

**Introduction to Polymer Physics**  
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**Lecture – 14**  
**Branching Network Formation and Gelation**

Hello. So, in the previous lecture we started discussing branching and we specifically looked at the case of hyperbranched polymers. We developed few expressions involving the number average degree of polymerization and weight average degree of polymerization of such hyperbranched polymers with respect to the extent of reaction as well as the functionality of the monomers involved.

So, in today's lecture we will continue our discussion of branching and branch polymers further, where apart from the randomly branched hyper polymers that we have discussed till now. We will look at the case of branched polymer which is highly ordered and where the branching is very controlled and such polymers are referred to as dendrimers. So, we look at the specific case of dendrimer in today's lecture, as another example of a polymer that is highly branched, but highly ordered as well.

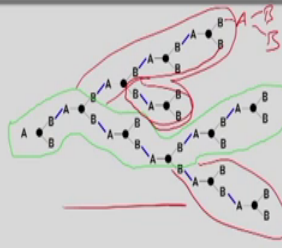
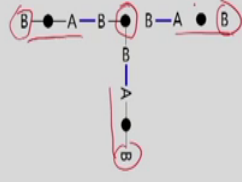
After that we will move on to discussing the case of network polymers and we will specifically look at how cross linking of polymer chains results in the formation of such network structures. We will talk about this transition where the formation of network results through the cross linking with between different chains. And this transition is that we will be discussing in this regard is referred to as gelation. So, the network polymer that form starting from the initial reaction mixture that network polymer is will refer to as gel and the transition, where the first network polymers spanning the entire system that we have appears this transition is referred to as gelation.

(Refer Slide Time: 02:14)

CONTENT	
Branching	
• Randomly Branched Polymers	
• Dendrimers	
Network Formation and Gelation	
• Crosslinking and Network Formation	
• Gelation	
• Mean-Field Model of Gelation	

Regarding the contents as discussed the randomly branched polymers will be briefly reviewed and after that we will talk about dendrimers which are also highly branched, but very ordered polymer structures. Then we will move onto the formation of networks high amount of branching can ultimately lead to cross linking between chains and formation of network structures and gels, and will briefly discuss a few results arising out of what is called the mean field model of gelation.

(Refer Slide Time: 02:46)

BRANCHING	
Branching	
Randomly Branched Polymers	
Dendrimers	
Network Formation and Gelation	
Crosslinking and Network Formation	
Gelation	
Mean-Field Model of Gelation	
	<p>Polymerization of <math>ARB_{f-1}</math> monomers: Hyperbranched Polymers for <math>f &gt; 2</math></p> <p>A and B are mutually reactive functional groups A can only react with B and vice versa <math>f</math>: Functionality</p> 
	<p>Polymerization of <math>ARB + B_3</math> monomers: Branched Polymers</p> <p>A and B are mutually reactive functional groups A can only react with B and vice versa <u>Bifunctional</u> + <u>small amount of trifunctional</u> monomers</p> 

To start with in the previous class we talked about the case of a hyper branched polymer that can form by polymerization of a monomer of type  $AR_{f-1}B$ . So, A and B here as we discussed earlier are the reactive functional groups and A can only react with B or B can react with A, but A cannot react with A and B cannot react with B that is the constraint that we have. So, if you look at this monomer here hyperbranched polymers we discussed will be formed if  $f$  is greater than 2. So, this  $f$  that we have that is referred to as the functionality of the monomer and that in this case, we can consider as a total number of functional groups present on a given monomer molecule.

We have  $f-1$  B functional groups and one A functional groups are total  $f$  functional groups are present per monomer molecules the functionality is  $f$ . So, that is what this  $f$  represents. Although strictly speaking the functionality for any given monomeric species is not necessarily equal to the number of functional groups present. It is equal to the number of chains that can arise out of a given monomeric unit. For our purposes it is the number of functional groups present the monomer is in our discussion will be equivalent to the functionality because all the functional groups present in our discussion will lead to the formation of or emanation of chains from the monomer.

This here was the small section of a typical hyperbranched molecule that can form if polymerization of  $AR_{f-1}B$  type of monomer is done and if we consider this encircled portion to be the mean a chain. So, in that case this part can be considered as a branch. Similarly this part can be considered as a branch and of this branch this further branch shown here that is also arising. And, if polymerization is carried out if we connect further A groups to and B groups that we have then further branching is of course, possible.

So, we end up getting a highly branched hyperbranched polymer. And, that is what we discussed in the previous class and we also derive the expressions for its weight average and number average degree of polymerization and how those quantities relate to the functionality and the extent of reaction. Apart from this kind of monomers we can also have other kind of monomer combinations which can result in branched polymers; if you consider a polymerization of a system containing two types of monomers  $AR_1B$  and  $B_3$ .

So, first monomer has one A functional group and one B functional group, the second monomer has just 3 B functional groups. So, such a and again A and B are mutually

reactive, but will not react with each other in the sensor the A will not react with A or B B will not react with B, but A and B will react together.

So, in this case the by functional monomer which contains two functional groups ARB and the trifunctional monomer B<sub>3</sub> is present. And typically if you have a small amount of trifunctional monomer present then such a system can also open polymerization leads lead to branch polymers and how that happens if we just look at a schematic if we consider a B<sub>3</sub> kind of monomer first containing three function groups of type B then reaction can of the exposed B functional groups can only occur with the a functional group of the bifunctional monomer that we have.

So, the B function group can react with a functional group and similarly for the other B function groups present. So, to start with we see that we have a structure where kind of a branching point is there. So, that this point which corresponds to the trifunctional monomer unit that acts as a branching point and for this the specific case it turns out that for given polymer chain only one branch will be formed. The reason is that once one stage of reaction is over and we have these AB monomers connected to the B<sub>3</sub> monomer. Then the next step of reaction will again involve the reaction of A groups of the AB monomer to the B groups at the end here, ok.

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BRANCHING	
Branching	Polymerization of ARB <sub>f-1</sub> monomers:
Randomly Branched Polymers	Hyperbranched Polymers for $f > 2$
Dendrimers	A and B are mutually reactive functional groups
Network Formation and Gelation	A can only react with B and vice versa
Crosslinking and Network Formation	$f$ : Functionality
Gelation	Polymerization of <u>ARB + B<sub>3</sub></u> monomers:
Mean-Field Model of Gelation	Branched Polymers
	A and B are mutually reactive functional groups
	A can only react with B and vice versa
	Bifunctional + small amount of trifunctional monomers

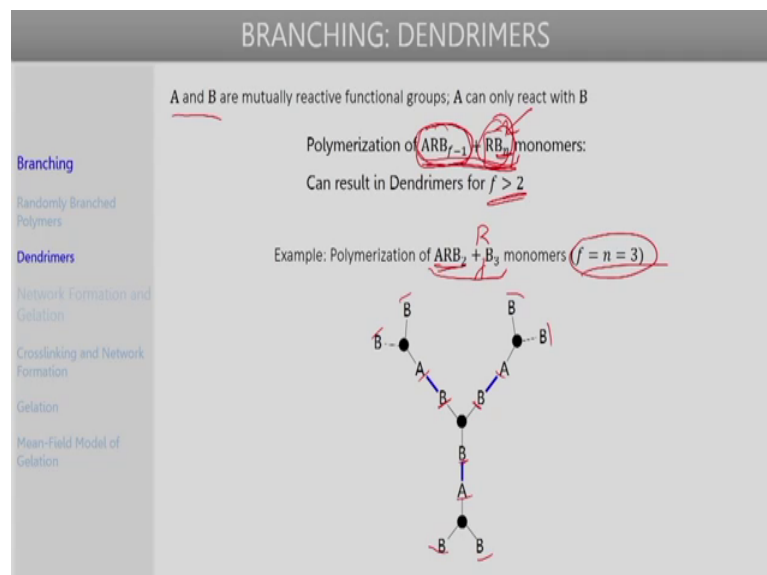
So, if we consider another stage in the reaction then the expose beam functional groups will react with the a functional groups of the AB monomer. And in that way the chain

size will increase, but that will not lead to the creation of any additional branch points. So, we see that we still have this only single branch point and the chains can continue growing larger in different directions, but there will just be single branch point per chain and if other chains are parallelly growing they will also have a single branch point. So, this kind of a monomer combination leads to branch polymers, but these are not highly branched these usually will contain single branch per chain, ok.

So, these are certain examples of monomer combinations where branch branching is possible and it can be the degree of branching can be small or it can be larger as in the case of hybrid branched polymers. And we see that it is necessary that one of the monomers have functionality greater than two only then branching is possible if all monomers have functionality too then a linear polymers will result,.

So, the cases that we have considered till now they involve kind of random branching, ok. So, there is no order involved in the kind of branching that is taking place. So, now, next we will consider a case of a type of polymer they are the where the branching is very ordered and controlled, so that the structure that we get the polymer structure that we get that also comes out to be very ordered.

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So, such polymers are referred to as dendrimers. And these are also highly branched structures, but as discussed the branching is not random and it is the structure. These are highly ordered molecules.

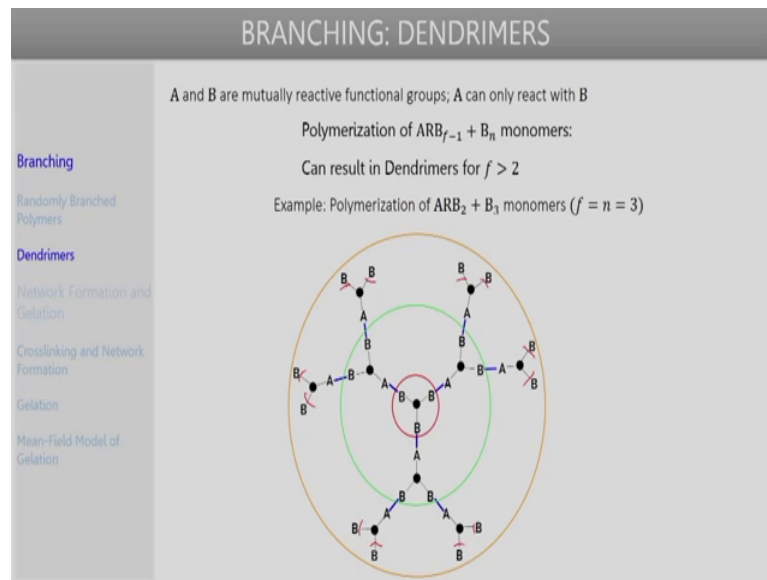
So, again we consider the same case where we have monomers containing A and B functional groups and this A and B are mutually reactive, but a and a will not react same B will B and B will not react. We consider the polymerization of this kind of combination of monomers  $ARB^{f-1}$  plus this  $RB^n$ . So, again here r is some group which is not involved in any polymerization reactions which R is not a functional group and the A and B are the functional groups participating in the reaction.

Now, if we carry out the polymerization of this kind of a monomer combination and if it is done in a controlled way then one can actually get dendrimer molecules out of such reactions. So, if the functionality again of this molecule is greater than 2 and we have this molecular. And typically will also be greater than 2, so, in such a case control reaction can be performed to form dendrimers.

This  $RB^n$  this monomeric unit that monomer molecule that we have typically this will form as what is called the core of the dendrimer molecule and starting from it  $ARB^{f-1}$  these monomer molecules will react with the B functional groups of the core and they will the molecule will progressively grow larger, but the an order kind of structure will be maintained. An example can be where f is equal to 3, so, an n is also equal to 3. So, in that case we have an  $ARB^2$  plus  $B^3$  or we can also call it  $RB^3$ . So, R was not mentioned explicitly here because that is not a functional group, but in any case a core monomer which contains 3 B functional groups. So, that is that can be an example of a system that if their reactions are done properly and in a controlled way can produce dendrimer molecules.

So, let us start with how the dendrimer molecule schematically; let us see how the dendrimer molecules form. So, we have this, for this case we have this  $B^3$  molecule which forms the core of the dendrimer or  $B^3$  monomer which forms the core of the dendrimer. And then at each of the B functional groups that we have here the a functional group of this  $ARB^2$  can react. So, if that is done we have this kind of a connectivity where all the 3 B groups here have been have reacted with these A functional groups and the molecule is grown in size. And now the instead of the initial 3 B functional groups of the core now we have 6 B functional groups at the periphery of our this growing dendrimer molecule.

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And, further those peripheral B groups can again react with the A groups of the  $ARB_2$  monomeric species present. And this will lead to further growth of the monomer of the dendrimer in an ordered fashion.

If another set of reactions takes place then we have we get more number of these B functional groups at the periphery again, so, there we had six. Now we see we have twelve and if we look at the core the B 3 that is as we discuss referred to as a core from which the growth of the dendrimer molecule starts and after all the B groups having of the core having reacted with the Aa groups of the other monomer then and one single layer is complete then that that is called the first generation of the dendrimer. And, similarly the B groups of the at the surface of this first generation if they once they are reacted with the A groups of the  $ARB_2$  type monomers, then the second generation will form and the second generation is what is shown here at the periphery.

So, we see that starting from the core which can be called as a zeroth generation as we increase a generation from 1 to 2 to 3 the dendrimer molecule grows in size. And the number of functional groups the B functional groups in this case present on the surface that also increases very rapidly. And, we can also notice that as the dendrimer molecule grow to higher generations the crowding at the surface of this molecule will become higher and higher because as the generation will increase more and more number of B functional groups will represent on the surface and ultimately there would not be enough

space to accommodate all the molecules at the surface. And this overcrowding is one of the problems associated with synthesizing very high generation dendrimers.

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**BRANCHING: DENDRIMERS**

Dendrimers: Polymerization of  $ARB_{f-1} + B_n$  monomers

**Branching**

Randomly Branched Polymers

**Dendrimers**

Network Formation and Gelation

Crosslinking and Network Formation

Gelation

Mean-Field Model of Gelation

Generation 0 (Core):  
Number of Monomers = 1

Generation 1:  
Number of Monomers =  $n$

Generation 2:  
Number of Monomers =  $n(f-1)$

Generation 3:  
Number of Monomers =  $n(f-1)^2$

⋮

Generation  $g$ :  
Number of Monomers =  $n(f-1)^{g-1}$

Let  $N_g$  be the total number of monomers up to generation  $g$ :

$$N_g = 1 + n + n(f-1) + n(f-1)^2 + \dots + n(f-1)^{g-1}$$

$$N_g = 1 + n \left[ 1 + (f-1) + (f-1)^2 + \dots + (f-1)^{g-1} \right] = 1 + n \left[ \frac{(f-1)^g - 1}{f-2} \right]$$

$(f = n = 3)$

So, as we discuss the dendrimers can be found by polymerization of this general kind of combination of monomers provided that  $f$  is greater than 2 and for the simple case where  $f = n$  and both are 3 we can have a dendrimer that up to the second generation looks like this. So, now let us consider each generation of the dendrimer in more detail and see how the number of monomers involved per generation that actually increases as we go higher in generations.

So, for the 0 generation which is the core we have just one monomer molecule which is a  $B_3$  type molecule in this case or the  $B_n$  molecule for the general case. And then in the next generation which is the first generation the number of monomer molecules will be  $n$ . The reason for this is the  $A$  in the core we have  $n$  functional groups of type  $B$  and when this first generation forms then all these  $n$  functional groups of type  $B$  would have reacted with each  $B$  functional group would have reacted with one molecule of this type. So, in the first generation will have  $n$  number of monomer molecules of this type?

And, once we have  $n$  number of monomer molecules in this first generation the number of  $B$  functional groups which will again each react with one monomer molecule. So, the number of  $B$  functional group on the surface of this first generation dendrimer will simply be  $n$  times  $f$  minus 1, because if you have  $n$  monomer molecules of this type each



monomer molecule of this type has  $f - 1$  in the functional groups of type B. So, total number of B functional groups on the surface at first generation will be  $n$  times  $f - 1$  and when the second generation forms all these B groups would have reacted with one monomer molecule each of again the ARB  $f - 1$  type.

So, in generation 2 the number of monomers that that will be present will be  $n$  times  $f - 1$ , because this is a number of surface B groups present on the in the first generation. So, if we take the example of the schematic shown here then we can see that in generation 0 at the core we have one a monomer molecule in generation 1, which is represented by the green circle here we have these three monomer molecules. And in the next generation, generation 2 which is shown by this orange circle here we can see that we have 1 2 3 4 5 6 monomer molecules involved and these are consistent with the expressions that we have here. So, a generation 0 we have one B 3 in generation one we have  $n$  which in this case is 3. So, that is what we got we got the three monomer molecules.

In generation 2 since  $n$  and  $f$  both are 3 this product will simply be 6 and that is what we got for generation 2. So, continuing in this fashion what we can see is that now in generation 2 again if we have  $n$  times  $f - 1$  monomer molecules and each monomer molecule has  $f - 1$  functional groups of type B. So, in the next generation all this type B functional groups will react with one monomer molecule again each 2 to form the next generation or the next layer of this dendrimer molecule.

So, we can say that for generation 3, the number of monomers will simply be this  $n$   $f - 1$  monomers multiplied by the  $f - 1$  B groups that each of these monomers have. So, we get  $n$  times  $f - 1$  square and continuing in this fashion for any general generation  $g$  of this dendrimer molecule we can then say that the number of monomers present only in this  $g$ -th generation is  $n$  times  $f - 1$  raised to the power  $g - 1$ , because for third generation we have power 2 for second generation we have power one here for first generation that power of this term  $f - 1$  is 0. So, for  $g$ -th generation we can see that it is number of monomers present in that generation is yes, and times  $f - 1$  raised to the power  $g - 1$ .

So, we see that with each generation the number of monomers present in that particular generation increases quite rapidly and also the number of functional groups present in the

surface also keeps in increasing very rapidly. So now, if we consider a dendrimer which has  $g$  number of generations, let us try to find out how many total number of monomer molecules are present where the dendrimer is perfect. So, if there are no disorders or imperfections in the dendrimer.

So, in that case let us say that this  $N_g$  represents the total number of monomers up to a generation  $g$  of the dendrimer. So, it is not just the number of monomer present in the  $g$ -th generation, but it is the sum of that all the monomers present up to  $g$ -th generation. So, that we can write as and the sum of all these quantities up to the  $g$ -th generation, therefore that should we have done 1 plus  $n$  plus  $n f$  minus 1 and so on, up to the number of monomers in the  $g$ -th generation. And we can see that from second term onwards in this summation we can take  $n$  as common. So, if we take  $n$  out then in the square brackets we are these terms and we can see that this is geometric progression which can be readily summed. So, taking the sum of this geometric progression we finally, get the expression for this  $N_g$  as 1 plus  $n$  multiplied by  $f$  minus 1 raised to the power  $g$  minus 1 whole divided by  $f$  minus 2.

So, this is the number of monomers present for a  $g$  generation dendrimer, the total number of monomers in that dendrimer molecule.

(Refer Slide Time: 21:37)

**BRANCHING: DENDRIMERS**

Polymerization of  $ARB_{f-1} + B_n$  monomers:

**Branching**  
Randomly Branched Polymers  
**Dendrimers**  
Network Formation and Gelation  
Crosslinking and Network Formation  
Gelation  
Mean-Field Model of Gelation

Total number of monomers up to generation  $g$ :

$$N_g = 1 + n \left[ \frac{(f-1)^g - 1}{f-2} \right]$$

Total number of monomers up to generation  $g-1$ :

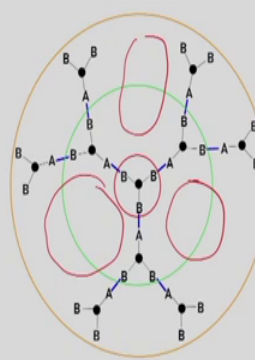
$$N_{g-1} = 1 + n \left[ \frac{(f-1)^{g-1} - 1}{f-2} \right]$$

Ratio of number of monomers in generation  $g$  to that in the rest of the dendrimer:

$$\frac{n(f-1)^{g-1}}{1 + n \left[ \frac{(f-1)^{g-1} - 1}{f-2} \right]} = \frac{(f-2)n(f-1)^{g-1}}{f-2 + n[(f-1)^{g-1} - 1]}$$

$$= \frac{(f-2)}{\frac{f-2}{n(f-1)^{g-1}} + 1 - \frac{1}{(f-1)^{g-1}}} \cong f-2 \quad \text{for } g \gg 1$$

E.g.:  $f = n = 3$   
 $0.923(f-2) = 0.923$  for  $g = 5$   
 $0.997(f-2) = 0.997$  for  $g = 10$



Using that same kind of argument we can say that if we consider only generation up to  $g$  minus 1 then the total number of molecules monomer molecules present in up to

generation  $g - 1$  that will simply be equal to this expression where all we have done is instead of  $g$  we have replaced it by  $g - 1$  here. So, this gives the total number of monomers present in the dendrimer molecule up to a generation  $g - 1$ ; so, up to the second last generation.

Now, let us see that for a given dendrimer what is the ratio of the total number of molecules present on the surface that is a number of molecules present in the in the last generation of the  $g$ -th generation to the number of molecules that is present in the up to the  $g - 1$  generation. So, it is a kind of a ratio of all the surface molecules divided by all the molecules which are inside and not exposed at the surface. So, what we will see is that the number of surface molecules actually are the fraction of monomer molecules on the surface is a quite high for dendrimers and it increases significantly as a number of generations increases.

So, the ratio of this number of monomers in generation  $g$  to that in rest of the dendrimer; so, the number of monomers in generation  $g$  that we had discussed in the previous slide that is just  $n$  times  $f - 1$  raised to the power  $g - 1$ ; and the number of monomers in the rest of the dendrimer excluding generation  $g$  is this  $n^{g - 1}$  the number of monomers up to generation  $g - 1$ .

So, the ratio of these two this is number of monomers only in generation  $g$  or the in the outer outermost layer and this is all the monomers up to  $g - 1$ . So, that is this term here. So, if we take consider this ratio and if we let us say take this  $f - 2$  term here. And then further in the numerator then we can write this term here in this form where  $f - 2$  you have taken the numerator.

And also here and then next what we can do is take this term in the denominator. So, divide each term of the denominator by this term here. So, if we do that again we end up with an expression of this kind and what we can see from here is that if the generation is large enough  $g$  is much larger than 1, then these quantities these two terms basically become very small in comparison to 1 and what we get is just  $f - 2$  as this ratio.

So, for the number of generation  $g$  much higher than 1, the ratio of the total number of monomers on the surface in the  $g$ -th generation to the number of monomers in the rest of the dendrimer molecule that is pretty much equal to  $f - 2$  approximately, and for a simple case simplest case where  $f$  equal to 3 that is a minimum required for dendrimer

formation. So, for that case we can see that this  $f - 2$  will just be 1. So, what that suggests is for a simple case of a dendrimer formed where this functionality of the monomer is 3 for such a case out of the total number of monomers present in the dendrimer molecule almost 50 percent will be on the surface or in the last generation, and if this  $f$  is a greater than 3.

So, if the functionality is 4 let us say then this percentage will be even higher. So, in for a functionality of 4 the number of monomers on the surface or in the last generation can actually be more than the number of remaining monomers present inside the dendrimer. So, we see what we see is that the number of as the generation increases the number of molecules monomer molecules or monomer units on the surface increases significantly and if you consider the example of a simple case where  $f = n$ ,  $n$  are 3. And if you try to evaluate this ratio then we see that if  $g$  is 5 for the fifth generation dendrimer molecule this ratio comes out to be 1.923 times  $f - 2$ , 0.923. And as if increase this generation from 5 to 10 then this ratio becomes equal to 0.997 which is pretty much one or unity.

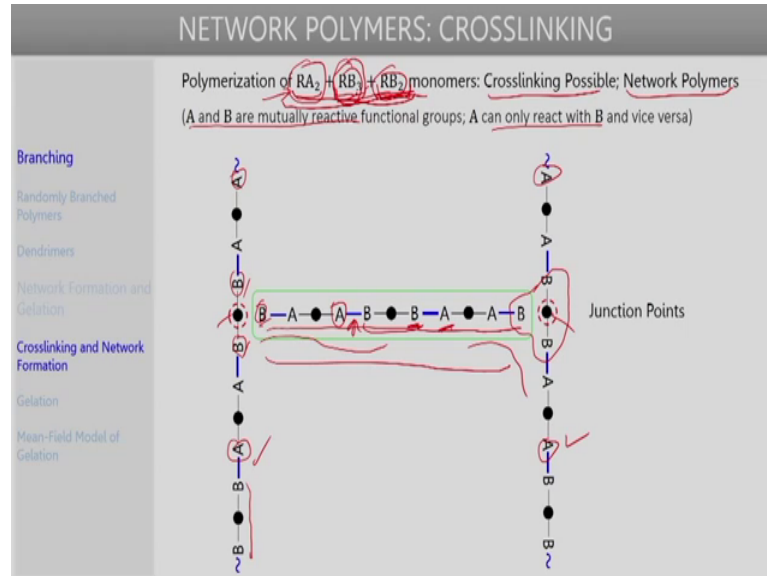
So, we see that for any dendrimer molecule as with high enough generation the number of monomer molecules on the surface is quite large and ultimately there will be as a number of generation increases, there will be a lot of county crowding on the dendrimers molecule surface and that limits largest size that you can get for a dendrimer molecule. And another thing that we can see is that the surface is crowded, but inside the dendrimer molecule there is lot of empty space, because if we look at the initial generations from core core to the first to the second we see that all this portion is unoccupied.

So, on the surfaces lot of crowding, but this is an white space in the interior of the dendrimer molecule, and this dendrimers actually are I have very interesting properties they have a lot of surface functional groups that can be further functionalized for many kinds of applications. So, in therapeutic start delivery people are exploring the use of such dendrimer molecules.

So, with that will conclude our discussion of branched polymeric system. And we have where we have talked specifically in detail about hyperbranched polymers and dendrimers. And next we will look at the case where if the branching goes on in such a way that chains start to get connected with each other or cross linked with each other.

Then we will have the formation of network polymers such a transition is referred to as gelation. And we will see different aspects of this gelation transition.

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If we consider now the polymerization of this kind of a monomer system they are apart from this  $RA_2$  and  $RB_2$  which are bifunctional monomers we have this trifunctional monomer as well. So, now for this kind of this represents a type of monomer combination for which cross linking is actually possible and we can get network polymer formation. So, let us just again schematically see how cross linking for this kind of a system is possible.

So, again we will start with this  $RB_3$  or  $B_3$  kind of type of monomer molecule and the B units here can react with the A units of  $RA_2$  of course. So, again A and B are mutually reactive, but a can only react with B. So, in that case these B units will react with the A in functional groups of  $RA_2$  and in that way the polymer chains can increase in size. And once it has reacted then we have this A groups at the end other terminal points. So, next this A groups will can react with either this  $RB_3$  or  $RB_2$ . So, let us say that this a groups reacted with this  $RB_2$  type of monomers next. So, in that case will again have this  $RB_2$  an  $RB_2$  monomer appearing here and this bond formation between a and B types.

So, let us say this is the way in which a chain is growing and there is some branching and let us say that another chain again starts for simplicity let us say that we are starting with again this  $B_3$  kind of monomer molecule and again it since it has B at the as the end

groups and functional group. So, it will react with the RA 2 monomers only and in that way the polymer will grow.

And once we have this as are the end these as can react again with either RB 3 or RB 2. So, let us say again that these are reacting with one of these two, and the chain grows further. Now, the A here this we see that this is in close proximity to this B group here of this branched polymer that they have formed. So, these two it can represent branched polymers and this A B groups, if they are in proximity they can also react form a bond and once this happens what we can say is that this chain here. And this chain here they have become linked together through this intermediate section of a polymer chain. So, this collection of a monomeric units here they actually have linked the other two chains shown in this schematic and what we say is that a cross link has basically formed between the chains. And, the two points here this and these represent other junction points at which that cross linked section connects with the chains.

So, in this way of course, as reaction takes place many such cross links can form. And formation of such cross links ultimately results in the formation of a network kind of structure and we get a network polymer in that case. So, this kind of a combination RA 2 plus RB 3 plus RB 2 that is one combination which can give a cross linked polymer which ultimately can form a network. They can be awakened monomer combinations also of course, which will result in network formation. So, this network formation phenomena is actually physically quite important and in the next few slides we will take a look at this transition where this initial branch polymers that have formed ultimately lead to a network will look at that kind of a transition in more detail.

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GELATION	
	Crosslinking of polymer chains results in the formation of network polymers.
	Linking of chains results in larger branched polymers.
<b>Branching</b>	At a certain extent of reaction, a molecule will form that spans the entire system.
Randomly Branched Polymers	This very large molecule (or infinite polymer) is called <u>gel</u> or <u>network</u> .
Dendrimers	
Network Formation and Gelation	<b>Gelation:</b> A sol-gel transition from a polydisperse mixture of branched polymers (sol) to a system containing one 'infinite' system-spanning molecule (gel) along with the finite branched molecules.
Crosslinking and Network Formation	
<b>Gelation</b>	<b>Gel Point:</b> The critical point (extent of reaction) at which <u>gel first appears</u> .
Mean-Field Model of Gelation	Just beyond the gel point, system will consist of finite branched molecules and the infinite molecule. This incipient gel <u>percolates through the entire system</u> .
	Theories describing Gelation:
	→ Mean-field theory developed by Flory and Stockmayer
	Critical Percolation theory

So, we have seen that cross linking of polymer chains. So, for some special kind of monomer combinations can result in formation of network polymers if enough cross linking is there. And so, initially when the linking between polymer chains takes place one can say that branched polymers are forming and ultimately as the polymerization reaction proceeds there will be a certain extent of reaction that will be reached at which at least a one molecule will form in the entire system which spans the size of the whole system, ok.

So, we will cross linking if enough cross linking takes place at least one network structure will form this network polymer and it molecule which is like a network it will span the entire system. So, once this occurs the transition known as gelation actually takes place. This very large molecular network that is found that which spans the entire system that we have and it said to be an kind of an infinite molecule with a infinite molar mass. So, this is referred to as a gel or a network and the gelation is basically this transition,.

So, if we look at gel try to define gelation more formally. It is a kind of a sol gel transition where initially before this transition we have a collection of branched polymers which we can term as the sol because ideally such polymers can be dissolved in a solution and upon further reaction just when this gelation transition takes place this collection branch polymers will connect in such a way that at least one system spanning

network structure will form and this molecule is referred to as a gel and this transition from a collection of branch polymers or the sol phase to a phase where a single system spanning molecule has formed which is a gel. So, this transition is called as a gelation transition.

So, right after this system spanning in gel molecule or network molecule has formed, even after that we will still have many other branched polymers present in the system. So, right after the gelation transition the system can be thought of as consisting at least one infinitely large molecule or the gel and also several branched polymer molecules. So, not all the branched polymer molecules will immediately connect to form a single gel molecule a system spanning molecule forms. But other branched polymer molecules which will in a finite size will still be present. And as the reaction further progresses beyond this gelation transition at high enough extents of extent of reaction almost all monomer will ultimately get connected to in this network structure and that will basically be the formation of what is called a fully developed network.

So, gelation transition the gel point marks the gelation transition. So, this is the critical point across which the gelation transition takes place and this will correspond to an extent of reaction. So, as the polymerization reaction continues an extent of reaction will be reached at which gelation is observed and that point is referred to as a gel point and this critical extent of reaction it is typically represented as  $P_c$ .

Gel point corresponds to the point where the first gel or the first network molecule spanning the whole system appears. And as we discussed just beyond the gel point close enough to the gel point, but just at an extent of reaction just above the gel point we will have a system we continuing a large molecule a gel which is the incipient gel. And the system will also contain many branched polymer molecules which have not formed part of the network yet, and as the reaction progresses further the fully developed network containing most of the monomers in system will form. So, this incipient gel is system spanning what; that means, is that it percolates through the entire system. So, whatever system we have it will span the whole system it percolates through the entire system.

So, the theories that described gelation used this concept of percolation of bonds across the entire system for this network polymer or the gel phase. And, traditionally the mean



field theories developed based a Flory and Stockmayer were introduced in around 1950s to describe gelation phenomena and later on theories based on critical percolation. So, critical percolation theories were introduced in the 1970s to further describe the gelation phenomena in a better way and then of course, further theories have come up to capture the kinetics of a gelation phenomena as well.

So, a towards end of this lecture we will briefly discuss a few important results from this mean field theory of Flory and Stockmayer related to gelation gelation when gelation takes place physically there the gel basically is a almost infinite large molecule. So, what would happen is that initially if the system is in any kind of a solution and the reaction is taking place and ultimately gelation happens then as liquid to solid kind of transition can be observed.

So, a common everyday example is the case of gelatin dissolved in water. So, if we dissolve gelatin in water. And let us say boil it and then cool it. So, upon cooling that liquid gelatin water solution will turn into a solid gel. So, that is also a kind of a gelation transition where a kind of a cross linking occurs. Although, in that case the cross linking not strictly speaking a chemical cross linking, but some kind of physical cross linking occurs which leads to the formation of a gel.

This typical gello kind of a material formed using this gelatin water solution. So, these material we see are behave like a more like elastic solids than liquids. So, a liquid to solid kind of transition can be observed when gelation takes place.

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**TYPES OF GELATION**

**Physical Gelation:** Gelation due to physical linking of polymer chains

**Strong Physical Gels:**  
Strong physical connections between polymer chains  
Glassy nodules, microcrystalline domains, helices etc.

**Weak Physical Gels:**  
Temporary weak association between chains  
Hydrogen Bonds, Ionic associations etc.

**Chemical Gelation:** Chain linking through covalent bonds; Strong gels.

**Condensation (Step) Polymerization**  
E.g.: Condensation of bifunctional carboxylic acid with trifunctional alcohol

**Addition (Chain) Polymerization**  
E.g.: Monomers with two double bonds

**Vulcanization:** Crosslinking of long linear chains  
E.g.: Crosslinking of natural rubber using sulphur

Now, the different types of gelation that is possible. So, one can have a physical gelation or chemical gelation. So, physical gelation as a name suggests it involves a formation of the network use using physical interaction or physical link. So, no chemical bonds are formed in this network physical network formation and chemical gelation of course, involves the formation of linking of chains through covalent bonds, ok.

So, if we talk about different types of physical gelation, there we can identify a few important types. So, the two important type of physical gelation is a strong the gelation resulting in the formation of strong physical gels and that which forms weak physical gels. So, if you talk about strong physical gels here the linking between the polymer chains is through some kind of physical linking only, but the linking is quite strong. So, such examples of such strong physical gels can be thermoplastic elastomers and this gelatin as well as the gello that we just discussed.

So, here the cross linking points are actually not chemical bonds do not have chemical bonds, but some physical association is there, but the physical connections in this case are quite strong. So, if we talk about thermoplastic elastomers. So, these are materials which normally are made up of block copolymers where one of the blocks actually prefers to stay in the amorphous phase where the as the other blocksion might be in the glassy state or might have been a kind of crystalline state as well. So, these glassy

nodules or the crystalline domains of one of the blocks that is kind of scattered in this matrix of an amorphous phase of the other block of this copolymers.

So, these glassy nodules or the crystalline domains kind of act as the junction points and these provide the necessary physical connection between the chains present in amorphous phase. So, this actually leads to the kind of to a kind of a network structure formation whether the junction points are this glassy nodules or crystalline domains. And, upon stretching this material actually do show some kind of elastomeric behavior where they stretch to a good percentage of their initial dimension, but the other good thing about these materials is that at if the temperature is high enough they can be molded like a thermoplastic into different shapes.

So, processing is easier at high temperature there is a thermoplastic part and they can be stretched like an elastomer also. So, such materials are called as thermoplastic elastomers and these are quite these are examples of this strong kind of physical gels. For the case of gelatin, if we consider this third type of physical connection shown here; so for the case of gelatin forming this gello kind of a gel there these helical polymer polymer chains in certain parts are arranged in the double helix kind of an arrangement. And these points form as these basically act as physical connections between the other amorphous chains present in the system. So, such connections also lead to strong physical gels.

Similarly, weak physical gels are form where there are weak transient kind of associations present in the in the system that we have. So, if you have weak physical gels can be weak associations between molecules or groups of atoms. And they can act as these linking points and formation of this kind of a network structure which is transient and can actually the network structure can actually be lost with the passage of time or with the application of heat or that is a some mechanical force. So, such examples of such weak gels are those gels where the association is due to forces like hydrogen bonds or ionic associations, but no covalent bonds.

So, these are examples of physical gels. Then if we talk about chemical gelation where actually covalent bond formation takes place and that results in cross linking. So, of course, these gels are quite strong and there are different ways in which such gels or polymer networks can be formed. So, one is just through condensation or a step polymerization. So, again step and condensation polymerization are not strictly speaking

identical bit, but they are similar enough. So, here we will not distinguish between the two terms.

So, these condensation a step polymerization offer as an example by functional carboxylic acid with a trifunctional alcohol. So, something like that actually can ultimately lead to the formation of a network structure which is which can be classified as a chemical gel. Similarly, addition polymerization can also be used. So, addition or chain polymerization can also be used to form this network polymer kind of polymer structure where the cross links are covalent bonds or cross links involve covalent bonds.

So, here if we have a monomers having multiple unsaturation points so monomers having let us say two double bonds. So, during polymerization one of these double bonds actually will convert to a single bond and polymer chains will form whereas, the other double bond might still be there in the polymer backbone. So, during polymerization this second this double bond present in the polymer backbone can also have be attacked by let us say radical if the mode of polymerization is radical polymerization and then from there branching and further cross linking can take place. So, this is another approach which can lead to network formation which again can be classified as chemical gelation.

And, the third type is where instead of starting from monomers and polymerizing the system we can start with the system which is already a polymer. So, we have long linear polymer chains present which are overlapping. And in there some the chain linear chains at a present can be cross linked by the addition of some other component and this again will lead to the formation of a network structure.

So, an example of this is basically the cross linking of natural rubber using sulfur this kind of a cross linking is referred to as vulcanization. So, that some broad outline of the different types of gelations that are there and the different types of gels ways in which network polymers or gels can form. Next, we will just talk a bit more about the gelation phenomenon.

(Refer Slide Time: 46:25)

**GELATION**

Gelation: Connectivity transition; can be described using a bond percolation model

Consider the monomer molecules placed on the sites of a lattice.

**Branching**  
Extent of reaction,  $p$ , is the fraction of all possible bonds that have formed at any point.

Randomly Branched Polymers  
Dendrimers

Network Formation and Gelation  
Crosslinking and Network Formation

**Gelation**

Mean-Field Model of Gelation

A connectivity transition occurs at the gel point or the percolation threshold.

If  $p = p_c$  denotes the extent of reaction at the gel point:

Slightly below  $p_c$ , the system consists of a polydisperse mixture of branched polymers (sol).

Slightly above  $p_c$ , the system consists of mostly branched polymers with one system-spanning structure that percolates through the entire system (incipient gel).

Much above  $p_c$  (as  $p \rightarrow 1$ ), polymer is a fully developed network.

**Gel fraction,  $P_{gel}$**  Fraction of monomers belonging to the gel ( $P_{gel} = 0$  for  $p \leq p_c$ ).

$$P_{gel} + P_{sol} = 1 \quad (\text{where } P_{sol} \text{ is the sol fraction})$$

Gelation as we discussed is marked by appearance of a network kind of structure which spans the entire system. So, we can think of it as a kind of a connectivity transition where at the transition point a structure appears that is connected across our entire system.

So, a model which is called the bond percolation model that a model of that kind can be used to describe the gelation phenomena and has been used by researchers to study gelation in more detail if we let us say- consider the simple case of monomers present on a lattice. So, we have each lattice site being occupied by monomer and as the reaction progresses that is represented by the formation of links between these lattice sites which represents the formation of bonds between monomers. So, as reaction progresses more and more bonding between the different monomeric species present on the lattice takes place. And the extent of reaction  $p$  in this case is simply the fraction of bonds that are formed compared to the total number of possible bonds that can form in this system. So, that is the extent of reaction  $p$  for this kind of a representation.

And, and as we discussed this gelation is this connectivity transition that occurs at the gel point where the extent of reaction reaches to such a point there where. So, that a large system spanning structure basically or network basically appears in the system. So, this gel point is also referred to as a percolation threshold and this is the point across which the gelation transition takes place. Now, the critical extent of reaction which marks the onset of this gelation transition that is typically represented as  $p_c$  and what we have

already discussed is a slightly below this critical extent of reaction system is in the sol phase. So, it just contains a poly dispersed mixture of branched or highly branched polymer chains.

But, as we as gelation transition takes place as we cross  $p_c$  this extent of reaction  $p_c$  then slightly over the above this  $p_c$  we will still have many highly branched polymers present, but apart from that we will also have one system spanning gel structural network structure that will form in the system and this system spanning structure will percolates to the entire system. And, as we discuss it is referred to as the incipient gel and as the extent of reaction goes further above this gel point or this critical extent of reaction then as it approaches. Let us say one almost all the monomers present will form part of the single network structure. And, this a fully developed network that is what we get as the extent of reaction approaches one which is typically much higher than the point at which gelation begins.

If we talk about let us say a point above the gelation transition. So, above the gelation transition we will have a 2 fractions one can identify 2 fractions one will be the gel phase. And one will be the phase which is just the all the branched polymer molecules present in the system, but which have not yet attached to the gel molecule or the network molecule. So, for fraction of monomers which are part of the gel that we refer to as a gel fraction of  $P_{gel}$ . So, if we have a bunch of monomers in the system in the fraction monomers that constitute the gel molecule or the network molecule is the that is represented as  $P_{gel}$  and we of course, by definition we know that this value will be 0 for  $p$  less than  $p_c$ , because below  $p_c$  there is no gelation there is no gel formation. So, no monomer has formed no monomer is actually part of the gel.

So, it is a  $P$  the fraction of gel fraction is less than is equal to 0 for  $p$  less than  $p_c$  and the other thing is that if the if you represent the gel fraction by  $P_{gel}$  and the sol fraction by  $P_{sol}$  where sol is again the all the branched polymer molecules which are not which has not found a network yet or attached to the network  $n$ . So, the sum of these two will be 1, ok. So, in the system here either had this gel which is the system spanning network and we have a collection of a this branch molecules which constitute the sol.

So, this there is some of those fractions will simply be 1 and what we will do next is just try to discuss what is called the mean field theory of gelation; and will not going to the

details of any derivation associated with the theory, but will identify some important results that come out of that mean field theory of gelation.

(Refer Slide Time: 51:28)

**MEAN-FIELD MODEL OF GELATION**

→ Flory-Stockmayer theory

Assumption: Each bond between two monomers is formed randomly.

Neglects cyclic bonds.  
Neglects excluded volume effects, steric hindrance.

Branching  
Randomly Branched Polymers  
Dendrimers  
Network Formation and Gelation  
Crosslinking and Network Formation  
Gelation  
Mean-Field Model of Gelation

→  $p_c = \frac{1}{f-1}$

→  $p_{sol}^{1/f} = 1 - p + p p_{sol}^{1/f}$

For  $f = 3, p > p_c$

→  $p_{sol} = \left(\frac{1-p}{p}\right)^3$

→  $p_{gel} = 1 - p_{sol} = 1 - \left(\frac{1-p}{p}\right)^3$

$p_{sol} = 1$   $p < p_c$   
 $f < 3$

The mean field model of gelation: let us say is due to the theory by Flory and Stockmayer of this gelation process. So, here the assumption is that on let us on a lattice if polymerization reaction is taking place then the formation of any bond is unaffected by the formation of any other bond in the system. So, what this says is that each one between two monomers is found randomly. So, if a certain monomer having a multiple functionality is already from a few number of bonds, then the next bond forming with this monomer is unrelated to any other bonds that have already formed and due to this assumption what it leads to is that the cyclic bonds are neglected. So, no bonds or one can say no intra molecular bonds are being formed as such between.

So, if we let us say A and B are reacting and then that B again reacts with A. So, that this new A functional group A will not react with any other functional group B which is part of that same molecule. So, no cyclic kind of bonding occurs and the steric hindrance a fluid volume effects these are also neglected in this theory. So, this theory has a involves assumptions and has shortcomings, but it makes some important qualitative predictions about gelation process. So, that is why it is important to study. Without going into the details what we can identify is that the theory predicts the critical extent of reaction  $p_c$  is

just  $1/(f-1)$  where  $f$  is the function monomer functionality in this case which has to be greater than 2 for network formation to take place.

And, apart from this the gel fraction and sol fraction those also can be expression for them can be obtained from this theory. So, the expression falls or equation for calculating sol fraction is this. And if you know the functionality of the monomer involved then the specific dependence of this  $P_{sol}$  on the extent of reaction that can be obtained. So, what when we can see from this equation is that this  $P_{sol}$  this equation has a solution  $P_{sol}$  equal to 1. So, if we solve this equation for  $P_{sol}$  then  $P_{sol}$  equal to 1 is a trivial solution and that is a solution which will be there for  $p < p_c$ .

So, if the extent of reaction is less than the critical extent of reaction and new gelation has taken place then the sol fraction will be equal to 1, because there is no gel present, ok. So, this for  $p < p_c$  they of course, this will be the only solution at solid and also if  $f$  is less than 3. So, if  $f$  equal to 1 of course, does not make much sense for polymerization, but let us see if  $f$  is 2. So, in that case also we know that network formation will not take place and  $f$  equal to 2 if we substitute  $f$  equal to 2 here again that will also give  $P_{sol}$  equal to 1. So, there also no gel formation is predicted.

But, if  $f$  is greater than 3 or greater than or equal to 3 and also  $p$  is greater than this critical extent of reaction then gel formation is expected and then we can actually this equation that way here we can be solved for value of  $P_{sol}$  which is less than 1. So, for let us say  $f$  equal to 3 for this specific case and  $p > p_c$ , so, that gel formation has taken place upon solution upon substitution of these here this  $f$  equal to 3 here we will get a quadratic equation which can be solved for  $P_{sol}$  and this is the expression that we get.

So, we see that that it depends on the extent of reaction as  $1 - p$  over  $p$  to the power 3 and the if the sol fraction is given by this the gel fraction is simply 1 minus of this. So, the gel fraction is 1 minus this quantity. So, if we let us say try to plot this  $P_{sol}$  as a function of the extent of reaction  $p$ , ok. So, if you are doing this plot and let us say this point represents a  $p_c$ . So, this point represents an extent of reaction where above which marks are a gelation transition. So, we will see that up to and let us say this is 1. So, the fraction  $P_{sol}$  will be 1 up to this gelation transition of course, and then after it will start decreasing and get to 0 at as  $p$  tends to 1.



Similarly, if we. So, this is the graph for P sol; similarly if we plot P gel also the gel fraction. So, that will be 0 up to  $p_c$  because there is no gel present and then it will rise up and approach one as  $p$  tends to 1. So, this is the graph for P gel or the gel fraction and the mean field model predicts this kind of a behavior. So, we see that mean field model always involves a certain assumptions it can predict to some important parameters associated with gelation like the extent of reaction beyond the generation takes place, and also the gel fraction in the sol fraction.

We will conclude this lecture here in the next lecture where you are take this discussion on gelation further. And we will also look at the swelling of polymer networks or gels in the presence of liquids. So, with that we conclude this lecture.

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MEAN-FIELD MODEL OF GELATION: CORRIGENDUM

<ul style="list-style-type: none"> <li style="color: #4a7ebb; font-weight: bold;">Branching</li> <li style="color: #4a7ebb;">Randomly Branched Polymers</li> <li style="color: #4a7ebb;">Dendrimers</li> <li style="color: #4a7ebb;">Network Formation and Gelation</li> <li style="color: #4a7ebb;">Crosslinking and Network Formation</li> <li style="color: #4a7ebb;">Gelation</li> <li style="color: #4a7ebb; font-weight: bold;">Mean-Field Model of Gelation</li> </ul>	<p>Flory-Stockmayer theory</p> <p>Assumption: Each bond between two monomers is formed randomly.</p> <p>Neglects cyclic bonds. Neglects excluded volume effects, steric hindrance.</p> $p_c = \frac{1}{f-1}$ <div style="border: 2px solid #4a7ebb; padding: 5px; margin: 10px 0;"> <math display="block">p_{sol}^{1/f} = 1 - p + p p_{sol}^{1-1/f}</math> <p style="color: #c00000; font-weight: bold; margin: 0;">CORRECTION: Exponent of <math>p_{sol}</math> in the last term is <math>(1 - 1/f)</math> and NOT <math>1/f</math></p> </div> <p>For <math>f = 3, p &gt; p_c</math></p> $p_{sol} = \left(\frac{1-p}{p}\right)^3$ $p_{gel} = 1 - p_{sol} = 1 - \left(\frac{1-p}{p}\right)^3$
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Thank you.