Introduction to Polymer Science

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Module No # 08
Lecture No # 36
Thermal Properties: Crystalline State

Welcome back, in this lecture I will continue my discussion on thermal properties and in today's lecture I will cover crystalline state of polymers

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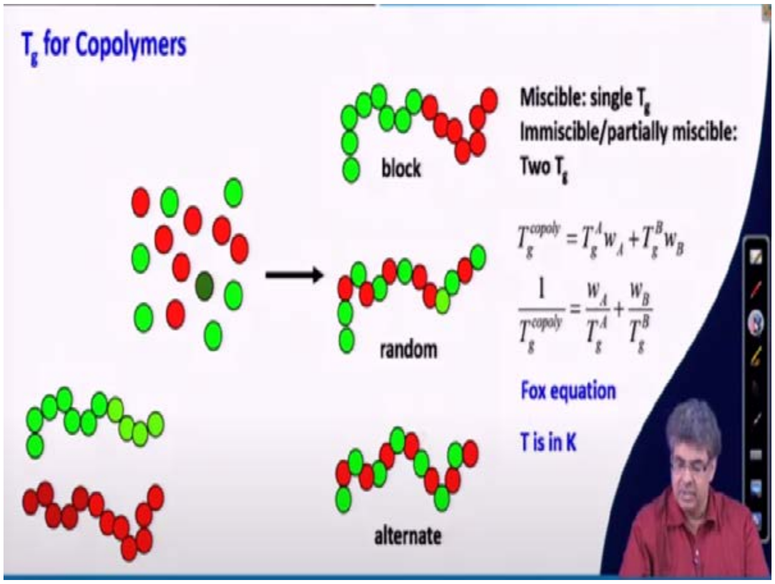

T_g for Copolymers

Miscible: single T_g
Immiscible/partially miscible: Two T_g

$$T_g^{copoly} = T_g^A w_A + T_g^B w_B$$

$$\frac{1}{T_g^{copoly}} = \frac{w_A}{T_g^A} + \frac{w_B}{T_g^B}$$

Fox equation

T is in K

Before moving to crystalline state, let us discuss on glass transition temperature. Let us consider the glass transition temperature for copolymers. If I have two monomers which are getting incorporated in a polymer forming random polymer, then the T_g of the copolymer can be expressed by various equations, one of such equation is shown here.

$$T_g^{copoly} = T_g^A w_A + T_g^B w_B$$

$$\frac{1}{T_g^{copoly}} = \frac{w_A}{T_g^A} + \frac{w_B}{T_g^B}$$

where W_A and W_B are the weight fractions of A and B in the copolymer. T_g^A is the homopolymer T_g made from A and T_g^B is the glass transition from the homopolymer made from B. This equation generally overestimates the T_g of the copolymer. Hence, another equation proposed by Fox and the equation is given by this expression where again W_A and W_B are the weight fractions of A and B respectively in the copolymer and T_g^A and T_g^B are the homopolymer T_gs. Remember, in this case we need to express the temperature always in Kelvin not in centigrade or Fahrenheit. It has to be always expressed in Kelvin. Now this is about random copolymer, if I have a block copolymer then what will be the T_g of the block polymer? Now this T_g depends on the miscibility behavior of the two blocks I have shown here. If the two blocks are miscible, completely miscible with each other then, the resulting T_g will be obtained by this expression as well.

If they are completely immiscible then we will have two T_g s, one corresponds to this block and the other corresponds to the other block, which means T_g^A and T_g^B, there could be a small deviation from the homopolymer T_g but it will be very close to these T_gs. If they are miscible then a single T_g is given by this expression, and if it is immiscible or partially miscible then we have two T_gs. If we have alternate copolymer then obviously it is a 1 is to 1 copolymer by mole. So, from the knowledge of the molar mass of the comonomers we need to find out what would be the weight fraction of corresponding monomers and we can use this expression to find out the T_g of the copolymer.

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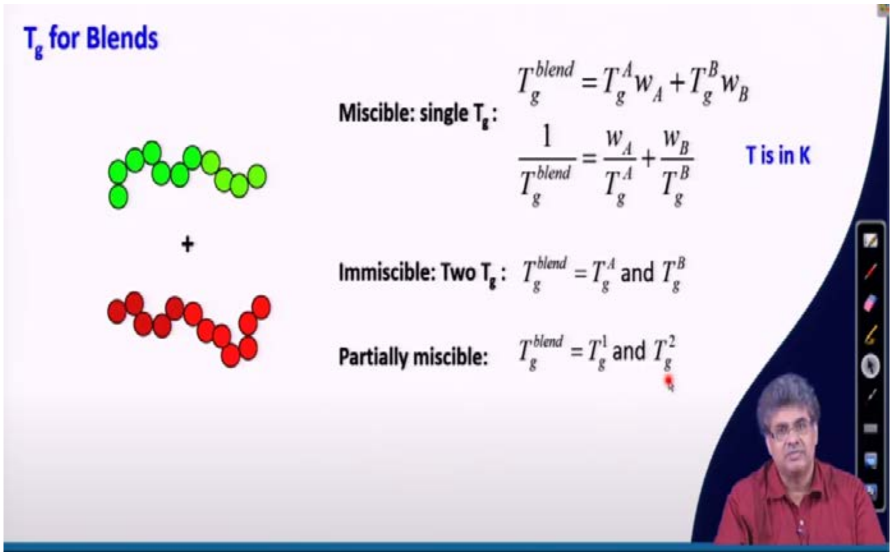

T_g for Blends

Miscible: single T_g:

$$T_g^{blend} = T_g^A w_A + T_g^B w_B$$

$$\frac{1}{T_g^{blend}} = \frac{w_A}{T_g^A} + \frac{w_B}{T_g^B}$$

T is in K

Immiscible: Two T_g: $T_g^{blend} = T_g^A$ and T_g^B

Partially miscible: $T_g^{blend} = T_g^1$ and T_g^2

Similarly, we can also use this expression to find out T_g for polymer blends Polymer blends are physical mixtures of one or more polymers. In this case, I have shown mixture of blends of two polymers. In this case, again if these two polymers are completely miscible with each other then we have single T_g and the T_g will be given by this expression. This is the expression, which is most frequently used, which is Fox equation and again remember that T is in K.

$$Miscible : single\ T_g\ , \quad T_g^{blend} = T_g^A w_A + T_g^B w_B$$

$$Immiscible : two\ T_g\ , \quad T_g^A \text{ and } T_g^B$$

$$Partially\ miscible: \quad T_g^{blend} = T_g^1 \text{ and } T_g^2$$

If it is completely immiscible then two T_gs are given by T_g^A and T_g^B, and if they are partially miscible then there will two T_gs, but they are different form T_g^A and T_g^B. There will be two T_gs, they will be different, they will slowly merge with each other as the miscibility increases. This two T_g actually merge with each other to form single T_g as miscibility goes up.

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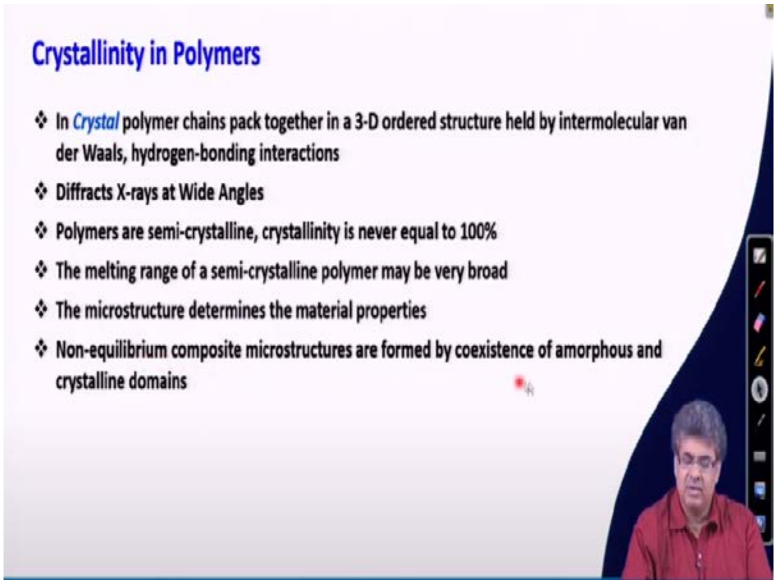

Crystallinity in Polymers

- In Crystal polymer chains pack together in a 3-D ordered structure held by intermolecular van der Waals, hydrogen-bonding interactions
- Diffracts X-rays at Wide Angles
- Polymers are semi-crystalline, crystallinity is never equal to 100%
- The melting range of a semi-crystalline polymer may be very broad
- The microstructure determines the material properties
- Non-equilibrium composite microstructures are formed by coexistence of amorphous and crystalline domains

Now I have moved to the topic on crystallinity of polymers. Now in a crystal, polymer chains pack together in a 3-D ordered structure held by intermolecular van der Waals forces like hydrogen bonding interactions. Crystals diffract X-rays at wide angles as have been discussed earlier that polymers are only semi-crystalline, 100% crystalline polymers are not possible because of the large molecular weight of the polymer. In general, in a polymer melt the polymer chains remain as an entangled mass. The melting range, unlike the small molecules where the melting point is a very sharp, in case of polymer the melting point is not very sharp. There is a melting range and that is because of presence of these amorphous regions between the crystalline domains. Those amorphous regions actually affect the T_g of the polymer T_m of the polymer and hence, this T_m is generally more broad in nature.

The microstructure of the polymer sample containing both amorphous and crystalline domains that actually determine the material property. In effect when you talk about semi-crystalline polymer, we have a non-equilibrium composite microstructure. Remember, we are using the term non-equilibrium because when you form a polymer sample from a melt, then we hardly get equilibrium structure because of the large molecular weight we do not usually given enough time to reach a thermodynamically equilibrium state. Non-equilibrium composite microstructures are formed by coexistence of amorphous and crystalline domains.

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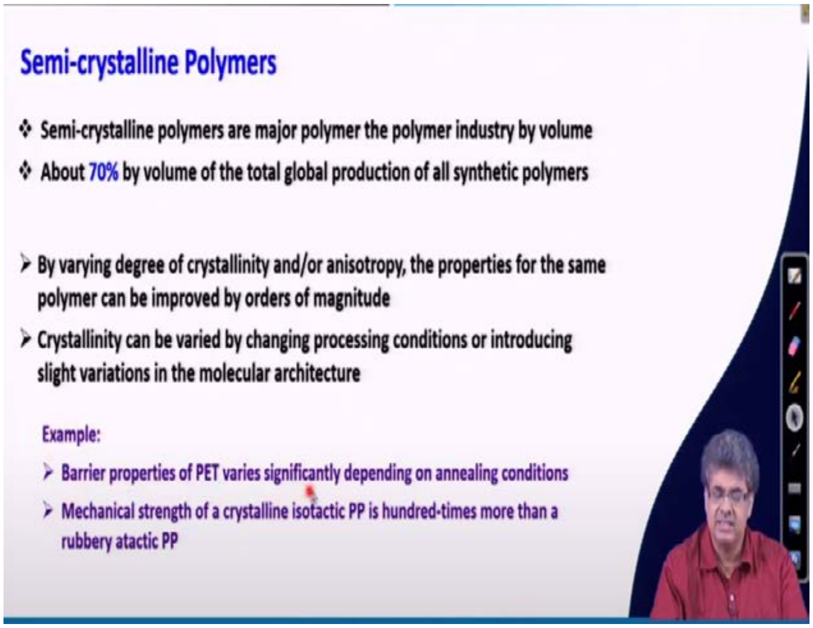

Semi-crystalline Polymers

- Semi-crystalline polymers are major polymer the polymer industry by volume
- About 70% by volume of the total global production of all synthetic polymers

- By varying degree of crystallinity and/or anisotropy, the properties for the same polymer can be improved by orders of magnitude
- Crystallinity can be varied by changing processing conditions or introducing slight variations in the molecular architecture

Example:

- Barrier properties of PET varies significantly depending on annealing conditions
- Mechanical strength of a crystalline isotactic PP is hundred-times more than a rubbery atactic PP

Semi-crystalline polymers are major polymers in polymer industry. About 70% of the total global productions of all synthetic polymers are semi-crystalline. Which means that completely amorphous polymers account for about 70% by volume when we talk about synthetic polymer industry. By varying degree of crystallinity and/or anisotropy, properties of the same polymer having same chemical structures can be improved by order of magnitude by changing the microstructure or degree of crystallinity.

Crystallinity can be varied by changing processing condition or introducing slight variation in the molecular architecture. For example, barrier property of PET varies significantly depending on annealing condition. Annealing conditions actually induce crystallinity in the polymer. So, if we change the annealing condition the extent of crystallinity also changes. As a result the barrier property of PET significantly changes depending upon the type of or time of annealing, we are providing to the sample.

Similarly, mechanical strength of a crystalline isotactic polypropylene is hundred times more than rubbery atactic polypropylene. That is understandable because this crystalline domain will give more rigidity to the polymer. Hence, the mechanical strength goes up tremendously as we increase the crystallinity in the sample.

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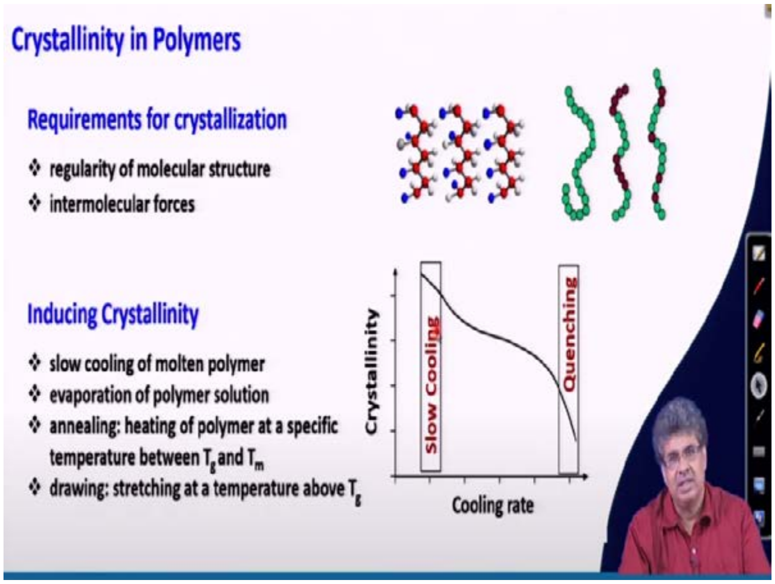

Crystallinity in Polymers

Requirements for crystallization

- regularity of molecular structure
- intermolecular forces

Inducing Crystallinity

- slow cooling of molten polymer
- evaporation of polymer solution
- annealing: heating of polymer at a specific temperature between T_g and T_m
- drawing: stretching at a temperature above T_g

We know that in polymer melt, polymer chains are having different orientation and they are entangled like this. Now if you want to make this polymer melt or polymers in solution to crystallize, then the polymer structures have to be regular. So, unless the structures are regular, they cannot pack in a 3-D crystal. Hence this regularity of the molecular structure is a must and also if these polymers interact with each other or attract each other, which means the intermolecular forces is high between the polymer chains, then also the sample becomes more crystalline or crystallinity becomes easier to get induced in the sample.

There are other indirect ways also we can induce crystallinity. If we compare the crystallinity of a homopolymer, block copolymer and a random copolymer, obviously because of the structural regularity, homopolymer and block copolymer will crystalize more easily whereas for the random copolymer it is very difficult to crystallize. Similarly, when we talk about about tacticity, when we have isotactic or syndiotactic polymer there is a possibility that these will crystallize whereas the atactic polymers generally do not crystalline because of irregularity in their molecular structure.

As I was discussing that there are ways we can induce crystallinity, and first thing is that if you give enough time for polymer chains to rearrange themselves and then align with each other to form crystalline domain, then obviously we are giving opportunity to the polymer chain to crystallize. Hence, slow cooling of the molten polymers will induce crystallinity. If we do fast cooling, like we do in injection molding or in an extrusion machine, it is basically we quench the sample, we bring down the temperature of the polymer samples very quickly. That will hardly induce any crystallinity because we are not giving enough time to polymer chains to rearrange themselves and align with each other to form crystalline domains. Similarly, if we evaporate polymer solution then evaporation being a slow process, as the polymer solution evaporates the polymer chains comes close to each other and they can align themselves and they can actually form crystalline domain. Similarly annealing is heating a polymer sample at a specific temperature between T_g and T_m. So polymers we will have enough mobility, because it is above T_g but it will have tendency to crystallize because it is below T_m.

Hence if we give enough time and if we give enough mobility, then polymers actually have crystallizability. If, the tendency of crystallization in the polymer sample exists, then by annealing we can induce crystallinity. There is the term crystallization and there is a corresponding temperature called T_c, crystallization temperature related to this annealing process or the crystallization process.

Similarly if you stretch a sample above T_g and give enough time then while stretching if you are aligning the polymer chains above $T_{g,}$ that means polymers have some mobility and they can actually now re-orient easily and form crystalline domains. So, these are some of the techniques or some of the indirect ways by which we can induce crystallinity in the sample.

This is a just to show that how crystallinity varies with cooling rate, if we cool a polymer melt slowly then the crystallinity will be higher because, we are giving more time to polymers to rearrange and align with each other. If we quench the polymer, for example as I said, in an injection molding or an extrusion process when we cool the polymer melt very fast, then we are not providing enough time, which means the extent of crystallinity is much lower compared to cooling where it will slower process.

So, if we basically slow the polymer melt cooling process, we induce more crystallinity in the sample.

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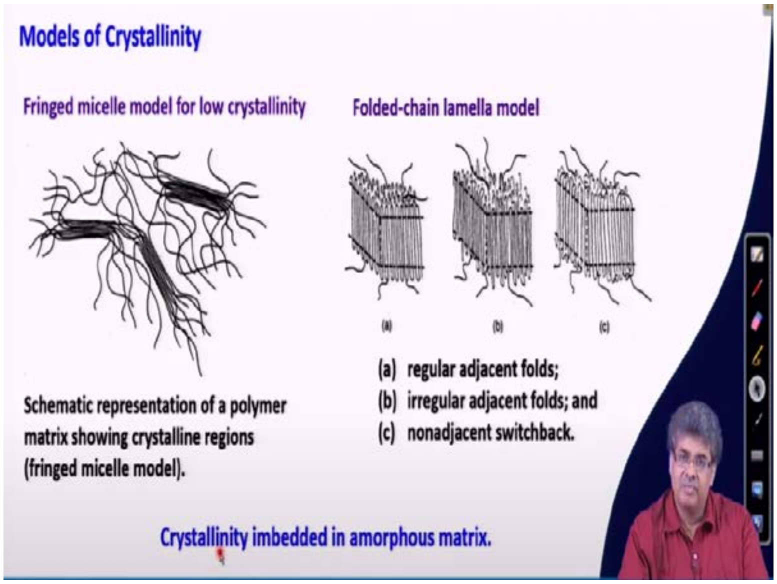

Models of Crystallinity

Fringed micelle model for low crystallinity

Folded-chain lamella model

Schematic representation of a polymer matrix showing crystalline regions (fringed micelle model).

(a) regular adjacent folds;
(b) irregular adjacent folds; and
(c) nonadjacent switchback.

Crystallinity imbedded in amorphous matrix.

We will talk about models of crystallinity, the two popular models - one is a fringed micelle model for low crystallinity. As you can see that this is a fringed micelle model where we have crystalline domain as well as amorphous domain. This crystalline domain is formed by various polymer chains and also a single polymer chain can contribute to two crystalline domain or more than two crystalline domains.

For example, this particular chain is part of this crystalline domain as well this crystalline domain. These are kind of micelles what we have learned in our colloid classes that they form a kind of self-aggregation in this case. This is some of crystalline domain and this is an amorphous domain. This is another model for crystallinity, folded chain lamellar model. While these lamellae are formed, crystalline lamellae are formed by arrangement of folded chain.

Again, one lamella will contain many more polymer chains, and similarly one polymer chain can be part of more than one lamella. There could be three possible lamella models, one is regular adjacent folds, irregular adjacent fold where folding is irregular. Third one is non-adjacent switch back. In this case, this switching back like one segment, polymer segment is coming and switching back, in this case this switching back is not adjacent to each other.

These are the three possible models for folded chain lamella and as we know from our previous knowledge as well that crystallinity embedded within amorphous matrix, hence we called semi-crystalline sample which have both T_m for the crystalline domain and T_g for the amorphous domains.

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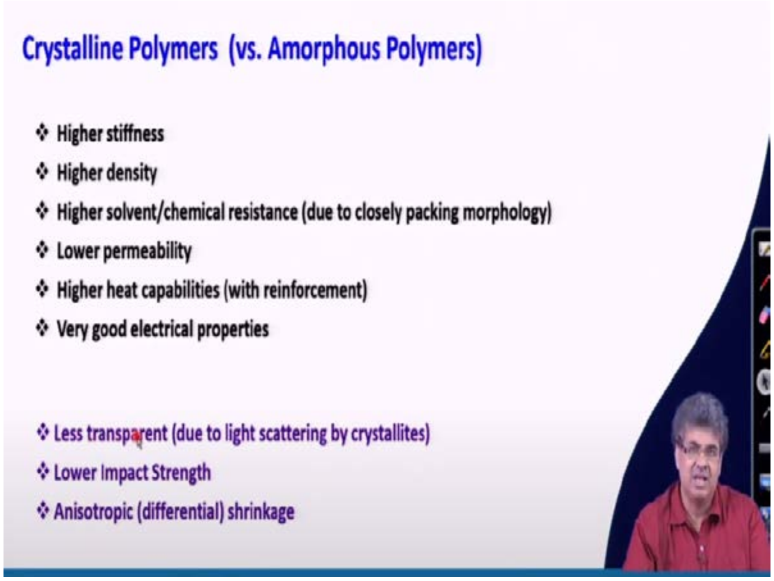

Crystalline Polymers (vs. Amorphous Polymers)

- Higher stiffness
- Higher density
- Higher solvent/chemical resistance (due to closely packing morphology)
- Lower permeability
- Higher heat capabilities (with reinforcement)
- Very good electrical properties

- Less transparent (due to light scattering by crystallites)
- Lower Impact Strength
- Anisotropic (differential) shrinkage

Now if you compare crystalline polymer versus amorphous polymer we see that owing to crystalline domains, polymers have higher stiffness, higher density, higher solvent or chemical resistance. Because of the close packing, solvent or the chemicals cannot diffuse in and harm the polymer chains. Because of the presence of crystalline domains it actually hinders the movement of gases through the polymer chains.

Hence, it has lower permeability or more barrier property, so the semi crystalline polymers are used as a container or as a storage of perfume bottles or some applications where you need to have a barrier property to prevent gases from diffuse out from the sample. Similarly, crystalline polymers have higher heat capabilities and very good electrical properties. Not everything is good for crystalline polymer, there are few inferior properties compared to amorphous polymer as well.

The most important is loss of transparency because of the crystalline domains present in a sample. They scatter light and as a result, the transparency comes down depending upon the extent of crystallinity. This is very important because, some applications where transparency is a must, these semi crystalline polymers are not very useful. Because the polymer chains are tied up with each other or they are partly crystalline, their impact strength actually comes down

To achieve a higher impact strength the polymer chains must be flexible enough to absorb the sudden impact or sudden input of mechanically energy and diffuse that, which is not possible for semi crystalline samples. And also, because their density is not homogenous in the sense that some part is less dense than the crystalline part which are more dense, it is also anisotropic or has differential shrinkage because it shrinks more in one direction compare to the other directions.

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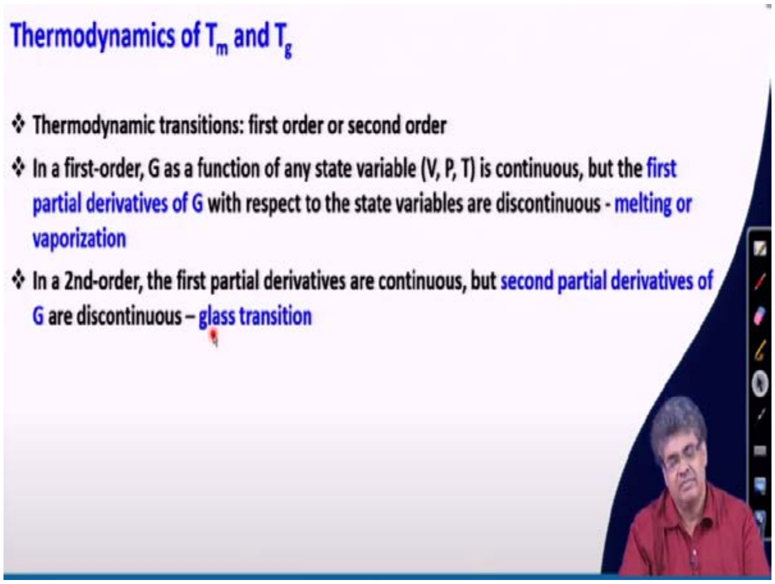

Thermodynamics of T_m and T_g

- Thermodynamic transitions: first order or second order
- In a first-order, G as a function of any state variable (V, P, T) is continuous, but the first partial derivatives of G with respect to the state variables are discontinuous - melting or vaporization
- In a 2nd-order, the first partial derivatives are continuous, but second partial derivatives of G are discontinuous – glass transition

We will talk about thermodynamics of T_m and T_g now. In thermodynamics, we talk about two transitions, two types of transition - one is first order, another is second order transition. First order transition gives energy as a function of any state variables like volume, pressure and temperature. G varies with V, P or T in a continuous manner, there is no discontinuity. But, the first partial derivative of G with respect to these variables, they are discontinuous. The first derivative is discontinuous, so we call this a first order transition like melting and vaporization. In fact, these are the proper thermodynamic transition. The second order transitions are those transitions where these first derivatives are not discontinuous but the second derivatives are discontinuous. For example, glass transition. I will just discuss more quantify in the next slide.

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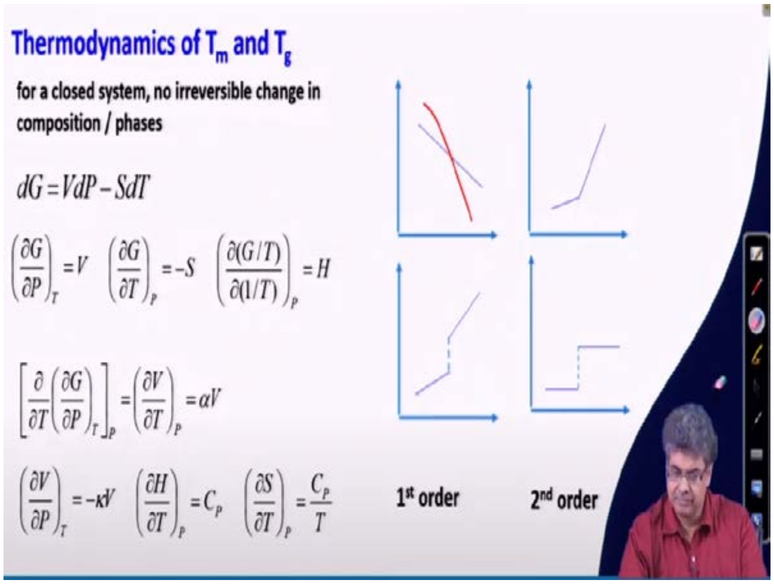

Thermodynamics of T_m and T_g

for a closed system, no irreversible change in composition / phases

$dG = VdP - SdT$

$\left(\frac{\partial G}{\partial P}\right)_T = V \quad \left(\frac{\partial G}{\partial T}\right)_P = -S \quad \left(\frac{\partial (G/T)}{\partial (1/T)}\right)_P = H$

$\left[\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T\right]_P = \left(\frac{\partial V}{\partial T}\right)_P = \alpha V$

$\left(\frac{\partial V}{\partial P}\right)_T = -\kappa V \quad \left(\frac{\partial H}{\partial T}\right)_P = C_P \quad \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$

We know from our knowledge of thermodynamics that for a close system and no irreversible change in composition, phases, we have this expression.

$$dG = VdP - SdT$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad \left(\frac{\partial G}{\partial T}\right)_P = -S \quad \left(\frac{\partial\left(\frac{G}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right)_P = H$$

$$\left[\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T\right]_P = \left(\frac{\partial V}{\partial T}\right)_P = \alpha V$$

$$\left(\frac{\partial V}{\partial P}\right)_T = -kV \quad \left(\frac{\partial H}{\partial T}\right)_p = C_P \quad \left(\frac{\partial S}{\partial T}\right)_p = \frac{C_P}{T}$$

For a first order transition, if we plot G versus either T, V or P, we will not have a discontinuity. If we talk about G vs T at first, then this side is melt and this side is solid. This is a melting point but in this case the transition is not discontinuous, but the first derivatives which are ∂G/∂P = V or -S or H. So, if we plot instead of G, if we plot say either V, S or H with say T or V or T or V or P then we get a discontinuity at melting point T_m. In this case the first derivative is discontinuous where the original G is not discontinuous. Similarly, so we called this as a first order transition.

But in case of second order transition, these values do not change discontinuously at transition, but the second derivatives like α or K or the heat capacity, they actually change discontinuously with temperature, pressure, volume. For example, in this case if we plot V, S or H against T then this is T_g. This case, these do not vary discontinuously, whereas in C_p versus T plot it actually changes discontinuously at T_g.

So T_g is a second order transition whereas T_m or melting is a first order transition. In true sense the melting or vaporization are actually thermodynamic transition, true thermodynamic transitions whereas a second order transition like glass transition is not true thermodynamic transition. The value of this transition temperature depends on the rate of cooling, how fast or how slow we cool a sample.

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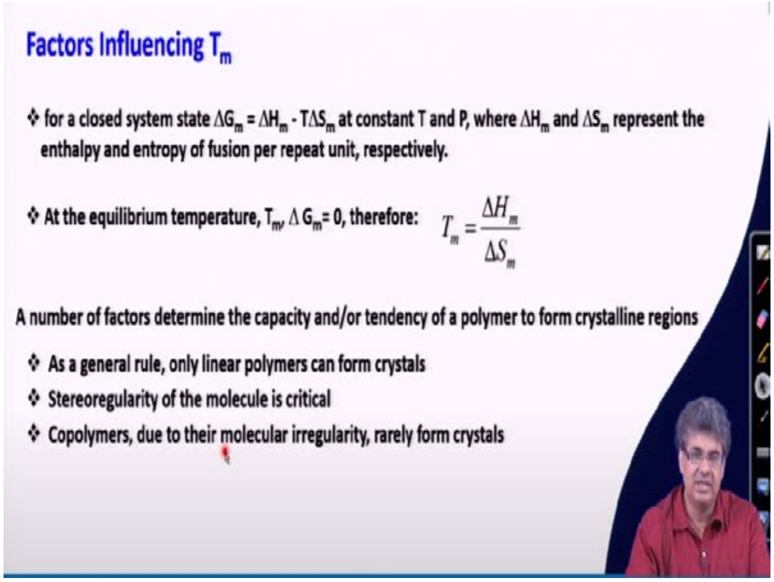

Factors Influencing T_m

- for a closed system state $\Delta G_m = \Delta H_m - T\Delta S_m$ at constant T and P, where ΔH_m and ΔS_m represent the enthalpy and entropy of fusion per repeat unit, respectively.
- At the equilibrium temperature, T_m, $\Delta G_m = 0$, therefore: $T_m = \dfrac{\Delta H_m}{\Delta S_m}$

A number of factors determine the capacity and/or tendency of a polymer to form crystalline regions

- As a general rule, only linear polymers can form crystals
- Stereoregularity of the molecule is critical
- Copolymers, due to their molecular irregularity, rarely form crystals

We now look at the factors with influence T_g. Now we know for a closed system, ΔG_m is given by $\Delta H_m - T\,\Delta S_m$ and m indicates melting process. So, these ΔH_m and ΔS_m represent the enthalpy and entropy of melting or fusion per repeat unit, respectively. At the equilibrium, at melting point, at equilibrium temperature, ΔG_m is zero, hence melting point is given by $\Delta H_m / \Delta S_m$.

$$T_m = \frac{\Delta H_m}{\Delta S_m}$$

Now, as the polymer chains are cooled from molten state, it form a crystalline domain. The polymer chains have a random orientation, much more flexible, becoming stiff and in oriented arrangement. Then, ΔS must be negative in this case, and because there are inter molecular attractions between the polymers chains, ΔH_m is also negative in this case. Depending on the magnitude of ΔH_m or and ΔS_m, T_m will vary. Higher the value of magnitude of ΔH_m, higher will be T_m. Smaller is value of ΔS_m, the higher will be T_m. Which means that the if we have a steep polymer chain, and then we are taking a stiff polymer chain from molten state to a crystalline state the amount of entropy loss it will incur will be lower compared to when you convert a polymer melt having more flexible chains to a crystal domain.

In the first case, when the polymer chains are more stiff, much more, easier to crystalline the polymer chain than a flexible polymer chain. If the interaction between, inter molecular attraction between, the polymer chain increases then it is easier for polymers to become crystalline. A number of factors determine the capacity or tendency of polymers to form crystalline region. As a general rule, only linear polymers can form crystalline as you can understand, for branched polymer the arrangement is difficult thing. So it is not possible to form crystalline. Atactic polymer generally do not crystallize. Stereoregularity is also very critical. As I discussed earlier, that random copolymer generally does not crystallize but, if you have a regular block type copolymer then it is possible to crystallize and again, this also we have discussed that slower cooling promotes crystal formation and growth.

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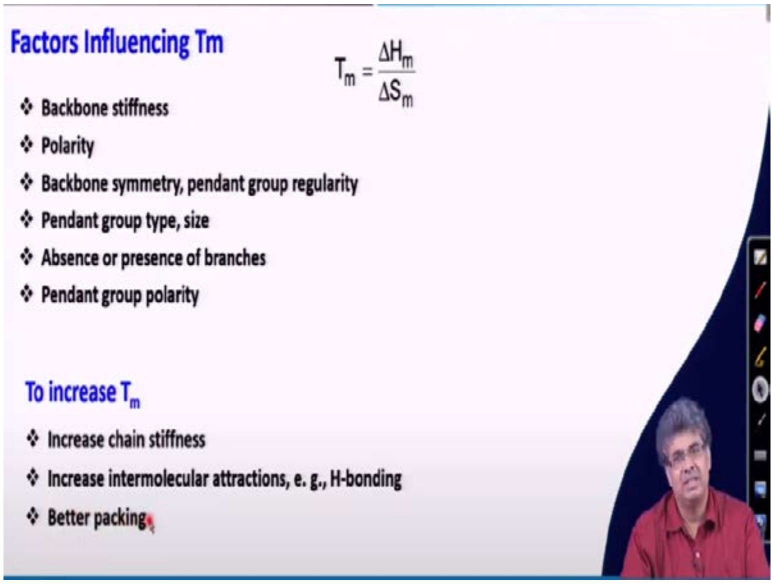

Factors Influencing Tm

$$T_m = \frac{\Delta H_m}{\Delta S_m}$$

- Backbone stiffness
- Polarity
- Backbone symmetry, pendant group regularity
- Pendant group type, size
- Absence or presence of branches
- Pendant group polarity

To increase T_m

- Increase chain stiffness
- Increase intermolecular attractions, e. g., H-bonding
- Better packing

So, what are the factors that determine T_m? The factors will determine is the backbone stiffness, polarity, backbone symmetry, pendant group regularity, pendant group type and size, absence and presence of branches, pendant group polarity. Basically, these all affect either ΔH_m or ΔS_m. As I discussed that if stiffness increases in polymer chain, then this becomes less negative. So, T_m will go up i.e. it is easier for the polymer chains to crystalline.

Similarly, as the polarity increases, which means there will be more intermolecular attraction, magnitude of ΔH will go up that also will increase the value of T_m because it will become easier for the polymer chains to crystallize. Similarly, backbone symmetry will help in crystallization and if there are regular pendant groups, small size will help in crystallinity. Absence of branch will help in crystallinity; presence of branch will inhibit any crystallization.

Pending group polarity also matters, if the polarity is higher for the pending groups, which helps in crystallization. So, to increase T_m or melting point, we should increase the chain stiffness, we should increase the intermolecular attractions, and if we have some groups, which can contribute in hydrogen bonding, then it helps in crystallinity. If you have molecular regularity, which helps in packing, then also it helps in crystallization.

So, in next lecture we will dicsuss about the factors that affect crystallinity of some polymer structures.