Introduction to Polymer Physics
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Lecture – 16
Amorphous State of Polymers

So in the polymeric materials that we have been studying these materials typically exist as a combination of crystalline and amorphous domains.

So, and typical polymer is usually semi crystalline where which contains both crystalline parts and amorphous parts. In this week, we look at the characteristics of the amorphous phase of the polymer as well as a crystalline state and we will also discuss the different kind of thermal transitions that are exhibited by these states of a polymer.

And this week we will also briefly define some of the important mechanical properties that are relevant for the study of polymeric materials towards the end of this week. So, today our focus is on the Amorphous State of Polymers. So, we will look at the amorphous state which is a kind of a disordered state of the polymeric materials in today's lecture.

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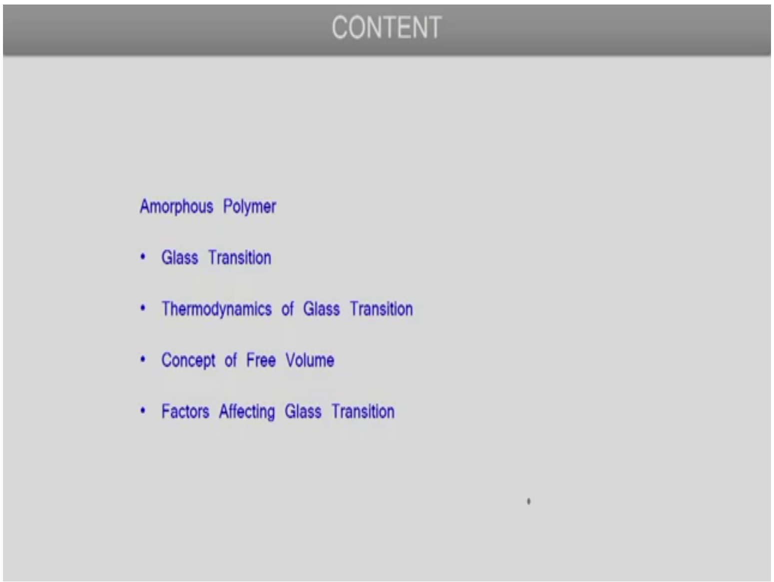

CONTENT

Amorphous Polymer

- Glass Transition
- Thermodynamics of Glass Transition
- Concept of Free Volume
- Factors Affecting Glass Transition

So, the content of today's lecture include discussion on the what is called the glass transition behavior of amorphous polymers. So, we will look at this special kind of a thermal transition behavior, which is a distinct from a melting transition that that is observed for crystalline polymers.

So, we look at glass transition we will also explore glass transition more detail by studying and the thermodynamics of glass transition. We will look at the molecular viewpoint, look at the look at glass transition from your molecular viewpoint by considering what is called the free volume theory and apply the free volume concepts to understand glass transition a little better.

And towards the end of this lecture we will focus on the different factors which affect the glass transition temperature of polymers.

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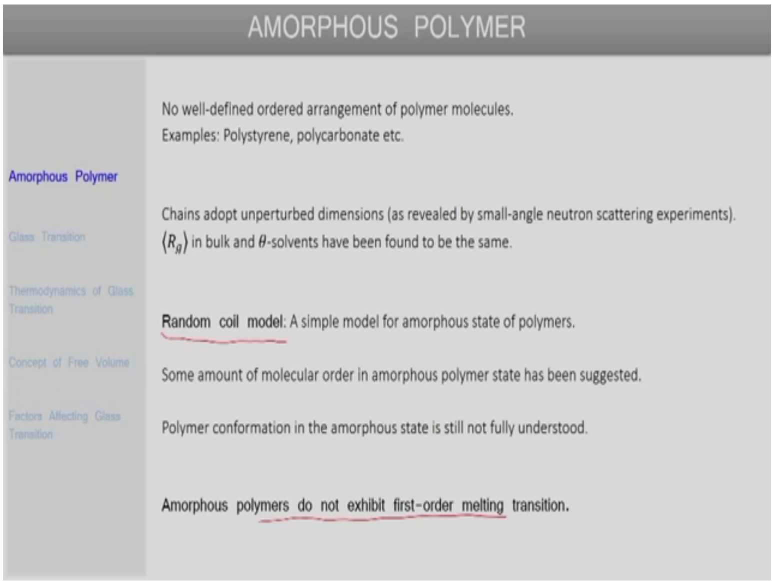

AMORPHOUS POLYMER

- Amorphous Polymer
- Glass Transition
- Thermodynamics of Glass Transition
- Concept of Free Volume
- Factors Affecting Glass Transition

No well-defined ordered arrangement of polymer molecules.
Examples: Polystyrene, polycarbonate etc.

Chains adopt unperturbed dimensions (as revealed by small-angle neutron scattering experiments).
$\langle R_g \rangle$ in bulk and θ-solvents have been found to be the same.

Random coil model: A simple model for amorphous state of polymers.

Some amount of molecular order in amorphous polymer state has been suggested.

Polymer conformation in the amorphous state is still not fully understood.

Amorphous polymers do not exhibit first-order melting transition.

So, to begin with as you may know the word amorphous normally signifies a disordered kind of a state. So, when we say amorphous state of a polymer what we mean is that; there is no well defined or ordered arrangement of polymer chains in this state.

And there are some polymeric materials which are almost completely amorphous at room temperature. So, that it is a polystyrene, polycarbonate these are commonly used polymeric materials that can be considered as amorphous. Similarly, there other elastomeric or rubbery materials which also do not show any significant molecular ordering and they are also amorphous.

Polystyrene for example, is the glassy what is called a glassy polymer at room temperature; whereas, poly butadiene would be rubbery polymer, but still an amorphous polymer at room temperatures. So, the key feature of this amorphous state is there is no molecular order present that can be easily discerned. The fact that there is not much molecular ordering present in amorphous state of polymers that has been sort of validated by certain neutron scattering experiments

So, small angle neutron scattering experiments on amorphous polymers as well as the moltens some molten polymers. So, these experiments have revealed that the conformation of polymer chains in this bulk amorphous state is almost identical to what is observed in a theta solvent ok.

So, we have earlier discussed that in a theta solvent the polymer chain adopts its unperturbed dimensions or the ideal dimensions. So, in the amorphous state also it has been revealed through small angle neutron scattering that polymer chains exist such that their end to end distances and the radius of gyration these correspond to the unperturbed dimensions.

These findings actually suggest that the in the amorphous state; the polymer chains are in a in a highly disordered arrangement and there is no well defined order present in the polymeric samples. Such findings have lay led to the reinforcement of what is called the random coil model, which is a simple model describing the amorphous state of polymeric materials.

And what is state is that in the amorphous state the polymer chains are present as random coils; which are strongly interacting and that is a inter penetrating each other. But still the coils the polymer chains themselves exist as random coils and they do not show any well defined ordered arrangement.

However, there is they have been many researchers who have actually disputed this contention that the amorphous state of a polymer contains entirely of disordered collection of polymer chains. So, instead what they have suggested is some degree of order ordering might be present and to that effect some experimental evidence say in the form of electron microscopy measurements have been presented.

But this argument that some sort of ordering exists in the amorphous state of polymers this; there is no clear cut obvious evidence which points to the fact that some ordering is present. So, at the status at the present is such that the amorphous state, the confirmation of polymers chains in amorphous state is not fully understood at present. And whether some degree of ordering might be present that that itself is a matter of contention and further experimentation and development of this field needs to be done before anything concrete can be said.

So, for our purposes we will assume the amorphous state to be almost completely disordered state; with the understanding that there are arguments by researchers for the presence of some degree of ordering even in the amorphous state. So, apart from this the fact that amorphous state is mostly disordered, another distinguishing feature of the amorphous state of polymers is that it does not exhibit any first order melting transitions.

So, amorphous polymers they do not show any first was called the first order melting transition. So, if we have a crystalline polymer on the other hand and if we heat it the crystalline domains will ultimately melt and begin to flow as a liquid. So that kind of transition is referred to as a melting transition and in the amorphous polymer state such transitions are absent.

This is another important distinguishing characteristic of the amorphous polymer phase that it amorphous polymers do not melt. So, if they do not melt then with change in temperature what kind of thermal transition do they show? Let us try to explore that now.

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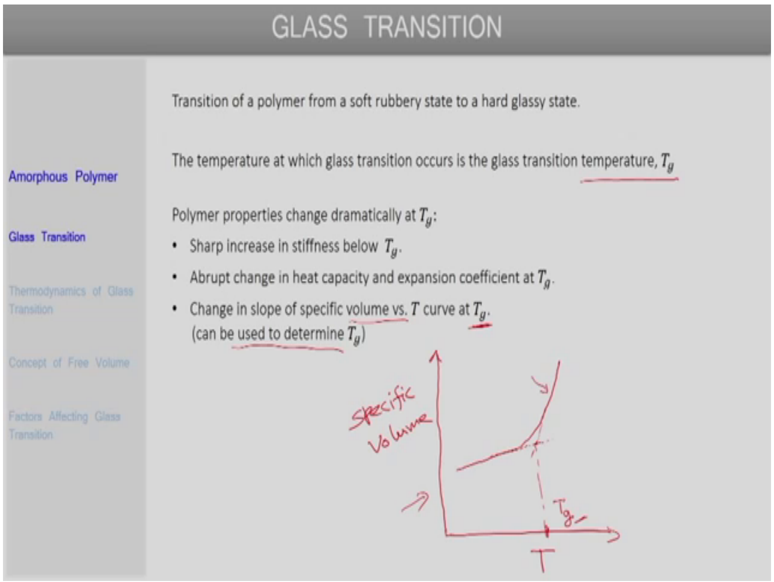

GLASS TRANSITION

Amorphous Polymer

Glass Transition

Thermodynamics of Glass Transition

Concept of Free Volume

Factors Affecting Glass Transition

Transition of a polymer from a soft rubbery state to a hard glassy state.

The temperature at which glass transition occurs is the glass transition temperature, T_g

Polymer properties change dramatically at T_g:

- Sharp increase in stiffness below T_g.
- Abrupt change in heat capacity and expansion coefficient at T_g.
- Change in slope of specific volume vs. T curve at T_g. (can be used to determine T_g)

For amorphous polymers, the thermal transition that is observed with change in temperature is what is called the glass transition. So, this glass transition is a transition that is characterized by change from a hard glassy state of the material to a soft rubbery state.

Below a certain temperature which is known as a glass transition temperature is amorphous polymers exist as glassy materials which are hard and brittle if these materials are heated above their glass transition temperatures.

Then they change into kind of rubbery substances and their hardness also decreases. So, this transition; this glass transition is the characteristic thermal transition exhibited by amorphous polymers. And as we discussed the corresponding temperature at which the transition takes place is called the glass transition temperature; it is denoted typically by T g. So, this glass transition is actually mark by significant change in the properties of the polymer.

So, as we go from above the glass transition to below the glass transition temperature that is from the rubbery state to the glassy state; the polymer stiffness of the polymeric material significantly increases. So, the material becomes harder, stiffer, but more brittle as well.

So, it will be its strength will be higher, but it will also break more easily. So, that is one characteristic that changes and so typically if you are looking for applications of polymers; where hard strong materials are required and we have amorphous polymers then we would prefer to use a glassy amorphous polymer ok.

So, typically the polystyrene the example that we discussed in the previous slide; often amorphous polymer and that is polystyrene. So, at room temperature it exists as a glassy polymer. Apart from the stiffness and other properties like and the heat capacity or the thermal expansion factor. So, these things also change as we move across this glass transition temperature. So as we go from the glassy state to the rubbery state, the thermal expansion coefficient typically increases and other properties like the heat capacity the isothermal compressibility these things also has are seen to change.

Some properties sure abrupt changes as just discussed; if we consider let say now the variation of specific volume of a amorphous polymer and see how a the specific volume changes with temperature. Then the specific volume versus temperature graph actually shows a change in slope at a certain temperature. So, as we change the temperature the specific volume increases with increase in temperature, but beyond a certain temperature the rate of change actually increases.

So, that temperature which marks a difference in a change in slope of this specific volume versus temperature curve that can be identified as the glass transition temperature of the polymeric material. The specific volume versus temperature curve that shows a change in slope and the point at which that slope changes marks T g.

Sothis something that that can be used as a technique to determine the glass transition temperature of amorphous polymers; so, if we let us say try to represent that through a plot; then let us say if you are plotting the specific volume versus temperature and we are trying to see the behavior glass the behavior of an amorphous polymer.

Then at low temperatures a specific volume increases with temperature, but the rate of increase is not that high. And then at high enough temperatures actually the curve this curve actually changes slope. And at higher temperatures the rate at which the specific volume changes with temperature that increases.

So, now we can identify actually two kind of linear regions and if we extrapolate the slope of these two regions; then the point at which these two slope intersect that this point actually can be identified as a glass transition temperature of the material. So, above the glass transition temperature the specific volume changes quite rapidly with increasing temperature whereas, below the glass transition temperature; the specific volume changes very gradually with increase in temperature.

So, this is how glass transition temperature can be identified. One thing to note what this glass transition is that the actual measurement; the temperature glass transition temperature that is measured that also depends on the rate at which the heating was cooling is being done.

So, the rate of change of temperature actually does affect the value of glass transition temperature being measured. So, if we are measuring if you are changing the temperature at a certain rate and we get the curve shown here; we will get a value of T g as shown here if the rate of temperature change is different, then the glass transition value obtained from such a curve that also will be slightly different.

So, the glass transition value measurement actually depends on the rate at which the temperature is being varied. Now that we have looked at the basics of glass transition and glass transition temperature; let us del the bit more deeper into the thermodynamics of this glass transition.

To understand the thermodynamics of glass transition, we need to first identify the two kinds of glass thermodynamic transitions that are typically observed. So, the most common type of thermodynamics transition that many of you might be familiar with is what is called the first order transition.

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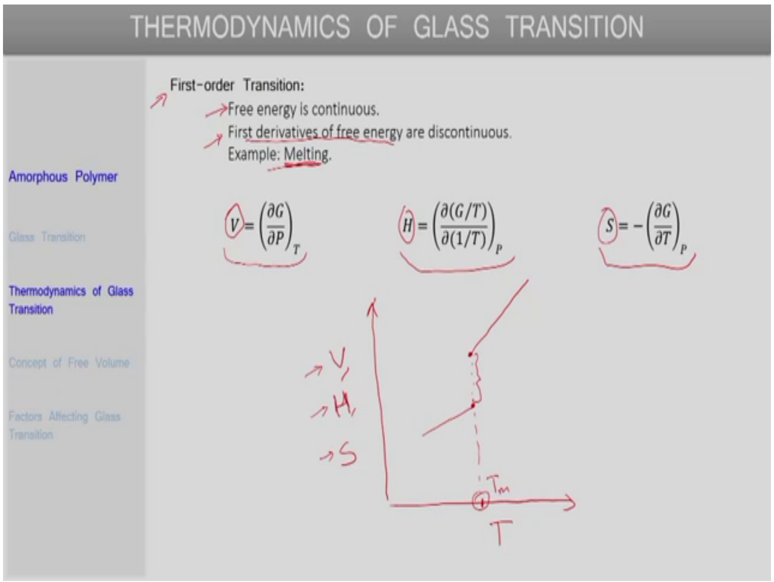

THERMODYNAMICS OF GLASS TRANSITION

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Concept of Free Volume

Factors Affecting Glass Transition

First-order Transition:

- Free energy is continuous.
- First derivatives of free energy are discontinuous.

Example: Melting.

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

And this first order thermodynamic transition is marked by the characteristics that the free energy change in changes continuously.

So, if free energy let us say is expressed function of a state variables like temperature and pressure, then free energy will change continuously with it let us a change in temperature or pressure. So, it will not show any discontinuity and even if a first order transition takes place; a cross that first order transition also the free energy will change continuously; it will not show any abrupt change.

But at the first order transition the first derivatives of the free energy they are discontinuous. So if we plot the first derivatives of free energy or let us say their change with change in temperature, then we will see that at the point of first order transition there will be an abrupt change in the value of these first derivatives and they will show discontinuity at this first order transition point.

So, an example of first order transition is a typical melting transition even vaporization from liquid to vapor that transition is also a first order transition. So, these first order transitions are typically these first order transitions typically involve what is called latent heat ok. So, this latent heat is a kind of energy that is added, but that does not lead to any change in temperature of the system; it just leads to change in the phase.

So this first order transitions involves some kind of a latent heat as well; so, now, if we look at the this first derivatives of free energy look at this term. And let us try to identify what are the typical thermodynamic variables that can be expressed as first derivatives of free energy.

So, that will help us identify common thermodynamic variables which actually are discontinuous in across a first order transition. So, from standard thermodynamic; so one can identify that the volume that is nothing but the first derivative of this energy with respect to pressure at constant temperature. Similarly enthalpy and entropy can also be expressed as first derivatives of the free energy; Gibbs free energy.

So, these thermodynamic quantities volume enthalpy are entropy these are actually the first derivatives and these are a discontinuous across a first order transition. So, if let us say we try to plot or; if we measure how the volume or the enthalpy or the entropy changes with temperature, then with temperature the typically the volume will increase in the normal cases.

And if we reach a transition point let us say this T m marks this first order transitions some kind of melting transition. So, at this temperature there will be a discontinuity and above this temperature again these will change with a different slope.

So, this gap here this is a abrupt change that we are talking about. So, these first derivatives volume enthalpy entropy these quantities will be discontinuous at the point of a first order transition and they will show an abrupt change. So, for a typical first order transitions like melting and vaporization these things are have been widely observed. So experimentally also this kind of an abrupt discontinuity changes observed in these variables at a first order transition point. So, that is what first order transition is.

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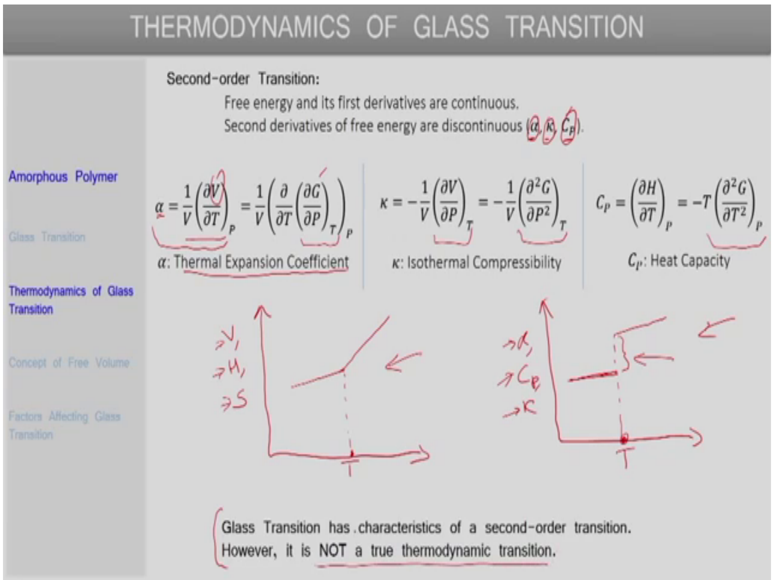

THERMODYNAMICS OF GLASS TRANSITION

Second-order Transition:

Free energy and its first derivatives are continuous.

Second derivatives of free energy are discontinuous (α, κ, C_P).

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V}\left(\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T\right)_P$$

α: Thermal Expansion Coefficient

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial P^2}\right)_T$$

κ: Isothermal Compressibility

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_P$$

C_P: Heat Capacity

Glass Transition has characteristics of a second-order transition.
However, it is NOT a true thermodynamic transition.

Now, if we talk about the second order transition. So, second order transition as the name suggests involves transitions where the free energy actually is continuous across a transition and the first derivative of free energy those are also continuous across a transition.

But the second derivatives of free energy these are discontinuous across a transition. So, if we talk about second derivatives of Gibbs free energy; we can identify three common such quantities this alpha is what is called the thermal expansion coefficient, kappa is isothermal compressibility C p is the heat capacity constant pressure.

So, these one can actually relate them to second derivatives of Gibbs free energy and these are seen to be discontinuous in a second order transition. Whereas, the first derivatives of Gibbs free energy like volume, enthalpy or entropy these are continuous across a first order transition. So, alpha by standard definition is 1 by V del V del T at constant P the thermal expansion coefficient. And since volume we had expressed as del G del P at constant T in the previous slide. So, this alpha can be expressed as a second derivative of G.

Similarly, the kappa isothermal compressibility also is related to change in volume with respect to pressure at constant T. So, that again can be related to a second derivative of Gibbs free energy and C p which is nothing, but del H del T at constant pressure that also again can be related to second derivative Gibbs free energy. So, heat capacity that is equal to minus T times del square G del T square at constant pressure. So, all these quantities which are second derivatives they are discontinuous across second order transition whereas, the first derivatives are continuous.

So, for a second order transition if we again try to plot the first derivatives of Gibbs energy like volume enthalpy or entropy against temperature; then what is observed is they change and at that point of transition. Let us say if this point master for second order transition then they do not show a discontinuous or abrupt jump only the slope will change though. So, the curve will still be continuous only the rate at which these quantities are changing with temperature that actually changes.

So, a second order transition is characterized by continuous variation of these first derivatives of free energy with respect to temperature or even pressure. So, here we have just used a single curve to in general denote V H or S. So, if we specifically plot V or H or S, then the actual values or the actual curves will be different, but all of them will show the same kind of behavior where the there is no discontinuity at the first order second order transition point and there is a usually change in slope.

Now, if we consider the second derivatives of Gibbs free energy which are alpha or it is a C p or kappa these kind of things. So, this these will these are usually are will show let us as a some change with temperature and at the second order transition point. So, let us see if again this is the second order transition point; these will show discontinuous jump.

So, there will be a gap here and below and above this transition point of course, the rate at which these quantity other quantities are changing with temperature that can change. But the characteristic feature here are the important point is that the at the second order transition point at that temperature these quantities show discontinuous and abrupt jump.

So, if you recall the our discussion the glass transition temperature and how the specific volume was changing with temperature; that specific volume versus temperature curve actually looked pretty much similar to what we have here ok. And it has been observed that for glass transition these we have quantities do shows this kind of a discrete or discontinuous jump or change.

So, these things lead us to believe that the glass transition actually is a kind of a second order thermodynamic transition. But because a across a glass transition also the first derivatives of Gibbs free energy are continuous they do not change abruptly. Whereas, the second derivative like alpha or C p they change abruptly and they are discontinuous.

So, these things lead us to believe that glass transition is a second order thermodynamic transition. But strictly speaking glass transition cannot be considered as a thermodynamic transition at all because it does not involve the transition between two phases which are in equilibrium. So, typically when you talk about melting or vaporization we have solid liquid equilibrium or a liquid vapor kind of equilibrium present then and those transitions have proper thermodynamic transitions.

Here in glass transition we have transition from a glassy to a rubbery state and these two states are not across a transition in true thermodynamic kind of equilibrium. So, strictly speaking the glass transition is not a true thermodynamic transition at all although it has features which has similar to a second order glass second order thermodynamic transition.

So, one can roughly treat it as a second order thermodynamic transition with the knowledge that strictly speaking; it is not a true thermodynamic transition. So, that is what we have mentioned here that it is not a true thermodynamic transition although it has characteristics of a second order transition.

So, now that we have we have talked about the thermodynamic foundation related to glass transition; let us discuss a little bit from the molecular viewpoint. So, what happens at the level of polymer chain molecules when glass transition takes place.

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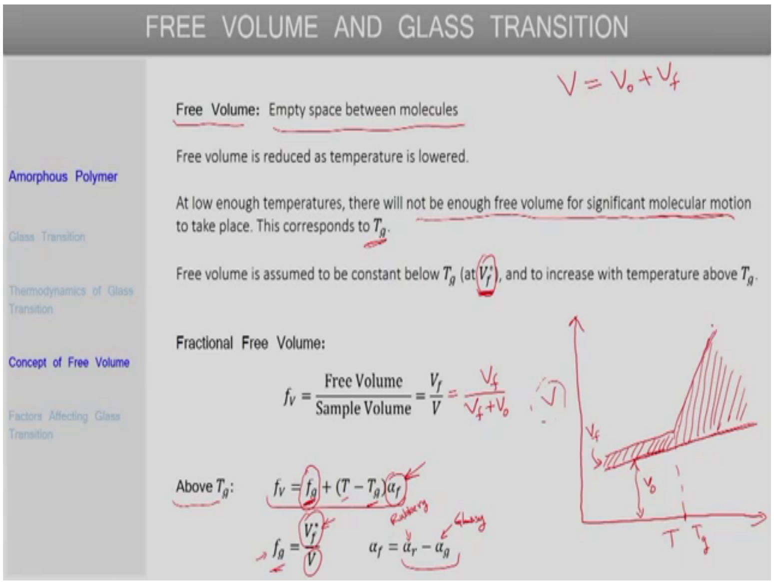

FREE VOLUME AND GLASS TRANSITION

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Factors Affecting Glass Transition

$V = V_0 + V_f$

Free Volume: Empty space between molecules

Free volume is reduced as temperature is lowered.

At low enough temperatures, there will not be enough free volume for significant molecular motion to take place. This corresponds to T_g.

Free volume is assumed to be constant below T_g (at V_f^*), and to increase with temperature above T_g.

Fractional Free Volume:

$$f_V = \frac{\text{Free Volume}}{\text{Sample Volume}} = \frac{V_f}{V} = \frac{V_f}{V_f + V_0}$$

Above T_g: $f_V = f_g + (T - T_g)\alpha_f$

$$f_g = \frac{V_f^*}{V} \qquad \alpha_f = \overset{\text{Rubbery}}{\alpha_r} - \overset{\text{Glassy}}{\alpha_g}$$

So, for that typically the free volume theory is a popular theory that is used to understand and describe the glass transition behavior from using a molecular viewpoint. So, if we talk about free volume; so, free volume is basically defined as the empty space that is present between the molecules.

So, whether we have a liquid or even amorphous polymer; the volume that is not occupied by the molecules of the system that constitutes the free volume. So, for an amorphous polymer the polymer chains will occupy some amount of space and whatever remaining empty space is there that that is the free volume of the system. So, if we denote the volume of the given sample to be, then that we can write as V naught plus V f where V f is the free volume and this V naught is the volume occupied by polymer molecules.

So, now, this free volume of the system actually if the temperature is lowered, the free volume reduces. So, if you are let us say are above the glass transition temperature and we start bringing the temperature down. So, free volume of the system will keep on decreasing and there will reach a point where the free volume will become so small that the motion of the polymer chains will not be possible because of the shortage of available free volume.

So, normally what this free volume theory proposes is that above the glass transition temperature there is in a plenty of free volume so that the polymer molecules can show some kind of long range segmental motion. So, they can wriggle about or move about a bit not in the true translational sense, but in the in a sense that the molecules show long way in segmental motion; that is a long parts of the polymer chain can show coordinated motions of the glass transition temperature.

So, the free volume theory what it proposes is that the presence of the reasonable amount of free volume above the glass transition temperature facilitates or rates in the movement of the polymer chains. And as a free volume is reduced with reducing temperature; the movement of polymer chains also becomes more difficult because of the low availability of free volume. And the free volume decreases to a kind of a critical value so that the polymer chains stop moving all the long range segmental motion in the polymer chains basically stops and the polymer chains get trapped in a kind of frozen configuration.

Then this critical point is referred to as a glass transition temperature. So, if the free volume decreases with temperature at certain low enough temperature there will not be any in enough free volume to allow for significant molecular motion. And that temperature requires will correspond to the glass transition temperature according to this concept of free volume ok.

Now, another assumption here in this free volume theory is that above the glass transition temperature as a temperature is raised, the free volume changes it actually increases. But below the glass transition temperature it is assumed that the free volume does not change much with temperature and one can assume it to be pretty much a constant ok.

Based on these kind of considerations where the where below the glass transition temperature this free volume we can represent at V f star and V assumed to be constant. And above the glass transition temperature it actually increases with T and this fractional free volume is the free volume present in a given sample divided by the total sample volume.

So, this V f by V we can just write it as V f by V f plus V naught where again V naught is the volume being occupied by the polymer chain molecules ok. So, this fractional free volume is a fraction of the total volume that is that is free.

So, again with respect to the fractional free volume typically the assumption is that below the glass transition temperature the even the fractional free volume is does not change much and it is pretty much a constant with respect to temperature. And above the glass transition temperature the fraction free volume increases as temperature is increased.

So, again one can write above the glass transition temperature; the variation of free volume with respect to temperature one can write in this form, where this f g is the free volume or the fractional free volume present in the glassy state. So, we said that in the glassy state the fractional free volume is pretty much a constant. So, this f g is that approximately constant fractional free volume in the glassy state. Of course, T is a temperature T g is the glass transition temperature and alpha f this is what is called the thermal expansion coefficient of the free volume.

So near the glass transition temperature if your if we know that thermal expansion coefficient of the rubbery phase and of the glassy phase; then the difference between that the thermal expansion coefficient of the rubbery phase and the glassy phase that can give us the thermal expansion coefficient of the free volume alpha f. So, as we discuss this f g is the free volume fraction free volume in the glassy state and that will just be V f star by V where V f star is the free volume available in the glassy state or below the glass transition temperature.

And we are assuming that this f g or V f star is relatively constant and this alpha f is this difference where this alpha r is the thermal expansion coefficient for the rubbery; polymer above the glass transition temperature and this is for the same polymer below the glass transition temperature that is a in the glassy state.

If you want to understand this free volume concept graphically then what one can do is; let say make a plot of a volume versus temperature plot again. And we have seen that this kind of a plot actually shows a change in slope at the glass transition temperature this we have already discussed before the lot of specific volume versus T shows change in slope and at T g.

So, now if we talk about the concept of free volume what this free volume theory that we have discussed here suggest is that below the glass transition if we represent the free volume present as the shaded region. So, below the glass transition this free volume is pretty much a constant ok. Whereas, above the glass transition the change in this volume of the entire sample; this increase in slope that is primarily because of the fact that the free volume start starts expanding quickly with temperatures.

So, above the glass transition the free volume actually is increasing ok. So, whatever we have in this shaded region that we are calling as the free volume. And this the volume characterized by this line here that will refer to as a this will be the V naught or the volume occupied by the polymer molecules; that will not change much with temperature, it is the expansion of the free volume that actually leads to change in the volume of the sample. So, that is what this free volume suggests.

And below the glass transition temperature the free volume does not change must be temperature. Whereas, above a this characteristic temperature the free volume starts changing quickly and that is why due to the increased free volume; the polymer chains are allowed greater degree of freedom to move about and that is why they become more mobile and the system goes from being a rigid kind of glassy solid to a soft rubbery material.

That is a kind of qualitative description of glass transition from a molecular viewpoint using the free volume theory. Next let us try to look at some of the factors that affect the glass transition temperature of polymers. So, when we talk about factors that can affect the glass transition temperature; there are many different factors that can be identified. So, we can have factors which involve the chemical structure of the polymer molecule.

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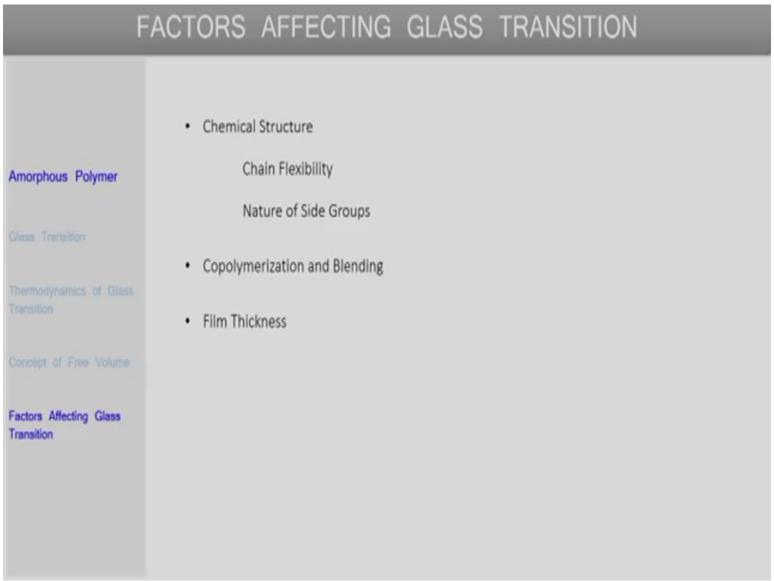

FACTORS AFFECTING GLASS TRANSITION

- Chemical Structure
    - Chain Flexibility
    - Nature of Side Groups
- Copolymerization and Blending
- Film Thickness

So, if we are talking about the chemical structure then there the chemical structure will also of the main chain will also dictate its chain flexibility. So, that main chain flexibility is an important factor; also the type and nature of the side groups that are present in a given polymer chain, they also are important factors for in determining the glass transition temperature.

Apart from this if we let us say have a copolymer or a blend; so, for copolymers and blends there also the glass transition temperatures will be different from the homo polymers that are used to make the copolymer the blend. So, the copolymerization or blending is also something that can affect the glass transition temperature.

The; if you are talking about very thin films of polymers; there also it has been seen that the glass transition temperature of polymers which exists as very thin films is different from glass transition of polymers which exists as bulk materials ok.

So, if you are talking about polymer films which are let us say thinner than 100 nanometer. So, of the orders of 10s of nanometers; so, let us a 20, 30 even 10 nanometer thin. So, for such very thin polymer samples it has been observed that the glass transition temperature is reduced compared to the glass transition temperature of the bulk polymer and the reduction in many cases is significant.

So, this how thin the polymer film is that can also affect the glass transition temperature, but usually this only becomes important when the film thickness is very small typically of the order of 10s of nanometers. And there the reason why the glass transition temperature is lowered is that in a very thin film majority of the polymer chains actually will be present on the film surface.

So, at the film surface since the surface of the film is exposed to the surrounding atmosphere. So, the chains at the surface actually are less restricted due to their surroundings. So, they can show a greater degree of molecular motion. So, that has been postulated as an explanation for this decrease in glass transition temperature as the film thickness reduces to let us say below 50 nanometer.

Apart from these factors another very important factor is actually the molecular architecture of the chain. So, whether the how long is the chain which will be defined by the molar mass of the chain; how much branching is there whether is any cross linking presents. So, these kind of features of the molecular architecture of the polymer chain; they also significantly affect the glass transition temperature. So, let us try to discuss some of these factors in more detail now.

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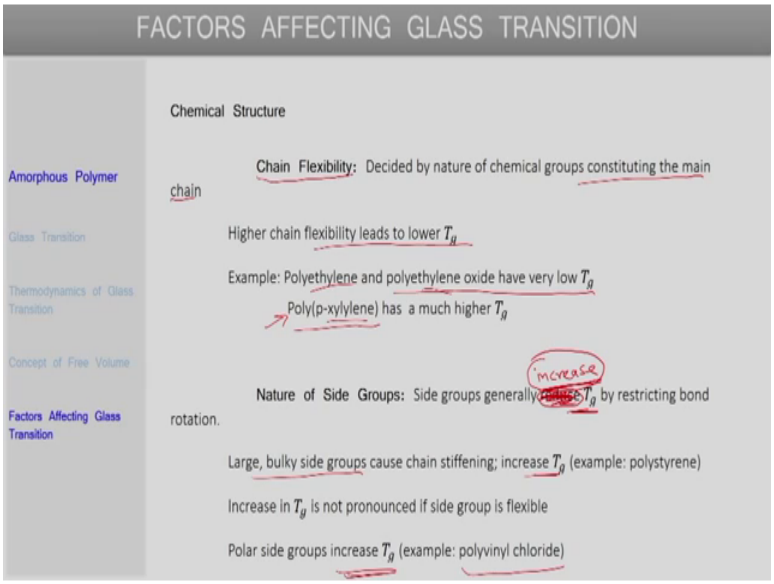

FACTORS AFFECTING GLASS TRANSITION

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Chemical Structure

Chain Flexibility: Decided by nature of chemical groups constituting the main chain

Higher chain flexibility leads to lower T_g

Example: Polyethylene and polyethylene oxide have very low T_g

Poly(p-xylylene) has a much higher T_g

Nature of Side Groups: Side groups generally ~~reduce~~ increase T_g by restricting bond rotation.

Large, bulky side groups cause chain stiffening; increase T_g (example: polystyrene)

Increase in T_g is not pronounced if side group is flexible

Polar side groups increase T_g (example: polyvinyl chloride)

So, if we talk about chemical structure ok. So there are couple of things that we can identify as affecting glass transition temperature. The most important thing being the flexibility of the main chain or the polymer backbone; so, if we are talking about the change flexibility with respect to the polymer backbone; then the flexibility of the chain is also defined by the kind of the or the nature of chemical groups that are present in the main chain of the polymer.

So, the groups that constitute the main chain of the polymer; they will define how flexible the main chain is. And the more flexible the polymer chain is the lower will be the glass transition temperature because the chain is more flexible. Then even at lower temperature with the lower thermal energy; it can start moving and hence the glass transition temperature will be lower.

As we discussed high chain flexibility will result in lower glass transition temperature of course. And as an example if we consider polyethylene or polyethylene oxide; so, these have, so polyethylene has CH 2 CH 2 the groups in their main chain and polyethylene oxide as CH 2 CH 2 O repeated in its main chain.

So, these polymer molecules basically are highly flexible because their main chains consist of these small groups which allow first which through easy bond rotation allow for great flexibility of the polymer chain.

So, these have very low T gs polyethylene the T g is not very easy to measure, but a typical estimates are in the range of minus 130 degree Celsius to minus 30 degrees Celsius polyethylene oxide has a T g of around minus 67 degrees Celsius. So, these are very low T gs because their main chains are highly flexible.

If we contrast that with the T g of poly p is xylylene; this has a much higher T g because in its main chain apart from the CH 2 CH 2 groups that are present in both p and po this poly p xylylene also contains a phenylene group.

So, an aromatic ring is also present in the main chain which is bulky and it hinders a rotation bond rotation. So, that is why the chain flexibility is significantly hampered by the presence of the phenylene group in this polymer and the subsequently that consequently the T g is much higher it is around almost 80 degrees Celsius. So, much higher than what we see for polyethylene or polyethylene oxide.

So, chain the main chain flexibility of course, of xtg; apart from that the side groups that are present, they also have a significant effect on the glass transition temperature of the polymer. If the side groups are bulky or heavy large side groups, then they again hinder that would bond rotation and reduced chain flexibility and thereby increase the glass transition temperature.

So, this should actually be not reduced, but increased; so, the presence of side groups actually hinders chain rotations reduces flexibility and increases a glass transition temperature. And especially that if the side groups are bulky or large then their effect on in on hindering the bond rotation, strain rotation and chain flexibility will be more pronounced and hence the glass transition temperature will be even higher.

So if you have large bulky side groups they can cause a significant stiffening of the polymer chains and they increase glass transition; so, typical example is polystyrene where the main changes pretty much similar to what we have for polyethylene. The main chain just contains CH 2 CH 2 groups, but every and on every other carbon atom of the main chain, there is a phenyl ring attached to it which is the bulky size group that we are talking about.

So, due to the presence of that the glass transition temperature of polystyrene is significantly increased and it is approximately almost 100 degrees Celsius. So, again the side groups increase the glass transition temperature and this error you should ignore it should be increase. So, side groups increase the glass transition temperature and how much increases the glass transition temperature depends on how bulky the side group is; so, that is one factor.

So, if instead of being bulky that the side group itself is quite flexible then the glass transition temperature might not actually in be affected that much. So, if we have a side groups which look like a short chain branch which are which have internal flexibility. So, because of that internal flexibility; the glass transition temperature is not significantly affected by such flexible side group. So, they do not lead to significant increase in T g whereas, if you have just bulk or rigid side groups they will lead to significant increase in T g.

Apart from the bulky nature if the side groups are polar. So, the polarity of the side group also plays a role on the glass transition temperature. So, if the side groups are polar then the glass transition temperatures are usually higher because the polar side groups will interact more strongly. And then again will lead to or again will hinder the change flexibility and chain rotation and movement.

So, if we have polar side groups; they also typically increase T g a typical example is polyvinyl chloride where the side group is a chlorine atom which is a polar group. So, there again the main chain is similar to what we have for polyethylene, but because of this polar chlorine side group; the glass initial temperature is around 80, 85 degree Celsius. So, it is much higher than what we have for a simple polyethylene polymer.

So, bulky side group polar side group these tend to increase the glass transition temperature. If the side group is itself is flexible, then the increase in the glass transition temperature need not be very pronounced.

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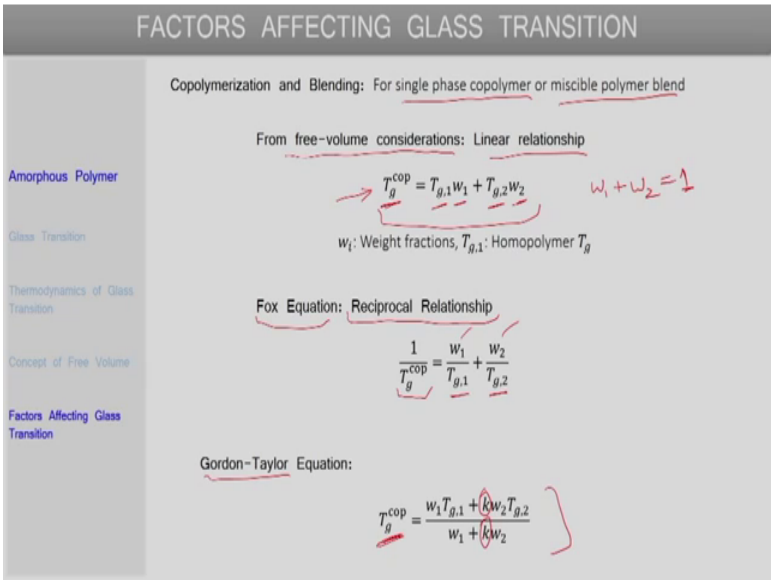

FACTORS AFFECTING GLASS TRANSITION

Amorphous Polymer

Glass Transition

Thermodynamics of Glass Transition

Concept of Free Volume

Factors Affecting Glass Transition

Copolymerization and Blending: For single phase copolymer or miscible polymer blend

From free-volume considerations: Linear relationship

$$T_g^{cop} = T_{g,1}w_1 + T_{g,2}w_2 \qquad w_1 + w_2 = 1$$

w_i: Weight fractions, $T_{g,i}$: Homopolymer T_g

Fox Equation: Reciprocal Relationship

$$\frac{1}{T_g^{cop}} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}}$$

Gordon-Taylor Equation:

$$T_g^{cop} = \frac{w_1T_{g,1} + kw_2T_{g,2}}{w_1 + kw_2}$$

So, apart from chemical structure the other thing is copolymerization and blending. So, if we have two homo polymers we are blending them together to form a miscible blend or if we form a let us say random copolymer or some kind of statistical copolymer, then in such cases the copolymer typically will exist as a single phase or the polymer blend also if it is a miscible polymer blend will exist as a single phase and the material will show a single glass transition temperature.

On the other hand if the polymer blend is immiscible and it actually contains two distinct phases or if again our copolymer is internally immiscible. For example, block copolymers which show micro phase separation. So, for such cases if there is in inherent immiscibility there and presence of two phases then the glass transition temperatures that these such immiscible copolymers or blends exhibit are more than 1.

So, depending on the components present the individual or characteristic glass transition temperature of individual polymers present in those immiscible blends or immiscible wakow polymers will be exhibited. However, we will restrict ourselves to the miscible polymer blends or copolymers also which exist in single phase; so, typically random or statistical copolymers.

And for such cases, the glass transition temperature for the blend or copolymer can be predicted from the glass transition temperatures of the respective homo polymers; using many different kind of relations. So, simple relation which is the based on very simple free volume theory arguments is just a linear kind of relationship and one can derive it from free volume considerations.

So, here the copolymer or the blend glass transition temperature is given as a glass transition temperature of the first homo polymer times its weight fraction and plus the glass transition temperature of the second homo polymer times the weight fraction of the second homo polymer. So, here it is important to realize that w 1 plus w 2 is 1; we have a binary polymer blend or a copolymer containing just two types of repeat units.

So, here if we know the T g 1 and T g 2 which are the glass transition temperatures have the respective homo polymers. And if we know the weight fraction, we can estimate the glass transition temperature of the blend or copolymer. But what seen usually is that this kind of a linear relationship usually overestimates the glass transition temperatures of the blend or copolymer.

So, instead of this other relationships which agree better with experimental findings have been proposed. So, Fox equation is one such equation which contains a kind of reciprocal relationship between the glass transition temperatures. So, here 1; 1 over the glass transition temperature of the copolymer or blend that is equal to the weight fraction of first homo polymer by divided weights glass transition temperature, plus weight fraction of the second homo polymer divided by its glass transition temperature; so, that is the Fox equation.

Many other equations are possible or are have been proposed. So, another widely used equation is what is called a Gordon Taylor equation; here the glass transition temperature of the blend or copolymer is again related to the weight fractions and the glass transition temperatures of the homo polymers using this kind of relation. But apart from the glass transition temperatures of homo polymers and the weight fractions this factor or this constant k is also present.

So, these are some typical relationships that can be employed to find out the glass transition temperature, if we have formed statistical or random copolymer or a miscible polymer blend. So, apart from co pollination or blending the; we discussed that the molecular architecture also affects the glass transition temperature.

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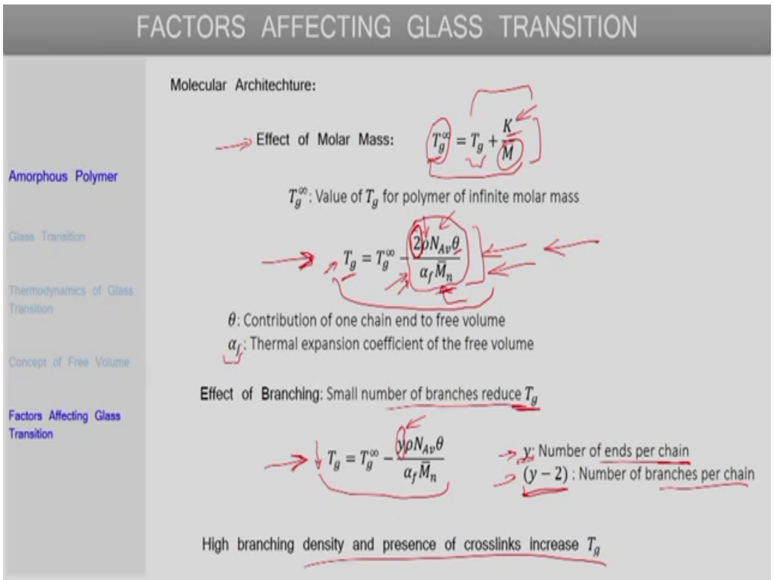

FACTORS AFFECTING GLASS TRANSITION

Amorphous Polymer

Glass Transition

Thermodynamics of Glass Transition

Concept of Free Volume

Factors Affecting Glass Transition

Molecular Architechture:

Effect of Molar Mass: $T_g^\infty = T_g + \frac{K}{M}$

T_g^∞: Value of T_g for polymer of infinite molar mass

$$T_g = T_g^\infty - \frac{2\rho N_{Av}\theta}{\alpha_f \bar{M}_n}$$

θ: Contribution of one chain end to free volume

α_f: Thermal expansion coefficient of the free volume

Effect of Branching: Small number of branches reduce T_g

$$T_g = T_g^\infty - \frac{y\rho N_{Av}\theta}{\alpha_f \bar{M}_n}$$

y: Number of ends per chain

$(y-2)$: Number of branches per chain

High branching density and presence of crosslinks increase T_g

So, in terms of molecular architecture we can this first consider the effect of molar mass on the glass transition temperature. So, molar mass is if we considering linear polymers, the molar mass will typically be directly related to the size of the polymer chains.

So, longer the polymer chains higher will be the average molar mass. So, it is observed that higher the molar mass larger is the glass transition temperature. So, typically the relation between the glass transition temperature and the molar mass is expressed by a relationship like this. Here this T g infinity is a kind of hypothetical value of the glass transition temperature for polymer with infinite molar mass and this k is a constant ok.

So, we can see from this relation that if T g infinity and K these are constant for a given polymer; then T g is T g will increase if M is increased. So, if M is increased this ratio will decrease and to keep T g infinity constant then if M increases then T g also has to increase; so, that this sum is maintained constant.

So typically the explanation for this increase in T g with molar mass is can be made through the free volume considerations. So, here what we can say is that the free volume associated with polymer chains and it is typically higher than the free volume associated with portions of polymers, which are not at the chain ends. So, near the chain ends is expected that the corresponding associated free volumes at is higher.

So, based on this kind of postulate that the chain ends are associated with larger free volumes, one can basically say that if the polymer molar mass is small then for a given polymer sample the number of chain ends will be higher; we will have many small chains and so, the number of chain in present will be larger. So, essentially the free volume present will be larger than the glass transition temperature will be lower.

On the other hand if the polymer chains are very long. So, in a given polymer sample the number of chain ends present in that case we lower. So, the corresponding associated free volume for if the chain ends will also be lower and that will lead to a larger glass transition temperature. So, based on this kind of arguments; one can actually derive an expression for this T g relation between T g and the number average molar mass.

So, the relation between T g and number average molar mass is given by this expression here where this N of average is Avogadro number rho is the density of the polymer. Theta is what is called the contribution that a single chain end makes to the free volume. This alpha f as we have discussed before is the thermal expansion coefficient of the free volume itself and it can be obtained as a difference between the thermal expansion coefficient of the rubbery and the glassy polymer.

Again from this relation we can see that as M n is increased T g will also increase because as M n is increased this term actually decreases. So, if this term is decreasing then T g will increase and as M n tends to infinity, this term will become 0 and T g will tend to T g infinity in that case. So, apart from molar mass the branching the degree of branching and cross linking; these can also have an effect of effect on the glass transition temperature.

So, if that degree of branching is small. So, if you have a small number of branches present on the poly polymer main chain, then that actually can lead to a reduction in the glass transition temperature. The reason for that is if we have a few branches present on each chain; then for each chain the number of chain ends present increases because each branch will contribute an extra chain end. So, and we have talked about the fact that each chain end is associated with larger free volume than the remaining parts of the polymer molecule.

So, since we are now more number of chain ends polymer molecule. So, that will increase the overall free volume and here thereby reduce the glass transition temperature. So, this will be true if we have a small amount of branching in the polymer chain.

So, small number of branches reduces T g as we discussed and the expression again relating T g and the degree of branching that can be obtained again from free volume considerations. So, the this expression that we have discussed before; this can actually be modified considering the fact that if we let us say have a branching the polymer chains; then for each polymer chain the number of chain ends will be more than 2.

So, here in this expression the number of chain ends is 2 that is why this factor two appears here. For a branched polymer the number of chains ends per molecule will be higher. So, instead of this expression here the expression that we can use is something like this. So, it is a similar in form to the previous expression only thing is instead of 2; we have y here. So, y is the number of chain ends per polymer molecule or number of chain ends per polymer chain.

So if the number of chain ends per polymer chain is y then the number of branches for the polymer chain molecule will be y minus 2 because two ends are we contributed by the main chain and remaining y minus 2 ends have being contributed by the individual y minus 2 branches present.

So, number of branches per chain will be y minus 2 number of chain ends per chain is y and the T g then is given by this expression. So, we see that as y is increased T g will go down, but this holds only if the number of branches is small; if the number of branch degree of branching is large, then the high amount of branching actually again starts interfering with chain motion and ultimately the T g is increased.

So, if we have a high amount of branching that T g will be increased the effect or the additional free volume due to the presence of extra chain ends; that will be more than offset by the hindrance to chain motion that will be presented by the high level of branching present.

So, for high amount of branching that T g will again increase; similarly if cross links are present then cross links again restrict the chain motion. So, that in turn leads to increase in glass transition temperature as well. So, high amount of branching was a present of cross links actually increases the glass transition temperature.

So, and if the cross linking density cross linking density is quite high then it might happen that the polymer does not show a glass transition at all and before showing a glass transition upon heating the polymer actually degrades. With this we will like to wrap up our discussion of the amorphous polymer phase where we have discussed the fact that amorphous polymers have mostly disordered. And to an extent one can describe the chain configurations as being similar to random coil or similar to what is observed in theta solvents where unperturbed chain dimensions are present.

So, in a polymer amorphous bulk polymer also similar chain dimensions are observed. The amorphous polymer does not show any melting transition, but it shows a glass transition way from a hard glassy state to a soft rubbery state. And this glass transition is shows characteristics that is similar to a second order thermodynamics transition.

Although strictly speaking glass transition is not a thermodynamic transition; one can understand glass transition from a molecular viewpoint using the free volume theory. And there are several factors that affect glass transition like the nature of chemical nature of the polymer chain, the nature of the side groups that are present, the flexibility of the main chain, whether we have a copolymer or blend the thickness of a polymer film that also can affect the glass transition temperature. And also the molecular architecture of this polymer chain in terms of the chain length its molar mass, the degree of branching cross linking.

So, all these factors can have significant effect on the glass transition temperature and we have explored those effects in the present lecture. So, in the next lecture we will discuss the other important state present in polymer molecules which is a crystalline state of polymers.

Thank you.