Introduction to Polymer Science
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Lecture - 25
Polymers in Solution: Solubility Parameter, Polymer Phase Separation and Fractionation

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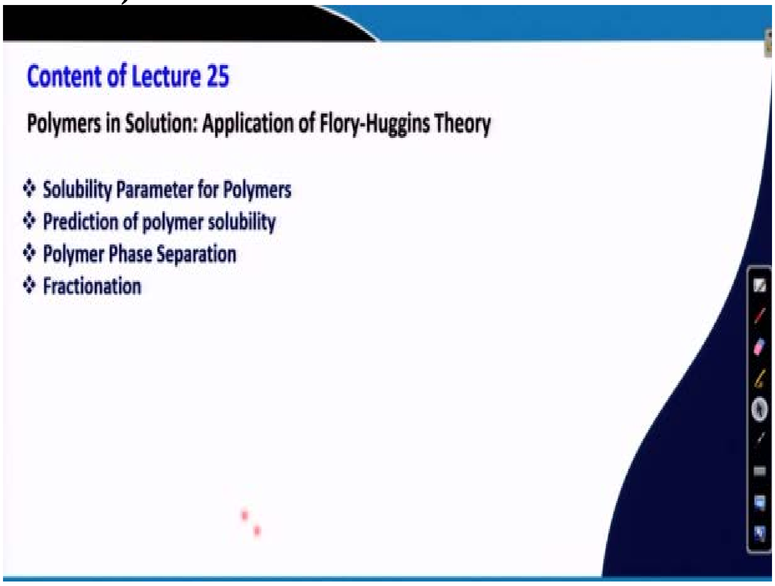

Content of Lecture 25

Polymers in Solution: Application of Flory-Huggins Theory

- Solubility Parameter for Polymers
- Prediction of polymer solubility
- Polymer Phase Separation
- Fractionation

Welcome back, in this lecture 25, we will continue our discussion on polymers in solution. We will introduce the term solubility parameter for polymers which will be utilized to predict the polymer solubility. A quick discussion about polymer phase separation and fractionation will also be taken up.

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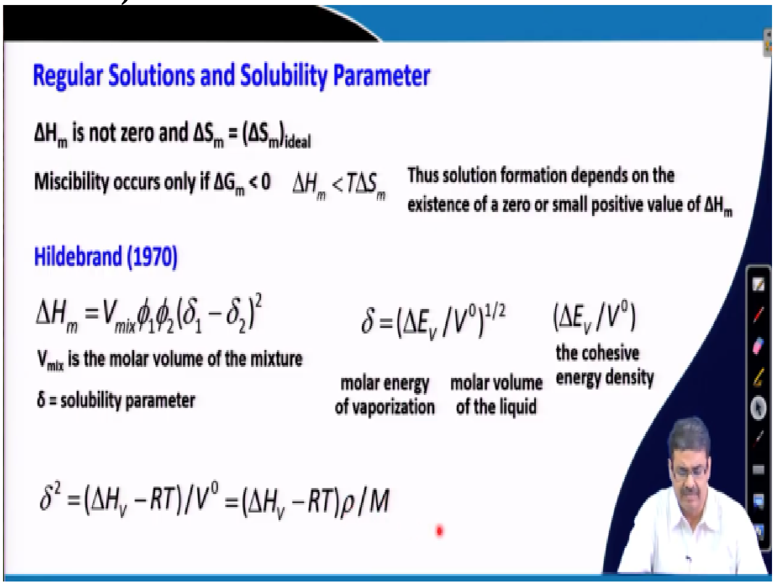

Regular Solutions and Solubility Parameter

ΔH_m is not zero and $\Delta S_m = (\Delta S_m)_{ideal}$

Miscibility occurs only if $\Delta G_m < 0$ $\Delta H_m < T\Delta S_m$ Thus solution formation depends on the existence of a zero or small positive value of ΔH_m

Hildebrand (1970)

$\Delta H_m = V_{mix}\phi_1\phi_2(\delta_1 - \delta_2)^2$ $\delta = (\Delta E_V / V^0)^{1/2}$ $(\Delta E_V / V^0)$

V_{mix} is the molar volume of the mixture

δ = solubility parameter

molar energy of vaporization

molar volume of the liquid

the cohesive energy density

$\delta^2 = (\Delta H_V - RT)/V^0 = (\Delta H_V - RT)\rho / M$

Now, we have defined different types of solutions earlier and one of those were regular solutions. In this lecture and several lectures before and later also we are generally using ΔH_m, ΔG_m, ΔS_m as enthalpy of mixing, Gibbs free energy of mixing and entropy of mixing respectively. So, for the regular solutions, ΔH_m is not 0 and $\Delta S_m = (\Delta S_m)_{ideal}$ for an ideal solution, which means that miscibility occurs if ΔG_m is less than 0 which means that the enthalpy of mixing must be lower than the term T multiplied by ΔS_m from thermodynamic knowledge. This is a negative term bsecause we know from an ideal solution ΔS_m is given by the combinatorial entropy which is always positive, hence the $T\Delta S$ term will be negative. Hence, this should not be a positive term having high value. So, the formation of solution depends on existence of ΔH_m as 0 or small positive value. If it is 0 then obviously, ΔG_m will be negative and formation of solution will be feasible. Even a small positive value will also allow the solution to form, but if the value of ΔH_m is large positive, then it will not allow the solution to form.

Now, to predict the value of ΔH_m, Hildebrand in 1970 basically proposed an expression for ΔH_m which is given by or which is shown below, where V_{mix} is the molar volume of the mixture and δ is solubility parameter. What is solubility parameter? It is given by this expression where ΔE_v is the molar energy of vaporization and V^0 a molar volume of the liquid.

$$\Delta H_m = V_{mix}\phi_1\phi_2(\delta_1 - \delta_2)^2$$

Now, this term within the bracket is also called cohesive energy density. It is related to enthalpy or energy of vaporization which basically quantifies the cohesive forces between the molecules.

Hence this term is generally expressed or called as cohesive energy density. Now, if the vapor is an ideal gas, then we can write ΔE_v as $(\Delta H_v - RT)$ and the molar volume of the liquid can be expressed as the density of the liquid divided by the molecular weight of the liquid or the solvent.

$$\delta = (\Delta E_v/V^0)^{1/2}$$
$$\delta^2 = (\Delta H_v - RT)/V^0 = (\Delta H_v - RT)\,\rho/M$$

Hence, using this expression, we can actually experimentally determine the value of solubility parameter of the solvent or a liquid, we can get the enthalpy of vaporization from experiment and we can get the molecular weight and density from the experiment as well.

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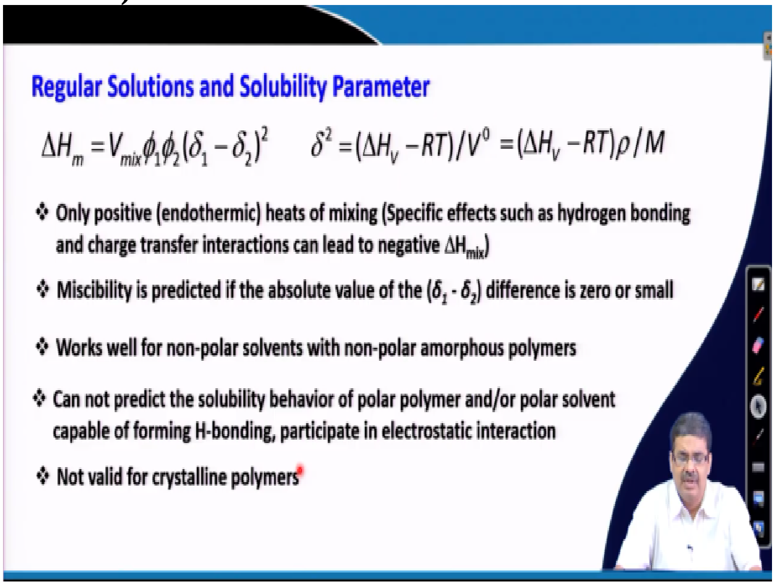

Regular Solutions and Solubility Parameter

$$\Delta H_m = V_{mix}\phi_1\phi_2(\delta_1 - \delta_2)^2 \qquad \delta^2 = (\Delta H_v - RT)/V^0 = (\Delta H_v - RT)\rho/M$$

- Only positive (endothermic) heats of mixing (Specific effects such as hydrogen bonding and charge transfer interactions can lead to negative ΔH_{mix})
- Miscibility is predicted if the absolute value of the $(\delta_1 - \delta_2)$ difference is zero or small
- Works well for non-polar solvents with non-polar amorphous polymers
- Can not predict the solubility behavior of polar polymer and/or polar solvent capable of forming H-bonding, participate in electrostatic interaction
- Not valid for crystalline polymers

Now, because this is a squared term $(\delta_1 - \delta_2)$, this only allows the value of ΔH_m either 0 or a positive number. But in some specific cases, where there is a strong hydrogen bonding between the solvent and the solute in this case polymer or a charge transfer interaction between the solute and solvent then that can lead to negative enthalpy of mixing which is not captured by the expression proposed by Hildebrand.

Hence, this value will be 0 or lower positive number if the value of δ_1 is close to δ_2, if they are equal, then this would be 0. If they are very close to each other, then the value will be lower. Hence, the miscibility of the solvent and the polymer or a solute is preferred when the solvent and the solute have solubility parameter value close to each other. So, miscibility is predicted if the absolute value of δ_1 and δ_2 the difference is 0 or small.

Now, this works well, for non-polar solvent and non-polar amorphous polymer where these interactions like hydrogen bonding, charge transport interaction or electrostatic interactions are absent. This cannot predict the solubility behavior of polar polymer and polar solvent capable of forming hydrogen bonding or participating in electrostatic interaction as we discussed earlier, as well. It is not valid for crystalline polymers because in case of crystalline polymer, the dissolution process also need energy for crystallites to become amorphous before it dissolves in the solvent. So, the energy of crystallization is also required to be supplied before the polymer, the crystalline polymer can be dissolved in the solution in solvent.

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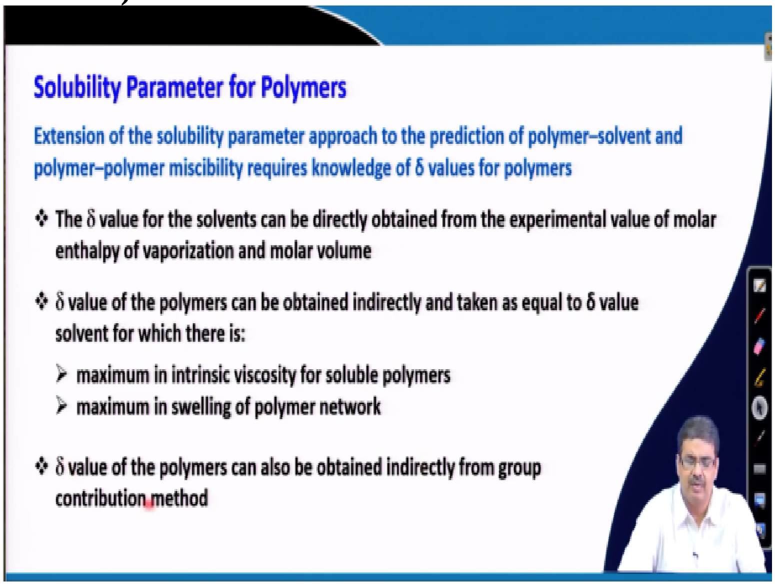

Solubility Parameter for Polymers

Extension of the solubility parameter approach to the prediction of polymer–solvent and polymer–polymer miscibility requires knowledge of δ values for polymers

- 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

The solubility parameter of polymers can predict the polymer solvent and polymer-polymer miscibility as well and it requires the knowledge of solubility parameter values for the polymers. As we discussed the solubility parameter for the solvent can be directly obtained from the experiments, the value of molar enthalpy of vaporization and molar volume, but for polymers the enthalpy of vaporization cannot be measured. Polymers cannot be vaporized using higher temperature, since before that temperature of vaporization, the polymers easily get degraded. Hence it is experimentally not possible to determine the enthalpy of vaporization value for polymer samples. Hence, the solubility is maximum when δ_1 and δ_2 are equal. Using that concept, we can actually determine or predict the solubility parameter value for polymers indirectly. The value of solubility parameter of polymer can be taken equal to the solubility parameter value of the solvent in which the intrinsic viscosity is maximum for that particular polymer. Or if we are talking about polymer network or cross-linked polymer network, then the solvent in which the polymer is swelling to a maximum extent can be taken as the solubility parameter value of that particular solvent, same as the solubility parameter value of the polymer. However, the solubility parameter value of polymers can also be obtained indirectly by group contribution method, which we will discuss now.

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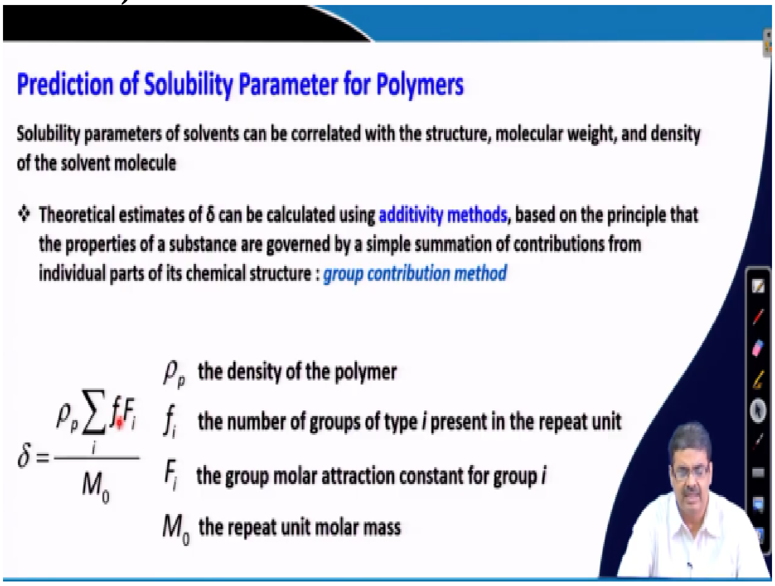

Prediction of Solubility Parameter for Polymers

Solubility parameters of solvents can be correlated with the structure, molecular weight, and density of the solvent molecule

- Theoretical estimates of δ can be calculated using additivity methods, based on the principle that the properties of a substance are governed by a simple summation of contributions from individual parts of its chemical structure : *group contribution method*

$$\delta = \frac{\rho_p \sum_i f_i F_i}{M_0}$$

ρ_p the density of the polymer

f_i the number of groups of type *i* present in the repeat unit

F_i the group molar attraction constant for group *i*

M_0 the repeat unit molar mass

Solubility parameter values of the solvents can be correlated with the structure, molecular weight and density of the solvent molecules. For the polymers, we can use this expression to estimate theoretically the value of solubility parameter following the principle that the property of a substance are governed by a simple summation of contribution from individual parts in this case different groups present in polymer of its chemical structure. Commonly we call this as group contribution method, which means, each group present in the substance, in this case polymer molecule, contributes and we get the value of the particular property by summing the values for all the groups present in the substance. This is the expression which is used to calculate the solubility parameter of polymer this can be used to calculate solubility parameter for solvent as well.

$$\delta = \frac{\rho_P \sum_i f_i F_i}{M_0}$$

Whereas, rho is the density of the polymer, M_0 is the repeat unit molar mass and F_i is the group molar attraction constant for that particular group i and f_i is the number of such group i present in the repeat unit.

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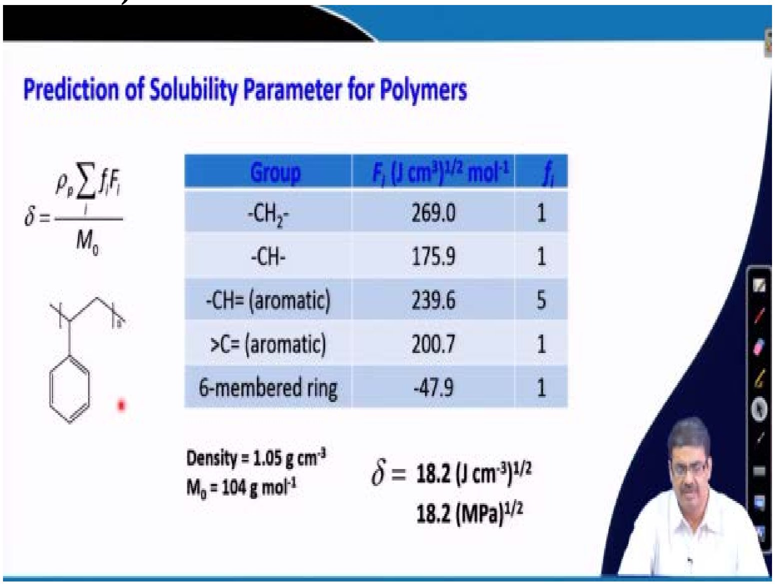

Prediction of Solubility Parameter for Polymers

$$\delta = \frac{\rho_p \sum_i f_i F_i}{M_0}$$

Group	F_i (J cm^3)$^{1/2}$ mol^{-1}	f_i
$-CH_2-$	269.0	1
-CH-	175.9	1
-CH= (aromatic)	239.6	5
>C= (aromatic)	200.7	1
6-membered ring	-47.9	1

Density = 1.05 g cm^{-3}
M_0 = 104 g mol^{-1}

δ = 18.2 (J cm^{-3})$^{1/2}$
18.2 (MPa)$^{1/2}$

For example, take the polymer polystyrene. Now, if we count the number of groups present in this repeat unit there is one CH_2 group, 1 CH group and these 5 aromatic CH groups double bonded and one aromatic C, plus we have a 6 membered ring. Now, each of these groups contribute some number for molar attraction constant which are available in literature. So, we can actually add all these numbers to get this expression and with the knowledge of the density of the polymer and molar mass of the repeat unit, we can get the solubility parameter. So, in this case, we can multiply f_i with this F_i and to sum to get this summation and density value we know and M_0, which is the molar mass of the repeat unit which is 104 grams per mole from that we can get the value as 18.2, you can do yourself and find out and verify this number and this is the unit.

This is SI unit, also sometimes we express this as Mega Pascal to the power 1/2. So, for any unknown polymer if we can count the number of groups present in the repeat unit and sum this molar attraction constant for all the groups present and also we can count this additional structural features like 6 membered ring in this particular case, present in the repeat unit then we can determine or calculate the value of solubility parameter provided we know the value of density of the polymer and the molar mass of the polymer repeat unit.

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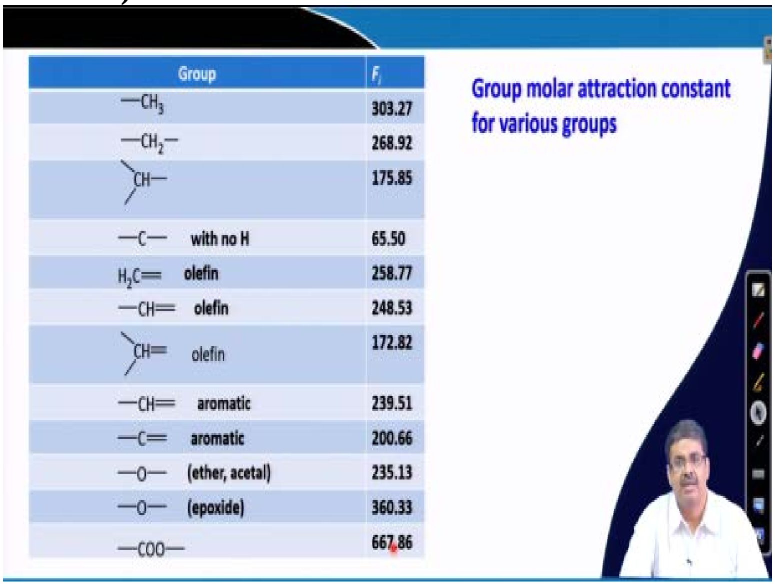

Group molar attraction constant for various groups

Group	F_i
$—CH_3$	303.27
$—CH_2—$	268.92
$>CH—$	175.85
$—C—$ with no H	65.50
$H_2C=$ olefin	258.77
$—CH=$ olefin	248.53
$>CH=$ olefin	172.82
$—CH=$ aromatic	239.51
$—C=$ aromatic	200.66
$—O—$ (ether, acetal)	235.13
$—O—$ (epoxide)	360.33
$—COO—$	667.86

These are some examples just to make you aware that these values are available in the literature. So, these are the functional groups or different groups which make a polymer molecule and corresponding molar attraction constant values are available in the literature.

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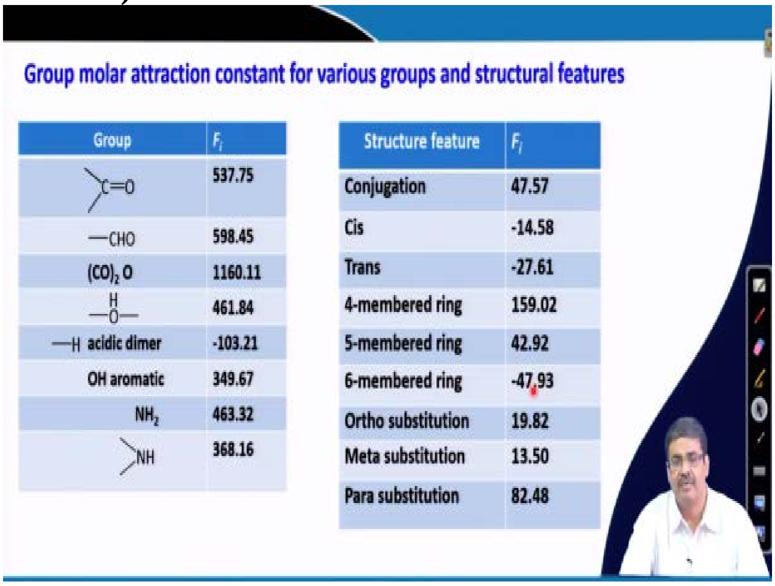

Group molar attraction constant for various groups and structural features

Group	F_i
$>C=O$	537.75
$—CHO$	598.45
$(CO)_2O$	1160.11
$—\overset{H}{O}—$	461.84
$—H$ acidic dimer	-103.21
OH aromatic	349.67
NH_2	463.32
$>NH$	368.16

Structure feature	F_i
Conjugation	47.57
Cis	-14.58
Trans	-27.61
4-membered ring	159.02
5-membered ring	42.92
6-membered ring	-47.93
Ortho substitution	19.82
Meta substitution	13.50
Para substitution	82.48

More values for different groups are shown and these are the structural features which you also need to include, while summing up all the molar attraction coefficients. If we have a conjugation like this, if we have cis, we have this contribution, 4 membered ring this, 6 membered ring as we as have just shown in the case of polystyrene.

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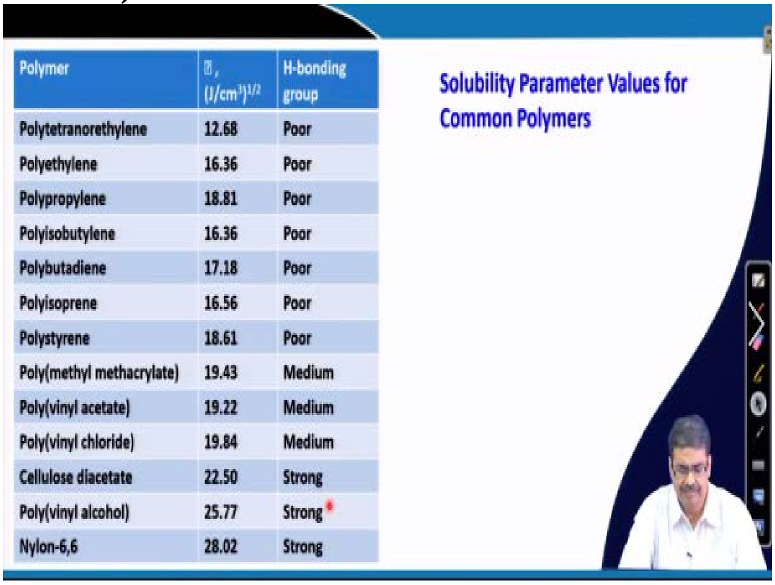

Solubility Parameter Values for Common Polymers

Polymer	▯, $(J/cm^3)^{1/2}$	H-bonding group
Polytetranorethylene	12.68	Poor
Polyethylene	16.36	Poor
Polypropylene	18.81	Poor
Polyisobutylene	16.36	Poor
Polybutadiene	17.18	Poor
Polyisoprene	16.56	Poor
Polystyrene	18.61	Poor
Poly(methyl methacrylate)	19.43	Medium
Poly(vinyl acetate)	19.22	Medium
Poly(vinyl chloride)	19.84	Medium
Cellulose diacetate	22.50	Strong
Poly(vinyl alcohol)	25.77	Strong
Nylon-6,6	28.02	Strong

Now, to find out, these are the values obtained for these polymers using this group contribution method, these are available in the literature and you can find from any standard textbook. Along with this value, the solubility parameter value, we also need to remember or keep in mind the hydrogen bonding capability of these polymers and these are generally estimated from the hydrogen bonding capability of the monomers from which the polymers are synthesized. For example, ethylene is a poor hydrogen bonding molecules so, polyethylene is also poor hydrogen bonding capability, vinyl acetate, vinyl chloride, they have medium hydrogen bonding capability and like polyvinyl alcohol, it has strong or nylon which has a strong hydrogen bonding capability.

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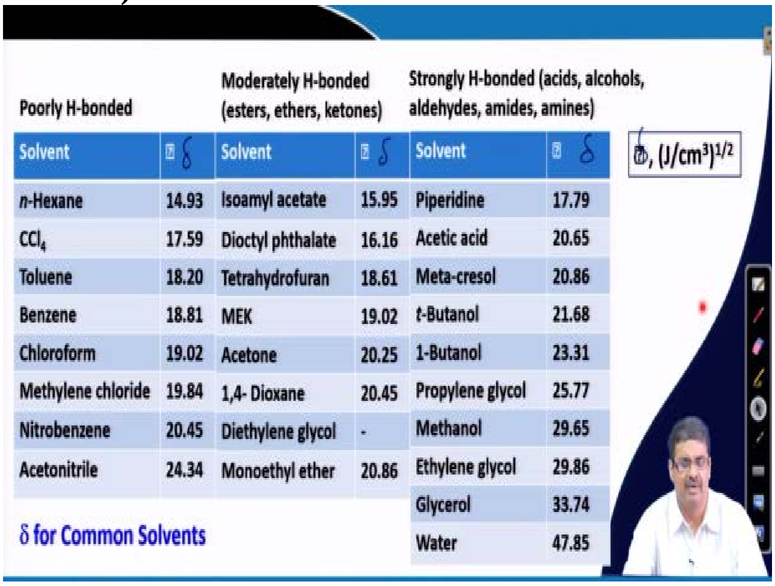

Poorly H-bonded

Moderately H-bonded (esters, ethers, ketones)

Strongly H-bonded (acids, alcohols, aldehydes, amides, amines)

Solvent	δ	Solvent	δ	Solvent	δ
n-Hexane	14.93	Isoamyl acetate	15.95	Piperidine	17.79
CCl_4	17.59	Dioctyl phthalate	16.16	Acetic acid	20.65
Toluene	18.20	Tetrahydrofuran	18.61	Meta-cresol	20.86
Benzene	18.81	MEK	19.02	*t*-Butanol	21.68
Chloroform	19.02	Acetone	20.25	1-Butanol	23.31
Methylene chloride	19.84	1,4- Dioxane	20.45	Propylene glycol	25.77
Nitrobenzene	20.45	Diethylene glycol	-	Methanol	29.65
Acetonitrile	24.34	Monoethyl ether	20.86	Ethylene glycol	29.86
				Glycerol	33.74
				Water	47.85

δ, $(J/cm^3)^{1/2}$

δ for Common Solvents

Similarly, we also need to find out or we need to be aware or keep in our mind the hydrogen bonding capability of the solvents also. For solvents, these are the values for solubility parameter δ, the value for solvent solubility parameter and generally solvents are arranged or classified into three types where some solvents are poorly hydrogen bonded, some are moderately hydrogen bonded and some are strongly hydrogen bonded.

Now, these classifications are done because we know like dissolve like. So, if we want to dissolve a non-polar polymer like which has a poor hydrogen bonding capability, then you should look for solvents, which also have poor hydrogen bonding capability and we will look for a solvent which has close value of solubility parameter of the polymer. If we want to find a solvent for a particular polymer we will basically match the solvent which the polymer in terms of hydrogen bonding capability, as well as, we will try to match the solubility parameter values close to each other. In that case, it is possible to find out a pair of polymer and solvent which will dissolve or which will be miscible with each other.

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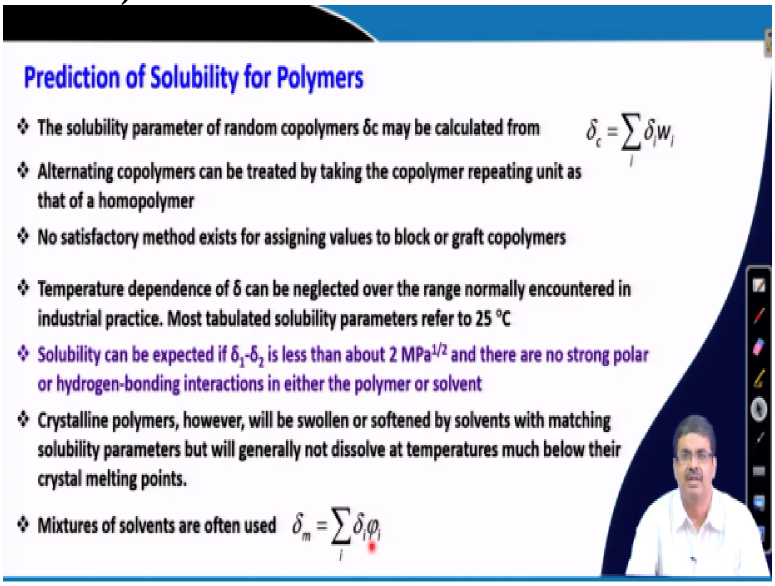

Prediction of Solubility for Polymers

- The solubility parameter of random copolymers δc may be calculated from $\delta_c = \sum_i \delta_i w_i$
- Alternating copolymers can be treated by taking the copolymer repeating unit as that of a homopolymer
- No satisfactory method exists for assigning values to block or graft copolymers
- Temperature dependence of δ can be neglected over the range normally encountered in industrial practice. Most tabulated solubility parameters refer to 25 °C
- Solubility can be expected if δ_1-δ_2 is less than about 2 MPa$^{1/2}$ and there are no strong polar or hydrogen-bonding interactions in either the polymer or solvent
- Crystalline polymers, however, will be swollen or softened by solvents with matching solubility parameters but will generally not dissolve at temperatures much below their crystal melting points.
- Mixtures of solvents are often used $\delta_m = \sum_i \delta_i \varphi_i$

$$\delta_c = \sum_i \delta_i w_i$$

So, the solubility parameter for a random copolymer can be calculated by this expression where this is solubility parameter for the individual homo-polymers and this is the weight fraction for the homo-polymers. We can find out the solubility parameter value for alternating copolymer, they may be considered as a 50-50 composition, but there is no satisfactory method exists for assigning value of solubility parameter to block or graft copolymers.

Generally, the temperature dependence of the solubility parameter can be neglected over the range normally encountered in industrial practice. Most of the solubility parameters which we discussed are and also reported in the literature are done at 25 ºC. As we mentioned that solubility can be expected if the difference between the solubility parameter of the solvent and of the solute, in this case polymer, is less than about 2 MPa$^{1/2}$.

There is no strong polar or hydrogen bonding interaction between either the polymer or the solvent. Crystalline polymers however, will be swollen and softened by the solvent with matching solubility parameter, but will generally not dissolve at temperature much below their crystal melting point. That is the reason polyethylene molecules are dissolved in solvent at higher temperatures like at 80 ºC where the temperature is close to the melting point of the polymer.

Sometimes, we can match the solubility parameter value of the solvent by combining more than one solvents and we can find out the solubility parameter of mixture of solvents by simply summing up their solubility parameter values multiplying by the volume fraction of that particular solvent and then summing up as shown here.

$$\delta_m = \sum_i \delta_i \varphi_i$$

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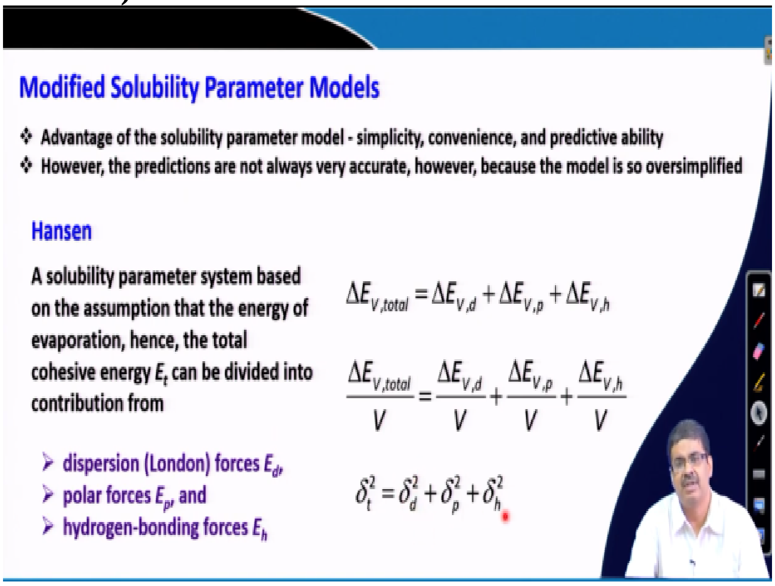

Modified Solubility Parameter Models

- ❖ Advantage of the solubility parameter model - simplicity, convenience, and predictive ability
- ❖ However, the predictions are not always very accurate, however, because the model is so oversimplified

Hansen

A solubility parameter system based on the assumption that the energy of evaporation, hence, the total cohesive energy E_t can be divided into contribution from

- ➤ dispersion (London) forces E_d,
- ➤ polar forces E_p, and
- ➤ hydrogen-bonding forces E_h

$$\Delta E_{V,total} = \Delta E_{V,d} + \Delta E_{V,p} + \Delta E_{V,h}$$

$$\frac{\Delta E_{V,total}}{V} = \frac{\Delta E_{V,d}}{V} + \frac{\Delta E_{V,p}}{V} + \frac{\Delta E_{V,h}}{V}$$

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$

Now, as we have seen that the advantage of solubility parameter model as proposed by Hildebrand is that it is simple, convenient and it has predictive ability, but the predictions are not always accurate because the model is very oversimplified. It does not consider negative value of ΔH_m. Now, later on Hansen has proposed another modification of solubility parameter by understanding that a solubility parameter system is based on the assumption that the energy of evaporation, hence, the total cohesive energy can be divided into three contributions, one is dispersion, London forces, polar forces and hydrogen bonding forces. Hence the total energy of vaporization can be divided into these three components, hence the cohesive energy density can be also divided into three components and the solubility parameter can also have three contributions, from dispersion forces, polar forces and hydrogen bonding forces. Now, there are ways which we can calculate or determine these values, which we are not discussing in this course.

$$\Delta E_{V,total} = \Delta E_{V,d} + \Delta E_{V,p} + \Delta E_{V,h}$$

$$\frac{\Delta E_{V,total}}{V} = \frac{\Delta E_{V,d}}{V} + \frac{\Delta E_{V,p}}{V} + \frac{\Delta E_{V,h}}{V}$$

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$

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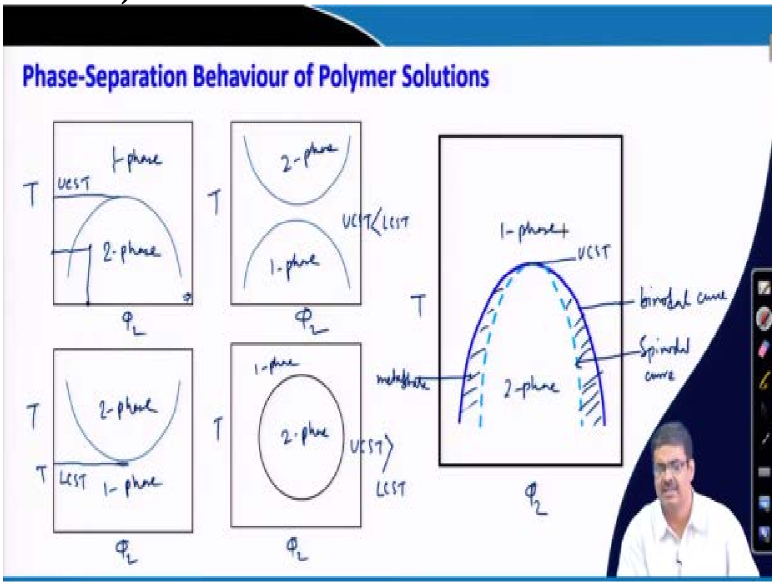

Phase-Separation Behaviour of Polymer Solutions

Next, we will move to the phase separation behavior of polymer solutions, and when we dissolve a polymer in a solvent and the solution can have these four possible phase behaviors. In this case, we are plotting temperature T with mole fraction of the polymer, for example, now 1 phase that means, the there is a miscible solvent and the region inside is a 2 phase. What does it mean? That if a composition with mole fraction the polymer in this region, any of these values will produce a miscible solution. Above this particular temperature, all the composition - any proportion of solvent and polymer will form a 1 phase system which means, it will be completely soluble system, it will make a solution.

Whereas, if you take point corresponding to a 2 phase system, that means it will be forming a polymer rich phase and a solvent rich phase. Now, the temperature above which all the composition of these polymer solvent system is miscible, we call this temperature as UCST upper critical solution temperature, which is defined as the temperature above which the polymer and the solvent is miscible in any proportion.

Similarly, in some cases it is the reverse scenario where below this temperature the polymer and the solvent is miscible in all proportions and we call these temperature as lower critical solution temperature defined as the temperature below which the polymer and the solvent is miscible in any proportion, there is a possibility that we can have either UCST is less than

LCST or UCST is greater than LCST. It is not that every polymer solvent system will have all these 4 phase possible phase behavior. This is an overall possible phase behavior for any combination of different polymer and solvent systems, this is general behavior, a particular solvent polymer pair may show one of this behavior or more than 1 behavior depending upon the particular pair we are discussing. In this case if we are just considering this UCST case, this is the temperature and this is the volume fraction of the polymer and this is UCST. We can also have this 2 lines which is called binodal curve and this is called spinodal curve and this region is actually a metastable region, and this is 2 phase and this is 1 phase system. Now, we will try to use polymer Flory Huggins equation to basically derive this or explain this type of phase behavior.

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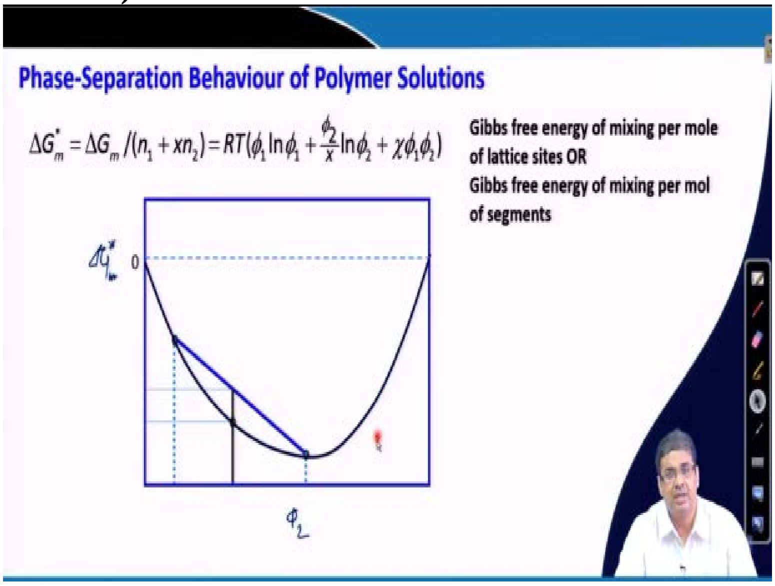

Phase-Separation Behaviour of Polymer Solutions

$\Delta G_m^* = \Delta G_m/(n_1 + xn_2) = RT(\phi_1 \ln\phi_1 + \frac{\phi_2}{x}\ln\phi_2 + \chi\phi_1\phi_2)$

Gibbs free energy of mixing per mole of lattice sites OR

Gibbs free energy of mixing per mol of segments

$$\Delta G_m^* = \Delta G_m/(n_1 + xn_2) = RT\left(\phi_1 \ln \phi_1 + \frac{\phi_2}{x} \ln \phi_2 + \chi\phi_1\phi_2\right)$$

This is Gibbs free energy of mixing per mole of lattice sites or we can describe this term as a Gibbs free energy of mixing per mole of segment and we can get this by dividing the Gibbs free energy of mixing by total number of segments, polymers segments plus the solvent molecules and this is given by this expression from Flory Huggins equation. Now, there could be 2 general types of variation of ΔG_m* with polymer volume fraction in a solution and first one is of this type. In this case, we are plotting ΔG_m* in Y axis and polymer mole fraction in X axis. Now, if you consider a point here, see in this case, the point here is to know whether the composition corresponds to this mole fraction, volume fraction of polymer in the solution, whether it is stable solution or not. For that, let us imagine that this solution will phase separate into 2 different solutions one with solvent rich, and another will be polymer rich and we can choose any 2 such composition for example, let us choose these 2 composition.

So, this is solvent rich and this is a polymer rich phase. Now, to know whether this composition will spontaneously phase separate and form these 2 compositions, we can find out jn the following way. First, we need to draw a straight line connecting these 2 points, which is called tie line and then, we need to draw a vertical line passing through this point. So, we draw this line and the intersection point between this tie line and this vertical line passing through this point.

We should compare the ΔG_m* value to this point corresponding to these original points. So, we can compare these 2 points. Now, for going from this composition to these 2 compositions the ΔG_m is actually becoming higher which means, this is not a spontaneous phenomenon, which means that a polymer solution of this composition is a stable solution. We can think in the same logic for all these points across this composition, which means for this type of behavior, the polymer is soluble in all proportions with the solvent.

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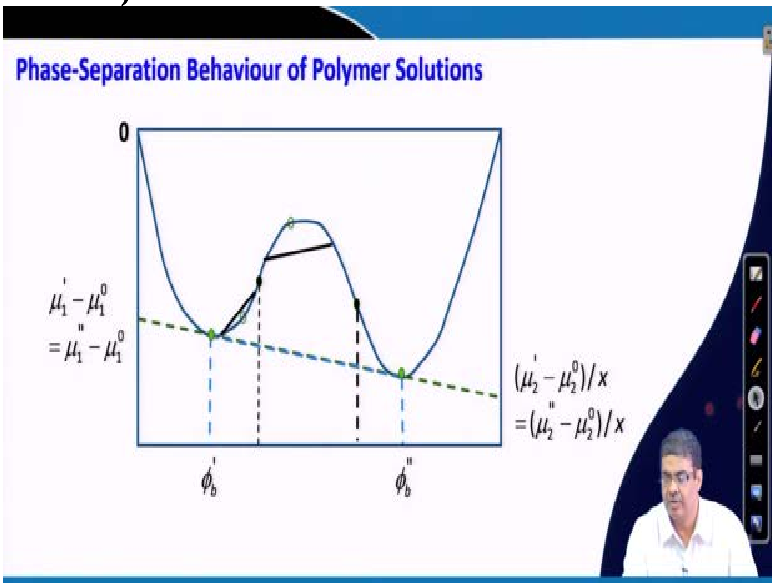

Phase-Separation Behaviour of Polymer Solutions

Now, there is another possibility, where again we plot ΔG_m* with the mole fraction and this is a possibility. Obviously, the compositions below this point is stable as we discussed in the last slide. Similarly, compostions beyond this point are also stable. Now, let us compare the situation or let us consider a situation a polymer solution having a mole fraction, or volume fraction of the polymer corresponds to this point.

Now, if this has to phase separate between say these 2 points, we can draw a tie line and from the same logic which we have given in the last slide, we know that this is a stable composition which means, the polymer is soluble in the solvent for this particular composition, because, this the intersection between the tie line and this vertical line through this point will have ΔG_m positive value.

Now, let us consider another point here, for this if we consider that it phase separates between this point and this point, then in this particular case ΔG_m will actually come down if it is phase separates, which means a polymer solution containing this composition will spontaneously phase separate to a polymer rich phase and a solvent rich phase. Now, it will stop where? It will phase separate till these 2 points which corresponds to the minimum of these curve.

Now, why it will not phase separate further or these 2 points correspond to equilibrium composition. These are the 2 compositions which should be the phase separated equilibrium concentration which have corresponding volume fraction values, we call these phase as single prime and these phase as double prime and these are the volume fraction of the polymer corresponds to these 2 points.

Now, it can be shown that this line if we extend upto $\phi_2 = 0$ point which means, the intersection of this tangent to this point and Y axis will correspond to these ΔG_m value which is for this particular point it is given by $\mu_1' - \mu_1^0$. Similarly, for this particular point, we can write this as $\mu_1'' - \mu_1^0$. Now, because this is a common tangent, it means that these 2 terms would be equal which also means that $\mu_1' = \mu_1''$ which means, the chemical potential of solvent for this composition is same as chemical composition of the solvent in this composition which means, they are in equilibrium. Similar logic can be given for the polymer also in this case also we can write that $\mu_2' = \mu_2''$, which means, the chemical potential of polymer for this particular composition is same as this particular composition which means these 2 phases are in equilibrium. Now, if you consider this point, which is the inflection point, then all the compositions between these equilibrium points, and this inflection point, are actually metastable situation because if somehow we can apply more energy, it phase separates beyond this point, then it will spontaneously phase separate and come to these 2 equilibrium phases.

So, the region in this area and also correspondingly this composition is actually metastable, because if we apply enough energy, so that the composition moves beyond this then it will spontaneously phase separate to this equilibrium points. So, these points we call spinodal points and these 2 equilibrium points we call binodal points. If we increase the temperature or decrease the temperature obviously, the nature of this curve will change and let us consider how it can change and what will be the effect of temperature on these binodal points and spinodal points.

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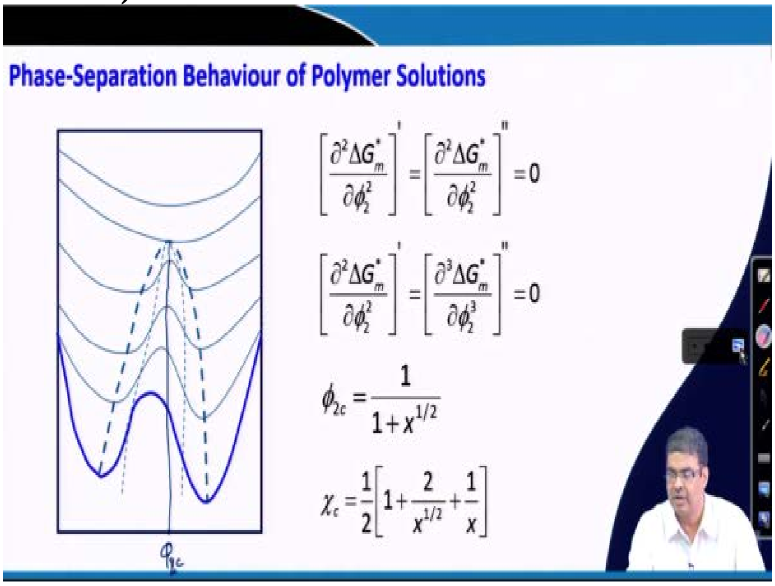

Phase-Separation Behaviour of Polymer Solutions

$$\left[\frac{\partial^2 \Delta G_m^*}{\partial \phi_2^2}\right]' = \left[\frac{\partial^2 \Delta G_m^*}{\partial \phi_2^2}\right]'' = 0$$

$$\left[\frac{\partial^2 \Delta G_m^*}{\partial \phi_2^2}\right]' = \left[\frac{\partial^3 \Delta G_m^*}{\partial \phi_2^3}\right]'' = 0$$

$$\phi_{2c} = \frac{1}{1 + x^{1/2}}$$

$$\chi_c = \frac{1}{2}\left[1 + \frac{2}{x^{1/2}} + \frac{1}{x}\right]$$

So, we this is the graph we described and if we increase the temperature, then the nature of the curves changes and at some temperature this curve corresponds to the first type of curve which we discussed a few minutes back which means for this temperature the polymer is soluble in the solvent in all proportion whereas, for this particular curve the polymer is soluble beyond this point. Whereas, at intermediate point this is metastable and in this region, this is actually not soluble. So, we have 2 phases in this region, and this region we have 1 phase. So, this is 1 phase and this is 1 phase and this is a region we have 2 phases situation and these are the binodal points and these are the spinodal points. Now, similarly, we have binodal points for these all the other curves and spinodal points for all other curves as well.

So, if we can connect these spinodal points and binodal points, this gives you the phase diagram where we are plotting temperature versus volume fraction. So, beyond this temperature the polymer is soluble in the solvent at all proportions, but, when the temperature goes below this particular temperature, then this phase separates depending upon the volume fraction of the polymer in solution, if the volume fraction is either left side of this curve or right sides of this cure, then it remains soluble, but if it is in between, then it phase separates whereas, this region is actually metastable region and we call this temperature as UCST upper critical solution temperature. Now, for these inflection points, we can write this expression and for the critical points, because it is the spinodal curve is turning around in this, in this point.

$$\left[\frac{\partial^2 \Delta G_m^*}{\partial \phi_2^2}\right]^{I} = \left[\frac{\partial^2 \Delta G_m^*}{\partial \phi_2^2}\right]^{II} = 0$$

$$\left[\frac{\partial^2 \Delta G_m^*}{\partial \phi_2^2}\right]^{I} = \left[\frac{\partial^3 \Delta G_m^*}{\partial \phi_2^3}\right]^{I} = 0$$

$$\phi_{2c} = \frac{1}{1 + x^{1/2}}$$

$$\chi_c = \frac{1}{2}\left[1 + \frac{2}{x^{1/2}} + \frac{1}{x}\right]$$

We can write this expression and from the expression of ΔG_m^*, as we have written in few slides back, we can get, we can get this expression where this is the critical concentration or critical volume fraction, which basically corresponds to this so, this is ϕ_2. So, this is the critical concentration and which is given by this expression x is the number of fragments in 1 polymer chain. Similarly, we can also get the critical value of polymer solvent interaction parameter from this expression by solving these equations.

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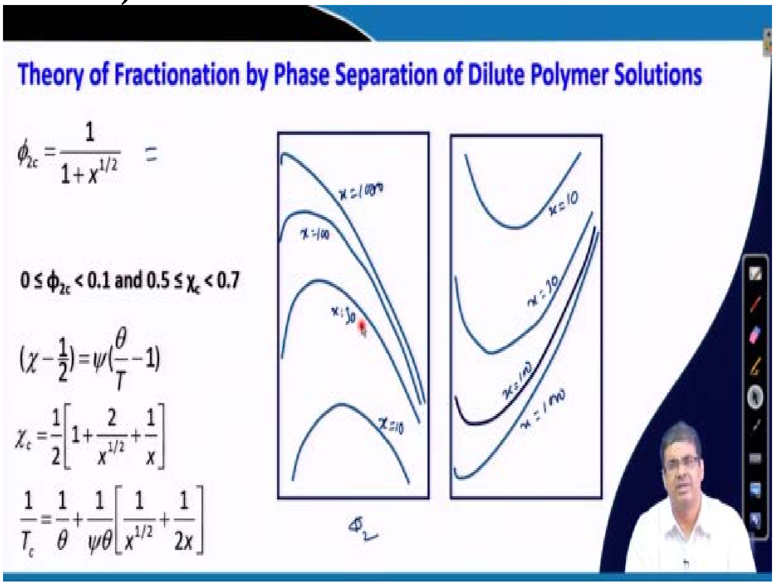

Theory of Fractionation by Phase Separation of Dilute Polymer Solutions

$\phi_{2c} = \frac{1}{1+x^{1/2}}$ =

$0 \le \phi_{2c} < 0.1$ and $0.5 \le \chi_c < 0.7$

$(\chi - \frac{1}{2}) = \psi(\frac{\theta}{T} - 1)$

$\chi_c = \frac{1}{2}\left[1 + \frac{2}{x^{1/2}} + \frac{1}{x}\right]$

$\frac{1}{T_c} = \frac{1}{\theta} + \frac{1}{\psi\theta}\left[\frac{1}{x^{1/2}} + \frac{1}{2x}\right]$

$$\phi_{2c} = \frac{1}{1 + x^{1/2}}$$

$$\left(\chi - \frac{1}{2}\right) = \psi\left(\frac{\theta}{T} - 1\right)$$

$$\chi_c = \frac{1}{2}\left[1 + \frac{2}{x^{1/2}} + \frac{1}{x}\right]$$

$$\frac{1}{T_c} = \frac{1}{\theta} + \frac{1}{\psi\theta}\left[\frac{1}{x^{1/2}} + \frac{1}{2x}\right]$$

Now, we know that the critical volume fraction is considered here. x is number of fragments which is proportional to the molecular weight, so, x is proportional to the molecular weight of the polymer. If I write M as molecular weight, then $x^{1/2}$ be proportional to $M^{1/2}$ and if x is large as the molecular weight is very high, then we can simply ignore this 1 and we can take ϕ_{2c} proportional and to 1 over $M^{1/2}$.

So, as the polymer size increases, this critical volume fraction actually comes down and for a normal size polymer which is beyond say 100,000 or 50,000, the typical value of critical volume fraction comes between 0 to 0.1 and critical value for these polymer solvent interaction parameters comes in this range. If we change the size of the polymer, we get lower value of the critical polymer fraction. So, as the size increases, as predicted from this expression, the critical volume fraction actually reduces. Similarly, if we consider a situation where we are talking about lower critical solution temperature, then also we can get similar behavior.

So, this would be for a LCST type polymer behavior in this case. Also the critical volume fraction of polymer for phase separation actually comes down in value. Now, we can correlate from this expression to find out the polymer solvent interaction parameter and from that we can also find out the relation between the critical temperature and θ temperature and entropy factor from this expression. We can actually use this principle for fractionating polymers. So, if we have a polymer solution, then if we reduce the temperature in case of a UCST type behavior or we add non-solvent, then at the beginning the polymers having large molecular weight actually phase separate and when we reduce the temperature further or if we keep on adding the non solvent, then next sized polymer actually gets fractionated.

So, in practice, to a polymer solution, an appropriate non solvent is added just to bring the start of phase separation and once that happened, the temperatures increased a little bit to make the solution clear and then slowly that temperature is reduced to phase separate out the different fractions. Also the polymer solution is poured on top of a column having glass beads which are having different temperature. As we go down the column, the temperature generally comes down which helps to collect different fraction of polymers. So, this is the way typically we do polymer fractionation. With this we come to end of this lecture in next lecture, we xwill start chain dimension.