalyzed,

Reaction:

$$\sim COOH + \sim OH \underset{}{\overset{K}{\rightleftharpoons}} \sim CO\text{-}O\sim + H_2O$$

where the initial concentrations of the hydroxyl group and the carboxyl group are $[C]_0$.
The concentration at equilibrium of ester groups [COO] is $Ce[C]_0$,
where Ce is the degree of equilibrium reaction.

At equilibrium, Ce[C] also represents $[H_2O]$. The equilibrium concentrations of the hydroxyl and carboxyl groups are each $([C]_0\text{-}Ce[C]_0)$.

And that is represented as COOH OH plus H_2O. Now, here the initial concentration of hydroxyl group and the carboxyl group are represented as C naught. The concentration of equilibrium of ester group that is COO is represented as Ce Cl_2. Now, at equilibrium Ce C is represented by H_2O. So, the equilibrium concentration of hydroxyl and carboxyl group are each having this C naught minus Ce C naught.

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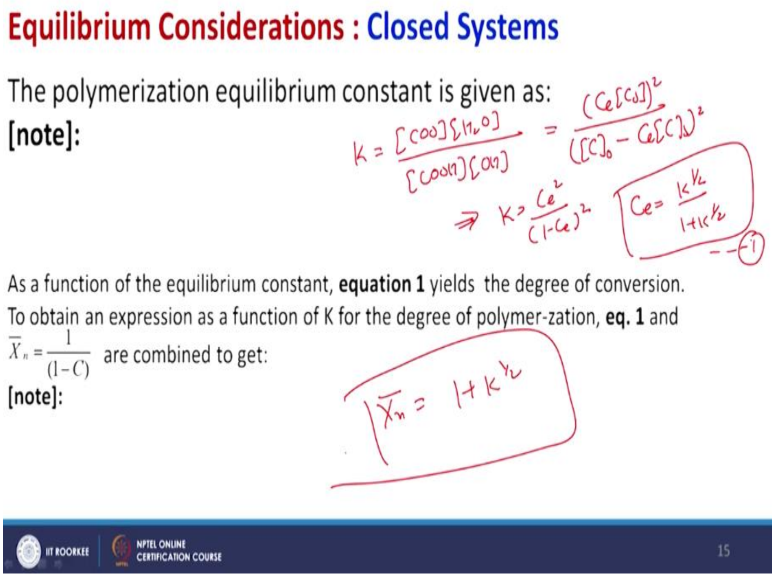

Equilibrium Considerations : Closed Systems

The polymerization equilibrium constant is given as:

[note]:

$$K = \frac{[COO][H_2O]}{[COOH][OH]} = \frac{(C_e[C_0])^2}{([C]_0 - C_e[C]_0)^2}$$

$$\Rightarrow K = \frac{C_e^2}{(1-C_e)^2} \qquad \boxed{C_e = \frac{K^{1/2}}{1+K^{1/2}}} \text{ -- } ①$$

As a function of the equilibrium constant, **equation 1** yields the degree of conversion. To obtain an expression as a function of K for the degree of polymer-zation, **eq. 1** and $\bar{X}_n = \frac{1}{(1-C)}$ are combined to get:

[note]:

$$\boxed{\bar{X}_n = 1 + K^{1/2}}$$

Now, so, the polymerization equilibrium constant, because ultimately, we are looking for that particular thing, so, the polymerization equilibrium constant is given as K is equal to H 2 O and that is upon concentration of C at time t is equal to 0 and then this C C naught square. So, if we simplify this then it can give you the K is equal to Ce 1 minus Ce square. Now, if we solve it for the Ce then this can be K and a half 1 plus K and half.

That can be represented as equation number 1. So, now, as a function of equilibrium constant this equation yields the degree of conversion to obtain the expression as a function of K for the degree of polymerization. This particular equation may be this particular equation and the bar X n is equal to 1 upon 1 minus C. So, in that case this can be represented as 1 plus K to the power half. So, this particular equation gives you a good knowledge about the K the rate constant etcetera.

$$k = \frac{[COOH][H_2O]}{[COOH][OH]} = \frac{(C_e[C_o])^2}{[C_o - C_e[C_o]]^2}$$

$$k == \frac{{C_e}^2}{[1 - C_e]^2}$$

$$C_e = \frac{K^{\frac{1}{2}}}{1+K^{\frac{1}{2}}} \qquad (1)$$

$$\overline{X_n} = 1 + K^{\frac{1}{2}}$$

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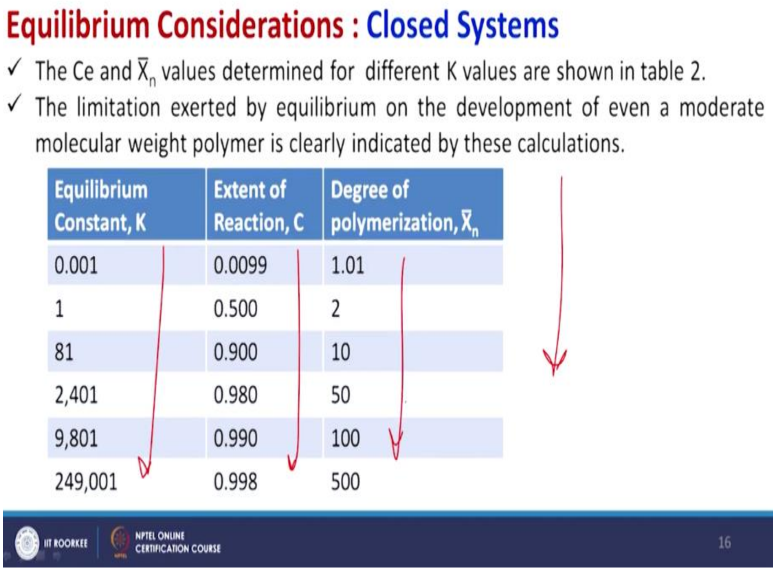

Equilibrium Considerations : Closed Systems

- ✓ The Ce and $\bar{X}_n$ values determined for different K values are shown in table 2.
- ✓ The limitation exerted by equilibrium on the development of even a moderate molecular weight polymer is clearly indicated by these calculations.

Equilibrium Constant, K	Extent of Reaction, C	Degree of polymerization, $\bar{X}_n$
0.001	0.0099	1.01
1	0.500	2
81	0.900	10
2,401	0.980	50
9,801	0.990	100
249,001	0.998	500

Now, Ce and bar X n values usually determined for different K values. They are represented in this table too. The limitation usually exerted by the equilibrium on the development of even a moderate molecular weight is indicated by this one. Now, you here you see that we have represented the equilibrium constant and the extent of a reaction. Extent of reaction is again very vital that you know that what is the efficacy of your polymerization reaction?

In view of this, this determination is extremely important. And then we have listed the degree of polymerization.

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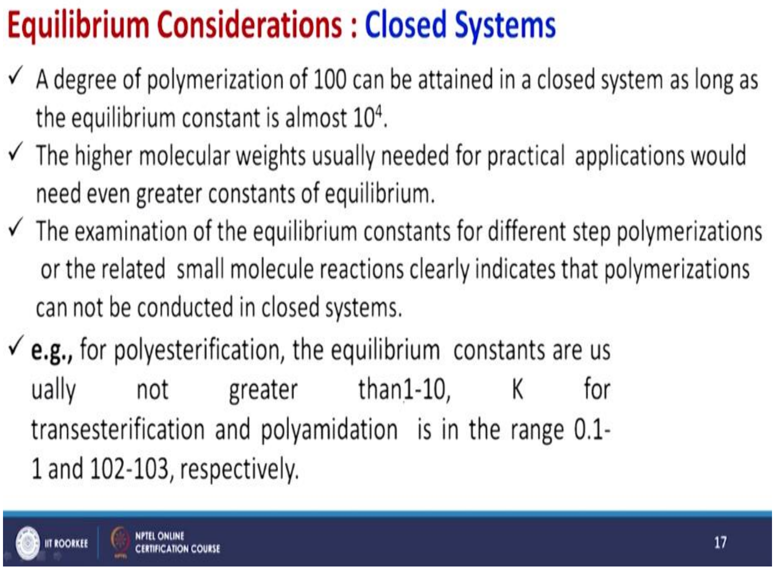

Equilibrium Considerations : Closed Systems

- ✓ A degree of polymerization of 100 can be attained in a closed system as long as the equilibrium constant is almost 10^4.
- ✓ The higher molecular weights usually needed for practical applications would need even greater constants of equilibrium.
- ✓ The examination of the equilibrium constants for different step polymerizations or the related small molecule reactions clearly indicates that polymerizations can not be conducted in closed systems.
- ✓ **e.g.,** for polyesterification, the equilibrium constants are us ually not greater than1-10, K for transesterification and polyamidation is in the range 0.1-1 and 102-103, respectively.

Now, the degree of polymerization of 100 this 100 can be achieved in a closed system as long as the equilibrium constant is almost 10 to the power 4. So, the higher molecular weight usually needed for the practical application would need even greater constants of equilibrium. Now, the examination of equilibrium constants for different step polymerization or related small molecule reaction clearly indicates that the polymerization cannot be conducted in a closed system.

Let us take an example of polyesterification. The equilibrium constants are usually not greater than 1 to 10 K for this transesterification and polyamidation that is in the range of 0.1 to 1 and 102 to 103 respectively. Now, let us talk about the open system. Because we previously we discussed about the closed system. Now, removal of at least one of the products, because if you recall that in the closed system, we are not removing any product but here we are removing.

So, the removal of at least one of the products of the forward polymerization reaction in the open system, this helps to move the equilibrium towards the higher molecular weight. So, the removal of this small molecule by a product is typically more convenient instead of polymer. Now, if water is a by-product, a combination of temperature, reduced pressure and inert gas purging sometimes will eliminate it.

Now, step polymerization they are often efficiently conducted at a temperature near or sometimes above the water boiling point. Now, this is typically performed to attained the required reaction rates but it has the additional benefit of enabling water removal. So, just to maintain the desired molecular weight, just to maintain the extent of a reaction, now, it takes a considerable attempt to move an equilibrium towards the polymer.

Because water or hydrogen chloride or other small molecule they must diffuse through and out of these reaction mixtures. Now, sometimes diffusion it is not so simple as a at a very high conversion the standard step polymerization method is somewhat viscous. So, the degree to which the system must be move in a forward direction this can be considered by measuring the declination in the small molecule concentration and sometimes needed to achieve a certain molecular weight. Now, let us take the example for the kinetic study of this polyesterification.
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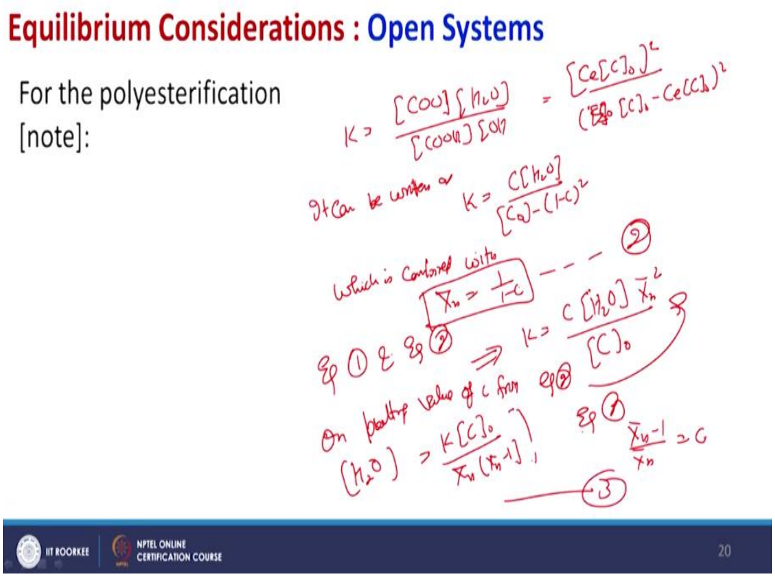

Equilibrium Considerations : Open Systems

For the polyesterification
[note]:

$K = \frac{[COO][H_2O]}{[COOH][OH]} = \frac{[C_e[C]_0]^2}{([C]_0 - C_e[C]_0)^2}$

It can be written as $K = \frac{C[H_2O]}{[C_0]-(1-C)^2}$

Which is combined with $\boxed{\overline{X}_n = \frac{1}{1-C}}$ --- ②

Eq ① & Eq ② $\Rightarrow K = \frac{C[H_2O]\overline{X}_n^2}{[C]_0}$

On putting value of c from Eq ② Eq ① $\frac{\overline{X}_n-1}{X_n} = C$

$(H_2O) = \frac{K[C]_0}{\overline{X}_n(\overline{X}_n-1)}$ — ③

$$K = \frac{[COO][H_2O]}{[COOH][OH]} = \frac{[C_e[C]_o]^2}{([C]_o - C_e[C]_o)^2}$$

It can be written as

$$K = \frac{[C][H_2O]}{[C]_o - [1-C]^2}$$

$$\overline{X_n} = \frac{1}{1-C} \qquad (2)$$

From equation (1) and (2) we have

$$K = \frac{[C][H_2O]\overline{X_n}^2}{[C]_o}$$

$$[H_2O] = \frac{K[C]_o}{\overline{X_n}(\overline{X_n}-1)} \qquad (3)$$

Now, here the K COO H_2O then COOH OH. And this can be represented as based on the previous notation Ce C naught sorry C naught. Now, it can be written as K is equal to C and C square, now, which is combined with. Now, if we consider the equation 1 and equation 2 then it may become K is equal to C H_2O X n square upon C naught. Now, on putting value of C from equation 2 in the equation we may have H_2O K C naught upon.

Now, here if you see that from equation 2, we have bar Xn minus 1 upon Xn C and that may be termed as equation number 3.

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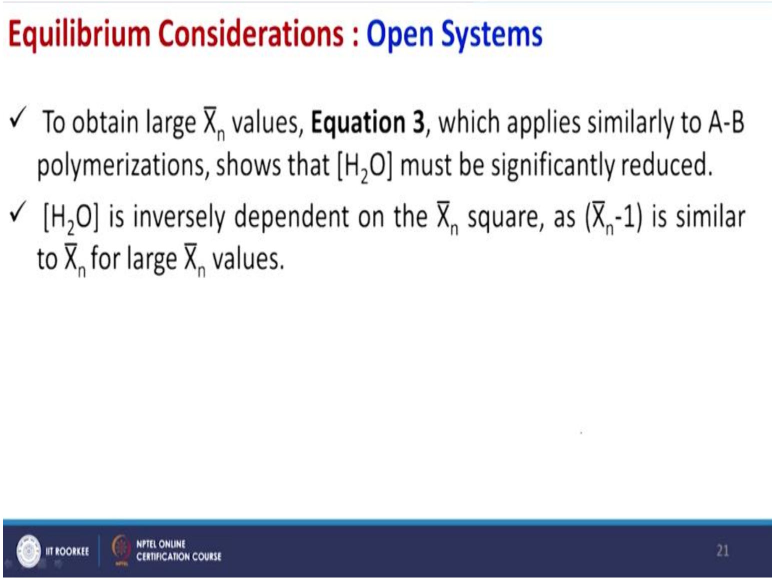

Equilibrium Considerations : Open Systems

- ✓ To obtain large $\bar{X}_n$ values, **Equation 3**, which applies similarly to A-B polymerizations, shows that $[H_2O]$ must be significantly reduced.
- ✓ $[H_2O]$ is inversely dependent on the $\bar{X}_n$ square, as $(\bar{X}_n-1)$ is similar to $\bar{X}_n$ for large $\bar{X}_n$ values.

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Now, to obtain the large X n value, the previous equation number 3 which applies similarly to AB type of a polymerization. This shows that the concentration of water must be significantly reduced. Now, the concentration of water is inversely dependent on bar Xn square as bar Xn minus 1 is a similar to bar Xn for a larger Xn values. Now, this particular approach is quite useful and for the determination for the explanation of various values of K.

Now, it is also found that with increasing K the initial reactant concentration a particular degree of water concentration that must be reduced to accomplish a certain degree of polymerization. This is sometimes also being having the increasing trend. Now, the previous this particular table represents the calculation of what concentration of water values for chosen value of K and X n at an initial concentration of 5 molar.

Now, here you see that the K values Xn and concentration of water in moles per liter (()) (21:05) the different values.

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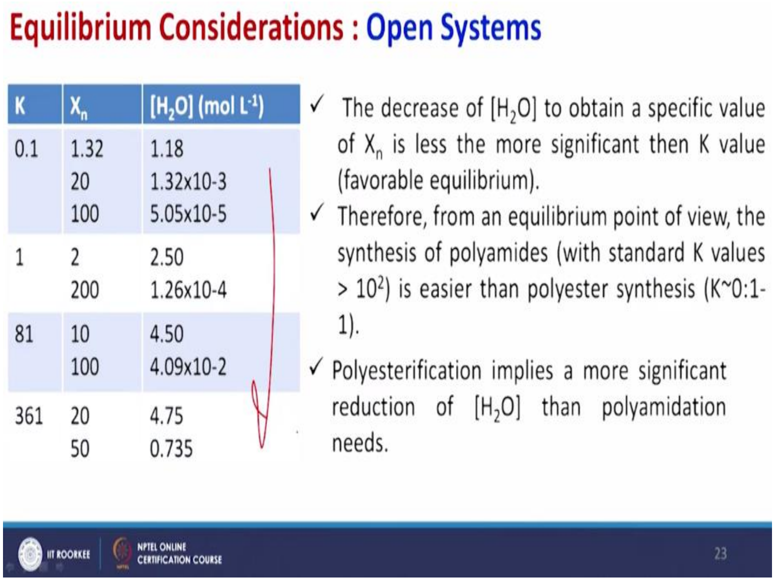

Equilibrium Considerations : Open Systems

K	X_n	$[H_2O]$ (mol L^{-1})
0.1	1.32 20 100	1.18 1.32x10-3 5.05x10-5
1	2 200	2.50 1.26x10-4
81	10 100	4.50 4.09x10-2
361	20 50	4.75 0.735

- ✓ The decrease of $[H_2O]$ to obtain a specific value of X_n is less the more significant then K value (favorable equilibrium).
- ✓ Therefore, from an equilibrium point of view, the synthesis of polyamides (with standard K values $> 10^2$) is easier than polyester synthesis (K~0:1-1).
- ✓ Polyesterification implies a more significant reduction of $[H_2O]$ than polyamidation needs.

Now, the decrease of the concentration of water to obtain a specific value of Xn is less the more significant than K values. That is a favorable equilibrium. Therefore, from an equilibrium point of view the synthesis of polyamides with the standard rate constant values greater than 10 10 to the power 2 is easier than polyester synthesis. That is somewhere around 0.1 to 1.

Polyesterification this implies a more significant reduction of H_2O than polyamidation needed.

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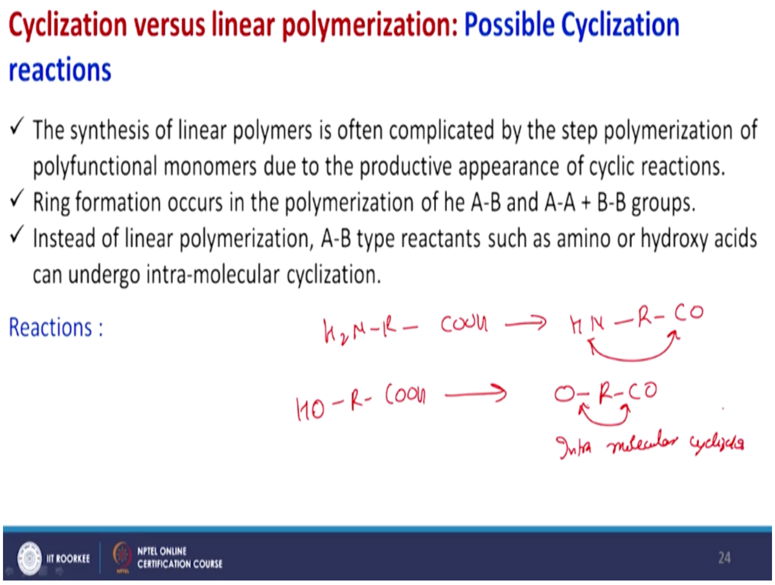

Cyclization versus linear polymerization: Possible Cyclization reactions

- ✓ The synthesis of linear polymers is often complicated by the step polymerization of polyfunctional monomers due to the productive appearance of cyclic reactions.
- ✓ Ring formation occurs in the polymerization of he A-B and A-A + B-B groups.
- ✓ Instead of linear polymerization, A-B type reactants such as amino or hydroxy acids can undergo intra-molecular cyclization.

Reactions :

$H_2N-R-COOH \longrightarrow HN-R-CO$

$HO-R-COOH \longrightarrow O-R-CO$

Intra molecular cyclization

Now, let us talk about the cyclization versus linear polymerization. And first thing is that the possible cyclization. Now, the synthesis of linear polymer it is all often complicated by the step polymerization of a polyfunctional monomer. That is due to the productive appearance of cyclic reactions. Now, the ring formation occurs in the polymerization of the A B and A A or B B groups.

So, instead of linear polymerization A B type reactions or reactants such as amino or hydroxy they can undergo the intramolecular cyclization. Let us have an example. That is H 2N R COOH and this HN R CO. Similarly, HO R COOH O R CO. That is the intramolecular cyclization.

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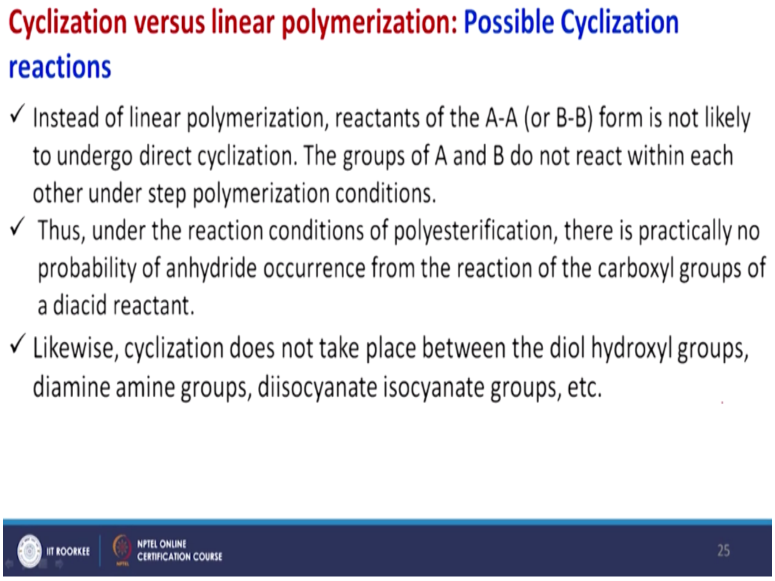

Cyclization versus linear polymerization: Possible Cyclization reactions

- ✓ Instead of linear polymerization, reactants of the A-A (or B-B) form is not likely to undergo direct cyclization. The groups of A and B do not react within each other under step polymerization conditions.
- ✓ Thus, under the reaction conditions of polyesterification, there is practically no probability of anhydride occurrence from the reaction of the carboxyl groups of a diacid reactant.
- ✓ Likewise, cyclization does not take place between the diol hydroxyl groups, diamine amine groups, diisocyanate isocyanate groups, etc.

Now, instead of linear polymerization, reactants of A A or sometimes B B they form is not likely to undergo the direct cyclization. The groups of A and B do not react within each and other and they undergo the step polymerization conditions. Therefore, under the reaction conditions of polyesterification, there is practically no probability of anhydride occurrence from the reaction of carboxyl group of a diacid reactant.

Likewise, cyclization sometimes does not take place between the diol hydroxyl group, diamine amine groups, or diisocyanate isocyanate groups, etcetera. Now, when the linear polymerization has achieved the dimer level, the intramolecular cyclization is a probability across A B.

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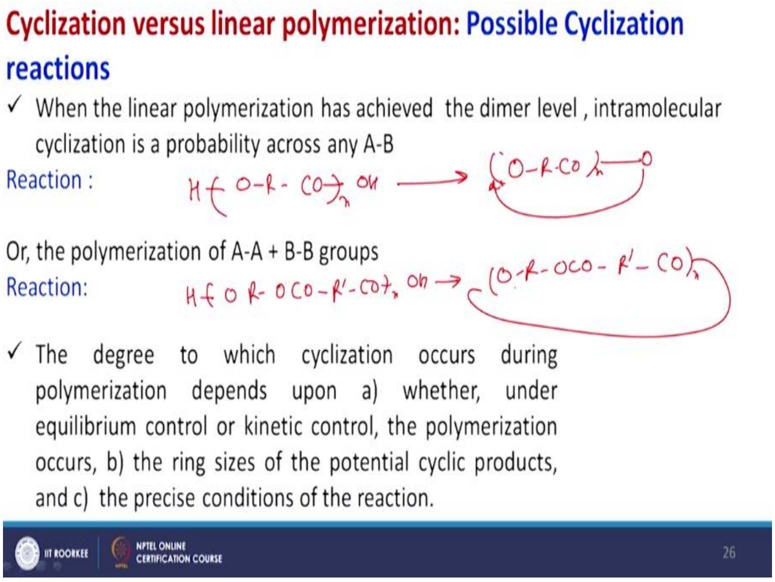

Cyclization versus linear polymerization: Possible Cyclization reactions

- ✓ When the linear polymerization has achieved the dimer level , intramolecular cyclization is a probability across any A-B

Reaction : $H(O-R-CO)_n OH \longrightarrow (O-R-CO)_n-O$

Or, the polymerization of A-A + B-B groups

Reaction: $H(O\,R-OCO-R'-CO)_n OH \rightarrow (O-R-OCO-R'-CO)_n$

- ✓ The degree to which cyclization occurs during polymerization depends upon a) whether, under equilibrium control or kinetic control, the polymerization occurs, b) the ring sizes of the potential cyclic products, and c) the precise conditions of the reaction.

So, when we talk about the intramolecular cyclization, let us give one reaction that is H O R CO n OH. And that means that gives the O R CO O and this moves over here. Now, on polymerization of say A A and B B or plus B B type of groups that can be represented as H O R OCO R dash CO O R OCO R dash CO. Now, this is, now, here this cyclization took place.

Now, the degree to which the cyclization occurs during the polymerization it depends on whether under equilibrium control of or kinetic control the polymerization occurs or the ring size of the potential cyclic products and that also depends on the precise condition of the reaction. Now, let us give a comparative note with the cyclization versus linear polymerization under the head of cyclization tendency versus the ring size.

Now, the cyclization is a comparable with the linear polymerization for a specific reactant or combination of reactants that depends on the thermodynamic and kinetic control of the size of the ring arrangement and that may occur. Sometimes that may occur. So, selection of sources provides an understanding of the relative ease of cyclization or linear polymerization. Now, let us discuss in 2 aspect.

One is that the thermodynamic stability of various size ring arrangement. Second is the heats of combustion of cyclic compounds. Now, the increasing the strain in the ring arrangement the thermodynamic stability decreases as calculated sometimes by the difference in the combination or the combustion heats per methylene group of the cycloalkene or and normal alkane.

Now, for 3 and 4 membered rings the strain in cyclic structure is very high. Reduced to 5-, 6- or 7-member ring significantly and sometimes it increases for 8 to 13 membered ring and decreases again for the larger rings. So, there are 2 kinds of strain in the ring structure. One is the angle strain and second is the conformational strain. Now, due to the high degree of angle pressure the ring structure of less than 5 atoms are highly impacted.

For ring larger than 5 atoms, the pressure will be extreme for planar ring owing the bond angle distortion. Now, in 5- or 6-member ring the strain occurs due to the variation in conformation strain. Now, let us talk about that in case of 6-member ring the torsional pressure occurs from eclipsed conformation on neighboring atom of the ring. Now, when we talk about the 8 or more-member ring, the transannular strain occurs due to the repulsive relation between the hydrogen and other groups that are compared to (()) (28:03) position within the ring structure.

So, therefore when we talk about the thermodynamic stability of various size of ring that is given by 3, 4 usually less than less than 5, then 7 to 13 is less than less than 6 and 14 and larger. Now, let us talk about the kinetic feasibility. So, usually the kinetic feasibility is essential in determining the competitiveness of the cyclization relative to linear polymerization.

The kinetic feasibility of cyclization reaction depends on the possibility that the reactant molecules functional end group will encounter one another. Now, as the probability of 2 functional groups reaching each other decreases the possibility of ring formation declines. The impact is usually expressed in an increasingly unfavourable activation entropy. Therefore, with increasing ring size, the kinetic factor becomes less favourable.

Now, when we talk about the reaction conditions the cyclization is a unimolecular referred as a intramolecular reaction whereas the linear polymerization is bimolecular or referred as intermolecular reaction. High monomer concentration usually supports the linear polymerization. So, when we talk about the ratio of cyclization to the linear polymerization varies inversely.

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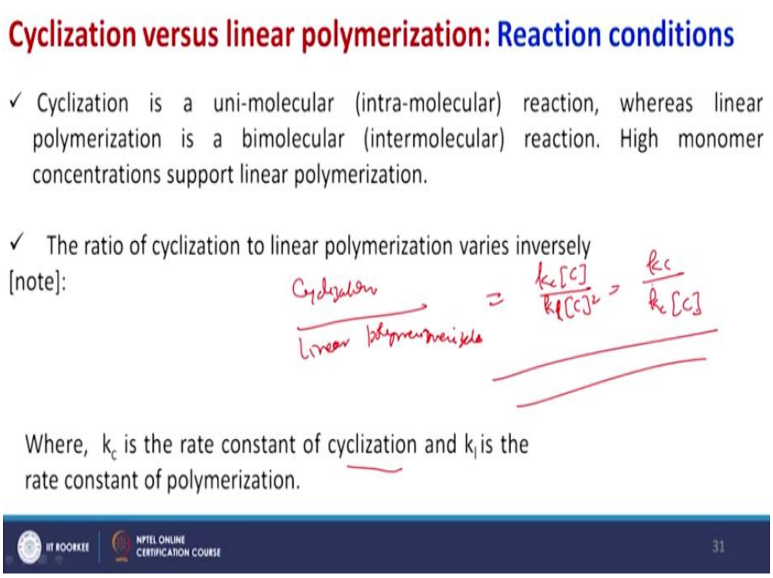

Cyclization versus linear polymerization: Reaction conditions

- ✓ Cyclization is a uni-molecular (intra-molecular) reaction, whereas linear polymerization is a bimolecular (intermolecular) reaction. High monomer concentrations support linear polymerization.
- ✓ The ratio of cyclization to linear polymerization varies inversely [note]:

$$\frac{\text{Cyclization}}{\text{Linear polymerization}} = \frac{k_c[C]}{k_l[C]^2} = \frac{k_c}{k_c[C]}$$

Where, k_c is the rate constant of cyclization and k_l is the rate constant of polymerization.

And that case, the cyclization upon linear polymerization. That is k c upon C kc C. That is the rate constant upon C. That is kc upon kc. So, this is where kc is the rate constant for the cyclization and kl is this kl is the rate constant for the polymerization.

$$\frac{Cyclization}{Linear\ polymerization} = \frac{k_c[C]}{k_P[C]^2} = \frac{k_c}{k_P[C]}$$

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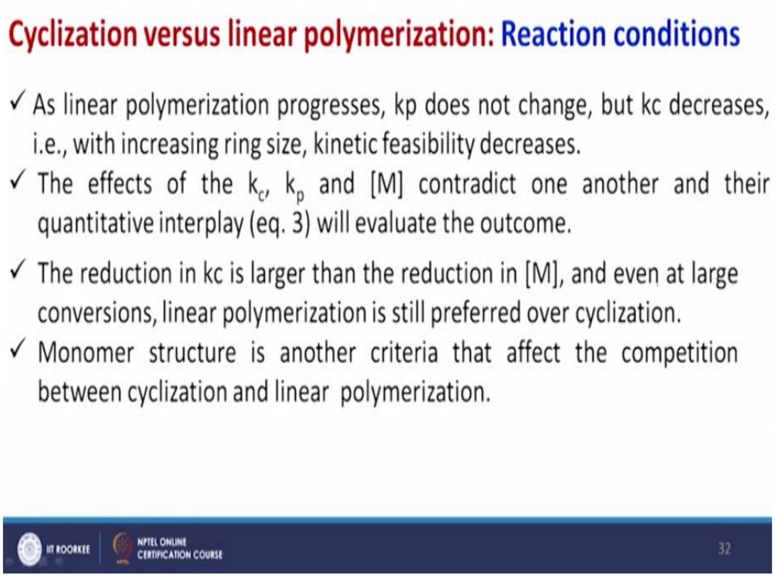

Cyclization versus linear polymerization: Reaction conditions

- ✓ As linear polymerization progresses, kp does not change, but kc decreases, i.e., with increasing ring size, kinetic feasibility decreases.
- ✓ The effects of the k_c, k_p and [M] contradict one another and their quantitative interplay (eq. 3) will evaluate the outcome.
- ✓ The reduction in kc is larger than the reduction in [M], and even at large conversions, linear polymerization is still preferred over cyclization.
- ✓ Monomer structure is another criteria that affect the competition between cyclization and linear polymerization.

Now, as a linear polymerization progresses the kp does not change. But kc increases that is with increasing ring size, the kinetic feasibility decreases. So, the effect of this kc, kp and the concentration of M this contradict one another and the quantitative interplay. This will evaluate the outcome. The reduction in kc is larger than the reduction in the concentration of monomer.

And even at large conversion the linear polymerization is still preferred over cyclization. Now, monomer structure is another criterion that affect the competition between the cyclization and linear polymerization.

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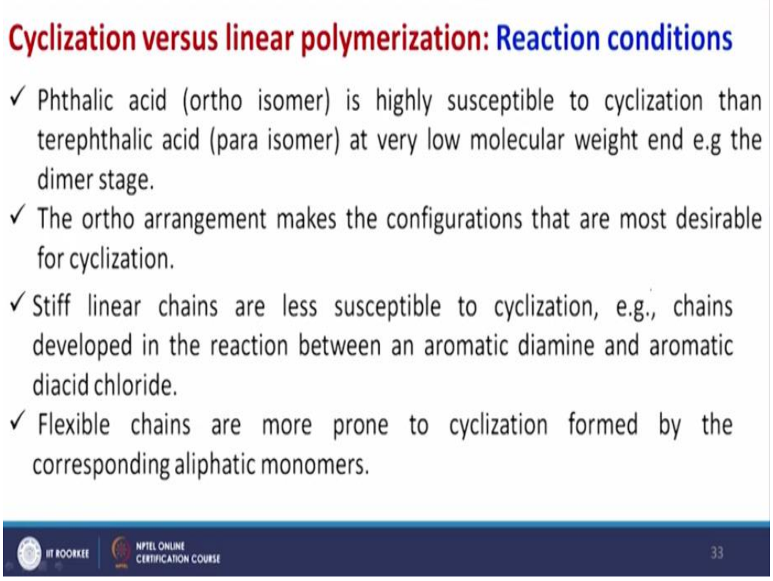

Cyclization versus linear polymerization: Reaction conditions

- ✓ Phthalic acid (ortho isomer) is highly susceptible to cyclization than terephthalic acid (para isomer) at very low molecular weight end e.g the dimer stage.
- ✓ The ortho arrangement makes the configurations that are most desirable for cyclization.
- ✓ Stiff linear chains are less susceptible to cyclization, e.g., chains developed in the reaction between an aromatic diamine and aromatic diacid chloride.
- ✓ Flexible chains are more prone to cyclization formed by the corresponding aliphatic monomers.

Now, again under the head of a reaction conditions, the phthalic acid that is ortho isomer is highly susceptible to cyclization than the terephthalic acid usually referred as a para isomer at a very low molecular weight. And that is the dimer stage. The ortho arrangement makes the configuration that are most desirable for the cyclization. Sometimes the stiff linear chains they are less susceptible to cyclization.

That is the chains developed in the reaction between an aromatic diamine and aromatic diacid chloride. The flexible chains are more prone to cyclization formed by the corresponding aliphatic monomer. Now, when we talk about the thermodynamic versus kinetic control, the polymerization through the thermodynamic control progress with an equilibrium among the cyclic and linear product.

The polymerization through kinetic control sometimes progresses without an equilibrium among cyclic and linear products. So, in any kind of a reaction system where the small molecular by-product does not react with the interconnections in the cyclic or a linear product, the kinetic control rather than thermodynamic control does exist. Thermodynamic control usually conducts the polyesterification among diacid and diol whereas the polyesterification among diacyl chloride and diol proceeds with the kinetic control.

Now, at last in this particular chapter we discussed about the concept of cyclization and we gave the comparative note of this cyclization versus linear polymerization under the various aspects like thermodynamic versus kinetic control, the reaction conditions etcetera.

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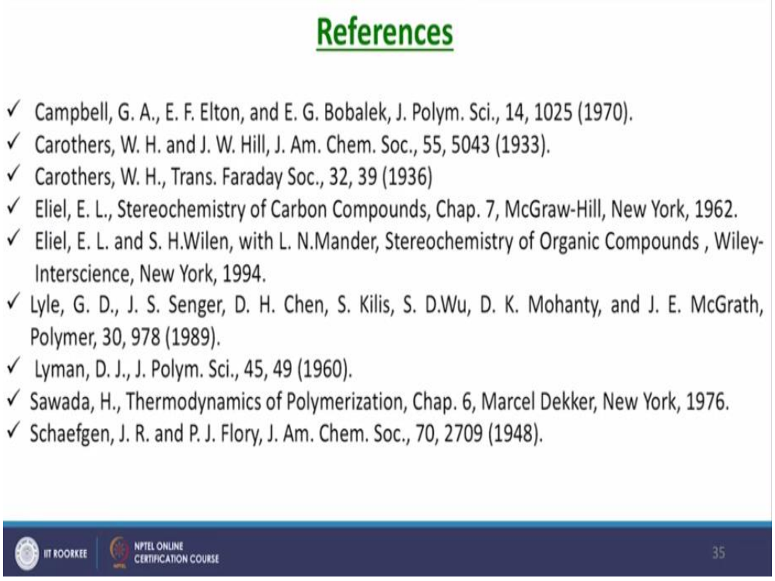

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For your convenience, we have listed a large number of references for further studies if you wish to carry on. Now, with this concept note, thank you very much.

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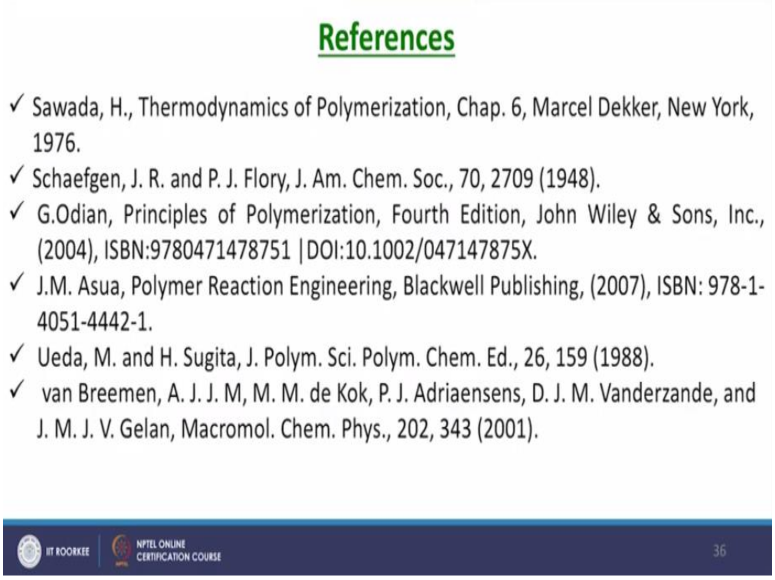

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