Polymeric Materials of Different Kind
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Lecture - 29
Blends II

Hello we have discussed a lot about macromolecular nature and its complicated behavior based on the giant molecule that it is over and above the tunability aspect of macromolecular system is what leads so many applications based on it. And therefore we are discussing polymer materials of different kinds and in the last lecture we looked at the blends and their definitions and so in this lecture we will try to look at some of the properties associated with blends and mainly the thermodynamics of mixing.

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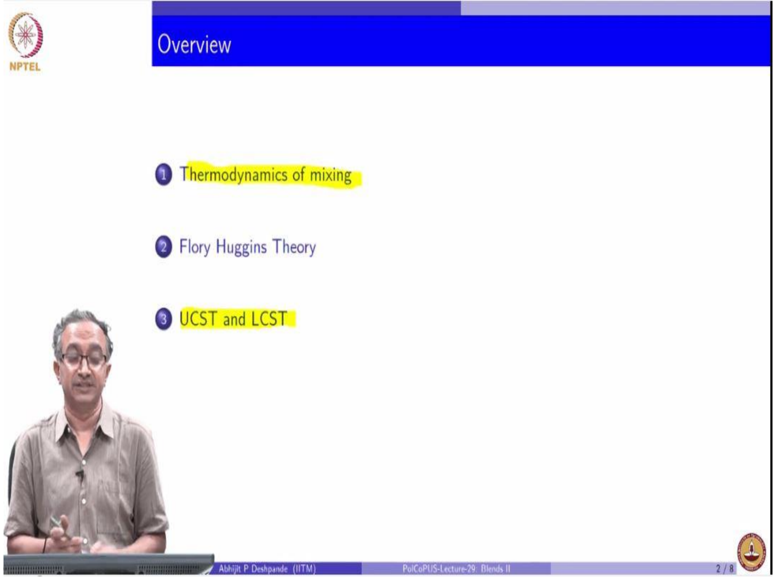

Overview

1. Thermodynamics of mixing
2. Flory Huggins Theory
3. UCST and LCST

So therefore we will begin by looking at thermodynamic aspects of looking at free energy of mixing for a blend systems and understanding the basic Flory Huggins theory which is proposed for understanding the miscibility of 2 polymer systems. And then finally we will end with looking at critical temperatures which are present which demarcate the boundary between miscible and partial miscible and immiscible regions in a polymeric blend system.

Some of these are also similar to small molecular systems. So from a thermodynamic point of view the theories are very similar depending on the nature of molecules and the interactions the details. So what constitutes for example the energy internal energy of interaction or enthalpy of interaction between molecules may change from one system to the other. Similarly the entropy of mixing may change depending on the type of molecule we have because the arrangement of the molecule for example in case of macromolecule we have a very large molecule.

So the way different monomers will organize themselves with the constraint of covalent bond between different monomers is different compared to all these monomers were separate objects. So therefore the details regarding the entropy and enthalpy of mixing will differ for polymers compared to small molecules however the broad framework of analysis of thermodynamics remains largely similar.

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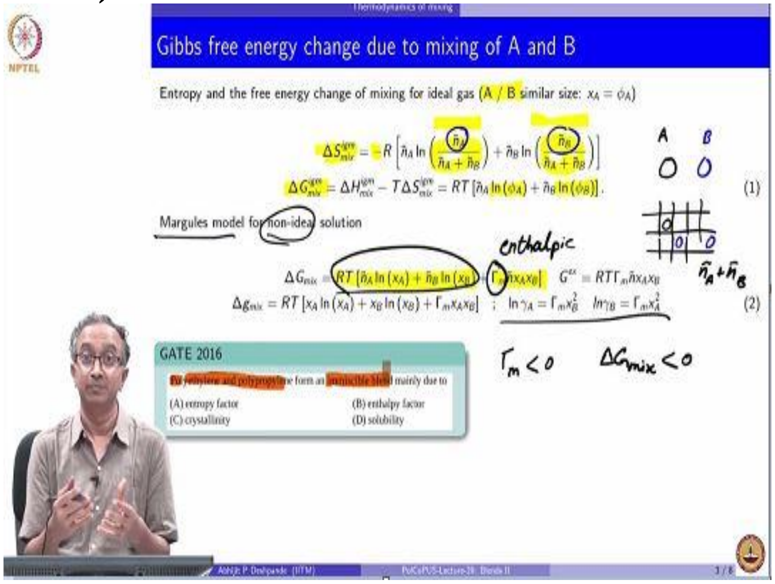

Thermodynamics of mixing

Gibbs free energy change due to mixing of A and B

Entropy and the free energy change of mixing for ideal gas (A / B similar size: $x_A = \phi_A$)

$$\Delta S^{igm}_{mix} = -R\left[\tilde{n}_A \ln\left(\frac{\tilde{n}_A}{\tilde{n}_A+\tilde{n}_B}\right) + \tilde{n}_B \ln\left(\frac{\tilde{n}_B}{\tilde{n}_A+\tilde{n}_B}\right)\right]$$

$$\Delta G^{igm}_{mix} = \Delta H^{igm}_{mix} - T\Delta S^{igm}_{mix} = RT\left[\tilde{n}_A \ln(\phi_A) + \tilde{n}_B \ln(\phi_B)\right]. \qquad (1)$$

Margules model for non-ideal solution

enthalpic

$$\Delta G_{mix} = RT\left[\tilde{n}_A \ln(x_A) + \tilde{n}_B \ln(x_B) + \Gamma_m \tilde{n} x_A x_B\right] \quad G^{ex} = RT\Gamma_m \tilde{n} x_A x_B$$

$$\Delta g_{mix} = RT\left[x_A \ln(x_A) + x_B \ln(x_B) + \Gamma_m x_A x_B\right] \;;\; \ln\gamma_A = \Gamma_m x_B^2 \quad \ln\gamma_B = \Gamma_m x_A^2 \qquad (2)$$

$\tilde{n}_A + \tilde{n}_B$

$\Gamma_m < 0 \qquad \Delta G_{mix} < 0$

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Polyethylene and polypropylene form an immiscible blend mainly due to

(A) entropy factor (B) enthalpy factor

(C) crystallinity (D) solubility

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So for example ideal gas mixing is something which we have seen from various physical chemistry and chemical physics courses where the entropy of mixing is basically given by the mole fraction of A and B. And if you notice this this is a negative quantity and since this is a fraction mole fraction this is less than 1. And so logarithmic of mole fractions will be negatives and so therefore entropy of mixing will always be positive and so we know that ideal gases will always mix with each other.

And the other hand the free energy of mixing is always negative because both of these quantities are individually negative and therefore ideal gases are always miscible with each other. Now this kind of a problem can be looked at as a problem of probability and combinatorics so you have 2 objects A and B. So let us say we could think in terms of 2 balls so if we have let us say ball A and then we have ball B and we have some numbers of them so in this case for example n A and n B are the numbers of these balls and then what we have is a this is called lattice theory.

So we have certain slots and then we could put each of these balls in each of these slots so now basically the total number of such slots available of course are let us say $n_A + n_B$. So this is the total number of slots and n_A and n_B is the number of individual molecules of A and B so then what is different number of ways in which we can distribute these objects in these slots. So it is a problem of combinatorics and the answer to this ΔS comes from analysis.

You basically get a binomial distribution and if n_A and n_B is large then we can show that it will be a gaussian distribution based on which we can then find what is ΔS. So generally this is only valid for ideal gases where A and B do not interact with each other so they are in they can both occupy slots which are same also if there is an A molecule. The probability of B being next to it is the same as probability of A being next to it so therefore in this case the probability of observing A or B on any slot is equally there.

But if let us say B likes to interact more with B and A likes to interact more with A then what will happen is in that case it is more likely that neighbor of B is likely to be B so this is a situation where there is interaction. And so in that case the overall Gibbs free energy of change has the entropic contribution and it also has an enthalpic contribution or internal energy of interactions. So this is the enthalpic contribution and this Γ_m is a parameter which tells us how much is the interaction if Γ_m is 0.

This is a simple model called Margules model of a non-ideal mixing between A and B. And so those of you who have done activity studies earlier will be quickly able to see that activity coefficient for such non-ideal systems are related to the compositions and this parameter Γ_m if Γ_m is 0 then we have an ideal system the other thing to notice here is if Γ_m is negative or positive if gamma is negative then what happens is ΔG will always be negative.

Because the term related to entropy is anyway negative so if gamma m is negative overall

ΔG_{mix} is negative. So clearly systems will be miscible so gamma m negative implies that A and B interact favorably with each other so if there is a B then it is more likely that A will be next to it. And so this is something for us to just ponder about as to why poly propylene and polyethylene form a immiscible blend given that interactions between them are very similar and this is something for you to ponder about.

Because if we have ideal gases where there is not much interaction or similar in so in that case the molecules like to mix but why is it that in case of polyethylene and polypropylene there is a tendency to form immiscible blends.

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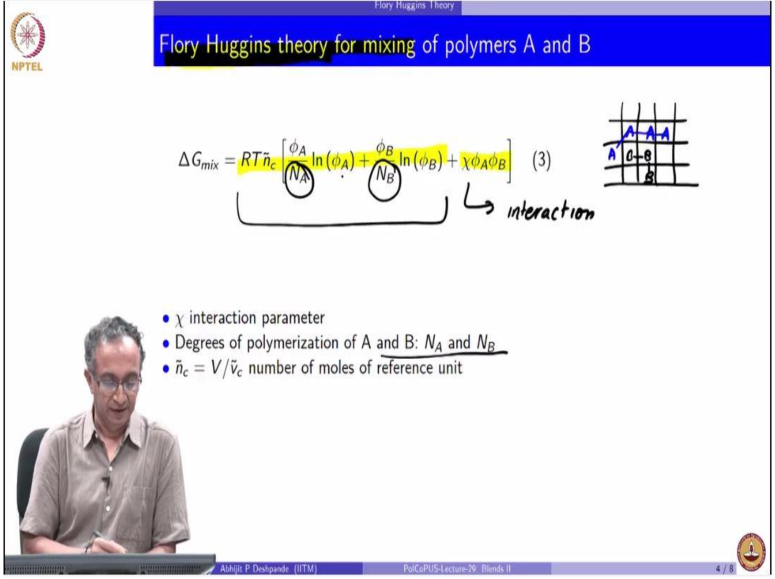

Flory Huggins Theory

Flory Huggins theory for mixing of polymers A and B

$$\Delta G_{mix} = RT\tilde{n}_c\left[\underbrace{\frac{\phi_A}{N_A}\ln(\phi_A)+\frac{\phi_B}{N_B}\ln(\phi_B)}+\underbrace{\chi\phi_A\phi_B}_{\text{interaction}}\right] \quad (3)$$

- χ interaction parameter
- Degrees of polymerization of A and B: N_A and N_B
- $\tilde{n}_c = V/\tilde{v}_c$ number of moles of reference unit

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So we can look at this by looking at the Flory Huggins expression similar to what I talked about in terms of a lattice. So if we have a lattice where there are many slots and there is a molecule A so there is A and then there is a covalent bond and A and then covalent bond and A. So what you can see is in this case because of the covalent bond of A and A there is a chain of A. The neighborhood cannot all be B one of the neighbor has to be A.

Because the A chain is continuing so therefore if B chain is there then there is a very limited set of slots which B can occupy because again there is a constraint of B being bonded to B. And then of course there is a chain of A which is also there so if you again do statistics of this distribution of how A and B will fit together in such slot. And that is what was done by Flory Huggins decades ago in terms of the lattice theory we come up with a very similar expression to what we saw for mixing of ideal gas.

So this is the entropic contribution and this is the enthalpy contribution. And just like gamma m we saw this χ interaction parameter is tells us about interaction between A and B if this is 0 then we fall back on basically only the entropy contribution. Now one of the things that you notice is that N_A and N_B these are nothing but degree of polymerization or it is the length of the macromolecule. And in case of macromolecules clearly this is a large number degree of polymerization or number of repeating units can be in 1000s.

So therefore you can see that this term is going to be exceedingly small because $\log\varphi_B$ and $\log\varphi_A$ are basically logarithms of volume fractions and volume fraction can vary between 0 and 1. So therefore the entropic contribution is extremely minimal in case of mixing of macromolecules. And so any amount of interaction which is not favorable will immediately induce immiscibility in macromolecular system that is the reason polyethylene polypropylene are also immiscible.

So unless we have on the 2 chains some molecules which will favorably interact with each other like we saw in case of polystyrene and polyphenylene oxide the miscibility is generally not present.

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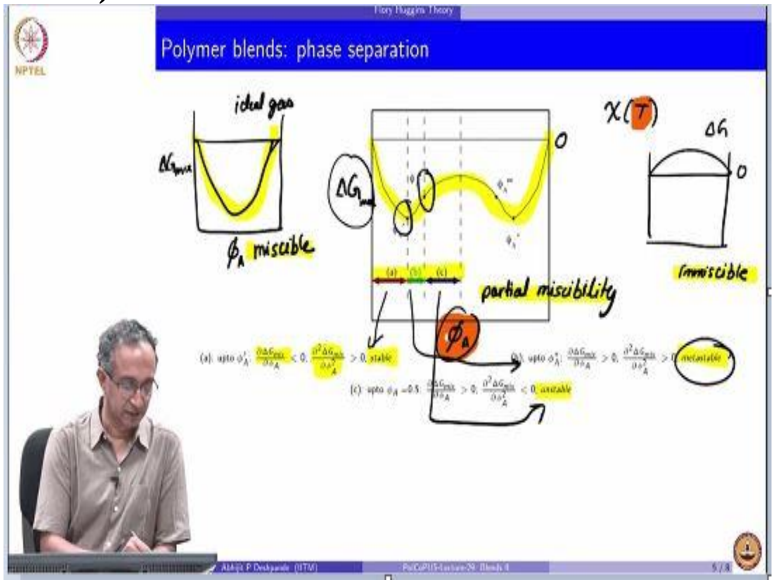

Flory Huggins Theory

Polymer blends: phase separation

(a): upto ϕ_A': $\frac{\partial \Delta G_{mix}}{\partial \phi_A} < 0$, $\frac{\partial^2 \Delta G_{mix}}{\partial \phi_A^2} > 0$, stable

(b): upto ϕ_A'': $\frac{\partial \Delta G_{mix}}{\partial \phi_A} > 0$, $\frac{\partial^2 \Delta G_{mix}}{\partial \phi_A^2} > 0$, metastable

(c): upto $\phi_A = 0.5$: $\frac{\partial \Delta G_{mix}}{\partial \phi_A} > 0$, $\frac{\partial^2 \Delta G_{mix}}{\partial \phi_A^2} < 0$, unstable

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So this can be also shown on a plot where we have ΔG the Gibbs free energy of mixing being plotted as a function of volume fraction of one of the substances and depending on the Flory Huggins expression. And where the χ is so χ is a strong function of temperature and this is understandable. Because if we change the temperature we can manipulate the miscibility basically temperature changing is with respect to the interactions between the 2 macromolecules.

And the more the thermal energy is and the interaction in relation to that thermal energy will determine whether miscibility is present or not. And χ can increase with temperature or decrease with temperature also so that gives you a hint that polymer mixing may be enhanced when you increase the temperature or polymer mixing may be actually decreased when you increase the temperature. So in these cases of mixing when we have ΔG of mix for a ideal gas mixture the behavior is just like this so this is for ideal gas.

So you can see that for all proportions of φA ΔG is negative. So in case of a polymer blend with partial miscibility also what you can see is ΔG is negative throughout. Because this is the 0 value and so ΔG is negative throughout but the shape is interesting so not only the magnitude of ΔG which is required to be negative for mixing to be spontaneous. But we also need to look at the first derivative and second derivative.

So whether there is a maximum or minimum and also what is the curvature of ΔG and this determines what is the nature of miscibility in the system. So if it is like this then this is a perfectly miscible system if the ΔG is like this then this is partial miscible. And we can have a situation where ΔG is completely positive so this is an immiscible system so therefore depending on the quantity of χ we can achieve all of these 3.

And therefore interaction between polymer A and B determines whether we have a miscible system partially miscible system or an immiscible system. So Flory Huggins theory is a very useful theory to try to understand these different regimes of behavior shown by different polymeric system and we can analyze this also from the point of stability so those of you who have learned about the concept of stability based on looking at the curvature you can understand this that we can split the overall region into 3 regions A B and C.

Where A is the stable region so that means any mixing of A and B in this region will lead to complete miscibility but if you have B and C then there is a partial miscibility observed and B state is fairly important in terms of its metastable state which means if we do not disturb the sample then it is possible for us to maintain the mixing but as soon as there is a small fluctuation. And in all real systems there are always small fluctuations the partial miscibility will set in and we will get A rich and A lean phase.

And of course in case of C region we have basically unstable so we will get phase separation of A rich and A lean phases. And so if you see here what are being denoted are these points so one which is the basically denotes between A and B the demarcation. So that is really the boundary of phase separation so we can plot this information of this diagram instead of plotting it with ΔG and φ we could plot it with respect to φ and temperature and this is called the phase diagram in terms of temperature and composition.

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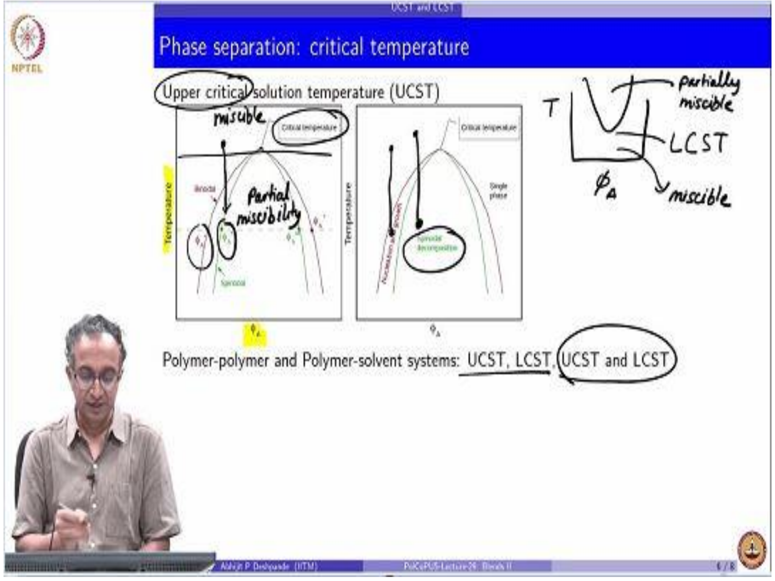

UCST and LCST

Phase separation: critical temperature

Upper critical solution temperature (UCST)

Polymer-polymer and Polymer-solvent systems: UCST, LCST, UCST and LCST

And generally this is how the phase diagram looks like so where we are plotting temperature as a function of the φ_A and what we do is all the points which were there on the previous slide. Because as soon as you change χ then ΔG will keep on changing and so we will get different family of these curves and so for each of them we can denote for at each and every temperature we can note the φ and construct the phase diagram.

And then what we see is in phase diagram we can recognize a region which is completely miscible. Then there is a region where there is partial miscibility or it is also called miscibility gap and the φ is φ' and φ*. That we had mentioned φ* is where there is an inflection point or the curvature changes and φ_A' is where there was a minimum in Gibbs free energy. So if I prepare a blend here and then start lowering the temperature basically a miscible blend will go to a partially miscible blend.

And so this is the temperature above which miscibility is there no matter what composition I mix. So that is why it is called a critical temperature and since it is a higher temperature it is also called an upper critical temperature which implies that in many polymeric systems you may have a phase diagram which looks like this so temperature as a function of composition you will have what is called an LCST or lower critical solution temperature.

So in this case lower temperature is where there is miscible behavior. And when you increase the temperature this becomes partially miscible so polymeric solvent system or 2 polymeric systems all these behaviors are possible that we may have UCST or LCST alone it is also possible that we have a combination of both UCST as well as LCST. And what is critical from a polymer application point of view is we our target is to achieve a certain set of properties by mixing polymer A and B.

And it is of our interest to know how A and B are distributed in the final engineering part that is going out. And this will be depending on how does the phase separation happen? So, for example if I take a polymer sample and cool it suddenly to this where there is unstable behavior and we will get what is called spinodal decomposition. Where everywhere simultaneously phase separation will happen. And we generally will get a co-continuous phase or if I cool the sample to a region where there is Meta stability.

Then generally what we get is nucleation and growth. So few points the phase separation will start happening and it will grow so nucleation and growth so in the end the final polymer part will have signatures of what was the phase separation mechanism.

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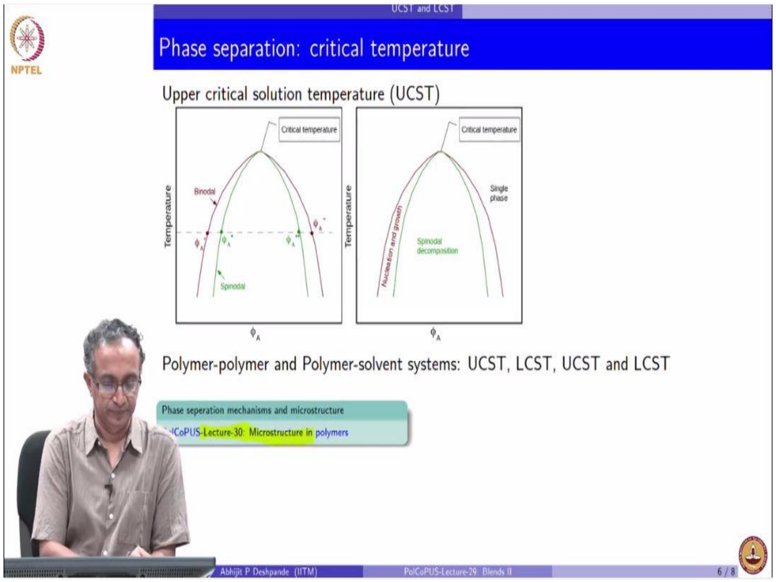

UCST and LCST

Phase separation: critical temperature

Upper critical solution temperature (UCST)

Polymer-polymer and Polymer-solvent systems: UCST, LCST, UCST and LCST

Phase seperation mechanisms and microstructure

lCoPUS-Lecture-30: Microstructure in polymers

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So this is something which is of great interest from an application point of view and this is what we will see in the lecture on microstructure in polymeric systems.

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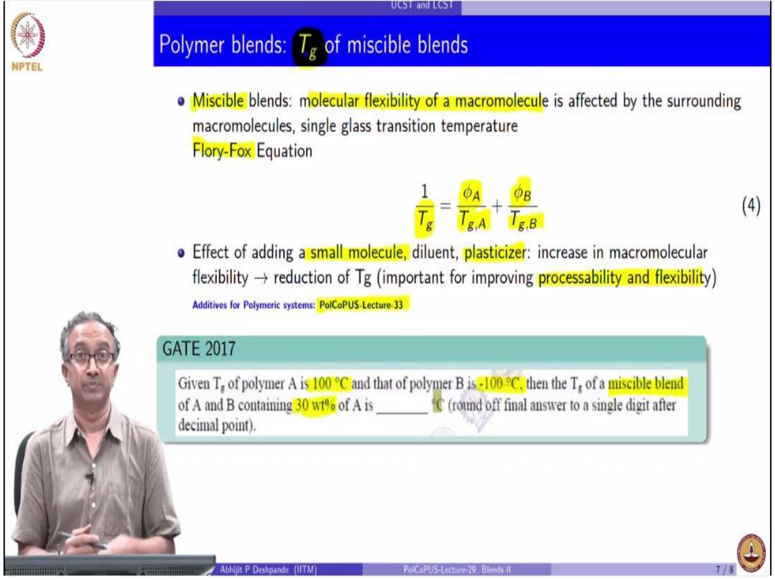

UCST and LCST

Polymer blends: T_g of miscible blends

- Miscible blends: molecular flexibility of a macromolecule is affected by the surrounding macromolecules, single glass transition temperature
  Flory-Fox Equation

$$\frac{1}{T_g} = \frac{\phi_A}{T_{g,A}} + \frac{\phi_B}{T_{g,B}} \tag{4}$$

- Effect of adding a small molecule, diluent, plasticizer: increase in macromolecular flexibility → reduction of Tg (important for improving processability and flexibility)

Additives for Polymeric systems: PolCoPUS-Lecture-33

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Given T_g of polymer A is 100 °C and that of polymer B is -100 °C, then the T_g of a miscible blend of A and B containing 30 wt% of A is _______ °C (round off final answer to a single digit after decimal point).

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So let us close this lecture by finally looking at the miscible system itself once more and looking at how do we estimate the properties and one important characteristic as we have already seen is the glass transition temperature. And since if it is a miscible blend a molecular flexibility of molecule is basically surrounded affected by the other molecule. And so if we have a glass transition temperatures of A and B we can have the glass transition temperature of mixture in proportion to whatever volume fractions we are adding and this is called a Flory-Fox equations.

And there are several other empirical relations also available semi-empirical theoretical relations because estimating the segmental mobility of a macromolecular system is of paramount importance from an application point of view so generally we can add a small molecule and again use similar phenomena as I have mentioned. Miscibility in a polymer-polymer solvent and polymer solvent system the basic framework remains the same and so what is called a plasticizer.

We will again discuss it is an important additive which is added in many polymeric systems to improve processability and flexibility. So the idea of adding polymers and then estimating properties is very standard and so for example in this question the T_g of 2 polymers pure polymers is given and then it is mentioned that it is a miscible blend. And it contains 30 percent of A so then what is the glass transition temperature so therefore we can use equations of Fox-Flory or other equations to try to estimate this.

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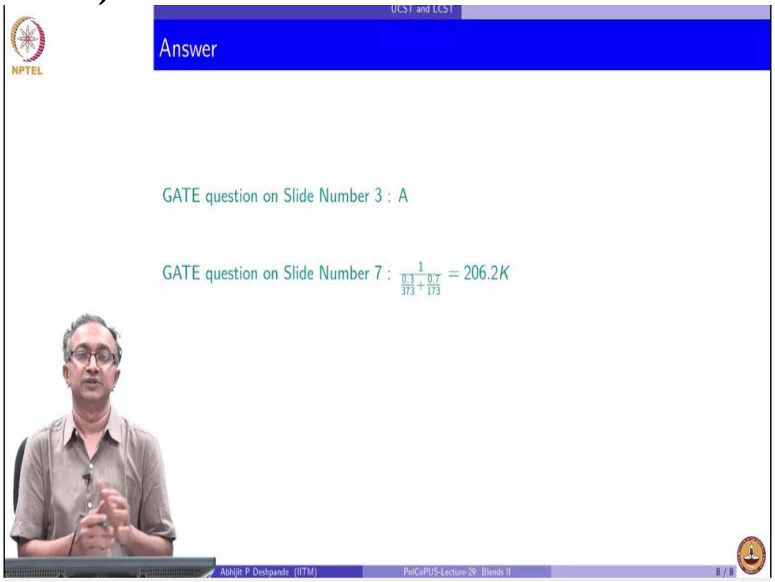

UCST and LCST

Answer

GATE question on Slide Number 3 : A

GATE question on Slide Number 7 : $\frac{1}{\frac{0.3}{373}+\frac{0.7}{173}} = 206.2K$

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And so I will leave you to do the algebra and do the calculations and so with this we have come to close on the discussions of the blend and now with the lecture 30 we will look at microstructure in many of the polymeric systems and finally we will have a lecture on composites so these are all our survey of polymeric materials of different kinds. Thank you.