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

Lecture – 08
Phase Behaviour of Polymer Blends and Copolymers

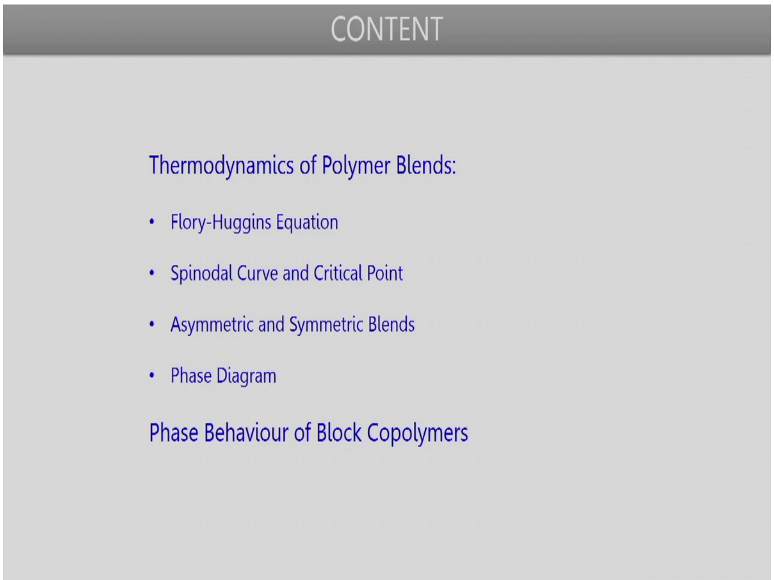
So, hello everyones. In the last lecture we were discussing the phase behavior of polymer solutions. So, specifically we look looked at the conditions under which polymer solution can become unstable and phase separated into 2 different phases. We considered the Gibbs energy versus composition diagram and on that diagram we marked the points which correspond to the stable meta stable and unstable regimes.

Basically the regions demarcated by the binodal points there represent the regions of a stability of homogenous solutions. The region between the binodal and spinodal points they represent represent the metastable region, where the thermodynamically the favorable state would be a phase separated 2 phase state.

But for that to happen this a barrier that needs to be crossed and then phase separation can take place through nucleation in growth. Further we also identified unstable region which is the region between the 2 spinodal points and this region any tiny fluctuation can result in the phase separation of a homogenous solution into 2 different phases.

So, we also developed mathematical expression starting from the Flory Huggins equation. For the spinodal curve as well as for the critical composition the critical temperature and the critical Flory Huggins interaction parameter. Further we also briefly started discussing the thermodynamics of polymer blends. So, in this lecture we will continue that discussion on the thermodynamics of polymer blends and we will also briefly talk about the thermodynamic and phase behavior of block copolymers.

(Refer Slide Time: 02:26)



CONTENT

Thermodynamics of Polymer Blends:

- Flory-Huggins Equation
- Spinodal Curve and Critical Point
- Asymmetric and Symmetric Blends
- Phase Diagram

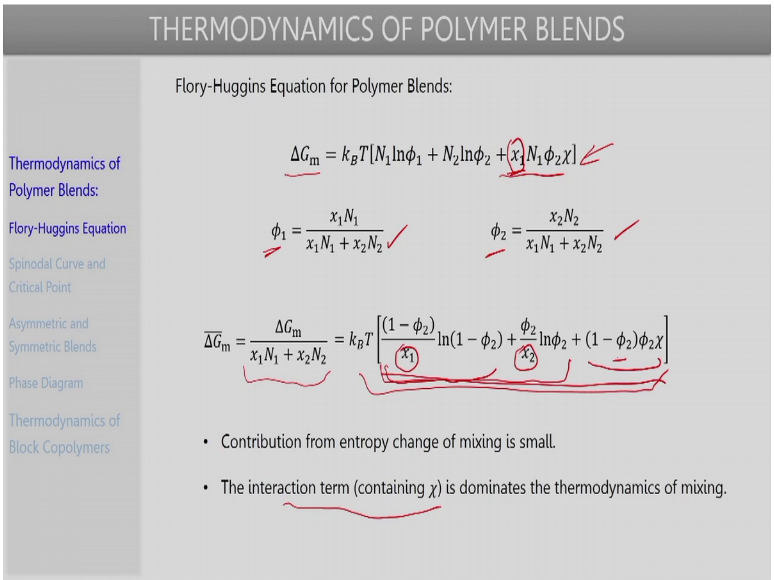
Phase Behaviour of Block Copolymers

So, the content of this lecture is briefly summarized here we will start with the Flory Huggins equation for polymer blends which we introduced in the previous lecture. Then we will use this Flory Huggins equation to derive the expressions for a spinodal curve as well as for critical point which is the approach will be similar to what we discussed in the previous lecture for polymer solutions. We will also look at the case of asymmetric as well as symmetric blend.

What these are and how the behaviors are be different. And finally, for polymer blends we will look at the phase diagram a typical phase diagram for polymer blends and we will see that it has features which are very similar to what we already observed for polymer solution phase diagrams and towards the end of this lecture, we will briefly also discuss the phase behavior of block copolymers and we will see that it shows some interesting features.

So, as discussed in the last lecture the Flory Huggins equation for a polymer blend.

(Refer Slide Time: 03:31)



THERMODYNAMICS OF POLYMER BLENDS

Thermodynamics of Polymer Blends:

Flory-Huggins Equation

Spinodal Curve and Critical Point

Asymmetric and Symmetric Blends

Phase Diagram

Thermodynamics of Block Copolymers

Flory-Huggins Equation for Polymer Blends:

$$\Delta G_m = k_B T[N_1 \ln\phi_1 + N_2 \ln\phi_2 + x_1 N_1 \phi_2 \chi]$$

$$\phi_1 = \frac{x_1 N_1}{x_1 N_1 + x_2 N_2} \qquad \phi_2 = \frac{x_2 N_2}{x_1 N_1 + x_2 N_2}$$

$$\overline{\Delta G}_m = \frac{\Delta G_m}{x_1 N_1 + x_2 N_2} = k_B T\left[\frac{(1-\phi_2)}{x_1}\ln(1-\phi_2) + \frac{\phi_2}{x_2}\ln\phi_2 + (1-\phi_2)\phi_2\chi\right]$$

- Contribution from entropy change of mixing is small.
- The interaction term (containing χ) is dominates the thermodynamics of mixing.

It is very similar to the Flory Huggins equation for a polymer solution. The only difference is the appearance of this term x 1 here and this x 1 is nothing but the number of segments in the first polymer.

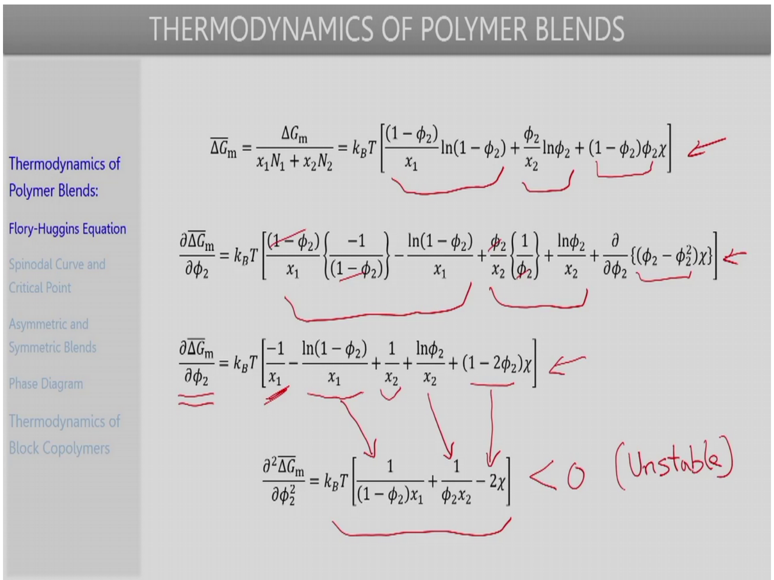
So, as we have already discussed polymer blends has a mixture of 2 different polymers. And x 1 denotes the number of segments in polymer one x 2 denotes the number of segments in polymer 2. So, the number of segments in polymer 1 x 1 that is the extra term that appears here as compared to the equation for polymer solution. And the volume fractions of the first and the second polymer the expressions for those also change a bit because now both components are polymers. So, the number of segments of both the polymers will come into the volume fraction expression.

So, we have phi 1 as x 1 n 1 by x 1 n 1 plus x 1 x 2 n 2 and similarly phi 2 as x 2 n 2 divided by x 1 n 1 plus x 2 n 2 if we take the delta gm and divide that by the total number of lattice sites total number of segments present which is x 1 n 1 plus x 2 n 2 what we can do is through this division reformulate the original Flory Huggins equation for a polymer blend into a a form where the right hand side only contains the volume fraction of the second polymer which is phi 2. So, this again is something that we discussed towards the end of the last lecture.

If you look at this expression the expression here, the first 2 terms here these 2 terms. These represent the contribution from the combinatorial entropy change of mixing. And we see that the difference from polymer solutions is here both these terms are actually contained either x 1 or x 2 in the denominator. So, that both these terms are small in magnitude what; that means, is that the entropy change of mixing is quite small for polymer blends and it turns out that it is actually the interaction term, which is a term containing chi this last term here that is the term which dominates the thermodynamics of polymer blends.

The entropy of mixing is small and that contribution does not significantly play a role in deciding the thermodynamics of polymer blends. It is an interaction in term which is the more important one

(Refer Slide Time: 06:09)



THERMODYNAMICS OF POLYMER BLENDS

Thermodynamics of Polymer Blends:

Flory-Huggins Equation

Spinodal Curve and Critical Point

Asymmetric and Symmetric Blends

Phase Diagram

Thermodynamics of Block Copolymers

$$\overline{\Delta G}_m = \frac{\Delta G_m}{x_1N_1 + x_2N_2} = k_BT\left[\underbrace{\frac{(1-\phi_2)}{x_1}\ln(1-\phi_2)} + \underbrace{\frac{\phi_2}{x_2}}\ln\phi_2 + \underbrace{(1-\phi_2)}\phi_2\chi\right] \leftarrow$$

$$\frac{\partial\overline{\Delta G}_m}{\partial\phi_2} = k_BT\left[\underbrace{\frac{(\cancel{1-\phi_2})}{x_1}\left\{\frac{-1}{(\cancel{1-\phi_2})}\right\} - \frac{\ln(1-\phi_2)}{x_1}} + \underbrace{\frac{\cancel{\phi_2}}{x_2}\left\{\frac{1}{\cancel{\phi_2}}\right\} + \frac{\ln\phi_2}{x_2}} + \frac{\partial}{\partial\phi_2}\{(\underbrace{\phi_2-\phi_2^2})\chi\}\right] \leftarrow$$

$$\frac{\partial\overline{\Delta G}_m}{\partial\phi_2} = k_BT\left[\frac{-1}{x_1} - \frac{\ln(1-\phi_2)}{x_1} + \frac{1}{x_2} + \frac{\ln\phi_2}{x_2} + (1-2\phi_2)\chi\right] \leftarrow$$

$$\frac{\partial^2\overline{\Delta G}_m}{\partial\phi_2^2} = k_BT\underbrace{\left[\frac{1}{(1-\phi_2)x_1} + \frac{1}{\phi_2x_2} - 2\chi\right]} < 0 \quad \text{(Unstable)}$$

So, again if we start with this reformulated Flory Huggins equation, in where delta gm is expressed in terms of phi 2 only and if we as before as discussed in the last lecture; if we again try to look at the condition for stability. So, the condition for stability we know is decided by the sign of the second derivative of this delta gm with respect to phi 2. So, what we can do is differentiate this expression twice again then see the what expression we get and how equating it to 0 can lead us to the expression for the spinodal curve.

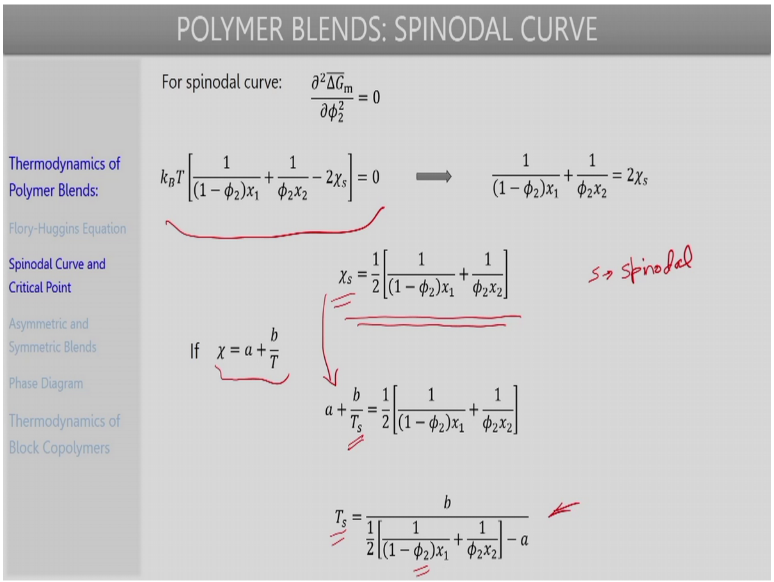
So, differentiating it once we will give us the expression here, where the these 2 terms here these 2 terms come from the differentiation of this term here and similarly these 2 terms come from the differentiation of this term here. And finally, this term comes to us just by the multiplication of 1 minus phi to with phi 2. So, again we see that these can be cancelled similarly the phi 2 here that can also be cancelled.

So, we end up with an expression which looks something like this and, now if we differentiate this expression one more time because we are interested in the second derivative of the Gibbs free energy change that is the term who sign decides the stability of the polymer blend. So, the stability will be decided by the second derivative and this second derivative is obtained by just differentiating this quantity one more time with respect to phi 2.

So, if we do that this term derivative of this with respect to phi 2 is 0 differentiation this is respect to phi 2 will give us this term again if we differentiate 1 over x 2 with this 2 phi 2 that is also 0 because x 1 and x 2 are constants as far as change with respect to phi 2 is concerned and differentiating this will give this term and finally, differentiating this will just give minus 2 chi term. So, the second derivative of the Gibbs free energy change is just respect to the composition which here is represented by phi 2.

So, the expression for that second derivative is this and as we have discussed before if this quantity is less than 0, then we know that the blend will be unstable and such a blend will not actually remain in a mixed state it will phase separate into 2 different phases.

(Refer Slide Time: 09:03)



POLYMER BLENDS: SPINODAL CURVE

Thermodynamics of Polymer Blends:

Flory-Huggins Equation

Spinodal Curve and Critical Point

Asymmetric and Symmetric Blends

Phase Diagram

Thermodynamics of Block Copolymers

For spinodal curve: $\frac{\partial^2 \overline{\Delta G_m}}{\partial \phi_2^2} = 0$

$$\underbrace{k_B T\left[\frac{1}{(1-\phi_2)x_1} + \frac{1}{\phi_2 x_2} - 2\chi_s\right] = 0}_{} \Longrightarrow \frac{1}{(1-\phi_2)x_1} + \frac{1}{\phi_2 x_2} = 2\chi_s$$

$$\chi_s = \frac{1}{2}\left[\frac{1}{(1-\phi_2)x_1} + \frac{1}{\phi_2 x_2}\right]$$

s → spinodal

If $\chi = a + \frac{b}{T}$

$$a + \frac{b}{T_s} = \frac{1}{2}\left[\frac{1}{(1-\phi_2)x_1} + \frac{1}{\phi_2 x_2}\right]$$

$$T_s = \frac{b}{\frac{1}{2}\left[\frac{1}{(1-\phi_2)x_1} + \frac{1}{\phi_2 x_2}\right] - a}$$

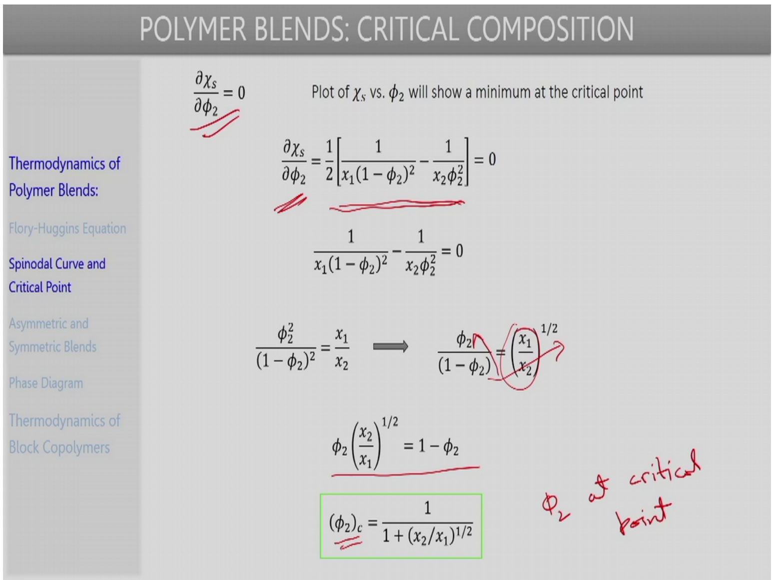
Now let us look at a condition where the second derivative is actually 0. So, the second derivative being 0, that is the condition for the spinodal point as we have discussed in the previous lecture for polymer solutions.

So, for polymer blends also the same condition will apply and the second derivative setting the second derivative to 0 that will provide us the location of the spinodal points. And so, if we use the expression for the del square delta gm del phi 2 square that we derived in the previous slide, we said that expression to 0 then from that by rearranging the terms finally, what we get is the chi which is a Flory Huggins polymer-polymer interaction parameter because we are talking the blend now.

So, here this chi s, where the subscript s denotes again spinodal. So, chi s is given by half of 1 over 1 minus phi 2 x 1 plus 1 over phi 2 x 2. So, this equation basically is the equation of the spinodal curve. So, if we plot chi s as a function of phi 2 using this equation that will give us the spinodal curve as predicted by Flory Huggins equation for a given polymer blend. Now if we assume that chi depends on temperature using a functionality of this form that is chi is equal to a plus b by T, then we can substitute that expression for chi s which is a plus b by T. And again instead of t we are writing T s we because we are dealing with the condition for spinodal.

So, that subscript s again denotes temperature denotes a spinodal condition and if we rearrange the terms again, we what we get is the expression for temperature this temperature T s at the spindle condition as a function of phi 2. So, from this equation as well we can plot the spinodal curve where as phi 2 changes how the temperature is changing that behavior can be obtained from this equation and then it can be plotted to get the spinodal curve.

(Refer Slide Time: 11:25)



POLYMER BLENDS: CRITICAL COMPOSITION

Thermodynamics of Polymer Blends:

Flory-Huggins Equation

Spinodal Curve and Critical Point

Asymmetric and Symmetric Blends

Phase Diagram

Thermodynamics of Block Copolymers

$$\frac{\partial \chi_s}{\partial \phi_2} = 0$$

Plot of χ_s vs. ϕ_2 will show a minimum at the critical point

$$\frac{\partial \chi_s}{\partial \phi_2} = \frac{1}{2}\left[\frac{1}{x_1(1-\phi_2)^2} - \frac{1}{x_2\phi_2^2}\right] = 0$$

$$\frac{1}{x_1(1-\phi_2)^2} - \frac{1}{x_2\phi_2^2} = 0$$

$$\frac{\phi_2^2}{(1-\phi_2)^2} = \frac{x_1}{x_2} \Longrightarrow \frac{\phi_2}{(1-\phi_2)} = \left(\frac{x_1}{x_2}\right)^{1/2}$$

$$\phi_2\left(\frac{x_2}{x_1}\right)^{1/2} = 1 - \phi_2$$

$$\boxed{(\phi_2)_c = \frac{1}{1 + (x_2/x_1)^{1/2}}}$$

ϕ_2 at critical point

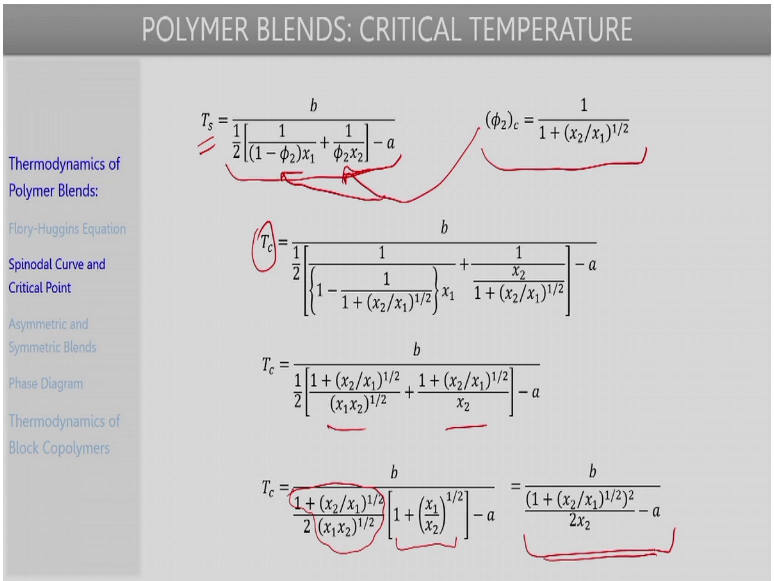
Next again as similar to what we did for a polymer solution for polymer blends also. If we want to determine the critical point the condition for that is the derivative of this chi s with respect to phi 2 is 0 what that means, is that if we plot chi s as a function of phi 2, then the critical point will correspond to the point where the curve will show a minimum.

So, the if we plot the spinodal curve then the minimum of that curve corresponds to the critical point and that is what we are trying to mathematically determine using the this condition here. So, applying this condition and we already have derived an expression for chi s in the previous slide. So, if we differentiate that expression with respect to phi 2, we get this expression here and for the critical composition or the critical point the condition is that this expression that is this derivative should be equal to 0.

So, setting it equal to 0 and again rearranging the terms what we get is phi 2 square over 1 minus phi 2 the whole square is equal to x 1 by x 2. And again in the next step we can just take the square root on both sides and then finally, rearrange the terms one more time take this term up here and this term up here. So, we get this expression and from this finally, the expression for phi 2 at the critical point. So, this phi 2 c, which is the critical composition or the value of phi 2 at critical point.

So, that is what we obtain and the expression for this critical composition is 1 over 1 plus x 2 by x 1 raised to the power half. So, next now that we have an expression for this critical composition, we can use this expression to obtain expressions for critical temperature as well as the critical value of the Flory Huggins interaction parameter.

(Refer Slide Time: 13:38)



POLYMER BLENDS: CRITICAL TEMPERATURE

Thermodynamics of Polymer Blends:

Flory-Huggins Equation

Spinodal Curve and Critical Point

Asymmetric and Symmetric Blends

Phase Diagram

Thermodynamics of Block Copolymers

$$T_s = \frac{b}{\frac{1}{2}\left[\frac{1}{(1-\phi_2)x_1} + \frac{1}{\phi_2 x_2}\right] - a} \qquad (\phi_2)_c = \frac{1}{1 + (x_2/x_1)^{1/2}}$$

$$T_c = \frac{b}{\frac{1}{2}\left[\frac{1}{\left\{1 - \frac{1}{1+(x_2/x_1)^{1/2}}\right\}x_1} + \frac{1}{\frac{x_2}{1+(x_2/x_1)^{1/2}}}\right] - a}$$

$$T_c = \frac{b}{\frac{1}{2}\left[\frac{1+(x_2/x_1)^{1/2}}{(x_1x_2)^{1/2}} + \frac{1+(x_2/x_1)^{1/2}}{x_2}\right] - a}$$

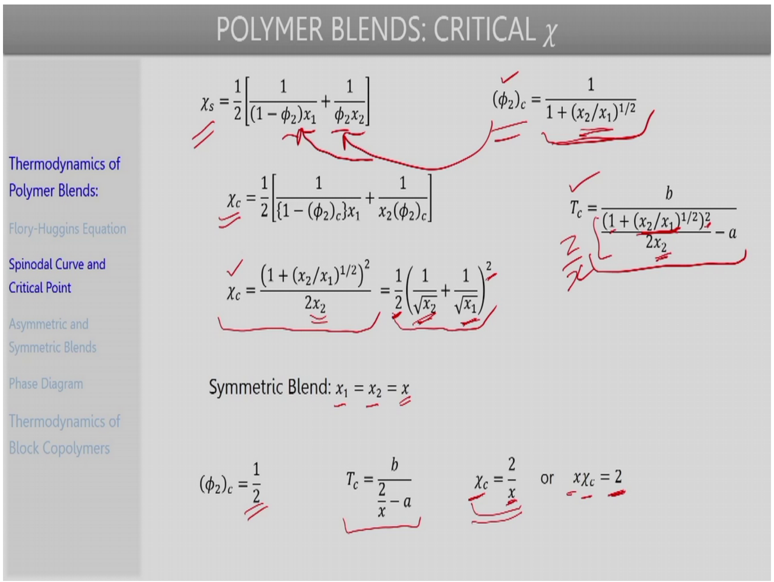
$$T_c = \frac{b}{\frac{1+(x_2/x_1)^{1/2}}{2(x_1x_2)^{1/2}}\left[1 + \left(\frac{x_1}{x_2}\right)^{1/2}\right] - a} = \frac{b}{\frac{(1+(x_2/x_1)^{1/2})^2}{2x_2} - a}$$

Earlier we have already derived that the temperature corresponding to the spinodal condition is this and the expression is given the right hand side here and since we have we already know that at the critical point in the composition is given by an expression like this we can substitute this phi 2 here at both the points where phi 2 appears on in this expression, we can we substitute the expression for phi 2 c at both those points. Then upon substitution we will get an expression for the temperature and that temperature basically is the critical temperature.

So, that is the temperature at the critical point and again upon simplifying. So, some simple rearrangement of their terms and then further taking some factor outside the brackets that is this factor is common to both their terms here finally, the expression for T c or the critical temperature we will get as something like this.

So, we see that this expression also contains the number of segments of both the polymers is present in the blend as well as the parameters A and B, which relate the Flory Huggins interaction parameter to the temperature. Next now that we have an expression for critical temperature we can also obtain an expression for the critical value of chi.

(Refer Slide Time: 15:03)



POLYMER BLENDS: CRITICAL χ

Thermodynamics of Polymer Blends:

Flory-Huggins Equation

Spinodal Curve and Critical Point

Asymmetric and Symmetric Blends

Phase Diagram

Thermodynamics of Block Copolymers

$$\chi_s = \frac{1}{2}\left[\frac{1}{(1-\phi_2)x_1} + \frac{1}{\phi_2 x_2}\right]$$

$$(\phi_2)_c = \frac{1}{1+(x_2/x_1)^{1/2}}$$

$$\chi_c = \frac{1}{2}\left[\frac{1}{\{1-(\phi_2)_c\}x_1} + \frac{1}{x_2(\phi_2)_c}\right]$$

$$T_c = \frac{b}{\frac{(1+(x_2/x_1)^{1/2})^2}{2x_2} - a}$$

$$\chi_c = \frac{\left(1+(x_2/x_1)^{1/2}\right)^2}{2x_2} = \frac{1}{2}\left(\frac{1}{\sqrt{x_2}} + \frac{1}{\sqrt{x_1}}\right)^2$$

Symmetric Blend: $x_1 = x_2 = x$

$$(\phi_2)_c = \frac{1}{2} \qquad T_c = \frac{b}{\frac{2}{x} - a} \qquad \chi_c = \frac{2}{x} \text{ or } x\chi_c = 2$$

So, we already have in have derived an expression for chi s which corresponds to chi at the spinodal points. And we know that the expression for the critical composition that is the composition at which this curve shows a minimum that expression is already derived to be this. So, again if you substitute the these this expression for phi 2 c at both these points here then upon that substitution the chi, that we get that chi is a critical Flory Huggins interaction parameter which is the value of chi at the critical composition

So, again upon substitution and rearrangement the expression that we end up with is something like this, this is a critical chi expression. For that for critic and we can further simplify it by dividing both the terms numerator by x 2, and the final expression that we get for critical chi is half multiplied by 1 over square root of x 2 plus 1 over square root of x 1 whole raised to the power 2. So, this expression again is the expression for the critical Flory Huggins interaction parameter. The expression of a critical temperature we have already derived to be this in the previous slide.

So, now this these expressions apply to any blend which can be described by the Flory Huggins equation. Now if you consider special case where the blend that we have is symmetric ok, we say that the blend is symmetric when both the polymers have the same number of segments. So, both the polymers constituting the blend have equal number of segments. So, what that means, is that x 1 and x 2 will be equal for a symmetric blend and let us say that we represent x 1 and x 2 both has by a this common symbol x.

So now let us see what happens to the expression for the critical composition the critical chi as well as the critical temperature for the special case of a symmetric blend. So, if we substitute x 2 equal to x 1 here this second term just becomes one. So, for critical composition the value that we get is just half. So, for a symmetric blend the critical point always will correspond to a composition of 0.5 and what that implies is that minimum in that in that curve at the minimum the spinodal curve will correspond to a composition of phi 2 equal to 0.5.

Next if we consider the critical temperature T c. So, again in this expression if we set x 2 equal to x 1. So, this term becomes 1. So, we get 1 plus 1 2 and this is squared here. So, 2 square will get 4 in the numerator here and we have a 2 here in the denominator. So, we will end up with a 2 by x 2 term. So, this x 2 we are since x 1 and x 2 are equal we are representing both as x. So, this term will simply become 2 by x. So, the critical temperature that expression reduces to b over 2 by x minus a and finally, the critical chi parameter.

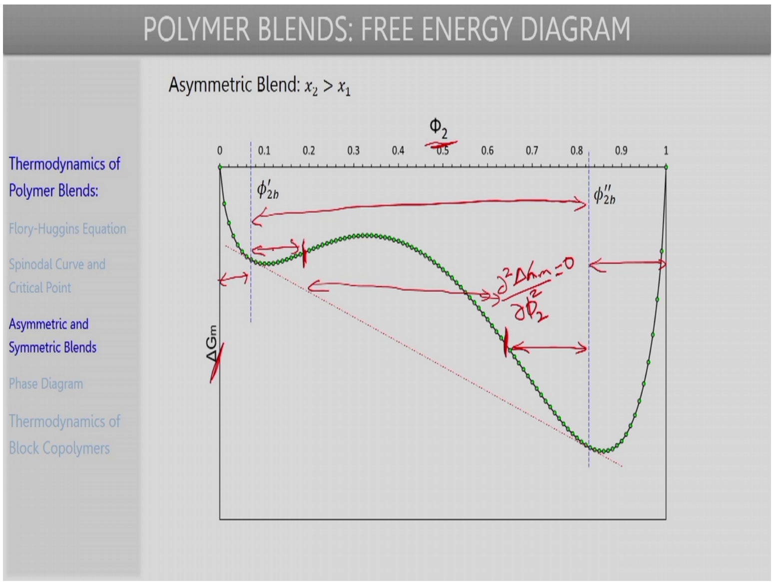
So, again in the expression that we had here if you substitute x 1 and x 2 to be equal and replace them by just x and take that out s common then in here inside the bracket we will be left with 1 plus 1 which is 2 n it is squared. So, we will get 4 again and we have a factor of 2 dividing it here.

So, we will end up with a factor of 2 in the numerator and this square root of x when it is taken out since there is a square present here that will become just x in the denominator. So, this xc simply reduces to 2 by x for the case of a symmetric blend. Now the larger the value of x the smaller will be the value of this critical chi parameter and if we just rearrange the terms here then this product of x time chi c.

So, this x time chi c where chi c is a critical clearing it is parameter that product is equal to 2. So, what this tells us is that this product x times chi c at the critical point, the value of this product is 2 for a symmetric polymer blend. Now that we have discussed the equation for spinodal curve as well as the expressions for critical point, now let us again try to look at the phase behavior as well as the delta g diagrams of this polymer blend graphically as we did in the case of polymer solution.

So, that we get better understanding of this topic.

(Refer Slide Time: 20:27)



POLYMER BLENDS: FREE ENERGY DIAGRAM

Thermodynamics of Polymer Blends:

Flory-Huggins Equation

Spinodal Curve and Critical Point

Asymmetric and Symmetric Blends

Phase Diagram

Thermodynamics of Block Copolymers

Asymmetric Blend: $x_2 > x_1$

So, let us consider an asymmetric blend first where x 2 is greater than x 1, which means that the second polymer has the number of segments in the second polymer is larger than the number of segments in the first polymer that is the second polymer is longer than the first polymer or. So, for such a case if we let us say consider that polymer blend to be at a temperature, where the delta G m versus phi 2 graph looks something like this it shows again 2 convex regions and kind of concave region in the middle.

So, if we have an asymmetric blend of this type. So, as before for the case of a polymer solution we can here also start by drawing a common tangent to the 2 portions of this curve. So, the common tangent that is represented by a dashed line here that basically will touch the curve at 2 different points.

And the 2 points at which this common tangent touches the curve correspond to the binodal points as we have already discussed, when we are talking the polymer solution case. So, polymer blends also a similar kind of construction can be used to identify the binodal points.

Now, that we have the binodal points as before the regions marked by these arrows here if you have a, the polymer composition in this these regions, then this line that forms will be a stable blend or it will be a miscible blend; however, if the blend forms outside this region.

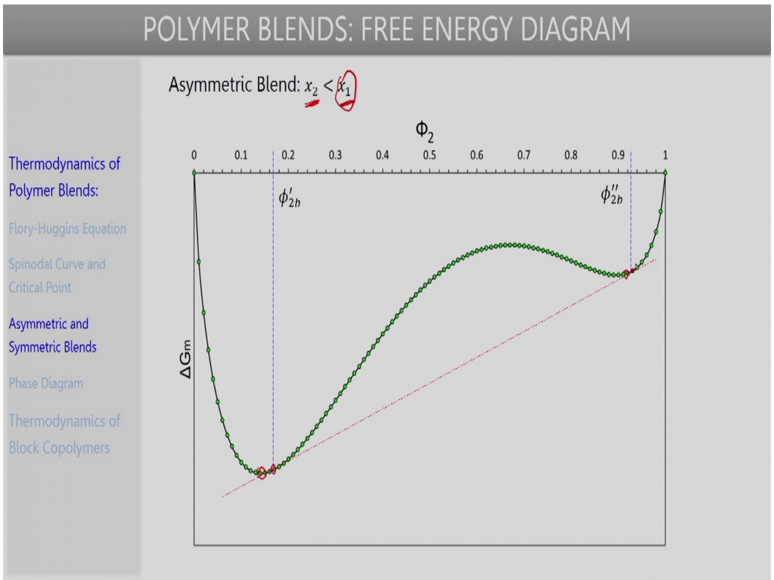
So, if the blend is found in with a composition of the second polymer phi 2 in this region, which is again the miscibility gap for this case. So, in this region the blend will not be stable in the sense that it can it will have a tendency to phase separate into 2 different phases.

So, again we are not going to discuss in too much detail because we have already had a discussion of the different aspects of such a diagram, when we are talk in polymer solution, but again in this case also we can identify 2 points which correspond to the condition of del square delta gm del phi 2 square equal to 0.

So, these 2 points where the second derivative delta gm becomes 0 these 2 points again will correspond to the spinodal points for the polymer blend. And if we have a blend that that has a composition lying between the spinodal points between these 2 points then that blend will be unstable and will tends to spontaneously phase separate and again the region between the binodal and the spinodal.

So, these 2 regions here they correspond to the metastable state.

(Refer Slide Time: 23:21)



POLYMER BLENDS: FREE ENERGY DIAGRAM

Thermodynamics of Polymer Blends:

Flory-Huggins Equation

Spinodal Curve and Critical Point

Asymmetric and Symmetric Blends

Phase Diagram

Thermodynamics of Block Copolymers

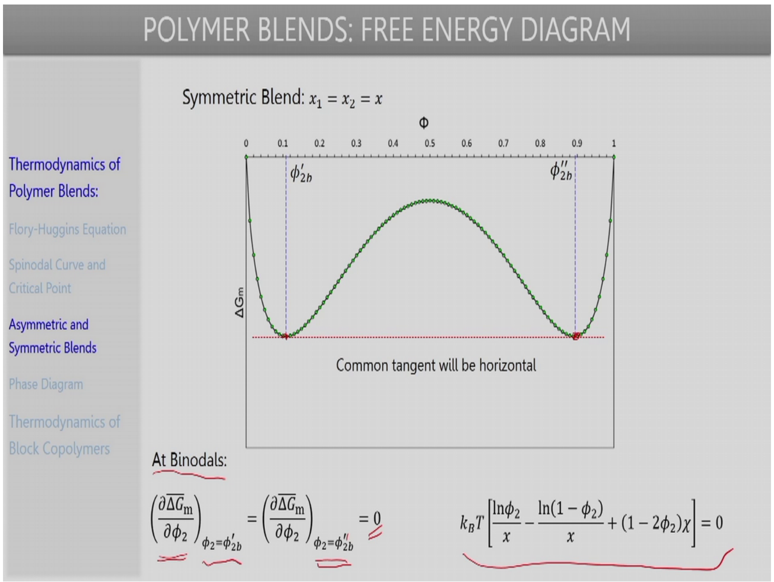
Asymmetric Blend: $x_2 < x_1$

If we consider an asymmetric blend which where the number of polymer segments is smaller in the second polymer than the first polymer. So, first polymer has more number of segments x 1 is larger than x 2 and if other things remain the same, then the phase or the Gibbs free energy diagram has function of phi 2 that will appear to be just inverted form of what we saw in the previous case.

So, in this case now the phase diagram or the free energy diagram actually will show deeper minima on the left side and a shallower minimum at the right side, which is opposite to what we saw in the previous case where x 2 was larger than x 1 and again by using a common tangent construction we can identify the binodal points and again one thing to remember is that the binodal points need not correspond to the points at which the this curve actually shows minimum.

So, the minimum might be somewhere here where the binodal point is somewhere here similarly the minimum here might be somewhere here and binodal point is somewhere at a slightly different location. So, if you have asymmetric system the binodal points will not necessarily correspond to the points of minimum on the free energy versus phi 2 diagram.

(Refer Slide Time: 24:47)



POLYMER BLENDS: FREE ENERGY DIAGRAM

Thermodynamics of Polymer Blends:

Flory-Huggins Equation

Spinodal Curve and Critical Point

Asymmetric and Symmetric Blends

Phase Diagram

Thermodynamics of Block Copolymers

Symmetric Blend: $x_1 = x_2 = x$

Common tangent will be horizontal

At Binodals:

$$\left(\frac{\partial \overline{\Delta G}_m}{\partial \phi_2}\right)_{\phi_2=\phi'_{2b}} = \left(\frac{\partial \overline{\Delta G}_m}{\partial \phi_2}\right)_{\phi_2=\phi''_{2b}} = 0$$

$$k_B T\left[\frac{\ln\phi_2}{x} - \frac{\ln(1-\phi_2)}{x} + (1-2\phi_2)\chi\right] = 0$$

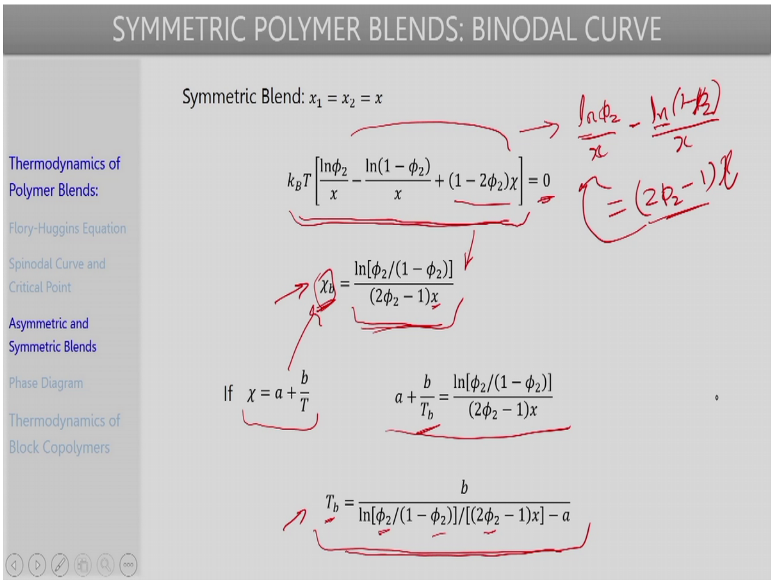
So, next consider let us consider the case of a symmetric blend, where x 1 and x 2 are equal and let us represent both x 1 and x 2 as x since the blend is symmetric, we see that the delta G m versus phi 2 that diagram is also symmetric and if we again make a common tangent do a common tangent construction what we see is that, the common tangent in this case is horizontal the reason for that is the since a blend is symmetric the free energy diagram is also symmetric. And both the minima actually have the same depth.

So, if we draw a common tangent which touches the curve at both these points then, that common tangent will be horizontal. So, for a symmetric blend, the common tangent is horizontal and mathematically. If we consider the first derivative of the Gibbs free energy, which is an expression, that we have derived previously in this lecture. So, instead of x 2 and x 1 we can replace both of them by just x.

So, that is what we have done and the expression for this first derivative which will correspond to the slope of this curve. So, that expression changes to or simplifies to this. And now we see that these 2 terms since x 1 and x 2 are equal these 2 terms actually will cancel each other. So, a simplified expression now becomes what shown here. So now, that the common tangent is horizontal the binodal points that we have identified we will coincide with the points at which the curve will display minima.

So, that makes things easier mathematically in the sense that at the binodals, now since both the binodal points also correspond to the points of minima on this curve. So, therefore, at the binodal points this one should be phi to be double prime. So, at the both the binodal points the slope of this delta G m versus phi 2 curve which is the first derivative that will be 0 at both the binodal points. Then since we already have an expression for this first derivative, we can set that equal to 0 and that will help us in determining the equation for the binodal curve.

(Refer Slide Time: 27:12)



SYMMETRIC POLYMER BLENDS: BINODAL CURVE

Thermodynamics of Polymer Blends:

Flory-Huggins Equation

Spinodal Curve and Critical Point

Asymmetric and Symmetric Blends

Phase Diagram

Thermodynamics of Block Copolymers

Symmetric Blend: $x_1 = x_2 = x$

$$k_B T \left[\frac{\ln\phi_2}{x} - \frac{\ln(1-\phi_2)}{x} + (1-2\phi_2)\chi \right] = 0$$

$$\frac{\ln\phi_2}{x} - \frac{\ln(1-\phi_2)}{x} = (2\phi_2 - 1)\chi$$

$$\chi_b = \frac{\ln[\phi_2/(1-\phi_2)]}{(2\phi_2-1)x}$$

If $\chi = a + \frac{b}{T}$

$$a + \frac{b}{T_b} = \frac{\ln[\phi_2/(1-\phi_2)]}{(2\phi_2-1)x}$$

$$T_b = \frac{b}{\ln[\phi_2/(1-\phi_2)]/[(2\phi_2-1)x] - a}$$

So, for a symmetric blend again if we are setting the this expression which is the first derivative of the Gibbs energy to be 0 that will give us the equation for the binodal curve because the condition that the first derivative is 0 that condition is satisfied at both the binodal points. So, if we again rearrange the terms finally, the chi parameter corresponding to the binodal point that, chi parameter expression one can derive to be this in going from here to here all we need to do is just rearrange the terms a bit.

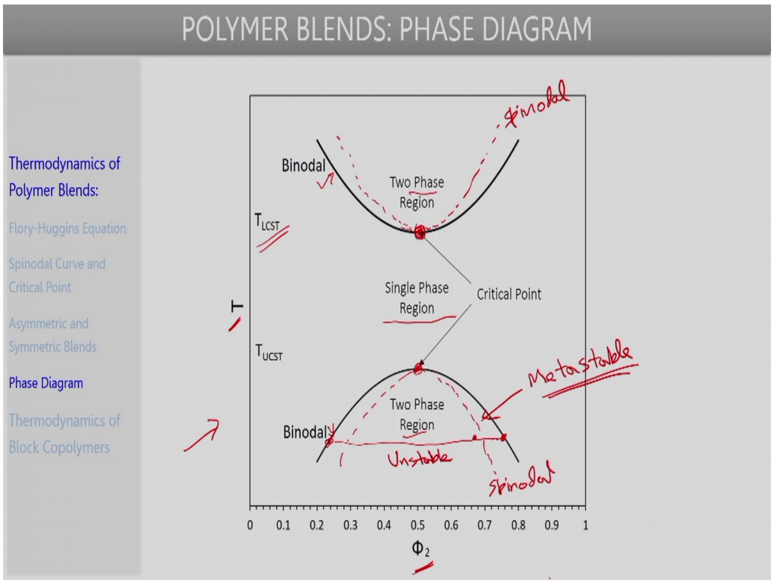
So, if, if we consider this term here and if you are setting it equal to 0 then what we can say is that l n phi 2 by x minus l n 1 minus phi 2 by x that will be equal to 2 phi 2 minus 1 times chi where we have taken this term on the other hand side. And then just let us we will just take this on the other side as the denominator. So, that will give us an expression for chi b and these 2 terms log a natural log terms can be combined because they have the same denominator.

So, this x will come out as common in the denominator. And ln phi 2 minus l n 1 minus phi 2 will give us this ratio l n phi 2 over 1 minus phi 2. So, that is how we can obtain this expression for chi b which is the Flory Huggins interaction parameter at the corresponding to the binodal condition. And if we now again use the expression for chi as a plus b by T, then the temperature for the binodal curve that expression can also be obtained. So, we just substitute this here and that will give us this expression. And then finally, we really arrange the terms and the expression for the temperature is what we have obtained here.

So, this equation or equivalent to this equation these 2 equations basically are the equations for binodal curve for a symmetric polymer blend. So, if we plot t the temperature or T b as a function of phi 2 using, this equation the curve that we will get will be the binodal curve for our symmetric blend.

So now that we have identified the equations for binodal curve for the special case of a symmetric blend let us now talk about the phase diagram a typical phase diagram of a polymer blend.

(Refer Slide Time: 30:02)



POLYMER BLENDS: PHASE DIAGRAM

Thermodynamics of Polymer Blends:

- Flory-Huggins Equation
- Spinodal Curve and Critical Point
- Asymmetric and Symmetric Blends
- **Phase Diagram**
- Thermodynamics of Block Copolymers

So, what we will see is that for a polymer blend also the phase diagram will contain features which are very similar to what we see saw for a polymer solution. So, the phase diagram that shown here this phase diagram is a generic case where we are considering a polymer blend that basically shows both the upper critical solution temperature and a lower critical solution temperature.

We can have polymer blends which show either one of these 2 or some can show both these critical points. So, we are just discussing a general case where both these critical points are present on the same phase diagram.

So, if we have a phase diagram shown here, which is a just a plot of temperature versus phi 2. And we are just representing the binodal curves here which mark the mark the boundary between the single phase and the 2 phase region or the single phase stable region and the 2 phase region which can contain both metastable and unstable regions. So, if we look at the phase diagram the single phase region is basically the region lying outside the 2 binodal curves.

So, these 2 are the binodal curves here and here. And the region outside the binodal curve correspond to the corresponds to the single phase region and the regions being enveloped by the binodal curve these correspond to the 2 phase regions

So, if we have a polymer blend at a certain composition and temperature which corresponds to this point, then it will basically phase separate into 2 different phases one having these 2 compositions ok. The 2 points here this point of maximum on this curve and this point minimum this curve these 2 points are the critical points for this case and because these 2 points are correspond to the maximum or minimum on the binodal curve. So, the lower point is what is called the upper (Refer Time: 32:16) critical solution temperature.

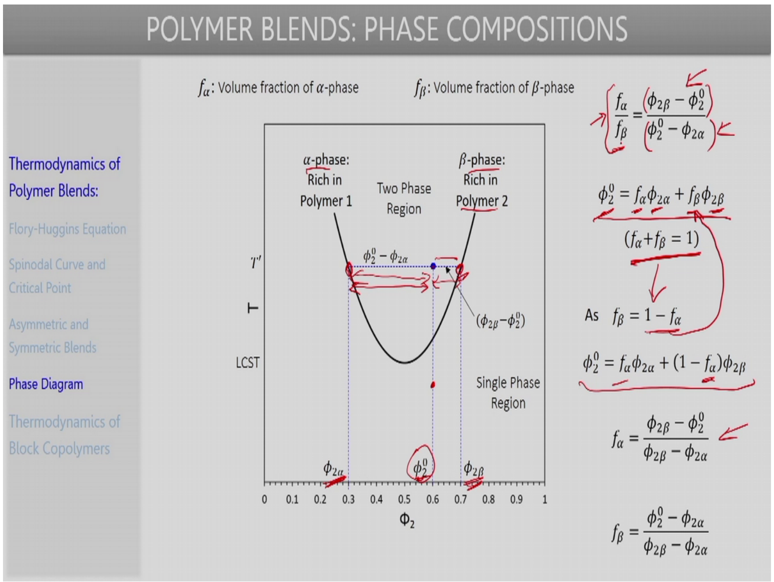
So, this is the maximum temperature up to which a 2 phase region can be seen or phase separation can be seen. So, above this upper critical solution temperature, the polymer blend will become miscible throughout the composition range, but if we keep on increasing the temperature for this particular case we can again hit the 2 phase region at a much higher temperature. And that the minimum of this curve is corresponds to a temperature which is called the lower critical solution temperature or LCST.

So, this terminology was already introduced when we discuss polymer solution and the same applies to polymer blends as well UCST and LCST. So, this lower critical solution temperature again corresponds to temperature below which we will have the complete miscibility of the polymer blend throughout the composition range. And above this temperature the polymer blend actually can become immiscible or can phase separate over a certain composition range which is basically the miscibility gap.

So, here we have not we have only shown the binodals, but one should remember that just like for the case of polymer solution, for polymer blends also if we try to draw the spinodal curves the spinodal curve will lie inside the binodal curve and they will touch the binodal curve at the minimum point.

So, the spinodals will also show a minimum at the same point as a binodal which is a critical point LCST and for the lower curve also a spinodal can be drawn which will show maximum at the same point as the maximum for the binodal which is the UCST point and the region. So, this is the spinodal curve similarly this also we have drawn the spinodal curve here and the region between the binodal and spinodal we have already discussed before is the metastable region in the same applies a and inside the spinodal we have the unstable region where spontaneous phase separation can occur in the presence of the tiniest of fluctuations.

(Refer Slide Time: 34:38)



POLYMER BLENDS: PHASE COMPOSITIONS

Thermodynamics of Polymer Blends:
- Flory-Huggins Equation
- Spinodal Curve and Critical Point
- Asymmetric and Symmetric Blends
- Phase Diagram
- Thermodynamics of Block Copolymers

f_α: Volume fraction of α-phase

f_β: Volume fraction of β-phase

$$\frac{f_\alpha}{f_\beta} = \frac{(\phi_{2\beta} - \phi_2^0)}{(\phi_2^0 - \phi_{2\alpha})}$$

$$\phi_2^0 = f_\alpha \phi_{2\alpha} + f_\beta \phi_{2\beta}$$

$$(f_\alpha + f_\beta = 1)$$

As $f_\beta = 1 - f_\alpha$

$$\phi_2^0 = f_\alpha \phi_{2\alpha} + (1 - f_\alpha)\phi_{2\beta}$$

$$f_\alpha = \frac{\phi_{2\beta} - \phi_2^0}{\phi_{2\beta} - \phi_{2\alpha}}$$

$$f_\beta = \frac{\phi_2^0 - \phi_{2\alpha}}{\phi_{2\beta} - \phi_{2\alpha}}$$

Let us consider the case of phase diagram which shows an LCST for a polymer blend. And let us see how the phase compositions can be determined. So, again we have a 2 phase region enveloped by the binodal curve here and the single phase region outside. So, the 2 phase region one arm of the 2 phase region let us call that the alpha phase, which will be rich in polymer 1. So, this corresponds to a lower volume fraction of polymer 2 phi 2 will have values less than 0.5 on this side.

So, that will be rich in polymer one because polymer will have one will have a higher volume fraction in that part of the phase diagram. And let us consider the other phase let us call it the beta phase and this phase will be rich in polymer 2 that is the volume fraction of polymer 2 will be higher in the beta phase than that of polymer 1. So now, in that we have identified these 2 phases let us see how let us first consider the LCST point, which is the minimum of this curve and let us consider a point on this phase diagram which lies inside the 2 phase region.

So, let us at some temperature T prime and some composition phi 2 naught we are at a point on the phase diagram, which lies inside a 2 phase region. So, if you are inside that 2 phase region the phase separation will take place. And we will end up with 2 phases one having a composition given by phi 2 alpha and the other having composition given by phi 2 beta. So, they will correspond to the 2 point (Refer Time: 36:30) marked here.

So, in the 2 phase region if we let us say initially where in the single phase region and if we increase the temperature up to this point, then in the 2 phase region that homogeneous single phase of the polymer blend will split into 2 phases and the 2 phases will have corresponding compositions one will be rich in a polymer 1 which is the alpha phase the other will be rich in polymer 2 which is the beta phase. So now, let us see how we can determine the phase composition which means some we can determine how much of which phase alpha phase and beta phase will form.

So, clearly the length of this line here is phi 2 not minus phi 2 alpha and the length of this line here is phi 2 beta minus phi 2 naught. That is obvious from the diagram. And let us represent the volume fraction of alpha phase by the symbol f alpha and the volume fraction of the beta phase by the symbol f beta. So, what can be shown is that is that the ratio of f alpha and f beta that ratio is equal to the ratio of these 2 quantities here.

So, if we look at the phase diagram this, the numerator here is the length of this part and the denominator here is the length of this part. So, using the phase diagram one can actually identify the volume fractions of let us say the second polymer in the 2 phases that are formed as well as the overall volume fraction of the entire 2 phase system. And using these volume fractions the ratio of the fractions of the 2 phases either present as f alpha and f beta they the ratio can be found.

So, if we just rearrange the terms and note that this f alpha plus f beta this sum is one, then we will get this expression for relating phi 2 naught with phi 2 alpha and phi 2 beta. Here phi 2 naught is again the overall composition, if you consider that 2 phase system together and phi 2 alpha and phi 2 beta the volume fractions of the second polymer in the alpha phase in the beta phase separately. F alpha and f beta as we have discussed is the volume fraction of the entire alpha phase and the entire beta phase.

So, there since we have only 2 phases present then their some of their volume fractions will be one which is shown here. So now, if from this what one can see is that f beta can be written as 1 minus f alpha, and that we can substitute in place of this f beta here to get this expression and if we rearrange the terms. So, that all the f alpha terms come on one side only then we can obtain an expression for f alpha here. And the expression for f alpha is this similarly f beta is 1 minus f alpha. So, using that the expression for f beta can also be obtained.

So, what we see is that using the different compositions from the phase diagram, these 3 we can not only determine the ratio of the phases that are formed the 2 phases alpha and beta, but we can also find the individual volume fractions of the 2 phases that are formed. So, we can find the expression for f alpha f as well as f beta. With that we will like to conclude the discussion of thermodynamics behavior and phase and diagrams of polymer blends.

So, what we saw is that for polymer blends much of the theory is similar to what we already discussed for polymer solution. The only difference is that in the case of polymer blends both the components are polymers. So, both are long chain molecules and hence the Flory Huggins theory gets or the Flory Huggins equation gets modified slightly, by the inclusion of the number of segments of the other polymer as well.

And due to this what happens is that, the entropy change of mixing that for polymer blends is quite small and does not play a significant role in the phase behavior. Instead the interaction term containing the Flory Huggins polymer-polymer interaction parameter.

That is the term which plays a dominant role in determining the thermodynamics of mixing or de mixing of polymer blends. The other thing that is different between polymer solution and polymer blends is that polymer blends in many cases are actually immiscible.

So, if we mix 2 polymers which are not very similar then mostly they will end up being phase separated that is the will not mix with each other ; however, there are cases where polymers are almost completely miscible with each other as well. Also if we have an immiscible polymer blend then phase separation might lead to the formation of 2 different phases in a given material.

So, although the 2 polymers are immiscible and strictly speaking have not formed blend, but still such immiscible polymer blends are actually also have some applications.

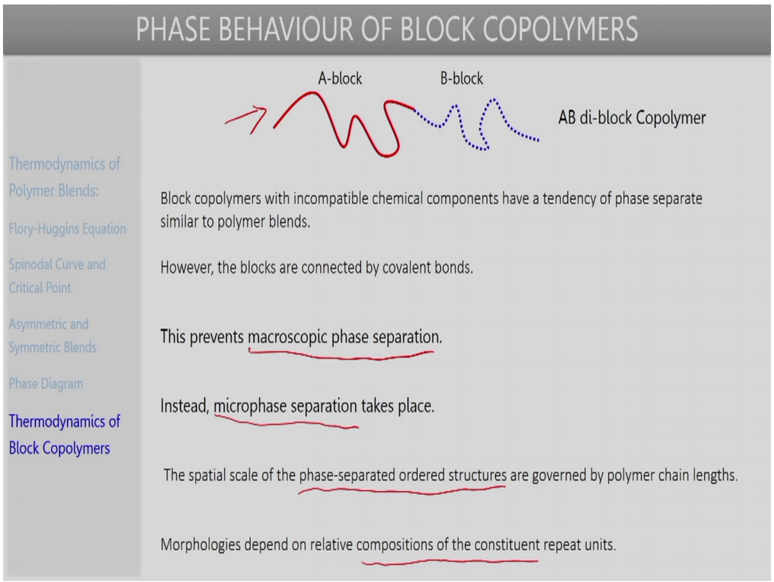
So, even upon mixing if the polymer blends are not miscible, thus material that that forms still can show some favorable properties and in fact, there are many cases in which immiscible polymer blends are also used in applications further if we have 2 polymer blends which are not very miscible with each other and which show phase separation, then their compatibility with each other can be increased by the process of what is called compatibilization, where a third component may be added which is a the compatiblizer to this polymer blend.

And what this third component can do is go and sit at the interface and basically improve the interfacial interaction between the 2 phases of this immiscible polymer blend.

So, here the compatiblizer that we add one example of compatiblizer material can be a copolymer where one part of the copolymer basically is miscible in one of the polymers of the polymer blend, whereas, the other part is miscible in the other polymer of the polymer blend. So, if we have such a case, then what will happen is that at equilibrium this block copolymer. So, we are talking block copolymer here. So, this block copolymer one block, which is which prefers the one of the polymers of the blend will try to reside in that phase whereas, the other block will reside in the other polymer phase of the blend and that will improve the interfacial interaction.

So, even for immiscible polymer blends the compatibility can be improved by the incorporation of compatiblizers. With that we will conclude the discussion of polymer blends and we will just briefly discuss the thermodynamic behavior and phase behavior of block copolymers next.

(Refer Slide Time: 44:06)



PHASE BEHAVIOUR OF BLOCK COPOLYMERS

Block copolymers with incompatible chemical components have a tendency of phase separate similar to polymer blends.

However, the blocks are connected by covalent bonds.

This prevents macroscopic phase separation.

Instead, microphase separation takes place.

The spatial scale of the phase-separated ordered structures are governed by polymer chain lengths.

Morphologies depend on relative compositions of the constituent repeat units.

So, a block copolymer if we have a block copolymer let us say as shown in this diagram, here which consists of 2 blocks.

So, if we have a di block copolymer where one block is let us say is called block A and the other block is called block B. Then if the blocks A and B are the repetitions in the blocks say A and B if they are not chemically compatible with each other which means that if they are not interacting favorably with each other then they will the such a copolymer will also have a tendency to phase separate a however, unlike a blend in the case of block copolymers the blocks of the copolymer are actually linked by the presence of covalent bonds.

So, if we have a blend where that we the 2 polymers are not liking each other then the 2 the blend can basically phase separate easily into 2 different phases at the macroscopic level. However, in the case of poly block copolymer since the 2 blocks which let us say are not chemically compatible, these 2 blocks do not like each other, but since they are covalently linked at a point, they are not free to just phase separate at the macroscopic level. So, what instead happens in the case of such block copolymers is that the macroscopic phase separation is does not occur because of the constraint of covalent bonding between the blocks however, the micro phase separation can take place.

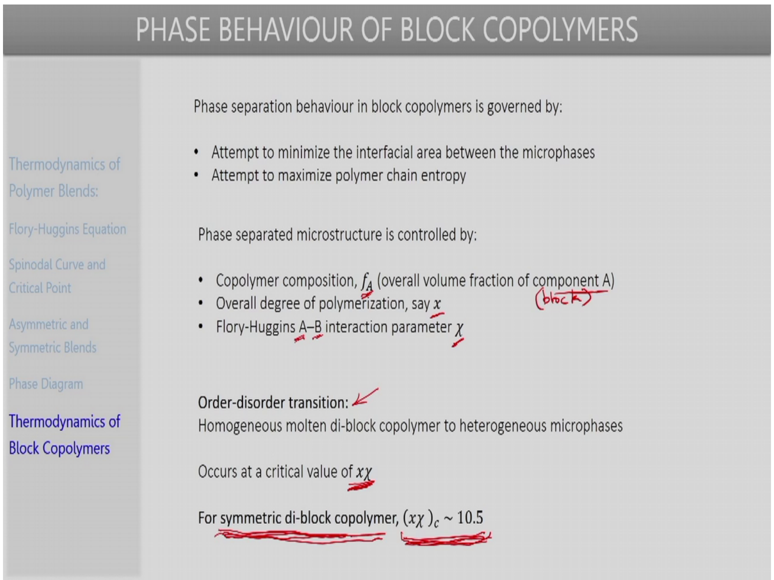
So, at a microscopic scale or even at the nanometer length scale the phase separation is actually observed for block copolymers. So now, when phase separation occurs at the microscopic scale, then spatial scale or the length scale over which structures are formed in such phase separated material that length scale is comparable to the size of the polymer chains that are present in the system.

So, the at the when micro phase separation takes place, the phase separated ordered structures can form and we will look at some of the order structures very soon. So, these phase separated structures that are formed their length scale will be determined by the lengths of the polymer chains that come constitute the system.

Whereas, the morphologies. So, apart from the length scale of these order structures that are formed the morphology of the order structures. So, whether we get kind of a lamellar morphology or a cylindrical morphology or some other kind of morphology, what kind of morphology will form that is governed by the composition of the constituent repeat unit.

So, what we mean by the this is that, the relative amounts of A and B present inside the block copolymer that will basically dictate what kind of morphology will be observed if we if the block of copolymer phase separates at the microscopic level.

(Refer Slide Time: 47:13)



PHASE BEHAVIOUR OF BLOCK COPOLYMERS

Thermodynamics of Polymer Blends:

Flory-Huggins Equation

Spinodal Curve and Critical Point

Asymmetric and Symmetric Blends

Phase Diagram

Thermodynamics of Block Copolymers

Phase separation behaviour in block copolymers is governed by:

- Attempt to minimize the interfacial area between the microphases
- Attempt to maximize polymer chain entropy

Phase separated microstructure is controlled by:

- Copolymer composition, f_A (overall volume fraction of component A) (block)
- Overall degree of polymerization, say x
- Flory-Huggins A–B interaction parameter χ

Order-disorder transition:
Homogeneous molten di-block copolymer to heterogeneous microphases

Occurs at a critical value of $x\chi$

For symmetric di-block copolymer, $(x\chi)_c \sim 10.5$

When we talk about phase separation block copolymers there are 2 factors which are governing this phase separation behavior or the microscopic phase separation behavior.

So, first factor is the fact that the interaction between the 2 blocks is not favorable, the 2 blocks are not chemically compatible.

So, the interfacial area of contact between the micro phases are formed containing there 2 different blocks, that interfacial area should be minimum ok. So, the system attempts to minimize this interfacial area. So, as to reduce the number of unfavorable contact interactions; however, since the polymer is phase separating where one block forms part of one phase and the other block forms part of another phase at the Nano scale level, this kind of phase separation can lead to stretching of the polymer chain.

So, this chain stretching actually is entropically unfavorable because stretching the chain will reduce the entropy change associated with the process and which is not favorable for mixing. So, there these 2 computing are opposite effects where the interaction basically is unfavorable. So, that will try to minimize the interfacial contact area, but in doing. So, the stretching of the polymer chain should not be such that the system loses too much entropy.

So, these are the 2 competing factors which are important in the phase separation behavior of block copolymers. And from the point of view of the different parameter system parameters that are important for the phase separation behavior and the structure side of formed up on the phase separation. So, there are 3 parameters that are important from that perspective. One is the amount of let us say amount of a block of one time that type that is present in the system. So, if we have blocks of 2 type A and B.

And let us say if f A represents the volume fraction of the total blocks of type a, then and that that composition which is represented by f A that will be one factor which will govern the phase behavior and the ordered structures that form upon phase separation. Another important parameter is again the Flory Huggins interaction parameter and this Flory Huggins interaction parameter chi is the interaction parameter between the A and B blocks of the system.

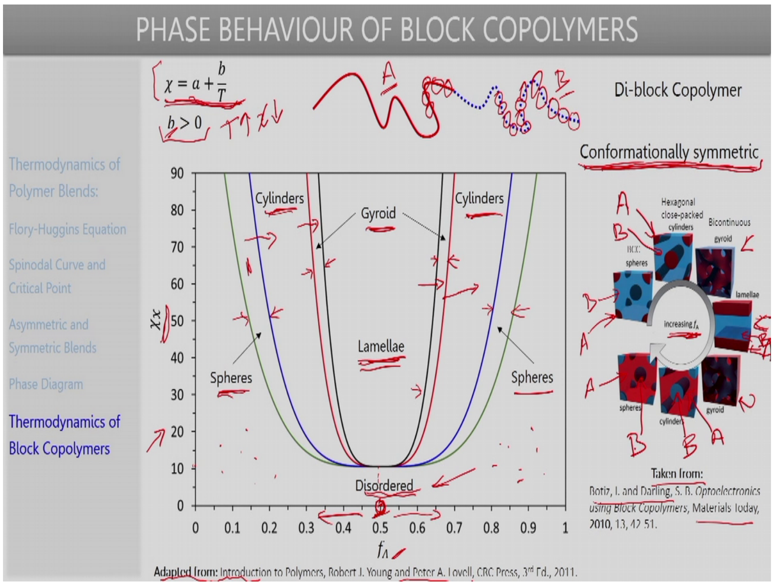
And finally, the third parameter that is important is the overall degree of polymerization of the system. So, how long the polymer chains are? So, these 3 parameters the composition which is characterized by f A the volume fraction of instead of component a we should may be using that terminology block A will be more appropriate here. So, the copolymer composition will be an important factor the overall degree of polymeration x and the Flory Huggins interaction parameter chi these are the important parameters.

Now the phase separation that micro phase separation that takes place in block copolymers that is typically referred to as order disorder kind of transition, where homogeneous molten di block copolymer can phase separate into heterogeneous micro phases of different morphologies.

So, this order disorder transition that we have this is seen to occur at a critical value of this product x times chi. So, this product x times chi the if the critical value of at a critical value of around 10.5, the or disorder disorder transition from molten homogeneous copolymer phase to a phase separated micro phase separated heterogeneous phase that is observed for symmetric di block copolymer. And this is actually predicted by a theory which involves a mean field approximation.

So, if the value goes above this then micro phase separation is expected to take place and if the value of this product is less than this critical value, then we will we will have an homogeneous molten state of the polymer solution or the block copolymer. So, when we say symmetric di block copolymer what we mean is that the di block copolymer has equal numbers of or equal sizes of the A and B block. So, essentially f A is equal to 0.5 in this case that is what the term symmetric here means.

(Refer Slide Time: 52:05)



PHASE BEHAVIOUR OF BLOCK COPOLYMERS

$\chi = a + \frac{b}{T}$

$b > 0$ $T\uparrow \chi\downarrow$

Di-block Copolymer

Conformationally symmetric

Thermodynamics of Polymer Blends:

Flory-Huggins Equation

Spinodal Curve and Critical Point

Asymmetric and Symmetric Blends

Phase Diagram

Thermodynamics of Block Copolymers

Adapted from: Introduction to Polymers, Robert J. Young and Peter A. Lovell, CRC Press, 3rd Ed., 2011.

Taken from:
Botiz, I. and Darling, S. B. *Optoelectronics using Block Copolymers*, Materials Today, 2010, 13, 42-51.

Finally, if we try to look at the phase behavior of a block copolymers from using a some kind of a phase diagram, then if we consider the Flory Huggins interaction parameter is dependent on dependence on temperature to be given by this expression.

Which we have been using for other systems as well and for block copolymers also such a dependences found to be the most common kind of dependence. For such a system for such a dependence of chi on temperature, for block copolymers mostly this quantity or parameter b is greater than 0. So, T increases for these systems an increase in T actually leads to a decrease in chi. So, a decreasing chi will mean an increasing temperatures and increasing chi means are decreasing temperatures.

For the case that we will discuss and the for the diagram that we will discuss next the condition under which the diagram has been drawn is that the system is conformationally symmetric. So, this actually should not be confused with the symmetric block copolymer that we discussed in the previous slide, conformationally symmetric means that the size of a let us say a given segment. So, let us say this block B that we have here and the block A here. So, let us say the size of the segments that constitute this block B and the size of segments that constitute block A.

So, the A and B blocks segment sizes are equal that is what this condition implies it has nothing does not imply that the amount of A and B block is the same. A typical phase diagram or something that is representative of a phase diagram for a block copolymer system is what is shown here in it has been adapted from this textbook by young and level. So, here on the x axis we are plotting f A, which is the composition of or the amount of volume fraction of the A block in the system, and on the y axis you see we are plotting this product chi times x ok.

So, as we discuss in the previous slide the critical value of this chi times x is around 2 10.5 for a symmetric block copolymers. So, symmetric block copolymer will correspond to this 0.5 composition, where f A is equal to f B and both are 0.5.

So, we see that at this composition the value of this chi times x is actually close to 10.5 in this plot as well and we can identify different regions in this phase diagram. So, the region here region in close by this the black curve here. So, that region basically corresponds to a micro phase separated system where lamellar kind of morphology is observed.

Similarly the region on this phase diagram lying between the black curve and the red curve on both sides. This corresponds to what is called a by continuous gyroid kind of marpho morphology in the phase separated micro phase separated block copolymer. And if we go further away from the symmetric condition which is f A equal to 0.5 if you go further on either side, then other morphologies can be seen. So, next at higher f A values as well as on the other side lower f A values also this cylindrical kind of morphology can also be observed. And finally, between this blue and the green curve here on both sides.

The micro phase separated copolymer will can show sphere like morphology. So, and the region that is outside the phase envelope that we have here, the region here this is this represents the disordered state. So, in all the points outside the phase envelope that we have drawn the system will be in a disordered the state which means it will basically be a homogeneous single phase system at the macroscopic as well as a microscopic level.

Whereas, in the microscopic phase separated domains all the macroscopically the system any phase separation might not be visible, but at the microscopic level which is at the scale of 1 to 100 nanometers let us say, the distinctive ordered structures representing phase separation will be can be observed.

And. typically experimental techniques such as transmission electron microscopy or small angle x ray scattering these techniques can reveal these micro phase separated morphological features in such block copolymers.

So, if. So, all the different morphological states that we have identified here, if we try to visualize them then this diagram here, which has been taken from this article by Botiz and Darling from materials today, this article this figure very nicely shows what the different kind of morphologies are which can be expected as we change this composition of the A block which is changed by increasing this f A. So, if f A is a small which is which let us say at small f A.

Let us say if we are in this region at small values of f A then the be the what we discussed earlier is that spheres will spear like morphology will form. So, what will happen is spherical domains spherical domains of a will form in a continuous phase from white B.

So, the blue region here is the B and the spherical domains that we see that is A. And as the value of f A is increased we will move from sphere to the cylindrical morphology where the again a will form this cylinder hexagonal close pack cylindrical phase and B will still remain as the continuous phase as shown by the blue part here.

And at if the composition of A is further increased a gyroid kind of by continuous gyroid kind of morphology as shown here will be seen and upon further increase lamellar morphology will be seen where the 2 blocks A and B will arrange themselves in flat layer by layer kind of morphology ok.

So, here the red layer represents again A and the blue layer represents B. And if we keep increasing the composition of a further then again we will move back into the gyroid kind of morphology, but the only difference is that now since the poly amount of the block is higher now.

So, that A block that will form the continuous phase and the B will form the discrete phase and similarly at again higher f A we will get going to the cylindrical morphology, but now the cylinders will be of B, A will be the continuous phase. And finally, at higher morphologies we will get A as a condensed phase again and spherical morphology of B. So, we see that for the case of block copolymers many interesting order structures can be observed at the microscopic level.

So, the phase behavior of block copolymers is actually quite interesting and leads to a very nice and a variety of morphological structures of whose length scale typically is of the range of a few nanometers to few tens of nanometers.

So, again the type specific type of morphology that will form depends on the composition. So, how much of the block copolymer is actually block of type A or how much is block of type B, that relative composition basically dictates the type of morphology form. And as we discussed earlier the size of the polymer chains that are present, that will dictate the length scales of the these ordered structures like sphere or cylinder or laminar that are formed.

So, what we can conclude is that for block copolymers, macro phase separation has as seen in the case of blends does not occur, because they are covalently bound the blocks are covalently linked to each other, but if the blocks constant elements of the blocks do not like each other they are not chemically compatible, then at the microscopic level or at the of the order of a few nanometers the polymer will actually phase separate.

So, a microscopic phase separation will take place and interesting ordered morphologies can be observed. So, with that we conclude our discussion of thermodynamics of polymer solutions as well as though that of blends and block copolymers and to summarize what we have discussed is the description mathematical description of the thermodynamic behavior of polymer solutions as well as blends using the Flory Huggins equation we have also discussed the solubility parameter approach, which can give a good estimate for the miscibility of a polymer in a solution and the solubility parameter approach can also be applied to blends in a similar way. So, if 2 the polymers constituent blend have similar solubility parameters they will be more miscible.

So, apart from that we have discussed the phase separation behavior the regions of stability unstability and meta stability in detail. We have also talked about how to identify the binodal points the spinodal points as well as constructing the phase diagrams and identifying the critical points on these phase diagrams. And for the case of copolymers we have also discussed that different kinds of interesting microscopic morphologies can be observed upon phase separation at the microscopic level.

So, that is a summary of what we have discussed under the thermodynamics of polymer solutions and blends and copolymers. In the next lecture what we will do is start discussion on the different techniques that can be used to measure the molar mass of polymers.

So, polymer molar mass as we will see is a very important characteristic of any polymer sample. And it actually a lot of macroscopic properties depend on the polymer molar mass. So, good knowledge of the polymer molar mass is important and in the next few lectures, we will discuss different techniques that can be used to measure the different types of average polymer molar masses that we have introduced in the very first lecture of this course.

Thank you.