Polymer Chemistry
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Lecture - 35
Amorphous and Crystalline State: Tg and Tm

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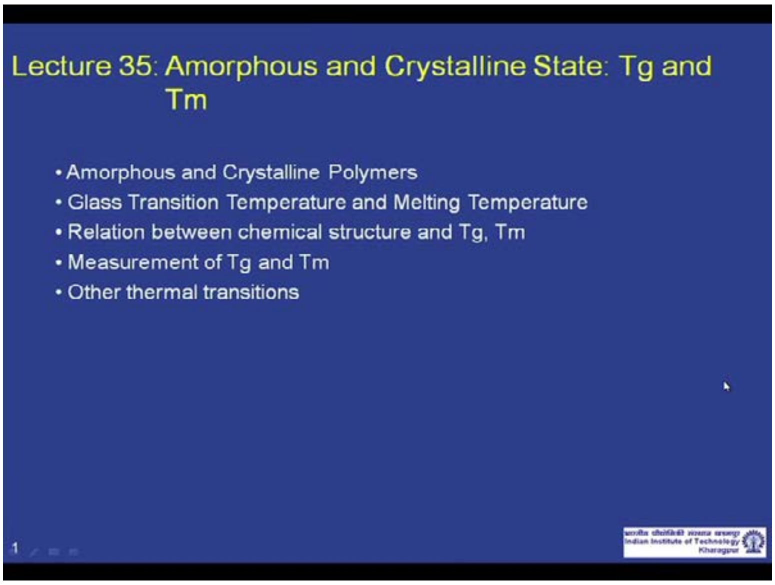

Lecture 35: Amorphous and Crystalline State: Tg and Tm

- Amorphous and Crystalline Polymers
- Glass Transition Temperature and Melting Temperature
- Relation between chemical structure and Tg, Tm
- Measurement of Tg and Tm
- Other thermal transitions

Welcome back to this course on Polymer Chemistry. In today’s lecture we are going to discuss about amorphous and crystalline states of polymers. And with related to that, we will talk about the glass transition temperature and the melting point of polymers and then we will talk about the relationship between chemical structures of polymer chain and how it is effects the values of glass transition temperature and melting point. I will brief discuss about the measurement techniques of T g and T m.

Before we start today's content, let me just take two to three minutes to explain the last slide or last slide page in my previous lecture, last lecture; because I thought that I did, because of time it was completed hurriedly. I just want to spend five minutes there.

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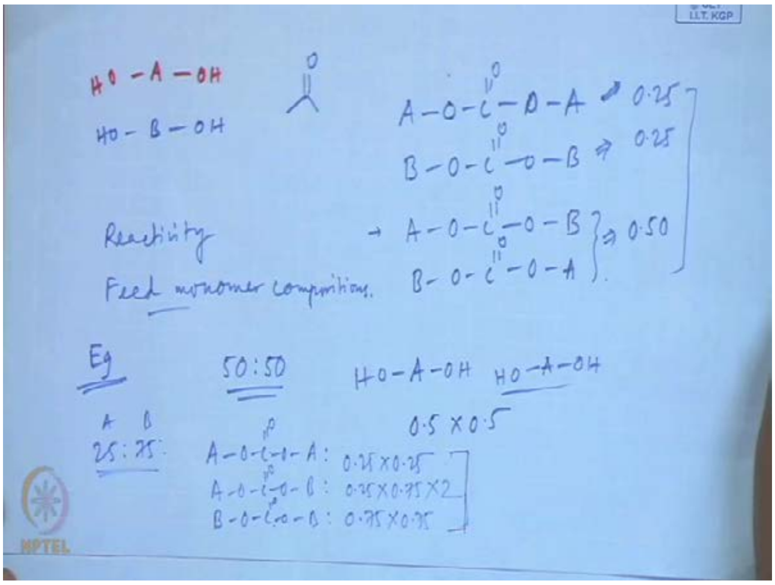

Now if, for example, what we were doing yesterday that I discussed that if I for example, have two phenol; bisphenol in this case and now they may react with some carbonate source to make to form polycarbonate. Now, this example I am giving for polycarbonate, but this is, this analysis is applicable for any polymer, any copolymer specially for poly condensation copolymers; where you have, you can find out a carbon which are signal, anymore signal dependent on the two two groups which is holding that bond.

Now, you can have the three types of carbonate linkage. ‘A O C O O A’, I just give it example here, and B O C O O B and you can have A O C O O B. Now, this is this is similar to having B O C O O. Now, this two are similar. Now, in a polymer copolymer chain which will be favorable? Of course they depend upon the reactivity of the monomers in this A and B and obviously the feed monomer composition.

Now for example, if we assume first that the reactivity of this two monomers is same, then if I take a fifty-fifty ratio of the feed monomer composition by more person, by number, then obviously the chances of that A O H will react with another A O H to form a carbonate; will be given by 0.5 in to 0.5. There, these are fifty percent of this bisphenols are this type. So, the chances of this type of carbonate linkage is forming 0.25, if I have fifty-fifty ratio in the feed. Similarly, the chances of this type of carbonate linkage is given by again 0.25, if I have fifty-fifty ratio in the feed. Similarly, the chances of this type of carbonate linkage is given by again 0.25 and individually these two are again 0.25, so together they get 0.5.

So, obviously if I having a random polymerization where it is only dictated by the feed monomer composition, not by the reactivity of the two monomers, then a fifty-fifty feed composition will produce these three carbonate linkage. Similarly, if I have a, say 25 A; A is to be 25 and 75, then chances of forming A O C O O A will be 0.25 multiplied by 0.25; A O C O O B, 0.25 into 0.75 again; twice because for the other way round and for B O C O O B will be 0.75 into 0.75.

See, if for A this small ratio; so if I found after the polymerization is made from our carbon that the ratio for these three carbonated is for fifty-fifty feed ratio, monomer ratio, then we will know that it is a random copolymer. So, the reactivities are not different.

Similarly, if we have a this ratio of these three carbonates, then we will know that this is a random arrangement. And if the obtained signal ratio is different from any of the values, it will be suppose to for a statistical random copolymer, then we will know that block is there in the polymer.

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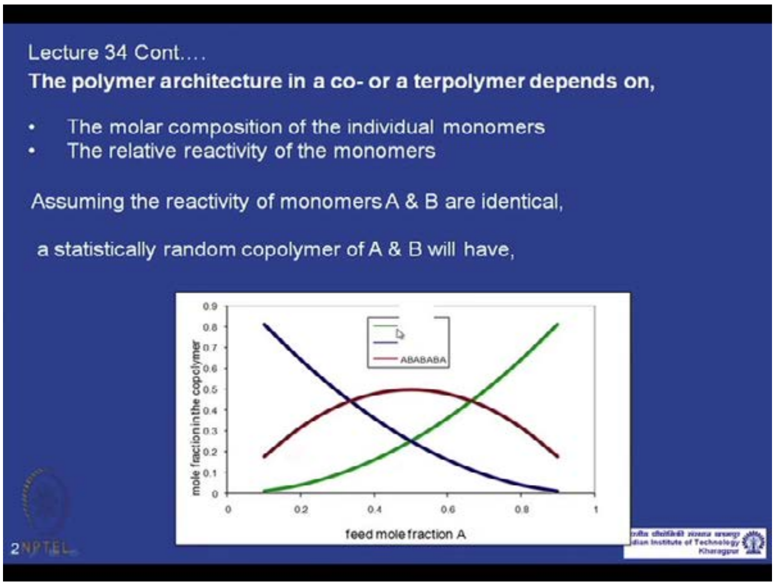

Lecture 34 Cont….

The polymer architecture in a co- or a terpolymer depends on,

- The molar composition of the individual monomers
- The relative reactivity of the monomers

Assuming the reactivity of monomers A & B are identical,

a statistically random copolymer of A & B will have,

So, this exactly has been shown by plotting in this. So, if you change the feed ratio, what will be the ratio? This is for A A and this is for B B, this is for A A. So, this A for carbonate or any other… polymer; this is for B B and this is for A B A B linkages. This is the plot of monomer mole fraction verses feed mole ratio.

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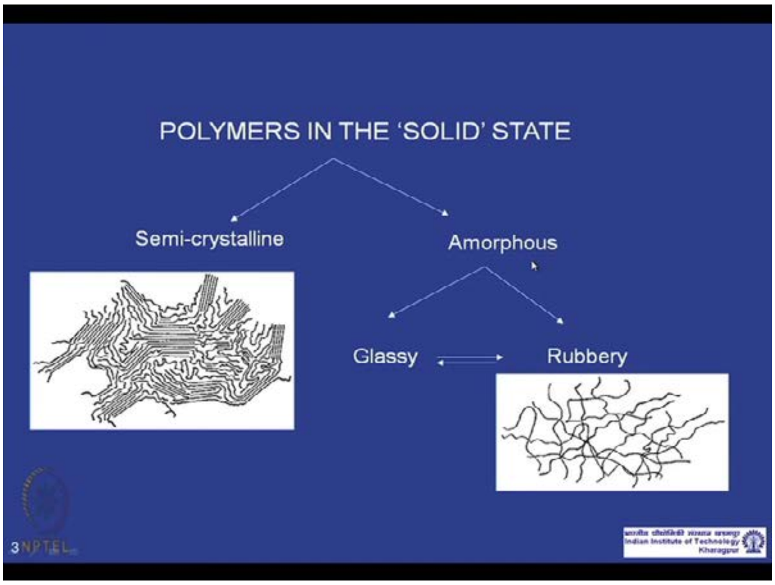
POLYMERS IN THE 'SOLID' STATE

Semi-crystalline

Amorphous

Glassy

Rubbery

Ok. Now, let us come back to today's topic of lecture about amorphous and crystalline state. Till now what we have done? We have already made the polymer. We know how to make the polymer from our understanding of polymer synthesis and then we know that how it behaves in solution. And with that knowledge, we were able to find out the chemical composition of the polymer. And if it is a copolymer what is the composition, what is the, what is the sequence of monomer present in the monomer in the polymer and we know what is the molecular weight of the polymer.

So, we know all the basically what are the information needed for the polymer. We know by this time. So, what is what we will do this? What we will do now with the polymer? Obviously, we want to use this polymer for some applications. And, I have discussed in the very beginning that polymers are utilized in mainly two O H bonds. These polymers after synthesized are added in some formulations along with the other components like in detergent, paint, ink, emulsions; where polymers are added with some other compounds. So, polymer is one of the components among many.

Secondly, which is almost the majority of the application of polymeric material or polymers is where the polymer is the main component. It is almost close to hundred percent polymers and you have the additives or fillers, which basically are the property enhancer or stabilizers or color and dye. Those are the added components. So, mainly it is the polymer. So what, how do you make those polymers like if you feel disc, if you want to make a CD or DVD out of a polymeric material? We have synthesized the polymer and characterized; now we have to give or you to make a polymer in a different shape, which is the shape of the final applications of that polymers.

So, for that we must know the behavior of a polymer in solid state. Solid state in the sense, where the polymer is applied in room temperature, it is not viscous. What it is not a as we will discuss that "solid state" may not be the thermodynamically correct terminology in case of Polymer Science. What solid by state, I mean that it is not flowing in the condition where we are using. So in polymers, polymers in that solid state can be mostly in two types. Where, they can be semi-crystalline; Semi- crystalline, when it has this crystalline regions and which are basically ordered. And amorphous region, where amorphous material, where there is no order.

We all know what is a crystal? And we know crystalline solid, liquid and gaseous state of matters; three state of matters. Where in case of crystalline state, solid state, we have long-range order; in case of liquid state we have short-range order and in gaseous state we do not have any order. And, we have sub-temperature or sub-temperature conditions, where these two transitions takes place from gas to liquid state at volume point and from a liquid to solid state as a freezing point. So, you know that there are three states possible for a matter.

In case of polymers, this solid state is not actually a proper. in true sense, solid states because in most cases, either it is fully amorphous, no long-range order is present and in second case they could be partly crystalline; partly, there could be long range order exists and partly there will be no order. So, it is a combination of amorphous and crystalline region. So, we call this as a semi crystalline state. It is not practically possible to get purely hundred percent crystalline polymer, because of your size is mainly because of size or large molecular weight. So, we mostly delete semi-crystalline polymer, which is basically partly crystalline and partly amorphous. And amorphous, which is hundred percent amorphous, zero percent crystalline region.

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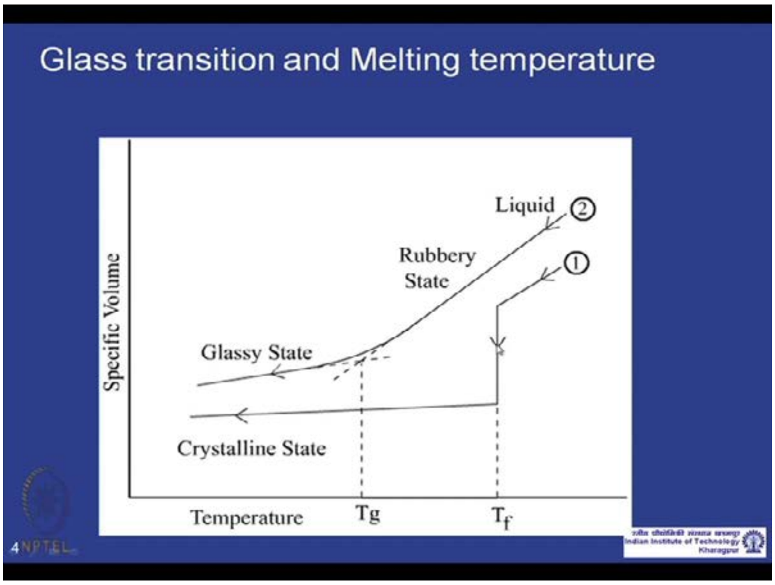

Glass transition and Melting temperature

Now, what happened if we take water and cool it down? Say, for example, this one, case one; if we take a water vapor and then the water, just consider water, liquid water and then cool it down. The specific volume will go down. It will happen for most of the basis. There could be some disturbance for water, but I am talking about in general any liquid. Just consider a general liquid; with decrease in the temperature, the specific volume will decrease and at a particular temperature freezing point, the specific temperature will go a discontinuity and then it will form a crystalline state. And again, the specific volume will decrease with the decrease in temperature, but in a much slower rate than it was in case of liquid state.

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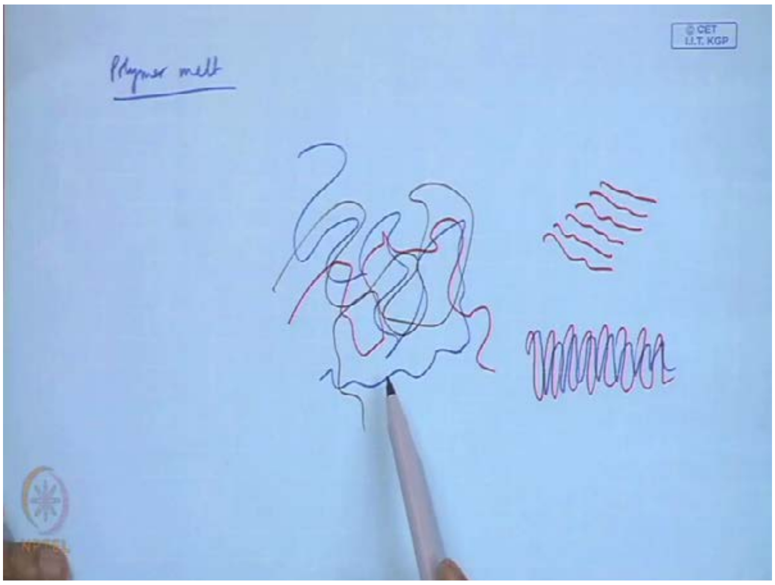

Now, what happened in case of polymer? See, if I have a polymer melt I have a polymer melt polymer melt, obviously there are many changes. I am drawing few changes here with different inks. Trying to draw polymer chains having different with different inks. Just imagine, these three are the different polymer chains in melt, then tangled. They have thermal motions; they have kinetic energy associated with them.

Now, if you cool this or reduce the temperature of this polymer melt, obviously this viscosity goes up and the polymers start flowing less. Now if you further cool down, what happened? In case of a small molecular liquid, they would have a certain temperature in freezing point or melting point, they would have arranged or form a crystal with long range order. But in case of polymers, when you are cooling these trans, these polymer chains do not have enough space or they do not have enough time to sort of arrange themselves and align themselves, so that they make a crystal.

So, to have a crystal, say for example, if I want to make a crystal, either these polymer chains should arrange in order or they can, a single polymer chain can fold like this and can make a order. So, basically if you are talking about two, three polymers, they can form like different crystalline states. So, what I am trying to explain? That when you cool a polymer melt, it is not possible for the entire polymer must, to crystallize mainly because of there is not enough space or you are not giving enough time to the polymer chains to arrange or align themselves in a crystalline manner or maybe the polymer chemical structures do not allow them to align in a regular manner.

So, if it does not crystallize at melting point and you keep on decreasing the temperature, what will happen? The viscosity will further decrease. And one point of time, the mobility, the thermal energy of this polymer chains will not be sufficient to have any mobility, any long range mobility of the polymer chain. So, the polymer chain will become like a glass. So, if you cool a polymer sample, they can crystallize partly in this temperature or if they do not crystallize at all and if further reduced, then they can undergo, the viscosity can go up, they can become a rubbery material.

And with further drop in temperature, their mobility becomes effectively very low and they become a glassy state. So, this temperature where you have a conversion or transformation of the rubbery state; transition from a rubbery state to glassy state, this is not a particular temperature, but a particular range of temperature; this is called glass transition temperature. And the temperature at which the polymer melting happens, that is the melting temperature of a polymer.

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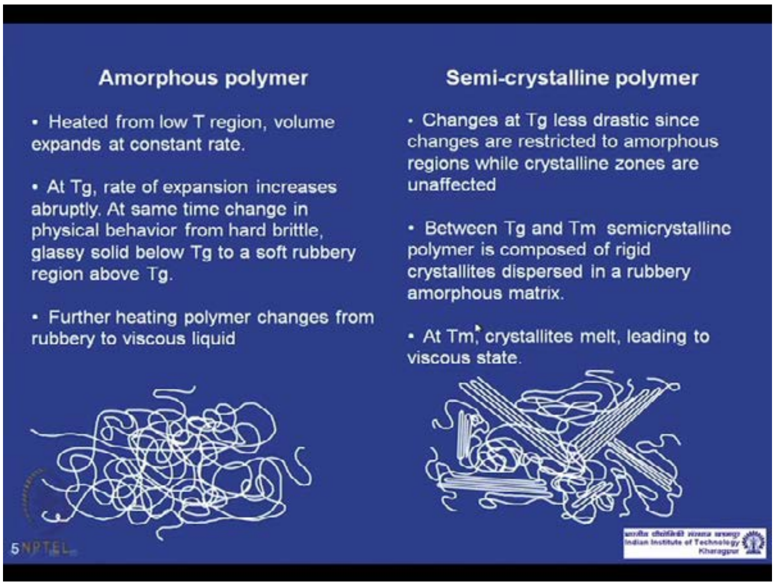

Amorphous polymer

- Heated from low T region, volume expands at constant rate.
- At Tg, rate of expansion increases abruptly. At same time change in physical behavior from hard brittle, glassy solid below Tg to a soft rubbery region above Tg.
- Further heating polymer changes from rubbery to viscous liquid

Semi-crystalline polymer

- Changes at Tg less drastic since changes are restricted to amorphous regions while crystalline zones are unaffected
- Between Tg and Tm semicrystalline polymer is composed of rigid crystallites dispersed in a rubbery amorphous matrix.
- At Tm, crystallites melt, leading to viscous state.

So, a polymer can have amorphous material. Now, we are talking about heating. What happened in case of a polymer material? For a amorphous polymer, if we heat from a lower temperature region, the volume expand at the constant rate. And at glass transition temperature, rate of expansion increases abruptly. And as the result of this chain mobilities, a bunch of physical behavior or the mechanical, a property of this polymeric material changes, it becomes hard material, to a hard glassy materials to a soft rubbery material. And if you continue heating, some point of time this rubbery material become like a viscous liquid.

Similarly, if you take a semi-crystalline polymer and heat it after the T g, the change in the polymer behavior is less compared to a pure amorphous, because they are part of the polymer material is amorphous; part is crystalline. So, changes at T g are less drastic, since the changes are restricted to amorphous regions only, where the crystalline regions are unaffected. So, between T g and T m the semi crystalline polymer is composed of rigid crystallites; like rigid crystallites which are composed, which are dispersed in a rubbery amorphous matrix. And at T m where the crystallite melts, which leads to a viscous state.

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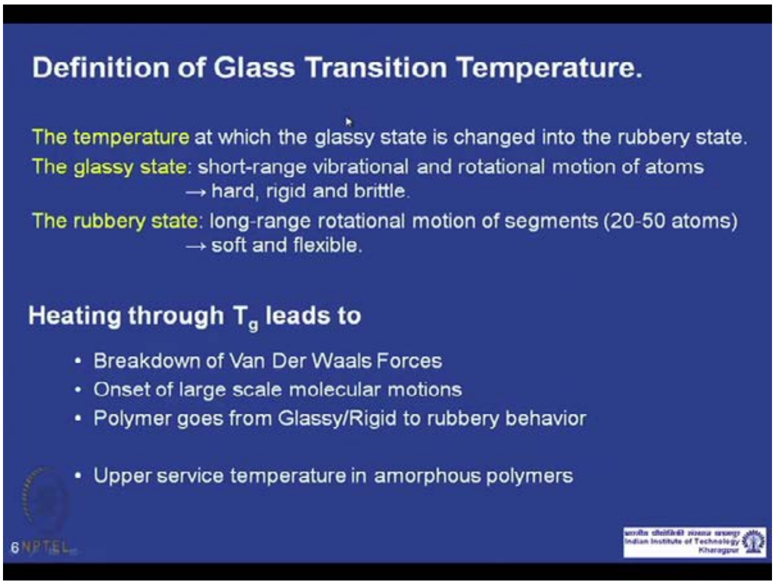

Definition of Glass Transition Temperature.

The temperature at which the glassy state is changed into the rubbery state.

The glassy state: short-range vibrational and rotational motion of atoms
→ hard, rigid and brittle.

The rubbery state: long-range rotational motion of segments (20-50 atoms)
→ soft and flexible.

Heating through T_g leads to

- Breakdown of Van Der Waals Forces
- Onset of large scale molecular motions
- Polymer goes from Glassy/Rigid to rubbery behavior

- Upper service temperature in amorphous polymers

So, if I want to define a glass transition temperature, that it is a temperature at which the glassy state is changed into the rubbery state. What is the glassy state? It is basically, we know this; the slide glass is hard rigid material, which have only a short-range vibrational and rotational motion of the atoms which is a hard, rigid and the brittle material. And the rubbery state is basically having a long-range rotational motion of polymer segments and it is a soft and flexible. So, at T g what are the transition takes place at in terms of molecular and if you think about polymer molecules, the intermolecular Van Der Waals forces they breakdown. And this is the temperature on set of large scale molecular motions. And we know that it undergoes glass to rubbery behaviour change. And that is, for amorphous polymer, obviously that should be highest temperature of usage because after that, the polymer becomes so soft that it cannot be useful.

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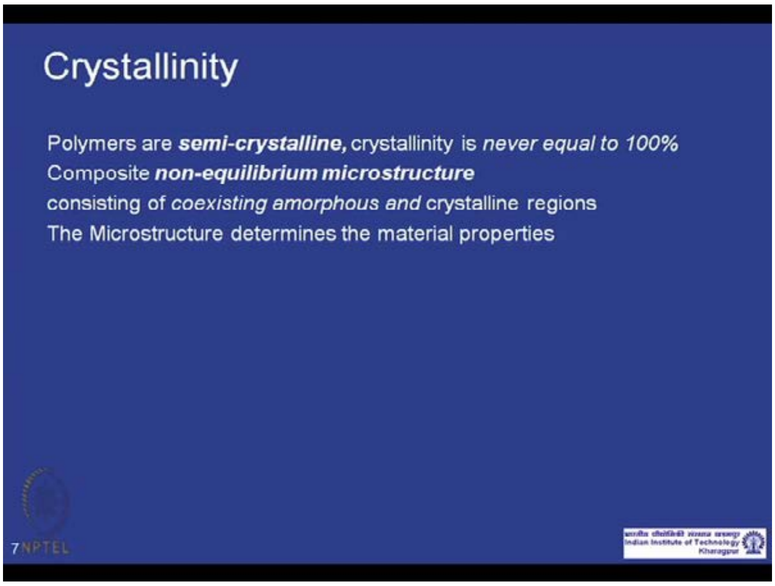

Crystallinity

Polymers are ***semi-crystalline,*** crystallinity is *never equal to 100%*
Composite ***non-equilibrium microstructure***
consisting of *coexisting amorphous and* crystalline regions
The Microstructure determines the material properties

We talk more about polymer crystallinity. Polymers as I said, it is never, the polymer crystallinity is not never up to hundred percent, it is always up to semi-crystalline. And the nature of polymer crystalline in the semi crystal material depends on how fast your cooling, what is the condition of you that the crystallization generalization. So, the crystallization size, the crystallites, the crystalline dimension of the shape of the crystalline regions, as well as the fraction of the inter material which are crystallize; they all depends on several factors. So finally, whatever crystalline material we have, that is non-equilibrium microstructures. And in case of semi crystalline material, there is existence, coexistence in amorphous and crystalline region. And this is the micro structure actually determines the material property.

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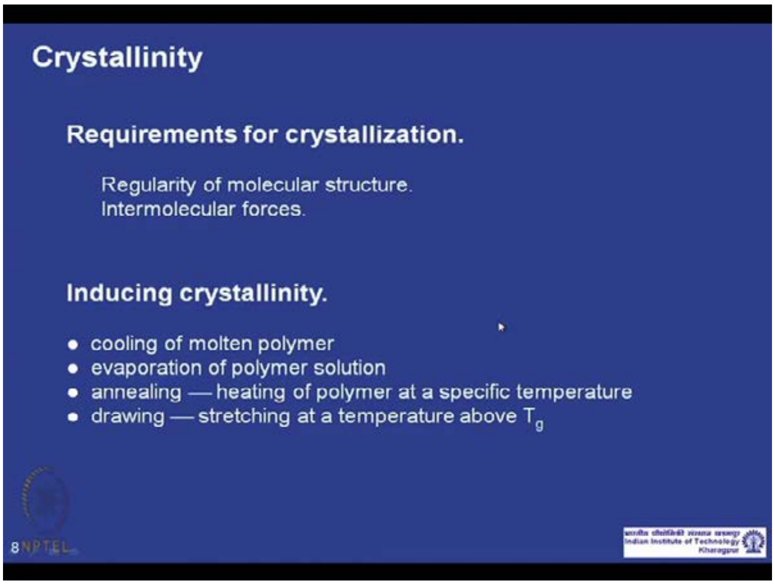

Crystallinity

Requirements for crystallization.

Regularity of molecular structure.
Intermolecular forces.

Inducing crystallinity.

- cooling of molten polymer
- evaporation of polymer solution
- annealing — heating of polymer at a specific temperature
- drawing — stretching at a temperature above T_g

How do you induce crystallinity in the material? We obviously can do it by cooling the molten polymer. When we evaporate a polymer solution, then the polymer chains can align themselves up because evaporation is a slow step, slow process... polymer chains in the solution have more time to align themselves. So, they can form crystalline regions. Annealing; annealing is nothing but heating a polymer at particular temperature. And basically what we get when we heat the polymers? At a certain temperature, we are providing some thermal energy. With the help of that, the polymer chains can slowly align themselves and form crystalline regions.

And another way, we can induce crystallinity in a polymer material by drawing. When a stretch, like stretch a amorphous polymers, then the amorphous polymer align just because it is between stretching the polymer. We the chains can come closer and direct; align themselves in a particular direction which basically induces crystallinity. So, these are the example how we can… these are the different ways we can induce polymer crystallinity. And as this emphasizes the fact that the final crystallinity in the polymer with… extend and the nature will depend upon several processes. So, final state is a non-equilibrium state.

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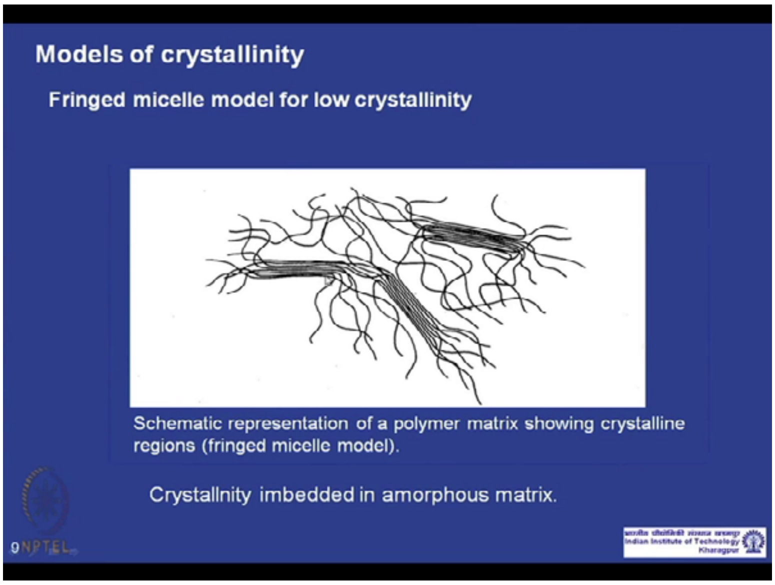

Models of crystallinity

Fringed micelle model for low crystallinity

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

Crystallinity imbedded in amorphous matrix.

There are different models available for polymer crystallinity. This is fringed micelle model, which is like these crystalline domains are micelle like structures. So, and this crystalline regions are formed by different polymer chains. And also, one single chain can be part of different crystalline regions. So, crystalline regions are embedded with or embedded in these amorphous regions, which are not crystalline.

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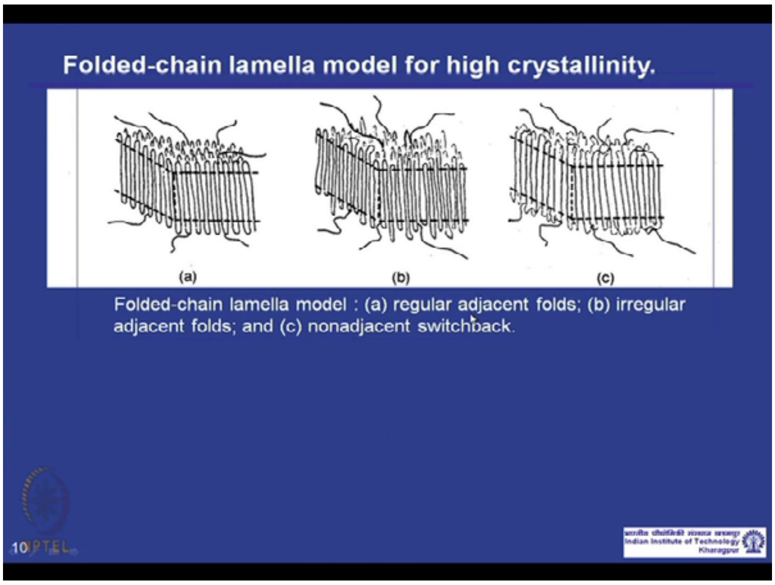

Folded-chain lamella model for high crystallinity.

Folded-chain lamella model : (a) regular adjacent folds; (b) irregular adjacent folds; and (c) nonadjacent switchback.

The other models it can form; just like I was explaining it can form folded chains and align themselves to form high crystalline material. And there are different models available like regular adjacent folds, irregular adjacent folds and nonadjacent switchbacks.

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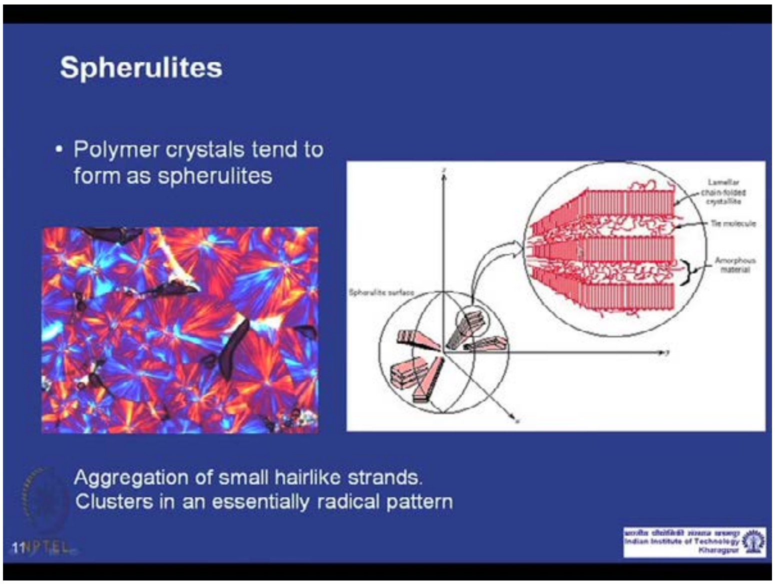

Spherulites

- Polymer crystals tend to form as spherulites

Aggregation of small hairlike strands.
Clusters in an essentially radical pattern

And, other module of polymer crystallines is Spherulite; where these polymer crystallites are arranged in this manner. As the Polymer Chemistry may not be very much interested in this that the morphology of the crystalline polymers, but we to understand the polymer properties and the structure properties relation, we must know the crystalline behaviour and different types of models in polymer material.

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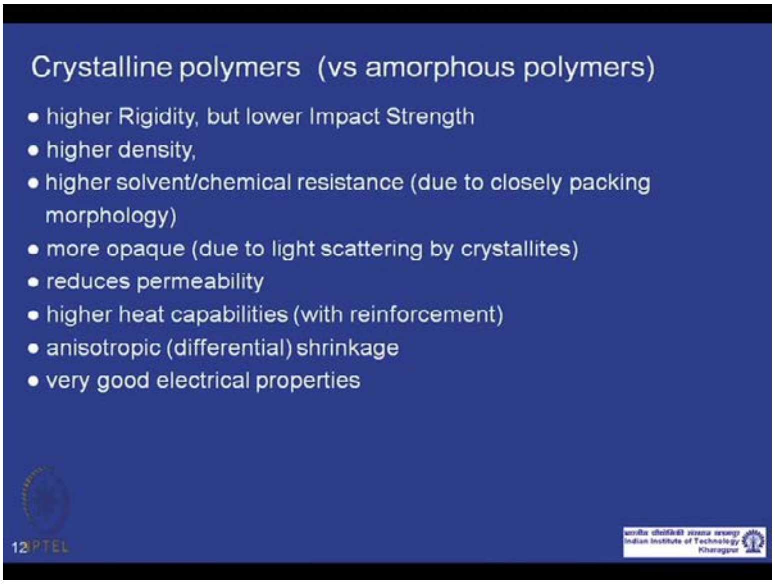

Crystalline polymers (vs amorphous polymers)

- higher Rigidity, but lower Impact Strength
- higher density,
- higher solvent/chemical resistance (due to closely packing morphology)
- more opaque (due to light scattering by crystallites)
- reduces permeability
- higher heat capabilities (with reinforcement)
- anisotropic (differential) shrinkage
- very good electrical properties

Now, how if the crystalline polymers is different than amorphous polymer? As you can understand that crystalline regions, semi-crystalline polymers will have crystalline regions of high stiff regions which basically gives you higher rigidity, but lower impact strength; obviously, you can imagine from the structure that it will give higher density. Crystalline polymers or semi-crystalline polymer give you a higher density to amorphous polymers. Because of the presence of the crystalline regions, it gives resistance, higher solvent or chemical resistant.

Obviously, this because of the presence of crystallites, catalyte and invariably we get translucent to opaque material. Presence of crystallites helps in reducing the permeability of different gases. The crystalline polymeric material gives high heat capabilities because of the reinforcement made by the crystalline regions. And some other properties like anisotropic and all good electrical properties you can get as a result of crystalline regions.

This is not all desired. It should not have a perspective that all crystalline polymers are semi-crystalline polymers… better properties than amorphous polymers. They have some better properties, but in a cost of something else. Like it always comes, it always becomes opaque or translucent. If you want to have applications where you need where you need a transparent polymeric material, then it is very difficult to do with a crystalline polymers. You always stand up for choosing amorphous material. So, there is always a balance between what you need for the final applications. Now, let us talk about the thermodynamics of this glass transition temperature and the melting point in brief.

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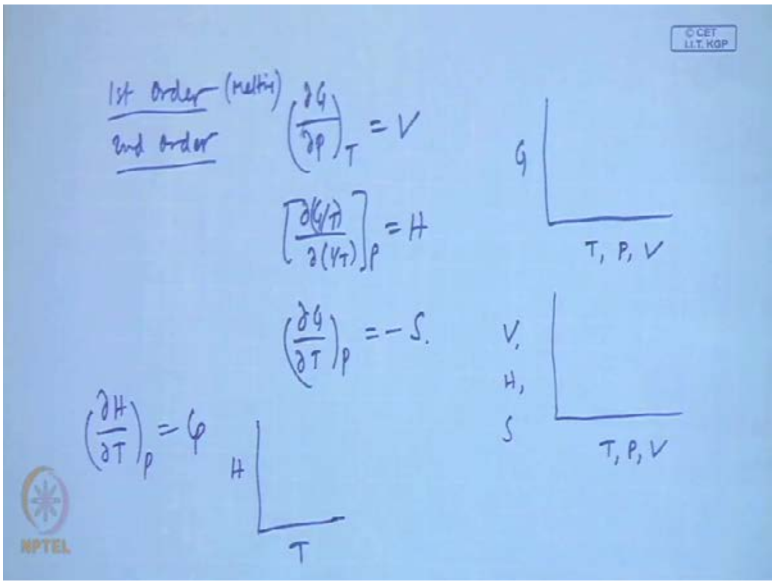
1st Order (melting)

2nd order

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

$$\left[\frac{\partial(G/T)}{\partial(1/T)}\right]_P = H$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$\left(\frac{\partial H}{\partial T}\right)_P = C_p$$

Now in Thermodynamics, we can have two types of transition; first order phase transition and second order phase transition. Now, from our thermo dynamical knowledge we can write these expressions. Now, in first order transitions what happened? If we plot G verses any of the straight parameters like temperature, pressure, volume, then it changes continuously. This is a continuous change of free energy with the state parameters like pressure, temperature, volume. Whereas if we plot any of the first derivative of the Gibbs energy function like V or H or S with any of this parameter, then we are we get a discontinuity in this plot. So, basically first order transitions gives continuity in G verses T, P, V plot, whereas the first derivative of G is discontinuous when we plot against these state parameters.

Whereas in second order transition; in case of second order transition both of these are continuous functions, but the second derivative of the Gibbs free energy function G is varies with these parameters discontinuously. For example, if I consider a H and then plot a H verses say T, we will have the discontinuity in the in this variation of a H with temperature. So, basically what does it mean? It mean that the first order transitions which, in case of first order transitions like melting where G is a linear function of basically it varies with temperature, pressure and volume continuously. And the first derivative will vary discontinuously, whereas in case of second order transition, the second derivative of the Gibbs free energy function varies discontinuously.

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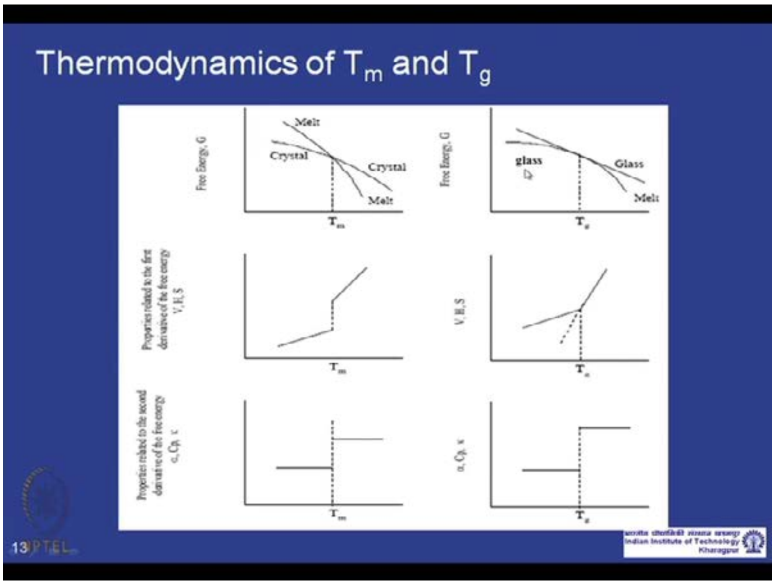

Thermodynamics of T_m and T_g

So, if you just look at this curve one more time, the melting is a first order transition, where G varies with temperature, the x-axis is the temperature, with G varies continuously with temperature and the first derivative of G, V, H, S, they varies discontinuously. Whereas in T g, the glass transition temperature which varies discontinuity with the second derivative of the Gibbs free energy function. Let C p and so C, this is to be C p; C p verses T would be discontinuous function because this is the second derivative of G and these are the first derivative of G. So it, does it mean that we know that T m from this curves we know that glass transition melting temperature is a melting is a first order transition, thermodynamic first order transition, but whether does this mean that glass transition is a second order transitions thermodynamically? The answer is no because the fact that the glass transition temperature depends upon also the rate at which we cool the polymer matrix or polymer melt.

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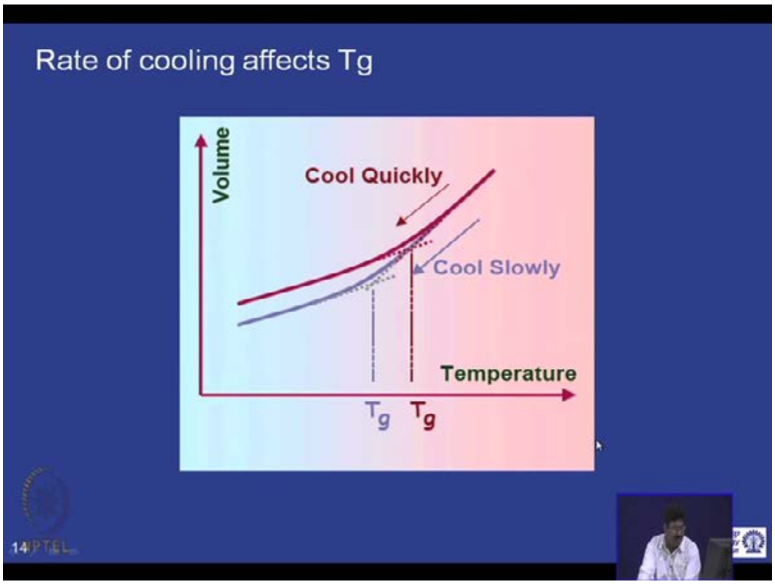

Rate of cooling affects Tg

If you cool fast, then T g will be higher; if we give more time, the polymer chains to arrange themself and give more time, which means cool slowly, then T g will be lower; which means is that, these curves will look like same, but this temperature glass transition temperature will vary, if we change the cooling rate or incase of reverse direction heating rate. So, this is not a… Hence this is not a true second order thermodynamic transition, but for a particular heating rate the phase transition between the glassy state, and the rubbery state is resembles with a second order thermodynamics transition.

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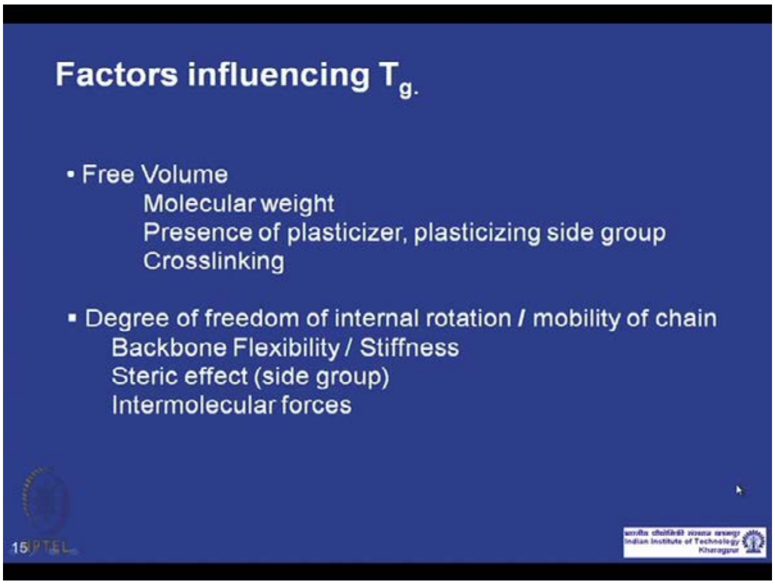

Factors influencing $T_{g.}$

- Free Volume
  - Molecular weight
  - Presence of plasticizer, plasticizing side group
  - Crosslinking
- Degree of freedom of internal rotation / mobility of chain
  - Backbone Flexibility / Stiffness
  - Steric effect (side group)
  - Intermolecular forces

Now, what are the factors from a Polymer Chemistry point of view? In, especially in Polymer Chemistry course, we must know what are the factors that responsible or that affects the value of T g. So, we can design the polymers of certain structure, certain chemical structure to get a desired value of T g. Now, the main factors: the T g depends on the free volume. Free volume is the volume occupied by not occupied by the polymer. If you are talking about polymer melt, it is the volume which is not occupied or the way the polymer chains. So, if you consider just a liquid, then there will be lots of you know, then there will be lots of intermolecular spaces which are not occupied by the molecules; that those are free volumes. And if you increase the temperature typically, if the free volume increases, the polymer becomes lesser than or the materials becomes less dense.

So, free volume of a polymer material depends on molecular weight, presence of plasticizers or plasticizing side group cross linking. We will discuss this, effect of this little detailed with examples. Another very important factor which determine the value of T g is the mobility to rotate or the mobility of the polymer chains. If the polymer for example, if it is very stiff, the rotation between the single bond, around the single bond is restricted, then the mobility of the polymers comes down. So if that happens, then the polymer chain have much less mobility compared to a much flexible chain.

So, basically the degrees of freedom for internal rotation or the mobility of the chain effect the value of T g. And this rotation or the mobility of the polymer chain depends upon the stiffness of the backbone or the flexibility of the backbone, steric effect, side group, which is basically governed by the side group present and inter molecular forces; the more intermolecular forces, the less is the freedom to move. So, what I will do? I will take these factors one by one and give examples; few real examples to emphasize or convince you or the how this factors effects the T g of a polymer material or a polymer.

Now, we must remember that it is very difficult to change only one of these parameters, just only one parameter; because changing one parameter, these are all interlinked sometime. So, they may changing one parameter may also change the effect on the other parameter. So, it is very difficult always to attribute one change in value of glass transition temperature, T g for a particular reason. But, at least we can estimate, we can find out the direction that, if we do certain changes of a certain polymer structure of what the expected change in the glass transition should be.

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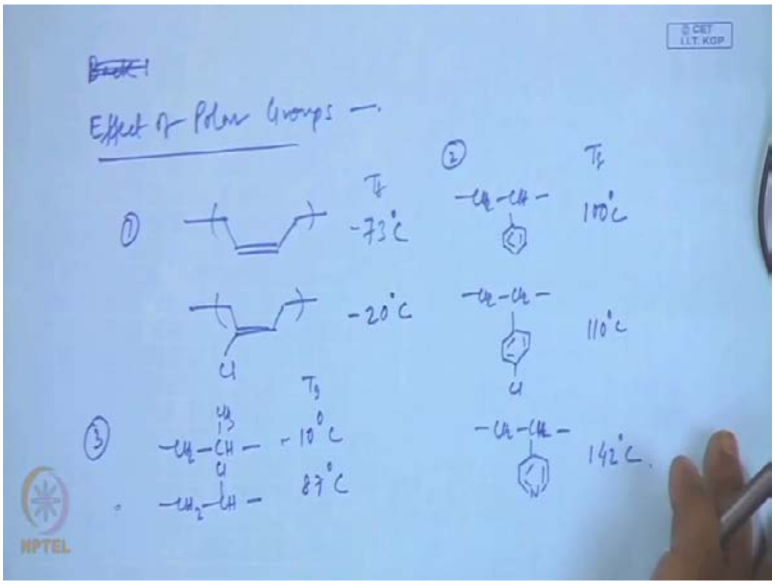

So, let us first talk about the chain backbone stiffness. So, let us first talk about the effect of polar groups. Consider this iso poly isoprene and poly chloroprene; this is chloroprene and this is isoprene. This has the T g 73 minus 73 degree centigrade and this is minus 20 degree centigrade. Compare another set of polymer polystyrene four poly four vinyl chlorobenzene, the values for the T g are given by 100 degree centigrade, 110 and 142. This is one set; this is second set.

Let us compare another set; polypropylene and polyvinyl chloride. This is around 10 degree; this is only around 87 degree. So, for example, here the effect of this chlorine and methyl group on the rotation, basically if the steric effect caused by this two or more similar. So, any change in these T g values are because of the most likely because of the interaction between the intermolecular forces between the two chains. This is having more, more polar, the intermolecular forces between the polyvinyl chloride chains are much higher compared to polypropylene chains. So, the T g goes up.

Similarly, you can get the other side of examples. The more is the polarity of these bonds, the more is the inter molecular forces between the polymer chains, which causes in effect more stiffness in the chains which makes the T g, which decreases the polymer mobility and which makes the T g higher. Same here the more polar, the more intermolecular forces and more higher T g. So, which means if we increase the polarity of the bonds, more will be the intermolecular attraction; T g will go up.

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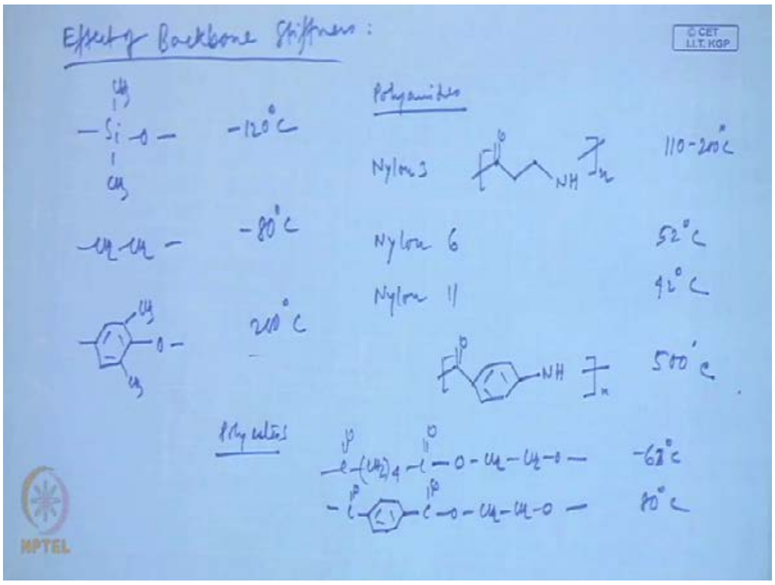

Let us talk about the effect of backbone stiffness; backbone of the polymer chain. Let us compare example of polydimethylsiloxane or P D M S. This is having T g of minus 120, polyethylene minus 80 and say it is a much rigid backbone; polypropylene oxide P P O, 200 degree centigrade. Let us compare another set of polyamides; same class of polymers. Polyamide; nylon 3, T g is 110 to 200 degree centigrade. Similarly we can write, we can know what is the… this is the number of… carbon atom which gives this number; so 3 carbon atom; nylon 3. So, similarly we can write nylon 6, nylon 11, which gives T g of 52 degree centigrade, 42 degree centigrade and one very rigid polyamide, polybenzamide, T g is 500 degree centigrade.

And, another set of example is the polyester. The T g is minus 63 degree, whereas if I replace this with a rigid phenyl backbone keeping everything else same, then the T g goes up. Now, look at these three set of example. We can clearly see. Here, we only change this (C H 2) 4 backbone with a much stiffer backbone, which basically restrict the rotational freedom around this chain, which makes the polymer backbone much stiffer. And hence, the T g goes up. Similarly, the example here; these two are stiff components. So, more C H 2 groups we put in between the polymer chains, more flexible or less stiff. So T g comes down, whereas again if we instead of a normal alkene chain in between, if you have a rigid… groups which is basically restrict rotation around single bonds, the T g drastically goes up.

Similarly, silicon oxygen bond is a very flexible bond. So, T g is very low; minus 120 degree. There is no side group present, which basically does not restrict at all the rotation around the single bond which polyethylene chain is very flexible. And T g is minus 80, whereas putting rigid group in the backbone makes the polymer very stiff, which keeps the T g very high. So, basically again if the backbone of the polymer chain increases, the stiffness of the backbone of the polymer chain increases or the T g goes up or the flexibility increases, the T g comes down.

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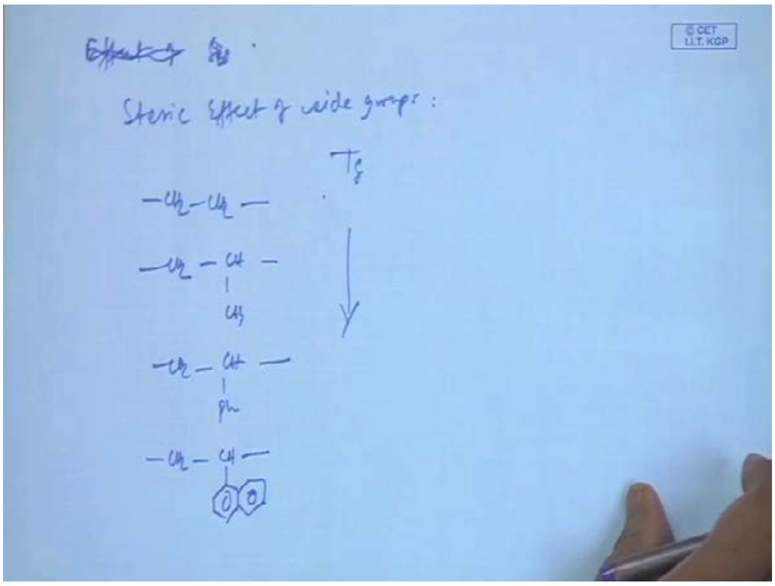

Steric effect of side groups :

Let us now discuss the effect of steric effect. Basically, steric effect or let me write steric effect of side groups. So, if you just compare a simple example of polyethylene, C H 2 C H 3 polypropylene, polystyrene and four vinyl anthrosin. Obviously, if you look at these structures, the rotation because of the substitute present, the bulky substituent present as a carbonate term, the rotation becomes more and more with the increase in the size of this substituent. Now, we can always argue that with the increase in the size; most likely when there was interaction between the chains, also increases which causes increase in intermolecular forces. That may be also true, so that continuity in some extent of this cause of increase in T g with more bulky group.

But, most likely the increase is in T g. The increase in T g, which increase in size of the side groups is mainly because of the restriction of the rotation. So, the polymer because of the increase in the size, the polymer chain goes, the polymer stiffness goes up and hence the T g goes up. So, which means that if we have bulky side groups, the polymer chains becomes more stiff. The as a result, the T g goes up.

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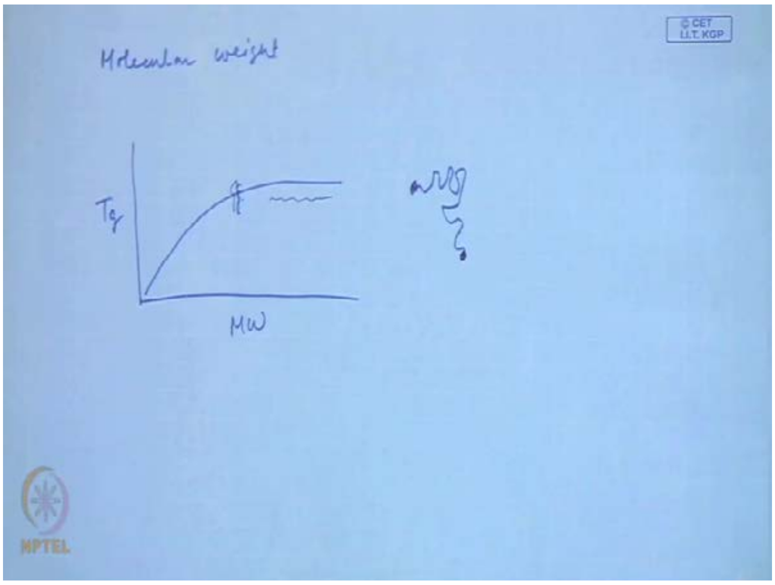

Molecular weight of a polymer chain also contribute in the value of T g, but it effect the molecular weight actually dies down after some molecular weight. So, basically with increase in the molecular weight, the T g goes up to certain point. And then basically the value of T g becomes independent of molecular weight. It can be explained for the fact that the chain ends, for the polymer chain the ends are more mobile, more flexible because in case, the one of the sides it is not tied up from both sides, whereas some, any segments in between they are tied up by both the sides.

So, ends are more mobile and have more free volume and hence they has they have more free volume. And if you increase the free volume, polymer has more space to basically more space to chain with contribution and it becomes more mobile and the T g goes down. So for a chain, the more is the contribution from ends, the more is the free volume; hence the T g is slower.

So, for shorter molecular weight the contribution from chain, hence the significant, hence the T g is low. And with increasing the chain length, the molecular weight, the contribution from the ends goes down progressively. And after a certain molecular weight, the chain, hence do not contribute too much. So, the value of T g becomes steady value.

Generally, we compare in for polymer application. We take molecules use or use polymers having molecular weight much above than these, so for practical purposes at the practical range of molecular weight, which usually used for applications of polymers. They are they do not change the T g with molecular weight.

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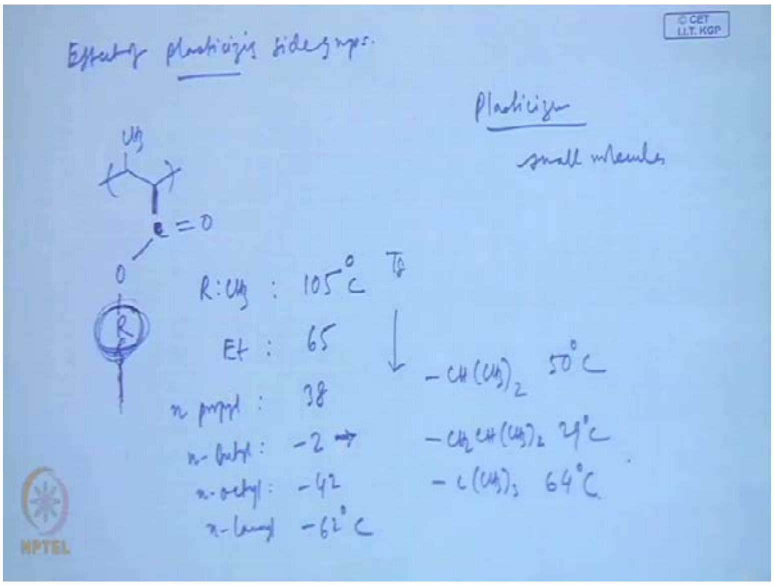

Effect of plasticizing side groups.

Plasticizer

small molecules

R: CH_3 : 105°C Tg

Et : 65

n propyl : 38

n-butyl : -2 →

n-octyl : -42

n-lauryl -62°C

$-CH(CH_3)_2$ 50°C

$-CH_2CH(CH_3)_2$ 29°C

$-C(CH_3)_3$ 64°C

Next, talk about the effect of plasticizing side groups. Let us take particular example of methyl methacrylate. So, let us talk about example of methyl methacrylate. If R C H 3 which is methyl methacrylate and T g is around 105; if we ethyl is 65; n-propyl 38; n-butyl minus 2; n-octyl minus 42; n-lauryl minus 62 degree centigrade. So, look if we, if you further apart from the backbone, they keep on increasing the chain length. What happens? With a further increase in the chain polymer side chain, they do not contribute too much in the restriction of the bond rotation; whatever restriction have been imposed in the bond rotation, they have done by first few atoms.

So, if you put further substitution, reaction do not contribute much in the terms of a restriction in bond rotation. But because of their mobility, the side chains, they generate lots of free volume and hence the entire polymer chain becomes more mobile. So, as a result the T g drops. So, if the side chain molecular weight goes up or size goes up, the T g grows some. This is nothing but sort of plasticizing effect. As if these molecules are dissolved in the polymer of this. But if we compare, like compare n-propyl substitution with isopropyl substitution, then the T g goes up little bit; 38 to 50 degree centigrade.

Compare n-butyl with isobutyl and tertiary butyl substitution; this is 29 and tertiary butyl is 64 degree centigrade. Whereas this n-butyl is minus 2; isobutyl is 29; tertiary butyl is 64 degree centigrade. So, look here because now this, when you have this isobutyl and tertiary butyl group, they are becoming bulky in this way and whereas n-propyl groups, they are becoming bulk or increasing size. So, the free volume because of this long chain is much more compared to the free volume produced by bulky groups having a spherical type shape or coil type shape. So, they give actually less free volume to the polymer chain and also they may contribute little bit about the restriction chain rotation. So, they actually increase in the polymer, increasing the restriction.

So, next talk about the plasticizing, the plasticizer. Plasticizers are nothing but small molecules which basically dissolve in the polymer matrices and like the solvent or some added molecules. If some residue on solvents present in the polymer matrix, then what happened? Because of the solvent molecules or small molecules or the free molecules, the solvent goes up. And hence, the polymer mobility goes up and T g also goes down. So, presence of plasticizer makes the polymer T g comes down.

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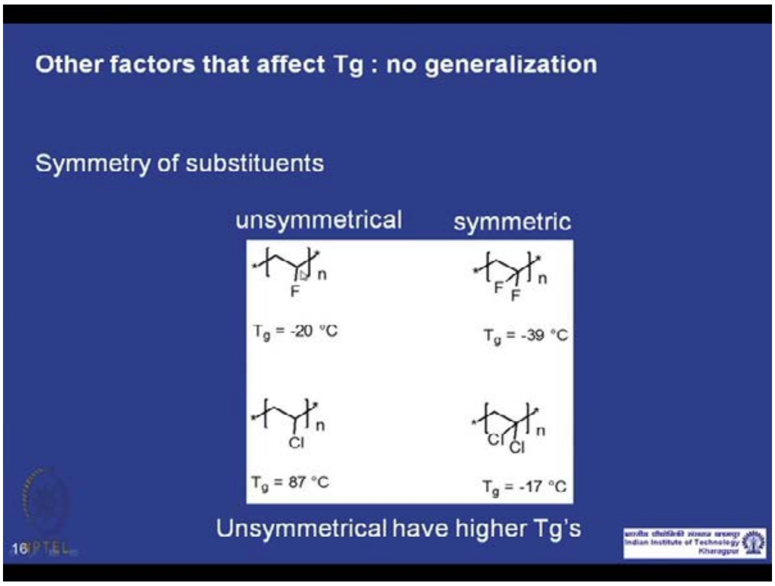

Other factors that affect Tg : no generalization

Symmetry of substituents

unsymmetrical symmetric

T_g = -20 °C

T_g = -39 °C

T_g = 87 °C

T_g = -17 °C

Unsymmetrical have higher Tg's

There are few other factors which affect T g which does not have any generalization. I just quickly go through that. For example, if I have compare two symmetric substitution like two substitutes, a F verses 1 and substitutes a F; the unsymmetrical have the higher T g. This is the two example.

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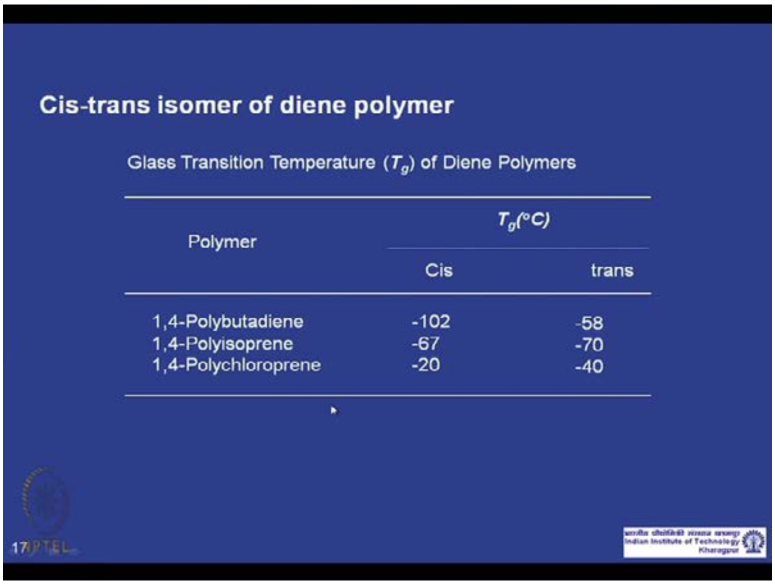

Cis-trans isomer of diene polymer

Glass Transition Temperature (T_g) of Diene Polymers

Polymer	T_g(°C)	
	Cis	trans
1,4-Polybutadiene	-102	-58
1,4-Polyisoprene	-67	-70
1,4-Polychloroprene	-20	-40

And now the Cis-trans isomer of diene polymer, they have different T g s. Now, these are all specific examples. No generalization can be possible. So explanation, general explanation is little difficult to give.

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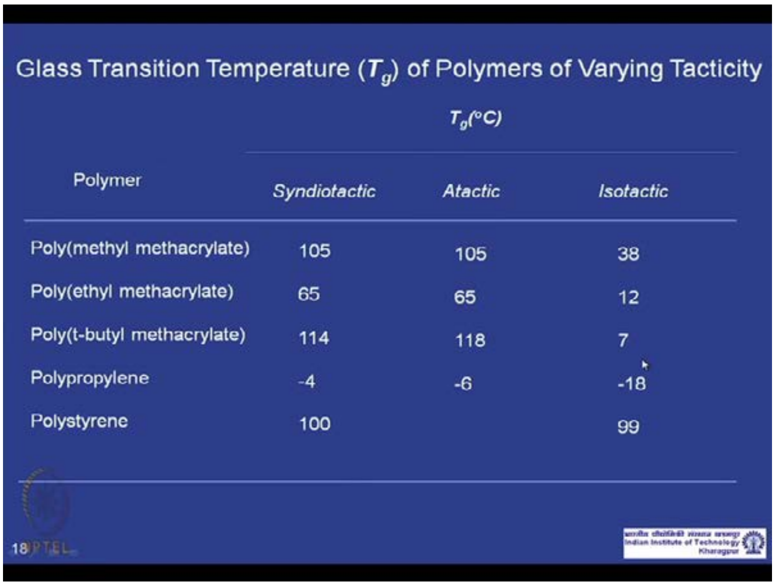

Glass Transition Temperature (T_g) of Polymers of Varying Tacticity

Polymer	T_g(°C)		
	Syndiotactic	*Atactic*	*Isotactic*
Poly(methyl methacrylate)	105	105	38
Poly(ethyl methacrylate)	65	65	12
Poly(t-butyl methacrylate)	114	118	7
Polypropylene	-4	-6	-18
Polystyrene	100		99

And if the glass transition temperature also depend on the T g, sorry, tacticity of the homopolymers, and for example if you look at the T g of syndiotactic of poly methyl methacrylate is different than isotactic, whereas copolystyrene is not different.

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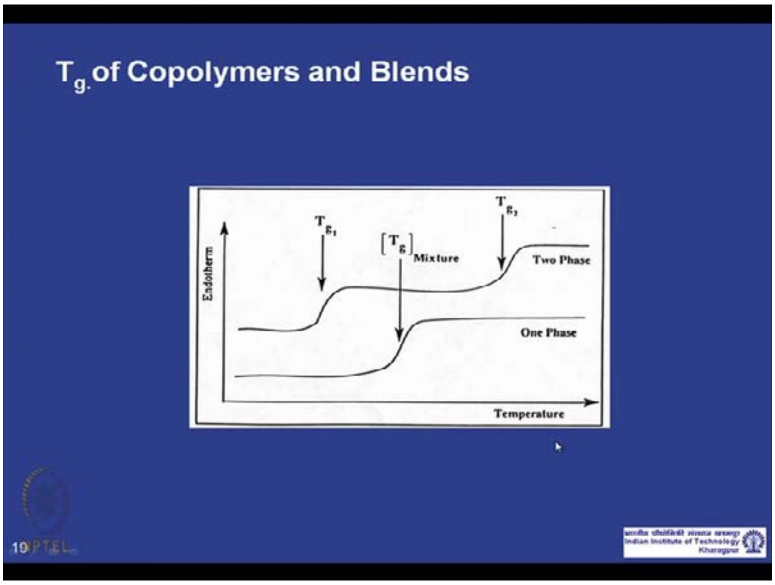

T_g of Copolymers and Blends

So, what I will do, I will stop today and we will start in the next lecture.