Principles of Polymer Synthesis
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Lecture – 09
Principles of Step Growth Polymerization (Contd.)

Welcome back to this ninth class of the NPTL course on principles of polymer synthesis. We have been discussing the topic of step polymerization the principle of step polymerization. And in this class, we are going to continue with that.

So, in the last class, the point where we left you is the talk of the molecular weight distribution. So, I told you that there is a statistical approach, that you could use in order to find the distribution the number fraction distribution with respect to the degree of polymerization or the weight faction distribution of the different species that are represent in the polymer sample as a function of the degree of polymerization.

So, degree of polymerization is nothing but the average number of structural units per polymer chain. Again, as I am telling you this is directly correlated with the molecular weight. So, you multiply the degree of polymerization with the average molecular weight of the structural unit and then you get your average molecular weight, which is which might be a number average molecular weight or weight average molecular weight we will come to that in a little while.

So, let us then begin our discussion today.

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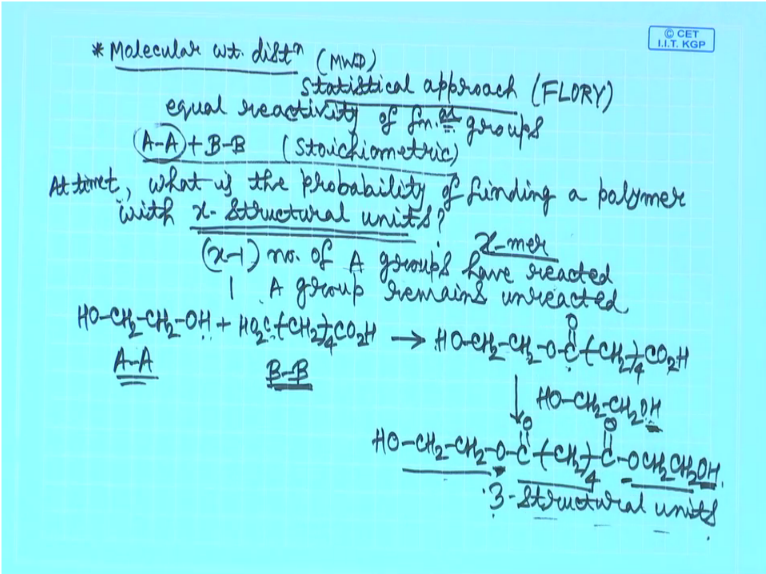

So, what we are looking for is a is to derive an expression for the molecular weight distribution or derive expressions that give you a fair bit of idea of that. So, for that we are going to use a statistical approach, Florys statistical approach. And of course, this is going to assume equal reactivity of functional groups, the same assumption that we had made when we analysed the kinetics of these reactions.

So, let us begin with 2 by functional monomers like this A A and B B and the assumption is that we are taking stoichiometric amount. So, most of the times this we typically take stoichiometric or near stoichiometric amount in practical situations also.

So, we begin by asking the following question. Say the reaction has progressed up to a time t. So, at time t, what is the probability of finding a polymer with x structural units? So, the polymer is going with time. The question that we are going to ask is that suppose the reaction has progressed up to time t. So, at this point of time, what is the probability that we will find a polymer that is having x number of structural units. So, as you know we are looking at averages.

So, when we are saying that we are trying to find a polymer which x number of structural units. That would also mean that all the polymer chains that have been produced up to that time. All of them do not have the same number of structural units. Some of them have x number of structural units, some of them has say y number of structural units some of them have say z number of structural units so on and so forth.

That is why the concept of average comes you have polymer chains of different lengths. Now how different the lengths are that is another question. That is given by the distribution of the molecular weight. If you can control it more precisely; that means, if your polydispersity index is; I mean closer to one. So, the closer to one it is the more evenly distributed I mean the more uniform the length of the polymers are, but it is another thing that you cannot actually control the distribution beyond a beyond a certain limit in certain polymerization reactions. This is a very vague statement that I am making you might thinking, but hopefully after I have finished this analysis, it will give a justification of this kind of statement that you cannot control the molecular weight beyond a certain control the distribution of the molecular weight to be more precise beyond a certain limit.

I mean which actually means that the PDI or the polydispersity index which is the ratio of weight average degree of polymerization to the number average degree of polymerization. That ratio you cannot sometimes control beyond a certain limit. You want it to be one right all the polymer chains to be of same length, but in reality, for certain class of polymerizations, especially say we are talking about say step polymerization, you cannot go to 1, it will be higher than 1. It will in fact, be close to 2. You cannot go to lower than say you cannot go to say 1.5 or close to one it will be close to 2 those reasons will be discussing here, after this analysis it should become clear.

So, at time t what is the probability of finding a polymer with x structural units? So, in order for this situation to unfold, what should happen to the a functional units? For a polymer of x structural units or an x mer to be produced, you basically need x minus 1 number of A groups to react. So, when you are you have formed an x mer, actually to form the x mer x minus 1 number of A groups have reacted, and one A group remains unreacted. In the x mer in the formation of x mer in the process of formation of x mer x minus 1 number of A groups have reacted and one A group remains unreacted. Let me explain this thing little bit more. Say, you are reacting ethylene glycol with adipic acid. So, first reaction will produce. So, this reaction of alcohol with carboxylic acid will produce a dimer like this O C O C H 2 whole 4 C O 2 H.

Now, let us say this particular molecule reacts with so, this is a dimer let us say this reacts with another molecule of ethylene glycol. So, it will react here. So, what will be the product O H C H 2 C H 2 O C O C H 2 whole 4 C O O C H 2 C H 2 O H.

So, you have created a trimer. So, in this trimer how many structural units are present. This is one structural unit, this is a second structural unit, this is the third structural unit. So, it is a it is a trimer it has 3 structural units, it has 3 structural units. Let us say this ethylene glycol I am turning it as the monomer A A in accordance with this, and adipic acid as the monomer B B. So, in the formation of a an oligomer, in this case with 3 structural units, how many A groups; that means, how many alcohol groups have reacted. So, in the first step one alcohol group has reacted. So, this alcohol group has reacted. In the first step in the second step another alcohol group has reacted.

So, basically in order to create 3 structural units, 2 alcohol functionalities have reacted. And how many alcohol functionalities remain unreacted. How many alcohol functionalities remain unreacted one alcohol functionality remains unreacted on this side for example here. So, in this particular scenario then in order to create the 3 structural units here if you are looking at A A. So, you have 2 number of A groups that have reacted. One number of A group that remains unreacted. So, if you I mean this is just a comparison to tell you. So, if you are looking at for example, if you if you looked at this as A A or this as A A the similar situations would arise.

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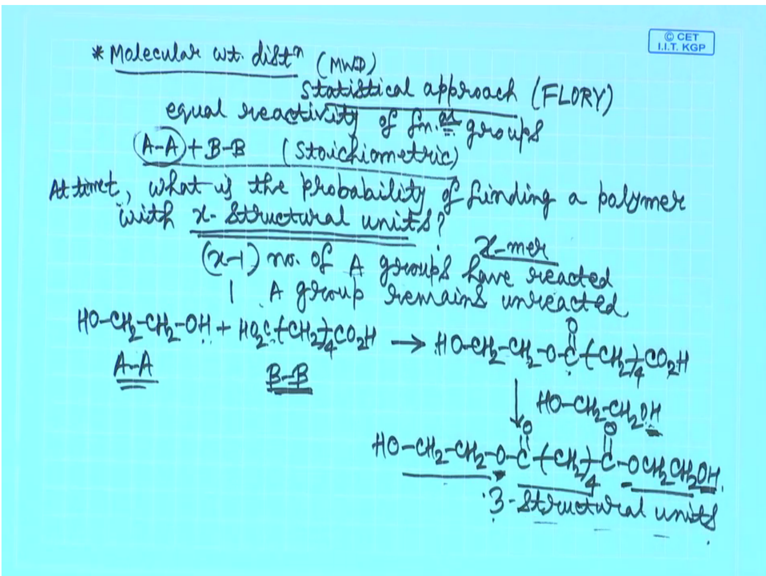

Now so x minus 1 number of A groups have reacted, and one A group remains unreacted.

So, what is the probability that one A group has reacted. Let us say p is the extent of conversion in keeping with whatever we told before, let us say p is the extent of conversion. So, p can also be termed as the probability that one A group has reacted. So, p can be also termed as the probability that one A group has reacted at time t. Everything is that time t so, this is the probability that one A group has reacted at time t.

So, what is the probability that 2 A groups have reacted at time t? That is p into p equals to p square. Now why it is p into p and not p plus p? Now this is p into p because, these events are independent of each other. Why these events are independent of each other? Since the reactivity of one functional group does not change when the other functional group has reacted, this is independent of each other this 2 events are independent of each other.

And when you were looking at probability of 2 events occurring simultaneously, if the 2 events are independent of each other, then the total probability is basically the multiplication of their individual probabilities it can be shown. So, probability that one A group has reacted at time t is p. So, probability that 2 A groups will react is p into p is p square. So, probability that x minus 1 A groups have reacted is p to the power x minus 1. But one A group has not reacted. So, what is the probability that one A group does not react that is 1 minus p? Because the probability that one A group reacts is p.

So, the probability that one A group does not react is 1 minus p. So, what is the probability that all these events so, ultimately what is the probability that all these events occurs simultaneously? Because we have to look for probability of finding the x mer, the x mer will be produced in all these events occur simultaneously; that means, x minus 1 A groups have reacted, and one A group has not reacted. So, what is the probability of finding an x mer? Now because this reactions this probabilities are independent this events are independent again there would be multiplication. So, that will be multiplication of 1 minus p with p to the power x minus 1.

So, that is the probability of finding an x mer. And this is nothing but the number fraction or mole fraction. So, let us say small n x is the number fraction. That will be equal to so, number fraction that will equal to 1 minus p into p to the power x minus 1. So, this is this is something that gives you the variation of the number fraction with respect to the x, which is the degree of polymerization because x average x structural units. So, if you have a polymer with x mer that is having a degree of polymerization of x. So, small n x is the number fraction distribution. So, small n x if it is nothing but number fraction or mole fraction that will be equal to capital N x by capital N, where capital N x is basically the total number of polymer molecules which have x number of structural units, and capital N is total number of polymer molecules.

So, capital N contains all the polymer molecules which have different number of structural units. Capital N x because x is the subscript capital N x tells you, that this is the number of polymer molecules which have x number of structural units. So, this ratio will give you the mole fraction of polymer molecules or the number fraction of polymer molecules with x number of structural units with x number of structural units. So, that is equal to 1 minus p into p to the power x minus 1. Now what is capital N we know the value of capital N is nothing but n 0 into 1 minus p, where p is the extent of conversion n 0 is the total number of molecules to start with. So, if you put those values here then your n x is nothing but n x is nothing but n 0 into 1 minus p square into p to the power x minus 1. So, this is the main expression.

So, this is the number fraction distribution this equation gives you number fraction distribution as a function of your degree of polymerization. So, number fraction distribution. So, what is the weight fraction distribution?

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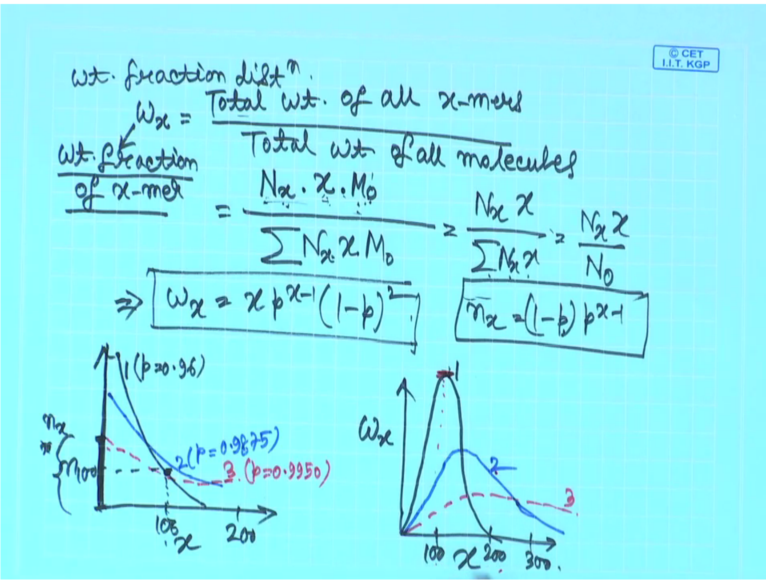

Let us say I put small w x. So, basically let us say weight fraction w small w x is weight fraction of x mer. Just like the number fraction of x mer. So, weight fraction of x mer is nothing but equal to total weight of all x mers divided by total weight of all molecules that is the fraction weight fraction in this case, which is nothing but total weight of all x mers. So, what is the total number of x mers? That is N x each x mer contains x structural units. So, multiplied by x multiplied by M 0 where M 0 is the molecular weight of the structural units.

So, total weight of all x mers is nothing but N x into x into M 0. Because what is the total number of structural units that we are dealing with? That is x into N x because N x is the number of molecules which of which each of them have x number of structural units and what is the total weight that is multiplied by M 0, because M 0 is the weight of one structural unit. So, what is the weight of N x into x number of structural units that is this it is total weight of all x mers divided by total weight of all molecules. So, you sum it up over all x all the xs either x can be of different values. So, when you are talking about all the molecules you actually encompassing molecules with all different number of structural units.

So, that is this so, M 0 goes. So, this is nothing but N x into x divided by sum over N x into x, and this is total weight of all the molecules was this. Now what is the sum over N x into x? Sum over n x into x is nothing but N 0 because you are actually summing up all the number of molecules here. And this is N x into x. Now this N x by N 0 already you know from the previous. So, this N x by N 0 is nothing but 1 minus p square into p to the power x minus 1. So, that if you put there your w x becomes x into p to the power x minus 1 into 1 minus p square. So, that is the final expression of weight fraction of x mer.

So, if you now. So, here, I am also putting the number fraction distribution 1 minus p into p to the power x minus 1 that is the number fraction distribution. So, if you plot this number fraction or n x, as a function of x that is the degree of polymerization, and you are actually multiplying by some factor say 10 cube or something like that. So, you are multiplying by some factor I am not putting the values here say 10 20 30 so on and so forth, just want to give you a principle the understanding of that say x is 100 here, x is 200 here. So, what you will have is something like this. So, I am going to draw certain things for you and then I will explain to you what they mean. So, I am going to draw this graph, and then I will draw something like this. And then thirdly so, let us say this is curve 2 I will draw something like this. Let us say this is curve 3. And this is curve one. So, these 3 curves you know here is p also in this particular expression. So, these 3 curves they are at different values of the conversion that is p. So, first curve is for p equals 0.96 96 percent conversion. The second curve is for theoretical p equal to 0.9875 90 around 99 percent conversion less than that. And the third curve is for p equal to 0.9950. So, what this graph tells you is that so, if your x is equals to say if you are looking for a an explanation of this curve that is right there.

As you go further and further down the graph. So, this graph this graph this graph. So, this graph is for a lower conversion, lower extent of reaction this this graph blue is for a higher extent of reaction. This rate curve is for even higher extent of reaction. So, and this number fraction this corresponds to with respect to the degree of polymerization. Here it tells you this graph tells you say for example, the graph one this tells you that at 96 percent of conversion this is the number fraction distribution of different oligomers or polymers oligomers everything. So, that means, if you are going towards here, you are going towards a monomer.

You know x is very small oligomers or even monomers when it is getting very close to the y axis. And this is the amount of monomer that will be present at p equals 0.96, and then say for example, this is the number fraction this is the number fraction of 100 mer so on and so forth. And even when you have say 99.5 percent of conversion, this is the this is the number fraction of the monomer that will be remaining, which tells you that you will at all point of time regardless of the extent of reaction. You will have more number of monomer molecules in terms of number more number of monomer molecules than any other polymer species.

So, this may appear to be little bit countering to it if to you, but this is what we will actually get here and it is also verified afterwards I will tell you how the full theory is verified in one way or the other. So, this graph actually tells you. So, the graph falls like this towards higher degree of polymerization. So, at the lowest degree of polymerization, you have a value of number fraction that is higher than any higher value of degree of polymerization then x n equals to so, 1. So, that means, at any extent of polymerization, even if it is 98 percent, 99 percent, 99.5 percent if you just look at the numbers of different species present the number monomer molecules the number of dimer molecules, the number of trimer molecules, the number of tetramer molecules, the number of monomer molecules is the highest among all the polymer species. What about the weight? This is the number. So, what about the weight? So, if you look at the weight fraction. So, you are plotting w x as a function of x. So, what you will get is the following. So, this is for curve one again one corresponds to this. So, approximately so, this will be like 100, this will be like 200, 300 so on and so forth. And this will be for curve 2.

So, like this say curve 2 corresponds to this. And this will be for curve 3. So, weight fraction. So, if you are looking at the basis as the weight here, the basis was number. So, the number of monomer molecules at any point of time for the polymerization is the highest with respect to all the other polymeric species. Here if you look at on the basis of weight, the proportion of low molecular weight species this side is the low molecular weight species this side is the higher molecular weight because x is the number of structural units. So, proportion of the low molecular weight species is very small. So, if you are looking at curve one. So, at 96 percent conversion weight wise the proportion of 100 mer say for example, if you look at this graph the proportion of say 100 mer, it is the highest or if you are looking at curve 2 which is 0.9875 98 percent conversion.

I have closed to 99 percent conversion the proportion of somewhere between 100 and 200 that many structural units will be there per polymer molecule the proportion of those species in terms of weight is the highest. And this maximum roughly corresponds to the number average molecular weight. So, this is the difference. So, these 2 curves tell you that the number fraction of the monomers is the highest, no matter what is the extent of polymerization; however, in terms of the weight fraction it is the different. Issue the weight fraction of the low molecular weight species is very, very small. So, even if the number is the highest the weight, weight wise the contribution to the total sample is very, very small and the contribution to the total sample in terms of the weight is maximum, close to the number average molecular weight value.

So, some of this graphs can be verified, because you know this kind of distributions we could experimentally get say the molecular weight distribution we will get from the GPC curve and all. But something that echos with this particular class in a very simple way we can also verify.

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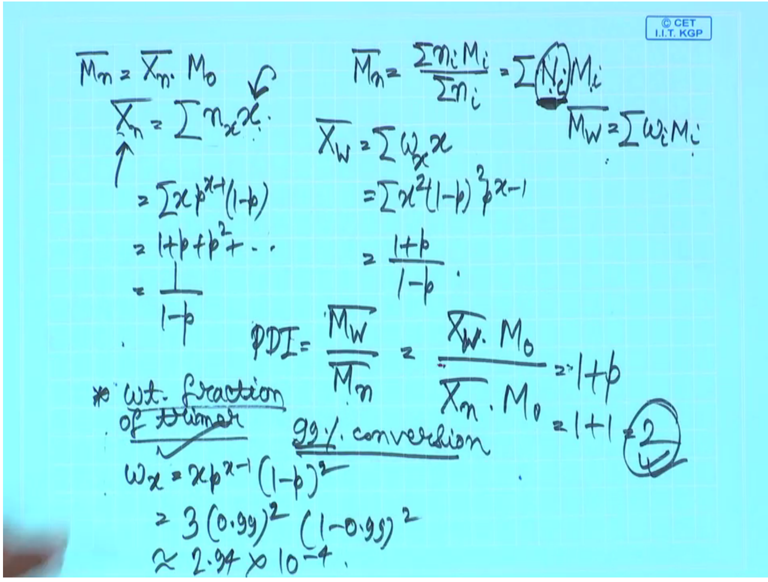

Say, let us say what will be the value of M n? We will go to the expressions here what will be the value of M n that will be X n bar into M 0. We have already talked about that. What is the value of X n bar after all these analysis what is the value of X n bar we will get let me write down first, and I will explain to you that is this. This is a number fraction of x mer, and this is the number of structural units.

So, this is basically so, this x is your degree of polymerization. And here so, this is the degree of polymerization. This is number average degree of polymerization. And so, when you are averaging this basically you are averaging you are weighing this particular thing with the number fraction. So, basically this is also the concept of average, let us say when you talked about the expression of M n, that was summation n i M i divided by summation n i if you remember. So, this is basically nothing but you can also write it down as let me say capital. N I mean it depends on the symbols that you are using you can use different symbols as long as you know what the symbols are let us say capital N i into m i.

So, this N i is basically the mole fraction. This is the mole fraction. So, you could also write this as summation of mole fraction into the corresponding molecular weights. The same way that you have written the Mw, which is the summation of weight fraction into molecular weight. So, you are weighing the molecular weights with weight fraction, and then you are getting the weight average; you are weighing this with weight fraction and that gives you weight average. You are weighing the molecular weight with number fraction that gives you the number average. So, you are weighing the molecular weight to get an average of molecular weight. So, here you are weighing the degree of polymerization to get average degree of polymerization.

So, when you are weighing the degree of polymerization with number average with the number fraction, then you are getting number average degree of polymerization. When you are weighing the degree of polymerization with the weight average, then you get weight average degree of polymerization. So, the same concept of average, this is the number average degree of polymerization. So, summation of the number fraction into x over all xs, if you put the corresponding values here that becomes x into p to the power x minus 1 into 1 minus p, and that is equal to 1 plus p plus p square so on and so forth. And this can be approximated as one divide by 1 minus p.

And similarly, if you are putting all the values here, that will be sum over x square into 1 minus p square into p to the power x minus 1, that will be equal to 1 plus p divided by 1 minus p. And now what is the polydispersity index? Polydispersity index is nothing but Mw by M n. And Mw is basically X w into M 0. M n is basically X n bar into M 0.

So, the number average degree of polymerization into molecular weight average molecular weight of the structural unit, and this is weight average degree of polymerization into average molecular weight of structural unit. And again, to repeat when you are looking for degree of polymerization average, you weigh the corresponding degree of polymerizations with the corresponding number fraction, when you are going for number average degree of polymerization. You way the x that is the degree of polymerization with corresponding weight fraction, when you are going for weight average degree of polymerization.

So, if you put those values here ultimately what you will get you will get 1 plus p, p is the extent of conversion surprise PDI is nowhere near 1. As I told before you need a very high value of p in order to get molecular weight of any importance as per as the practical utility is concerned, p has to be as close to one as possible for your purpose. So, if p is so, p can be 1 or less than 1. So, if p is 0.5. Does that serve your purpose? No, you look at the x n bar value the number average degree of polymerization is extremely low you only a oligomers does not work for you. You need at least 99 percent of conversion go close to 1. So, that means, your PDI or polydispersity index can never be close to 1.

So, the maximum value of PDI can be 1 plus 1 equals to 2 when p equals to 1. And it has to be close to 2. Whether you desire it or not it has to be close to 2. Because in other ways because otherwise you cannot get high molecular weight, polymer that is your first priority to get high molecular weight polymer, and then your PDI is automatically close to 2. So, of course, then there is a way to find out if this theory is right or wrong try to find out the PDIs from the GPC for example, or some say use the suitable standard for calibration. And try to find out the PDIs for different state polymerisations. And you will see that many of them are close to 2. In fact, they are sometimes more than 2 like you know 2.22 2.3 so on and so forth.

There are reasons for that that if you have impurities present in the sample, because the impurities that changed the number of particles in the system, that have a greater effect on the value of M n that is a number average molecular weight. That will reduce the number average molecular weight and correspondingly your PDI will go up. So, that will be higher than 2. So, in practice for many step polymerization reactions you get close to 2. So, that serves as a validation for this theory. It has not been validated for all the reactions, but for many systems it has been found that this particular theory has a sound basis. So, what we will do is that, we will do a small problem very small problem. Just we are going to use the formula and this will give you an idea of how to tackle some of this different simple questions.

Let us say you are asked what is the weight fraction of trimer in a step polymerization that is carried out to 99 percent conversion? So, what is the weight fraction of trimer in a step polymerization that is carried out to 99 percent conversion? I mean these are the utilities. You have done the reaction to a certain extent, and then you want to find out what is the weight fraction of different species you can find out using some of these equations. So, what is the equation for weight fraction w x equals to x into p to the power x minus 1 into 1 minus p whole square. So, this is the expression and your x, you are looking for trimer. So, your x is 3 and your p is 99 percent. So, it is 0.99 square into 1 minus 0.99 square, and it will be approximately you know 2 point I have worked this out. So, to save some time I do not want to calculate it again serves no purpose.

So, these are some of the very simple problems that you can tackle with this it is also informative, and you can find out also for yourself that what will be the number fraction for a dimer trimer so on and so forth. You will find that some of them are higher than the big polymeric species; however, the big polymeric species actually contribute more in terms of weight much more in terms of weight rather than some of these very small species. That is more evident when you are plotting the weight fraction as a function of the x.

So, we will stop here, and in the next class what I want to discuss is a particular site reaction that could be detrimental to the processing to the process of step polymerization. And then finally, we will talk about interfacial polymerization, because that is also an important industrial industrially used process.

So, thank you for your attention in this class. And see you in the next class.