Principles of Polymer Synthesis
Prof. Rajat K Das
Material Science Centre
Indian Institute of Technology, Kharagpur

Lecture – 08
Principles of Step Growth Polymerization (Contd.)

Welcome back to lecture 8 of this course on principles of polymer synthesis. The topic of this lecture we continue with the principle with the discussion of the principle of step polymerization. So, we will start right where we left in the previous class that was we started talking about molecular weight control by having slight stoichiometric imbalance between the monomers. So, let us say what I mean by stoichiometric imbalance is this.

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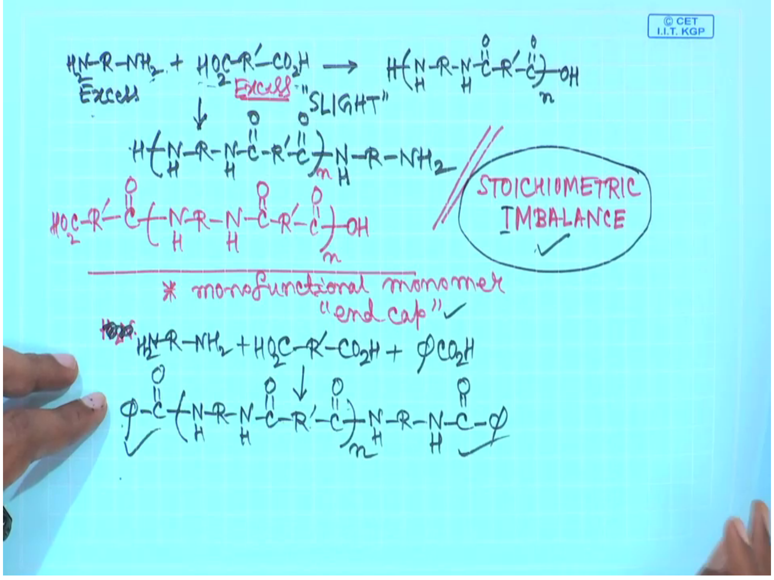

Let us say you start with a diamine, you react this diamine with a dicarboxilic acid. You are preparing a polyamide. So, when you are drawing the polymer structure it is very important to know what the repeat unit is. So, many times people will do mistakes in that. So, you have to take care of that. So, you have N H R N H, then you have C O R prime C O whole n, that is it.

Now, if you have both of them both the amine and the carboxylic acid in stoichiometric amount. Then what you will have is at the end of this particular chain on one end it will be amine, and another end it will have carboxylic acid. So, 2 such chains can react because this amine can react with this carboxylic acid under specific conditions they could react. This is something you wanted to avoid, because otherwise the molecular weight cannot be controlled.

Now, suppose you take a slight excess, I will tell you what the meaning of this term slight is in terms of the present concept. Let us say you take an excess of this. Then what will happen? What will be the product you will have the same repeat unit here same repeat unit, except that both sides will end with amine. Now this side you have a carboxylic acid if you did not have an excess amine how to end this side with amine? So, you have an O H here that will become an amide.

So, that will become an amide, and then you finish with this amine on this site. So, this will be the product. So, what you what do you have on both sides you have amines. So, this particular polymer now does not have end groups which can react with themselves. So, the polymerization is stopped.

If you had instead of this, if you had a an excess of this particular (Refer Time: 03:09) say you have a dicarboxilic acid which is excess. Then what will be the product? Again, you draw the same repeat unit here. Now both ends will end with acid of course, here I forgot to put n, you have to put n. And then you have O H on this side. Now this side you have an amine you have to form an amide bond because it has to end with an acid. So, you have to react this with another molecule of the acid. So, this will be an amide bond here. So, C O R prime C O 2 H.

So, this could be a problem also that people can ask you. So, when they are trying to know if you have a clear concept of this or not. If you are using one of them in x s what are the end groups draw the complete polymer structure. Then the n groups will be like this if you are using this as excess and if you draw this that will be incorrect, and if you draw this that will be incorrect. And if you draw this that will be incorrect because this this is only possible when you have stoichiometric amount. So, is the principle for this. So, one of the ways then in which you can control the molecular weight by is by introducing a stoichiometric imbalance.

Now, the other way you could do a control of molecular weight you could achieve is by using a mono functional monomer mono these are all bi functional you know mono functional monomer that will end cap the polymers. So, if you had a mono functional monomer. So, instead of a diamine if you have a mono function, this end there is no functional functionality left. So, that way also you can actually end cap both sides.

So, for example, if you are reacting so, I will go back to the black pen, because that concept has been already discussed. So, we come back to our the original colour. So, if you a diamine like this, and you are reacting this diamine with say carboxylic acid, usually I am taking the same reaction because I am trying to illustrate the concept and it becomes easier if you already know the kind of reaction that we are dealing with I mean for the starters.

And let us say we take benzoic acid as the mono functional monomer. So, this phi is basically used as a substitute for the benzene ring. So, a benzoic acid this is a mono functional monomer because this does not have 2 C O 2 H units it has only one C O 2 H unit. Now when you are using this mono functional monomer what will be the product structure again draw the repeat unit. So, you draw the repeat unit like this.

Now, this side you have an amine it will react with this carboxylic acid. So, it will form an amide and benzene ring. This side there is no function left because this is a mono functional monomer this has reacted, now this side you have an acid these acid cannot react with this acid. So, then basically this acid if you have to finish this particular structure you have to put an amine again amide bond here with this end caper. So, what you do here is this.

So, you put the amine again and form the amide bond N H R N H and then you end cap with this. So, this is also a way now this cannot react with itself because both ends there are no functional groups left; only functional group in the mono functional monomer that has been used up to react with the polymer. So, these are the 2 ways through which you can control the molecular weight, for our purpose what we will do is that we will discuss the stoichiometric imbalance the analysis of that in little more detail, and we would not further discuss as far as the analysis of mono function monomer is concerned.

So, let us go back. So, let us actually go forward to discussion of this stoichiometric imbalance this situation.

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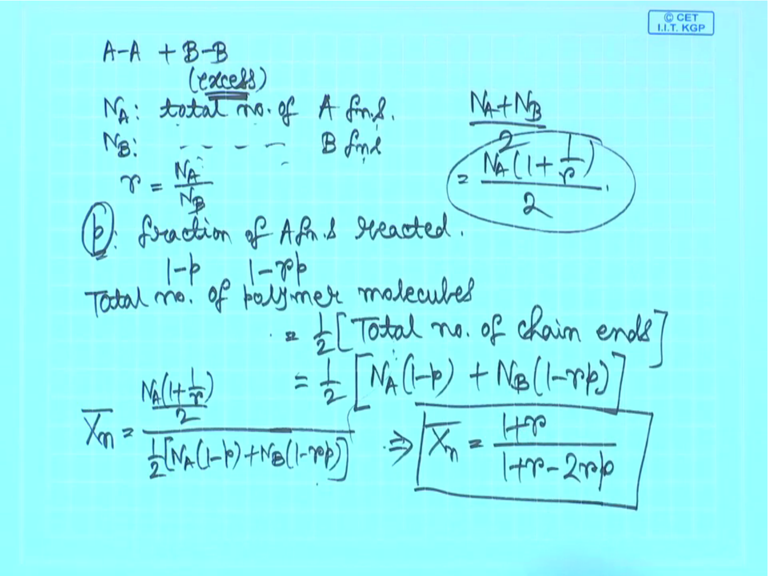

A-A + B-B
(excess)

N_A: total no. of A fn.s.

N_B: - - - - - B fn.s

$r = \frac{N_A}{N_B}$

$$\frac{N_A+N_B}{2} = \frac{N_A\left(1+\frac{1}{r}\right)}{2}.$$

(p): fraction of A fn.s reacted.

$1-p \quad 1-rp$

Total no. of polymer molecules

$$= \frac{1}{2}\left[\text{Total no. of chain ends}\right]$$

$$= \frac{1}{2}\left[N_A(1-p) + N_B(1-rp)\right]$$

$$\overline{X_n} = \frac{\frac{N_A\left(1+\frac{1}{r}\right)}{2}}{\frac{1}{2}\left[N_A(1-p)+N_B(1-rp)\right]} \Rightarrow \boxed{\overline{X_n} = \frac{1+r}{1+r-2rp}}$$

Let us say you take a bifunctional monomer like A A, another bifunctional monomer B B, this could be an amine diamine this could be di carboxylic acid. Let us say you take this in excess.

Now, remember this terms like that I told, if you take one of the monomers in large excess then what will happen is that before the polymer could develop into a substantially long chain already both sides that majority monomer will react. And those functions will be there. Say if you take diamine in a very large excess with respect to the di carboxylic acid. All the di carboxylic acid will react before a long chain has been produced, and then at the end the diamine will react on both sides. And that will stop. That will be an oligomer at based.

So, that is why it is very important to maintain a very slight difference in the stoichiometry. Say 0.1 mole percent excess of one of them or one mole percent excess of one of them. And maintaining this value of r is very important and it is not very straight forward. Suppose you are reacting a diamine with diacid. Problem of diamines is that they might be volatile. So, as the reaction progresses the concentration of diamine may change and then your small r will change. And you will find through the analysis of course, that so that means, the r that you started with is changing. And the problem they are then there is an error in the r if there is an error that will be manifested much more when you are going to high degree of polymerisation which actually means when you are going to high extent of reaction. Rather than when you are actually settling for a very low molecular weight which you seldom do.

So, maintain this r is very important in that case people will do what you call as a batch process; that means, you are doing the reaction and you replenish from time to time maybe the diamine. So, as to have carefully maintain the concentration which we will in turn maintain your value of r. R I am telling r, r all the time, but I did not introduce what is r. In fact, I already introduced to you this r is a measure of the stoichiometric excess. I just give the symbol and I did not tell you what r is before.

Because now I am going to go in to this analysis, if you have excess of this, let us say let us give some symbols here. N A is the total number of A functional groups, total number of A functionals functional group here present N B is the total number of B functional groups now B is in excess. So, your stoichiometric imbalance in fact, you say stoichiometric ratio, ratio from ratio the term r comes the later small r this is stoichiometric ratio that is N A divided by N B. This ratio is never greater than 1. So, if you have one of the monomers in excess that comes in the denominator. The monomer which is not in excess that comes in the numerator on the up. So, N A divided by N B.

Now, if N A is the total number of A functions and N B is the total number of B functions, then what is the total number of monomer molecules, N A plus N B by 2, because each monomer molecule contains 2 functions. So, N A plus N B by 2 is total number of monomer molecules which is equal to N A into 1 plus. So, from here you replace the N B 1 divided by r by 2 total number of monomer molecules.

Now, let us say you have done the reaction to an extent p; which is the fraction of a reacted fraction of A functions reacted. Then how much fraction of A functions is not reacted that is 1 minus p, this much fraction of A function is not reacted. How much fraction of B function is not reacted? That is 1 minus r p. So, what is the total number of polymer molecules that is present in the system at this point of time? When you say polymer molecules basically you mean everything oligomers all oligomers all big polymers everything that is present, because all this species will be present at all the time molecular weight will actually develop very slowly now.

So, what is the total number of polymer molecules at this point when extent of reaction is p. Total number of polymer molecules at this point will be equal to will be equal to half the total number of chain ends if you have one polymer it has 2 chain ends. So, if you can count the number of chain ends, then you divide by 2 and you find the total number of polymer molecules.

So, what are the total number of chain ends total number of chain ends is equal to the total number of un reacted A and B groups because those un reacted groups are at the end of chains. So, then that will be equal to half into total number of un reacted groups. So, your 1 minus p is the fraction of a that has not reacted. So, the total number of un reacted groups will be fraction into N A. So, N A into 1 minus p plus N B into 1 minus r p.

So, what is the expression of X n bar degree of polymerization. X n bar is total number of molecules that are present initially divided by total number of molecules that are present at this time. All those molecules you are actually terming as polymer. So, n 0 by n I already told you n 0 is total number of monomer molecules to start with. So, that n 0 by n that n 0 is this thing total number of monomer molecules to start with. So, that will be N A into 1 plus 1 by r divided by 2, divided by total number of polymer molecules, because it is number of structural units per polymer molecule. So, you divide by this.

Now, if you replace this N B by you know N A by r, and then you remove the r and do the all the final analysis I will just write down the final expression. This is just mathematics you can do it X n bar becomes 1 plus r divided by 1 plus r minus 2 r p. That is the expression. So, that is how the degree of polymerization will vary with respect to the extent of conversion and with respect to the stoichiometric excess that you have stoichiometric imbalance that you have taken or the stoichiometric ratio that you have taken.

Now, let us say you are, let me draw this particular expression again in discussed to special situations for the moment.

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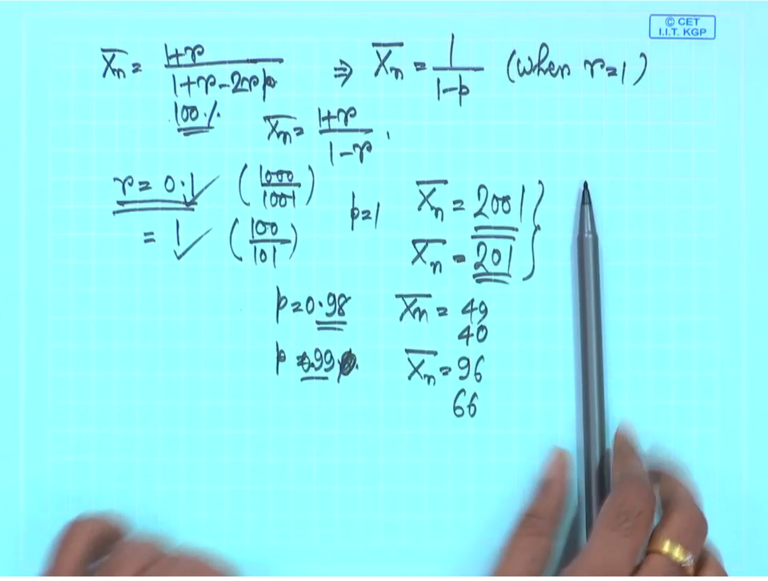

Let us say your r is 1; that means, there is no stoichiometric imbalance. Both the reactants you have taken in the same amount. Then what happens is that your X n bar will reduced to 1 divided by 1 minus p when r is equals to 1. This is the same expression that we got through Carothers equation. So, this is another way this is a special case of this general expression. And the other case is the when your reaction is 100 percent complete, then your p is nothing but 1 then your X n bar is equals to 1 plus r divided by 1 minus r.

Now, let us say I am going to give you a specific example which is going to tell you when you vary the r, how that will affect the X n bar. So, let us say your r is 0.1. So, that will happen when you have say thousand moles of one of the reactants, and thousand and one moles of the other 1. Or let us say your r is 1. So, this is 0.1 mole percent or 1 mole percent. So, that will be 100 divided by 101. So, this is 101 moles of one of the reactants and the other one is 100 moles and if you are. So, you consider 2 situations in one situation your r is 0.1 in another situation is r is 1.

So, r is 0.1, let us say you put p equals to 1; that means, 100 percent reaction. So, what will happen is that at 100 percent reaction, your X n bar if you are putting r equals to point 0.1, your X n bar will become 2001. If you put r equals to 1, your X n bar will be equal to 201. So, you see the large difference that will come. So, if you have some error of the r, that will manifest here significantly, now what happens if you have say 98 percent reaction or say 99 percent reaction? Say you have 99 percent reaction, then your X n bar will be 96 when your r is 0.1 and 66 when r is 1. When you have 99 percent reaction, p is actually 0.99 is the fraction. So, percent you can put 99 percent when p equals to 0.98 then your X n bar will be 49 for 0.1 when r equals 0.1 here X n bar will be 49, when r equals 1, your X n bar will be 40.

So, you see as the extent of reaction increases, the difference between the 2 X n bar values that correspond to a small r value and a big r value also increases; that means, as you go to towards more and more completion of the reaction as you go towards higher and higher molecular weight as your target. You have to more precisely control your r value. If your r value becomes one from 0.1, then if you have done say 98 percent reaction, then your X n bar does not vary much between 49 and 40. If you have done 99 percent reaction, then if you have this much error then there is some difference 66 and 96.

If you go to 100 percent if it typically do not go to 100 percent, this is just in principle I am showing you have this much huge difference. So, then the point is as you go towards the finalisation. I mean the completion of the reaction finalization is not the right word. So, completion of the reaction, you have to actually precise the more precisely control the value of r. If you that means, if you are looking for a very high molecular weight, you need that much of precision in the value of small r, which is your stoichiometric ratio.

So, these also tells you how we can control actually the molecular weight, because you know the value of X n bar you want. So, correspondingly you choose your small r value, which is a very you want to you want to actually take that value as close to one as possible, but not one because there is slight stoichiometric imbalance that you want to introduce.

And then you know what is the extent of reaction that you have to go actually you can plot a graph with respect to this also, but I think the principle already I have described. So, I do not want to you know go into much more details that you can actually ultimately figure out after. We also give some problems may be in the assignments in exams.

So, let me at this point once we have developed this particular thing. Let me do a problem for you. So, I have actually worked out this problem already because calculations actually take time lot of time, but I want to discuss the principle for you.

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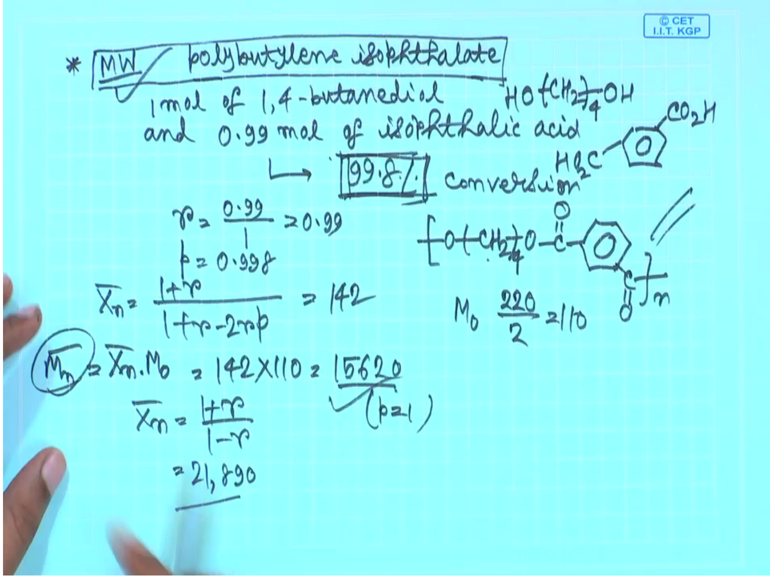

* MW / polybutylene isophthalate

1 mol of 1,4-butanediol and 0.99 mol of isophthalic acid

$\hookrightarrow \boxed{99.8\%}$ conversion

$r = \frac{0.99}{1} = 0.99$

$p = 0.998$

$\bar{X}_n = \frac{1+r}{1+r-2rp} = 142$

$M_0 \; \frac{220}{2} = 110$

$\bar{M}_n = \bar{X}_n . M_0 = 142 \times 110 = 15620$

$(p = 1)$

$\bar{X}_n = \frac{1+r}{1-r}$

$= 21,890$

Let’s say we this is a problem. You are trying to find out the molecular weight, molecular weight of polybuthylene isophthalate, poly butylenes isophthalate. And the problem here is you started with 1 mol of 1 4 butane diol and 0.99 mole of iso phthalic acid. So, one for butane diol is this, and your isophthalic acid is this. So, you are doing reaction with one mol of one for butane diol and 0.99 mol of isophthalic acid. And these reaction you have done up to 99.8 percent of conversion. You have achieved this is the conversion.

So, the question is what will be the molecular weight of the product. So, in order to determine that, you know your small r value, that is the question your small r value is 0.99 I am trying to work it out 0.99 divided by 1 which is actually 0.99. That is the small r value your small p which is your extent of reaction is 0.998 because that is 99.8 percent conversion that is 0.998.

Then what is the degree of polymerisation, we use the formula 1 plus r divided by 1 plus r minus 2 r p. And you put all these values here and then the value of X n bar is 142 as I have worked out already it is 142. So, what will be the molecular weight of the product in order to do that you have to draw the repeat unit structure, and be careful when you are drawing the repeat unit structure, that you do not make mistake. So, this is the diol part and then this is the di acid part.

And if you take the molecular weight of the repeat unit is 220, but there are 2 structural units per repeat unit. So, average molecular weight per structural unit is 220 by 2 is 110 which is M 0. So, your X n bar into M 0 will give you your average molecular weight number average molecular weight that is what you want. So, it will be 142 into 110. So, it will be 15620.

And then if I ask you what is the maximum molecular weight that is achievable. So, maximum molecular weight is only achievable when you have, 100 percent conversion in this kind of situation because this problem is only defined. So, what is the maximum molecular weight? You can get so; that means, your p value is 1. So, your X n bar is 1 plus r divide by 1 minus r you put the value of r here and what you will get is 21890.

So, you know then this is something that you can control to start with. And then you can actually find out the conversion, because ultimately how much of concentration of carboxylic acid is remaining from there you can find out the conversion. So, because the concentration is equals to M 0 which is the initial concentration minus M 0 into p, where p is the conversion, and that will be equal to your M which is the final concentration that you can find out you can measure the carboxylic acid concentration through titration. And then you will know what is the value of p correspondingly, and then the question is what will be the molecular weight number average molecular weight that you want and you will get this.

And in practice what you will do is that after doing the reaction many times in many situations, I mean after doing the reaction many times in many situations, I mean after doing the reaction this is the calculation that you have after doing the reaction you take out the sample and do find out this value of M n through one of the different means that. I have described you can do a GPC. I mean this is not only for the specific reaction for other different molecules you can do a GPC, or you can actually find out by vapour pressure osmometry GPC will give you the full distribution depending on what kind of samples you are using for calibration how much error will be there typically if you are using polystyrene for calibration linear molecules. So, what you want is that your unknown structure I mean unknown molecular weight structure will also be linear then there will be some better correlation so on and so forth.

So, then this particular problem I hope has illustrated the importance of the preceding discussion that why do we need to know this kinetic analysis; that means, we know now how the degree of polymerization varies with temperature yeah sorry, with time we also know that we have to do this particular reaction. In an open system with an external catalysis if possible, because if it is an you know if you do not have an external catalyst if the acid itself is catalysing the reaction, then your molecular weight the way it develops the development of molecular weight with time is extremely slow. And it is much more acceptable development of X n bar or the molecular weight. Whatever way you want to explain that with time when you are looking for external catalysis.

So, you have to go to external catalysis number one and number 2, you need open system you have to remove the water continuously. And number 3 you need as high equilibrium constant as possible for your particular reaction in question. Because high equilibrium constant will ensure that you will need to remove less amount of water which therefore, becomes more easily miserable. In order to get your desired high molecular weight and also, we told that how we can introduce his small stoichiometric excess, and correspondingly you can look for your desired molecular weight at a very high extent of conversion. And how you do not allow the molecular weight to go out of control by this kind of you know end capping for example, with mono functional monomer or you use one of the monomers in excess.

So, this completes this full analysis as far as the molecular weight control is concerned. So, let me discuss something that I can consider as a prelude to our next class at the moment. So, you know that the molecular weight distribution is something that you really want to have for a polymer sample. Because as I have argued before, if you have only the number average molecular weight. You have determined that may underestimate the molecular weight of the system. So, at least you need to get M w that is the weight average molecular weight, or you get M w and M n both and then find you have an idea about the polydispersity of the sample. And then you can also be GPC to have the distribution.

But is there a way to derive this molecular weight distribution from theory from a statistical approach. Let us say it turns out there is Flory in I believe in 1950, he has used this concept again of equal reactivity of functional groups. In order to develop an approach that actually gives you an expression of your molecular weight distribution. And this expression is useful, because that will tell you like we say that most of the monomer has reacted already before the reaction as proceeded to a large enough conversion to give you large molecular weight. For a step polymerization because you know the monomers will react with dimers they will react with trimers and all this species are present. So, mostly there will be different oligomers present at different points of time and the molecular you will develop slowly first step polymers.

But you will see after this analysis that the molecular weight distribution the way we will show is we will actually determine the number fraction distribution of different species that are present in the polymer sample, and the weight fraction distribution of different species that are present in the polymer sample. And it turns out that all though this is theoretical there are many experimental verifications. So, we will come to those discussions in the next class. So, this is the approach of Flory and there we will have an approach with probability, and we will say that the reactivity of the functional groups are the same. That is very important whether you have a small molecule or whether you have a big molecule.

So, thank you for your attention for this class. And look forward to seeing you in the next class.