

Polymer Chemistry
Prof. Dibakar Dhara
Department of Chemistry
Indian Institute of Technology, Kharagpur

Lecture - 27
Polymer Solution (Contd.)

Welcome back to the course on polymer chemistry and in today's class.

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Lecture 27: Polymers in Solution (cont.)

- Cohesive energy density
- Solubility parameter
- Phase-separation behavior of polymer solutions

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Polymers in Solution : Recap

$$\Delta G_m = RT(n_1 \ln \phi_1 + n_2 \ln \phi_2) + RT(n_1 \chi \phi_2)$$

Flory-Huggins equation

- Represents effect of combinatorial entropy
Always < 0, always favors mixing
- Represents effects of enthalpy and entropy change due to polymer-solvent contact
- Decide whether mixing will occur or not
 - < 0 – mixing
 - > 0 and large – no mixing
 - > 0 and large – depends

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We will discuss we will basically continue our discussion having polymers in solution and the topics, we plan to cover today this lecture is now cohesive energy density and solubility parameter. How we can use the knowledge from solubility parameter and we can estimate or predict the solubility behavior of a polymer in a solvent. And then we will follow up our discussion with a phase separation behavior of polymer solutions.

Now, let us begin just recapping few minutes what we discussed in last class or last lecture. Now, this is what we found we derived the Flory- Huggins equation where now this is Gibbs free energy of mixing given by two terms this term was coming from purely combinatorial entropy and this is always negative. And so this is always favors mixing this is always gives you negative contribution towards Gibbs free energy mixing, this is always favors mixing.

And this coming from a combination of enthalpy and entropy change due to polymer solvents contacts. And it will decide because it is always negative and it is always contribute in favor of mixing. So, the value of this basically determines where polymer will mix or becomes soluble in a solvent or not. And if the value becomes less than zero negative obviously mixing will happen, if it is positive and large no mixing and if it is slightly positive small I did not change from. So, this is if it slightly positive and this is and the value is small and it depends between the completion of this two to which will decide whether the polymers will go in to solution or not.

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Polymers in Solution : Recap

Dilute Polymer solution

$$\mu_1 - \mu_1^0 = (\mu_1 - \mu_1^0)^{id} + (\mu_1 - \mu_1^0)^{E_{mix}}$$

$$(\mu_1 - \mu_1^0)^{E_{mix}} = RT\left(\chi - \frac{1}{2}\right)\phi_2^2 = RT\psi\left(\frac{\theta}{T} - 1\right)\phi_2^2$$

At theta temperature, solution behaves like an ideal solution, polymer exists in solution with unperturbed dimensions

- $\chi = 0.5$ - ideal solution, mixing; $T = \theta$
- $\chi < 0.5$ - coil expands, promotes mixing; $\psi > 0, T > \theta$ or $\psi < 0, T < \theta$
- $\chi > 0.5$ - against mixing

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In dilute polymer solution we had found that the excess contribution excess chemical potential, we got this relationship. And at related temperature this term the contribution of excess chemical potential becomes 0 and the solutions become ideally. If you look at this expression if this contributes negatively, obviously μ_1 this difference would be lower than the ideal. That means polymer will the solution or the mixture of polymer and the solvent will be favored, if this is positive then it will be higher than the value of ideal. So, it will be it will have effect against solution.



So, theta temperature the this becomes 0, so the solutions become ideal solutions and polymer exist in solution with unperturbed dimensions. Now, we will come in a next lecture what is unperturbed dimensions, but what does it mean in brief as if polymers are present as such without no interference or no interaction from the other polymer molecule or the solvent molecule, which will discuss what the meaning of unperturbed dimensions in detail in next lecture.

Obviously as I said that when theta is temperature is theta temperature value of polymer solvent interaction parameter χ becomes 0.5. So, the solution will be the polymer and solvent mix like ideal solution, if this is if the value of χ becomes lower than half then the coil expands polymer expands in solution, which promotes mixing. Ψ was if you recollect the this was entropy parameter now to have this term negative, for a positive entropy factor or parameter, T has to higher than the theta temperature to have mixing.

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Polymers in Solution : Recap

Polymer	Solvent	θ °C	ψ	mixing
Polyethylene	Biphenyl	125	> 0	$T > \theta$
Polystyrene	Cyclohexane	34	> 0	$T > \theta$
Poly(vinyl acetate)	Methanol	6	> 0	$T > \theta$
PMMA	Butylacetate	-20	> 0	$T > \theta$
Poly(vinyl alcohol)	Water	97	< 0	$T < \theta$
Poly(acrylic acid)	1,4-Dioxan	29	< 0	$T < \theta$

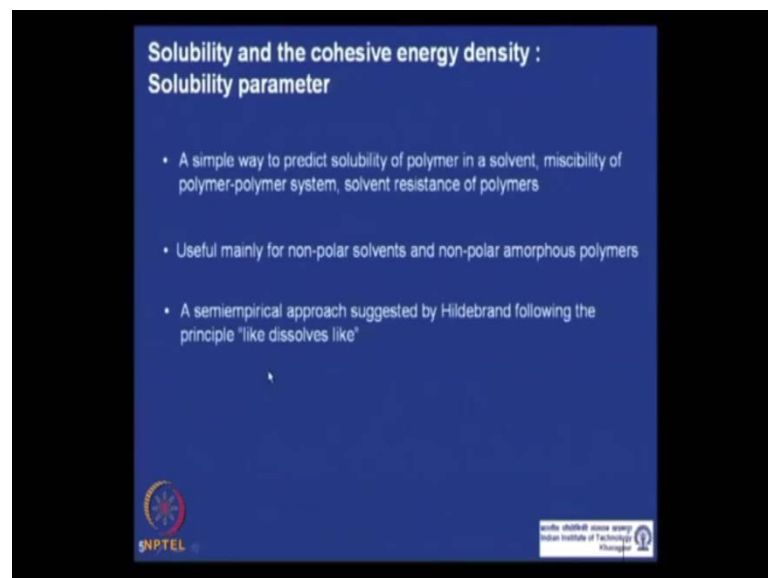



Whereas, if the entropy factor is negative than T has to be lower than the theta temperature to have mixing possible. And the other cases, where the opposite case or the reverse case where chi polymer solvent interaction parameter is higher than 0.5, it against mixing. Just to give few data for polymer solvent polymer solvent system having different values of χ and theta...

Let us look at some data of different polymers and with different solvents as we are mentioning, for all this cases the interaction parameter value chi is less than 0.5. That means this is all this examples we are talking about favoring mixing so as I mentioned, if χ is positive then for mixing to happen temperature has to be higher than theta. And examples where there are strong interaction between the solvent and the polymer, the entropy factor becomes negative. In that case the temperature has to be lower than the theta temperature to have the mixing possible. And these are two examples where the χ factor is negative and theta has to be lower than theta two to get the mixing possible.



Now, let us move to the one more topic on solubility which is determined cohesive energy density and solubility parameter. Now, if you look back the Flory-Huggins expression we have two terms the first term from the combinatorial entropy, which can predict theoretically if you know the volume fractions of the polymer and the number of moles of the polymer molecules. The second term which actually determines the polymer will get solubilized in the solvent, you need to find out the value of that.

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**Solubility and the cohesive energy density :
Solubility parameter**

- A simple way to predict solubility of polymer in a solvent, miscibility of polymer-polymer system, solvent resistance of polymers
- Useful mainly for non-polar solvents and non-polar amorphous polymers
- A semiempirical approach suggested by Hildebrand following the principle "like dissolves like"

And there are some approach some approaches from the different, different scientist made and one of the important and important contribution from this towards this is by Hildebrand, Hildebrand who basically introduced the concept of cohesive energy density...

And relations to solubility parameter, and this is simple way to predict the solubility of polymer in a solvent and miscibility also can predict the miscibility the behavior of polymer polymer system. And we also can because it as if it can determine the solubility of polymer, it can also simultaneously detect the solvent resistance behavior of the polymer.

It mainly useful for as we see it is mainly useful for non-polar solvents and non-polar amorphous polymers, it is not very useful for polar molecules and polar solvents. It is basically a semi-empirical approach as suggested by Hildebrand following the principle like dissolves like. This means basically as we know that like the polymers which are a similar structure or similar sort of interaction behavior with a solvent will dissolve in that solvent.

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Cohesive energy density : Solubility parameter

Cohesive energy density (CED)

$$= \frac{\Delta E_v}{V} \quad \Delta E_v = \text{molar energy of vaporization}$$

$$= \frac{\Delta H_v - RT}{V} \quad \Delta H_v = \text{molar enthalpy of vaporization}$$

Solubility parameter, $\delta = (\text{CED})^{1/2} = \left[\frac{\Delta H_v - RT}{V} \right]^{1/2}$

Enthalpy of Mixing, $\Delta H_m = V_m(\delta_1 - \delta_2)^2 \phi_1 \phi_2 > 0$

Hildebrand suggests that compatibility between components 1 and 2 increases as $\delta_1 \rightarrow \delta_2$

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Quantitatively this cohesive energy density is defined by this which is ΔE_v is molar energy of vaporization, it can be written by this expression also where ΔH_v is molar enthalpy of vaporization, this is molar enthalpy of vaporization and this is molar enthalpy of vaporization V is the molar volume of the substance. Now, as you

know cohesive energy is basically, it gives idea about the interaction or the force of attraction between the similar type of molecule.

So, if the cohesive energy density is the higher than the attraction of the attraction between the similar molecules is higher. So, as we know from our previous understanding that cohesive energy is the energy of interaction between the similar molecules. So, higher cohesive energy density means higher attraction between the molecules. Now, one defined the term solubility parameter which is basically square root of cohesive energy density. So it is given by this expression and this is what we are looking for the enthalpy of mixing is given by, if you know the values of the solubility parameter then the enthalpy of mixing can be obtained by this expression. We know the contribution from the combinatorial entropy which is always favoring mixing.

Now, this is the term will give you the enthalpy of mixing the way this expression has been proposed, it always gives the entropy the enthalpy of mixing. Enthalpy of mixing ΔH_m is positive or 0, if δ_1 is equals to δ_2 the drawback of these approach is that it cannot predict any negative enthalpy of mixing, which sometimes happen if there are strong specific interaction between the polymer and the solvent. V_m is the average molar volume of the polymer and the solvent.

So, if you if you think about the Gibbs energy of mixing which is $\Delta H_m - T\Delta S_m$. So, obviously the lower is the value of ΔH_m the better is the mixing and if it is negative then obviously it favors the most in this case because it is positive or 0, then the case where ΔH_m would be 0, it will be most favorable for mixing. And if it is positive then the lower is the value of ΔH_m it will be it will be better for mixing.

So, as Hildebrand suggests that that compatibility between components one which is the solvent and two which is the solute the polymer in this case arises, as you have the less differences between the solubility parameter of the two components. So, if this they are same that is the best case where ΔH_m would be equals to 0.

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Cohesive energy density : Solubility parameter

$$\chi = \chi_s + \chi_H$$
$$\chi_H = V_1(\delta_1 - \delta_2)^2 / RT$$

Works well for non-polar solvents with non-polar amorphous polymers

Not valid for crystalline polymers

Can not predict the solubility behavior of polar polymer and/or polar solvent capable of forming H-bonding, participate in electrostatic interaction

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Now, we have we have seen before that the polymer solvent interaction parameter can be actually have two component, the entropy component and enthalpy component. It can be shown that enthalpy component is can be expressed by this expression as well, and this term entropic contribution towards the polymer solvent interaction parameter is most cases, it happens the value of 0.2. So, if this is close to or at least less than 0.3 then chi would be less than 0.5, which means it will promote mixing and which means the closer this the value of delta 1 and delta 2. Then obviously the difference it will be nearer to 0 the chi H value would be nearer to 0.

So, from this expression also you can predict that the polymer solvent interaction parameter will be lower than 0.5, which means the polymer will promote or it will dissolve in the solvent you are using. Now as I said that before that this box will for polymers of or for a non-polar solvent the non-polar amorphous polymer. It is not valid for crystalline polymers because you know this, this expression or this approach we are talking about talks about liquid solvent and liquid polymer. Means amorphous polymer so in if you want to dissolve a crystalline polymer then you have to also include the contribution for the enthalpy of crystallization. So, in this case the enthalpy of crystallization is not taken in to account.

So, that is why this is this approach is not valid for crystalline polymers this is added already for amorphous polymer. In case of polar solvent you can have specific

interaction between the polymer and the solvent. For example, it can have hydrogen bonding, it can participate in the electrostatic interaction and which we can think that if there is specific interaction like hydrogen bonding attraction between polymer, and solvent. Then there is a possibility that there is ΔH_{mixing} would be negative and that as it approach the solubility parameter approach, does not predict any value any negative value of ΔH_{mixing} . So, this is not valid for polymer long polar a polar polymer and polar solvent as usually, which is usually valid for non polar solvent and non polar and non polar amorphous and non polar solvent.

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Cohesive energy density : Solubility parameter

The δ value for the solvents can be directly obtained from the experimental value of molar enthalpy of vaporization and molar volume

δ value of the polymers can be obtained indirectly and taken as equal to δ value solvent for which there is:

- maximum in intrinsic viscosity for soluble polymers
- maximum in swelling of polymer network

δ value of the polymers can also be obtained indirectly from group contribution method.

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Now, how to get these delta value, the value of the solubility parameter? Obviously as we you can recollect this the delta can the cohesive delta is the we see square root we see the cohesive density and cohesive energy density can be found from molar energy of vaporization or molar enthalpy of vaporization. For liquids or for solvents we can experimentally determine the molar enthalpy of vaporization and the molar volume. So, you can get the cohesive energy density and the value for the solubility parameter as well.

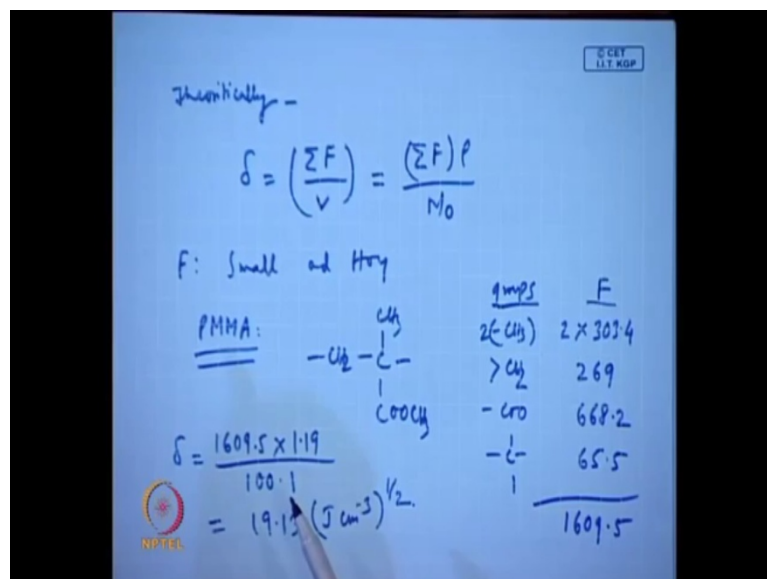
But for polymers because they cannot be vaporizable vaporize or polymers are not vaporizable, you cannot experimentally get the value of solubility parameter for the polymer because they are large in size. So, they are the value of delta the solubility parameter of polymer are typically determined indirectly and it is basically following the

approach, we took delta H becomes 0 as delta 1, delta 2 becomes same. So, a polymers are added if talking about linear polymer then the intrinsic viscosity of that polymer is measured in several solvents, several common solvents.

And the highest or the maximum intrinsic which is the in which the solvent in which the polymer gives, we the solubility parameter of the polymer is taken as the same solubility parameter of that particular solvent. Basically this indirectly telling that the delta 1, delt 2 are same. So, this give giving the maximum solubility or maximum intrinsic viscosity for that polymer if the polymers are crops linked or jelt, then we do the same experiment take the polymer and do series of put the polymer need to work in series of solvent and find out the maximum swelling ability. If the where that interaction is maximum, the maximum swelling happens. So, we take the solubility parameter of that particular solvent as the solubilitic parameter of the given polymer.

The value of solubility parameter of the polymers can be also indirectly obtained from group contribution method. As you know the group contribution methods are utilized to find out theoretically, the value for several other parameters several other properties of polymer. And this solubility parameter can be also obtained by group contribution method, and this how it is done there particularly the solubility...

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This is done theoretically delta is this, F is the contribution form or the value for different groups. If you can divide or bisects the polymer into different parts then these values for

F are available in literature. So, you can add those and this is molar volume so you can also write this as density and molecular weight, F can be on F value of F so given by a small an Hoy and this looks at one example we take P M M A poly method calculate the structure of which is as you know this is the structure.

So, how many groups it has we have to count groups there 2 C H 3 groups 1 C H 2 group. So, 1 C H 2 group 1 C O group and one motoring carbon in case of these are the groups there in this polymer, then values of these are separate these the contribution of these groups have already tabulated or theoretically find out by scientists like Small and Hoy, you have to just take those values and add up to get the this value. And then get the solubility value the F value which has been supplied in literature for this is 303.4. So, this gives you 269. So, sum up 1609.5, so delta would be given by multiplied the density 1.19 and by the molar mass, mass of the repeating unit.

Now, look at these values of the groups as I said that this is this gives this, basically the solubility parameter is basically the square root of the cohesive energy density. And cohesive density energy is nothing but measure for the interaction or attractive interaction between the molecules. If there are polar molecules, obviously the are attraction between the similar molecules become higher.

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Solvent	$\delta / 10^3 \text{ J}^{1/2} \text{ m}^{-3/2}$
acetone	20.3
CCl ₄	17.6
cyclohexane	16.8
xylene	18.0
Toluene	18.2
CHCl ₃	19.0
methanol	29.7
water	47.9
PS	18
PC	19 - 20.0

So, the contribution become higher and if the volume becomes higher there's no polar groups the volume becomes higher there is more Vander Wall forces between them

which also, increases the cohesive interaction between the groups. So, this C H_3 has higher than C H_2 than the vortronic carbon atom this is the size of the group so the size increases. Vander Waals force is increases so increases. So, the value of or fluctuation for this group increases. So, like this you can get the value for this interaction parameter for any of the polymers because the value of this are supplied by available in the literature.

Now, look at sum of the final sum of the polymers and solvent common solvent like acetone delta value 20.3 c c l 6, this example of take few polymer like polystyrene, this is some polymer polystyrene 18.5 and bis phenyl poly carbonate its around 19.5 to 20. Obviously if you look at this number 19.5 and to 20 this number 19.5 to 20, obviously look at this, this solvents. Now, as we have seen that if the delta value of the polymer is closer to the value of solvent that of solvent liquid that of mixing the polymer will be soluble in that solvent.

So, polycarbonate will obviously become soluble in chloroform, it is 19.5 and 19.19, 19.5. Obviously polycarbonate will not be soluble in methanol water or some of the non polar solvents, cyclohexene and sides carbon tetrachloride zylene and so on. Acetone 20.3 is basically this polycarbonate becomes soil it's not very good solvent for polycarbonate, but it is it is also a very non solvent either. So, the solubility of polycarbonate is a very low, but it's is not zero in acetone.

So, if basically if you know the solvents and the value of polycarbonate you can predict, you can estimate the whatever, whatever you want to know which application. For example, if you want to use some medical devices you know you in medical devices, like cringes and some other medical component like you most cases before use they are sterilized by applying some spirit rectified spirit, which contains alcohol. If you know the solubility parameter of that alcohol then you know what are the, you can estimate or you can basically zero down, narrow down the choices of your polymer which will not be soluble in that alcohol, which will be use wiping those or sterilizing those equipment. So, you can basically, reduce your number experiment which can, which you can already your choice of polymer by a prior knowledge of solubility parameter, and some value of solubility solvent and polymer.

Some cases this rubber gaskets are used for sealant in may be in aircraft applications, where a ceiling is very important. Now, obviously they come in case of car also they

clients are very important. So, how they come in the contact of the petroleum vapours, or they come in contact with liquid fuel. Now, if those rubbers or the sealants, rubbers actually gets solvents then there would be leakage or there in that sealing method. So, you do not want your material rubber material to swell in that particular gasoline or liquid fuels. So, you choose a polymer which would be non soluble polymer in that environment.

So, if you have prior knowledge of your solubility parameter of the polymer and solvent then you can narrow down the polymers, before you go the exact trail. If you look at the polis polystyrene obviously polystyrene will not soluble in water and methanol, but it polystyrene almost soluble in most of this solvents. So, it actually gives you idea it doesnt gives you exact sort of solubility behavior, but it this gives you guidelines or help you to understand, what is the solubility you know bring the solubility of the polymer in a solvent.

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Phase-separation behavior of polymer solutions

$$\Delta G_m = RT(n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \chi \phi_2)$$

per segment

$$\Delta G_m^* = RT\left(\frac{n_1}{n_1 + x n_2} \ln \phi_1 + \frac{n_2}{n_1 + x n_2} \ln \phi_2 + \left(\frac{n_1}{n_1 + x n_2}\right) \chi \phi_2\right)$$

$$\Delta G_m^* = RT[\phi_1 \ln \phi_1 + (\phi_2 / x) \ln \phi_2 + \chi \phi_1 \phi_2]$$

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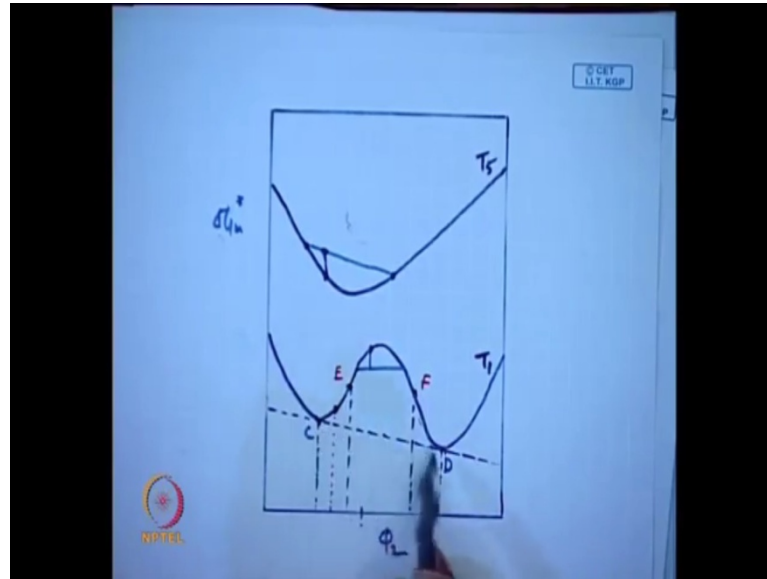
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Now let us move to the next topic where we talk about polymer phase separation behavior of polymer solution. And again going back to the Flory- Huggins expression Flory-Huggins equation, this is Gibbs energy of mixing. Now, if you want to convert it Gibbs energy mixing per segment or per unit then we will divide by the number of segments total number segments or number of lattice sign n 1 is for the solvent, and this is for the polymer. So, you divide that and get this as another expression for the poly

hybrid expression, where this Gibbs free energy of mixing takes place in terms of first segment of the polymer molecule.

Now, this gives the behavior of the or the how the Gibbs energy of mixing per segment varies with, say one of the say compositions in this pie 2, pie 1 can be converted into pie, pie 2 easily see if you plot say ΔG_{mixing} .

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If you plot ΔG_{mixing} first segment if you can get from this expression of what we just saw in this case, from this expression we will tell you it will give two general type of variation of this ϕ and G with in this case say pie 2, ((Refer Time: 31:47)) of the polymer. Now, let us consider this case, the temperature is T_5 , now in this case if you take any point say I will take at this point. Now, if this has to spontaneously phase separate to any of the other two compositions, say this composition and this composition two point. So, I consider a solution which corresponds to this particular pie 2.

Now, if that has to spontaneously phase separate in to in to two other composition obviously one has to be polymer rich and this one and other has to be solvent rich left hand side. Pie 2 comes down you can take any two point, now if that process of phase sep spontaneous phase separation happen the ΔG_{mixing} of that process would be given by the value of this, which is the distance between the interaction point of the tie line, this is tie line. Now, the tie line is the line straight line connecting two points in that curve and this line, which is a vertical line parallel to the y axis.

Now, this the value of this gives you the Gibbs free energy mixing I am telling again the value of this gives you the Gibbs free energy of mixing for the process of separating a composition corresponding to this to, to composition corresponding to this and this now this value, if you can see any of this points is positive. Which means that this process of spontaneous phase separation is thermodynamically not visible, which also means that each point or each solution in this line corresponds different π_2 , they are all stable. That means the polymer and the solvent is soluble across compositions.

So, If you take polymer and dissolve in the solvent it will be soluble for that particular temperature in this case T_5 for any at any composition, it will not face separate to any two composition I mean polymer rich and solvent rich, phases as that is thermodynamically not feasible. Now, consider another temperature T_1 you get this type of this is another general type curve.

Now, the region this side below this point say I if I write c and it is a point d below left hand side c and above d is similar to this expression. So, all the composition will be stable, so you will get soluble polymer will get solubilized in the solvent in this range and in this range, exactly like this. Now, look at another composition here any point here between this and this point any point in this curve, this is the tie line. So, if this has to phase separate this, this solution having polymer mole fraction of this value if that has two phase separate two, two composition having polymer mole fraction correspondence to this and this, the Gibbs mixing would be given by this value and that is negative.

So, which means that between this point and this point between this point and this point any composition, which immediately phase separate and come to this two points. So, if you have any solution having π_2 value in this region, immediately they will phase separate and form two equilibrium solution, one is polymer rich, one is solvent rich.

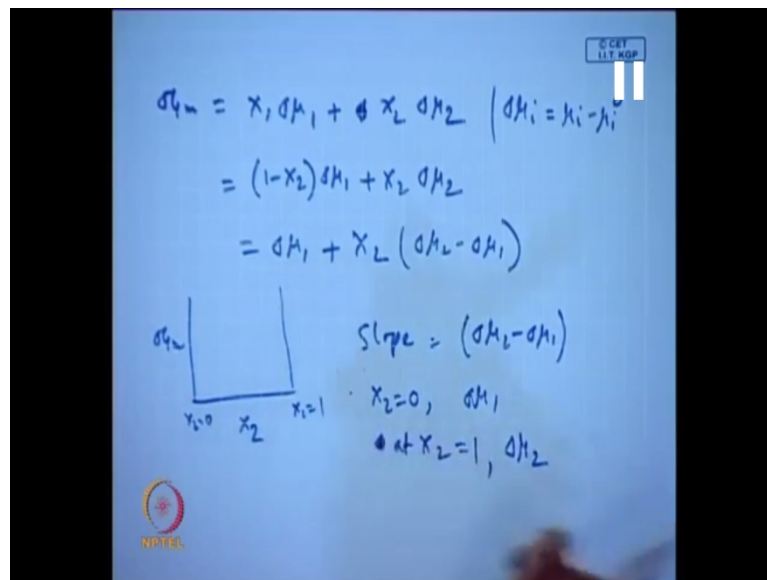
Now, look at point here any point between this two line this point and this point and this point and this point. So, this is $E f$ so any point between c and e and f and d now, if at if this has to phase separate to any of the slight changes in to slight changes in the composition. Say this point in this point it will be similar to this curve, similarly same in this case, but if this has to phase separate if I consider this point which has this value of π_2 , if this has to separate phase separate into two phases having composition between this point and this point. Then obviously Δg_{mixing} positive so that mean

unfavourable, but if this composition is phase separate into a point here and here, the ΔG be negative.

So, it will spontaneously phase separate, see if this any point in this region any composition any solution would be stable, for small change in composition, but it is not stable for a large changes composition beyond this, this point. So, this is region of metastable region where the composition are stable only for slight change in composition. So, this is meta stable region so these regions are metastable c to e and f to d and any composition between e to f is completely unstable, which will immediately phase separate into c and d. And any composition between this point and c and d to n would be stable, there will be clear solution. This is the inflection point this is the inflection point.

Now, if I change some other temperatures the solution will, you can draw some other lines. And then join these points, this points to get a bell safe curve which I just come in a minute. Now, let's talk little more about this two points and this two points c d and e f.

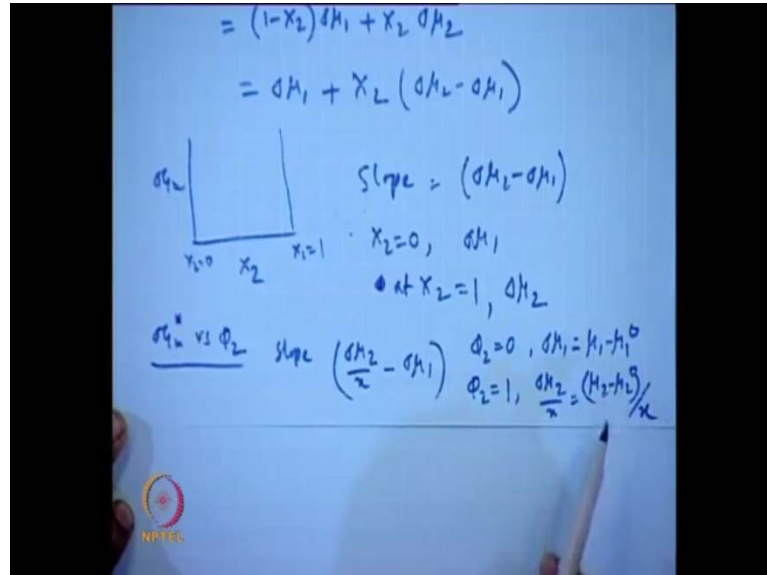
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Now, ΔG_m I can write $\Delta G_m = x_1 \Delta \mu_1 + x_2 \Delta \mu_2$ the mole fraction $\Delta \mu_1, \Delta \mu_2$ is $\mu_i - \mu_i^0$, it can be written as $\Delta \mu_i$ is an intrinsic quantity. So, I can write $x_1 \Delta \mu_1 + x_2 \Delta \mu_2$. So, if you plot ΔG_m versus x_2 you get the slope as $\Delta \mu_2 - \Delta \mu_1$ and the intercept will be at $x_2 = 0$, $\Delta \mu_1$ and at $x_2 = 1$, $\Delta \mu_2$.

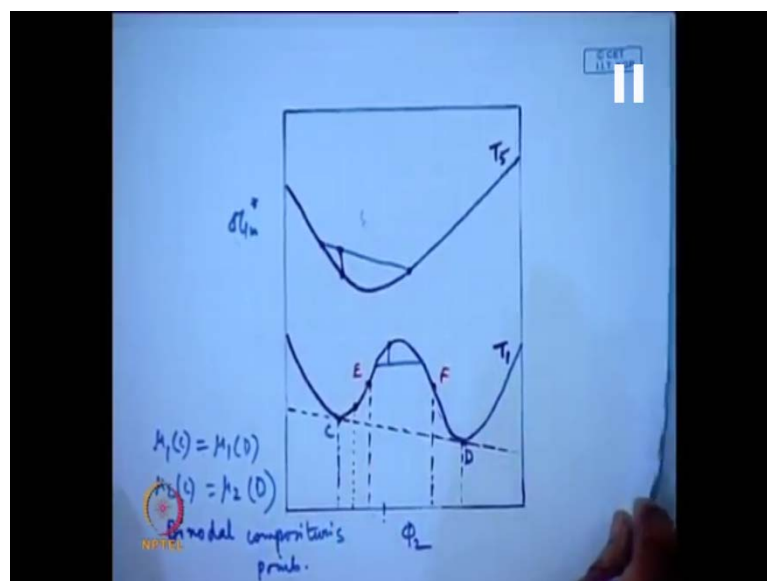
2 is equal to 1 we will get delta mu two till the intercepts, intercept at x 2 is equal to 0 and x 2 is equal to 1.

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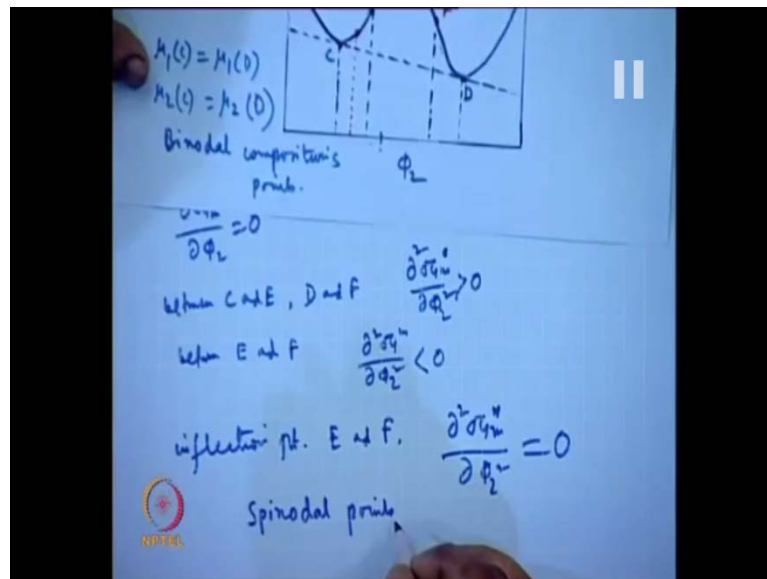
And if I want to do it for delta G m star which is for segment and pie 2, we can easily imagine that the slope would be slope at any point of that curve will be mu 1. And the intercept at pie 2 0 would be delta mu 1, which is mu 1 minus mu 0 that is the intercept at pie 2 is equal to 1 of the delta mu to x, this is a simple mathematic you can find out that.

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So, what means that if you plot these ΔG_m versus ϕ_2 then the slope will be given by this and the intercept would be given by this values. Now, if you look at this two point the tangent for those two point would meet at the same points, which means they have they must have a common tangent. So, these two point must have a common tangent so the and has the slope is given by this, which will also mean that μ_1 for the solvent at point c will be equals to μ_1 at d μ_2 at point c would be equals to μ_2 at d this two point will have same slope and have a common tangent. If the common tangent in the slopes will be same and from the slope, we have already seen you can write that $\mu_1 c$ equals to $\mu_1 d$. So, chemical potential of the solvent in this point is same as this point so as the chemical potential of the polymer in this point. And this means that c and d are two equilibrium, equilibrium composition and we name this as binodal, binodal compositions or binodal points.

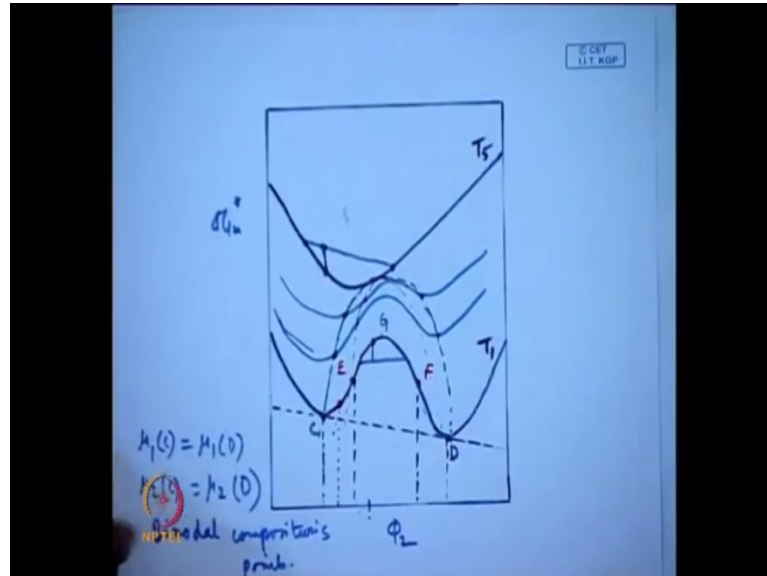
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Now, this is between c and d you can clearly see that c and d are the binodal points... where is 0 between c c and e d and f the slope is changing in positive way so d ϕ_2 is greater than 0. And between e and f this is the change of slope, sorry this is slope and this is the rate of change of slope this change of is coming in positive direction here, and negative direction here. And in the inflection point which is e and f, inflection point e and f would be 0, these two points which are inflection points is called spinodal points. Spinodal points or spinodal cum composition, basically it is the boundary between spinodal points, spinodal composition this is the boundary between a meta stable and a

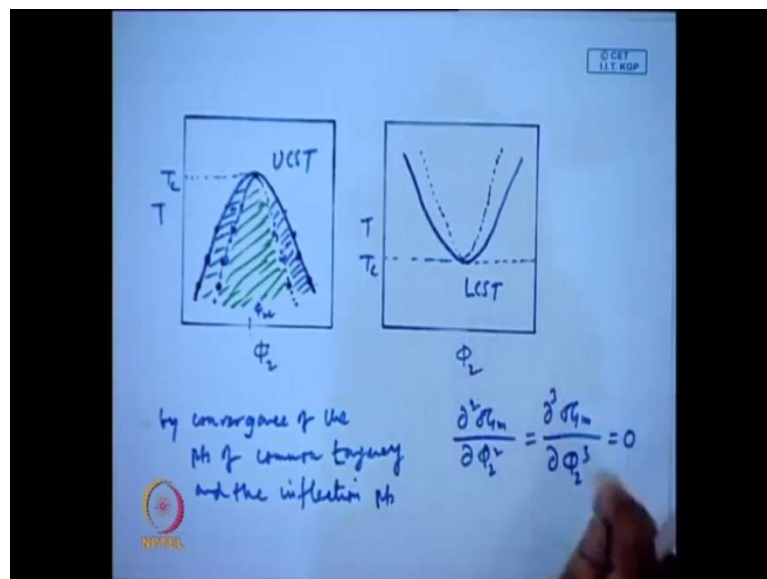
unstable composition. The inflection point is the boundary between the metastable and the unstable compositions and this gives why this expression.

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Now, I was telling little earlier that now you can draw similar lines like let me try and then join this spinodal points. And also join the you can join this spinodal points and you can also join the inflection points to get something like this.

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I have already drawn so you can just see form here, so you can get a curve like this are the locus of the bi nodal points at different temperature, at different temperature you

have different binodal points you have temperature these, you have temperature these like this at one point they will merge. Similarly, this line is the locus for the spinodal points, spinodal points these are the different points for the different temperature.

And at some points they converge so this point this is critical points is given by critical points is given by convergence of the points of common tangency and inflection points. Common tangency points are the spinodal points and inflection points are spinodal points. So, by converging you get T_c , and so you can write at that point at T_c both are zero, this way you can get this. I hope you got it this are this line this solid line is this you join different binodal points obtains in different.

So, if one temperature you got binodal points here and here another points you got binodal points here and here, the another one here and here you have just joined them and got a binodal curve. Similarly, this temperature you have spinodal points like here and here, this temperature you have here and here similarly, here you can join them and get a spinodal curve. And this is the point they converge. So, what about this regions then? Any composition above this curve this solid curves will be completely soluble they will have single phase. So, any point in this diagram will be having single, single phase any point within these. So, basically this region will be completely insoluble they face separate out.

And any region any point here would be meta stable one so in single curve, single diagram you can get complete phase diagram, it basically gives you the phase diagram of that polymer in that solvent. So, basically you are plotting a different temperature, the composition of the solution so at any point in this region, you get a single phase which is polymer soluble in the solvent. Any point this is temperature and this composition you get two phase polymer and in this case you get meta stable solution which will be stable to a small fluctuation in the composition, but not in the large fluctuation.

So, this basically gives you the phase diagram of a polymer in a solvent from that original Flory-Huggins equation, this point you call $U_C S T$ upper critical solution temperature, so above this temperature the polymer is soluble in that solvent at any composition. Below this temperature the polymer is the only soluble in

that solvent in this composition left hand of this point and in this composition, but above this temperature the polymer is soluble in the solvent at any composition, that is called upper critical solution temperature. And you can get the reverse also and in that case this point called L C S T is called lower critical solution. So, basically below this temperature everything is soluble, in a polymer soluble at every composition so if I take that Flory-Huggins expression this one and Flory-Huggins expression this one...

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The image shows handwritten mathematical derivations on a blue background. At the top right, there is a small box containing the text "© CBT 11/1/2017".

The first derivation is for the spinodal point, labeled "Spinodal m". It shows the second derivative of the Gibbs free energy with respect to the volume fraction ϕ_2 set to zero: $\left[\frac{\partial^2 \Delta G_m}{\partial \phi_2^2} \right] = 0$. This leads to the equation $\frac{1}{1-\phi_2} + \frac{1}{2\phi_2} - 2\chi = 0$.

The second derivation is for the critical point, labeled "Critical m:". It shows the second derivative of the Gibbs free energy with respect to the volume fraction ϕ_2 set to zero: $\left[\frac{\partial^2 \Delta G_m}{\partial \phi_2^2} \right] = 0$. This leads to the equation $\phi_c = \frac{1}{1+\chi}$.

The final equation shows the critical composition $\chi_c = \frac{1}{2} \left[1 + \frac{2}{\chi} + \frac{1}{\chi} \right]$. The NPTEL logo is visible in the bottom left corner of the slide.

And write the conditions from for spinodal id equal to 0, you get the spinodal points like $1 - \phi_2 + \frac{1}{2\phi_2} - 2\chi = 0$. And for the critical this was the critical point you get, again if you do this you have the expression for ΔG_m and star for if you do this you will get ϕ_c for the critical. And from these two you can write the critical these are just pure mathematics form you are getting these expression from Flory Huggins expression which we called earlier for the per segment Gibbs free energy per segment. So, you can get this expression what you will do is just.

In the next lecture we will take this and just complete the discussion of our phase separation of polymer solution. And then we will look in to it that how the molecular weight or the size of the polymer determine the solubility of polymer, and which can utilize to fraction fractionate the polymer of different molecular weight. We will just start form this in next lecture.