Polymer Chemistry

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Module - 1
Lecture - 36
Amorphous and Crystalline State: Tg and Tm (Contd.)

Welcome back to this course on polymer chemistry, and to this lecture we will continue our discussion we are having on amorphous and crystalline state, and we will have discussion on glass transition temperature, and melting point of polymers.

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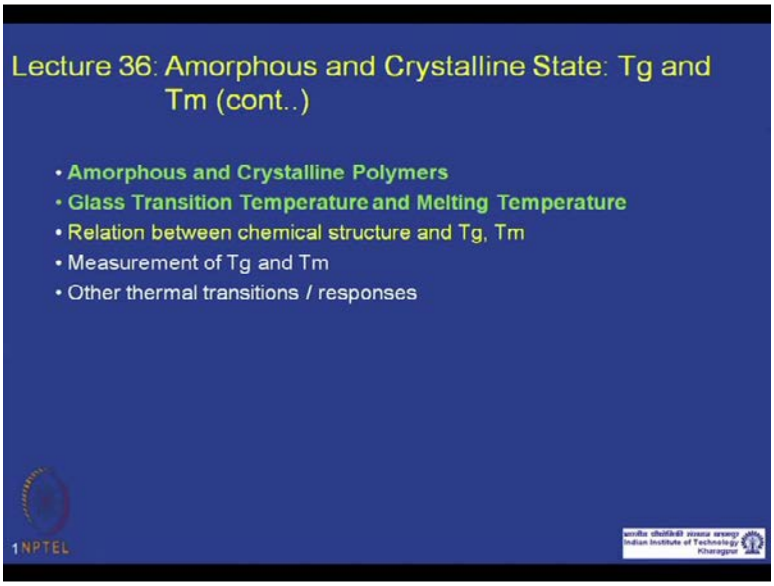

Lecture 36: Amorphous and Crystalline State: Tg and Tm (cont..)

- 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 / responses

Now, if you look at this slide, this is the topic these are the topics we thought of covering in this amorphous and crystalline state. We have covered in last lecture our introductory discussion on amorphous and crystalline polymers, and then we discussed what is glass transition temperature, and melting temperature for polymers. We discussed that glass transition temperature is a secondary transition, glass transition is a secondary transition, and melting is a first order transitions for polymers. We also discussed in detail about the relationship between chemical structure, and glass transition temperature. And in today’s lecture we are going to discuss the relationship between the chemical structure of a polymer, and the melting point. We will discuss today about, how the measurement techniques used for T g and T m, will not have detail discussion but the basic discussion, basic technique on determining T g and T m. And we will also discuss little bit about other thermal responses in other, other responses polymer shows when you heat up a polymer material.

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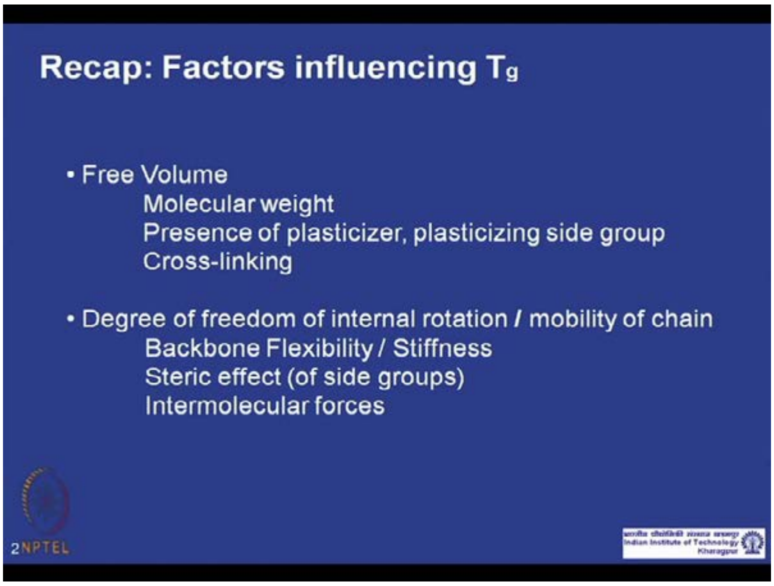

Recap: Factors influencing T_g

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

Just a recap, the factors which will that influence glass transition temperature, mainly we can divide in two factors; one is free volume, free volume is the volume in polymer material, which is not covered by the polymer molecules, and as we have seen that, if we increase the free volume content in a polymeric material or sample, the polymers has more space to move around, so mobility goes up. And hence the effect of, it affects the glass transition temperature, and will also (( )) effects the melting point. Second major of the main contribution in deter or determining factor in T g is the, freedom of the polymer chain to rotate around its single bond, which gives us the mobility of the polymer chain. So, if you increase the mobility, obviously polymer chain becomes more flexible, and T g goes down.

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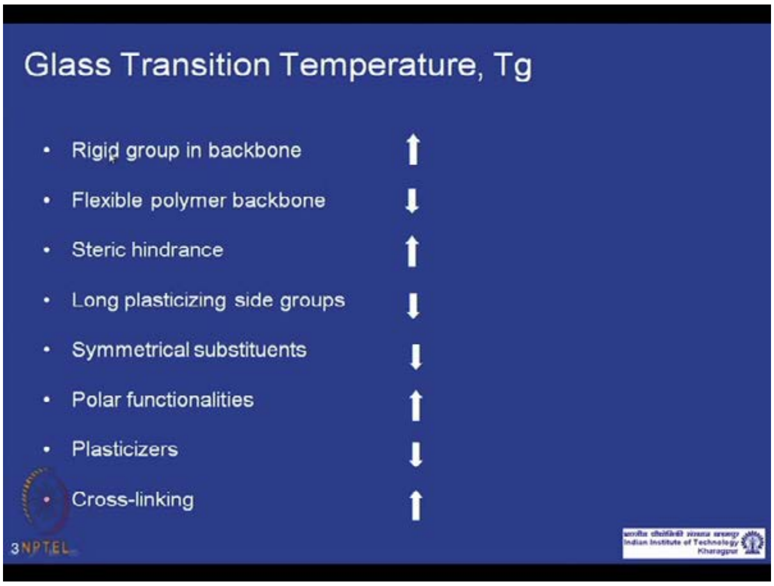

Glass Transition Temperature, Tg

- Rigid group in backbone ↑
- Flexible polymer backbone ↓
- Steric hindrance ↑
- Long plasticizing side groups ↓
- Symmetrical substituents ↓
- Polar functionalities ↑
- Plasticizers ↓
- Cross-linking ↑

So if you go back, and look at these factors we discussed in last lecture. If you have a digit backbone, digit group in the backbone, then T g goes up, as a result of increase stiffness. Flexible backbone, obviously T g goes down, if you have the steric hindrance, because of presence of bulky side groups or side bulky pendant groups, then the rotation around single bond becomes difficult, as a result stiffness goes up and T g goes up. If you have long plastizing side group, then obviously free volume goes up, and T g goes down. Similar symmetrical substituent we have seen, that T g brings down polar functionalities will increase the intermolecular or interpolymer attractions, which will increase the T g.

Plasticizer increase the free volume, T g goes down, and cross-linking also decreases the amount of free volume, so T g goes up. Now this are some of the factors, we try to include, and will see that most of this factors also influence the value of T m, because T m and T g (( )) are very closely related phenomenon, so this factors also will contribute, may be, may not be in same extent or same nature same way, but they also contribute, in determining value of the glass transition temperature.

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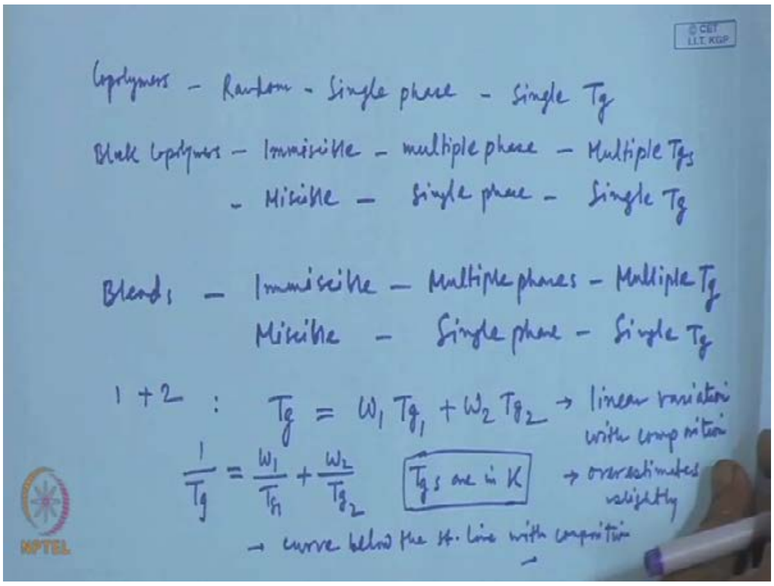

Copolymers - Random - Single phase - Single T_g

Block Copolymers - Immiscible - multiple phase - Multiple T_gs

- Miscible - Single phase - Single T_g

Blends - Immiscible - Multiple phases - Multiple T_g

Miscible - Single phase - Single T_g

1 + 2 : $T_g = W_1 T_{g_1} + W_2 T_{g_2}$ → linear variation with composition → overestimates slightly

$$\frac{1}{T_g} = \frac{W_1}{T_{g_1}} + \frac{W_2}{T_{g_2}}$$ $\boxed{T_g\text{s are in K}}$

→ curve below the st. line with composition

What about the T g of co polymer, we talked about mainly last class T g of homopolymers, now what about in the T g co polymers and polymer blends, if we talk about co polymers first. Now co polymers, you can have random co polymers. Now if you have random co polymers, obviously they form a single phase, because they individual monomers does not make a. They are not distinct to each other, in the sense that their statistical co polymer, so you have a single phase for that. And if you have a single phase, this gives as a single T g for the co polymer .If you have a block co polymer, now if the block is, the blocks involved here are invisible with each other, then we have multiple phases. For example, if we are talking about two blocks, then, if they are not miscible to each other or other way invisible to each other, then you have two phases. Then we have multiple T gs, each T g represents the T g for the corresponding homopolymer.

So, if you have two blocks, which are not visible, then we are going to get two T gs for the corresponding homopolymer. Now if, please remember that, if the sign this T g, the T g of the homopolymer in a block co polymer, will depend upon the size or the molecular weight of co polymers, as you we know that the T g also depends on the molecular weight, of the polymers, so if we talk about the small block, then we are going to get slightly less T g, then a large homopolymer, so that part you have to keep it in mind. That if you take a small block, then T g will be lower compared to the homopolymer, which have a higher molecular weight. If these blends are miscible sorry this co polymers the two blocks are miscible, then obviously you are going to get single phase, and which will give as a single T g. Similarly, if you take two homopolymers, and blend them, if we have invisible, again similar thing, then you have invisible multiple phases, multiple T gs.

If we are talking about, say two homopolymer blend, so multiple T g, if they are visible, obviously single phase, and you have single T g. For invisible blend, it does not matter that, you know that T g is for the homopolymers, obviously then you can know you will know the T gs for the block co polymer immiscible block co polymer, or invisible blends. What is the T g for invisible blend, if you mix; say component one and component two, and then mix with each other or you make a block co polymer of one and two, which becomes invisible, then what is the T g. The two equations which you can apply, this T g is for the resulting co polymer, or the blend, visible blend, which is given by W 1 T g 1 plus W 2 T g 2. T g 1 is the T g for the component one, W 1 is the weight fraction. Similarly, W 2 is the weight fraction for the component two, and T g 2 is the weight fraction for the second component.

Now this equation gives linear or straight line variation, linear variation with composition. So if you (()) composition, you get linear variation by this equation. Now this generally what estimates the T g of the co polymers or blends slightly (( )) slightly. So the other equations, used are given by this one by T g W 1 by T g 1 plus W 2 by T g 2. Again this terms are same, remember this t, this T g is are in Kelvin. So, don’t confuse that, for applying this equations, you must take the temperature in Kelvin. Now this case; obviously this equation, predicates the curve, a curve below the straight line, with composition. So, if you have a straight line here, it will little curve below that, and is typically under estimates, is basically to be little, under estimates little bit about the T gs for the miscible blends, or the co polymer.

Hence the actual T g lies between a T g which is somewhere between, predicted by this two expression. Now obviously if these two blocks, in a block co polymers or say two homopolymers in blends are partially visible, then what happens, you still gets two T g s, for a two component system, but if T gs comes down from the corresponding homopolymers, you get a somewhere intermediates. So, basically if you find out, or if you measure the T gs or deputed a defensive thermal kilometric, which will just stop in a minute. We will find depending how T g you are getting, you estimate, or you can predict or you know, whether the blends are miscible blends, or they are partially miscible blend or there completely miscible blend. Similarly, you can find this is whether blocks, that the two block in a block polymer, and miscible or partially miscible, or completely immiscible.

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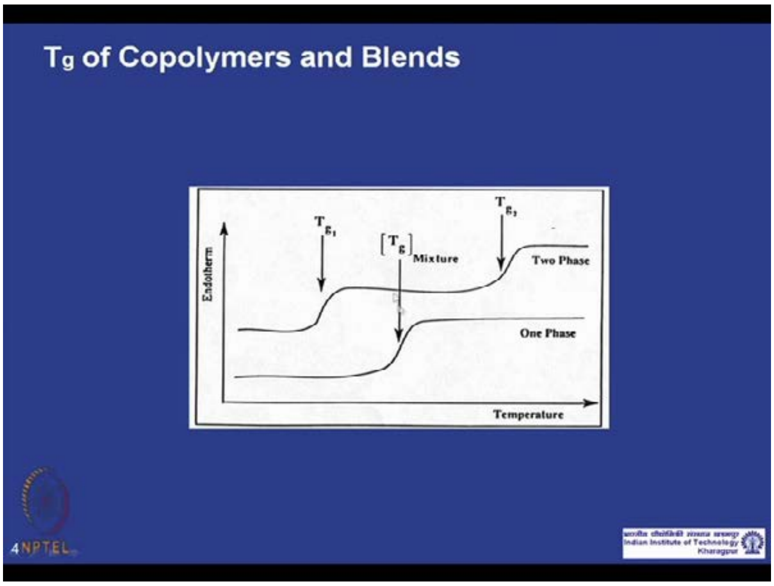

Tg of Copolymers and Blends

So if you want show this in peterocially, if you are two face system immiscibly system you get corresponding, two T g corresponding to the homo polymers, and if you have completely mixed or miscible blend, miscible copolymers, then you have T g intermediate between these two. The value of this T g is given by the two expressions I just wrote in it.

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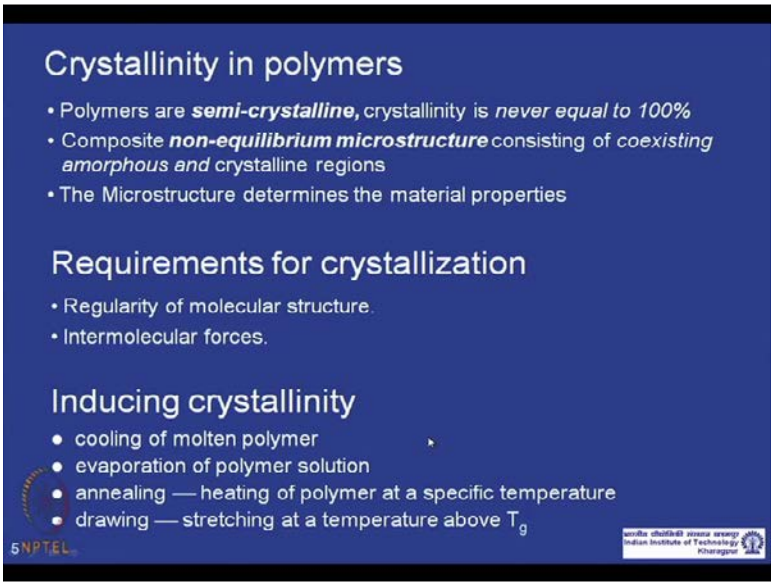

Crystallinity in polymers

- 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

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

We will come to T m and melting point, before coming to melting point discussion, let us just recap with the crystallizing polymer, which we discussed in length last lecture. Crystalinity polymer as you know as we discussed many times in this course; that polymer are hardly crystallize up to hundred percent, so most cases if they, the crystality varies from zero hundred polymers, so polymer are generally semi crystalline in nature. And you have non equilibrium micro structure, co existing the amorphous and the crystalline region. We talk about non equilibrium, because when we introduce crystalinity in the polymers, the amount and the nature of the crystalinity depends upon how you are inducing the crystalinity, whether it fast or it slow. So the micro structure you get consisting amorphous crystalline region, are basically non equilibrium structure. And that micro structure actually determined eventually, the properties of material.

We also discussed requirement for crystallization; basically the polymer chain has to have a regular molecular structure, so that the chains can pack close to each other easily, and obviously if the inter molecular force between the polymer chains higher, then they can pack easily, or if they remain pack easily, which are they. So these are the two criteria's must be fulfilled, so to get a crystalline polymers. How do you induce crystalinity in a polymer material. Remember we discussed last class that, generally we can introduced a by cooling a molten polymer, or annealing a semi crystalline or amorphous polymer is specific temperature, and then is just keeping a amorphous semi crystalline polymer at a particular temperature for a long time. You can introduce crystallinity by evaporating a polymer solutions slowly, and the another way we can introduce crystallite by drawing, which basically means stretching the polymer strain, so polymer chains at a particular temperature about T g, by which they can align, and then crystallize with each other. So what are factors that influence the value of melting point or melting temperature.

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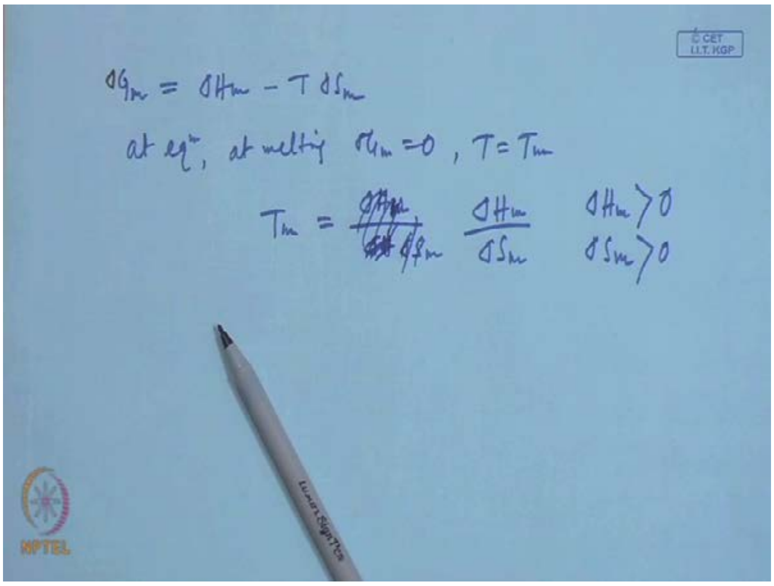

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$\Delta G_m = \Delta H_m - T\Delta S_m$

at eq^n, at melting $\Delta G_m = 0$, $T = T_m$

$T_m = \frac{\cancel{\Delta H_m}}{\cancel{\Delta S_m}\ \Delta S_m} \quad \frac{\Delta H_m}{\Delta S_m} \quad \Delta H_m > 0$

$\Delta S_m > 0$

Let us think about the thermo dynamics little bit, we know that. So if we consider delta G of melting, delta G of a processes, we can write T d S m. Now these are the delta G m, delta G, delta G m and delta S are the corresponding terms for particular, per unit for per. Now at equilibrium, which is a case of melting, so at melting, delta G m would be zero, T is T m melting point. Hence T m is given by delta H m, delta S m. Let me once delta H m by delta S m. Delta H m is melting is always endothermic processes, so this is a positive value.

Similarly, entropic change in melting processes, result in increasing in, mobility of the polymer chains, so at the entropic goes up. So if you, from this expression if you can increase the value of T m, either by increasing the value of del H, and by decreasing del S value. If del H can be increased, by improving the inter molecular attraction, if you increase the inter molecular attraction between the polymer chains, then obviously the delta h of melting goes up. Similarly, if the entropy denies term, can be reduced, then the T g goes up. We will discuss the specific example in a minute now.

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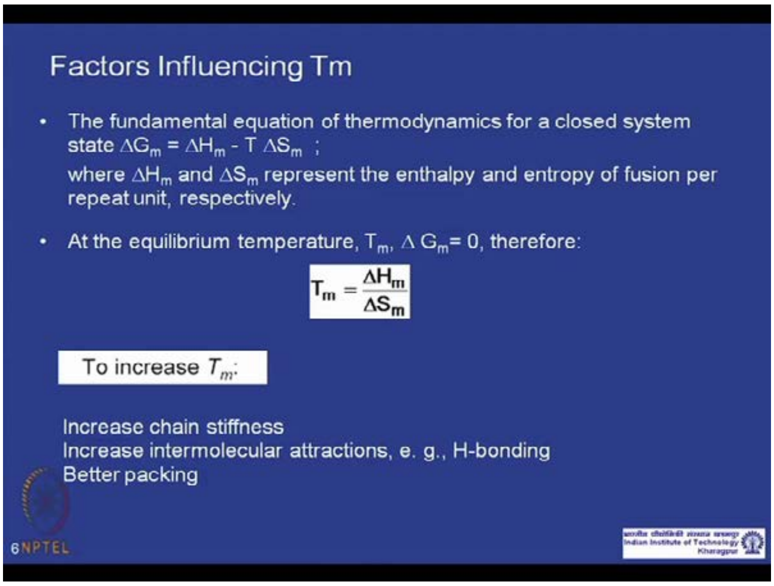

Factors Influencing Tm

- The fundamental equation of thermodynamics for a closed system state $\Delta G_m = \Delta H_m - T\ \Delta S_m$;
  where ΔH_m and ΔS_m represent the enthalpy and entropy of fusion per repeat unit, respectively.
- At the equilibrium temperature, T_m, $\Delta G_m = 0$, therefore:

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

To increase T_m:

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

So, this is what I discussed that delta G m is delta H m minus T deltas delta m enthaply and entropy of fusion, for melting per repeat unit, at equilibrium delta Gm zero, so this is zero. So to increase T m with this chain stiffness mobility, if we increase chain stiffness, we increase the chain stiffness, if we increase the chains stiffness what happened. When we melt these polymers, if they are stiff, if the polymer is stiff, then the increased entropies is not much. Obviously, if you have more flexible chain, then from to bring the chains from closeting to molten state, where the polymers have much more mobility. If the polymers are intrinsically more flexible; obviously for flexible polymer on melting delta is goes up more, than a polymer chains which are much stiffer.

So to increase T m, you prefer to have a stiffer chain, because if you have stiffer chain, then the entropies increase and melting is less, so T m goes up. Similarly, you can increase the inter more attraction, you can introduce some specific bonding; like hydrogen bonding, that will increase the enthalpy, the delta h of melting, and by that we can increase the melting point, and obviously better packing is always help in increasing the, you can understand better packing is always improve the T m melting point of the polymer.

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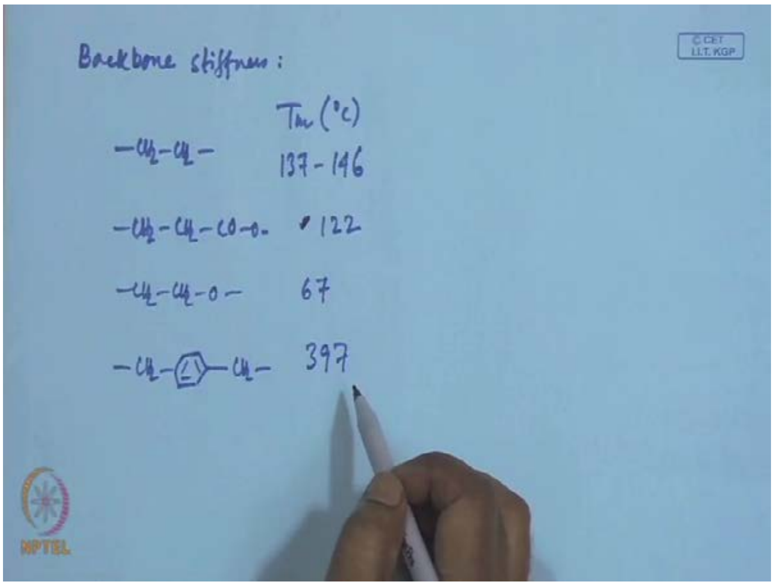

Backbone stiffness:

	Tm (°C)
$-CH_2-CH_2-$	137 - 146
$-CH_2-CH_2-CO-O-$	122
$-CH_2-CH_2-O-$	67
$-CH_2-C_6H_4-CH_2-$	397

So, what are the… If you look chain micro structure, or chain chemical structure, what are the factors, you can think of, which will affect the value of T m. Obviously, we discussed back bone stiffness, now I will give few examples, so that we can verify this concept. So let us talk about first this example; polythene have T m around 137 to 146 degree centigrade. If you introduced a flexible group in the back bone, then flexibility goes up, so delta S goes up, so your T m goes down so it comes around 122. If you just have a ether linkage, then flexibility goes up even higher, you get it drop in T m value. If you introduced a phenyl width in the back bone, your stiffness will go up, and you get a much higher T m value, increased T m value as a result of increase in the back bone polymer chain stiffness. We can give more example of back bone stiffness.

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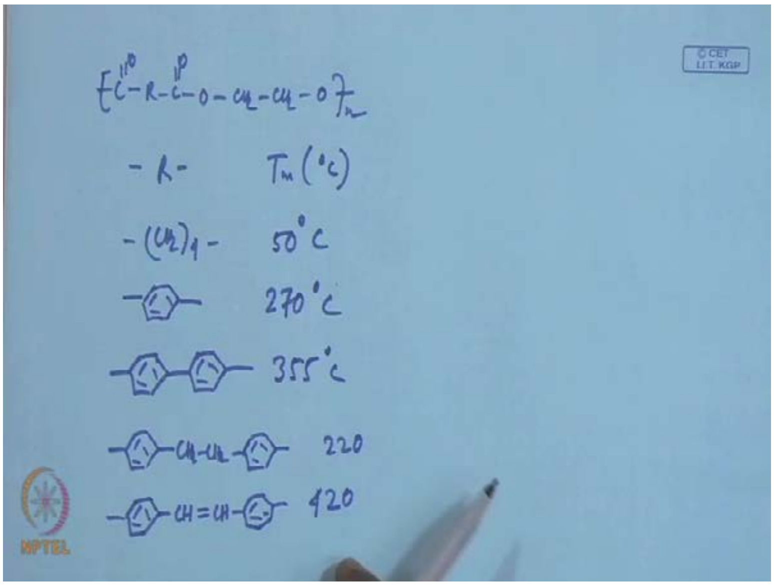

For example if we consider these polyesters, when R is c h 2 4, c h 2 4 is linear alkane. Normal alkane, which gives us very flexible chain, and T g T m is 50 degree centigrade, if you increase much stiffer molecule group. So we are giving example of this back bone stiffness, which will affect the value of T m, so if you have a much stiffer back bone, by introducing rigid phenyle group, the T m goes up to 70 degree centigrade. If you have more stiffer group, then the T g T m sorry T m goes up even higher. If you introduce a flexible group in between, then T m goes down. Whereas, instead of c h 2 c h 2, if you have alpine group, which makes the chain even stiffer, then your T m goes up drastically. So, the example we have seen in this page, and in this page, confirms the understanding that if we increase the back bone stiffness, the T m goes up.

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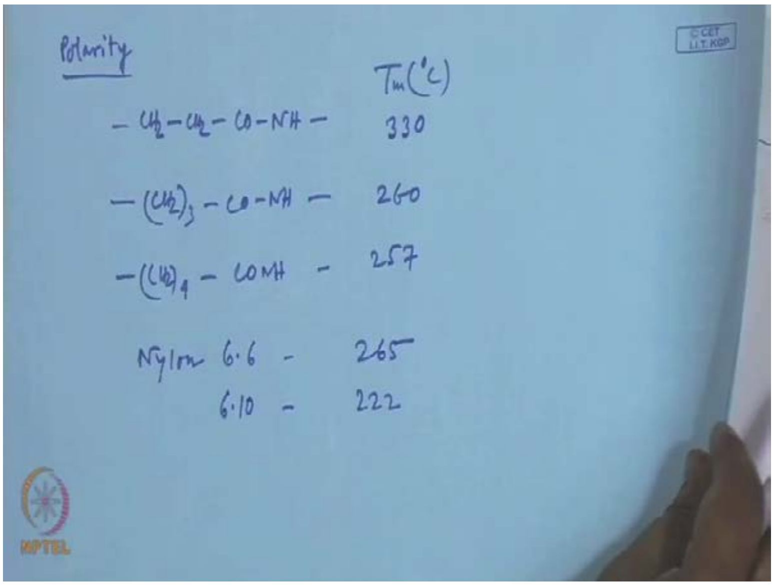

Polarity

	Tm(°C)
$-CH_2-CH_2-CO-NH-$	330
$-(CH_2)_3-CO-NH-$	260
$-(CH_2)_4-CONH-$	257
Nylon 6.6 -	265
6.10 -	222

Now let us talk about the second factor polarity, let us have some example about poly-amides. So, if you have more flexible group, instead of C H 2 C H 2, for examine three groups, three C H 2 groups, then the polymer becomes the contributions from this C O N H 2 group in this case, is higher compare to this case, because your adding more non polar groups. Hence the inter molecular attraction goes down, hence T m goes down, so 260 degree. If you increase further, then T m goes down further. Now in this case, you can argue that, this drop in T m could be, because of the increasing flexibility of the back bone, but you write it can cause some decrease in the T m, because of increase flexibility, but the amount of drop shown here, that can be only explain by the decrease in the inter molecular attraction, because of the fraction of the c u n h group, is less in this polymer chain, compare to the one shown here. Similarly, you can compare nylon 6 6 265 and nylon 6 10 is 222. Here also, because you have, for given molecular weight you have less number of C O N H group, the T m goes down.

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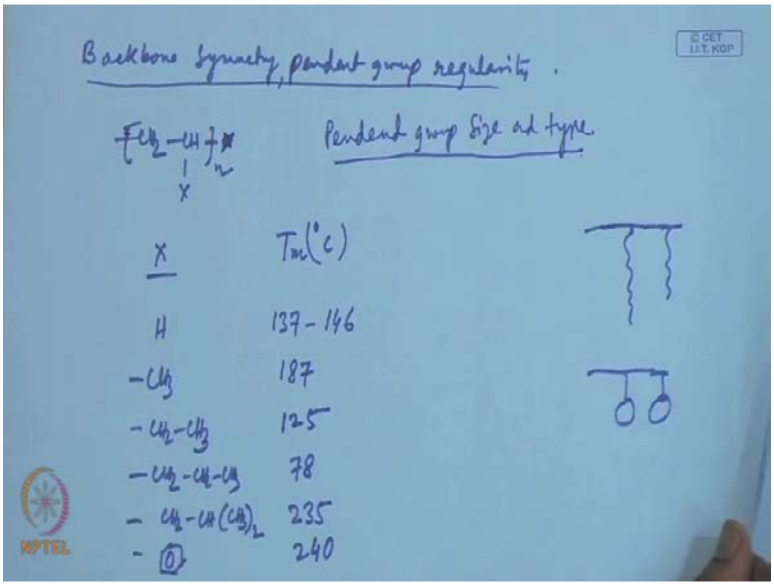

Backbone Symmetry, pendent group regularity.

$\left[CH_2-\underset{X}{CH}\right]_n$ Pendent group Size and type.

X	Tm(°C)
H	137 - 146
$-CH_3$	187
$-CH_2-CH_3$	125
$-CH_2-CH_2-CH_3$	78
$-CH_2-CH(CH_3)_2$	235
- ⌬	240

The third factor we can think of is, back bone symmetry, and pendent group regularity. If you consider this example, when x is 8; that means polyethylene T m is 137 to 146 degree. When this is C H 3, if you have C H 3 group, the polymer chain becomes more stiffer. Hence the T g goes up, but if you increase the length of the side chain, as you have seen in case of T g as well; that the chain rotation is mainly determine by first one or two pendent groups. If you have a longer pendent groups, it actually plasticizes the polymer molecules, by increasing the free volume. So if you increase this pendent group, what happened, it increase the free volume; hence the flexibility goes up, and as a result your T m goes down.

So if you increase further, your T m further goes down. However if you have same thing you have seen for T g, in case of T g, if you have bulky side group, not a long not long pending grouping from the chains, but if you have a bulky groups, then this contributes or gives steric hindrance in rotation, and which increases stiffness. Where in this case, its free volume increases, and flexibility of the polymer chain increases, because of the increase in free volume. So in case, the stiffness goes up, and as a result the T m goes up, and if you have, even bulkier group, then the T m goes up further. So it is basically the pendent group which. So, basically we are talking about pendent group size, we are not talking about this, we are talking about pendent group size and type.

So depending on what is the type and size of the pendent group, the melting point gets influenced. If you compare, give one example here. Not this one. So let us go back and look at this slide, we have discussed the back bone stiffness, we have discussed the polarity, we have discussed effect of pendent group size and type. Obviously if you have branches present in the polymer chain, it hinders in crystallization, so crystallization become difficult, so it affects the T m. And if you have pendent polar troops, then it effects, or if a pendent polar group obviously, the inter molecular attraction goes up, and as a result T m will go up. If you have pendent groups present on the substituent present regularly, then it is easy to pack or packing it becomes better, so T m goes up. If the pendent groups are not placed symmetrically, then the T m goes down.

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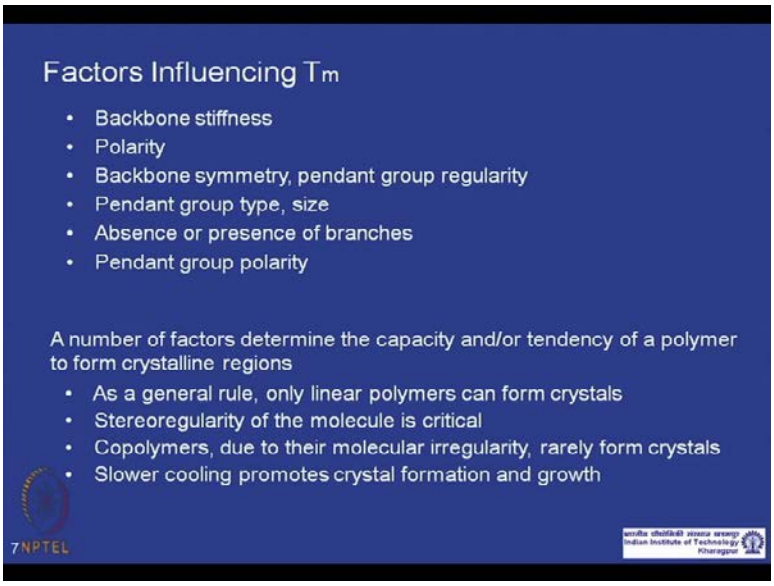

Factors Influencing Tm

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

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

- As a general rule, only linear polymers can form crystals
- Stereoregularity of the molecule is critical
- Copolymers, due to their molecular irregularity, rarely form crystals
- Slower cooling promotes crystal formation and growth

So, as a general factor we can say that, only linear polymers can form crystals, if the branches present in the polymer chain, it does not form crystals, or it does not crystallizes. Stereoregularity in a polymer molecule, is critical, so if syntactic or iso-tactic polymer will have bitter crystalline, crystal ability, then ataractic polymers co-polymers are. We talking about random co polymers, where their due to the molecular irregularity, they rarely form crystal. Obviously, if you have cool the polymer melt slowly then, the crystal, the polymers gets, polymers chains gets more time, and they can crystallize, and the crystallize crystallization take place easily, or the crystallize can grow in bigger size.

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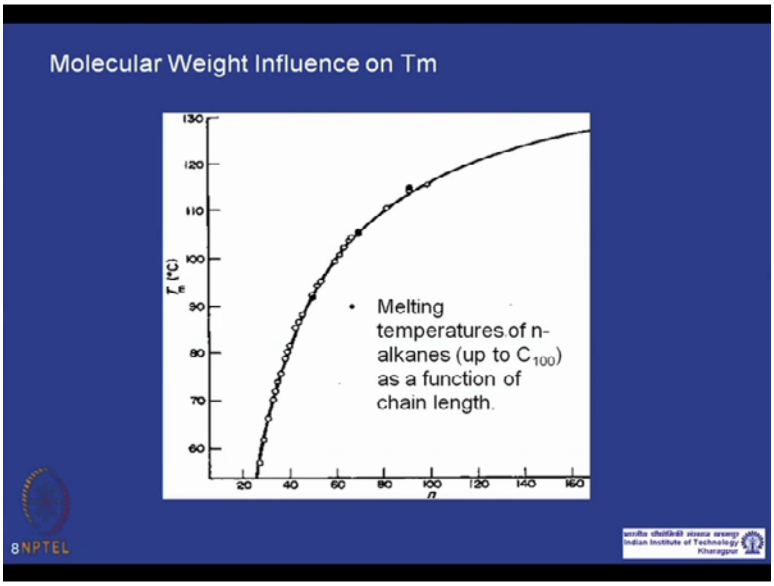

Molecular Weight Influence on Tm

- Melting temperatures of n-alkanes (up to C_{100}) as a function of chain length.

Molecular also influence the value of T m, this, because as you have seen in case of T g as well, that if we the chain ends are having much more free volume, so the end of polymer chains are much more flexible. So if you have a sorted chain, then the polymer is effectively more flexible, T g goes T m goes down, and if you have a higher chain the contribution from the ends is less, so T m goes up. So this is one example of normal alkanes as shown, that with increasing the chain length number of carbon atoms, the T m values goes up and eventually it is become a steady value. So if you want to compare between two polymer chains, it is preferably to compare in high molecule rate, so that the T m is almost independent of the molecular weight.

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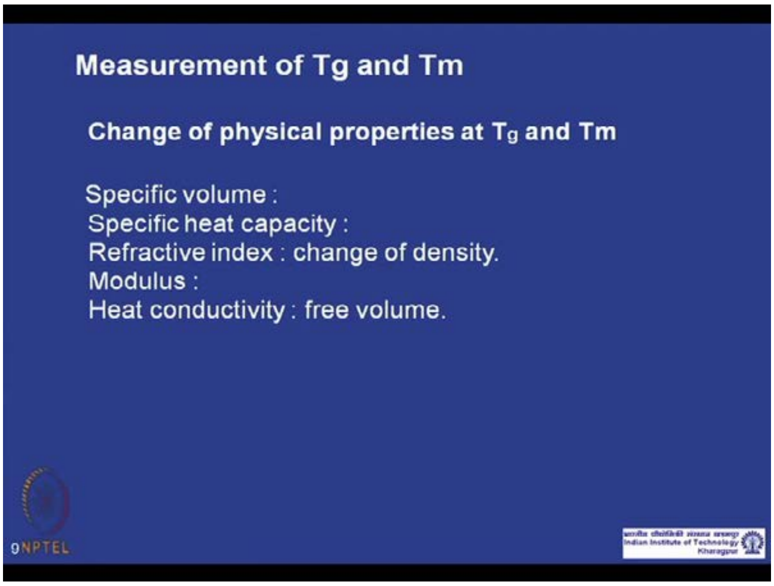

Measurement of Tg and Tm

Change of physical properties at T_g and Tm

Specific volume :
Specific heat capacity :
Refractive index : change of density.
Modulus :
Heat conductivity : free volume.

Now, we discussed the concept of T g and T m, and we also discussed the chemical, how the T g and T m depend on the chemical structure of a polymer chain. Now we will move and briefly discussed, how we determine, or measure T g and T m in laboratory. We have discussed this that, there are lots of physical properties changes, during the glass transition and melting, some of the them are listed here, specific volume changes, specific heat capacity, refractive index, modulus, heat conductivity. There are many others which can be in list, but these are some of the examples, some of the physical properties, undergo change their value during glass transition, and melting. So if you can follow any of this property with temperature, we can find out the glass transition temperature, and melting point. The most basic techniques, which are used in laboratory for determining T g and T m are, the D S C and D T A.

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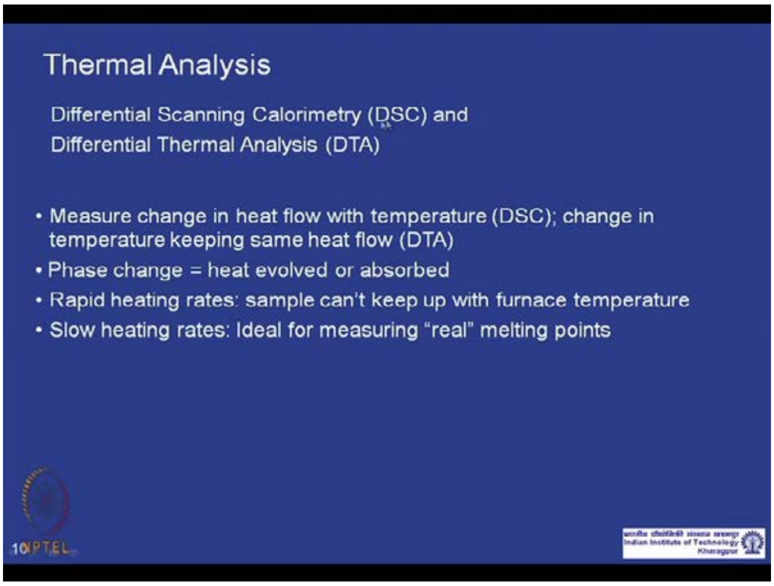

Thermal Analysis

Differential Scanning Calorimetry (DSC) and
Differential Thermal Analysis (DTA)

- Measure change in heat flow with temperature (DSC); change in temperature keeping same heat flow (DTA)
- Phase change = heat evolved or absorbed
- Rapid heating rates: sample can't keep up with furnace temperature
- Slow heating rates: Ideal for measuring "real" melting points

The D S C is different term; differential scanning calorimetory, and differential thermal analysis. So D S T stands for differential scanning calorimetory, and differential D T A stands for differential thermal analysis.

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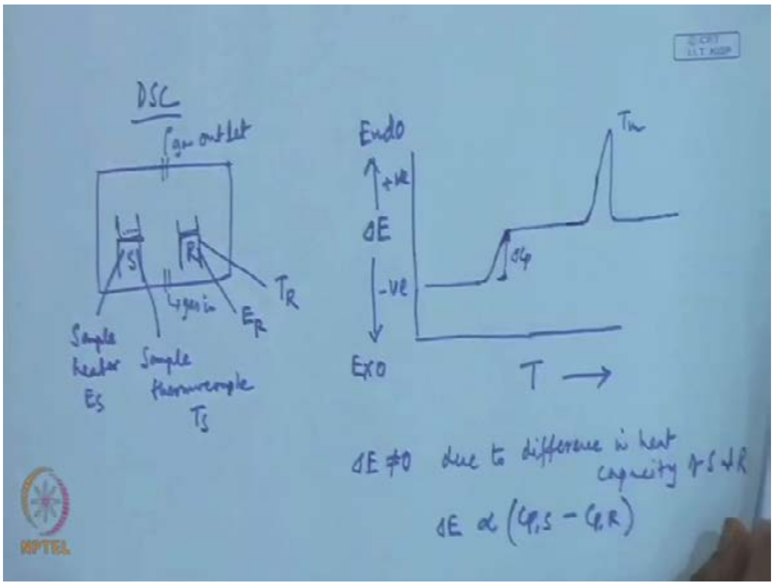

What is the principle of D S C and D T A. In D S C you typically have a chamber, where a sample is placed. So that is your sample S, and you have reference, which is empty. There is a heater, two sample heater, E s supplies energy, they is a thermo couple, sample thermo couple T s. Similarly, here you have a reference heater, and you have reference thermo-couple, which determines the temperature. Thermo-couple determines the temperatures of sample, and T r thermo-couple determine the temperature of the reference there is a gas inlet, typically with your experiments in inner atmospheric, so they is a gas inlet and a gas outlet. So what is done in this experiment; the sample and the reference which is just a blank. Sample are typically taken in a aluminum container, and then the aluminum container can be covered and creamed, so that nothing goes out, from the container, and parallelly they is a blank container without sample is kept. This two are heated, and the temperatures are maintained same. The temperatures for this sample, and the reference are kept maintain same. And to maintain the same temperature the heat or energy is supplied to the sample.

If there are something happen, some exothermic and endothermic reaction going on, so if there is some exothermic in exothermic transition or reaction happened here, then to maintain the temperature, the system has to supply more energy from outside, to maintain the temperature. So basically in this case, energy supplied is plotted against temperature. If they is a endothermic process goes on, in the sample, then you have to supply energy from outside. If some exothermic process goes on, then heat get evolves in the samples. So to maintain the same temperature between the sample and reference, you have take out some energy, so delta E becomes negative. So if you consider a process, typically what happened, there is always the delta is neighbor is zero, because there is always a difference between, difference in the heat capacity between the sample, and the reference.

So you have to always supply more heat, or at least different amount of heat, higher heat energy, to keep the sample at the same temperature as the reference. So delta S is always positive, neighbor is not equal to zero, due to difference in heat capacity of sample, and the reference, to keep. So this, again this delta is the amount of energy, or the heat we have to supply to the sample, to keep the sample and the reference temperature same. So delta will be proportional to the difference in the heat capacities, between the sample, heat capacities of the sample, and heat capacity of the reference. So if they is no change in heat capacity of the sample, then the value of the daily will remain same, which will give pass the base line. So if you start, daily will start somewhere and remain same, as long as the heat capacity of the sample remains same.

Now say, the sample is undergoing glass transaction temperature, if sample goes glass transaction temperature, which is a endothermic processes, so the system has to supply more energy, so delta will higher, and then once the glass transaction is over, then it will be same, again remain constant, because the heat capacity of the robbery state is higher, typically higher than the glassy state. The delta is e value will be higher in the robbery state, correspondence to corresponding to, or compare to a glassy state. And this difference will give the delta c p between the glassy state, and the rubbery state, now this if you increase further the temperature. Now if it continuing, a term, a time will come when these polymer samples undergo melting, and you get a peak correspondence to the melting of the polymer, so you get a curve like this.

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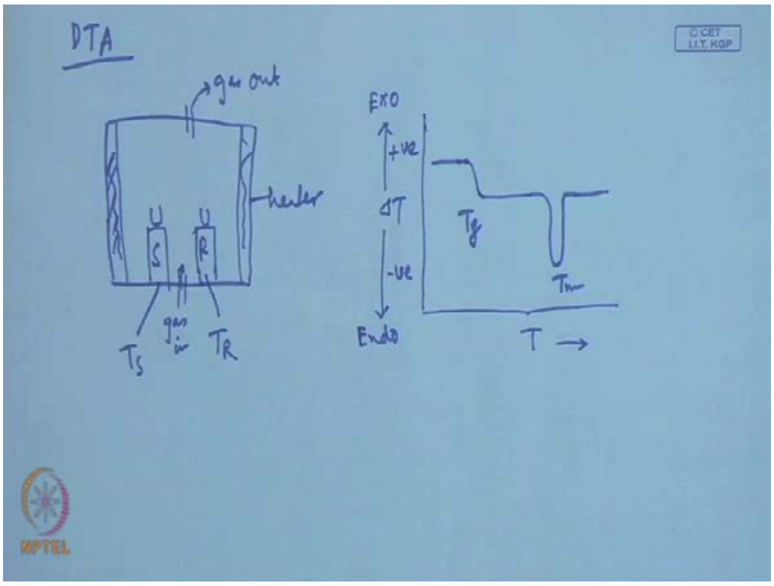

In case of D T A; differential thermal analysis, a similar concept is applied, where you have a chamber, which has a inbuilt heater. This is a heater, and you have sample, and again you have a reference, you have a thermo-couple for the sample, a thermo-couple for the reference. There is a place to put the gas inside, and there is a gas outlet is also there. In this case what happened heat is supplied, at a particular rate in the system, and difference in the temperature, between the sample, and the reference is observed. So in this case, delta T is a temporary difference between the same, and the reference is plotted against the temperature. So if there is a exothermic processes, delta T will be higher as a result of increase in heat, inside the sample. If there is a endothermic processes, there will be delta T will be lower correspondence to the difference, because you were supplying constant amount of energy to the system.

So if you plot the same graph, like we did for D S C, we get it deep at T g glass transaction temperature, and melting t you get exo peak, so this is T g and T m. So in the case of D S C, the temperature between reference and the sample is kept constant, and the required energy is supplied, so delta e is the amount of energy required, to keep the temperature between the sample and the reference same, is plotted against t. And in case of D T A difference thermal analysis, the same amount of heat is supplied to sample and reference, at a constant rate, and the difference in the temperature between the sample and the reference, is plotted against the temperature. So any face change, which involves any glass transaction or melting, which is endothermic processes, will require more heat, to maintain the temperature, and ideally this should be a sharp increase here.

But as all of us know, that the polymer sample consist of many chains of different length, so the T g corresponding to each chains are different, so that is why we get a board nature of this transition, because each higher size polymers will have slightly have T g correspondence to compare to a polymer chain having, lower size. Similarly, the T m is little less sharp, compare to a small molecular melting point, because the polymer chain has many molecular weight; basically consist of chains having many molecular weights. Now this T g, we will talk about this D S C, how T g obtained. Mathematically, if we draw this portion again we can, so that is end of...

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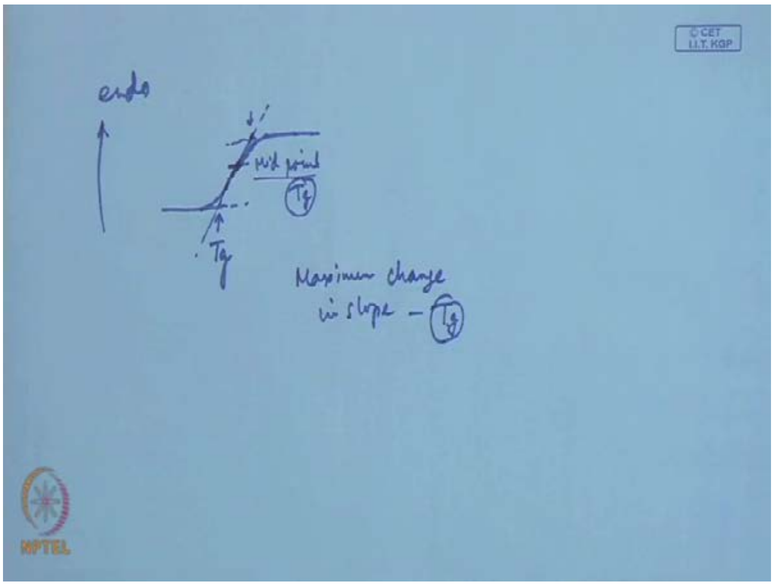

So, different scientists use different techniques or different techniques to find out the T g. Some uses this inflection point, the inflection point as T g. Many uses or that is the most used technique, where. There is an inflection point here, and there is a inflection point here. The midpoint of these two, some people consider this as a T g, and some cases what happened, the point where there is a maximum change in the slope, during this inter temperature in the slope changes, keep on changing. So the point where the maximum change in slope happens, some people consider that as a T g. Now this and this is very close to the midpoint of this change over. So generally if nothing is mentioned.