Introduction to Polymer Science
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Lecture - 08
Linear Step Polymerization: Kinetics (Contd.), Equilibrium Consideration, General Requirements for Achieving High MW, Non-linear Step Polymerization

Welcome back. In this lecture 8, we will continue our discussion on linear step polymerization.

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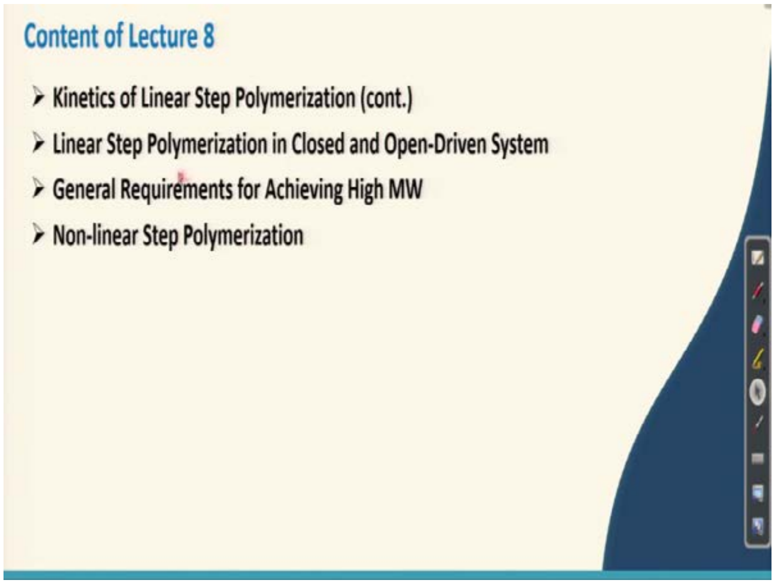

Content of Lecture 8

- Kinetics of Linear Step Polymerization (cont.)
- Linear Step Polymerization in Closed and Open-Driven System
- General Requirements for Achieving High MW
- Non-linear Step Polymerization

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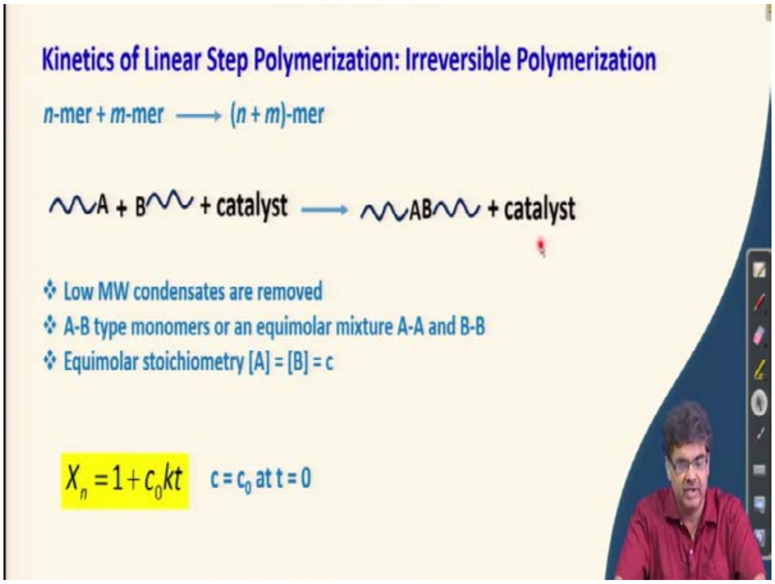

Kinetics of Linear Step Polymerization: Irreversible Polymerization

n-mer + m-mer $\longrightarrow$ $(n+m)$-mer

∿∿A + B∿∿ + catalyst $\longrightarrow$ ∿∿AB∿∿ + catalyst

- Low MW condensates are removed
- A-B type monomers or an equimolar mixture A-A and B-B
- Equimolar stoichiometry [A] = [B] = c

$X_n = 1 + c_0kt$ $\quad c = c_0$ at t = 0

In the last lecture, we discussed the kinetics of linear step polymerization in presence of external catalysts. We mentioned that irreversible polymerization means that in these reactions, low molecular condensates are removed completely out of the system. For the simplest case, we considered AB-type monomer or an equimolar mixture of AA and BB, so that the concentration of A is equal to concentration of B. We found that degree of polymerization was equal to $1 + C_0kt$, where k is the rate constant and C_0 is the concentration of functional groups at time zero.

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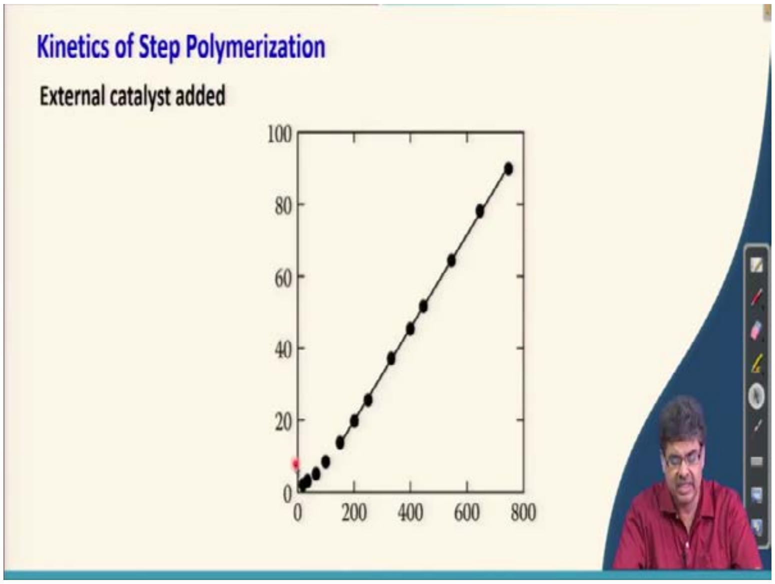

Kinetics of Step Polymerization

External catalyst added

In the plot between X_n^2 and time (minute), the result of the experiment was verifying, matching the expected data quite nicely except for the very low conversion region or low degree of polymerization region after that it matched very well.

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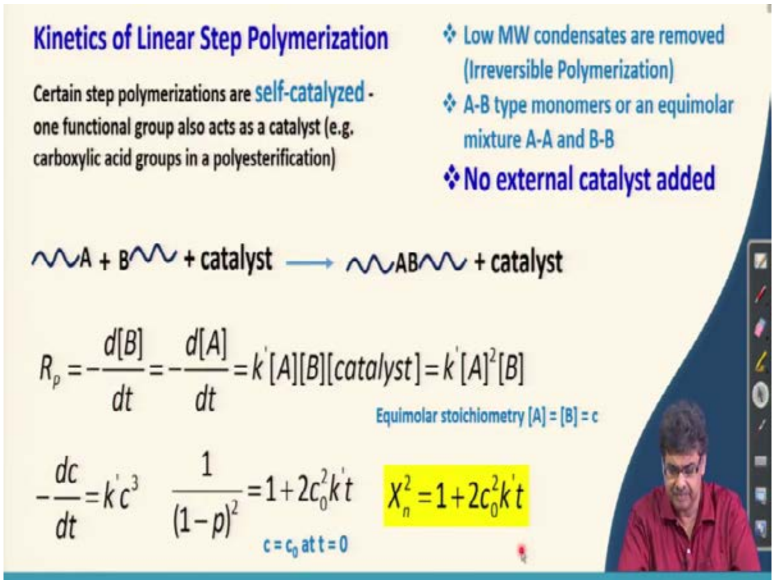

Kinetics of Linear Step Polymerization

Certain step polymerizations are self-catalyzed - one functional group also acts as a catalyst (e.g. carboxylic acid groups in a polyesterification)

- ❖ Low MW condensates are removed (Irreversible Polymerization)
- ❖ A-B type monomers or an equimolar mixture A-A and B-B
- ❖ **No external catalyst added**

$$\sim\sim A + B\sim\sim + \text{catalyst} \longrightarrow \sim\sim AB\sim\sim + \text{catalyst}$$

$$R_p = -\frac{d[B]}{dt} = -\frac{d[A]}{dt} = k'[A][B][catalyst] = k'[A]^2[B]$$

Equimolar stoichiometry [A] = [B] = c

$$-\frac{dc}{dt} = k'c^3 \qquad \frac{1}{(1-p)^2} = 1 + 2c_0^2k't \qquad \boxed{X_n^2 = 1 + 2c_0^2k't}$$

$c = c_0$ at $t = 0$

Now, there could be another possibility where we will consider a case when no external catalysts are added. Some of the functional groups present can act as a catalyst by themselves. So, we call these reactions as self catalyzed reactions. We are also considering that no low molecular condensates are present in the reaction with the mixture and the molar ratio of two functional groups is 1: 1 and no external catalyst is added from outside.

So in that case rate of polymerization is the rate of disappearance of the functional groups which is given by a rate constant, concentration of the functional groups, and concentration of catalyst. In this case, one of the functional groups, let us say A group, is behaving as a self catalyst. So, instead of catalysts concentration, we can put concentration of A group. So, R_p = k'$[A]^2$[B], and considering that [A] = [B] = C

We can get this expression like this,

$$-\frac{dc}{dt} = k'C^3$$

By integration, and considering that C is C_0 at t = 0, we get this expression.

$$X_n^2 = 1 + 2C_0^2k't$$

This k' is a separate rate constant from the 'k' we used for the previous case where external catalyst was added from outside.

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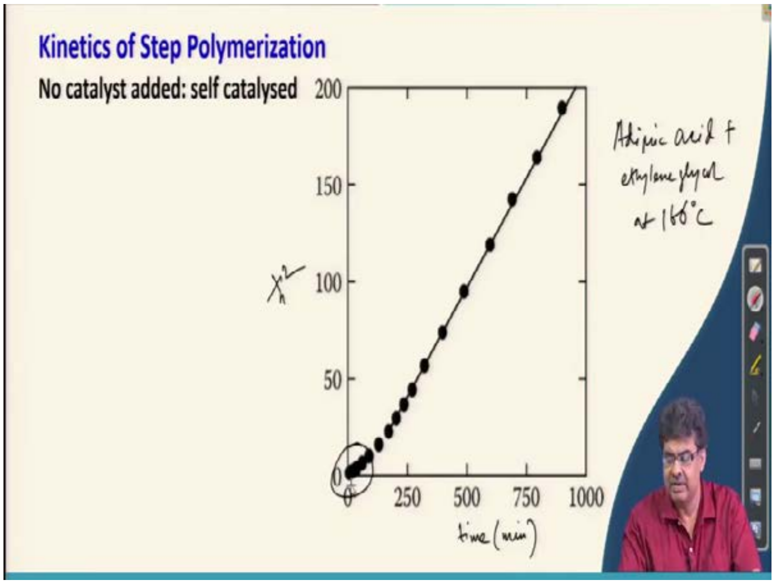

Kinetics of Step Polymerization

No catalyst added: self catalysed

This is experimental data for adipic acid and ethylene glycol at 166 ^{o}C. Now, in this case, we can see that the experimental data match quite well with the expected result except for the initial part where the number average degree of polymerization is quite low. This means that the assumptions we made that the reactivity of functional groups is independent of the size of the chain and the functional group present at the which end, are quite valid, except in the very initial stage where we have few monomers which got attached, the degree of polymerization is quite low. So our assumption of equal activity of function group is also quite valid.

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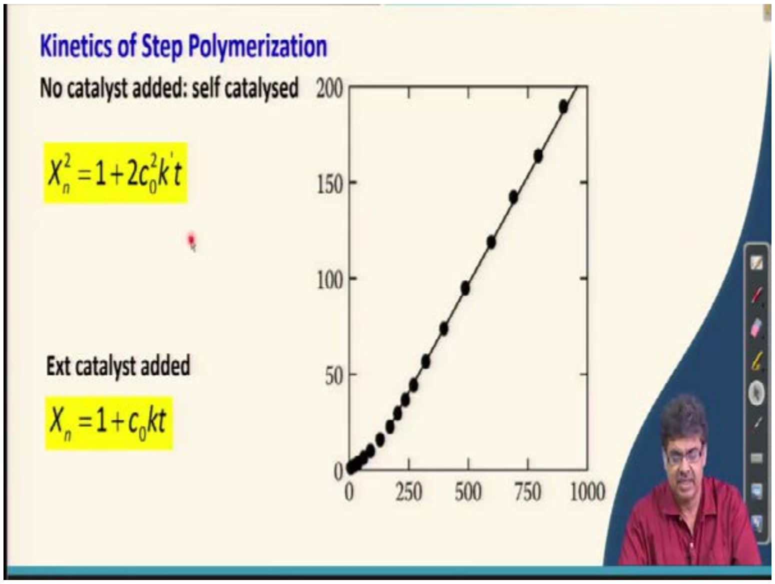

Kinetics of Step Polymerization

No catalyst added: self catalysed

$X_n^2 = 1 + 2c_0^2 k' t$

Ext catalyst added

$X_n = 1 + c_0 k t$

Now if we compare the results from the external catalyst reaction with self catalyzed reaction. For external catalyst reaction, we had the expression X_n=1+C_0kt. For example, if we increase the time of reaction by 4 times, in the self catalyzed reaction, Xn^2 increases approximately 4 times. The degree of polymerization increases by 2 times. Whereas, external catalyst reaction, if we increase the reaction time by 4, the degree of polymerization also increases by 4. So, to increase same extent of degree of polymerization, we need to run the reaction much longer time in the case of self catalyzed reaction. The conclusion is that we always prefer external catalyst reactions because this is a much faster reaction compared to the self catalyzed reaction.

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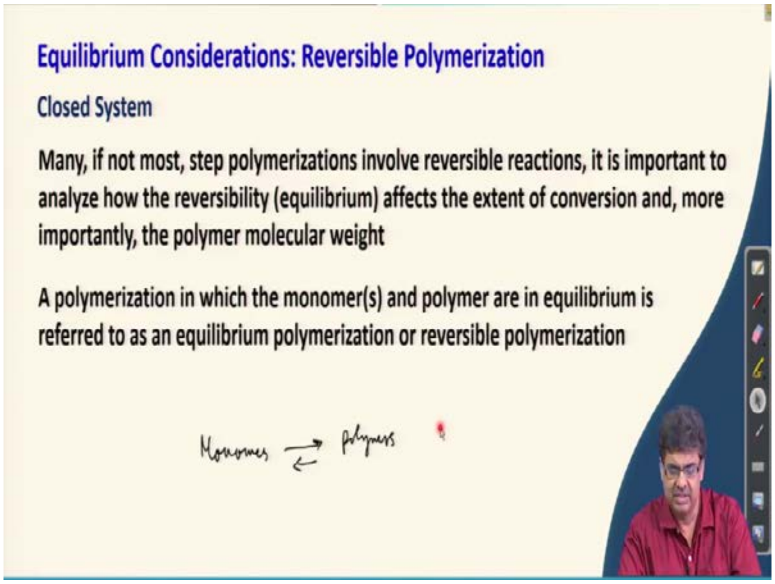

Equilibrium Considerations: Reversible Polymerization

Closed System

Many, if not most, step polymerizations involve reversible reactions, it is important to analyze how the reversibility (equilibrium) affects the extent of conversion and, more importantly, the polymer molecular weight

A polymerization in which the monomer(s) and polymer are in equilibrium is referred to as an equilibrium polymerization or reversible polymerization

Monomers ⇌ Polymers

In the last kinetics, we considered that it was an irreversible polymerization. No small molecular condensate like water or methanol which comes out during the reaction are present in the reaction mixture. So we did not consider the backward reaction at all. But in practice, it is impossible to take out everything from the reaction mixture, because of lot of engineering issues. In the case of step polymerization, we cannot remove the condensate completely, so there is always a possibility of backward reactions happening. We will consider them now and see how the presence of small molecular condensates in the reaction mixture affects the molecular weight or degree of polymerization of the resulting polymer.

Let us consider that the reaction is performed in a closed system, no condensate is taken out of the system. In this case we have reversible polymerization which means there is a possibility of monomer to polymer formation and polymer to monomer formation. And as it is in a closed system, the monomers and polymers are in equilibrium, the reaction is referred to as equilibrium polymerization or reversible polymerization.

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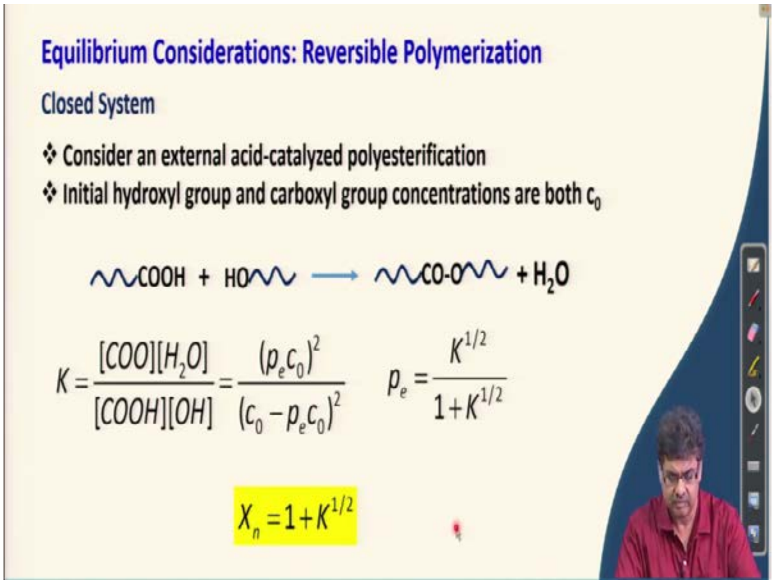

Equilibrium Considerations: Reversible Polymerization

Closed System

- Consider an external acid-catalyzed polyesterification
- Initial hydroxyl group and carboxyl group concentrations are both c_0

$$\sim\sim COOH + HO\sim\sim \longrightarrow \sim\sim CO\text{-}O\sim\sim + H_2O$$

$$K = \frac{[COO][H_2O]}{[COOH][OH]} = \frac{(p_e c_0)^2}{(c_0 - p_e c_0)^2} \qquad p_e = \frac{K^{1/2}}{1+K^{1/2}}$$

$$\boxed{X_n = 1 + K^{1/2}}$$

We first consider the acid-catalyzed reaction and consider that polyester is being synthesized by reacting hydroxyl group and carboxylic group, and this is the reaction between acid group and alcohol group resulting in ester and water. Now, in this case, the reaction is performed in a closed system, no water molecule is taken out of the reaction mixture. In this case, we will consider the equilibrium constant. So equilibrium constant will be given by K.

$$K = \frac{[COO][H_2O]}{[COOH][OH]}$$

Now at equilibrium, if we consider the extent of polymerization is p_e. the concentration of COOH and H_2O would be the extent of the functional group reacted multiplied by the initial concentration of the functional group. The equation can be written as,

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

By rearranging the equation, the conversion at equilibrium is given by this expression-

$$p_e = \frac{K^{1/2}}{1 + K^{1/2}}$$

where K is the equilibrium constant for this reaction

The degree of polymerization is given by $X_n = 1 + K^{1/2}$

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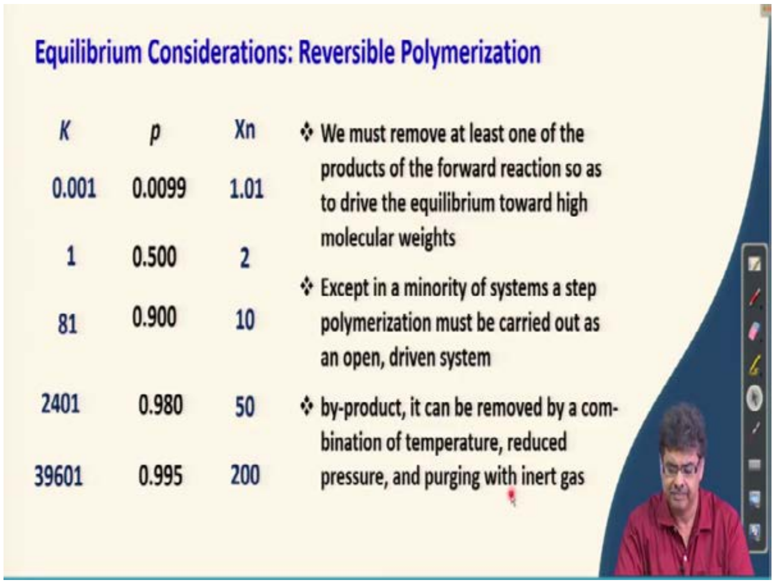

Equilibrium Considerations: Reversible Polymerization

K	p	Xn
0.001	0.0099	1.01
1	0.500	2
81	0.900	10
2401	0.980	50
39601	0.995	200

- We must remove at least one of the products of the forward reaction so as to drive the equilibrium toward high molecular weights
- Except in a minority of systems a step polymerization must be carried out as an open, driven system
- by-product, it can be removed by a combination of temperature, reduced pressure, and purging with inert gas

Now, if we consider this expression $X_n = 1 + K^{1/2}$ and plug in some numbers in the expression, we get that if *K* is very low, we almost get no polymerization. In case of *K* is 1, we get the degree of polymerization of only 2. Only half of the functional groups are reacted in equilibrium. As we increase the value of the equilibrium constant, we get a higher conversion and higher degree of polymerization.

But in most cases, step-growth polymerization is not having a high *K* value. They are in the range between say 1 to 81. Hence, if the reaction is done in equilibrium condition without taking the small molecular condensate out, high molecular weight polymer can not be synthesized. In this case, we must remove at least one of the products of the forward reactions, so that the equilibrium is driven towards high molecular weight. Most cases it is very difficult to remove the polymer. So, we take out the small molecular condensates. A step polymerization must be carried out as an open and driven system, open and driven means we drive out one of the products of polymerization. By-products can be removed by a combination of temperature, reduced pressure, or by purging inert gas.

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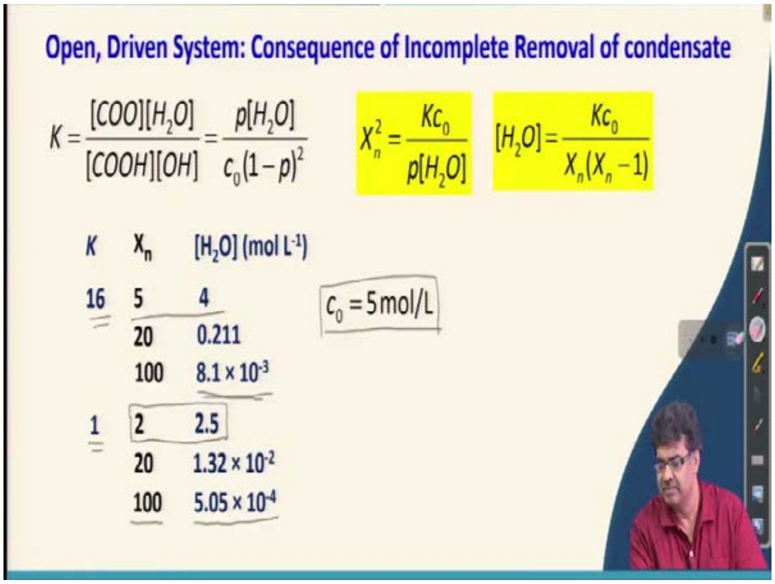

Open, Driven System: Consequence of Incomplete Removal of condensate

$$K = \frac{[COO][H_2O]}{[COOH][OH]} = \frac{p[H_2O]}{c_0(1-p)^2}$$

$$X_n^2 = \frac{Kc_0}{p[H_2O]}$$

$$[H_2O] = \frac{Kc_0}{X_n(X_n-1)}$$

K	X_n	$[H_2O]$ (mol L^{-1})
16	5	4
	20	0.211
	100	8.1×10^{-3}
1	2	2.5
	20	1.32×10^{-2}
	100	5.05×10^{-4}

$c_0 = 5$ mol/L

What is the consequence of open driven system? What is the consequence of incomplete removal of the small molecular condensate, H_2O for example in this case. In this case, we have the *K* value as,

$$K = \frac{[COO][H_2O]}{[COOH][OH]} = \frac{p[H_2O]}{C_0(1-p)^2}$$

$$X_n^2 = \frac{KC_0}{p[H_2O]}$$

$$[H_2O] = \frac{KC_0}{X_n(X_n-1)}$$

For a given *K* if we increase the amount of H_2O remaining in the medium, the degree of polymerization will come down. We should try to remove the small molecular condensates to the maximum possible extent to increase the molecular weight of the polymer. Let us see the consequences of this remaining H_2O in the system. If the *K* value is 1, then if we do the reaction in a closed system the degree of polymerization will be 2. and the concentration of H_2O remaining is 2.5 mol L^{-1}. We have considered, in this case, the initial concentration of functional groups are 5.0 mol L^{-1}. To build a polymer having X_n of 100, we need to reduce the water concentration in the reaction medium to 5.05×10^{-4} mol/L, which is quite low. So unless the H_2O concentration can be reduced to this level, we cannot build a degree of polymerization of 100 when the K value is 1.

If we increase the K value to 16 then we can afford to keep a little higher amount of H_2O. In this case the affordable concentration of H_2O is 8.1×10^{-3} mol/L.

This table shows that if the *K* value of the reaction is higher, then it will be affordable to keep a higher amount of H_2O in the reaction mixture to build a high molecular weight. That means, the evacuating system should be very good so that we can apply a high vacuum. Additionally, we have to do the reaction at quite a high temperature so that we can effectively remove the water or other condensates from the reaction mixture. We realize from this table and equations that if we want to make high molecular weight polymers in step polymerization, we have 2 options. We need to reduce the value of the small condensate in the reaction mixture and/or we have to choose a reaction that has a very high K value.

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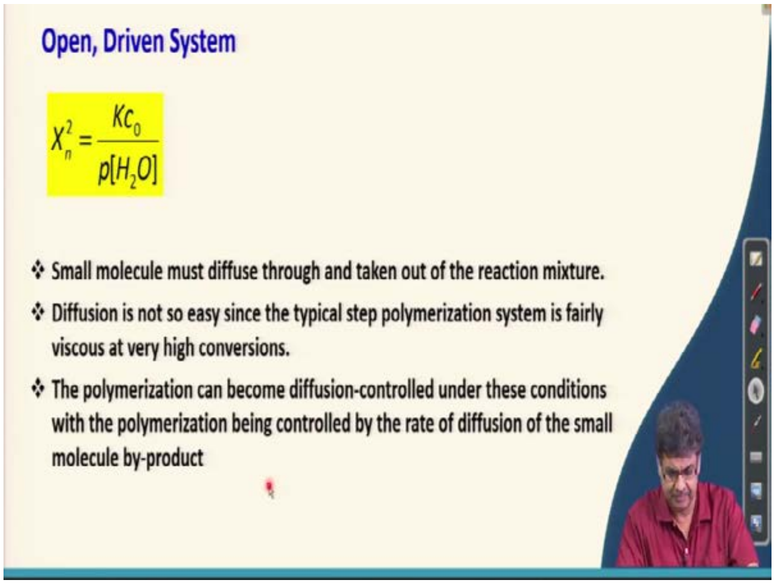

Open, Driven System

$$X_n^2 = \frac{Kc_0}{p[H_2O]}$$

- Small molecule must diffuse through and taken out of the reaction mixture.
- Diffusion is not so easy since the typical step polymerization system is fairly viscous at very high conversions.
- The polymerization can become diffusion-controlled under these conditions with the polymerization being controlled by the rate of diffusion of the small molecule by-product

So the small molecule condensates must be taken out. In this case, say water, for polyesterification reactions, are produced in the bulk. We cannot take the H_2O which is produced in the bulk directly to the vapor phase. H_2O molecules need to diffuse through to the surface, and from the surface, it can be removed. If the viscosity of the polymerization medium is very high, which may happen if the polymer molecular weight is quite high then, no matter what is the suction capability or the low pressure we apply, it is not possible to take out the water molecule or other small molecular condensate. It is limited by the diffusivity of the molecules through the high molecular weight polymer melt or polymer mixture present. At this point, the polymerization can become diffusion-controlled under these conditions and the polymerization rate or the molecular weight can be controlled by the rate of diffusion of the small by-products.

Engineers will try to build reactor with different designs with different stirring mechanism, because if stirring can be done properly then it can generate lots of new surfaces during the reaction so that the condensate can be taken out properly. These way, engineering aspects can be altered and maximum efforts can be made to reduce the amount of condensates in the reaction medium. But sometimes there is a limitation also. No matter how is the design of the reactor, what condition we apply, it is possible to remove the condensate to a limited extent.

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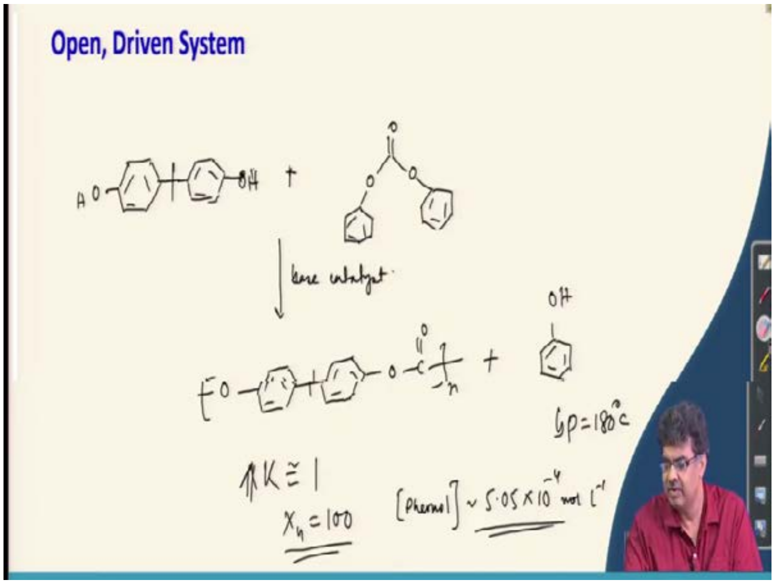
Open, Driven System

So in that case, it is the responsibility of the chemists to design monomer differently so that it can increase the *K* value. Now if the *K* value is increased, then we can afford to have a little higher value of the small condensate in the reaction medium to build the high molecular weight. Just take an example of Bisphenol A polycarbonate. Bisphenol A polycarbonate is synthesized by trans esterification reaction of Bisphenol A with diphenyl carbonate using a base catalyst. Phenol is the by-product in this case. Boiling point of phenol is 180 °C. The reaction is carried out above 180 °C so that this phenol can be taken out easily by applying vacuum. Now, the *K* of this reaction in a closed system is approximately close to 1. That means if we want to make a degree of polymerization of 100. We need to reduce the concentration of phenol to the level of 5.05×10^{-4}

mol/L. Now, as we discussed, sometimes it is not possible, no matter what is the reactor design or reaction conditions. In this case, then we need to change the chemistry. If we can change the chemistry and increase this *K* value, then probably, we will get high molecular weight polymer. How do we achieve that?

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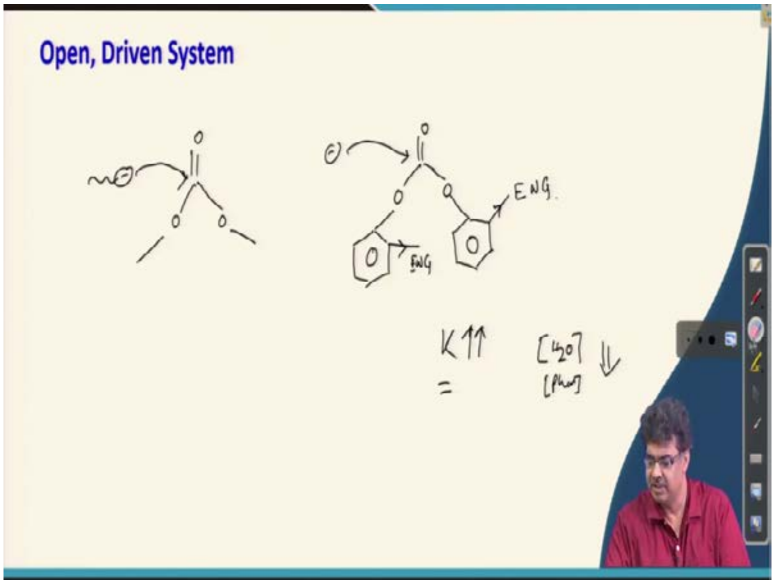

Open, Driven System

We can change the design of the monomer. The reaction occurs in presence of the base. This reaction take place by the nucleophilic attack of the phenolate. Base abstracts the H from the Bisphenol A, make it a phenolate and this does a nucleophilic attack, and the products are formed. If the tendency of the nucleophilic attack can be increased by increasing the electrophilicity of this carbon, then obviously, the K is increased. Now how to do that? The electrophilicity can be increased by adding some strong electron-withdrawing group in the ortho position. For this, the attack of the phenolate will be much easier, much more probable and as a result, the K value of this reaction increases.

This is the example of how a polymer chemist design the monomer to increase the K. Whereas the engineers change the design of the reactor or the condition of the reaction to reduce the level of condensates like water or phenol to lower level. The combination of these give a higher value of the degree of polymerization.

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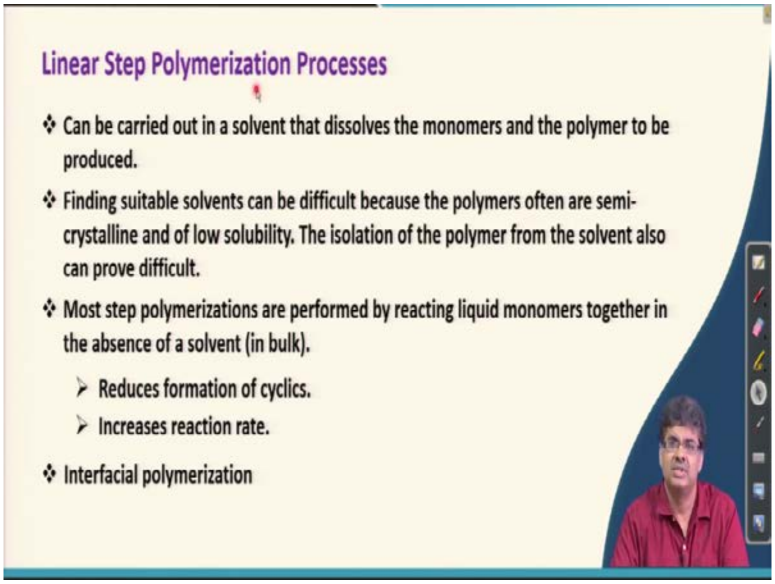

Linear Step Polymerization Processes

- Can be carried out in a solvent that dissolves the monomers and the polymer to be produced.
- Finding suitable solvents can be difficult because the polymers often are semi-crystalline and of low solubility. The isolation of the polymer from the solvent also can prove difficult.
- Most step polymerizations are performed by reacting liquid monomers together in the absence of a solvent (in bulk).
  - Reduces formation of cyclics.
  - Increases reaction rate.
- Interfacial polymerization

We know how to increase or control the molecular weight - by tweaking the stoichiometry or by adding a chain stopper. We also know the limitations of linear step-growth polymerization. The linear step polymerization is carried out in a solvent that dissolves the monomers and the polymers produced. But, it is always difficult to find a solvent that can dissolve both polymers as well as the monomers, because polymers often are semi-crystalline and have low solubility and after the reaction, the isolation of polymers from the solvent is also difficult due to involvement of some cost-prohibiting steps. So, most polymerizations are carried out by reacting the liquid monomers together in absence of solvents like in melt polymerization or bulk. This has 2 advantages, it reduces the formation of cyclics and also increases the reaction rate. Sometimes, interfacial polymerization is also employed in step polymerization to synthesize a high molecular weight polymers.

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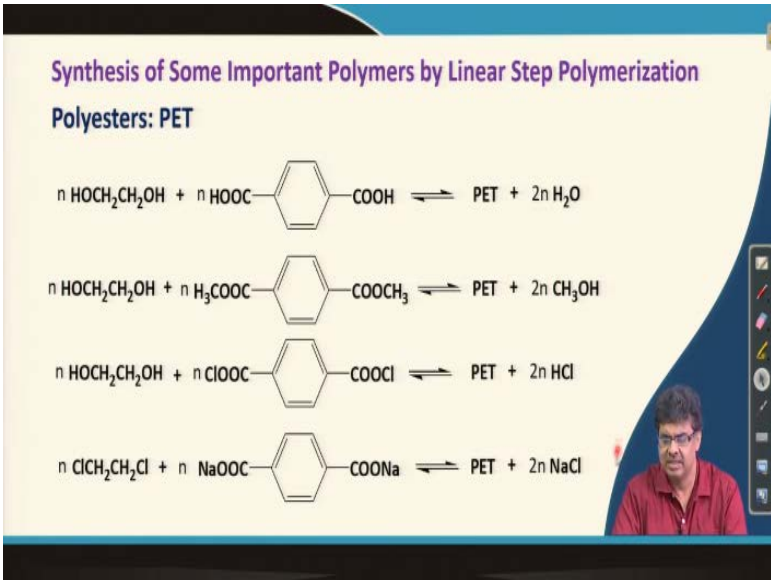

Synthesis of Some Important Polymers by Linear Step Polymerization

Polyesters: PET

n $HOCH_2CH_2OH$ + n HOOC– –COOH $\rightleftharpoons$ PET + 2n H_2O

n $HOCH_2CH_2OH$ + n H_3COOC– –$COOCH_3$ $\rightleftharpoons$ PET + 2n CH_3OH

n $HOCH_2CH_2OH$ + n ClOOC– –COOCl $\rightleftharpoons$ PET + 2n HCl

n $ClCH_2CH_2Cl$ + n NaOOC– –COONa $\rightleftharpoons$ PET + 2n NaCl

There are some examples of important polymers which are synthesized by linear step polymerization.

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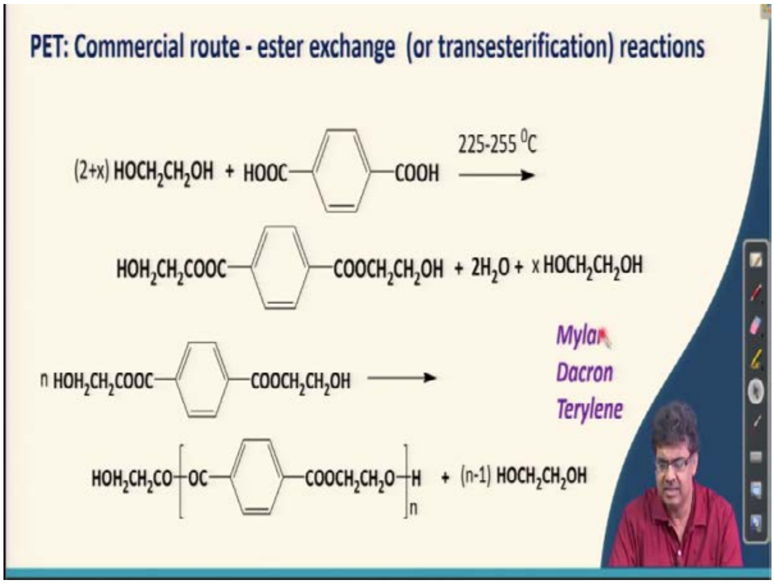

PET: Commercial route - ester exchange (or transesterification) reactions

(2+x) $HOCH_2CH_2OH$ + HOOC– –COOH $\xrightarrow{225\text{-}255\,^0C}$

HOH_2CH_2COOC– –$COOCH_2CH_2OH$ + $2H_2O$ + x $HOCH_2CH_2OH$

n HOH_2CH_2COOC– –$COOCH_2CH_2OH$ $\longrightarrow$

HOH_2CH_2CO–[OC– –$COOCH_2CH_2O$]$_n$–H + (n-1) $HOCH_2CH_2OH$

Mylar

Dacron

Terylene

This is the standard reaction, which is used for making poly(ethylene terephthalate) and this is the commercial route. The synthesis is typically done in 2 steps, in the first step, the terephthalic acid is reacted in excess of ethylene glycol, and the produced H_2O and the excess ethylene glycols are taken out of the system. In the second step, the molecules are taken at a high temperature to form the poly(ethylene terephthalate). Poly(ethylene terephthalate) is sold in the market with various trade names like Terylene, Dacron, Mylar, and so on.

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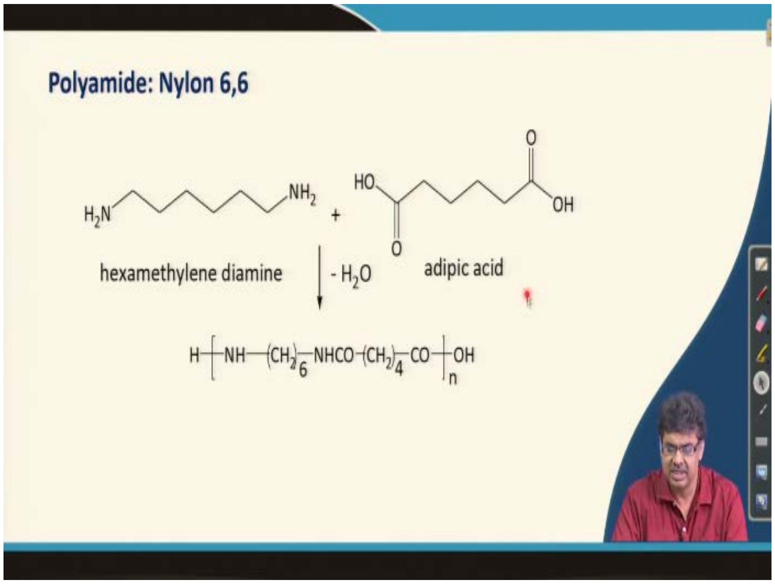

Polyamide: Nylon 6,6

$H\left[NH-(CH_2)_6-NHCO-(CH_2)_4-CO\right]_nOH$

Similarly, polyamides are known as, in this particular case, Nylon 6,6. This is the standard synthetic method of production of Nylon 6,6.

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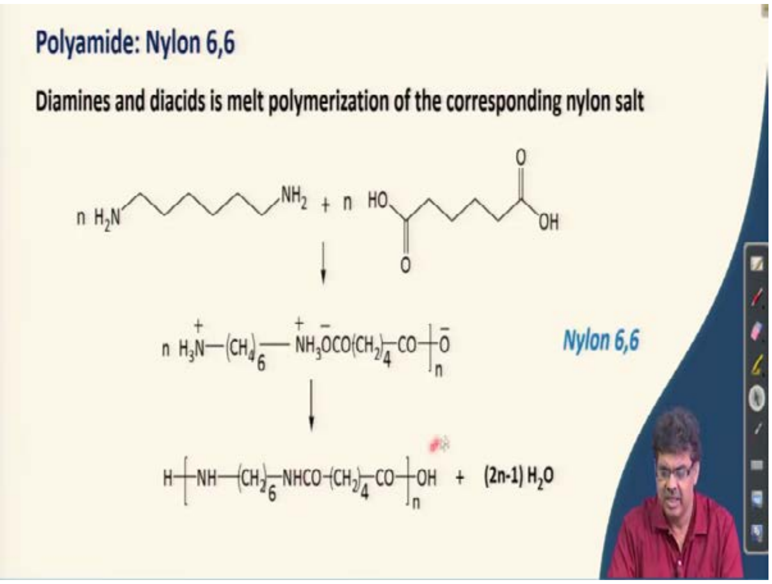

Polyamide: Nylon 6,6

Diamines and diacids is melt polymerization of the corresponding nylon salt

$n\ \overset{+}{H_3N}-(CH_2)_6-\overset{+}{N}H_3\overset{-}{O}CO(CH_2)_4-CO\left.\right]_n\overset{-}{O}$

$H\left[NH-(CH_2)_6-NHCO-(CH_2)_4-CO\right]_nOH + (2n-1)\,H_2O$

It is the commercial setup of preparation of Nylon 6,6. At the first step, in Nylon 6, 6 salts are produced which are then taken out of the system and purified, and then the second stage, these are heated at 277 °C to make Nylon 6, 6.

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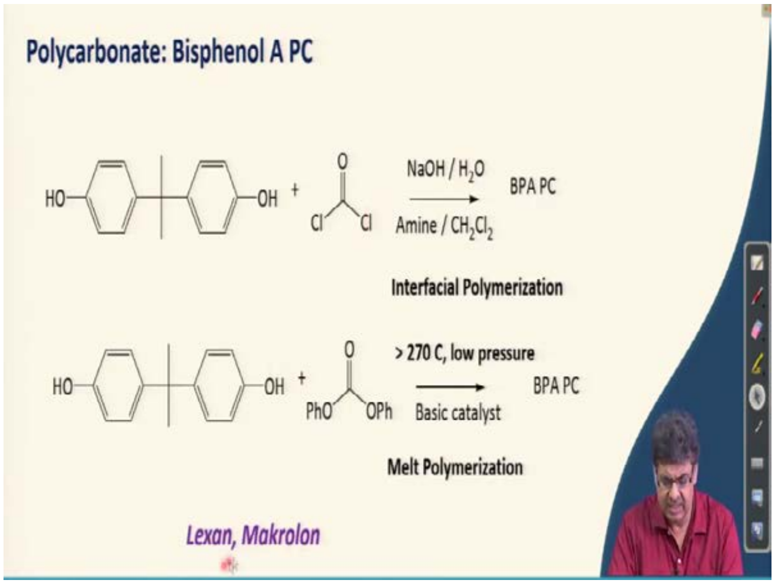

Polycarbonate: Bisphenol A PC

Lexan, Makrolon

Similarly, Bisphenol A Polycarbonate is prepared either by melt polymerization by reacting with Bisphenol A with diphenyl carbonate, or by interfacial polymerization by reacting with Bisphenol A with Phosgene. Polycarbonates are sold as trade names like Lexan, Makrolon, and so on.

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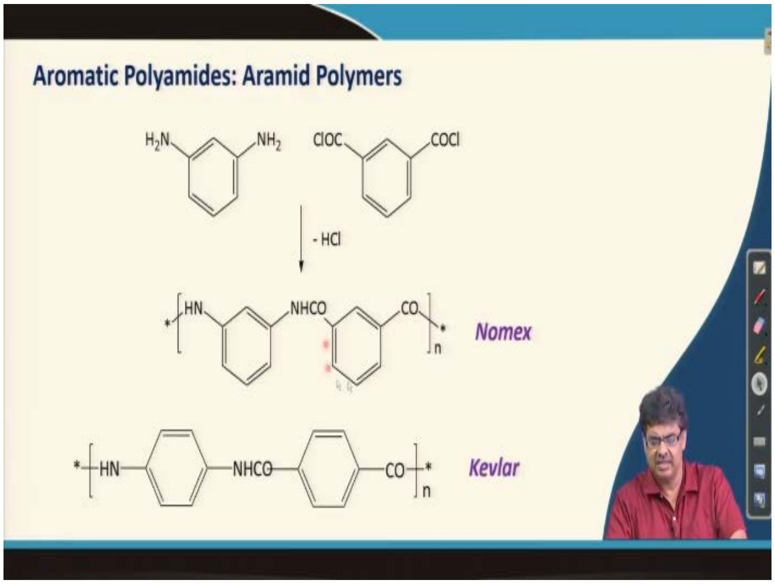

Aromatic Polyamides: Aramid Polymers

These are the processes of synthesizing aromatic polyamides named Nomex and Kevlar.

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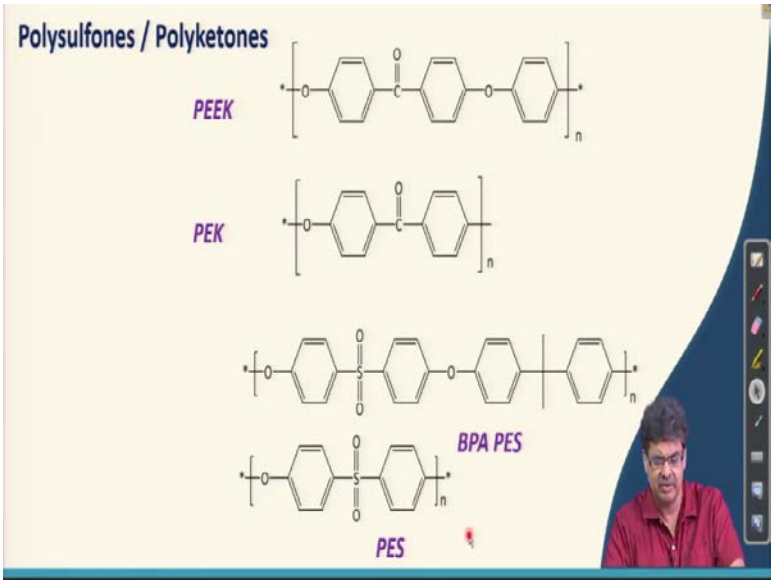

Polysulfones / Polyketones

These are some structures of polysulfones and polyketones named PEEK, PEK, BPA PES, PES, etc.

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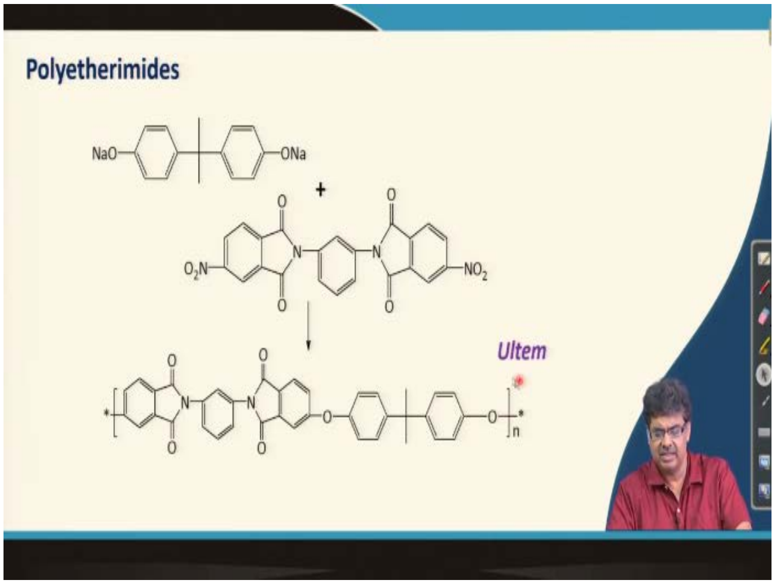

Polyetherimides

This is a polyetherimide. The structure is given and the trade name is Ultem.

So with this, we will end this lecture. In the next lecture I will start summing up the step-growth polymerization method and revise the conditions to build high molecular weight in linear step polymerization.