Principles of Polymer Synthesis
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Lecture - 06
Principles of Step Growth Polymerization

Hello and welcome back to this second week of classes of the NPTEL course on Principles of Polymer Synthesis. Just to recap what was discussed in the previous week we started with a discussion of the historical development of the polymer science and we emphasised upon the fact that polymers where known for a long long time, even in the early nineteenth century polymers were prepared except that the structure was not established. And not only that even as late as early 20th century people used to believe that it is the colloidal aggregates association of small molecules that is actually responsible for the all the properties of the polymers. For example, the high melt flow or high melt viscosity or you know material which sometimes you cannot crystallize those kinds of properties.

So, they used to believe that this is the reason and as we also had told that rubber used to be believed to be composed of cyclooctadiene dimethyl cyclooctadiene monomers, they were actually having interaction with their double bonds with the all these units together and that was what was believed.

So, then in came Dr Harmann Staudinger in the early 1920's and he was the person who coined the term macromolecules mind it he did not coin the term polymers, the term polymers was known from 1833 that was actually coined by Berzelius.

So, it was Hermann Staudinger who introduced this term macromolecule. And we have discussed about the resistance that he had to face from the scientific community, because crystallographers actually believed, that these kind of long molecules if the light house because it is actually believed that this kind of long molecules if they actually crystallized. How this full molecule can be incorporated into a small unit cell, but later on it was established by Staudinger and other scientists the crystallographers themselves, that the full molecule does not need to be incorporated into the unit cell a part of it will do.

So, those kinds of studies were done and that was the discussion of the first class and afterwards we had a discussion on the classification of polymers based on their structures, based on their mechanism, based on their properties, and also based on their sources. And then the discussion moved to the molecular weight of polymers and we emphasize the fact that molecular weight is very very important thing that you need to characterize for the polymers and different average molecular weights where introduced and some of the main techniques where discussed.

And you will see that we have not discussed all the techniques that will be the Moto that will be the theme of this course all throughout that whatever the basics some of the most important things that will be discussed and not all the detailed different aspects of say for example, we talked about molecular weight determination, average molecular weight weight, average molecular weight.

We talked about light scattering we did not go into details we talked about GPC where we discussed things in details. So, certain things we will discuss in as much detail as possible in a very simple and you know basic way. So, that will be the theme of this class all throughout.

So, this week we are going to start with the topic principles of step polymerization. So, if you recall when we classify the polymers on the basis of structures, we could say they are addition polymers or condensation polymers or on the basis of the mechanism of formation of the polymers, we could say they are step polymers or chain growth polymers.

And briefly we discussed what are step polymers or step growth polymers or step growth polymerization process and what is chain growth polymerization very briefly, but for now we will shift our attention completely to step growth polymers and later on we will come to the chain growth polymerization and the comparison of that will be also discussed in more detail probably. So, let us then start with step growth polymerization.

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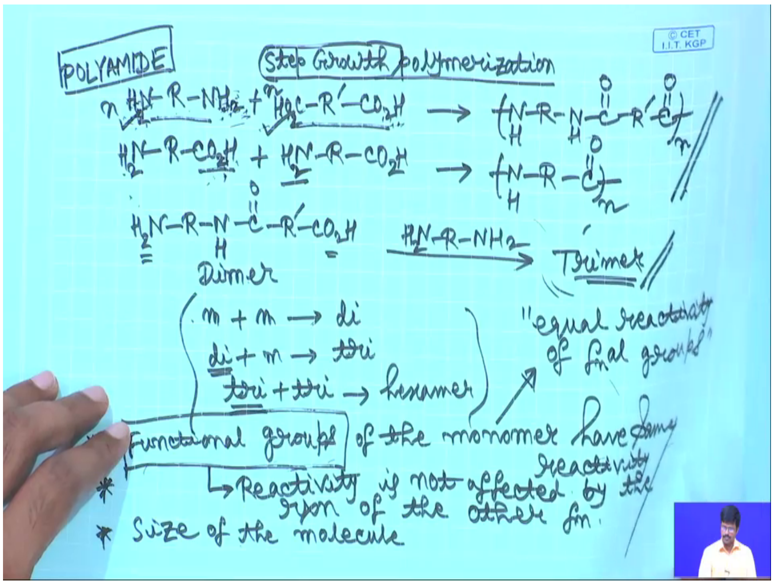

The reason it is called step growth is because it is basically you know monomers, which have more than one function and this functionality is they are reacting among themselves either they will belong to one monomer or they will belong to different monomers we will explain in a short while and this reaction between different functions that happens in a stepwise fashion. So, what do we mean by that?

So, what we can have is for example, we can have a monomer say we can have a monomer like this a Diamine R is some generic term it may be an alkyl group or you know long alkyl chain may be some aromatic units or whatever. And let us say we are trying to create a polyamide also the reason why we will study the step growth, in detail is many important industrial polymers are prepared through step growth polymerization same is also true for chain growth polymerization processes.

So, for example, first when you are applying step growth principle you can synthesize polymers such as polyethylene terephthalate which is polyester or you can synthesize you may know about the name nylon it is a household name I would say. So, those are a class of aliphatic those are actually class of polyamides which are aliphatic polyamides. So, those are synthesized to step growth polymerization or for example, this phenol a carbonate. So, those kinds of poly carbonates also those are also polyesters those are also synthesized by step growth polymerization.

Let us say we want to synthesise a polyamide. So, in that case what we can do is that we can take a bifunctional or we can take a more than bifunctional polyfunctional monomer. So, this monomer has both the functions same now amide formation is between amine and carboxylic acid that is the reaction. So, what you can have is that you can have a bifunctional monomer like this both the functions of the same and you can have a bifunctional monomer like this.

So, you have a Diamine and you have a diacid and when they react they will form a polymer which has a repeat unit something like this something like this or what we can have also is that in the same monomer. So, basically you are reacting a function amine this amine function you are reacting with carboxylic acid function. So, this is basically then the reaction between different functional groups or what you could have is that the same molecule could contain both the functions.

The same molecule could contain both the functions and then what will happen is that the, this molecule if you take. So, the functions will react among themselves between different molecules so in this case. So, you can have something like this. So, it is a same molecule is actually reacting it can be also called as self amidation. So, this carboxylic acid can react with the amine so on and so forth and then you will have a repeating unit which resembles something like this, say n number of units that is what I am just writing down if it is n molecules of this and N molecules of this.

So, that is in a sense the point of step polymerisation, that you will have reactions between different functional groups and those functional groups could be present in the same molecules same monomer or they could be present in different monomers. And, not only that the reaction will progress in a stepwise fashion which means that the functional groups will engage with themselves in a stepwise fashion.

So, maybe this monomer reacts with this monomer initially to create something like this. So, you will have N H C O. So, you have an amide unit now R prime C O 2 H. So, it is a dimer now this dimer you have a carboxylic acid here you have an amine here, this could also now react with another molecule of let us say amine on this site and it can form a amide bond here then what you will have is a trimer I am not drawing the structure you can work it out yourself.

So, like this step wise the molecular weight of the product will develop. So, this Trimer can reactivate with another dimer or it can react with monomer itself. So, what will happen is that very soon in the reaction process most of the monomer will be consumed and you will have different kinds of you know oligomers different kinds means the number say for example, you have trimer tetramer pentamer decamer so on and so forth. All these things will be present and the molecular weight will develop slowly, only towards the end of the reaction; that means, when you are achieved a very high conversion you will have molecular weight of any practical importance.

So, when we say molecular weight of practical importance we say at least you know 4,000 at least you should have a minimum molecular weight say for example, you can have 4,000 5,000 because if you remember the property versus molecular weight graph that we have drawn in the in the previously week, you will see that the properties will develop slowly and you need at least a minimum molecular weight in order for the properties to become you know significant in practical terms.

But the question then is that. So, it the molecular weight will be high you want high molecular weight, but what do you mean by then control of molecular weight. I mean then you would like to have as high molecular weight as possible is that the Moto, actually that is not the Moto the Moto is you want high molecular weight. So, that the properties that you want they will be manifesting themselves in a practical way significant manifestation.

And you want you know a range of molecular weight say very as much precise as you as you can be you want to be. So, you do not want to be having a molecular weight higher than that why because if you want to go as high as possible what can happen is that the process ability may be affected the melt viscosity may become so high that you cannot process the polymer. So, that is very important to understand. So, you have you a molecular weight in mind you want a certain molecular weight and you want to be as close to that as possible.

So, if you are looking towards that kind of situation, what you have to do is that you have to analyse the kinetics of this reactions because if you can analyse the kinetics then only you understand the principle fully the mechanistic aspects of that fully and then you know how you can control the molecular weight. And you will see that at least 99 percent of conversion is necessary from the monomers in the step polymers step polymerization. So, as to have polymers of any practical significance; that means, the molecular weight will be much much low.

If you are say you can have 95 percent conversion 95 percent 96 percent conversion maybe very good when you are reacting small molecules and preparing small molecules in your simple organic reactions simple organic transformations, but say 90 percent a conversion of 90 percent is a disaster in step polymerisation, because you will have very very low molecular weight polymer we will discuss all these things. So, you need to go beyond 98 percent of conversion and you have to go sometimes beyond 99.5 percent so on and so forth in order to have high molecular weight high enough that will meet your purpose.

So, to understand all those things the first thing you should do is to try and analyse the kinetics of these reactions. So, if you look at these reactions you know I am just drawing a symbol like this m is your monomer. So, at any time you have to actually analyse all these reactions that monomer will react with monomer to generate may be a dimer, now this dimer can react with a monomer to create a trimer. Trimer could react with another trimer to create hexamer and again this trimer can react with dimer to create pentamer so on and so forth.

So, all these reactions are according and all the species will be present in different amounts of course, at any point of time. So, you have to then take into account all these reactions when you are trying to analyse the kinetics which is a herculean task in order to simplify our analysis what we have done is we have made certain assumptions say, what are the kinds of assumptions we have made. So firstly, the functional groups functional groups of the monomer have same reactivity what do you mean by that I will go back to the same reaction say you have a monomer which has both the functional groups are same. So, when I say functional groups of the monomer has same reactivity all I am saying is that the same kind of functional groups, because your monomer can have both amine and carboxylic acid they obviously do not have the same reactivate.

So, if you have say for example, a Diamine which is a monomer both the amines have the same reactivity, if you are making an aster polyester then you are reacting a diacid with a diol instead of any history of O H both the O H they have the same reactivity and both the C O 2 H they have the same reactivity in the monomer.

Second thing is that the reactivity of these functional groups is not affected by the reaction of the other function what; that means, is that suppose you have a Diamine and you are reacting with a di carboxylic acid. So, first assumption says that both the amines have same reactivity, second assumption says if one of the amines have reacted the other amine will still at the same reactivity. So, the reactivity of the other amine will not be affected by the reactivity of the by the fact that this amine has already reacted.

And the third thing is that this reactivity of the functional groups will not depend on the size of the molecule what; that means, is that. So, at any point of time you will have all these species which has amines which has carboxylic acids let us take an example of only polyamide say and explain all through with this we stick to this particular reaction.

So, what will happen say you have say a hexamer you have a decamer or maybe you have an nmer, where N is maybe say 50 and say you have an amine at the end of that nmer and another side you have carboxylic acid.

Now, that amine the reactivity of that amine will be the same as the reactivity of the monomer. So, just because the size of the molecule has become large it will not affect the reactivity of your functional group that is an assumption. Now all these assumptions you can actually say this is basically called as an assumption of equal reactivity of functional groups that is the assumption equal reactivity of functional groups.

So, you might very reasonable ask this question is this actually true when you increase the size of the molecule does this not affect the reactivity of the functional group it should affect maybe it should decrease the reactivity of the functional group. Actually experimentally it has been shown that that is not the case and people usually believed that the reactivity is affected, because for some other reasons whatever the reasons might be the polymerization was not progressing at the rate that they want we will also discuss one or 2 points that will relate to this particular aspect a little while later.

So, let us take of course, whatever I am going to draw here is not generated by me this is an experimental result that just validates this particular statement of equal reactivity of the groups more precisely that the reactivity of the groups does not change with the size of the molecule. So, let us say you consider a reaction such as this small molecule.

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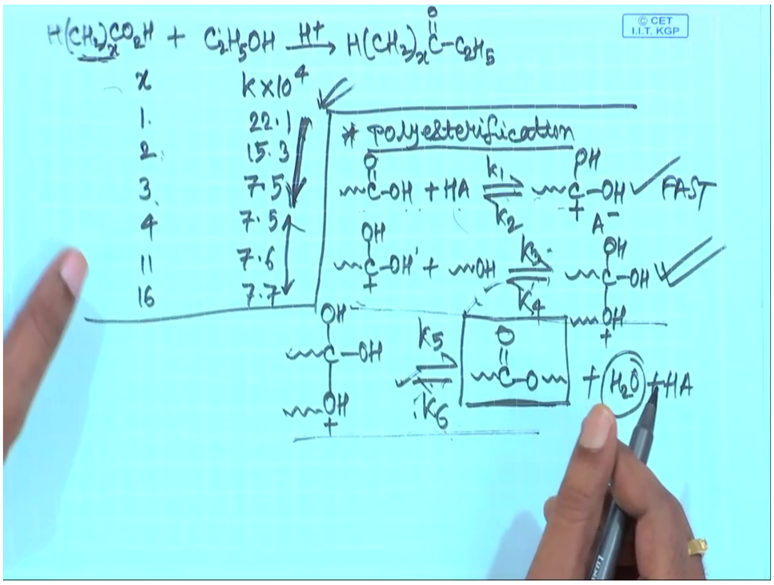

So, you have a carboxylic acid like this and you are reacting with say ethanol I mean for this reaction only the experiments the data are there in presence of an acid acid catalysed esterification reaction and you are making your product which is an ester C O O C 2 H 5.

Now, this particular reaction so I am going to draw a table here. So, this is a homologues series of carboxylic acid this reaction. So, if you have a table x versus k k is the rate constant for this reaction. So, k is the rate constant k into 10 to the power 4 because the value is small. So, you just multiply by 10 to the power 4 and scale accordingly. So, let us say x is 1. So, you have 1 C H 2 unit here than your k into 10 to the power 4 is 22.1, if it is 2 then it is 15.3, if it is 3 7.5, 4 7.5, 11 7.6, 16 7.7.

So, you will see that initially when you are increasing the size of this C H 2 from 1 C H 2 to 2 C H 2 to 3 C H 2 the effect is enormous the reaction rate is dropping rate constant is dropping enormously, but just after first few units here after that this affect is this situation is stabilized. So, after a certain size of this group is reached the rate constant of the reaction is no longer affected much or significantly by the size of the molecule.

So, this is one of the proofs that tells you that basically the functional group reactivity does not change significantly with the size of the molecule, I mean some of these assumptions will breakdown in case of special reactions, we will not discuss those we will discuss in general for many of the step growth reactions this is the truth that this principles are actually followed and this principle of equal reactivity of different groups will work for many reactions it will not work. For example, if you have already reacted one of the functions you have a Diamine say one of the amines you react it might affect the reactivity of the other amine in some cases there you should have special treatment those treatments we are not going to cover here .

So, now with this principle of equal reactivity let us proceed to try and analyse the kinetics of this particular reaction let us say we will take a Polyesterification reaction, we will try to analyse the kinetics this assumptions actually simplify our treatment. So, in a generic way let us draw out the reaction. So, you have the carboxylic acid and these reactions can be catalysed by acid. So, let us say H A is your acid.

So, these are typically reversible reactions k 1 and k 2 are the rate constants of the forward and backward reaction. So, you will have something like this this species and you have a minus, now these species these species can react with your alcohol now when I am drawing this lengthy line; that means, it may not be your monomer it can be some kind of oligomer or polymer which has an O H at the end of it and that is reacting with this intermediate. So, this is k 3 and k 4 and you have C O H O H O H plus this intermediate and in the final step what will happen is that this, will produce a product like this here one ester here and then you will have water produced and you will have acid generated acid is your catalyst it is generated back at the end.

Now, when you look at this particular reaction it has all this reversible sign here. So, these are typically you know equilibrium reactions and in order to have a high yield of the product what is essential is that you remove this water as it is produced, because then you can shift the equilibrium towards the product site. So, you should be keep removing water and then when you are doing that essentially this second step and this last step they become irreversible they can be treated as irreversible. So, k 4 is much smaller than k 3 and k 6 is much smaller than k 5. So, they can be essentially treated as irreversible reaction the fast reaction reaction between you know this protonation your carboxylic acid and this acid this protonation is a very fast reaction and it is a reversible reaction, but the other 2 reactions could be regarded as for all practical purpose purposes it can be regarded as irreversible reaction.

So, now what you can do is that you can follow the rate by simply looking at or following the disappearance of carboxylic acid the rate at which it disappears you could actually tighted it with a standard concentration with a base of known concentration and then you can see how it is disappearing. So, that is the rate of the reaction.

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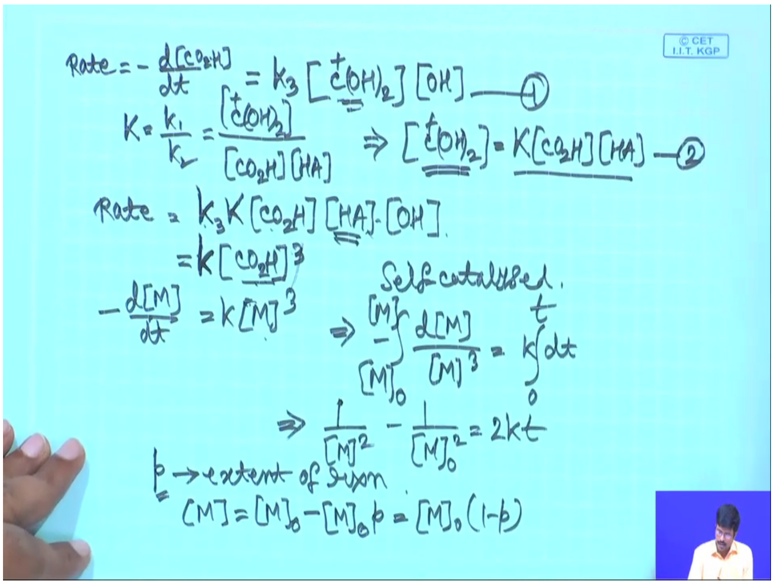

$$\text{Rate} = -\frac{d[\underline{CO_2H}]}{dt} = k_3[\underline{\underline{\overset{+}{C}}}(OH)_2][OH] \text{ — ①}$$

$$K = \frac{k_1}{k_2} = \frac{[\overset{+}{C}(OH)_2]}{[CO_2H][HA]} \Rightarrow [\underline{\underline{\overset{+}{C}(OH)_2}}] = \underline{K[CO_2H][HA]} \text{ — ②}$$

$$\text{Rate} = k_3K[CO_2H][\underline{\underline{HA}}]\cdot[OH].$$

$$= k[\underline{CO_2H}]^3$$

Self catalysed.

$$-\frac{d[M]}{dt} = k[M]^3 \Rightarrow -\int_{[M]_0}^{[M]} \frac{d[M]}{[M]^3} = k\int_0^t dt$$

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

$\underline{\underline{p}}$ → extent of rxn

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

So, the rate of the reaction is then minus. So, rate of disappearance of your carboxylic acid. So, that is the rate of disappearance of carboxylic acid and let me go back to the previous script. So, here you have to actually look at what is the rate determining step and that will govern the reaction rate the second step is actually, the rate determining step the first the first step is very fast it is not rate determining the slowest step in all the multi-step synthesis is the rate determining step this step is the rate determining step. So, so what you then have to do is follow this and draw the expression of the rate and that will be then equal to your k 3. So, this is k 3 k 3 into this intermediate let me draw it like this for the sake of convenience into O H alcohol.

So, this is the thing, but this is an intermediate and you do not always measure the concentration of these things. So, you have to replace this with more; more you know convenient quantity with a more convenient concentration.

So, if you look at the first reaction this is an equilibrium reaction k 1 and k 2 they are related by the equilibrium constant. So, for this particular reaction then you can write equilibrium constant for this reaction k is equal to k 1 divided by k 2 and that is equal to your C O H whole 2 plus concentration divided by C O 2 H into H A.

So, from here you can have an expression of this term and that term becomes equal to capital k into concentration of C O 2 H into concentration of H A so equation 2 equation 1. So, if you replace this term C O 2 H plus here by this expression then your rate becomes capital to k 3 into capital k C O 2 H h a into O H.

Now, what you can do is that this k 3 and k you can club together in A constant this K is capital this is small k. So, let us club together into a into a constant small k and then C O 2 H, now let us say you are taking equi molar quantity of the starting materials then C O 2 H and O H the concentrations at the same. So, basically you can say this is C O 2 H whole square and let us say you are not adding any acid from outside. So, that the reaction is basically self-catalysed; that means, your starting acid itself is catalyzing the reaction then this H a can be replaced by the concentration of C O 2 H. So, that will be then C o 2 H whole cube. So, if the concentration of the monomer is instead of this you just put M concentration of the monomer then this rate can be written as minus d M d t equal to k M cube M is the concentration of the monomer, which will be equal to the concentration of carboxylic acid groups which will be equal to the concentration of hydroxyl groups.

The starting materials because both of them are equimolar quantity that is what the our assumption is to simplify this matter which is M, let us say and this is a self-catalysed reaction we are now talking about a self-catalysed reaction. So, if you put this M here and you integrate so you integrate from M 0 initial concentration of the monomer to the final concentration of the monomer minus d M by M cube equals to k d t. So, you do the reaction from time 0 to time t and then if you integrate and afterwards organise this thing then what you will get is something like this, let me draw this thing out here M square minus 1 by M 0 square. So, if you put it like this self-catalysed reaction that will be equal to 2 k t.

Now, let us say p is the fraction of the starting monomer functional group that has reacted. So, you can actually say p is the extent of reaction p is the extent of reaction. So, p being the extent of reaction that is related to M by this your m the final concentration of the monomer is equal to the initial concentration of the monomer minus how much has reacted which is your m 0 into p. So, that becomes equal to M 0 into 1 minus p. So, if you replace this M by 1 minus p here and rearrange this thing M 0 square will come there then finally, what you will get is this expression 1 by 1 minus p whole square is equal to 2 M 0 square k t plus 1 2 M 0 square k t plus 1.

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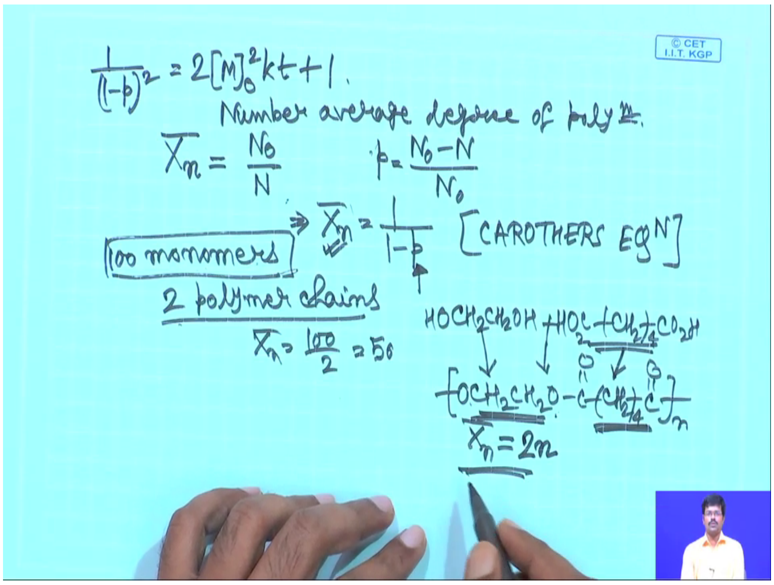

$$\frac{1}{(1-p)^2} = 2[M]_0^2 kt + 1.$$

Number average degree of polyᵐ.

$$\overline{X}_n = \frac{N_0}{N} \qquad p = \frac{N_0 - N}{N_0}$$

$$\Rightarrow \overline{X}_n = \frac{1}{1-p} \quad \text{[CAROTHERS EQ}^{\text{N}}\text{]}$$

$\boxed{\text{100 monomers}}$

2 polymer chains

$$\overline{X}_n = \frac{100}{2} = 50$$

$HOCH_2CH_2OH + HO_2C{-}(CH_2)_4{-}CO_2H$

$$\left[OCH_2CH_2O{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_4{-}\overset{O}{\overset{\|}{C}}\right]_n$$

$$\overline{X}_n = 2n$$

Now, is the time to introduce another concept which is very very important for our analysis here number average degree of polymerization number average degree of polymerization, which is denoted by x n bar. Now number average degree of polymerization is nothing, but the average number of structural units that are present per polymer molecule. So, basically this is nothing, but N 0 by N, where N 0 is the total number of molecules to start with N is the total number of molecules that are present after time t.

So, if you are doing a step polymerization reaction initially you have 2 monomers. So, when you are doing the reaction for a time t you may have some monomer some dimer some trimer whatever. So, everything is being considered within this degree of polymerization and with respect to that you will divide that. So, n 0 is the initial total number of molecules actually they are the monomers n is everything that is present the total number of all those molecules after time t and this ratio will give you the average number of structural units per polymer chain.

In this case it is also considering it is a dimer trimer in this particular situation because dimer trimer all this things can be present at a time t, all those things will be included in the summation when you are calculating the value of N. So, this is N 0 by N.

Now, if you consider the fact that p is related to N and N 0 by this 0 minus N by N 0, because this is the extent of reaction. So, N 0 minus N by N 0 and then if you replace that here what you will get is that your x n becomes equal to 1 divided by one minus p which is nothing, but Carothers equation that relates the average degree of polymerization number average degree of polymerization with the extent of reaction.

So, if you are looking are 0 chains let us say you do not any monomer left then it becomes easier for you to understand, but even if you have monomers left the principal is the same 100 monomers unit and then finally, you have only 2 polymer chains. So, what is the average degree of polymerization that will be hundred divided by 2 equals to 50? So, you have basically 50 monomer units per polymer chain.

So, if you are reacting say ethylene glycol ethylene glycol with adipic acid and then you have this kind of repeating unit C H 2 C H 2 O C O polyester C H 2 whole 4 C O like this.

Now, here what is the value of x n each repeat unit is actually containing 2 structural units? So, this is a structural unit that is donated by one monomer, this is another structural unit that is donated by other monomer. So, each repeat unit this is one repeat unit it contains 2 structural units. So, you have total n number of repeat units. So, your average degree of polymerisation is nothing, but 2 n.

So, I think our time is up for the day in the next class we will continue from this derivation where we left it. And then we will derived the full kinetic expression and try to understand the significance of that in our further understanding of the polymerization step polymerization.

Thank you.