

**Introduction to Polymer Physics**  
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**Lecture - 13**  
**Branching: Hyperbranched Polymers**

Most of the discussion that we have had in this course up till now applies primarily to linear polymers. So, when we talked about the various models for polymer chains; they were mostly restricted to linear polymers. Similarly for solution thermodynamics the development that we introduced a using the Flory Huggins theory, that was also using a model of linear polymers.

So, in this week what we will do is discuss the case of branched polymers primarily Hyper branched Polymers as well as network polymers. And we will see how the behavior of these is different and how from linear polymers and how that behavior can be described. So, for branched polymers we will the study what is the effect of branching on let us say the number average degree of polymerization or the weight average degree of polymerization.

And that will primarily be the focus of today's lecture in the other lectures this week we will also explore the concept of gelation in network polymers. So, how the formation of cross links leads to network polymers and at what point a kind of gelation phenomenon occurs, these are the topics that we will be exploring this week.

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So, in today's lecture we will focus primarily on Branching and the case of Hyperbranched Polymers. So, we will just introduce the case of hyperbranched polymers and then talk a bit about the how one can calculate the number average degree of polymerization or the weight average degree of polymerization for the specific case of such hyperbranched polymers.

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INTRODUCTION	
	Polymerization of $ARB_{f-1}$ monomers:
	A and B are mutually reactive functional groups
	A can only react with B
	Hyperbranched polymer will form if $f > 2$ .
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If we consider a let us say monomeric unit and let us represent that monomer by this  $ARB_{f-1}$  here A and B are functional groups which are mutually reactive. So, we

will be focusing primarily on branch or hyperbranched polymers that form through what is called step polymerization or condensation polymerization.

So, here A and B represent functional groups that are mutually reactive. So, A can react with B to form a link between the monomer units, but A and A cannot react; similarly B will not react with b. Now if we consider this case where here again the R that we have it just represents some other group might that might be present in the monomeric unit, but that is not a functional group; so, it is not participating the reaction as such in the polymerization reaction. Now if we look at the this kind of a monomeric monomer ARB  $f - 1$ ; so, it contains one A functional group and it also contains  $f - 1$  functional groups of type B.

Now, if  $f$  is equal to let us say see what happens when  $f$  can  $f$  takes different values. So, if  $f$  is equal to 2 in that case we will have an ARB kind of polymer because  $f - 1$  will be just one the monomer will have just one A functional group and one B functional group. So, when a polymerization reaction takes place for such monomers then they will invariably lead to the formation of linear polymers. So, any monomer that is bifunctional that its polymerization will result in the formation of linear polymers.

But if instead we have a monomer where this quantity  $f$  if this is a greater than 2 in that case branching can occur and we will get the formation of hyperbranched polymers. The condition for formation of branched polymers is that this  $f$  that we have it should be greater than 2. And if it is equal to 2 then we will just get linear polymers; if you want to just represent this schematically, then the monomer that we have that can be represented something like this where repeat units have been shown here. And the black dotted circle is any other group that might be present in the monomer, but which is not a functional group and which is not participating the polymerization reaction.

This monomer can react with another monomer and form this A B linkage ok. So, we have said that A can only react with B and or B can react with A only. So, we can have a reaction between the A and B functional groups of 2 monomers and we get this linkage. Similarly as the reaction proceeds we can the B groups that we had on this small monomeric unit that also can react with other monomer A groups of other monomers and in this way we can have a formation of a kind of a branched polymer. And if it proceeds

further on we will get a hyperbranched polymer, which will have a very high degree of branching.

So, even for this simple case we can see that we have branching over here as well as a small branch over here or if we consider this to be the main chain then instead this can be considered as a branch. So, in any case if this reaction proceeds further then we will have a polymer molecule that will be highly branched and that basically will can be referred to as a hyperbranched polymer. Let us look at how one can determine the number average degree of polymerization for such hyperbranched polymer formation.

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### NUMBER-AVERAGE DEGREE OF POLYMERIZATION

Hyperbranched Polymers

Introduction

Number-Average Degree of Polymerization

Weight-Average Degree of Polymerization

**Polymerization of  $ARB_{f-1}$  monomers:**

Each monomer has one functional group of type A and  $(f - 1)$  functional groups of type B.

Let the total number of monomers present initially be  $N_{tot}$ .

Let  $p$  represent the fraction of reacted B groups.  $p \Rightarrow$  Extent of reaction

Then, the number of B groups reacted is  $p(f - 1)N_{tot}$ .

Number of A groups that have reacted will also be  $p(f - 1)N_{tot}$ .

Fraction of A groups that have reacted will be  $p(f - 1)$ .

Fraction of unreacted A groups =  $1 - p(f - 1)$

Number of unreacted A groups =  $N_{tot} [1 - p(f - 1)]$ .

Every molecule present in the reaction mixture contains one unreacted A group.

Number of molecules present in the reaction mixture = Number of unreacted A groups

So, again we are considering the polymerization of a monomer which is of  $ARB_{f-1}$  type. So, it contains a single monomer molecule contains only one functional group of type A and  $f - 1$  functional groups of type B where  $f$  has to be greater than 2. So, in the schematic that we had drawn in the previous slide there  $f$  was equal to 3. So, that the monomers that we had were of  $ARB_2$  type, but the discussion that we will have and the theory that will develop it will be valid for any kind of polymerization where this  $f$  for it will be valid for any value of  $f$  in general.

So, as we discussed each monomer has one function group of type A and  $f - 1$  of type B. And then now if we consider a case where the reaction has proceeded up to a certain point and certain number of functional groups have reacted. So, let us say that the reaction has proceeded up to a point where a fraction of functional groups at a of type B

that have reacted let us say that, that fraction is referred to as  $p$ . Let  $p$  represent the fraction of groups of type B that have reacted and let us say that initially in the reaction mixture we had  $N_{\text{tot}}$  this number of monomers present.

So, initially to start with will have just a monomer molecules present and this once a reaction starts, then the functional groups will start reacting and that is A and B; these groups will start reacting and form start to form linkages between the monomeric units. And this will lead on to the formation of dimer trimer and larger polymeric molecular species.

So, if we are using this symbol  $p$  to represent the fraction of functional groups of type B that have reacted at a certain point; then using and also using the fact that we had initially  $N_{\text{tot}}$  number of monomers present; what when we what we can say is that the number of groups of type B that have reacted that is  $p$  times  $f - 1$  times  $N_{\text{tot}}$  ok.

So, how this comes about is if we consider a single monomeric molecule; a single monomer molecule then that contains  $f - 1$  functional groups of type B. Initially we if you have  $N_{\text{tot}}$  number of monomer molecules and the number of functional groups of type B present on the  $N_{\text{tot}}$  multiplied by this  $f - 1$ . And if at a certain point a fraction of  $p$  of these function groups of type B have reacted; then the number of groups that have reacted will be just this fraction  $p$ , times the total number of groups of type B that they are present initially; so, that will be  $p$  times  $f - 1$   $N_{\text{tot}}$ .

And similarly if the number of groups of type B that have reacted that will be equal to the number of groups of type A that have reacted. Because any reaction basically takes place between a group of type A and a group of type B. So, now, the number groups of each type that have reacted at a certain point; they will be equal. So, that is why the number of groups of type A that have reacted at this point where the fraction of B groups reacted is  $p$ .

So, that number will also be the same as what we have here and that will also be  $p$  into  $f - 1$  into  $N_{\text{tot}}$ . So, that is the number of a group that has that is reacted and initially if we have  $N_{\text{tot}}$  number of monomers; we know that in the type of monomer that we have we are considering each monomer molecule has only one group of type A.

So, initially in the reaction make sure the number of functional groups of type A present will also be simply  $N_{tot}$ . And if the number of A groups that have reacted is they given by this expression; then the number of groups or the fraction of a groups that that has reacted will simply be; whatever the number of groups of a type A that have reacted, divided by the total number of groups of type A that were present. So, this  $p f$  minus 1 times  $N_{tot}$  divided by  $N_{tot}$ ; so, that fraction of A groups that have reacted will simply be  $p f$  minus 1.

And generally this quantity  $p$  that we have which is represent representative of the fraction of B groups that have reacted; this quantity  $p$  is also referred to as the extent of reaction ok. So, it is a it is a measure of how far the reaction has proceeded and it is also called the extent of reaction. So, if the fraction of A groups that have reacted is this then the fraction of unreacted A groups that will simply be 1 minus the reacted fraction. So, the fraction of reacted plus the fraction of unreacted groups of type A will simply be equal to 1. So, the fraction of unreacted A groups will be 1 minus this  $p f$  minus 1 and since then total number of A groups present in the system is just equal to that number of monomers present initially which is  $N_{tot}$ .

So, the number of unreacted A groups will we will get by just multiplying this fraction by  $N_{tot}$ . So, that is what we have done here and this is what we get; so that is number of unreacted A groups. So, now, we can identify a couple of things here; so, at any point of time during the reaction if we consider the entire reaction make sure it will consist of collection of molecules are different sizes. So, at any point of time during the reaction we might still have some unreacted monomer molecules present as well as other molecules of different sizes present as well.

But one thing in common about all these molecules will be that all of them will contain only one unreacted A group. So, whether it is a single monomer molecule are a large branch polymeric chain that that has formed in either case the number of unreacted A groups will simply be 1 for per molecule. So, after identifying this fact what we can say is that the number of molecules present at any point of time will simply be equal to the number of unreacted A groups that are present.

Because each molecule contains just one unreacted A group, but that is what we have stated here is that number of molecules present in the reaction make sure at any point of

time where the extent of reaction is  $p$ ; that will simply be equal to the number of functional groups of type A which are still unreacted.

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**NUMBER-AVERAGE DEGREE OF POLYMERIZATION**

Number of molecules present in the reaction mixture = Number of unreacted A groups

Number-Average Degree of Polymerization =  $\frac{\text{Number of monomers present initially}}{\text{Number of molecules present in reaction mixture}}$

$\bar{x}_n = \frac{N_{\text{tot}}}{N_{\text{tot}}[1 - p(f-1)]} = \frac{1}{1 - p(f-1)}$

$\bar{x}_n$  diverges at  $p_c = \frac{1}{(f-1)}$

$p_c$ : Maximum possible fraction of reacted B groups

Again using this condition now what we can do is try to develop the  $\bar{N}$  expression for the number average degree of polymerization for such hyperbranched polymers.

So, if you recall the number average degree of polymerization that we can that we had introduced in the very first lecture and that is a measure of how many repeat units or monomeric units are basically present on average in a given polymer chain in our in a certain polymer sample. So, if a polymer sample can is poly dispersant has chains of different lengths; then on an average given the number of monomeric units or the repeat units present in a certain polymer molecule that is what this number average area of polymerization represents.

In the present case, so what we can identify is that this number average degree of polymerization will simply be equal to the number of monomers that were present initially, divided by the number of molecules that are present at any point of time in the reaction mixture. So, initially initially we will only have monomer molecules present and as they start reacting; some monomers will convert to dimer, trimers and larger molecules whether were some monomers will still remain unreacted and as the reaction proceeds; more and more monomers will react and larger polymer chains will form.

The number of molecules that have formed at any point of time during the reaction; if we can if we take that number and use that to divide the number of monomers at the initially present, then that ratio basically gives the number average degree of polymerization. So, this is something that you can just consider a test case where let us say initially you had 10 monomeric molecules.

And after a certain point of time you let us say end up with a system which has a 2 unreacted monomer molecules and also which has resulted in the formation of; let us say 3 2 dimers and as well as a tetramer. So, initially let us say we have a collection of 4 5 6 7 8 9 10.

So, initially let us say we have 10 monomer molecules present. So, that will be the numerator here and of course, in a real system the number of monomer molecules will be huge, but just for as an illustration for simple case we are considering 10 monomer molecules. So, that will be the numerator and at any point of time let us say what we have is let us say 2 dimers have formed like this and one tetramer has also formed. So, we have ah 2 unreacted monomer molecules as well as these 2 dimers and 1 tetramer. So, that gives us the total number of molecules present at this point is simply 1 2 3 4 5.

So, 2 monomer molecules which are unreacted; 2 dimers that is 4 plus 1 tetramer; so, 5 molecules are present at this at a certain point of time when the reaction mixture has this composition. So, in at this point of time the new denominator will simply be 5. And based on the ratio that we have 10 by 5 the number average degree of polymerization will simply be 2.

And similarly if the reaction proceeds further; so, that at some other point of time; now at some other point of time if the reaction mixture is such that we have hexamer which contains 6 monomeric units and a tetramer. So, now the number of molecules present in the reaction mixture has reduced to 2 and initially a number of monomers was 10. So, now, the number average degree of polymerization has increased to 5.

So, just by looking at this case where one this oligomeric species has 4 units and the other one has 6 monomeric units; so, on an average one would expect the number average degree of polymerization to be 5 and that is what we are getting from this relation as well.



So, now, we can use this relation and also the fact that the number of molecules present in the reaction mixture at any time that is equal to the number of unreacted A groups. So, the in the denominator that we have here we can replace this by the number of unreacted A groups. And if we do that the number of monomers initial initially present was  $N_0$  that is what we have considered. And the number of molecules present in the reaction mixture, we have replaced that by the number of unreacted A groups present and the expression for that we already discussed in the previous slide that is this.

So, that gives the number average degree of polymerization to be  $\frac{1}{1 - pf}$  where  $f$  is the number of functional groups per monomer. So, this is an expression that is valid for a hyperbranched polymer that forms, where the value of  $f$  should be greater than 2. But even if the value when the  $f$  value of  $f$  is 2, which will lead to the formation of linear polymers, even in that gives this general expression is valid. So, for the case where let us say the value of  $f$  is 2 and we get linear polymers. So, in that case this expression simply reduces to  $\frac{1}{1 - p}$  for when  $f$  is 2.

So, that equation for which is valid only for linear polymers that is called the Carother's equation and that was proposed long back in the probably in the 1930's by Carother's. A more generalized equation that is valid for branched polymers as well is this where  $f$  can have a value greater than 2 as well. And in general if  $f$  has a value greater than 2 only then one will get branched polymers and hyperbranched polymers.

So now, one thing to note here in this equation is that for a certain value of  $p$ . So, for a certain value of this extent of reaction  $p$ ; the  $\frac{1}{1 - pf}$  actually tends to diverge. So, the  $\frac{1}{1 - pf}$  or the number average degree of polymerization diverges when this  $p$  takes this critical threshold value of  $\frac{1}{f - 1}$ .

So, when the extent of reaction becomes equal to  $\frac{1}{f - 1}$  that corresponds to a point where this the expression that we have developed here diverges and that essentially what that tells us is that the branching has reached such a point that some kind of a gel formation or network formation resulting in gelation might begin.

But that condition this condition actually corresponds to the fact that the maximum possible fraction of B groups have already reacted. So, the maximum possible fraction of B groups would have reacted when all the A groups present in the system have all

reacted. So, when all the A groups are exhausted; the maximum number of B groups should also have been reacted and beyond that no further reaction can take place.

So, in general this point will not be reached and so gelation typically will not be observed in for a such a system and we will usually have a hyperbranched kind of polymers. Development of this expression for  $\bar{x}_N$  that we have done here we have used certain simple arguments and developed this expression and it saw it is fine. But if we want to extend this approach and try to find let us say the weight average degree of polymerization or the polydispersity index.

So, if you want to find some certain other quantities related to the hyperbranched polymers. So, the simple approach that we have adopted here actually is has its limitations and cannot be extended to obtaining other quantities like the weight average degree of polymerization.

We will next discuss a more kind of a more powerful approach in the sense that; it can it apart from giving us a number average degree of polymerization, it can also it will also allow us to obtain the weight average degree of polymerization as well as the polydispersity index for a given hyperbranched polymer.

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**NUMBER-AVERAGE DEGREE OF POLYMERIZATION**

In an  $N$ -mer containing  $N$  monomer/repeat units:

Total number of B groups present:  $(f-1)N$       Total number of reacted B groups:  $N-1$

Total number of unreacted B groups:  $(f-2)N+1$

Probability that a B group has reacted:  $p$       Probability that  $N-1$  B groups have reacted:  $p^{N-1}$

Probability that a B group has not reacted:  $1-p$       Probability that  $N-1$  B groups have not reacted:  $(1-p)^{(f-2)N+1}$

**Number fraction of  $N$ -mers:**

$$n_N(p) = a_N p^{N-1} (1-p)^{(f-2)N+1}$$

**Weight Average Degree of Polymerization**

$$\bar{x}_N = \frac{[(f-1)N]!}{N! [(f-2)N+1]!}$$

$$n_N(p) = \frac{[(f-1)N]!}{N! [(f-2)N+1]!} p^{N-1} (1-p)^{(f-2)N+1}$$

So, this approach that we will be discussing next is the kind of a statistical approach and for this discussion; we will again consider let us say  $N$  mer which is basically a polymer

which contains  $N$  number of monomer repeat units. So, we will consider the formation; we will start by considering the formation of a polymeric molecule which contains  $B$  number of monomer units and will refer to this polymeric molecule as  $N$  mer.

So, as we have discussed previously the schematic that we have here it contains if we count here it contains 10 monomeric units. So, this will correspond to a 10 mer. So, the expression that will develop will be for a general case of an  $N$  mer where the molecule contains  $N$  number of monomer units. Now in this  $N$  mer for any  $N$  mer that we have the total number of  $B$  groups present will be  $f$  minus 1 times  $N$ . The reason for this is  $N$  mer will contain a single  $N$  mer molecule will contain  $N$  number of monomer units and each monomer unit contains  $f$  minus 1 functional groups of type  $B$ .

So, so that the total number of  $B$  groups present in an  $N$  mer; that will be equal to just  $f$  minus 1 times  $N$ ; so, for the case that we have here if we see the  $N$  which is number of monomer units present in this  $N$  mer is 10 and the value of  $f$  for the monomeric unit that we have it is a  $B_2$  type of monomeric units. So, the value of  $f$  is 3 for this case; so, the number of  $B$  group present according to this formula will be  $3$  minus  $2$  which is  $2$  times  $10$ , so,  $20$ . And if we count here for this entire molecule will see that we have  $20$  functional groups of type  $B$ .

Out of that  $B$  groups that are present in this particular  $N$  mer; if we focus on the  $B$  groups that have reacted. So, we are not talking about the reacted  $B$  groups in the entire reaction mixture, we are just talking about the number of reacted  $B$  groups in this particular  $N$  mer molecule. So, that number of reacted  $B$  groups is simply  $N$  minus 1 because any  $N$  mer molecule which contains  $N$  monomeric units will have  $N$  minus 1  $A-B$  bonds.

So, each  $A-B$  bond corresponds to the reaction between the functional group of type  $A$  with that of type  $B$ ;  $N$  minus  $A-B$  bonds basically correspond to the number of reacted  $B$  groups and that is that can also be seen here where since we have a 10 mer. So, we will see that there are 9  $A-B$  bonds; so 4 5 6 7 8 9. So, there; so those many  $A-B$  groups have reacted. So, all the  $B$  groups that are part of these bonds these are the ones that have reacted and the remaining are of course, unreacted.

So, the number of unreacted  $B$  groups will be just the total number of  $B$  groups present, minus the number of reacted  $B$  group; so, that comes out to be this. And one more thing

to note is that the probability that a B group has reacted that is given by  $p$ . So, the extent of reaction that we have defined previously the same  $p$  we are using here. And that  $p$  earlier had been defined as the fraction of B groups in the entire reaction mixture that have reacted at a certain point of time.

So, now that fraction also is equivalent to the probability that a certain B group has reacted in the reaction mixture. So, if you just randomly select a B group and try to see if it has reacted or not in the reaction mixture; the probability that it has reacted at a certain point of time will simply be  $p$  and that that same probability can be applied to for the reaction of all the B groups that are present in this N mer.

So, for any B group that is present in this N mer; the probability that it has reacted is  $p$  and the probability that let us say all the  $N - 1$  B groups that have reacted in this N mer. So, then net probability that all of them have reacted is simply this  $p$  multiplied by itself  $N - 1$  number of times. So, that will just be  $p$  to the power  $N - 1$ .

Similarly, for the number of B groups that have that have not reacted is given by this number here and the probability that the B group has not reacted is given just by  $1 - p$ . So, the probability of that a B group has reacted is  $p$ . So,  $1 - p$  will just represent the probability that a certain B group has not reacted.

So, again the total number of unreacted B groups is this  $f - 2 \times N + 1$  and for a given N mer; what we see is that it should contain  $N - 1$  reacted B groups and  $f - 2 \times N + 1$  unreacted B groups. So, the probability that  $N - 1$  B reacted groups represent that is  $p$  to the power  $N - 1$ . Similarly the probability that  $f - 2 \times N + 1$  number of B groups are unreacted will simply be this  $1 - p$  raised to the power that quantity  $f - 2 \times N + 1$ .

The probability that this; N mer has formed is will just be given by  $ah$  or will be proportional to the product of these 2 quantities the probability that the  $N - 1$  B groups have reacted and the probability that the other B groups in the N mer have not reacted. So, if we combine take the product of these probabilities that will give us a measure of the probability that an N mer is has formed in the reaction mixture. And this probability that N mer has formed in the reaction mixture is simply equal to the number fraction of N mers that are present in the reaction mixture and this number fraction is equivalent to the mole fraction as well.

So, for a certain polymer molecule having  $N$  number of monomer units the probability; that it has found that is given by this expression here. And that is equivalent to the number fraction of such  $N$  mer polymeric molecules present in the entire reaction mixture and it will also be equivalent to the mole fraction of these  $N$  mers in the entire reaction mixture.

So, we said that the product of these 2 the 2 probabilities is actually a measure of this number fraction that we have. And because this extra term  $N$  also actually comes in here; so, apart from the product of these 2 probability that will lead to the formation of this  $N$  mer ah that will give the probability of formation of this  $N$  mer.

This extra a  $N$  term appears because even when an  $N$  mer forms; there are many different ways which this  $N$  monomeric units can be arranged to get different arrangements of the same  $N$  mer ok. So, this a  $N$  actually takes in into account that extra number of arrangements that are possible for this  $N$  repeat units or monomeric units to get different let us say different arrangements of the same  $N$  mer molecule.

So, this a  $N$  also we can evaluate. So, what we need to do is take the product of several these terms. And what each of these terms will just discuss briefly and we will see that this product which comes out to be this ratio that is actually related to this a  $N$  here the number of ways in which we can arrange this  $N$  monomer units to form our  $N$  mer.

Here if is this expression that we have is based on the fact that the number of different ways of arranging the  $N$  monomer units to form the  $N$  mer is basically equal to the number of different ways in which their respective or successive B groups can be chosen whose reaction with an a group will lead to the growth and formation of this  $N$  mer. So, the first term here basically represents the number of ways in which B group can be chosen for the first reaction in the first a B linkage to form.

So, we have  $N$  minus 1 linkages here in for the entire  $N$  mer. So, for the  $N$  mer to form the first linkage that forms the number of ways in which we can select the B group that takes part in this linkage formation; that is just  $f$  minus 1 times  $N$  because that is a total number of B groups that are present for us in this monomer  $N$  mer molecule.

So, now that we have chosen that one B group out of all the B groups present and that bond A B bond has formed. For the formation of next A B bond again we will see how

many way in different ways are there in which we can select an unreacted B group. So, one B group has already reacted; so, number of B groups that are available for the formation of second A B linkage is given by just this term which is  $f N f \text{ minus } 1 N \text{ minus } 1$  because 1 has already reacted to form the previous A B linkage.

Similarly, for the third A B linkage the number of B groups available for first selection is  $f N \text{ minus } 1 N \text{ times } N \text{ minus } 2$ . And if we go on in this direction in this way then the total number of reacted B groups is  $N \text{ minus } 1$ . So, this the last term that we get if you for continue this series the last term that we will get will be  $f \text{ minus } 1 N \text{ minus } N \text{ minus } 2$ .

So, that is number of ways in which B group can be chosen to form the last A B linkage of for this N mer. So, the product of all the different ways in which we can choose the successive B groups; to form the A B linkages that product is given by this expression and that product is actually can be used to find out this a N.

So, that the overall product that we have the number of different ways that we have counted that is given by this ratio. And, but in this ratio that we have obtained here the some extra counting has been done because the all the different N monomeric units present, which we are attaching to form this N mer they are indistinguishable there identical molecules. Their internal permutation actually will not lead to any distinct or distinguishable arrangement of a different N mer molecule.

So, we need to scale or divide this quantity that we have obtained by N factorial to account for the extra counting that has been done. So, this a N simply is equal to this term here divided or scale by the N factorial term which takes care of the fact that all the N monomer molecules that that are being arranged to form this N mer they are identical. So, their internal arrangement will not lead to a distinct or different confirmation of our N mer branch polymer.

So, with this expression for a N; we can write the overall expression for this number fraction of N mers as simply this here. So, this a N we have substituted here and there is the expression that we get. So now, starting from this in expression, which is the number fraction of N mers; that is present at a certain point of time in the reaction mixture when the extent of reaction is p.

So, starting from this expression we can next try and derive the expressions for the number average molar mass and number average degree of polymerization and the weight average degree of polymerization. And we will see that the number average degree of polymerization expression that we get is the same as what we already obtained using another approach, but using the this the current approach we can get other quantities as well.

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**NUMBER-AVERAGE DEGREE OF POLYMERIZATION**

Hyperbranched Polymers

Introduction

Number-Average Degree of Polymerization

Weight-Average Degree of Polymerization

$$n_N(p) = \frac{[(f-1)N]!}{N![(f-2)N+1]!} p^{N-1} (1-p)^{(f-2)N+1} = a_N p^{N-1} (1-p)^{(f-2)N+1}$$

$$\sum_{N=1}^{\infty} n_N(p) = 1 \qquad \sum_{N=1}^{\infty} a_N p^{N-1} (1-p)^{(f-2)N+1} = 1$$

$$\frac{(1-p)}{p} \sum_{N=1}^{\infty} a_N p^N (1-p)^{(f-2)N} = 1 \qquad \longrightarrow \qquad \sum_{N=1}^{\infty} a_N p^N (1-p)^{(f-2)N} = \frac{p}{(1-p)}$$

Let  $x = p(1-p)^{(f-2)}$   $\longrightarrow \qquad \sum_{N=1}^{\infty} a_N x^N = \frac{p}{(1-p)}$

$$\longrightarrow \left\{ \sum_{N=1}^{\infty} N^k a_N x^N = x \frac{\partial}{\partial x} \left\{ \sum_{N=1}^{\infty} N^{k-1} a_N x^N \right\} = x \frac{\partial}{\partial p} \left\{ \sum_{N=1}^{\infty} N^{k-1} a_N p^N (1-p)^{(f-2)N} \right\} \frac{\partial p}{\partial x} \right\}$$

This is just the expression that we obtain we have just obtained. What we can identify is that this number fraction of N mers that number fraction; if we sum these number fraction over all the possible N mers that might be present. So, if we sum it over N ranging from one to infinity; so, starting from monomeric species the molecules that are present at a certain point of time in the reaction mixture to very long let us say polymeric chains that have formed.

So, if we sum over all the cases possible then the number distance is a number fraction the overall sum should equal to 1. So, it should it is a normalized kind of distribution of the number fractions. So, using this fact that the number fraction their sum over all the possible N mers that can be present is 1. So, using the fact that this summation is 1 because the summation of number fractions, we can write down that this summation also is 1 because this number fraction is simply given by this expression here.

So, now, in this summation we can what we can do is take out the term  $1 - p$  over  $p$ . So, if we do that we have taken out this term  $1 - p$  over  $p$ . So, in here actually this  $p$  to the power  $N - 1$  that we had that changes to  $p$  to the power  $N$  because if we take this  $p$  inside the summation then this  $p$  to the power  $N$  will become  $p$  to the power  $N - 1$  here.

Similarly, this the plus 1 in the exponent of this  $1 - p$  that has been removed here and that  $1 - p$  has been taken out here. And since the summation is over  $N$  its the quantity  $p$  does not depend on the summation index  $N$ ; so, it can easily be taken outside. So, just by rearrangement what we can say is that the summation of this term which is a  $N$  times  $p$  to the power  $N$  times  $1 - p$  to the power  $f - 2$ ; the summation of this from  $N$  equal to 1 to infinity that is simply given by this ratio  $p$  over  $1 - p$ .

So, now that we have identified this expression this there is some substitution that we can make. So, what we can see here is that this  $p$   $N - 1$  minus  $p$  to the power  $f - 2$  both are raised to the power  $N$  in this term. So, if we simply replace this quantity;  $p$  times  $1 - p$  to the power  $f - 2$  by this ah symbol  $x$ ; then we can write this expression in a kind of a shorter format.

And the equivalent expression will simply be this where we have used; we have replaced this term simply by  $x$  and that is raised to the power  $N$ . And before we move on to actually developing the expressions for the number average and weight average molar mass, this mathematical identity or mathematical operation that we will just discuss quickly and which will be useful in further development of this theory.

The mathematical operation that or identity that we are we will we are discussing is that if we have a summation of this kind  $N$  to the power  $k$  a  $N x$  to the power  $N$  sum from 0 1 to infinity; then that equivalently can also be written as  $x$  times partial derivative with respect to  $x$  of this entire quantity where; where we have changed this  $N$  to the power  $k$  to the  $N$  to the power  $k - 1$ .

So, if we instead of  $x$  if we just replace  $x$  by what it stand for; then the that expression becomes this. And here instead of  $\frac{\partial}{\partial x}$  in the next step what we have done is taken  $\frac{\partial}{\partial p}$  and then to account for that change in the variable with respect to which we are differentiating; we have also multiplied this  $\frac{\partial p}{\partial x}$  term here. We will



see that the expression that we have developed here will be useful in developing expressions for both weight average and number average degree of polymerization.

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**NUMBER-AVERAGE DEGREE OF POLYMERIZATION**

Hyperbranched Polymers

Introduction

Number-Average Degree of Polymerization

Weight-Average Degree of Polymerization

$$\sum_{N=1}^{\infty} N^k a_N x^N = x \frac{\partial}{\partial p} \left( \sum_{N=1}^{\infty} a_N p^N (1-p)^{(f-2)N} \right) \frac{\partial p}{\partial x}$$

$k = 1:$

$$\sum_{N=1}^{\infty} N a_N x^N = x \frac{\partial}{\partial p} \left( \sum_{N=1}^{\infty} a_N p^N (1-p)^{(f-2)N} \right) \frac{\partial p}{\partial x}$$

$$\sum_{N=1}^{\infty} a_N p^N (1-p)^{(f-2)N} = \frac{p}{(1-p)}$$

$$\sum_{N=1}^{\infty} N a_N x^N = x \frac{\partial}{\partial p} \left( \frac{p}{(1-p)} \right) \frac{\partial p}{\partial x}$$

$$\sum_{N=1}^{\infty} N a_N x^N = \frac{p}{(1-p)[1-p(f-1)]}$$

$x = p(1-p)^{(f-2)}$

$$\frac{\partial p}{\partial x} = \frac{1}{\frac{\partial x}{\partial p}} = \frac{p(1-p)}{x[1-p(f-1)]}$$

$$\frac{\partial}{\partial p} \left( \frac{p}{(1-p)} \right) = \frac{1}{(1-p)^2}$$

So, the the same expression that we had in the previous slide has again been written here ok. And let us per consider a case where if this quantity k is equal to 1; so, for that case this summation N into a N into x to the power N that simply becomes this term where if we take k equal to 1; then N to the power k minus 1 that that term simply becomes 1.

So, now, let us see if we can obtain expressions for these 2 terms; we know from our previous discussion just by using the fact that the number fraction their sum is 1. So, from that we develop this expression that this summation is equal to p over 1 minus p; so, this we have already developed.

And; so the this equation here can be rewritten in this form where we have substituted p over 1 minus p in place of this summation here ok. Next if we try to carry out these 2 differentiations and substitute them back in this expression then we will get any an equation a useful equation for this summation. So, x we have already defined as in terms of p as this. Now del p del x one can write as del p del x is a term here one can write as 1 over del x del p. And this since x is a function of p of this form; then that del x del p through differentiation one can evaluate and upon simplifying that in the expression obtain finally, we get this expression for del p del x.

Similarly, for differentiation of the  $p$  over  $1 - p$  that is in even simpler differentiation and it upon differentiation will simply get  $1$  over  $1 - p$  square. So, now, if we substitute this expression here as well as  $1$  over  $1 - p$  square in place of this derivative then finally, this summation here will be given by  $p$  divided by  $1 - p$  times  $1 - p$  multiplied by  $f - 1$  as we have shown here. So, this equation that we have this will be useful in determining an expression for the number average degree of polymerization.

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**NUMBER-AVERAGE DEGREE OF POLYMERIZATION**

Hyperbranched Polymers

Introduction

Number-Average Degree of Polymerization

Weight Average Degree of Polymerization

$$\rightarrow n_N(p) = \frac{[(f-1)N]!}{N![(f-2)N+1]!} p^{N-1}(1-p)^{(f-2)N+1} = a_N p^{N-1}(1-p)^{(f-2)N+1}$$

$$\bar{x}_n = \sum_{N=1}^{\infty} N n_N(p) = \sum_{N=1}^{\infty} N a_N p^{N-1}(1-p)^{(f-2)N+1} = \frac{(1-p)}{p} \sum_{N=1}^{\infty} N a_N p^N (1-p)^{(f-2)N}$$

$$\sum_{N=1}^{\infty} N a_N p^N (1-p)^{(f-2)N} = \sum_{N=1}^{\infty} N a_N x^N = \frac{p}{(1-p)[1-p(f-1)]}$$

$$\bar{x}_n = \frac{(1-p)}{p} \cdot \frac{p}{(1-p)[1-p(f-1)]} = \frac{1}{1-p(f-1)} \quad \text{for } p < p_c = \frac{1}{(f-1)}$$

Again we have we will we have rewritten the expression that we obtained for the number fraction of an  $N$  mer present. And the number average degree of polymerization can simply be written as this  $N$  multiplied by this number fraction and the summation being taken from  $N$  equal to  $1$  to infinity.

So, if we look at this carefully this  $N$  is the number fraction which is nothing, but the mole fraction. So, we discussed a number fraction is equivalent to the mole fraction of these  $N$  mer polymeric molecules and if you multiply that mole fraction or the number fraction by the corresponding number and if we take the summation summation over all possible values of  $N$  that is what that is a different kind of a definition of the number average degree of polymerization.

So, that is what we have used and this kind of an expression this is also called the first moment of this quantity  $N p$ . Again by substituting this in place of  $N n p$  here we get this

summation and that that is the expression for  $\bar{x}_N$  which is the number average degree of polymerization. Next again as we did previously we can take this  $1 - p$  over  $p$  outside and that will change these 2 terms in here. So, instead of  $p$  to the power  $N - 1$  will have  $p$  now  $p$  to the power  $N$  now and instead this plus 1 here will not appear in this term anymore because that has come out here.

So, now we have this expression and we see that this term is nothing, but again  $x$  to the power  $N$ . So, I by identifying the fact that this term is simply  $x$  to the power  $N$  we can write the previous summation in this form. Now this summation we have already in the previous slide obtained an expression for this. And that expression was this  $p$  over  $1 - p$  multiplied by  $1 - p$  times  $f - 1$  since we have this value for this summation.

So, that can directly be substituted in this expression here and that will give us an expression for  $\bar{x}_N$ . So, the expression for  $\bar{x}_N$  upon substitution is. So, this term we have substituted here; so, this  $1 - p$  will cancel, this  $p$  will cancel this. So, the final expression is this for  $\bar{x}_N$  and we see this is the same as what we obtained earlier in the initial part of this lecture using a different approach. And for  $p$  this is only applicable for  $p$  less than  $p_c$  equal to  $1 / (f - 1)$ ,  $1 / (f - 1)$  because at  $p$  equal to  $p_c$  this will diverge.

(Refer Slide Time: 43:53)

**WEIGHT-AVERAGE DEGREE OF POLYMERIZATION**

Hyperbranched Polymers

Introduction

Number-Average Degree of Polymerization

Weight-Average Degree of Polymerization

$$n_N(p) = a_N p^{N-1} (1-p)^{(f-2)N+1} = \frac{(1-p)}{p} a_N x^N \quad x = p(1-p)^{(f-2)}$$

$$\bar{x}_w = \frac{\sum_{N=1}^{\infty} N^2 n_N(p)}{\sum_{N=1}^{\infty} N n_N(p)} = \frac{\sum_{N=1}^{\infty} N^2 a_N x^N}{\sum_{N=1}^{\infty} N a_N x^N}$$

$k = 2:$   $\sum_{N=1}^{\infty} N^2 a_N x^N = x \frac{\partial}{\partial p} \left( \sum_{N=1}^{\infty} N a_N p^N (1-p)^{(f-2)N} \right) \frac{\partial p}{\partial x}$

$$\sum_{N=1}^{\infty} N a_N p^N (1-p)^{(f-2)N} = \sum_{N=1}^{\infty} N a_N x^N = \frac{p}{(1-p)[1-p(f-1)]}$$

$$\frac{\partial p}{\partial x} = \frac{1}{\partial x / \partial p} = \frac{p(1-p)}{x[1-p(f-1)]}$$

$$\sum_{N=1}^{\infty} N^2 a_N x^N = \frac{[1-p^2(f-1)]p}{(1-p)[1-p(f-1)]^3}$$

Next using a similar approach we can also find out the weight average degree of polymerization. So, the good thing about this approach that we are following now is that apart from number average degree of polymerization; the weight average degree of polymerization can also be obtained.

So, again we start with the expression for the number fraction of an N mer that we have developed earlier and the expression for  $x$  in terms of  $p$ . And we note that the weight average degree of polymerization is simply the ratio of this summation  $\sum N^2 N_p$  by  $\sum N N_p$  and both summations are from  $N=1$  to infinity.

So, there is something that we are not explicitly proving, but it can easily be shown. So, this  $\sum N N_p$  is simply given by this. So, if you substitute instead of  $N N_p$  if you substitute  $1 - p$  over  $p$  times a  $N x^N$  to the power; then this  $1 - p$  over  $p$  will cancel in the numerator and the denominator here and  $N$  will get this ratio of these 2 summations.

And if you look at the denominator this summation we have already developed an expression for this summation in the previous slide ok. Now let us see how we can develop an expression for the summation in the numerator and once we have both we can just divide them and get an expression for  $\bar{x}_w$ . Again we go back to the general expression that we had earlier and use a  $k$  equal to 2.

So, for  $k$  equal to 2 we get  $N^2$  here and here we get  $N$  to the power  $k - 1$ . So, in this case it becomes just  $N$  and again other similar terms are there. So, this  $\sum N^2 N_p$  we have already discussed in the previous slide that its value can easily obtain and the value is simply this same as before. For this case first we need to find out the expression for this summation and then that expression can be differentiated respect to  $p$ .

So, now if we again note this term this is nothing, but again  $x$  to the power  $N$  and provided that we are using this definition for  $x$ . So, and this whole summation is nothing, but the summation that we have in the denominator here and that summation we have already developed the expression for it in the previous slide as we discussed this term is simply  $x$  to the power  $N$  and the value of this summation we have already discussed in the previous slide to be this.

So, now, this whole expression can be substituted here and the partial derivative is with respect to  $p$  can be taken. So, that will in this is a function of  $p$  and  $f$ , but since it is a

partial derivative f can be taken as constant and then one can differentiate and obtain the next entire an expression for this term and this del p del x is already known to be this. So, after doing these operations and combining all the terms finally, the expression for this summation it can be shown to be simply this.

So, now that we have an expression for this summation which is appears in the numerator here and the expression for this information the denominator which is this one was already discussed in the previous slide. So, we can combine these to take the ratio to obtain the weight average degree of polymerization.

(Refer Slide Time: 47:11)

**WEIGHT-AVERAGE DEGREE OF POLYMERIZATION**

Hyperbranched Polymers

Introduction

Number Average Degree of Polymerization

Weight Average Degree of Polymerization

$$\bar{x}_w = \frac{\sum_{N=1}^{\infty} N^2 n_N(p)}{\sum_{N=1}^{\infty} N n_N(p)} = \frac{\sum_{N=1}^{\infty} N^2 a_N x^N}{\sum_{N=1}^{\infty} N a_N x^N} = \frac{[1 - p^2(f-1)]p}{(1-p)[1 - p(f-1)]^2} = \frac{1 - p^2(f-1)}{[1 - p(f-1)]^2}$$

Polydispersity index:

$$\frac{\bar{M}_w}{\bar{M}_n} = \frac{\bar{x}_w}{\bar{x}_n} = \frac{[1 - p^2(f-1)]}{1 - p(f-1)} = \frac{1 - p^2(f-1)}{1 - p(f-1)} \quad \text{for } p < p_c = \frac{1}{(f-1)}$$

For ideal, randomly-branched N-mer:  $\langle R_g^2 \rangle \cong \frac{\pi(f-1)}{8(f-2)} b^2 N^{1/2}$

$R_g \sim N^{1/4}$  linear, ideal chain,  $R_g \sim N^{1/2}$

$b \rightarrow$  size of monomeric unit  
 $N \rightarrow$  No. of monomeric units

So, the expression for weight average degree of polymerization we have again written here. And if you substitute the expression for the expressions for that 2 summations one in the numerator and other in the denominator then what we see is this 1 minus p term will get cancelled; similarly this p will get cancelled here and this will change this exponent here to 2.

So, finally, the expression that we get for the weight average degree of polymerization is this. And we again see that this is also valid for p less than this p c equal to 1 over f minus 1 because at this value of p; this expression also diverges ok. So, this weight average degree of polymerization is also valid for extent of reaction less than this p c. And from here we can easily obtain an expression for the polydispersity index, which is a ratio of the weight average molar mass to number average molar mass.

And which can equivalently also be written as a ratio of the weight average degree of polymerization to the number average degree of polymerization. Because the weight average molar mass and weight average degree of polymerization; these 2 are just related by the molar mass of a monomer unit or a repeat unit, similarly these 2 are also related by the molar mass of a repeat unit.

So, in going from here to here that molar mass of the repeated will get cancelled and we can just say that the polydispersity index can also be re obtained as the ratio of the weight average degree of polymerization and the number average degree of polymerization. And if you substitute the expressions 2 expressions that we have obtained for these; then and if we simplify; so, this will cancel a change the exponent here to 1. So, ultimately we end up with this expression for the polydispersity index and again this diverges at this value of  $p_c$ ; so, it is valid for  $p$  less than  $p_c$ .

So, that is the expression for polydispersity index and we see that using the statistical approach; we can they are apart from number average degree of polymerization. The weight average degree of polymerization and the polydispersity index both we have been able to calculate. So, this approach or the statistical approach that we have discussed it is a more power approach because it gives us more information about the system.

Apart from these quantities another important quantity that is different for a branch polymer compared to a linear polymer is ah something that relates to its size and that is a radius of gyration. So, if we consider an randomly branched  $N$  mer ah which is ideal. So, if we are neglecting again the excluded volume effects; then the it can be shown we will not go through a derivation here, but we will just write down the final result is that this  $R_g$  square; the square mean square radius of gyration is equal to this quantity which is dependent on this  $f$  here multiplied by  $B^2 N$  to the power half. So, this  $B$  is nothing, but the size of the monomeric unit and  $N$  of course, if you are considering  $N$  mer is the number of monomeric units.

What we see here is that this  $R_g$  if we just considered  $R_g$  and its; how it scales with the number of monomeric units present in the in our  $N$  mer for this branched polymer randomly branched polymer. Then it scales actually as  $N$  to the power  $1/4$  because this mean square  $R_g$  scales as square root of  $N$ . So,  $R_g$  itself is scale as  $N$  to the power  $1/4$ . And this is in distinct contrast to the case of a linear ideal polymer ideal chain;

where  $R_g$  scales as  $N$  to the power half. So, this we have discussed earlier when we are talking about the chain models.

So, for linear ideal chains the radius of gyration scales as square root of  $N$  whereas, for this randomly branched  $N$  mer the radius of gyration scales as  $N$  to the power  $1/4$ . So, what this illustrates is that the branched polymers have a smaller size than the corresponding linear polymers; it both contain the same number of monomer units.

And also the branched polymer actually scales more weakly or the size of the branched polymer as quantified by it is a radius of gyration; it scales more weakly with the number of monomer units present compared to linear polymers. So, scaling here is  $N$  to the power  $1/4$  whereas, for linear its  $N$  to the power half.

So, this illustrates are the branched polymers of the same number of units will be more compact in size. And in their size will also scale more weakly with the number of monomeric units present. So, with that we will conclude our discussion of branching and branch a formation of hyperbranched polymers. And how one can use the either statistical approach or a simpler approach to obtain quantities like the number average degree of polymerization. And especially specifically for the statistical approach also the other quantities like the weight average degree of polymerization and the polydispersity index.

And in the next lecture, we will consider the case where if cross links actually form between polymer chains; how that can result in the formation of polymer networks. And at what point this gelation the phenomena of gelation; basically takes place in such network polymers.

Thank you.