Polymer Reaction Engineering
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Lecture - 29
Step-Growth Polymerization-II

Welcome to the lecture of kinetics of step growth polymerization, self-catalysed polymerization and external catalysis under the head of polymer reaction engineering. Now, before we start, let us have a brief look about what topics we covered previously. We discussed about the brief outlook of step growth polymerization with the help of certain commercially important polymers.

We discussed about the basic property of step growth polymerization process under the edges of melt polymerization, solution polymerization, interfacial polymerization.

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We discussed about the emulsion polymerization and solid-state polymerization, both. Now, apart from this we discussed the reactivity of functional groups.

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Topics to be covered in this lecture

- Kinetics of step polymerization
- Self-catalyzed polymerization
  - Experimental observations
  - Reasons for nonlinearity in third-order plot
- External catalysis of polymerization

Now, in this particular chapter, we are going to discuss with the kinetics approach of step growth polymerization. Then, we will have a discussion about the self-catalysed polymerization based on the experimental observation as well as the reasons for nonlinearity in third order plot. We will have a discussion about the external catalysis of polymerization.

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Kinetics of step 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.

✓ Just as kinetics can provide insight into other reaction mechanisms, It can also provide insight into how the polymerization occurs.

✓ Let us consider the polyesterification of a diacid and a diol to illustrate general form of the kinetics of a typical step polymerization process.

Now, let us have a look about the kinetics of step polymerization. Usually, it is imperative of to understand how reactions proceed over time. Now, this information can tell us about the time it takes for a polymer to reach to an optimum length that is related to the chain of that particular polymer. Now, let us have a look about the kinetics of step polymerization. It is imperative to understand how reactions proceed over time.

Now, this information can tell us about the time it takes for a polymer to reach an optimum length so that it can acquire the appropriate property as desired by the process. Now, just as kinetics can provide insight into the other reaction mechanism. It can also provide the insight into how the polymerization occurs. Now, let us consider the polyesterification of diacid and diol to illustrate general form of the kinetics of a typical step polymerization process.

Now, it is quite simple that the esterification is a well-known acid catalysed reaction and polyesterification follows the same course. Now, the reaction involves protonation of carboxylic acid followed by the reaction of protonated species I which with alcohol to yield any kind of ester.

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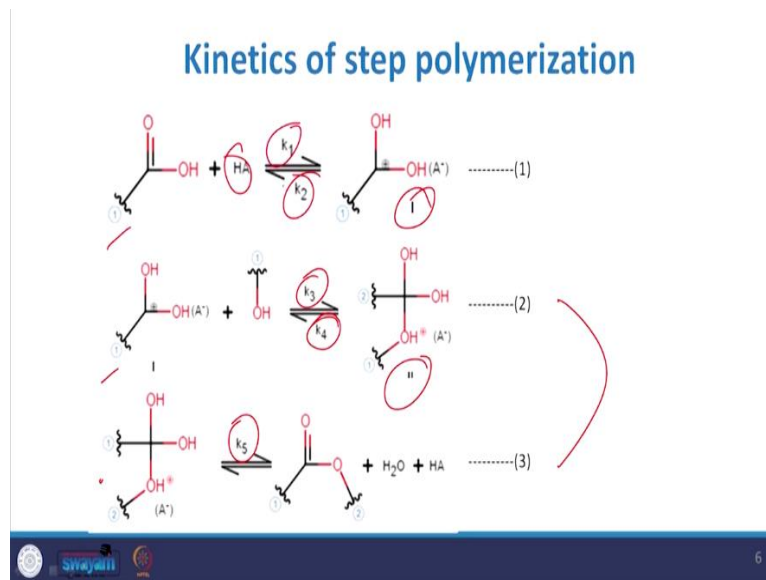
Now, you can see here that how we explain the kinetics of this step polymerization with the help of these 3 mechanisms.

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Kinetics of step polymerization

✓ 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 counterion derived from the acid HA.

✓ Polyesterification reactions are equilibrium reactions.

Now, see all acid or alcohol species like monomer, dimer or n mer in the reaction mixtures are indicated by 1 and 2 like here. You can see over here. Now, since polymerization often takes place in organic media of low polarity, species 1 and 2, they are shown in the form of this is 1 and 2, they are shown in the form of their associated ion pair. Now, A is the negative counterion derived from the acid HA.

The polyesterification reactions are equilibrium reactions and therefore, you need to address the things associated with the equilibrium criteria to have this type of a reaction.

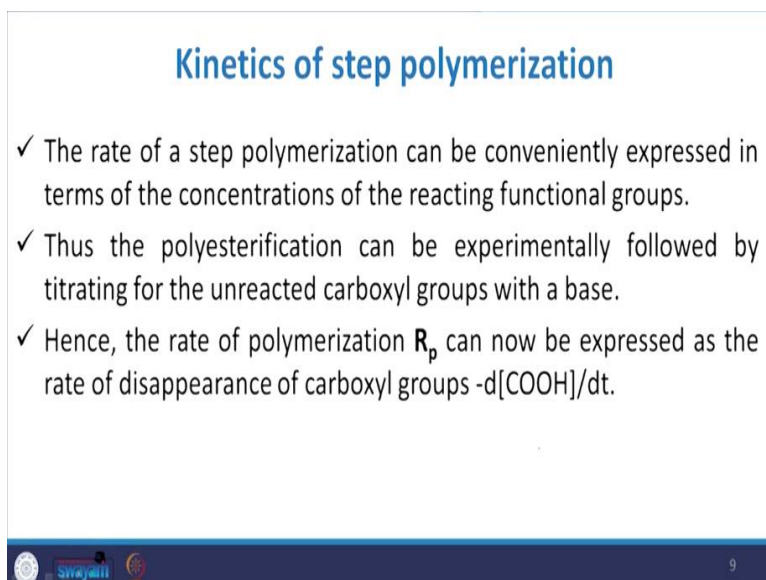**(Refer Slide Time: 04:04)**

Kinetics of step polymerization

✓ 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.

✓ This is accomplished by removal of water that is a by-product of the reaction species II (Eq. 3). The kinetics of polymerization under these conditions can be handled by considering the reactions in Eqs. **2** and **3** to be irreversible.

Now, considering the practical viewpoint of obtaining high yield of high molecular weight products, such polymerizations are run in a manner so as to continuously shift the equilibrium in the direction of the polymer. Now, this is accomplished by removal of a water that is a by-

product of a reaction species 2 as shown in the figure. The kinetics of polymerization under these conditions can be handled by the considering the reaction in equation number 2 and 3 needs to be reversible irreversible in this particular slide.
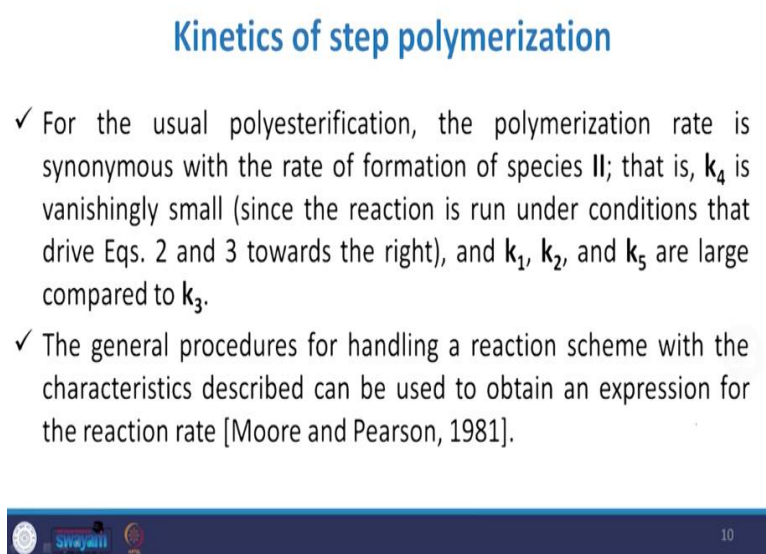
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Now, the rate of step polymerization can be conveniently expressed in terms of concentration of reacting functional group. Thus, the polyesterification can be experimentally followed by titrating the unreacted carboxylic group with a base. Therefore, sometimes when we need to find out the rate of polymerisation R p, this can now be expressed as the rate of disappearance of carboxylic group. That is sometimes referred as d COOH upon dt.

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Now, for the usual polyesterification, the polymerization rate is synonymous with the rate of formation of species 2 and that is the k 4 is usually vanishingly. Now, for ease of this again I

am showing the mechanism of that particular reaction over here. Now, here you see that there are the k_4, k_3 these are the rate constants for forward direction and backward direction. And sometimes when we talk about the irreversibility etcetera, then we need to address the equation 2 and 3 in that case.

So, when we talk about the reaction run under the condition usually that prevails under the equation number 2 and 3 towards the right, the k_1 and k_2, k_5 they are the large as compared to k_3. So, the general procedure for handling a reaction scheme with the characteristic describe, this can be used to obtain an expression for the reaction rate. Now, let us have a look about the rate of polymerization.

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Kinetics of step polymerization

✓ The rate of polymerization is given by
[Note]:

✓ 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.

So, the rate of polymerization is given by Rp.

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$$R_P = -\frac{d[COOH]}{dt}$$

$$R_P = k_3[C^+(OH)_2][OH] \quad (4)$$

That is equal to d COOH upon dt and Rp is referred as k_3 if you recall those equation C plus OH. This is this can be represented as equation 4. First 3 equations are represented in that particular mechanism, now, where this COOH and OH and C plus OH twice they represent the concentration of carboxylic, hydroxyl, protonated carboxylic groups respectively. And the concentration terms are in the unit of moles of the particular functional group per litre of solution.

Now, this particular equation which we represented in the previous one that it is inconvenient as the concentration of a protonated carboxylic group is not easily determined experimentally. So, one can obtain a more convenient expression for rate of reaction. Now, if we substitute if we have a substitute for C plus OH twice from the equilibrium expression for the protonation reaction, then we can have this particular equation.

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Like k is equal to k_1 upon k_2. That is C plus OH upon COOH HA. This can be represented as equation number 5.

$$k = \frac{k_1}{k_1} = [C^+(OH)_2][OH]/[COOH][HA] \qquad (5)$$

$$R_P = -\frac{d[COOH]}{dt}$$

$$R_P = k_3[C^+(OH)_2][OH] \qquad (4)$$

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

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Kinetics of step polymerization

✓ Combination of Eqs. **4** and **5** yields
[note]:

✓ Two quite different kinetic situations arise from Eq. **6** depending on the identity of HA, that is, on whether a strong acid such as sulfuric acid or p-toluenesulfonic acid is added as an external catalyst.

Now, if we combine both the equation, equation 4 and equation 5. For convenience, again I am writing the equation number 4 that is R p is equal to minus d COOH upon dt or Rp is equal to k_3 C plus OH OH. This is equation this was our equation number 5. Now, if we combine both

these equations, then we may have minus d COOH upon dt is equal to k 3 k COOH OH. That is equation number 6.

So, the 2 quite different kinetic situations arise from this equation number 6 depending on the identity of H. That is on whether a strong acid such as sulfuric acid or para toluenesulfonic acid is added as an external catalyst. Now, one of the most important properties in the condensation polymerization is the polymers molecular weight. As we discussed that polymer molecular weight play a very vital role in all kind of property determination approaches. So, consider a linear step growth polymerization of AB type here in this particular figure.

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Let A refer to the hydroxyl group and B refer to the carboxylic acid group. So, that a polyester is formed and the polymerization reaction can be represented like this.

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Kinetics of step polymerization

✓ In step-growth polymerization, it is common to use the symbol **p** (rather than **x**) to refer to conversion of the limiting functional group, 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:

[note]:

Now, in step growth polymerization, it is common to use the symbol p rather than x to refer the conversion of limiting functional group. Now, as the conversion is equal to the probability that a particular functional group say sometimes hydroxyl group OH group in the original reaction mixture, they had it has reacted with another functional group, sometimes carboxylic group like COOH. Therefore, the probability that a random molecule will have a chain length n would be p(n) is equal to p to the power n minus 1 into 1 minus p.

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Let us refer as this particular equation number 7.

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

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✓ 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.

So, the consumption of exactly n monomer to form this polymer chain requires n minus 1 independent chain linking reactions. Now, each will probably with the probability p and also that 1 hydroxyl group that is the one at the end of the resulting molecule. So, this has not been consumed and which has the probability of 1 minus p. So, the distribution in the previous equation that is equation number 7 is called the Most Probable Distribution or sometimes referred as MPD or Schulz Flory distribution.

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✓ 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

Now, the probability P n usually it corresponds to the mole fraction of n mer. That is sometimes referred as x n. Now, as conversion increases sometimes, we say that p tends to 1, the mole fraction of small molecules decreases and the mole fraction of larger molecules increase. But the species with the largest concentration is always the monomer. So, that the number CLD that is referred as a Chain Length Distribution.

Or, sometimes mathematically we can represent as equation number 7 is a decreasing function of chain length. Now, we can utilise this particular equation number 7 to develop an expression of the weight chain length distribution for this AB type of polymeric system. So, in that case, let us have that N be the total number of molecules remaining at conversion p and N naught be the initial number of monomers. Then N is equal to N naught 1 minus p and the mole fraction of n mer can be represented as.

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Now, it can be represented as x n N naught 1 minus p. Now, since this x n is equal to P n and that is equal to p to the power n minus 1 1 minus p that we have already represented, so, the number of moles of n mer can be represented as N n is equal to N naught p n minus 1 1 minus p to the power 2. And this can be represented as equation number 8. And this can be represented as equation number 9.

The mole fraction of n-mer is

$$X(n) = \frac{N_n}{N_o(1-P)} \qquad (8)$$

The number moles of n-mer is

$$N_n = N_n P^{n-1}(1-P)^2 \qquad (9)$$

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Kinetics of step polymerization

✓ The weight fraction of n-mer is:
[note]:

$$W(n) = \frac{N_n(nW_m)}{N_o W_m} = \frac{N_o(1-P)^2 P^{n-1}_n}{N_o}$$

$$= (1-P)^2 P^{n-1}_n \qquad ——(10)$$

✓ where w_m is the molecular weight of a repeat unit.
✓ **Assumption**: The total mass of the repeat units in the polymer chains is large compared to the mass of the end groups.

$$W(n) = \frac{N_n(nW_m)}{N_o W_m} = \frac{N_o(1-P)^2 P_n^{n-1}}{N_o}$$
$$= (1-P)^2 P_n^{n-1} \qquad (10)$$

Now, if go to the weight fraction concept, and we talk about the weight fraction of n mer. Sometimes it is quite useful. Then it can be represented as w n is equal to Nn nW_m upon N naught Wm. And this is N naught 1 minus p square p n minus 1 n upon N naught or upon rearrangement arranging we can write 1 minus p square p n minus 1 n. And you can write this as the equation number 10.

So, this here you can say the w m sometimes the molecular weight of a repeat unit. Now, you may take the assumption that the total mass of repeat unit in the polymer chain is large compared to the mass of end group. So, whatever end group is here, you can say that the total mass of this particular polymer chain is larger than the mass of this end group.

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Kinetics of step polymerization

✓ The Number-Average Degree of Polymerization (DP_n)

[note]:

$$DP_n = \sum_{n=1}^{\infty} n \times (n) = \sum_{n=0}^{\infty} (1-P)^2 P_n^{n-1}$$

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

$$= \frac{1-P}{(1-P)^2} = \frac{1}{1-P} \qquad (11)$$

So, sometimes we may talk about the number average degree of polymerization and referred as DP n. It is again quite important in case of the step growth polymerization. So, the number average degree of polymerization, this can be represented as DP n is equal to summation n is equal to 1 to infinity n x n. n is equal to 1 1 minus p np n minus 1 or this is 1 minus p 1 plus 2p plus 3p square plus and so on.

Or, this can be represented as if we adopt the proper mathematical tool to represent this degree of polymerization, it can be represented as 1 minus p upon 1 minus p square and that is 1 minus p. Now, this can be represented as let us say for the ease of calculation, we can represent that equation number 11a.

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

[note]:

$$DP_w = \sum_{n \geq 1}^{\infty} n\, w(n) = \sum_{n \geq 1}^{\infty} (1-p)^2\, n^2\, p^{n-1}$$

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

$$= \frac{1+p}{1-p} \quad --- \quad)\, (b)$$

✓ The polydispersity index ($PDI = DP_w / DP_n$) is $\boxed{1 + p.}$

✓ Since p is very close to 1.0 for linear HMW step-growth polymers, the polydispersity is very close to 2.0.

Now, the weight average degree of polymerization, the DPw, because, previously we talked about the number average degree of polymerization, now, sometimes the determination of weight average degree of polymerization DPw can also be a very important thing. And this can be calculated easily from the number and weight chain length distribution. So, it can be represented as DPw that is equal to n is equal to 1 to infinity nW(n).

n is equal to 1 to infinity 1 minus p square n square p n minus 1 or 1 minus p square 1 plus 2 square p plus 3 square p plus and so on. And this can be represented as 1 plus p upon 1 minus p. That is our equation number 11b. Now, the polydispersity index is usually referred as PDI is equal to DPw upon DPn. And in that case, it is 1 plus p. Since p is very close to 1 for linear then step the high molecular weight polymerize step growth polymerization or polymers the polydispersity index is very close to 2.

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Kinetics of step polymerization

✓ 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.

Now, this equation 11a and 11b, these 2 equations indicate that for this simple step growth polymerization, the molecular weight averages can be calculated easily from the conversion. And that the conversion p must be very close to 1 to obtain the high molecular weight polymer. So, this is a particular important thing is need to be look into while considering the kinetics of step polymerization.

Now, sometimes when we talk about the self-catalysed polymerization, then in the absence of an externally added strong acid or diacid monomer acts as its own catalyst for the esterification of reaction. That means, sometimes the reactant itself sometimes the product being developed in due course of time within the reaction mass they can act as a catalyst for the polymerization reaction.

They are clubbed under the head of self-catalysed polymerization. For this case, HA is replaced by COH and equation the original my original equation 6 this can be written in the usual form. **(Refer Slide Time: 18:11)**

Self-catalyzed polymerization

✓ In the absence of an externally added strong acid the diacid monomer acts as its own catalyst for the esterification reaction.

✓ For this case [HA] is replaced by [COOH] and Eq. **6** can be written in the usual form.

[note]:

$$-\frac{d[COOH]}{dt} = -k([COOH])^2[OH] \qquad (12)$$

✓ where K and k_3 have been combined into the experimentally determined rate constant **k**.

Like this minus D COOH. It is quite evident that why we are putting the minus sign because it is being consumed in the course of reaction. Then it can be OH. Let us represent that as equation number 12. Now, sometime here the K and k3 if you recall the original reaction condition, they are they have been combined into the experimentally determined rate constant k. So, that is the slight modification because it is a self-catalysed type of polymerization.

$$\frac{-d[COOH]}{dt} = -k(COOH)^2[OH] \qquad (12)$$

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Self-catalyzed polymerization

✓ Eq. **12** shows the important characteristic of the self-catalyzed polymerization.

✓ The reaction is third-order overall with a second-order dependence on the carboxyl concentration.

✓ The second-order dependence on the carboxyl concentration is comprised of two first-order dependencies—one for the carboxyl as the reactant and one as the catalyst.

Now, this equation this particular equation shows the important characteristics of self-catalysed polymer polymerization, the usually the reaction is the third order overall with a second order dependency on the carboxylic concentration. Now, the second order dependency on the carboxylic concentration is usually comprised of 2 first order dependency, one for the carboxyl as the reactant and one for the catalyst.

So, remember here the carboxylic group act as a twofold. One is acting as a reactant and another one is acting as a catalyst. So, there are 2 type of a dependency in the first order reaction you need to consider. For most polymerization, the concentration of 2 functional groups are very nearly stoichiometric. And my previous equation number 12 can be written as minus d M upon dt.

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Self-catalyzed polymerization

✓ For most polymerizations the concentrations of the two functional groups are very nearly stoichiometric, and Eq. **12** can be written as

[note]:

$$-\frac{d[M]}{dt} = k[M]^3 \quad ---- \quad 13\ (a)$$

$$\text{or} \quad -\frac{d[M]}{[M]^3} = k\,dt \quad ----- \quad 13\ (b)$$

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That is k M cube. That is let us say that this is my equation number 13a. Or, minus d[M] M cube. That is equation number (()) (20:16). That is equation number 13b. So, you can represent these 2 equations.

$$\frac{-d[M]}{dt} = -k(M)^3 \qquad (13.a)$$

$$\frac{-d[M]}{(M)^3} = -kdt \qquad (13.b)$$

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Self-catalyzed polymerization

✓ where [M] is the concentration of hydroxyl groups or carboxyl groups. Integration of Eq. **13b** yields [note]:

✓ where $[M]_0$ is the initial (at t = 0) concentration of hydroxyl or carboxyl groups.

✓ It is convenient at this point to write Eq. **14** in terms of the extent or fraction of reaction **p** defined as the fraction of the hydroxyl or carboxyl functional groups that has reacted at time **t**.

Now, where this concentration M is the concentration of hydroxyl group or carboxylic group and integration of this particular 13b.

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$$2kt = \frac{1}{[M]^2} = \frac{1}{[M]_0^2} \qquad (14)$$

This yields the 2kt is equal to 1 upon M square is equal to 1 upon M naught square. That may be represented as equation number 14. Now, here M naught is the initial concentration at time t is equal to 0 of hydroxyl or carboxylic group whatever you like. Now, it is convenient at this particular juncture to write equation 14 which we discussed over here in terms of extent of a fraction of a reaction.

p defined as a fraction of hydroxyl or carboxylic functional group that has reacted at time t. Now, sometimes p is also referred to as the extent of a fraction of conversion, the value of p is

calculated from determination of the amount of unreacted carboxylic group. So, the concentration M at time t of either hydroxyl or carboxylic group is can be given by M is equal to M naught minus M naught p.

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Self-catalyzed polymerization

✓ **p** is also referred to as the extent or fraction of conversion. (The value of p is calculated from a determination of the amount of unreacted carboxyl groups.)

✓ The concentration **[M]** at time **t** of either hydroxyl or carboxyl groups is then given by

[note]:

Or, this is M naught 1 minus p. That is equation number 15. So, if we combine the equation 14 and 15 then we may have 1 upon 1 minus p square. That is equal to 2M square kt plus 1. That is equation number 16.

$$M = [M]_o - [M]_o P$$

$$M = [M]_o(1 - P) \qquad (15)$$

$$\frac{1}{(1-P)^2} = 2[M]_o^2 kt + 1 \qquad (16)$$

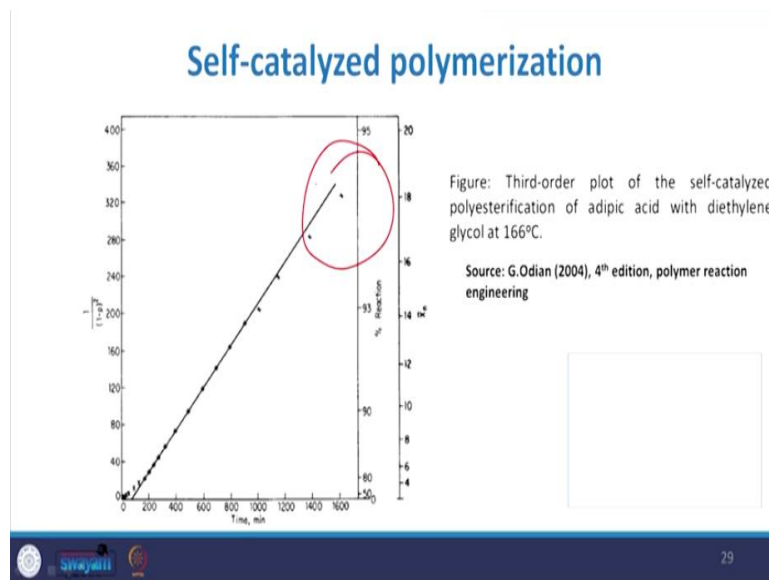**(Refer Slide Time: 22:27)**

Self-catalyzed polymerization

➢ **Experimental observation**

✓ Eq. **16** indicates that a plot of $1/(1-p)^2$ versus 't' should be linear.

✓ At first glance the plot does not appear to exactly follow the relationship. The experimental points deviate from the third-order plot in the initial region below 80% conversion and in the later stages above 93% conversion.

Now, sometimes the experimental observation plays a very vital role. Now, this equation 16 indicates that we try to plot graph of 1 upon 1 minus p square versus t. This should be linear. So, at a first glance the plot does not appear like this. It does not appear to exactly follow the relationship. So, the experimental points though deviates from the third order plot in the initial reason like this, here you can see.

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Self-catalyzed polymerization

Figure: Third-order plot of the self-catalyzed polyesterification of adipic acid with diethylene glycol at 166°C.

Source: G.Odian (2004), 4th edition, polymer reaction engineering

This is a third order plot of self-catalysed polyesterification of adipic acid with diethylene glycol. We have referred this figure from G Odian. Now, if we see that it deviates from third order plot in the initial reason below 80% conversion and the later stage about 93% conversion can be achieved over here. You can see.

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Self-catalyzed polymerization

✓ These deviations led various workers to suggest alternate kinetic expressions based on either 1- or $\frac{1}{2}$-order dependencies of the reaction rate on the carboxyl concentration, that is, 2 and $2\frac{1}{2}$ order dependencies according to

[note]:

So, these deviations sometimes led to the various worker to suggest alternate kinetic expression usually based on either 1 or half order dependencies of the reaction rate on the carboxyl concentration. That is 2 and 2 and a half order dependencies. So, when we consider all those things, then we may have another approach when we talk about these second and 2 second and a half order thing. Then, we may write this d COOH upon dt.

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That is k COOH. Let me write that this is equation number 17a. And minus d COOH upon dt that COOH 3 by 2 OH, therefore, referred as 17b.

$$\frac{-d[COOH]}{dt} = -k[COOH][OH] \qquad (17.a)$$

$$\frac{-d[COOH]}{dt} = -k[COOH^{3/2}][OH] \qquad (17.b)$$

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Self-catalyzed polymerization

✓ The experimental rate data fits Eq. **17a** well only in the region between 50 and 86% conversion with an excessively poor fit above 86% conversion. On the other hand, a plot according to Eq. **17b** fits reasonably well up to about 80% conversion but deviates badly above that point.

✓ Neither of the two alternate kinetic plots (Eq. **17a** and **17b**) comes close to being as useful as the third-order plot.

So, when you see that the experimental rate data fits in equation 17a well only in the region between 50 to 86% conversion with an excessively poor fit about 86% conversion. Now, on the other hand, a plot according to the equation 17b fits reasonably well up to about 80% conversion but deviates badly above that point. So, this point needs to be and that is why the experimental data also play a very vital role when we try talk about the validity or validation of those mathematically derived equation.

So, neither of these 2 alternative kinetic plots based on equations 17a and 17b come close to being as useful as the third order plots. So, the third order plot fits the experimental data much better than does either the of the other at the higher conversion. The fit of the data to the third order plot is reasonably good over a much greater range of the higher conversion reason. So, the reason of high conversion is of the prime importance.

Since high molecular weight polymer is obtained only at high conversion. So, if your target is to have to obtain the high molecular weight polymer, then you need to look this particular aspect. So, from the practical point of view, the low conversion region of the kinetic plot is of having very little significance. Now, sometimes people may talk about that what should be the reasons for nonlinearity in the third order plot.

So, the nonlinearity they are not inherent characteristics of the polymerization reason. There may be certain low conversion reasons. So, Flory PJ Flory in 1953 he attributed the nonlinearity in the low conversion reason to the large changes that take place in the reaction media. Now, the solvent for the reaction changes from an initial mixture to carboxylic acid and alcohol to an ester.

So, the reaction rate constant increases with decreased solvent polarity, since the transition rate is less charged than the reactant. So, it has also been suggested that the excessive or extensive association of both the diols and diacid reactant in low conversion reason, they lower the reaction rate by effectively decreasing the concentration of the reactive species and that is a free or sometimes unassociated OHRCOOH group.

So, the low conversion region usually fits an overall 2 and a half reaction order it is usually better than it does with 3 order re or third order reaction change from 2 and a half order to third order as a reaction medium becomes less polar is compatible with a change from specific yield

sometimes protonic catalysis to the general acid catalysis. The proton concentration is relatively high.

And H plus ion is more effective catalyst than unionized carboxylic acid in the polar regular and low converse conversion reason. Now, if we again go back to my equation number 1, 5 and 6. Especially with respect to HA, usually is replaced by H plus. So, the reaction rate becomes the first order in each carboxylic and hydroxyl group and H plus. So, the proton concentration may be usually given by H plus is equal to kHA.

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Because, we have replaced this one to the power half, this may be represented as my equation number 18. So, if we combine equation 6 previously discussed and equation 18, this may yield minus d COOH upon dt. That is k 3 kkH to the power half COOH 3 by 2 OH. That can be represented as equation number 19.

$$[H^+] = [K_H[HA]^{1/2} \qquad (18)$$

If we compare equation (6) and (18)

$$-\frac{d(COOH)}{dt} = k_3 K K_H^{\frac{1}{2}} [COOH]^{\frac{3}{2}} [OH] \qquad (19)$$

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Self-catalyzed polymerization

✓ HA in Eqs. **1**, **5**, and **6** is replaced by H⁺. The reaction rate becomes first-order each in carboxyl and hydroxyl groups and H⁺. The proton concentration is given by;

[note]:

✓ where K_{HA} is the ionization constant for the carboxylic acid. Combination of Eqs. **6** and **18** gives;

[note]:

So, here you see that K HA is the ionizing constant for the carboxylic acid. Now, another problem is the very high concentration of reactants those present in the low conversion reason. And that is again a most trivial problem. So, yet another possibility for the nonlinearity in the low conversion reason is the decrease in the volume of the reaction mixture with conversion. That is due to the loss of one of the products of reaction.

As we attributed that water in the case of esterification that sometimes referred as a condensation product. Now, it is unclear whether this is effect alone can account for the nonlinearity in the low conversion reason of esterification and polyesterification. Now, let us talk about the high conversion reason.

Now, the nonlinearity usually observed in the third order plot in the final stage of polyesterification is probably not due to any of the reason which we described earlier. Since, the reaction system is fairly dilute and relatively low polarity. Another possible reason for the observed nonlinearity is an increase in the rate of reverse reaction. The polyesterification reaction is an equilibrium reaction.

And it often becomes progressively more difficult to displace the equilibrium to the right, now, sometimes towards the polymer as long as we go the for the higher conversion or conversion increases. Now, this may be because of the greatly increased viscosity of the reaction medium at a very high conversion. Now, the large viscosity increase decreases the efficiency of water removal.

And sometimes may led to the decrease in the reaction rate with increasing conversion. Now, sometimes, we need to address the issues attributed to the external catalysis of this step growth polymerization. The slow increase in molecular weight was mistakenly originally thought to be the due to the low reactivity of functional groups attached to the large molecule. Now, it is however, simply a consequence of a third order kinetics of direct polyesterification reaction.

The realization of this particular kinetic situation sometimes led to the achievement of high molecular weight products in reasonably reaction time by employing the small amount of externally added strong acid, sometimes as a catalyst. So, that is the external catalysis type of scenario. So, under these conditions, the let us again refer to the previous equation number 6. HA in the that particular equation.

That is the concentration of the catalyst. Since this remain constant throughout the course of the polymerization. So, we can write the equation number 6 in a slightly modified way.

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External catalysis of polymerization

✓ Under these conditions, [HA] in Eq. **6** is the concentration of the catalyst. Since this remains constant throughout the course of the polymerization, Eq. **6** can be written as

[note]:

$$-\frac{d[M]}{dt} = k'[M]^2 \qquad (20)$$

✓ where the various constant terms in Eq. **6** have been collected into the experimentally determinable rate constant **k'**.

That is minus d M upon dt. That is k dash. Now, sometimes you may refer this as the equation number 20. Now, here the various constant terms in equation 6 have been collected into the experimentally determined rate constant k dash.

$$-\frac{d[M]}{dt} = k'[M]^2 \qquad (20)$$

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External catalysis of polymerization

✓ Eq. **20** applies to reactions between stoichiometric concentrations of the diol and diacid. Integration of Eq. **20** yields

[note]:

✓ Combining Eqs. **21** and **15** yields the dependence of the degree of polymerization on reaction time as

[note]:

Now, this particular equation which we discussed over here, this applies to the reaction between the stoichiometric concentration of a diol and diacid. So, if we integrate the equation 20 which we discussed, this can give us another approach.

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$$\frac{1}{[M]} - \frac{1}{[M]_o} = k't \qquad (21)$$

$$[M]_o kt = \frac{1}{1-P} - 1 \qquad (22.a)$$

$$X_n = 1 + [M]_o k't \qquad (22.b)$$

Like that k dash t is equal to 1 upon M upon 1 upon M. And then this is M naught at t is equal to 0. That may be equation number 21. Now, if I try to combine the equation number 21 and equation number 15. This may yield to give that M naught k dash t equal to 1 upon 1 minus p

minus 1. That may be referred as equation number 22a. And Xn is equal to 1 plus M naught k dash t. That may be represented as equation number 22b.

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External catalysis of polymerization

✓ The concept of functional group reactivity independent of molecular size has been highly successful in allowing the kinetic analysis of a wide range of polymerizations and reactions of polymers.

✓ Its validity, however, may not always be quite rigorous at very low or very high conversions.

Now, the concept of functional group reactivity independent of molecular size has been highly successful in allowing the kinetic analysis of a wide range of polymerization and reactions of polymers. So, it is validity however, may not always be quite rigorous at a very low or a very high conversion. So, in this particular segment, we discussed about the kinetic analysis of step growth polymerization with the help of various approaches.

Those who are extensively being used, maybe you can call that some self-catalysed polymerization, some sort of an external catalysed polymerization. And we gave the due respect to the low conversion as well as the high conversion.

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References

- G.Odian, Principles of Polymerization, Fourth Edition, John Wiley & Sons, Inc., (2004), ISBN:9780471478751 |DOI:10.1002/047147875X.
- J.M. Asua, Polymer Reaction Engineering, Blackwell Publishing, (2007), ISBN: 978-1-4051-4442-1.

Now if you wish to have further more discussion, we have listed several references for your convenience. You can refer those references and you can enhance your knowledge. Thank you very much.