Introduction to Polymer Physics
Dr. Amit Kumar
Department of Chemical Engineering
Indian Institute of Technology, Guwahati

Lecture – 15
Gelation and Swelling of Network Polymers

Hello, so in the previous lecture, we were discussing about Gelation and Formation of Network Polymers. Today we will continue that discussion, where we will focus on the theories that, describe Gelation and also some of the results from those theories. Apart from Gelation, we will also focus today on the swelling behavior of network polymers. So, network polymers, when solvent is mixed with them do not dissolve because of the network and cross link structure that they have.

But they tend to swell in the presence of solvent. So, we will see how that swelling behavior can be described. So, in today's lecture the focus will be initially, on the mean field model of Gelation that we are discussing in the previous lecture.

(Refer Slide Time: 01:10)

CONTENT

Mean-Field Model of Gelation
- Degree of Polymerization
- Number Density Distribution

Scaling Model of Gelation

Swelling of Network Polymers
- Flory-Rehner Equation

So, we had introduced this, model in the last lecture and today we will focus on the results related to the degree of polymerization, as well as the number density distribution that, arise from the mean field model of Gelation.

We will also very briefly look at the some a scaling results, from what is called a six scaling model of Gelation. So, this scaling model of Gelation is a bit more sophisticated than, mean field model. So, we are not going to details of this model or any theories associated with it, but we will just look at the key results that, this scaling model of Gelation predicts. And in the later part of today's lecture, we will focus on the swelling behavior of network polymers and specifically, we will look at an equation, which is known as the Flory Rehner equation and how that equation describes the swelling behavior of a network polymers in the presence of a solvent.

So, to start with this mean field theory by of Flory and Stockmeyer, it can and the results of this theory can be readily obtained, if we assumes that this polymerization process and subsequent branching network formation Gelation these processes are take are taken place on a special kind of lattice called the Bethe lattice. So, this Bethe lattice is a lattice which has a coordination number equal to the functionality of the monomer, which is involved in a polymerization reaction.

So, if we consider a Bethe lattice and we if we can say that, each lattice site is occupied by a monomer species then, the Bethe lattice is a lattice, where the monomer functionality that we have that equals the coordination number, that a lattice site has So, if the monomer functionality, that we are considering is f then, the Bethe lattice will have a coordination number of f, which means that each site will have a f number of nearest neighbors and any monomer present on any given site can connect with f other monomers present in the adjacent neighboring sites.

So, we are not going to any details of a derivation of the results starting from the monomer placement on the Bethe lattice and polymerization represented by connect connectivity between adjacent sites of a Bethe lattice. So, we are we are not interested in those derivations, but it considering such a lattice results can be readily obtained. So, we will focus more on the results that we obtained and the kind of scaling behavior that we get, which again will be further focus of the scaling model of Gelation.

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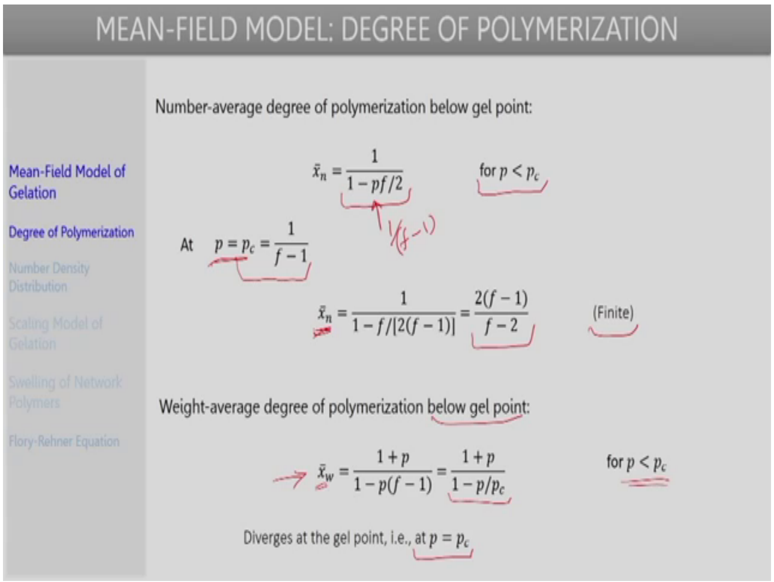

MEAN-FIELD MODEL: DEGREE OF POLYMERIZATION

Mean-Field Model of Gelation

Degree of Polymerization

Number Density Distribution

Scaling Model of Gelation

Swelling of Network Polymers

Flory-Rehner Equation

Number-average degree of polymerization below gel point:

$$\bar{x}_n = \frac{1}{\underbrace{1 - pf/2}_{\uparrow\, 1/(f-1)}} \qquad \text{for } p < p_c$$

At $p = p_c = \frac{1}{f-1}$

$$\bar{x}_n = \frac{1}{1 - f/[2(f-1)]} = \frac{2(f-1)}{f-2} \qquad \text{(Finite)}$$

Weight-average degree of polymerization below gel point:

$$\rightarrow \bar{x}_w = \frac{1+p}{1-p(f-1)} = \frac{1+p}{1-p/p_c} \qquad \text{for } p < p_c$$

Diverges at the gel point, i.e., at $p = p_c$

So, if we now consider the number average degree of polymerization below the gel point.

So, we are still continuing with this mean field model of Gelation and using this mean field model of Gelation, the result for the number average degree of polymerization below the gel point that is obtained is xn bar is equal to 1 1 over 1 minus pf by 2. And this is valid for p less than pc, so when we are below the gel point. From this number average degree of polymerization of course, one can also obtain the number average molar mass, simply by multiplying this xn bar by the molar mass of a monomer.

So, if we consider the point, where Gelation transition just takes is taking place or the gel point, where p equal to pc. So at that condition, we know the from this mean field model at peak, pc is equal to 1 over f minus 1. So, at p equal to pc, xn bar can be obtained by replacing this p by 1 over f minus 1. And if we do that the final expression for xn bar that we get is this. So, at that critical point of the point, where Gelation transition is taking place, we see that this xn bar or number average degree of polymerization is finite, it does not diverge or it does not become infinite.

Ah if we consider the weight average degree of polymerization and again without going through the derivation, if we just consider the result that we get from this mean field theory, the weight average degree of polymerization below the gel point, that this p less than pc is given by this expression. So, here we get a xw bar is equal to 1 plus p, over 1 minus p over pc So, one thing to note here is that, at the gel point when p is equal to pc, we see that the denominator of in this case becomes 0 and the xw bar diverges, so xw bar tends to infinity, as we approach the gel point ok.

So, another result arising out of the mean field theory of a Gelation is that, the number average the weight average degree of polymerization diverges, at the gel point and similarly, the weight average molar mass will also diverge. And this gel point is characterized by p equal to pc. Now that we have discussed, the number average and the weight average degree of polymerization there, one can just take the ratio to get an measure of the polydispersity index of the sample that we have.

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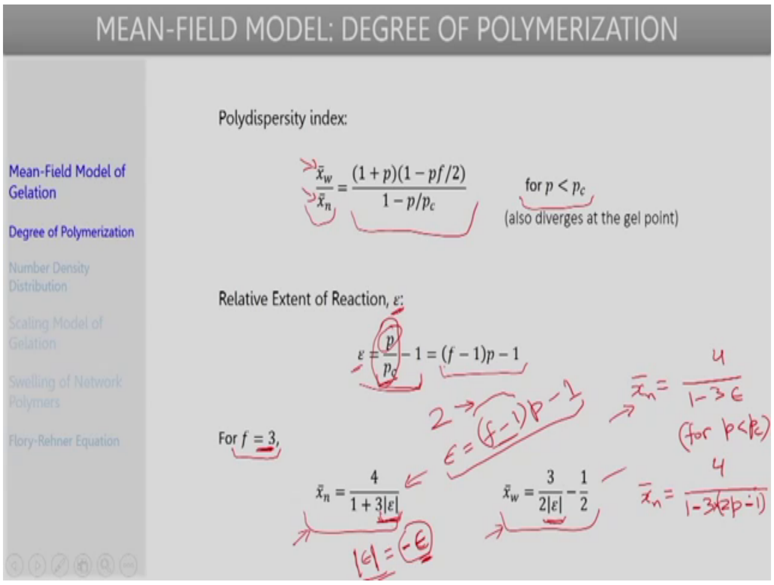

MEAN-FIELD MODEL: DEGREE OF POLYMERIZATION

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- Flory-Rehner Equation

Polydispersity index:

$$\frac{\bar{x}_w}{\bar{x}_n} = \frac{(1+p)(1-pf/2)}{1-p/p_c}$$ for $p < p_c$

(also diverges at the gel point)

Relative Extent of Reaction, ε:

$$\varepsilon = \frac{p}{p_c} - 1 = (f-1)p - 1$$

For $f = 3$,

$$\bar{x}_n = \frac{4}{1+3|\varepsilon|} \qquad \bar{x}_w = \frac{3}{2|\varepsilon|} - \frac{1}{2}$$

$2 \rightarrow$

$\varepsilon = (f-1)p - 1$

$|\varepsilon| = -\varepsilon$

$\bar{x}_n = \frac{4}{1-3\varepsilon}$

(for $p<p_c$)

$\bar{x}_n = \frac{4}{1-3(2p-1)}$

So, if we do that, the polydispersity in index as you know is defined as a ratio of the weight average molar mass to the number average molar mass. So, which can equivalently be stated as the ratio of the weight average degree of polymerization, to the number average degree of polymerization. And this ratio if, we substitute the expressions from the previous slide for xw bar and xn bar here and simplified that expression for polydispersity index, that we get is this and this again is for p less than pc or below the gel point.

So, now, here we again see that, the denominator is such that at the gel point, when p equal to pc, this polydispersity index also tends to infinity and it diverges. So, this pdi also diverges at the gel point ok. Now apart from these quantities, it is useful to define or introduce a quantity, which measures, how far away the system is from the gel point at a certain point of time. That is defined by what is called a relative extent of reaction and which will represent as epsilon.

So, this relative x extent of reaction is defined as p over pc minus 1 and if, we substitute pc equal to 1 over f minus 1 then, we get epsilon equal to f minus 1 times p minus 1 So, what does this relative extent of reaction represent? It actually represents, how far or near we are to the gel point ok. So, if we are exactly at the gel point then, this p will be equal to pc and epsilon will be equal to 0 in that case.

So, epsilon will be equal to 0 at the gel point and as we go away from the gel point in either direction whether, above the gel point or below the gel point the value of epsilon will increase or the absolute value of epsilon will increase. If you have below the gel point you can notice that, epsilon will be negative. So, below the gel point p will be less than pc, so this ratio will be less than 1 and epsilon by this definition will be less than 0.

Similarly, above the gel point, the epsilon will be a positive quantity. So, now, using this relative extent of reaction, the number average degree of polymerization and the weight of average degree of polymerization these two can all can be defined. If we consider the specific case where the monomer functionality is three that is, f equal to 3, so for that case, xn bar and xw bar are related to this epsilon, using these 2 relations that we have here.

So, you notice that we have used the absolute value of epsilon here because below the gel point the epsilon actually is negative. So, so if we consider these 2 equations and try to see if the these are consistent with the previous equations that, we had derived in the last slide for xn bar and xw bar. We can we can do that and we will see that we get the same results as before if, we substitute epsilon is equal to f minus 1 p minus 1 times p minus 1, which is the result that we have here.

So, if you substitute that here and also note that, below the gel point this absolute value of epsilon actually will be minus epsilon because, below the gel point epsilon itself is negative and this absolute value has to be positive. So, minus of this epsilon which is negative, will give us a positive value which will be the absolute value of epsilon below the gel point. So, if we do that so if, we let us say that, xn bar is equal to 4 over 1 minus 3 epsilon for p less than pc.

So, we are below the gel point that is why we have used minus epsilon in place of this absolute value of epsilon here. And if you substitute now this expression here then, xn bar upon simplification we will get to be the same as what we got in the previous slide, so if we do 4 over 1 minus 3 times. And this f minus 1 that we have, this will the in our case, it will be 2 because f is relating f to be 3, so f minus 1 is 2. So, 3 times this f minus 1, which is 2, so 3 times, 2 times p again, minus 1 in here inside bracket.

So, these relations that we have these are consistent with, what we had discussed previously. And these will be valid both below and above the gel point. So, below the gel point since, epsilon is negative absolute value of epsilon will be minus e above the gel point since, epsilon will be positive the absolute value of epsilon can simply be replaced by epsilon itself. So, now that we have define the relative extent of reaction. Let us see how the distribution or the number density distribution of the change that, we have in the system, how that changes or what is a relation for that.

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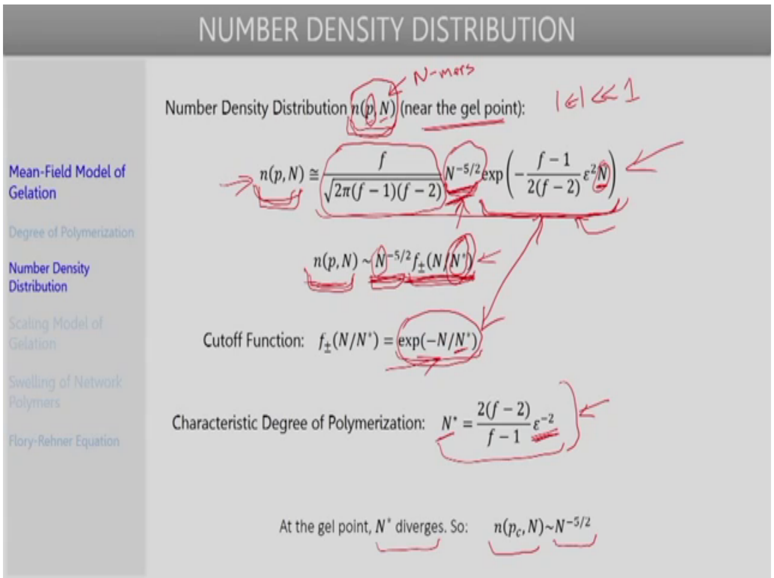

NUMBER DENSITY DISTRIBUTION

Mean-Field Model of Gelation

Degree of Polymerization

Number Density Distribution

Scaling Model of Gelation

Swelling of Network Polymers

Flory-Rehner Equation

Number Density Distribution $n(p, N)$ (near the gel point): $|\epsilon| \ll 1$

N-mers

$$n(p,N) \cong \frac{f}{\sqrt{2\pi(f-1)(f-2)}} N^{-5/2} \exp\left(-\frac{f-1}{2(f-2)}\epsilon^2 N\right)$$

$$n(p,N) \sim N^{-5/2} f_{\pm}(N/N^*)$$

Cutoff Function: $f_{\pm}(N/N^*) = \exp(-N/N^*)$

Characteristic Degree of Polymerization: $N^* = \frac{2(f-2)}{f-1}\epsilon^{-2}$

At the gel point, N^* diverges. So: $n(p_c, N) \sim N^{-5/2}$

So, if we consider the a number density distribution to be represented by this symbol, n which is a function of a pN capital N. So, this small N represents the number density distribution of N mers. This N represents that, we are talking about N mers or the polymer molecules, which have capital N number of monomer (Refer Time: 12:29) present in them. So, the number density distribution of this N mers at a certain point of time and the extent of reaction is p, that is what we are looking at when, we are considering this function here. And this number density distribution is defined basically, as the number of N mers per monomer at a certain extent of reaction ok.

So, now again, we are not going to the a detailed derivations here. One can again starting from by considering a Bethe lattice and using the mean field model, one can derive an expression for a general expression for this quantity. And from this quantity, other things like the degree of polymerization, such things can also be obtained.

So, we will not going to the derivation, we will just state the result that, we obtained for the case, when we are considering this number density distribution near the gel point in the mean field model. So, in this mean field model of gelation, if you are near the gel point which means that, we are talking about a condition where, this epsilon is much smaller than 1 ok, the absolute value of a epsilon. So, we can be near the gel point from either direction, whether we are above the gel point or below the gel point, the same relation applies here. Only thing is that, epsilon should have a very small values should so and we should be very close to the gel point.

So, if that is the case then, it can be shown that, the this density distribution of the N mers at any given extent of reaction p, which is very close to the gel point pc, so that is approximately given by this relation here. So, this is a kind of a pre factors, so this is not of that much interest to us. The what is more interesting are these two quantities, so this is a kind of a power law dependence of this number density distribution on the degree of polymerization of this N mers. So, if you are considering only N mers, the degree of polymerization will just be N.

So, this is a power log dependence of this number density distribution on the degree of polymerization. And this is a kind of a function that also contains the degree of polymerization N. So, this also affects the behavior of this number density distribution with N. Now if we just focus on the dependence on these two quantities, the power law as well as our exponential function, then we can write this number density distribution to be related to the this quantity N through, this power law dependence N to the power minus 5 by 2 along with a kind of a function.

And this function is a function of N and the another quantity N star which will define shortly. So, this f plus or minus n over n star, this function is referred to as the cutoff function and if we consider the form of the equation here then, the cutoff function for the mean field theory is of the exponential form and it is form is exponential minus N over N star.

Here the N star is called the character characteristic degree of polymerization. And again by comparing these 2, we can find that N star will be given by this relation, for through the mean field theory of Gelation. The number density distribution has a power law dependence on the degree of polymerization, but that is a kind of truncated by this the presence of this function, which is the cutoff function ok. And that will be the power law dependence will be truncated at this characteristic degree polymerization N star.

So, we see that, N star is again a function of this relative extent of reaction epsilon and it is related to E to the power minus 2. So, as a extent of reaction tends to zero or as we approach the gel point, we see that this N star actually again diverges. So, at the gel point this a characteristic degree of polymerization also diverges and since, this N star diverges or tends to infinity at the gel point, the cutoff function will tend to will tend to 1 ok.

So, we will get exponential of a 0 as a N star tends to infinity, we will get exponential of 0 as a cutoff function which is 1 So, at the gel point the number density distribution just simply scales as, N to the power minus 5 by 2, where capital N is the degree of polymerization and there is no cutoff function involved. So, this is these are some of the results, that we obtain if we consider the mean field model for the Gelation transition. So, next let us look at a different kind of model for this Gelation phenomena, which is known as the scaling model of Gelation. And the that model is a bit more sophisticated and advanced than this is the other simpler mean field model.

But we will see that the kind of a dependence that we have obtained from the mean field model, similar kind of scaling the dependence is also predicted by this scaling model of Gelation. So, we consider the scaling model of Gelation, which was developed by through the work of (Refer Time: 18:11) and others.

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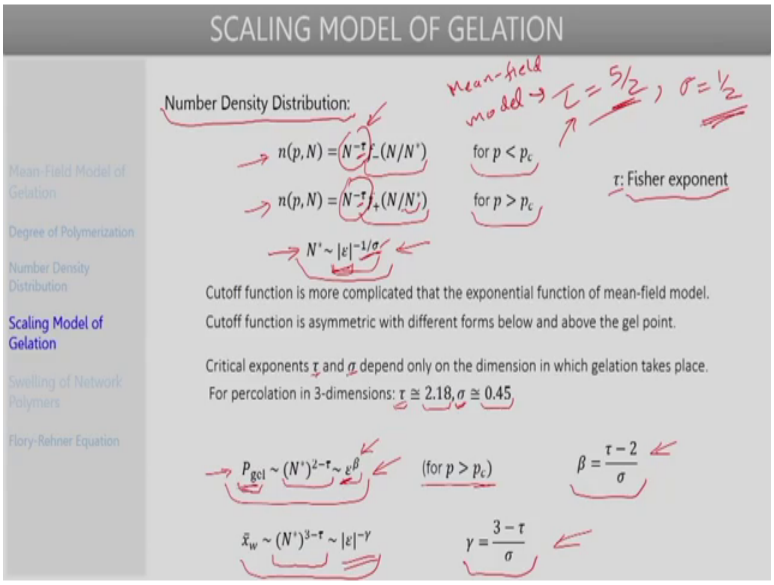

SCALING MODEL OF GELATION

Mean-Field Model of Gelation

Degree of Polymerization

Number Density Distribution

Scaling Model of Gelation

Swelling of Network Polymers

Flory-Rehner Equation

Number Density Distribution:

Mean-field model → $\tau = 5/2$, $\sigma = 1/2$

$n(p,N) = N^{-\tau} f_-(N/N^*)$ for $p < p_c$

$n(p,N) = N^{-\tau} f_+(N/N_+^*)$ for $p > p_c$

τ: Fisher exponent

$N^* \sim |\varepsilon|^{-1/\sigma}$

Cutoff function is more complicated that the exponential function of mean-field model.

Cutoff function is asymmetric with different forms below and above the gel point.

Critical exponents τ and σ depend only on the dimension in which gelation takes place.

For percolation in 3-dimensions: $\tau \cong 2.18, \sigma \cong 0.45$

$P_{gel} \sim (N^*)^{2-\tau} \sim \varepsilon^{\beta}$ (for $p > p_c$) $\beta = \dfrac{\tau - 2}{\sigma}$

$\bar{x}_w \sim (N^*)^{3-\tau} \sim |\varepsilon|^{-\gamma}$ $\gamma = \dfrac{3-\tau}{\sigma}$

If we talk about a number density distribution, which we were discussing in the previous slide for mean field model and if you talk about the scaling model of Gelation now, then the number density distribution actually has a similar kind of form as we saw for the mean field model but there are some important differences ok. So, the number density distribution that we have actually whether, if we are below the gel point or if we are above the gel point that actually dictates, what kind of number density distribution that we have because, the cutoff function in the 2 cases are different, when we are talking the scaling model of Gelation. In the mean field model of Gelation, that we just discussed previously the cutoff function is the same whether we are below the gel point or above the gel point.

But in the scaling model, we have different cutoff function. So, this cutoff function is basically a symmetric across the gel point. Apart from that we also with this power law kind of dependence and N to the power minus tau in both the cases. This exponent tau is the same for the case below the gel point and above the gel point and this tau is referred to as the fisher exponent. So, in the case of a mean field model, the power law dependence that we had was, N to the power minus 5 by 2, here that minus 5 by 2 is replaced by N to the power minus tau. So, kind of a more generic kind of a exponent which is and this exponent is referred to as the fisher exponent.

Apart from that the characteristic degree of pollination N star, so this N star scales as this absolute value of epsilon, which is a relative extent of reaction raised to the power minus 1 over sigma. So, this sigma is again or this 1 over sigma is also an exponent that appears in this scaling model of Gelation So, if we consider the mean field model, we see that for the mean field model the corresponding values of tau will be 5 by 2 and sigma will be just half, so if you are considering the mean field model.

So, if them in the mean field model the equivalent values of tau and sigma are 5 by 2 and half. In the scaling model, actually the value of tau and sigma it is, these are not constants, but depend on the dimension, in which the percolation is taking place. So, the percolation phenomena which describes this connectivity of the network polymer or the dimension of a per dimension, in which the percolation is taking place, that will actually dictate the value of tau and sigma these exponents for scaling model of Gelation; whereas, in mean field model these 2 are always taken to be constant at 5 by 2 and half.

So, as we discussed the difference from mean field model is that, the cutoff function here is more complicated and it is asymmetric with different forms below and above the gel point. And the cutoff function in the in the mean field model is a simple exponential function, but in scaling model the exact form of cutoff function, actually is not known. The exponents that we have tau, as well as sigma here these are called the critical exponents; tau has a special name of fisher exponent.

So, these are critical exponents and these depend on the dimension of the problem. So, dimension in which, percolation is being considered and dimension which the Gelation is taking place, that dimension dictates the value of tau in sigma. So, for percolation in 3 dimension approximately, the value of tau is 2.18 and sigma is 0.45 in the scaling model of Gelation.

And these values are not obtained from any analytical relation. So, these are not exact values, but these are approximate values obtained through, let us say computer simulation results. Similarly, if the percolation is happening in 2 dimensions, the value of tau and sigma will be different from these. If you are considering percolation in some higher dimension, the values will again be different. And if you are considering a limit where percolation is taking place in dimensions of 6 or above so high order dimensions then, the value of tau and sigma actually coincide with the values that we get from the mean field model.

Now in the scaling model, using the scaling model of Gelation, some other the kind of scaling relations can also be identified. So, again we will not go into the details of any derivation here, but just point out a few key important scaling results. So, the gel fraction the scaling model predicts that, the gel fraction is actually proportional to N star to the power 2 minus tau; again N star is the characteristic degree of polymerization.

And since N star itself is a related to the, relative extent of reaction epsilon, through this relation, so then, the p gel can also be related to the relative extent of reaction, as epsilon to the power beta. So, this beta is another exponent that comes in here and since we are talking about the gel fraction, this is all only valid at p above pc because, below the gel point, there will not be any gel and the gel fraction is 0. So, above the gel point this is a scaling relation for the gel fraction.

And since, we are above the gel point there is no need to use a absolute value for epsilon because, above the gel point epsilon will anyways be positive. Similarly, similar kind of scaling um result can also be obtained for the weight average degree of polymerization, so the weight average degree of polymerization if we consider, then the scaling result that we get is, it we xwr scalar a scales as N star to the power 3 minus tau.

So, again N star is related to epsilon through this relation, so we can also say that, x w bar are the weight average degree of polymerization, that scales as epsilon to the power minus gamma. Now the beta as well as the gamma, these 2 exponents can be related to the other 2 critical exponents tau and sigma through these two relations and that is obvious, if we consider if we consider either this relation on this relation in conjunction, with the relation for N star here.

So, if we combine them the then, we can obtain results for beta and gamma in terms of tau in sigma. So, these are some of the important results from the scaling model of Gelation. And what this scaling model predicts is that, the percolation phenomena the dimension, in which the percolation is taking place, that basically has a an effect on the kind of a exponents, that we get in the scaling relations, as well as the form of the cutoff function that we have. And the form of the cutoff function that actually is different, if we are below the gel point from that which, if we will be above the gel point, so the cutoff function is also asymmetric.

So, we will not discuss this model in any further detail, but we will just state that the model actually is more sophisticated and advanced than the mean field model of Gelation. And it predicts some important scaling relations for a various important parameters related to Gelation phenomena and network formation. So, the last in the last part of this lecture, what we will do is focus on this phenomenon of swelling of network polymers ok. So, we have considered Gelation phenomena, now and the formation of network polymers.

Now if you have a fully developed network for polymer that has formed, where almost all the monomeric units are part of this large network. And if we try to dissolve this network polymer in a solvent, then the since the network is almost infinitely large, this due to the presence of these cross links the polymer, network will not actually dissolve in the solvent, but instead it will swell in the presence of the solvent. So, the polymer network will imbibe the solvent molecules inside it and that will lead to the swelling of this cross linked polymer network.

So, we will next discuss some equations and theories that, that are used to describe such swelling behavior. So, as we discussed network polymers being a highly cross linked do not dissolve in the solvent, but this swell in the presence of solvents.

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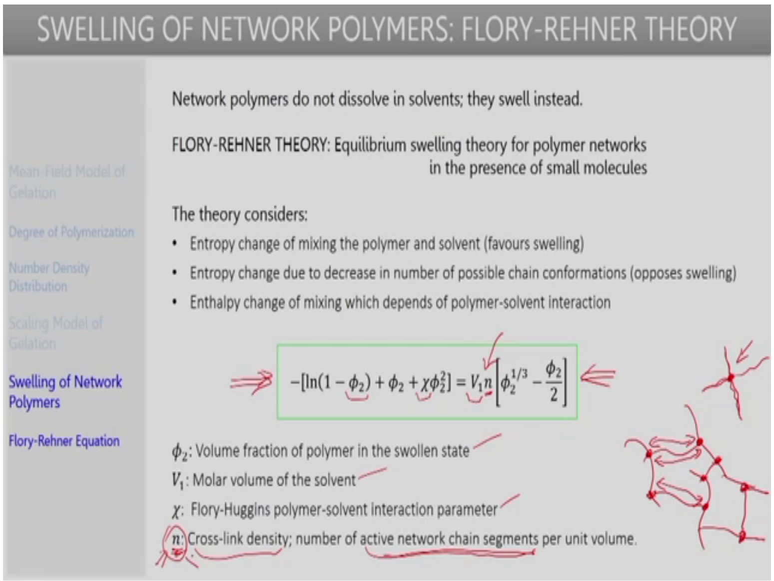

SWELLING OF NETWORK POLYMERS: FLORY-REHNER THEORY

Network polymers do not dissolve in solvents; they swell instead.

FLORY-REHNER THEORY: Equilibrium swelling theory for polymer networks in the presence of small molecules

The theory considers:

- Entropy change of mixing the polymer and solvent (favours swelling)
- Entropy change due to decrease in number of possible chain conformations (opposes swelling)
- Enthalpy change of mixing which depends of polymer-solvent interaction

$$\boxed{-[\ln(1-\phi_2)+\phi_2+\chi\phi_2^2] = V_1 n\left[\phi_2^{1/3}-\frac{\phi_2}{2}\right]}$$

ϕ_2: Volume fraction of polymer in the swollen state

V_1: Molar volume of the solvent

χ: Flory-Huggins polymer-solvent interaction parameter

n: Cross-link density; number of active network chain segments per unit volume.

So, typical examples of network polymers are elastomers and thermosetting polymers. So, if we consider elastomers, let us say, if we add some solvent to rubber, then that elastomeric material like rubber will swell ok. So, that the swelling, that is what we were interested in studying the swelling behavior.

Relatively simple, but the useful theory for describing the swelling behavior is due to Flory and Rehner. And this equilibrium swelling theory proposed by them is describes, the swelling of polymer networks, when exposed to solvent to containing small molecules ok. So, if you have a small solvent having small molecules and if we are adding it to a network polymer then, this kind of swelling, that we get that is described by this Flory Rehner theory. And in this theory, the basically three different kinds of a factors were considered by Flory and Rehner to come up with, the expression for the swelling behavior.

So, the different factors, which are considered are that, when we are mixing a solvent into a network polymer and the network polymer swells then, there are three different forces, that are at play. One is due to the entropy of a mixing, so since we are mixing 2 different substances that, just pure entropy of mixing will always a favor swelling because, it will be a negative quantity. So, the entropy of a mixing will favor the selling behavior.

On the other hand, upon swelling we have a network polymer. So, upon swelling, the chains basically get kind of stretched the chains are cross linked at different junction points. So, if in the presence of a solvent the chain the network polymer swells then, the different chain segments between the junction points they get stretched. And they would like to come back to their original dimensions and state so, as to increase or maximize the entropy that they have. So, that stretched polymer chain will lead to a loss in a entropy.

So, entropic factors due to the stretching of polymer chains that will actually not favor swelling and it will try to bring the network polymer back to its original size. So, that is a factor that is opposing the swelling behavior. And the third factor is the enthalpy of mixing, so that will depend on the interaction between the polymer and solvent and depending on what kind of interaction we have. It this factor can either oppose swelling or favor swelling.

So, based on these 3 considerations and using the Flory Huggins approach for the polymer solvent mixing behavior and the a kind of the theory of a elasticity of elastomers, for considering the stretching of the net network chain segments and considering these two these two theories together, Flory and Rehner came up with the expression for describing the swelling of network polymers ok.

So, the Flory Rehner equation, the final equation will not go through a derivation again. The final equation is shown here and in this Flory Rehner equation the different terms, some of these terms should be familiar to you. So, this phi 2 is just the volume fraction of the polymer in the swollen polymer network, so that is phi 2, chi is the Flory Huggins polymer solvent interaction parameter and that is also a something that we have come across previously one is the molar volume of the solvent ok.

So, that is also something, that will be known and the n is some n is an interesting quantity, so we will discuss what n is briefly. So, as we discussed phi 2 is the volume fraction of polymer in the swollen state, V 1 is the molar volume of solvent and Chi Huggins interaction parameter and the quantity n here parameter n this is a sometimes referred to as, the cross link density. And it describes a number of network segments, present per unit volume of our sample ok.

So, when we say active network chain segments, these this term basically describes a chain segments which are between 2 junction points. So, the chain segments connecting a 2 other chains that is that is, what we mean by this active network chain segments and this corresponds to a segment of a chain, that is bound at the 2 ends by 2 junction points ok. So, the density of such a network chain segments per unit volume, that number density is what this n is and it is also sometimes called the cross link density. And one should note that, this density, number density is actually different from the number density of the junction points that we will get.

So, if we consider a network polymer ok, and if we consider different kinds of a junction points ok, so these are junction points and this is the network acting network side segment that we are talking about. So, number of such network segments, these network segments between 2 junction points per unit volume that is what this n is. And if we are talking about the density of these junction points number density, then that actually will depend on the um the functionality of this each junction point.

So, for from each junction point, how many chains are propagating. So, one can have a tri functional junction point, from which three chains are where three chain, segments are connecting. One can have tetra functional also where 4 chains are connecting. So, depending on that the junction point density can be related to n, so for this tetra functional kind of case, so the junction point density will just be half of n.

So, this the cross link density, that we are talking about that, we can obtain if we know the density or polymer density, as well as the what is called the number average molar mass of these active network chain segments. So, the a number average molar mass of these kind of chain segments between 2 junction points, if you are averaging all the all such active network segments present in the system. So, that molar mass, if we divide the polymer density by that molar mass then, we will get the this cross link density n ok.

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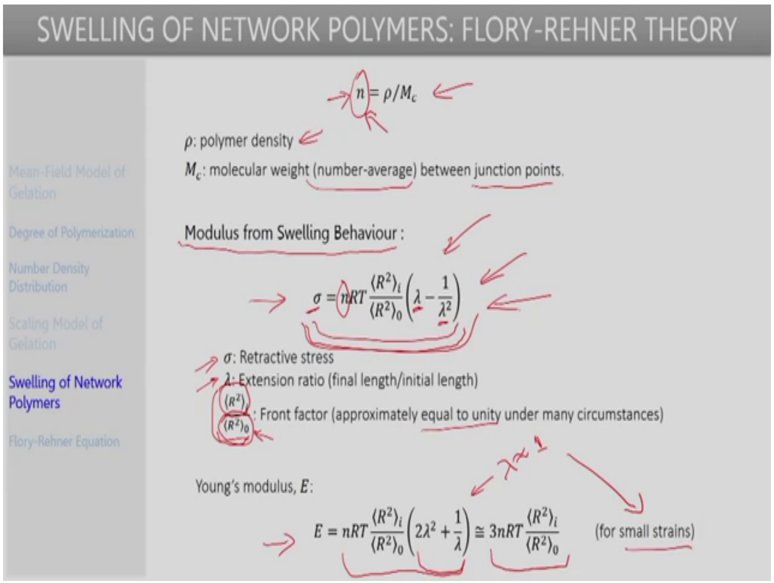

SWELLING OF NETWORK POLYMERS: FLORY-REHNER THEORY

Mean-Field Model of Gelation

Degree of Polymerization

Number Density Distribution

Scaling Model of Gelation

Swelling of Network Polymers

Flory-Rehner Equation

$$n = \rho / M_c$$

ρ: polymer density

M_c: molecular weight (number-average) between junction points.

Modulus from Swelling Behaviour :

$$\sigma = nRT \frac{\langle R^2 \rangle_i}{\langle R^2 \rangle_0} \left(\lambda - \frac{1}{\lambda^2} \right)$$

σ: Retractive stress

λ: Extension ratio (final length/initial length)

$\frac{\langle R^2 \rangle_i}{\langle R^2 \rangle_0}$: Front factor (approximately equal to unity under many circumstances)

Young's modulus, E:

$\lambda \approx 1$

$$E = nRT \frac{\langle R^2 \rangle_i}{\langle R^2 \rangle_0} \left(2\lambda^2 + \frac{1}{\lambda} \right) \cong 3nRT \frac{\langle R^2 \rangle_i}{\langle R^2 \rangle_0} \quad \text{(for small strains)}$$

So, this n is given by simply rho by M c, where rho is a polymer density, mc is the molecular weight or molar mass, which is the number average quantity between of the polymer active network segments between different junction points ok. Now the swelling behavior that we have, of course one can obtain, in the previous expression we saw that, the Flory Huggins interaction parameter also appears. So, the swelling behavior can be used to obtain the Flory Huggins interaction parameter data.

And if let us say we have a system where, the Flory Huggins interaction parameter is known then, the swelling behavior actually can be used to obtain the elastic modulus of this polymer net network or polymer gel ok. So, let us see how that that is done. So, if we want to obtain the modulus from swelling behavior then, we will need to use an expression that, describes the relation between the stress and strain. So, without again deriving we will just write down this expression for which relates the stress and the what is called the extension ratio lambda, which is a measure of the strain.

And we see that this number n, which is the same as this n here that appears in this relation ok. So, what this suggests is that, if we have this a value of this n for from the swelling behavior then, that can be used to obtain a modulus from an equation of this kind ok. So, this equation we have not derived, but we will try to briefly consider this later and in this course when we talk about rubber elasticity.

So, through theories of rubber elasticity, one can show that an expression like this under the certain assumptions is valid So, if you have this expression and this is the retractive stress, if the sample is being extended then, the retractive stress developed in the sample that is sigma. Lambda extension ratio is just the final length at any point divided by the initial length of the sample and it is a measure of the strain. And this front factor is this ratio, which is generally equal to 1, but can be different from 1 also in some cases.

And a here these 2 quantities, it is a ratio of these 2 quantities, so R square i is basically, a kind of a mean square, end to end distance of a active network segments between different junction points in the network polymer. And this R square naught is just the mean square into an distance, if these if these network segments were not bound at the junction points, but if their ends were free and if they are isolated and then, in that case what mean square into n distance they would have that is this r square naught.

And from this relation, we can a one can actually obtain the Young’s modulus directly. So, the Young’s modulus from this relation again will not go into the derivation, but then Young’s modulus, that we get is this and for a small strain, where the extension ratio lambda is close to 1. So, if lambda is approximately equal to 1, which corresponds to small strains we will get this track rate term as just 3. So, we will get this as the Young’s modulus.

So, if we know n again from the swelling data of the polymer network then, Young’s modulus can be estimated using this kind of an expression ok.

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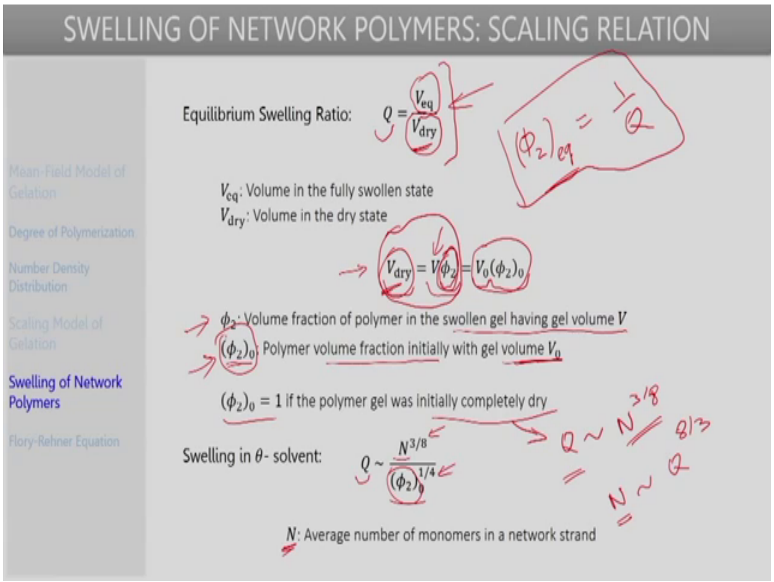

SWELLING OF NETWORK POLYMERS: SCALING RELATION

Mean-Field Model of Gelation

Degree of Polymerization

Number Density Distribution

Scaling Model of Gelation

Swelling of Network Polymers

Flory-Rehner Equation

Equilibrium Swelling Ratio: $Q = \frac{V_{eq}}{V_{dry}}$

$(\phi_2)_{eq} = \frac{1}{Q}$

V_{eq}: Volume in the fully swollen state
V_{dry}: Volume in the dry state

$$V_{dry} = V\phi_2 = V_0(\phi_2)_0$$

ϕ_2: Volume fraction of polymer in the swollen gel having gel volume V
$(\phi_2)_0$: Polymer volume fraction initially with gel volume V_0

$(\phi_2)_0 = 1$ if the polymer gel was initially completely dry

Swelling in θ- solvent: $Q \sim \frac{N^{3/8}}{(\phi_2)_0^{1/4}}$

$Q \sim N^{3/8}$

$N \sim Q^{8/3}$

N: Average number of monomers in a network strand

So, before we conclude we will just talk about a couple of other aspects related to, so are related to polymer network swelling So, a quantity known as the equilibrium swelling ratio Q that can be defined as the volume of the polymer network or polymers gel, when it is swollen and when it is at a equilibrium, divided by the volume of the dry polymer sample network polymer sample ok.

So, if you have dry network polymer and if, we add a solvent, it will take in some solvent somehow, the solvent and it will swell. So, the Veq is the volume of that, swollen polymer network and V dry is the volume of the dry polymer network in the absence of a any solvent in the system ok. So, what we can do is, identify a relation like this between the dry volume of the network polymer, as well as the volume fraction of the polymer ok, for any amount of swelling that has happened.

So, let us say if, you have a partially swollen sample, which has not fully swollen it is not yet had attained its equilibrium swollen volume. So, this even then the dry volume can be written to be equal to the volume of this partially swollen polymer sample network polymer sample, multiplied by the volume fraction of the network polymer in the sample. And this can be done because, swelling is taking place only because of the extra volume of the solvent, that s coming in the volume of this polymer itself is not changing ok.

And let us say that initially instead if instead of starting with a dry polymer in initially at the initial point, if the volume if the polymer itself had some solvent present and then, more solvent has added to swell it to a larger volume So, if initially the volume of a partially it is a swollen polymer or a polymer having some solvent is V naught and the corresponding volume fraction of polymer is phi 2 naught then, this product will also be equal to V dry. So, at any point, during the swelling behavior the V dry will be equal to just the corresponding volume of the swollen gel times the corresponding volume fraction of polymer in that swollen gel.

So, as we discussed this phi 2, we have already discussed in phi 2 not being the volume fraction of polymer in swollen gel, when the volume is of gel is V and the volume fraction initially this phi 2 naught, when the gel volume is and initially if the polymer is dry then of course, this phi 2 naught will be 1 ok. So, if the polymer is entirely dry, there is no solvent present in the volume fraction of polymer in the gel in that case will be just 1.

So, if the polymer is completely dry initially, this is 1 and without going into too much details, what we will do is, just identify a kind of a scaling relation again ok, between this equilibrium swelling ratio and some other quantity of interest for the particular case of a theta solvent ok. So, if we have a network polymer and in the presence of a theta solvent then, the kind of swelling that we get, that swelling equilibrium swelling ratio is actually related to this quantity n and phi 2 naught through these exponents ok.

So, if the phi 2, if the initially the polymer sample is dry phi 2 naught is just one, so in that case so for the completely dry case, Q will simply scale as this n to the power 3 by 8 ok. And this n is the average number of monomers in the network strand. So, if you are considering network strand between the different two different junction points, so the average number of monomers present in such a strand that is what is this n represents. And we see that, the equilibrium swelling ratio q actually scales as n to the power three by eight or in other words n is related to will scale as Q to the power 8 by 3.

So, if we have an idea of the equilibrium swelling ratio for a given from given swelling experiment, then we can estimate or get a measure of the average number of monomers present in a given network strand, between two junction points. One last thing to identify here is that, if we look at this equilibrium swelling ratio and if we consider phi 2 at equilibrium so, when the swelling complete swelling has taken place and we are at an equilibrium condition, then the corresponding volume fraction of the polymer in that swollen gel equilibrium swollen gel, we can we can identify that is just equal to 1 over q and that can be done by looking at this relation, as well as this relation here.

So, if you substitute this V dry here and we consider in case of this V the equilibrium swollen volume and this phi 2 then will be the volume fraction at in the equilibrium swollen gel. So, that will give us this kind of a reciprocal relation between, the volume fraction of polymer in the equilibrium swollen gel and the equilibrium swelling ratio Q ok. We will conclude our discussion of swelling of a network polymers here and before concluding the this lecture, will just let us just review and recap the different things, that we studied in during this week related to branching of polymers and Gelation.

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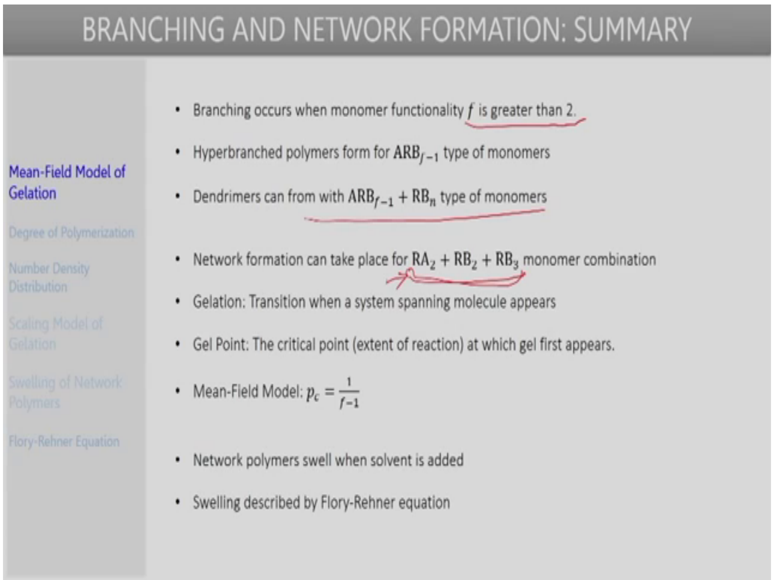

BRANCHING AND NETWORK FORMATION: SUMMARY

Mean-Field Model of Gelation
Degree of Polymerization
Number Density Distribution
Scaling Model of Gelation
Swelling of Network Polymers
Flory-Rehner Equation

- Branching occurs when monomer functionality f is greater than 2.
- Hyperbranched polymers form for ARB_{f-1} type of monomers
- Dendrimers can from with $ARB_{f-1} + RB_n$ type of monomers
- Network formation can take place for $RA_2 + RB_2 + RB_3$ monomer combination
- Gelation: Transition when a system spanning molecule appears
- Gel Point: The critical point (extent of reaction) at which gel first appears.
- Mean-Field Model: $p_c = \frac{1}{f-1}$
- Network polymers swell when solvent is added
- Swelling described by Flory-Rehner equation

So, with regards to branching we discussed that, branching occurs when we have at least a monomer having a functionality greater than 2 ok. So, at least f greater than 2 is required for branching. The in for a special case of kind of a monomer type, where we have a ARB f minus 1, type of monomer, where f is a functionality and A and B are the functional groups, that react. We can get a hyper branch polymer, so it will not form network polymers or will not result in Gelation, but we will get hyper branch polymers.

Similarly if we have a AB ARBF minus 1 plus RB n kind of monomer combination, then under control conditions, if properly done we can get the highly ordered polymer structures, branch polymer structures, called dendrimers ok, so that is what, we have here. We also have discussed Gelation or a network formation and Gelation in this week, so with respect to network formation, we discussed that if we have a monomer combination of this type then, network formation can take this through the formation of junction points. And this is not the only combination of monomer that will result in network formation.

So, if we just have a monomer RA 3, that will upon where, a can react with itself. So, if we have a some kind of polyol with where, the oh groups can react to form a ether linkage let us say. So such cases also can result in the formation of network polymers so this is a one example, but apart from this with other monomer combinations like RA 3 and some other combinations some can result in network form formation ok.

So, we discussed that, network formation is associated with this Gelation transition. And this Gelation is a transition from a sol to like state to a gel like state, where a system spanning large are almost infinite kind of molecule first appears, during this Gelation transition. And this assessment planning molecule has a connectivity, um across the entire microscopic system. And the gel point is a point, that marks its Gelation transition and it is the extent of reaction, corresponding to the gel point is referred to as a Pc.

The mean field model predicts this pc's 1 over f minus 1 and then, the mean field model can be used to obtain others kind of a relations for the number average and a weight average degree of polymerization, as well as the number density distribution. Most sophisticated scaling theories also are there and we have briefly discussed some results, some scaling results from those theories in today's lecture. And finally, we have considered consider the case of the swelling of network polymers in the presence of a solvent.

So, network polymers do not dissolve, but swell in the presence of solvents and such swelling behavior can be described by the Flory Rehner equation. So, these are some of the topics that, we have considered under the branching and network formation of polymers and we will conclude this lecture at this point.

Thank you.