**Science and Technology of Polymers**
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**Lecture - 5**
**Principles of Polymer Synthesis**

Today we shall the start basic principles of polymer Synthesis.

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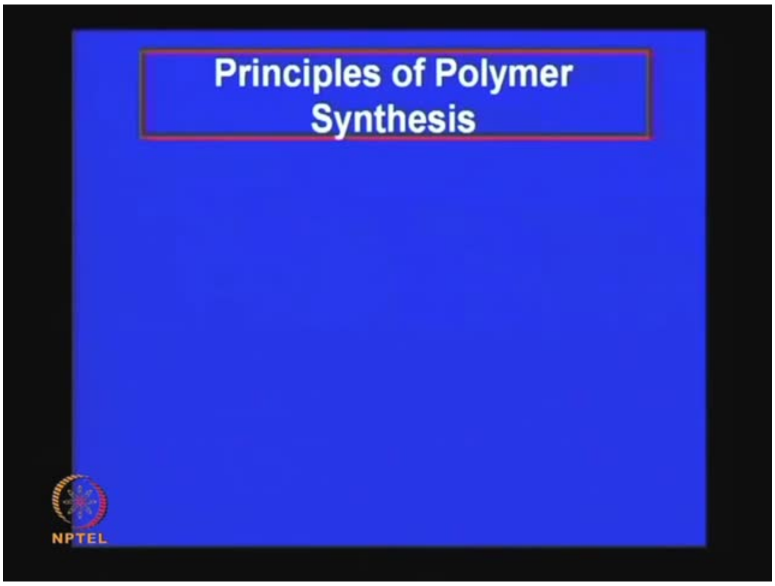


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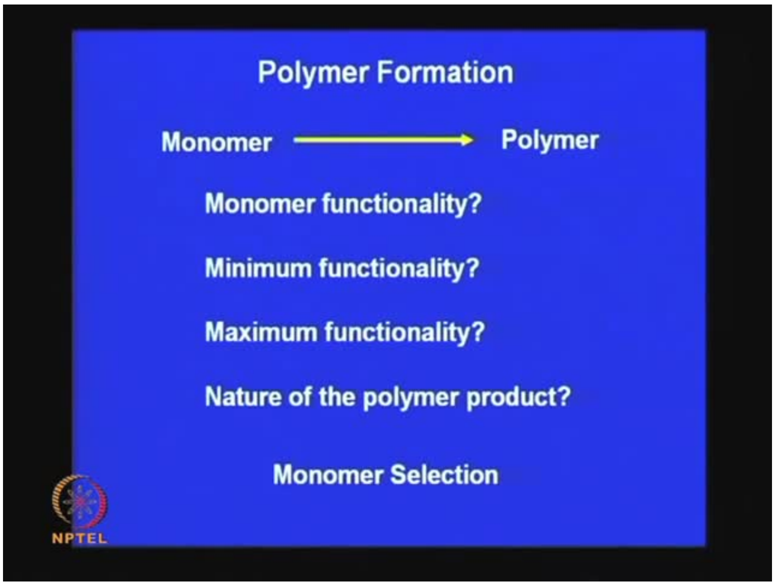

For any targeted polymeric product, we need some polymer raw material. Polymer has raw material and that polymer is converted to product by mixing it some functional additives. I have already mentioned this aspect to you in my last lecture. Now, we will concentrate our attention to the manufacture of that polymer as raw material or polymer raw material. That means the virgin polymer material, pure polymer material from its monomers. There are various principles which are followed for the manufacture of such polymers and you have seen from the classification scheme that, there are condensation polymers.

There are addition chain polymer you have seen because those condensation polymers or addition chain polymers are straight polymers, which are manufactured by following certain principles of synthesis. Here in this slide you see, monomer in general it is to be converted to a polymer. This is small molecule, this is macro molecule. Then in order to conversion of this monomer to polymer there are certain requirements; that requirement, the first and for most requirement is the functionality means, number of reactive functional groups or sides available in the monomer, then only we can converted to a polymer of large monocular weight, large monocular size.

Then what is that functionality? What is the minimum functionality required for getting a polymer? We can have a chemical compound whose functional group may be 1. Is it polymerisable to a high molecular weight product? No, so minimum requirement of functionality is 2, at least two sides should be there, then only with the help of those two reactive sides it can link up with one another, for being a very big macro molecule known as polymer materials.

Then, if there is minimum functionality of 2, then what is there any maximum requirement of functionality? Can it be 3, can it be 4, can it be 5? Yes, it is possible to have 4 or 5 or 3 reactive functional sides on a molecule, then what will happen to the polymer, structure, polymer product or what kinds some conditions are necessary to convert those poly monomer molecules having more than 2, 3 function groups leading to a polymer, those things would be considered.

Why I am telling these things? Because you would be may need to synthesize a new polymer may need to design a new polymer from a new monomer, so you have to concentrate your attention to the various functional groups present over there. How many function groups are present over there? Say for example, if the functionality more than 2, what will happen? If the functional sides are 2, then it is a bi functional monomer; it will lead to a linear macro molecular chain. If there is a third functional group, what will happened?

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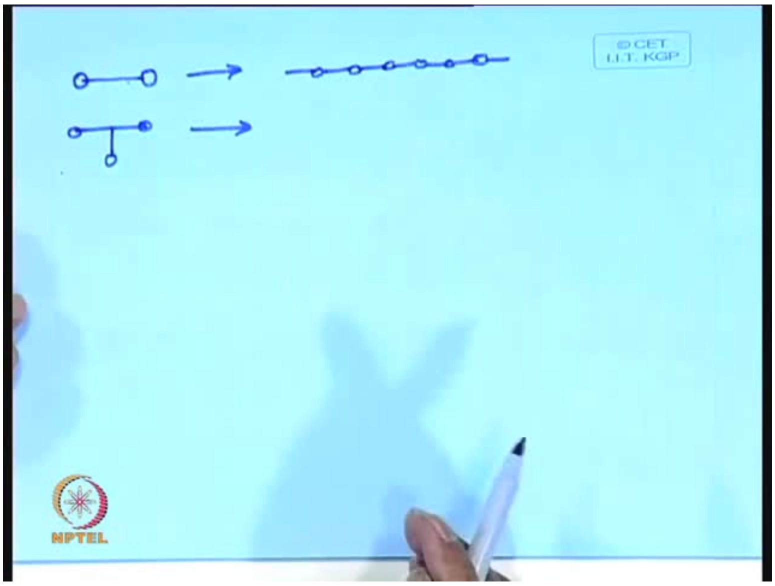


Suppose, this is a molecule having one functional group here another functional group here, so it will lead to a polymer like this, joining at this functional sides leading to a macro molecular chain or you can have molecule like this. All they are reactive, of course these the nature of this function group is different from the nature of this function group, otherwise can react. Say diode cannot lead to a polymer, but a hydroxyl alcohol sorry, hydroxyl acid link a polymer like that.

So, a tri function monomer in which one may be carboxyl group, another may be hydroxyl group and this may be again a carboxyl group. We go on thinking how to got might happened? Tri functional or you can have a tetra functional monomer, you can have a penta functional monomer. So, pentaerythritol of those who have this chemistry background, you know the formula of pentaerythritol. You know the formula of glycerol, that is also an alcohol. If you react glycerol with thalegon ndroid, what will be the nature of product?

What will happen during polymerization? So, these things will come cross casually and you will see, so we have to looking to the nature of polymer product looking at those points, they have to go for a proper selection of monomer before synthesizing a polymer. First of all you have to select, what polymer we are going to synthesize, a polyester or polyethylene? If you have to need a polyester, if want to have a polyester, then we should select a principle for step reaction polymerization involving some monomers, which will lead to an extra functional group up after reaction between the reactive function groups, all right? So, polymerization principle you know already, the step reaction principle I have explained, what is straight reaction principle, because these polymer synthesis involving reaction between a carboxyl group and hydroxyl group or a carboxyl group and amino group leading to ester or amide group.

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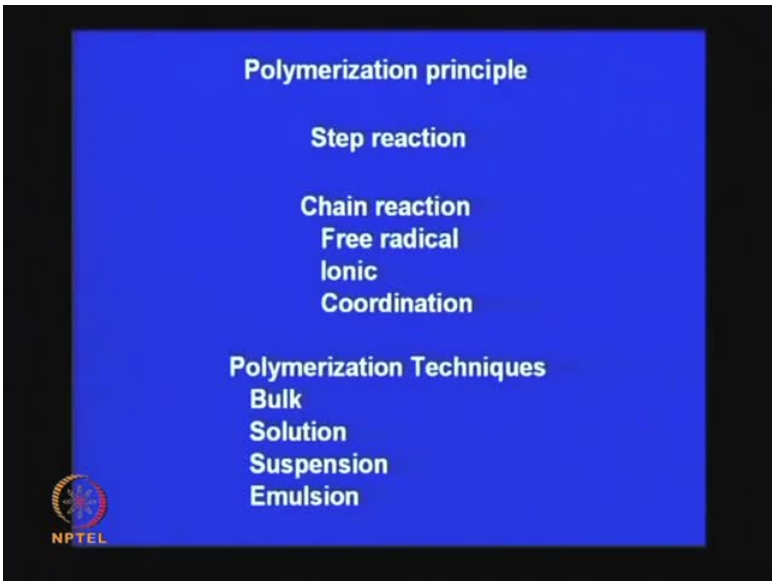


So, leading to polyester or polyamide and I mentioned that these occurs in steps means first of all 1 diol reacts with a diacid to form an intermediate, that inter mediate while react with either 1 diol molecule or 1 diacid molecule or both. So, this way you will have several numbers of intermediate compounds known as dimer, trimer, trettamer, pentamer, hexamer like this. So, those occur in steps that is why these polymerizations principle is known as step reaction principle. Yes, your question please.

Student: (( ))

Yes.

Student: (( ))

Diol and diacid you should also take a diol.

Student: (( ))

Look at this.

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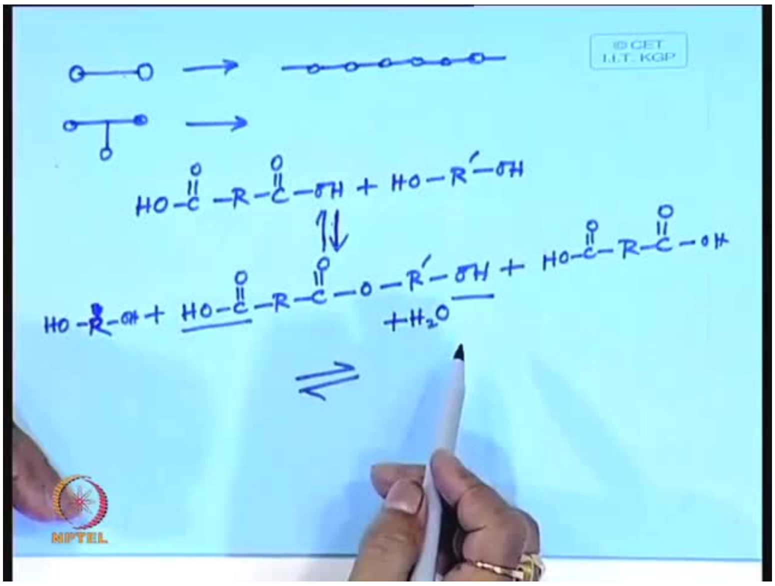


What is this? Diacid. What is this? Diol. So, it will lead to this is intermediate at these end and acid group and these set is a alcohol group. So, these will further react at this side with one acid functional group. These sides will react with an alcohol functional group, I am sorry I am sorry, all right? So, this intermediate has a capability of reactive with 1 diol molecule at one side, 1 acid molecule 1 diacid on the other side. So, this way it will continue to go on increasing the length and these reactions occurs in so many different steps. You know these esterification reactions or emitification reactions, are all equilibrium type reactions, the state in equilibrium after certain progress. So, equilibrium means?

Student: (( ))

That means the product can revert back to the reactants. That means there is a dynamic equilibrium between the reactants and the product, until and unless some of the products or any of the products are removed from the reaction mixes. That means you have to break the equilibrium by removing the reaction product. So, in this case some water molecule is produced as a byproduct. If that water molecule is remove from that reaction chamber, reaction medium, then this reaction will proceed towards the forward direction breaking equilibrium.

This is a principle you know, otherwise you cannot get the growth of progress of reaction, you will not get product until and unless you break the equilibrium equilibrium. Anyway this is straight, the nature of straight reaction polymerization and there are other principles, chain reaction polymerization, which can occur through free radical mechanism free radical mechanism or ionic mechanism or coordination reaction mechanism. Apart from this actually this we have various, we have to follow various techniques of polymer manufacture; bulk, solution, suspension.

That means polymerization in bulk polymerization in solution, bulk means without using any solvent polymerization. In solution means it dissolve the monomers in a suitable solvent, apply sufficient and necessary conditions, necessary and sufficient conditions, it will start polymerization and continue. Finally, you isolate the product and purify and product is a polymer. Then emonsons are polymerization technique and suspension polymerization technique. There are other techniques like sy, interfacial polymerization technique. If possible I will discuss little detail later.

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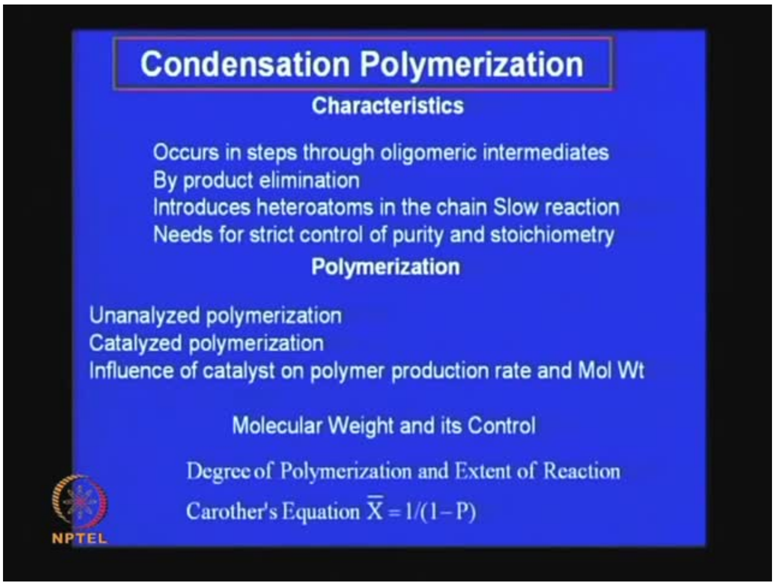


Actually I find there is certain changes that has occur during this copying and transferring this file from one computer to the other computer, there are something missing here. Now, let us concentrate our attention to this principles of condensation polymerization. As I mentioned earlier let us looking to the characteristics of this condensation polymerization. Once again I am telling, this condensation polymerization occurs in steps through oligomeric intermediates, oligomanse oligomeric means, oligo means small.

Smaller intermediate products, oligomeric intermediates, then there is a byproduct elimination. It introduce introduces heteroatoms in the polymer chain, it introduces some heteroatom in the polymer chain.0 The reaction is slow polymerization reaction is slow, polymerization reaction is slow. It is take long time to complete to get a product, polymer product. One most important parameter is, this kind of straight reaction polymerization, poly condensation reaction needs a very straight control of purity and reaction stoichiometry.

Stoichiometry I mean, here you see you are taking these monomer diacid monomer and this diol monomer, then what is the molar ratio or mole ratio of this monomers? It implies a for this particular case, it involves 1 mole of diacid with 1 mole of di alcohol, diol. In paper we are writing, but in real situation when you will be ask to synthesize a polymer using certain quantity of 1 mole of diacid and 1 mole of dialcohol, what you will do? You will calculate the molecular weight of these two compounds, then you have to way the amounts corresponding to one mole of each.

Then mix these two reactance in presence or absence of solvent. Apply polymerization conditions and it will start polymerization. But while you were weighing this two reactance, you have to be ensured that these react reactance are perfectly pure. Means having 100 percent purity, these diacid and diol. These are chemical compounds, so you have to know the purity level of these things. If they are not 100 percent pure, then the amount you are viewing can it be one more exactly. No, so there be certain something wrong ox, wrong amount you are taking.

So, there is no strict control of the ratio of the mole ratio of these two reactance, this ratio is called stoichiometric ratio, stoichiometric between the reactance. This is a problem in condensation polymerization. What will happen, you will see later. You will see if there is some impurity or if there is a mistake during viewing of this two reactance, then you may not get a polymer of high molecular weight. Those who will be doing lab class for synthesis of phenyl and formaldehyde or synthesis of other polymers, you will see may or may not get a polymer.

If you do not get polymer, then you have to enquire there is something wrong in weighing or some some impurities are there. So, you have doing very much careful, so you have to control, you have to ensure that these are pure as well as going you are taking the bites, the bites must be take in a right proportion. Then you go for polymerization. Now, when you go for start polymerization or when you going to, you go to start the polymerization. What is happening? There is something wrong, is should be un catalyzed polymerization. There is un catalyzed polymerization, there is un catalyzed polymerization here it is written unanalyzed polymerization. I corrected it, I do not know, somehow this wrong file has come.

Un catalyzed polymerization and catalyzed polymerization. Polyester synthesis it needs a catalyst. What are the catalysts? Sulphuric concentrated, a sulphuric acid, para toluene toluene sulphuric acid, fluoro sulphuric acid etcetera, any strong acid you have to take as a catalyst for this polymerization. Even you can do this polymerization without using any catalyst, provided if it is polymer verification reaction or polyester verification reaction, because one of the reactance is acid, so one of the reactance can perform as catalyst also, that we will see.

Then influence of catalyst on polymer production rate and molecular weight. Is there any influence of catalyst, on the production rate of the polymer? How fast it will be produced or not? We have to see with the theoretically calculate. Then this control of molecular weight; so in this molecular weight control you will see, what is the value of degree of polymerization that could be achieved after the polymer product is accelerated? You have to assist that you have to find out, you have to evaluate that. What is the extent of reaction? Means what is to, what percentage of monomers have been converted to a polymer? That is called extent of reaction. Then, one equation will evaluate that is Carothers equation. We will see the derivation.

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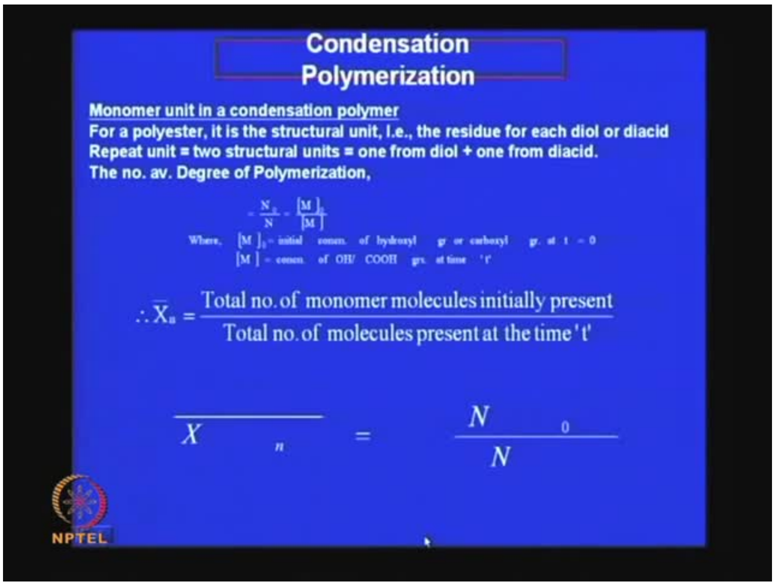


Again there is something wrong here, well do not worry I will explain. Now, this is a condensation polymer, we are synthesizing today, we are discussing here. If you take, if you go if you synthesize a polyethylene, that is no problem.

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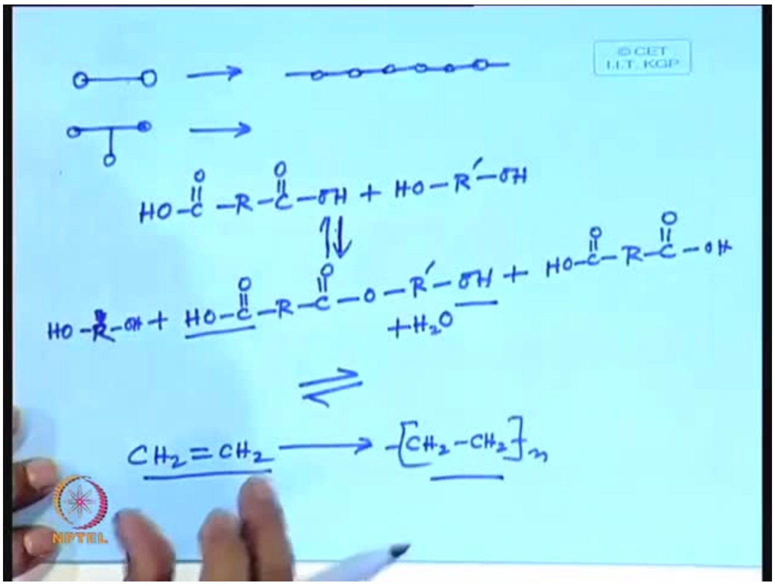

You take ethylene simply you can write the formula of polyethylene like this, but in case of polyester, the situation is little different. Here we are considering these as monomer, these as polymer. Then we have to starting with these two compounds, which one you consider as a monomer? What is the formula of the monomer then? Because as per the definition of the polymer, the monomer unit has to repeat large number of times along the polymer back bone chain. So, what is the formula of the monomer unit in the polymer in case of condensation polymer? So, for a polyester it is the structural unit for a polyester it is the structural unit. That is the residue for each diol or diacid, so this is a diacid. From diacid, what is removed?

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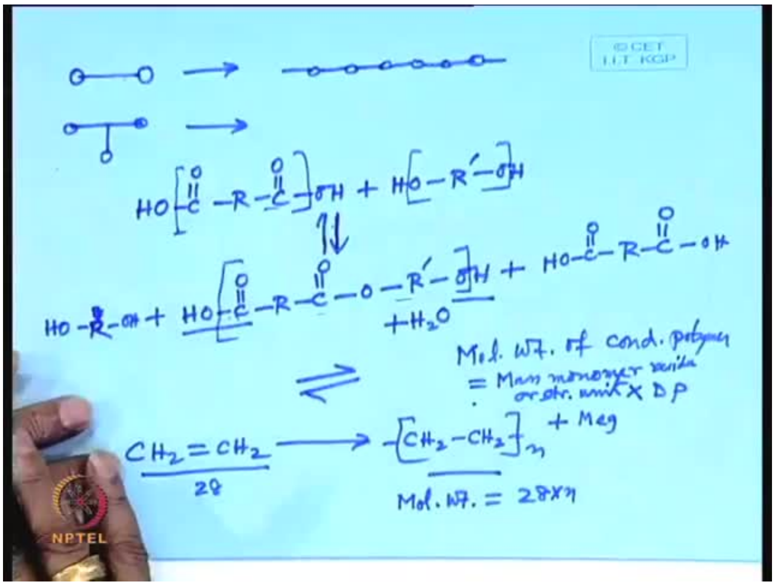


What is retained? This portion is retained. From di diol, this portion is retained. You see, so here R C O O, again R prime R prime is coming O H. So, this thing is coming. So, this is the residue for, from diol and diacid. This is the monomer unit in a condensation polymerization; this is the monomer unit from here to here. So, you in order to calculate the molecular weight of a polymer, how can you calculate in case of condensation of polymer and in case of addition chain polymer?

Here you see, the calculation of molecular weight of addition chain polymer it is very easy. Molecular weight of monomer is here 28, here are n number of 20 unit a units of mass 20 evening 28 are present in the polymer chain, so molecular weight in this case very easy to calculate. 28 n is the molecular weight. If n is 50,000 that is the molecular, if it is 10,000 that is the molecular weight multiplied by 28 in this case. So, you have to calculate the molecular weight, molecular mass taking from this C O R C O O R prime and O.

So, molecular weight of a polymer, condensation polymer, you should take the mass of monomer residue or structural unit or structural unit into degree of polymerization plus molecular weight of n group. What are the n groups? Because this will continued to increase repeating this portion residue within the parentheses, within the third bracket and outside the bracket there will be 1 O H and 1 H.

So, molecular molecular weight of the n groups here, 18. If it is a case of polyamide O H and H H, not N H O H and H acid and amine, you see, you verify. Sometimes it is H Cl sometimes it will be Na Cl depending on the reactive function reactive functional groups present in the monomeric unit, okay? Then, what is degree of polymerization then? How you can calculate?

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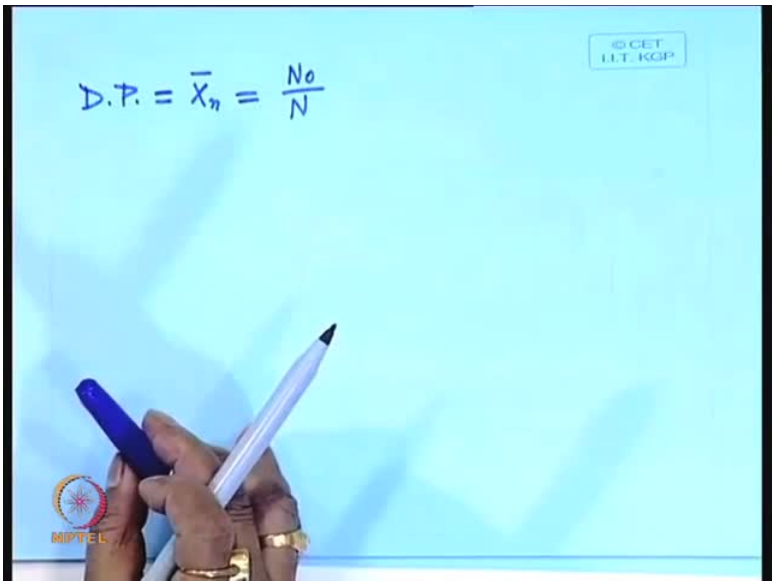


Degree of polymerization is equal to that is the number of molecules initially present divided by number of molecules present at any instant of time, dividing the polymer growth here it is written. So, degree of polymerization here later for the simplicity sake of simplicity, we write number average degree of polymerization. We clarify later what do we mean by number average molecular weight? There are other all average molecular weight designations with average molecular weight, viscosity average molecular weight. We are not coming to those complexity at this movement, I shall discuss in future lectures.

Today, for the time being, you see degree of polymerization is equal to number average degree of polymerization, means it is best on number count of molecules. The concept of average molecular weight in polymer comes from the situation. Already I explained in previous classes that these polymer molecules in a mass of polymer, in a sample of polymer does not contain the same molecular weight, do not contain the same molecular weight. There is a distribution of molecular size, here is a (( )) difference between discreet small molecular compounds and polymeric compounds.

A mass of polymer contains molecules of different sizes, a mass of discreet molecule contains molecules of same equivalent sizes, identical sizes and molecular weight, molecular formula. Here in polymer mass, the case is situation is different. Here there is distribution of sizes of different size molecules and you will get an average distribution. That is why you have to express this molecular mass or molecular weight as average. Might be number average based on number count or weight average based on weight count, all right? We will discuss later in detail.

So, that weight average a number average molecular weight, that is actually designated by X n bar is equal to N 0 by N, number of molecules initially present divided by number of molecules present at any time during the growth of polymer molecules, during polymerization, is it clear? Do not forget this, X n bar is equal to N 0 by N. If you start with by functional molecules, then is it total number of functional groups would be twice N 0 by twice N and basically this N, X n bar.

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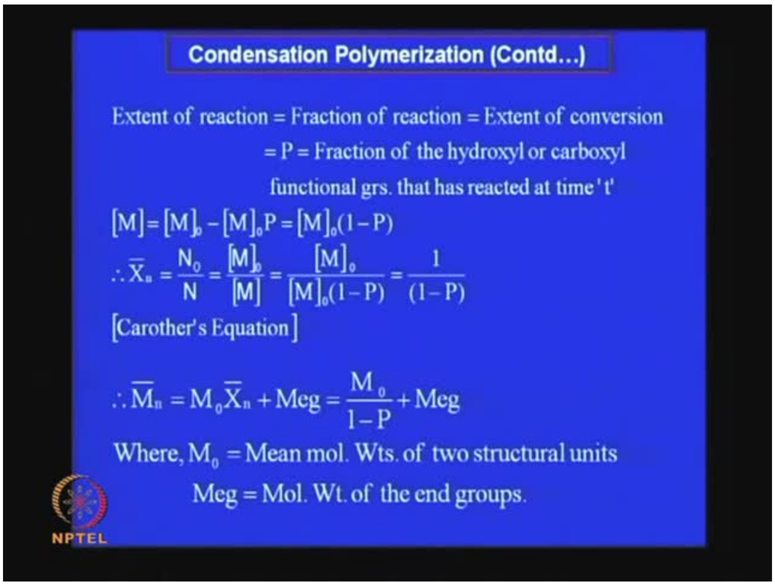


Now, let us have a concept now, extent of polymerization. What is this extent of polymerization? A very simple, extent of run, extent of growth. To what extent growth is there? 80 percent? 90 percent? 50 percent? 5 percent or no or 100 percent 100, cent percent growth? That is called extent of any function, extent of any function, say extent of reaction, that is called fraction of reaction or extent of conversion of the monomers to polymer, designated by p small p. It is a fraction of the either fraction of either hydroxyl groups or carboxyl groups are both are converted to a polymer, a reacted to a form a polymer at time t.

Here you see at all M under third bracket, that is the concentration of monomer. These designates concentration of monomer at any instant of time during polymer growth. How that can be calculated? That calculated from this thing, initial this is the initial concentration of the monomer and we have to find out how much monomer molecules have been consumed to from a intermediate or even some polymer? If there extent of reaction is p, the extent of reaction is p, so p multiplied with initial concentration gives you the amount of monomer that has been consumed or converted to polymer. So, the concentration remaining, then concentration monomer reaming then initial concentration minus the amount that has been reacted, okay? So, M 0 into 1 minus p, so this is the…

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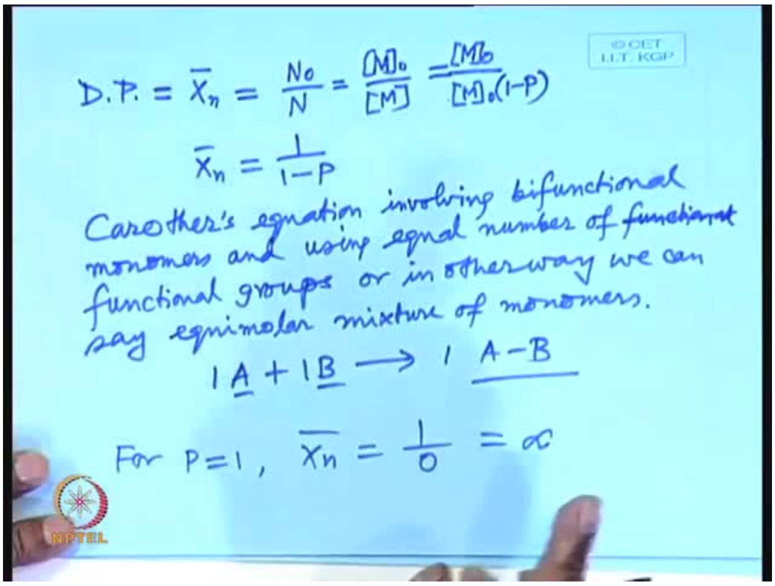


So, mass you can convert into mass, then number into mass of each. So, you can also write this way M 0 by M. So, if it is M 0 by M, then here what is M? This M 0 1 minus p means X n bar is equal to 1 by 1 minus p. This is a form of, the simplest form of Carothers equation involving by functional mono monomer molecules, involving by functional compounds.

1 A plus 1 B gets to 1 A B. Now, let us examine one thing here, 1 by 1 minus p A p is equal to 100 percent reaction. Means p is equal to 1, then theoretically if you take cent percent pure monomers with strict control of molar ratio stoichiometry, it is should lead to molecular size of infinite molecular weight. Now, one question I can ask you in that ideal situation, taking cent percent pure monomer and perfect stoichiometry and what will be the N groups present over there? How many numbers? How many molecules will be there?

If you can clarify this concept, then you will understand polymer otherwise it will become difficult. So, I am going very slowly for your understanding because your background is different, otherwise I could have finished this portion in half an hour, in 20 minutes time. How many molecules will be there? How many molecules will be there? Polymer molecule?

Student: One

One molecules. How many N groups will be there?

Student: (( ))

Two, simple. If there is in this ideal situation, ideal case you have taken cent percent pure monomer and strictly 1 is to 1 molar ratio, so one molecular form and at the there will be two ends only. At one end there will one carboxyl group and the other end one hydroxyl group, provided the reaction is 100 percent, clear? Then you you can move around anywhere, this is the ideal situation. You can deviate from this ideality to any other situation. So, you can have a mixer of molecules of different sizes. So, you can think of, you imagine the number of N groups that will be present, number of functional groups that will present.

Now, this gives you a clue, how to monitor the growth of such reaction? Here in this particular case you have studied with a diol and diacid. So, either you can go for estimation of alcohol or acid group by simple (( )) metric method, is it not possible? At any instant of a polymerization, polymer growth if you estimate the concentration of hydroxyl group, alcohol group or acid group, can you not say this is the growth? Initial you have taken you know that is you known value, at any time you are calculating, so what is the concentration remaining, you can know. So, can you can calculate the growth.

So the value of p, you can evaluate p maybe 0.3. 0.4. 0.5. 0.56 like this 0.8 0.9 like this. That means you can follow the kinetics, reaction kinetics. You can follow the reaction kinetics, is it clear? No ambiguity, no doubt? There will be numerical calculations from this things and I refer you a book principles of polymer chemistry by George Odian published by John Wilay.

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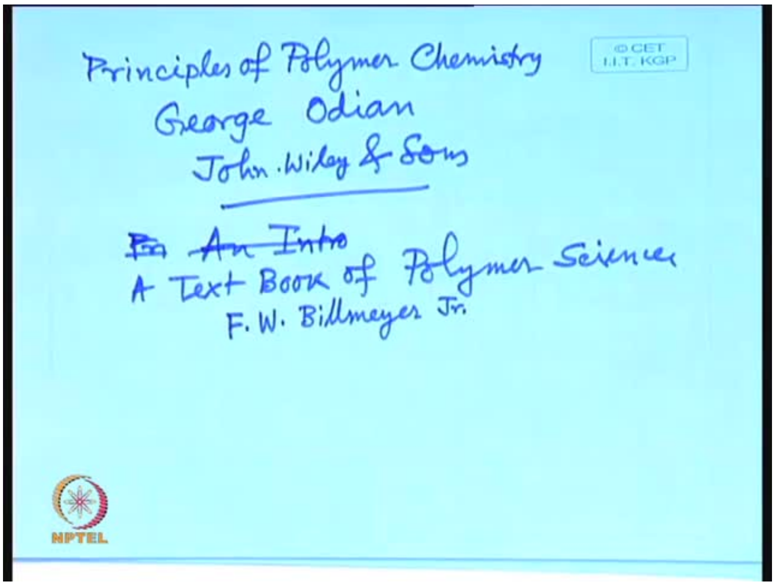


This is very good book, there are copies in the library or Indian addition is available. That is most authentic book or else you can see another book, I am sorry you to go for numerical calculations, calculation of polymerization rate, calculation of polymer growth, calculation of percent conversion, calculation of molecule weight of the per product.

Student: (( ))

Yes, please. (( )) of course. Sure.

Student: (( ))

This M n bar M n bar you see molecular weight, number of a molecular weight. This is the number average degree of polymerization multiplied by molecular of the monomer M 0 M 0. Where you see? Meg is there. The actually this M 0 here M 0 is the mean molecular weight of two structural units, I showed you, I showed in the previous structural units. That means the portion within the parenthesis. This is not a concentration at all.

This is not a concentration at all. Molecular weight, molecular of the structural unit enclosed within the third bracket, multiplied by this degree of polymerization, this degree of polymerization plus 2 N groups will be there, mass of the N groups. Left side right side and X n bar is equal to 1 by 1, 1 minus p. Very simple, but you have to do practice, okay? I am going to the next slide.

Student: (( ))

That is a very good question, which (( )), which parameters are responsible or dependent to form, he is asking leading to molecules sub difference sizes? Now, you know any reaction that occurs due to the collision of the random collision of the reactive spaces, any reaction chamber, am I correct? Out of 10 to the per 13 collisions, one collusion might be effective incurring out the reaction. So, in a chamber, in a reactor you have taken this monomers. Monomers are colliding with each other. Probably they are not achieving their sufficient activeness and energy to start the reaction, okay?

If one collusion achieves that activeness and energy in that you can start the reaction. So, that is a dimmer. Then that dimmer will be collected with monomer or a dimmer or a trimmer like this. So, this way there are random collision among the units present in a polymerization mass. You understand and this way growth occurs and some times which stop the growth, stop the polymerization to isolate the product. Otherwise, if you if you allow the reactions to completed for infinite period of time, because the step reactions polymerization is slow. There will be from your side you see cargo will like this, rate will be slope down, slope down (( )), it will continue for a infinite period.

I tell you one thing, suppose this is a polymer, made of say made by condensation process step reaction process. Somewhere the polymerization of this product was stopped, that does not mean that the polymerization of the reactive monomers taking for making this polymer was completed. Polymerization remained incomplete where you have frozen the polymerization. You stop the polymerization by freezing the reaction mixer of polymerization mass.

Then you have from this product, then you are using this thing. Now, this is subjected or exposed to these ambient conditions of temperature, pressure, humidity, life radiation so and so forth. So, these are again this environmental parameters become agencies to carry out residual polymerization reaction inside this polymer material, you understand? So, there is slow growth of this polymer inside this article. So, initially when this product was made it contain the set of properties, mechanical properties, thermal properties, optical properties all sets of properties, after certain period of its life the set of property changes because of this growth of this polymerization, you understand?

So, these are the agents for which defined a mixer of molecules of varying sizes, different sizes, am I clear to you? See these are collision reactions random collisions one with other. So, if I allow you to, allowing to start wrestling all this, fighting, what will be the product?

Student: (( ))

Only blood. You will find some of your finger is removed, some of your leg is removed, arm is removed, nose is removed and some teeth also goes out also. So, the products are different and then your mass will be different. A part if your body is removed, your weight maybe decreased by 1 kg or 2 kgs like this, it is like this. So, there are some reactions, interactions. If they are some interaction, if they are some interaction show it may not lead to it is of same size, a product of same size. Of course, if want to make one product only out of smashing all of you, all of us, then will get mass of tissues. So, I think I am clear to you.

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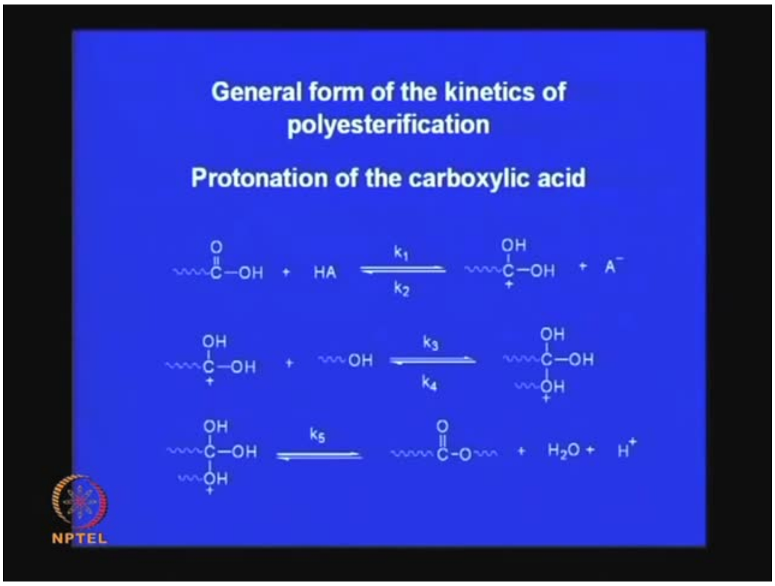


Now, the basic situation I have told, let us concentrate little bit into chemistry. If you do not like, I would not going detail. Now, what happens actually? You may be curious enough, what happens during this growth of polymerization involving an acid and alcohol. Know what you know what you bothers to think, but this is the situation here. You see a carboxylic group react with one alcohol sorry, I am sorry hydroxyl as acid as acid protonation, this is a acid. So, it can add some protein to this thing, so this carbon will be protonated.

Now, this protonated basis, this protonated basis will react with the alcohol forming again this intermediate. This intermediate is end itself to fall extra functional groups producing a byproduct molecule H 2 0 and releasing back the proton. See this proton acted here as a catalyst, you know the basic concept of catalyst function of catalyst is it is not consume to during the process, but it helps the process to load that activeness and energy, it helps a process to carry out. So, here acid is removed, means regenerated. So, this is the basic mechanism of esterification, how it occurs?

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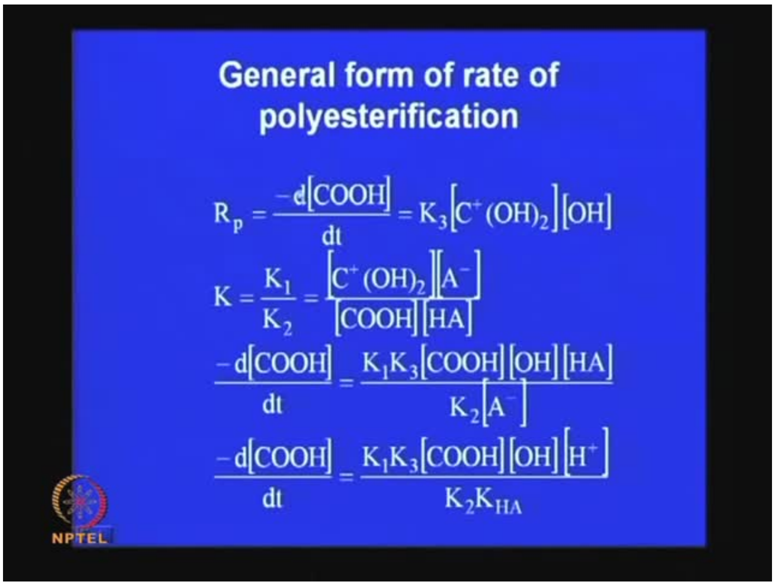


Here you see, how to write down the rate, rate of esterfication or rate of polymerization? Very simple. Now if I ask you, if some would ask you, do not be scared of, this polymerization reaction kinetics reaction there do not be scared of, please. This is very simple thing. Suppose, in this room, we are say 30 people are sitting in this room. Now, if you are told one by one go out of this room. So, there is only one door, one person will go out, then the second person will go, then the third person will go out. So, these way it will take some certain period of time to you have to evacuate this room.

Or all over sudden if there is a bomb outside your back side of you, there is a timer. If there is a timer, then you find only 5 second is left for the blast, then what will happened everybody will rush to the door and try to effuse you out of the door. So, the rate of this diffusion or effusion from this room will be different. The time required of this process to occur, how much time you are taking from going out of this room to the corridor, simple here also. Now, you consider yourself as reactance, you considered yourself as reactance, here carboxyl groups or hydroxyl groups reactance.

So, rate is calculated here the time taken by you people to go out of this room. Number of people going out divided by time, that is rate, that is a rate. Two persons in 2 seconds or 5 seconds, so 2 by 5 gives you the, gives your idea of the rate here also. How many carboxyl groups are exhausted or hydroxyl groups are exhausted? Because what is it called?

Student: (( ))

Disappearance of one carboxyl groups, means disappearance along with hydroxyl groups. Disappearance of one carboxyl groups means disappearance on hydroxyl group also, because of these disappearance occurs by as a result of reactance between carboxyl and hydroxyl group. So, either you can express in the form of disappearance of carboxyl group or hydroxyl group it is all same. Now, here you see, here you see this is this this is proportion of two or equal to some rate constant. And the concentration of the protonated (( )) and hydroxyl group. I have taken this thing from that Odian’s book, you please read that it very simple.

I have given you the background, how to understand. So, of this K is equal to K 1 by K 2. In the previous slide, here there are constants. These are all equilibrium type reactions. Now, in order to get this sector, this reaction, this step as to be revisable, is to be revisable. These step is to be revisable, otherwise you cannot get the product. So, these are the various red constants for different intermediates here. Ultimately all those red constants are involved in that equation and overall rate of esterification or overall rate of polymerization can can be calculated considerably the concentration of taking the concentration of carboxyl group, hydroxyl group and the say involving this acid is a concentration in the rate equation. There are certain regions it will I will explain later.

Thank you.