Polymer chemistry

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Lecture - 4
Step-growth Polymerization

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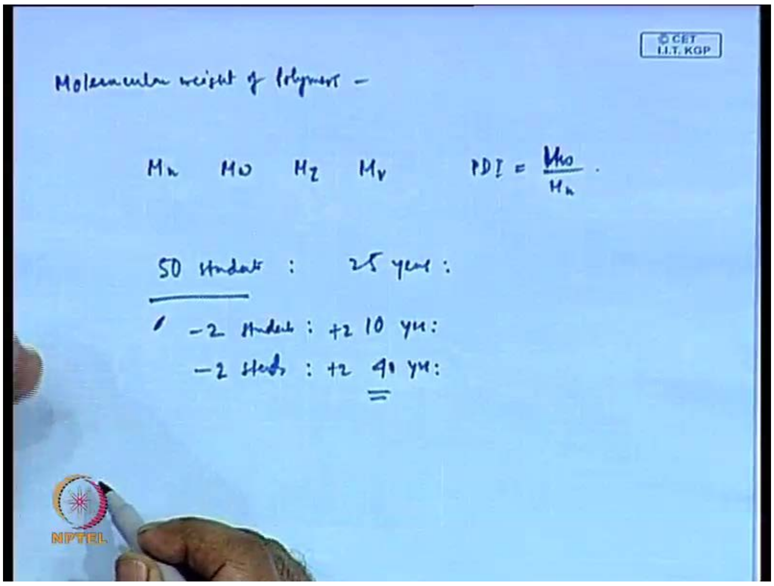

Molecular weight of polymers –

M_n M_w M_z M_v PDI = $\frac{M_w}{M_n}$.

50 students : 25 years :

−2 students : +2 10 yrs:
−2 students : +2 40 yrs:

In the last lecture, we were discussing about different types of molecular weight of polymers, and we defined number average molecular weight, weight average molecular weight, z average molecular or z average molecular weight, whatever you call, viscosity average molecular weight. And we also introduced the term polydispersity index, which was given by M w by M n. Now, you may ask me, what is the need for having more than one molecular weight? We can just simply say that polymer, this polymer has, this polymer sample has this M n.

Now, let us, let us begin with some real life example. Now, I have; so, for this class I have 50 students, 50 students on an average age, let us, 25 years, all of you. If I assume that your knowledge in polymer chemistry or other subject is related to the age, then you have some knowledge base. Now, from these students, now I take out two student and add 2, 10 year students; we have age of 10 years, class standard 10, student, 5 student. And, I take out 2 students and add 2, 40 years, say, professors from any college. So, what will be the average? Average would remain same, 25 years. I just taken out 2 student, added 2, 10 years; and, taken out another 2 student of 25 years, added 40 years.

So, what do you think the samples ability to score in any subject, which depends upon knowledge, would change or not? The average remains same which is same as 25 years as earlier. But, obviously, you can now understand that, because you added two 40 years professors, the ability to the knowledge or ability to score in exam is much more for this sample compared to the earlier one.

So, what I am trying; with this example, what I am trying to convince you that, may be the average remain same in two cases; in the first case, there was 25 years 20 50 students, and in this case, you have replaced 4 student with 4 another set of person. The average remains same, but the property; in this case, property being the knowledge or the ability to score marks, changed. That means property of a polymer sample cannot be always obtained from just single value of same end, which is the arithmetic or average, like this case. If you have a distribution, broader distribution or a narrower distribution, then the property is going to change. How do you determine this molecular weight?

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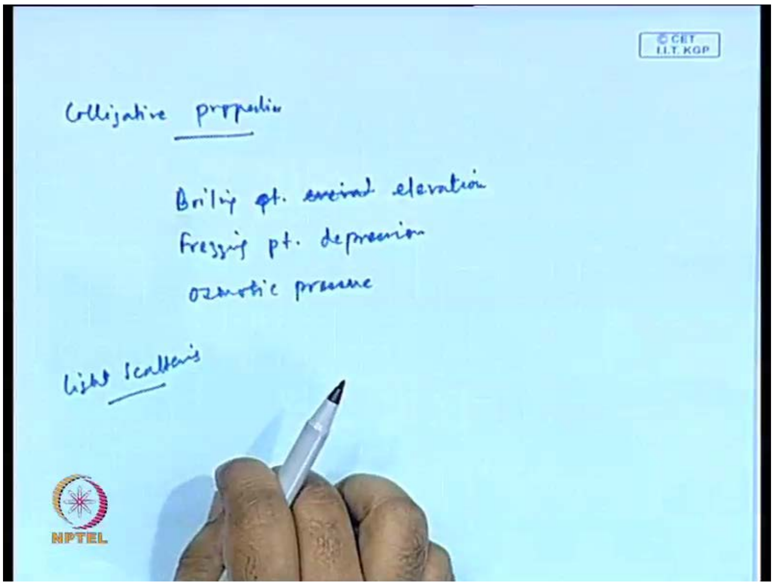

Colligative properties

Boiling pt. [illegible] elevation
Freezing pt. depression
osmotic pressure

Light scattering

For example, if I have these colligative properties, you know colligative properties, properties; these are like boiling point elevation of a solvent, freezing point depression, osmotic pressure, like this. These, you know that the property or the value of this colligative properties will depend upon the number of solid molecules.

So, if you add a polymer sample in a solvent, make a solution, the boiling point elevation for that solvent compared to pure solvent or a freezing point depression compared to pure solvent. We will now determine on the number of polymer molecules present in the solution; number of polymer molecules, which will give you M n, because M n is what concerns the number of polymer molecules.

Now, if I want to measure the light scattering from a polymer solution; as you know, the light scattering is dominated by the molecules having larger sizes or larger molecular weight. So, light scattering from a polymer solution will depend biased; it will be heavily dependent on the larger molecules, not the smaller molecules; which means, the property like lights catering depend more on a M w, not M n. Alter centrifugation would depend upon M z. Viscosity is depend upon M v, viscosity average molecular weight.

So, we need all these molecular weights as well as the distribution p d (( )) index, M w by M n, to completely under the sample; what you mean by understand, the properties of the sample. If I want to know the ability to scatter a light from that sample, it would, you know, we need M w value, rather than M n. And if you want to find out the colligative properties of that sample, then we know that this is M n which we need to know, rather than M w. And also, we will see later lectures that distribution matters for a given average if distribution changes, then the properties like melt viscosity and the strength, and the mechanical properties also changes with the distribution. So, keeping the average same, the polymer property will change, if the distributions also change.

So, these are the reason, why we need all this numbers, or the values of all this molecular weights, not only a single molecular weight, and also the distribution.

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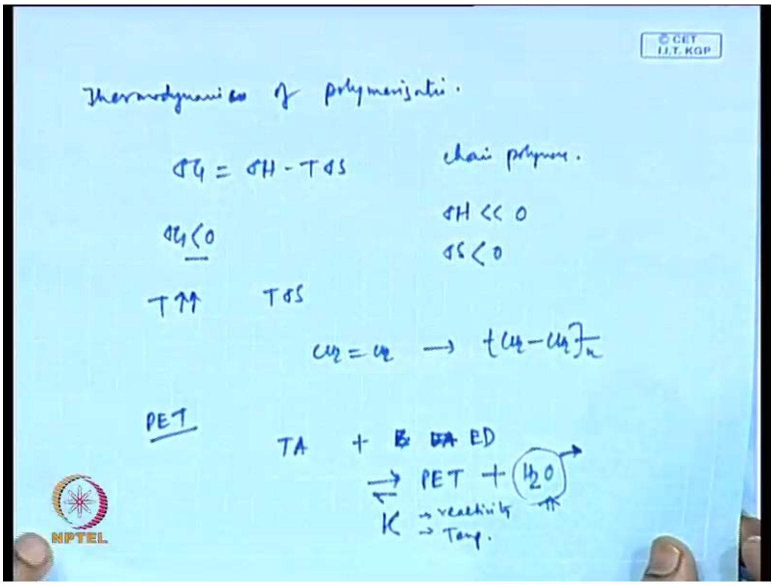

Thermodynamics of polymerization.

$\Delta G = \Delta H - T\Delta S$

chain polymers.

$\Delta H << 0$

$\underline{\Delta G < 0}$

$\Delta S < 0$

$T\uparrow\uparrow$ $\quad T\Delta S$

$CH_2 = CH_2 \rightarrow \{CH_2 - CH_2\}_n$

PET

TA + ~~B~~ ~~DA~~ ED

$\rightleftharpoons$ PET + H_2O

K → reactivity
→ Temp.

Now, before I move to the, this lecture's topic on temper polymerization, I just want to very briefly touch upon the thermo dynamics of polymerization. Now, you know, del G is del H minus T del S. When you making chain polymers, what you doing? We will making chain from the monomers. So, lots of bond formation is taking place; so, del H is highly negative, and because the monomers is getting tied up, del S is also negative.

So, depending upon the value of this del S and, del H and del S, the del G value will depend. And, at normal temperature, the temperature we work in the lab, del H is highly negative which makes del G is based on 0. So, the polymerization is highly favorable, same polymerization highly favorable. Now, at higher temperature, if we increase T temperature, then this second term, T del S, becomes higher and higher. So, minus T del S will become more positive; which means, at some point, at a very high temperature del z, del z will be the 0, and positive above certain temperature.

In that case, the reverse reaction would start taking place; that means, polymers will start unzipping. Because, in normal temperature, this reverse reaction is very insignificant for 10 polymers, but typically it do not represent, say, reaction like polyethylene formation with a reversible sign. Because, the temperature, we do normal 10 polymerization, this reverse, reverse reaction is insignificant.

Now, in case of step polymers, like we talked about PET, polyethylene teritarate, we have teritaric acid, so I have T A plus, ethylene, ethylene glycol plus, the dyol ethylene, dyol I write D A. So, I will, ethylene dyol ED, which gives you polyethylene teritarate, plus water. Now, in this case, these reactions are reversible, and you have a associated equilibrium constant with this reaction. Because, the re-activities of these accidents, accidental call, they form ester is, is not very highly, highly feasible reaction. So, often we need catalyst to make the reaction feasible. This K would depend on reactivity of the function group as well as the temperature. Higher the temperature, the K will go up, and your reaction will go to its right hand side.

Now, in most cases, in most practical cases, to make a high molecular polymer, you have to take this condenser out, because this is a equilibrium reaction, reversible action. In most practical cases, these are taken out by applying vacuum; and also increasing temperature, by increasing temperature; and doing that, you force the equilibrium move towards right hand side, which will gives you the polymer.

Just to mention these two features that this step growth polymers are reversible equilibrium reaction, and having at a PET K value, which depend on the reactivity and temperature. And, for a practical syntheses of step growth polymers, you need to take out this condensed from the reaction by applying high temperature and high vacuum, so that the reaction proceed to the product side. Whereas, in case of chain polymers, it is (()) feasible; only at very high temperature the reverse reactions becomes significant. Just remember this point; we will come to the detail turbulent polymerization when the proper time comes.

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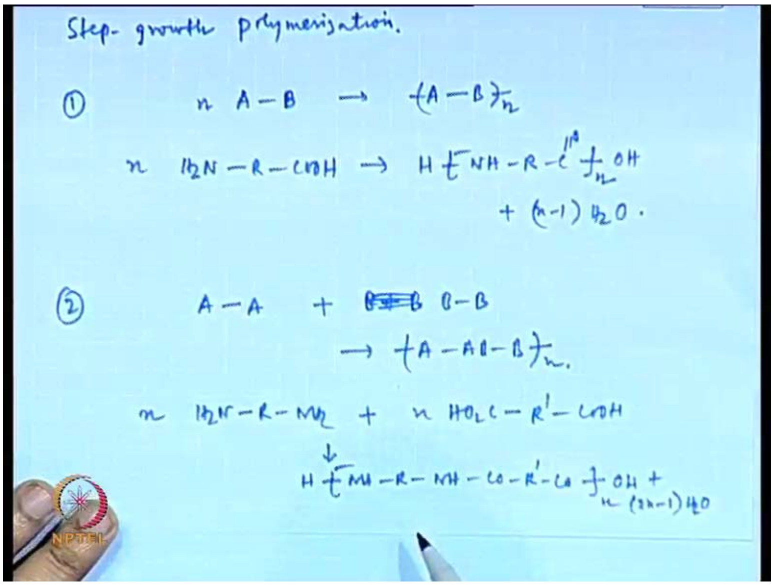

Step- growth polymerization.

① $n\ A-B \rightarrow \left(A-B \right)_n$

$n\ H_2N-R-CO_2H \rightarrow H\left[NH-R-\overset{O}{\overset{\|}{C}} \right]_n OH$
$+ (n-1)\ H_2O.$

② $A-A + \cancel{B-B}\ B-B$
$\rightarrow \left(A-AB-B \right)_n.$

$n\ H_2N-R-NH_2 + n\ HO_2C-R'-CO_2H$
$\downarrow$
$H\left[NH-R-NH-CO-R'-CO \right]_n OH + (2n-1) H_2O$

Now, we will move to the step growth polymerization and its kinetics and mechanism. Now, step growth polymerization can be classified in or grouped into types- one is, where you have polymerization done from single monomer having 2 different functional group; so, I write A B gives you this; for example, I can write, general reaction. And the second group is where you have, 2 different monomer having 2 different bifunctional monomer; I can write a general example as in the earlier case, gives you; plus, ok; and, 2 n minus 1, H 2 O.

And, as we have learned in last lecture that to make a high molecular weight of this polymers, the polymerization has to be pushed with, such a way that to the conversion of the monomers or functional groups are very high, more than 98 person. And, also we will see that another conditions required for this type of polymerization to make high molecular weight, is that the two functional groups has to be present, so, S symmetric amount; that means, the ratio of NH 2 O group and COH groups has to be 1 isto 1; that is another requirement. We will find out more about that in, little later.

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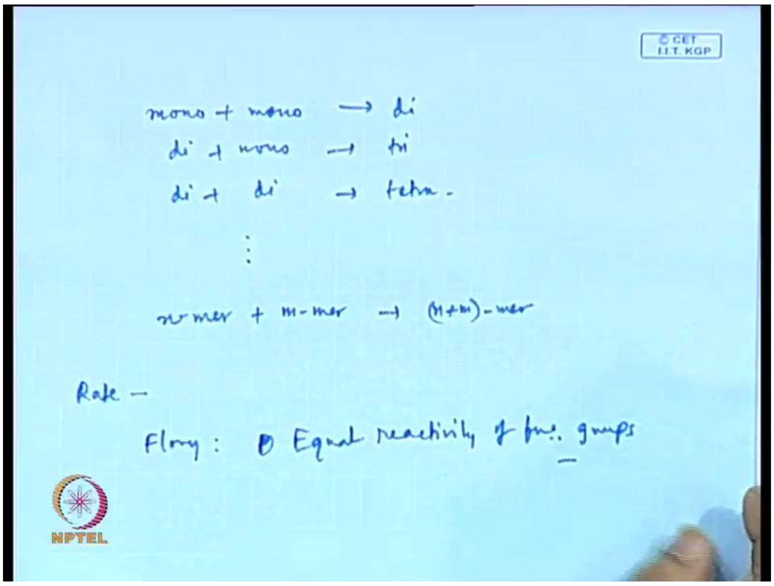

mono + mono → di
di + mono → tri
di + di → tetra.
⋮
n-mer + m-mer → (n+m)-mer

Rate –

Flory : Equal reactivity of fn. groups

So, as we had seen in earlier lectures that; we write this step wise reaction to describe a step growth polymers, or general you can write m r plus m r, gives you n plus m, m r. So, in a polyestrification reaction, when you are forming a polyester form the higher C than diol, or form a hydro oxide acid, at any point of time, we will find, in the mixture dioxides and very different size of dioxides, diol and hydro oxides acid, and so on. And, all this reactions happen between the functional groups; so, polyester case, reaction between OH and COOH.

If we want find out rate of this polyester exhibition reaction or the step growth polymerization, you need to know the rates of each step, and then sum up to get the rate of the final polymerization. But that is very difficult job; is in practical to find out rate for individual because there is so many reactions happening, different possibility. Then, if you want to know the reaction leads for each and individual steps and then finally, sum them to get the final rate; that is practically a impossible task.

So, this is simplified; it can be very simplified, if we imagine that rates of all this reactions are same. Now, this reaction is nothing but reaction between functional groups. Though the sizes of this species are different, but the final reaction is between OH group and COOH group for a polyester exhibition reaction. So, we can assume that the rates of this individual steps are different, and first it was proposed by Flory, and which is proposed as the equal reactivity of functional group, functional groups; Flory, who proposed first. Now, what are the, what does it mean by equal reactivity of functional group?

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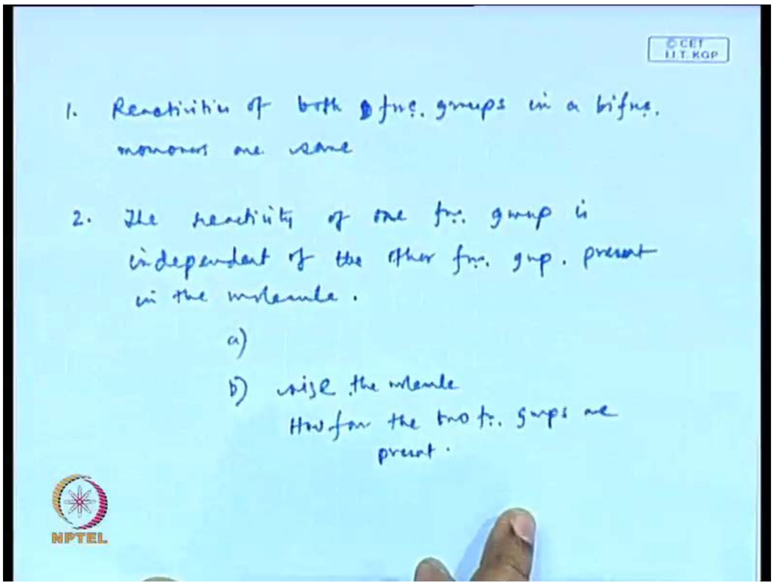

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1. Reactivities of both fnc. groups in a bifnc. monomers are same

2. The reactivity of one fn. group is independent of the other fn. gp. present in the molecule.

a)

b) size the molecule
How far the two fn. gps are present.

One: that reactivates of both functional groups in a bi functional monomers are same. For example, if we have a diol, or a di acid, or a hydro oxide acid, in case of the polyester is, reaction is just talking about; re-activities of both the functional group 1n the bi functional monomers are same.

Now, what is, the second point is that, the reactivity of one functional group is independent of the other function group present in the molecule; which means, whether the other functional group is reacted or not, if we have bi functional molecule with 2 functional group two side; now reactivity of one functional group is independent the other.

So, you can say that whether the other functional group, it present in other end of the molecule, whether that is reacted or not, that does not determine the reactivity of the other side, as the function group is in other side. And second, it is independent of size of the molecule, or how for the two functional group are present; whether they are present in the dimer, or in a octamer. So, the functional, the reactivity of more the functional group is independent of the other functional group irrespective of the length in between, which makes this, all the reaction as happens in the step growth polymers, polymerization process, they are same. Now, this assumption is a shear assumption, and it has been proven experimentally.

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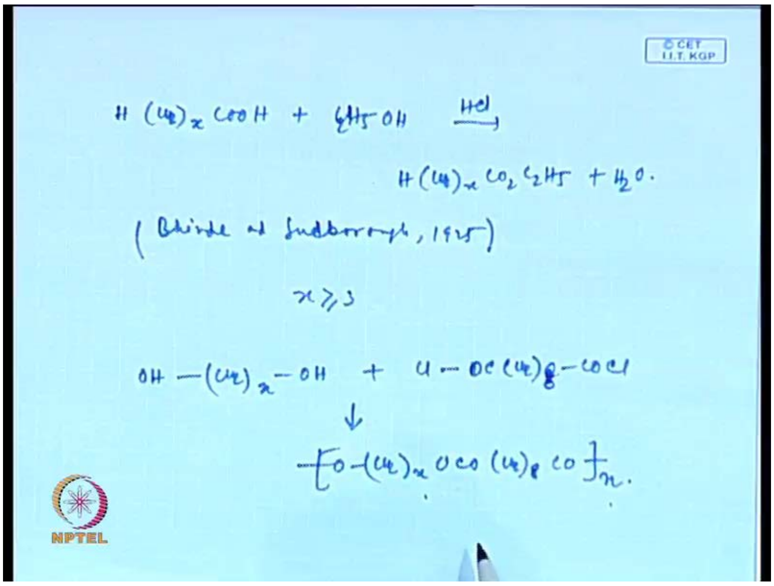

$$H(CH_2)_x COOH + C_2H_5OH \xrightarrow{HCl} H(CH_2)_x CO_2C_2H_5 + H_2O.$$

(Bhide and Sudborough, 1925)

$$x \geq 3$$

$$OH-(CH_2)_x-OH + Cl-OC(CH_2)_8-COCl$$

$$\downarrow$$

$$-\!\!\!\left[O-(CH_2)_x OCO (CH_2)_8 CO \right]\!\!\!-_n.$$

For example, this reaction; Long back, by this 2 scientists, it was shown that this reaction, this esterification reaction becomes independent; the rate of this in, esterification reaction becomes independent, when x is greater than equals to 3; which means, the reactivity of COH group is independent of the chain length. And, not only this is true for mono functional agent, this reaction can be shown through, if you have the another COH in the other side. So, if you have a dicarboxylic acid and reaction it has already proved experiment, that if you have a di carboxylic acid, a reaction with ethyl alcohol, again the rate is independent of the chain length of the di acid group. And, if the rate becomes limited, you know, when they becomes equal, whenever the chain grows, the significant number in this case, say 3.

Another example, we can show, the other, the other example where. Now, rate of this polyesterification reaction is again, it become independent on the value of x as well as the n. These examples prove that the assumption we made earlier, in terms of equal reactivity of function group, is valid. And that has been, it is not something here imagining to make our life simply, to my, make our life simplify. This has been experimentally proven fact, that the reactivity of the equal, the functional groups are equal when in (( )) molecular species s present in a step polymers state.

Now, this can be justified, if you think little more. For example, how the reaction takes place? In this case, between the two functional groups, between OH and CH for a esterification reaction; the reaction takes place by the collision between the 2 functional group; not all the collisions are useful; not every collision between the OH group and COH gives you esterification. But fraction of collisions which can work on the activation minutes will give you a pester. So, as we know that the reactivity, for the finally, the outcome of the reaction, it depends upon the collision frequencies.

Now, when, this functional group present in a small molecule, compare a situation if you have the functional group, 2 functional group present in a regal molecules; now, is under stood that regal molecules will have lower deficivity, they have lower deficient rate. So, the collision frequency between the 2 molecules, 2 oligomer in this case, we will (()); understand; I am talking about the collision frequency between the two molecules. In this case, 2 oligomers having 2 function groups at the end, they will work if you compare with this smaller, smaller molecule. But same times, same logic, when they come close, they will stay longer, because their rate of the fission is lower. And, if they stay longer, then the probability of collision between the functional groups which are present at the end also increases.

So, the collision frequency between the functional groups also increases. So, same time the collision frequency between the molecules coming down because of size being higher, but the collision frequency between the functional groups, they are becoming more. So, on effect, this two are rarifying each other, and so, final collision frequencies between the functional groups present in a smaller chain compared to a larger chain are equal; and, as the collision frequency, the final functional groups are equal, the reactivity or the rate of reactions also equal.

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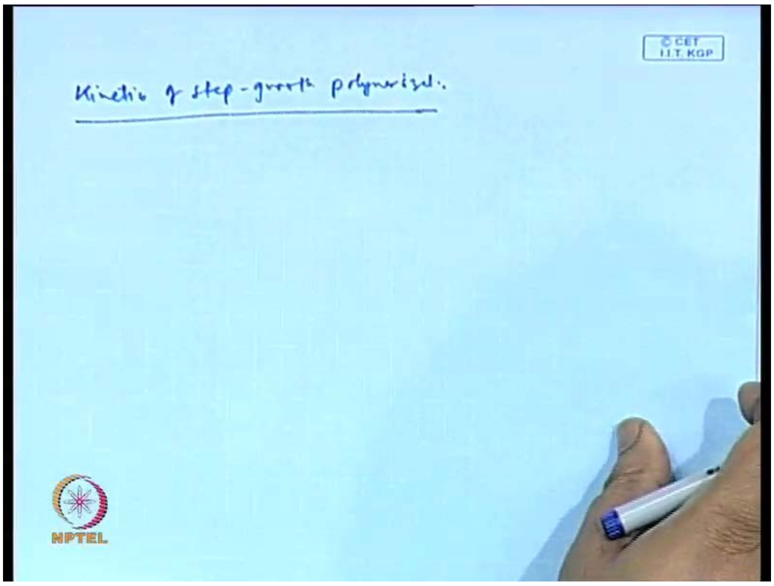

Kinetics of step-growth polymerization.

So, now we will move to the; with that example, I will go to the kinetics of step growth polymers.

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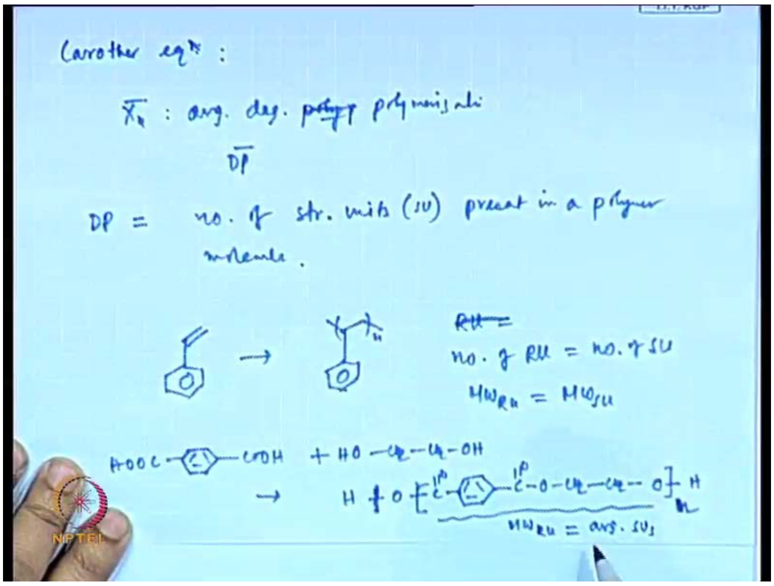

Carother eqn :

$\bar{X}_n$: avg. deg. ~~polym~~ polymerization

$\overline{DP}$

DP = no. of str. units (SU) present in a polymer molecule.

~~RU =~~

no. of RU = no. of SU

$MW_{RU} = MW_{SU}$

HOOC–C_6H_4–COOH + HO–CH_2–CH_2–OH → H[O–CO–C_6H_4–CO–O–CH_2–CH_2–O]$_n$H

MW_{RU} = avg. SUs

And, before we start kinetics of step group polymers, we define another term, or we talk about Carother equation, which gives you the average degree of polymerization; sometimes written as DP, is a average of polymer, degrees of polymerization. Now, what is degrees of polymers? We learned in the first lecture, is the number of structure units present in the molecule or in a polymer chain.

As I said in the first class itself that structure units and repeat units are different, and it will become more clear, I just give 2 examples. Let us talk about stirring. And, in this case, this is a repeating unit; it is same as a structure unit, structure unit is the residue of the monomer. So, in this case, repeating unit, or number of repeating unit is same as number of structure units; molecular weight of repeat unit is same as molecular of structure units. In case, polyethylene teritarate, this is the repeat unit.

So, what is the relation between repeat unit and structure unit, in this case; and each repeating unit contains 2 structure units. So, the molecular of repeat unit is the average of the structure units minus, the conducted which had gone out, in this case water molecules, because of the condensation reaction.

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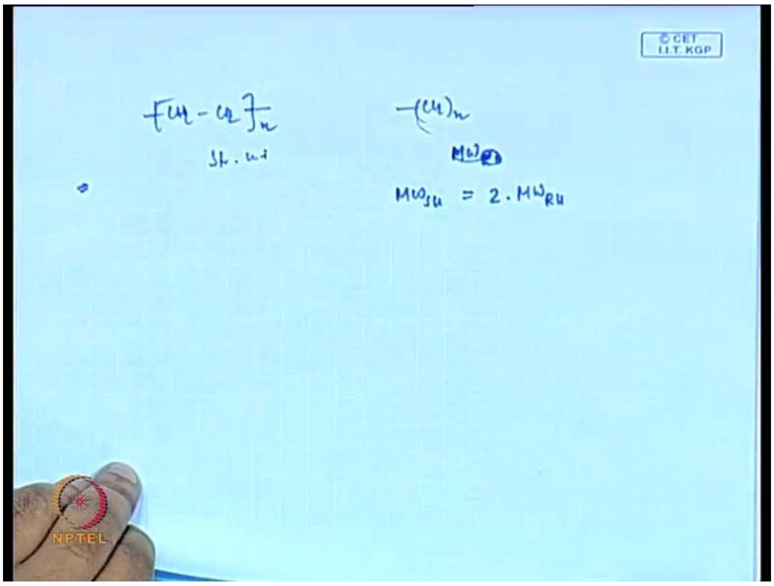

See, this is specific case as a polyethylene, this is structure units, and repeat unit is this. So, in this case, molecular of structure unit is twice the molecular of repeat unit; this is the repeat unit, and this is the structure unit. So, the molecular of structure units twice the molecular repeating. So, this is a specific case, this, this example is not, there are many many case. So, they, this two are more common, where the molecular of repeat unit is same as structure units; where, second case where molecular structure unit is the summation of the average server. So, basically we had to put twice; average multiplied by twice for this.

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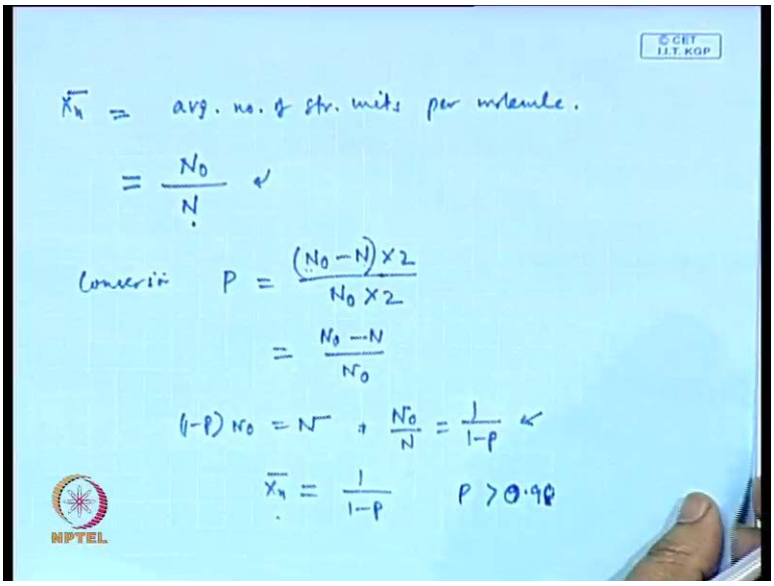

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$\bar{X}_n$ = avg. no. of str. units per molecule.

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

Conversion $P = \frac{(N_0 - N) \times 2}{N_0 \times 2}$

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

$$(1-P) N_0 = N, \quad \frac{N_0}{N} = \frac{1}{1-P} \swarrow$$

$$\bar{X}_n = \frac{1}{1-P} \qquad P > 0.98$$

So, the X n is the average number of structure units per molecule. Now, this can be given by N 0 by N; if N 0 is the total number of monomers at the beginning, and N is the total number of chains present at after polymerization or some time. How do you get? You just simply think that, say if you have 50 of your students, I ask to occupy 5 benches. Now, they are big benches; we can occupy any chairs if you choice; so, all 50 of you distributed in the 5 benches. Now, at the end I ask you to hold hand and tell me, what is the average, average number of student in a particular bench? So, you have total number of 50 students, in the 5 bench. So, average per bench is 50 by 5, that is 10.

Simply, if you are starting with N 0 of monomers and then finally, you have present, you are remain with N mono N chains, then each chain will have N 0 by N structure units; simple. Now, if we note, we define conversion or if conversion is P, now, how do you define conversion P? Total number of functional group reacted divided by total number of functional group present.

Now, N 0 was the number of molecules, or monomers at the beginning. And, now, N is the monomers present. So, N 0 minus N is the number of monomer or moles of monomers reacted, divided by, N 0 is the total number of monomers the beginning, and each monomer has 2 functional group. So, multiplied by 2 functional group, 2 each to make the total functional group reacted. So, this is the number of molecules present at this, at this movement, any time during the reaction.

So, N 0 minus N is the monomers which are reacted. So, you multiplied by 2 to get the number of moles of functional groups reacted, and N 0 was the monomers were present originally. So, N 0 by 2 is the number of functional group present at the beginning. So, this is the fraction which has reacted. So, I write N 0 by N, N 0; I can rearrange this to get N 0 by N as 1 by 1 minus p. So, if you compare this and this, I can write, the average degree of polymerization is given by 1 by 1 minus p.

Now, this is again giving the same information as we got in earlier cases, in earlier discussion. To have a high molecular weight polymer you need to have high value of X n, is the number one monomer unit or structure unit present in the system. How do you get a high value of X n? Only the p is high; if it is p is 0.98, may be 90 percent of the function groups has reacted, you get 50; X n is 50. If it is 0.99, there will be 99 percent of the functional groups are reacted, then you get 100.

So, look, how it is from 99, from 98 percent reaction to 99 percent reaction, you are getting jumping degree of, average degree of polymerization from 50 to 100. I should think about the lower values of p, 97 percent, or even 90. If 90 percent of the fractional groups are reactive, when normal organic reaction is in small molecules; say, we have an esterification reaction, a 90 percent reaction means, you all happy; if you not happy you increase, do something to make a 95 percent reaction, then very happy. Whereas, in case of polymers, if you do 90 percent, in step growth polymers we have a 90 percent conversion; p is 0.9, then this gives you 10; X n is 10. So, it is a oligomer. So, 90 percent conversion is not enough to give you high molecular polymer.

So, again stating it for getting high molecular polymer, you made a conversion p greater than 0.98 and so; 0.98 give you 50 and so, as increase will be p, the higher and higher value of X n.

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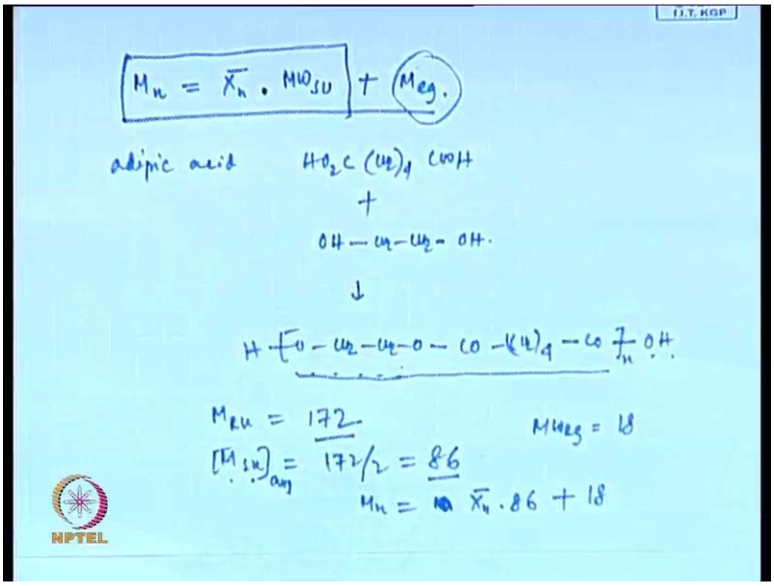

$$\boxed{M_n = \bar{X}_n \cdot MW_{SU}} + M_{eg}.$$

adipic acid $HO_2C(CH_2)_4COOH$

$$+$$

$$OH-CH_2-CH_2-OH.$$

$$\downarrow$$

$$H-\!\!\left[O-CH_2-CH_2-O-CO-(CH_2)_4-CO\right]_n\!\!-OH.$$

$M_{RU} = \underline{172}$ $M_{W_{eg}} = 18$

$[M_{SU}]_{avg} = 172/2 = \underline{86}$

$M_n = \bar{X}_n \cdot 86 + 18$

How do you get molecular x from, you got X n average degrees of polymers from this; you can get experimentally, p, q, can experimentally determine the fraction of molecule present. So, if you do it activation for curio oxide acid, you can get the fraction of (()) from beginning. So, you can get X n multiplied by the molecular unit of structural unit, plus, the molecular unit of, molecular unit of the groups of the end. So, if I take a example of adipic acid, plus ethylene glycol, you get a polymer of this. So, molecular weight of the repeating unit in this case, this is the repeating unit, is the molecular weight of this entire repeat unit, which is 172.

But, molecular weight of average molecular of the structure unit in this case, we have 2 structure units in this (( )) unit. So, the molecular weight of structure unit; in this case average, because 2 are different. So, I can write M s u average is 172 by 2, is 86. So, and what is the molecular weight of the n group? OH plus H, it gives you 18. So, the total unit of this polymer would be given by X n bar multiplied by 86 plus 18. So, this is, this is very important part.

Now, the molecule, relation between molecular weight and degrees of polymers; Molecular weight, M n, is degrees of polymer multiplied by the molecular rate of the structure units. If the polymer is made from 2 different monomers, like in this case adipic acid and its glycol, then molecular of structure will give the average of that, of that. Some people, or some students in, from our experience, you have seen that they confused this with the repeat unit; then they were confused that this is a molecular repeat unit, this is molecular rate of the structure unit. So, this is 86 not 172 for this example. And, in more of an, in all practical cases, we can ignore this contribution from n group. So, most often we write, M n is this.

Now again, this is molecular of structure units, if this is, this is synthesis from two different monomer in this case adipic acid and ethylene glycol. This is average of the residues of the monomer; the monomer minus the condensed, in this case H 2 O. And, average of that, so, this is 86; not the molecular rate or the repeating rate. If you take repeat unit, you will be doubling the calculated molecular weight M n for this.

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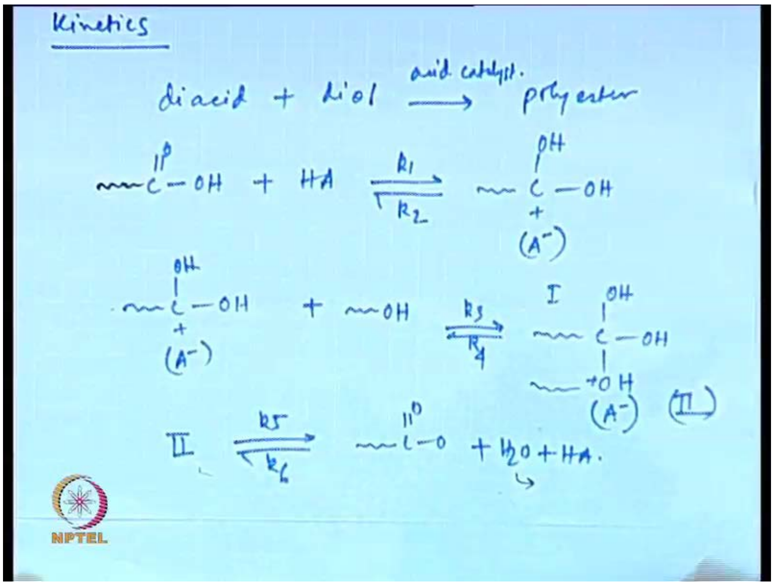

Now, let us come back to the kinetics of step growth polymers. Now, just to illustrate the general poly esterification; we will take a example of poly esterification as the example of step growth polymers. And, we take as earlier, di oxide plus diol gives you polyester. And, as I said that, in most cases for practical purposes, you need a catalyst to increase the reaction rate. So, I can write this X n (( )) reaction for this H A represents the acid.

This is the reaction scheme for a polyestrification process. And this waved lines means that it is applicable for any size; no, we are talking about general reaction, it could be a end of the dimmer or in dimmer and so on. And so, as this, the hydro oxide group; remember, we talked about the equal reactivity of functional groups; so, we are considering all this functional group present at the end of a molecules are equal. So, we consider this general reaction.

Now, for all practical purposes, as I said that, this are equilibrium reaction; this condensed are taken out from the reaction by applying high vacuum and high temperature. So, that this reactions are all most exclusively on the right hand side. So, the k 5, k 6 and k 4 are very small; k 6, value of k 6 and k 4 are insignificant; we can ignore them, because in most practical scenario, we take out this 2 from the system to make reaction move towards right hand side.

Now, we will come back to the cases where you cannot take out the entire amount of H 2 O produced; we will talk about the expression for those cases later. For this case we are ignoring this 2, and so that the value of k 6 and k 4 are very in significant. And, also this k 3 is the; the value of k 1, k 2 and k 5, they have much higher value compared to k 3. So, this reaction is your state, rate determining in state, which is given by the rate constant value of k 3.

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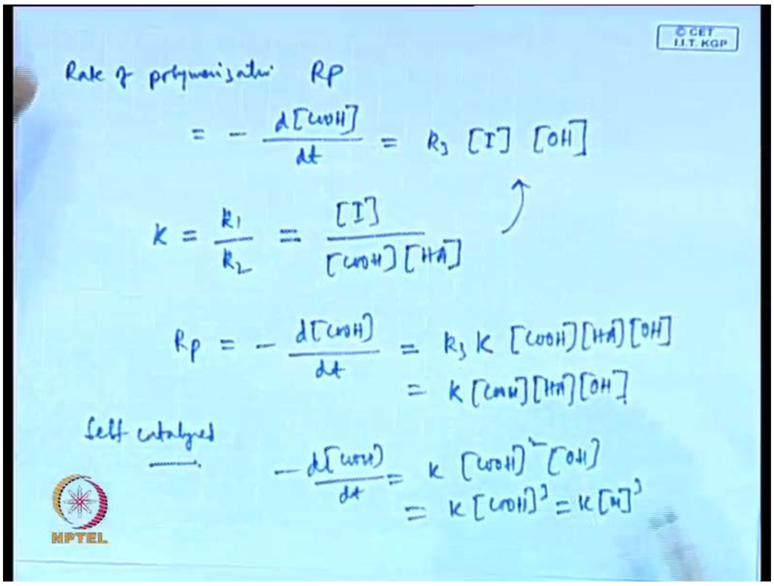

Rate of polymerization Rp

$$= -\frac{d[COOH]}{dt} = k_3\,[I]\,[OH]$$

$$K = \frac{k_1}{k_2} = \frac{[I]}{[COOH][HA]}$$

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

Self catalyzed

$$-\frac{d[COOH]}{dt} = k\,[COOH]^2\,[OH]$$
$$= k\,[COOH]^3 = k\,[M]^3$$

So, if I want a write a rate expression, rate of polymerization R p will be given by loss of acid group from the reaction; this is, we talked about this reaction. So, from this reaction you are getting the, this is 1. So, the rate of reaction is given by k 3 and the concentration product of this 1, and which 1 is this; number 1 is this. Now, from the first reaction, this one, we can write a equilibrium constant k 1 by k 2, is this 1 by concentration of COOH and HA; from this reaction, we can write equilibrium constant is this; concentration of this, divided by the concentration of this, and concentration of that.

So, I can, from this expression I can put the concentration I value to this expression, to get R p minus d COCH by d t, gives us k 3 K COOH HA and OH. I can write this as another constant OH. Now, we can consider two specific cases, where you have self catalyst; that means, you are not adding external catalyst, excess catalyst from outside; H is not, as said outside; the COOH groups present in the medium are acting as a catalyst; in that case, you can write this as K COOH square and concentration of OH.

Now, as you now that, most cases the reaction is carried out with the isometric amount of COOH and OH. So, you can replace OH by COOH concentration, which gives you this; and I write this as K M cube to make it simplified. So, M is concentration of either COOH or OH in this case, because both are used in isometric amount.

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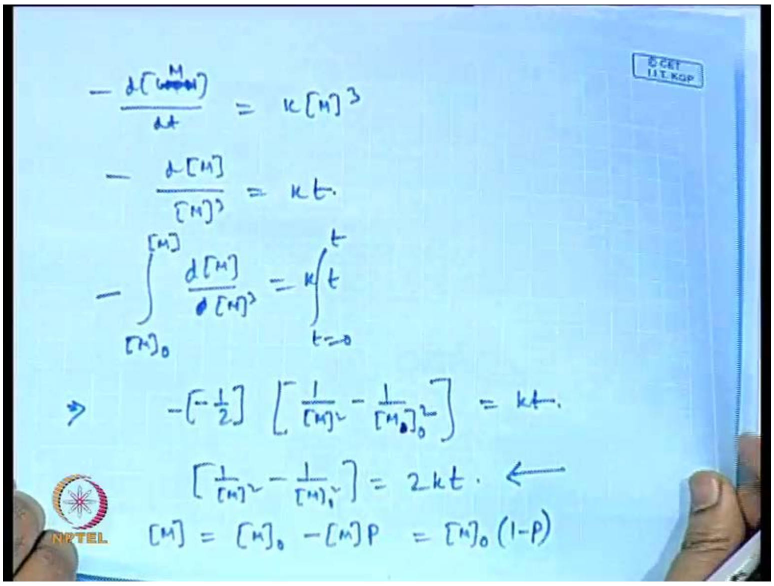

$$-\frac{d[\overset{M}{\cancel{\text{COOH}}}]}{dt} = k[M]^3$$

$$-\frac{d[M]}{[M]^3} = kt.$$

$$-\int_{[M]_0}^{[M]} \frac{d[M]}{[M]^3} = k\int_{t=0}^{t} t$$

$$\Rightarrow \quad -\left[-\frac{1}{2}\right]\left[\frac{1}{[M]^2} - \frac{1}{[M]_0^2}\right] = kt.$$

$$\left[\frac{1}{[M]^2} - \frac{1}{[M]_0^2}\right] = 2kt. \leftarrow$$

$$[M] = [M]_0 - [M]P = [M]_0(1-P)$$

So, I quickly integrate this expression, d CoOH by d t is k M cube; minus, this we can put M; minus M by M cube is k d t. I integrate from, at t is equal to 0, M is M 0, and at t is t, M is M, which leads you, minus, this minus here; minus of minus half 1 by M square, minus 1 by M 0 square is k t; or, 1 by M square, 1 by M 0 square is twice k t. Now, again, from definition of a conversion, we can write that amount of monomer present is, the amount of monomer present initially at t is equal to 0, minus conversion which makes this; and I am going little fast, but you can yourself go through it and understand no problem.

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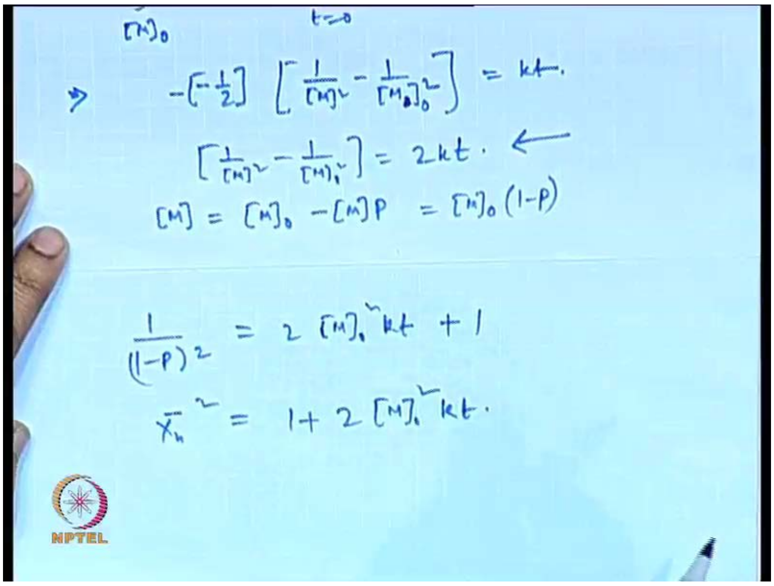

$[M]_0$ $\quad t=0$

$$\Rightarrow \quad -\left[-\frac{1}{2}\right]\left[\frac{1}{[M]^2}-\frac{1}{[M]_0^2}\right] = kt.$$

$$\left[\frac{1}{[M]^2}-\frac{1}{[M]_0^2}\right] = 2kt. \longleftarrow$$

$$[M] = [M]_0 - [M]P = [M]_0(1-P)$$

$$\frac{1}{(1-P)^2} = 2[M]_0^2 kt + 1$$

$$\bar{X}_n^2 = 1 + 2[M]_0^2 kt.$$

So, from this, I can now write; or, X n square, k t. Now, you can do yourself for an external catalyst reaction.

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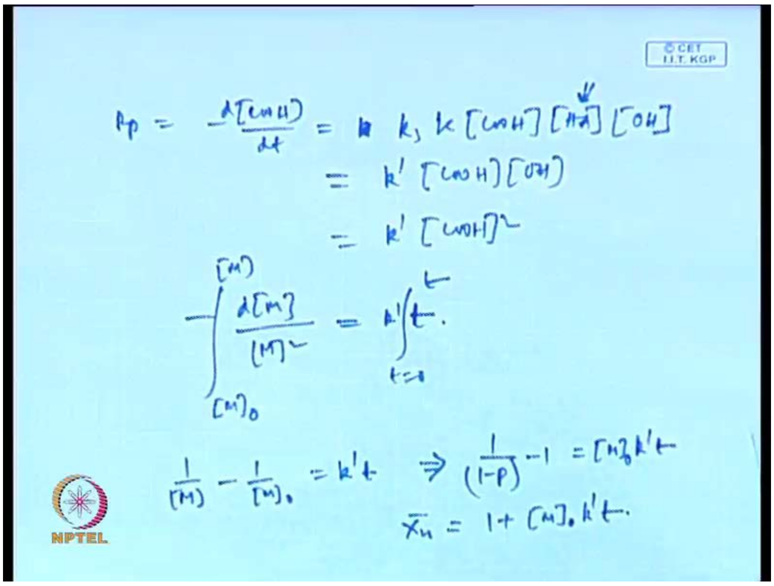

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$$R_p = -\frac{d[COOH]}{dt} = k_3 k[COOH]\overset{\Downarrow}{[HA]}[OH]$$

$$= k'[COOH][OH]$$

$$= k'[COOH]^2$$

$$-\int_{[M]_0}^{[M]} \frac{d[M]}{[M]^2} = k'\int_{t=0}^{t} t.$$

$$\frac{1}{[M]} - \frac{1}{[M]_0} = k't \Rightarrow \frac{1}{(1-P)} - 1 = [M]_0 k't$$

$$\bar{X}_n = 1 + [M]_0 k't.$$

We had the original rate equation R p is, d t is, k 3 k COOH HA and OH. Now, if this is added from externally; the concentration of this is 6. So, with this and this, you can take this; a new constant; put this. So, if this makes you, again COOH square. I can write, similarly, d M M square is t. Similarly, integrate form M 0 to M, t is equal to 0 to t; and you finally get, 1 by M minus 1 by M 0 we get as t, which will lead to 1 minus 1 by p minus 1 t; or, X n is 1 plus M 0 k dash t.

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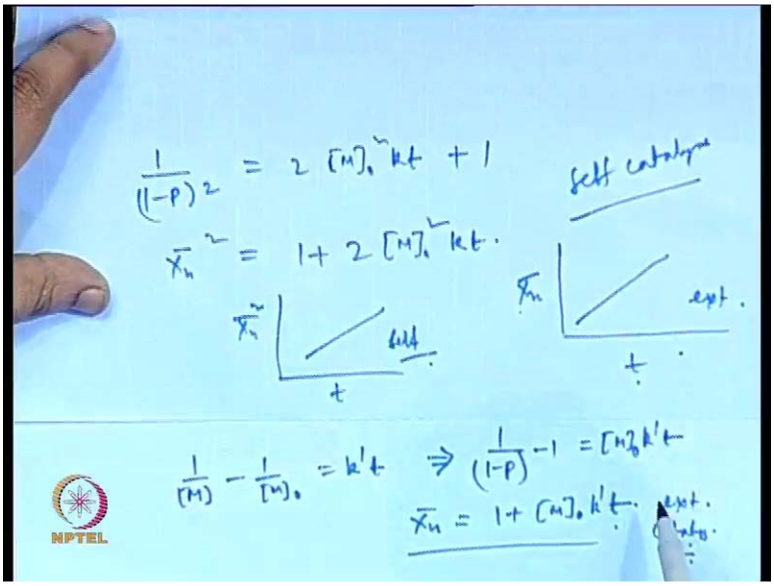

$$\frac{1}{(1-p)^2} = 2[M]_0^2kt + 1$$

$$\bar{X}_n^2 = 1 + 2[M]_0^2kt.$$

$$\frac{1}{[M]} - \frac{1}{[M]_0} = k't \Rightarrow \frac{1}{(1-p)} - 1 = [M]_0k't$$

$$\bar{X}_n = 1 + [M]_0k't.$$

Now this was for self catalyst, and this expression for external catalyst. See, if you can, you going to plot time with molecular width, in this case, for a external catalyst you get a straight line for X n by verses t plot; and in case of self catalyst you get, square verses t as a plot. As you can find out from this, to increase, if you increase the time, it is always, you get more increase in the molecular weight, when this is external catalyst. This was for external catalyst, this was self catalyst.

If you increase the time 4 times, the molecular weight also increases 4 times, in case of external catalyst. But if you increase the time 4 times, you are only double increasing molecular weight for a same catalyst reaction. That is a reason, it is always very difficult to get a poly conversion reaction by a self catalyst reaction, we always add, we always, typically in practice, we always add catalyst from outside.

Now, what we will do in next lecture is, we will take this, this two expression, and start from there in the next lecture. And we will talk about this plots, little more; and, how, what does it signify. And we will talk about the other aspects of step growth polymerization in next lecture. We will continue this step growth polymerization in the next lecture.