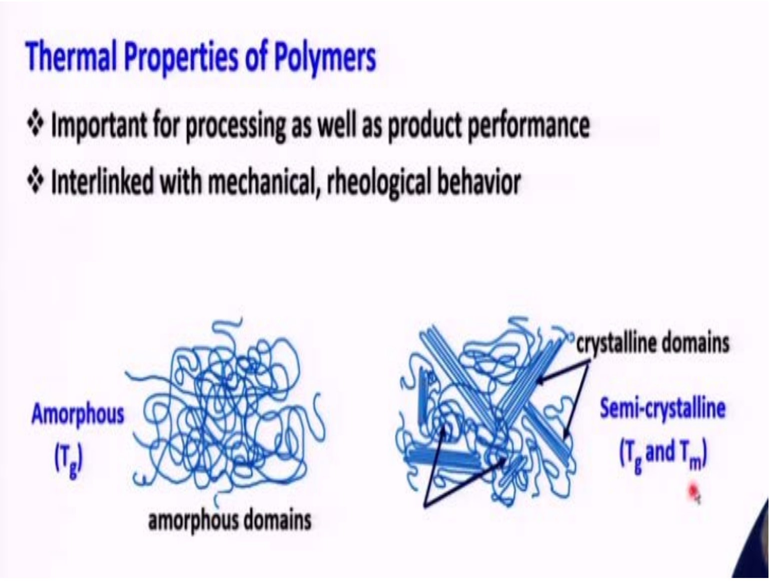
Introduction to Polymer Science
Prof. Dibakar Dhara
Department of Chemistry
Indian Institute of Technology – Kharagpur

Module No # 07
Lecture No # 35
Thermal Properties: Amorphous State

I have been discussing on properties of polymers and I have started discussion on thermal, mechanical and viscoelastic properties. In this lecture, I will focus mainly on thermal properties and on amorphous state.

(Refer Slide Time: 00:41)

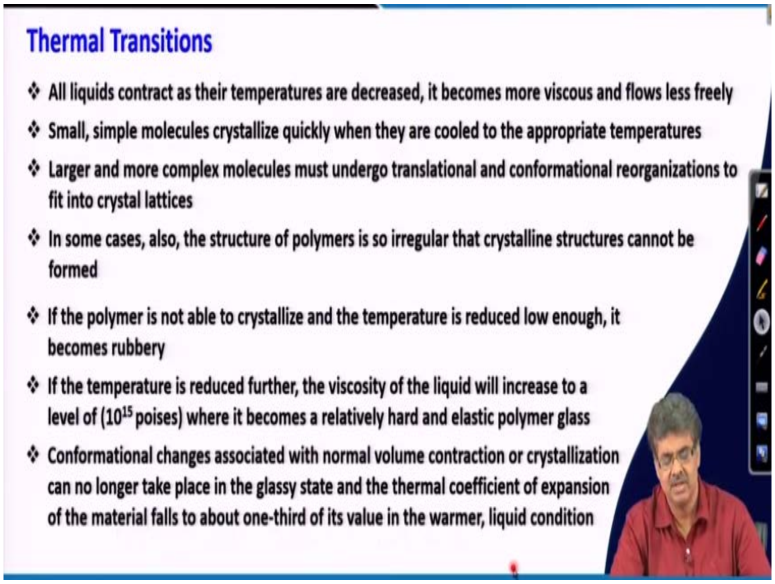


Thermal Properties of Polymers

- Important for processing as well as product performance
- Interlinked with mechanical, rheological behavior

As I was discussing at end of the last lecture that thermal properties of polymers are very important for processing as well as product performance, and the mechanical and rheological or viscoelastic properties of polymers are also well related with the thermal properties as I will discuss in coming lectures. Again, as we have discussed that amorphous polymers are entangled frozen mass with practically no order and these polymers are characterized by glass transition temperature. Similarly, for semi-crystalline polymer, we have both amorphous domain and crystalline domain which corresponds to T_g and T_m, glass transition temperature and melting temperature.

(Refer Slide Time: 01:43)



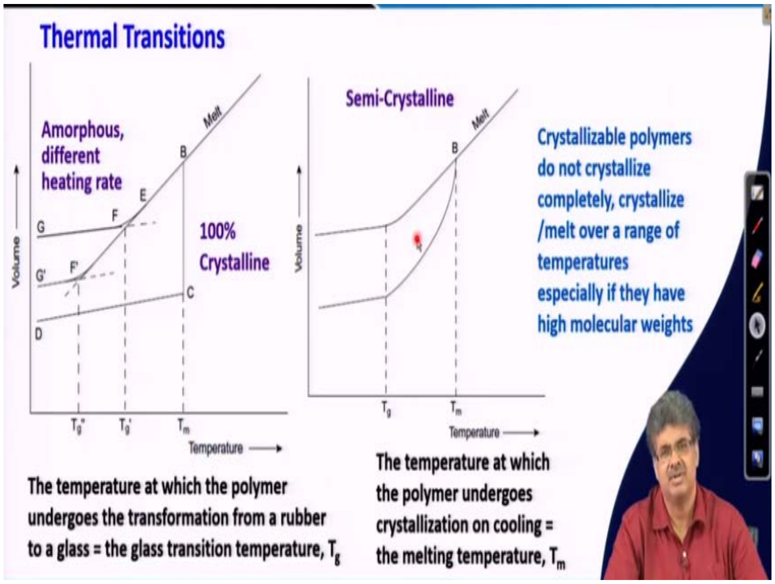
Thermal Transitions

- All liquids contract as their temperatures are decreased, it becomes more viscous and flows less freely
- Small, simple molecules crystallize quickly when they are cooled to the appropriate temperatures
- Larger and more complex molecules must undergo translational and conformational reorganizations to fit into crystal lattices
- In some cases, also, the structure of polymers is so irregular that crystalline structures cannot be formed
- If the polymer is not able to crystallize and the temperature is reduced low enough, it becomes rubbery
- If the temperature is reduced further, the viscosity of the liquid will increase to a level of (10^{15} poises) where it becomes a relatively hard and elastic polymer glass
- Conformational changes associated with normal volume contraction or crystallization can no longer take place in the glassy state and the thermal coefficient of expansion of the material falls to about one-third of its value in the warmer, liquid condition

So we have been talking about the glass transition temperature and melting temperature, these are the typical thermal transitions in polymer samples. Now if we think about a liquid, say water, and decrease their temperature what happens? When the temperature is decreased, it becomes more viscous and it flows less freely. Now when the temperature is sufficiently low then small molecules like water or other small simple molecules, crystallize at a particular temperature quickly to form a solid crystalline material and that temperature is called melting temperature as we all know that.

But if the sample or the molecules are present in this liquid state are quite large like polymer molecules and in complex shapes, then it is very difficult for these molecules to undergo translation and conformational reorganization to pack in a crystal-like manner. When a crystal is formed, the molecules have to align themselves in a particular order. Now if the polymers are very large then they are all entangled with each other in liquid state. So even we decrease the temperature sufficiently, it is also not possible for the polymer molecules to undergo translation or conformational reorganizational to fit into a crystal lattice. Also as the structures of the polymers are so irregular that crystallized structure cannot be formed. And if the polymers are not able to crystallize and if the temperature is reduced further and it goes below a certain temperature it becomes rubbery in nature. And if the temperature is reduced further, the viscosity of the liquid becomes so high that it is like a solid material, it does not flow at all, it becomes very hard and polymer glassy material. So it does not have a regular arrangement like a crystal structure but its viscosity so high that there is no mobility of the molecules and is almost like a solid material. In this case the conformational changes associated with the normal volume contraction or crystallization no longer take place in the glassy state, because there is no freedom at all, so the associated confirmation changes and volume contraction do not happen as temperature is decreased further. So the thermal coefficient of expansion of this glassy material falls to about one third of value in a warmer liquid condition. The molecules are large and they are almost like in a frozen state, they do not have any mobility. So they cannot contract during decrease in temperature, so the coefficient of thermal expansion for this glassy materials falls about one third of its value compared to warmer liquid condition.

(Refer Slide Time: 05:43)



Thermal Transitions

Crystallizable polymers do not crystallize completely, crystallize /melt over a range of temperatures especially if they have high molecular weights

The temperature at which the polymer undergoes the transformation from a rubber to a glass = the glass transition temperature, T_g

The temperature at which the polymer undergoes crystallization on cooling = the melting temperature, T_m

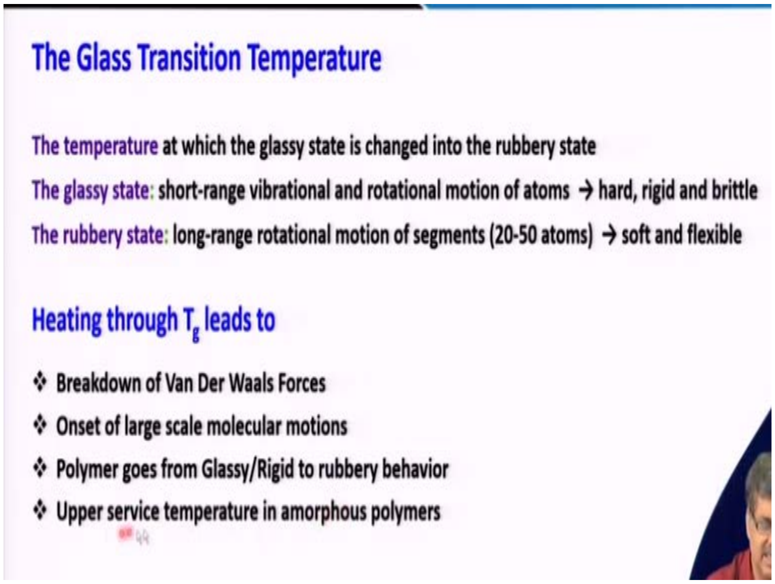
If we graphically represent the volume versus temperature curve, if we start from molten state and decrease temperature, the volume decreases. If the molecules can pack well, crystallize, then volume suddenly drops and a solid state is formed at melting point or melting temperature. And when, we decrease the temperature further, the volume changes negligibly small because it is in a solid state now. But as we said, if the molecules are large like large polymer molecules, then they do not have enough flexibility or enough freedom to rearrange themselves and pack in a crystal matrix. Hence, it will continue to decrease its volume without crystallizing, and a temperature will come, in fact a range of temperature will come, when the sample cannot contract further because of no practical mobility, viscosity is extremely high like a solid. This temperature is called glass transition temperature and below which there is not much contraction.

Now as we can imagine, if we cool the sample at different rate then this temperature, glass transition temperature will vary little bit. Because if we cool faster then we are giving less time to the polymers to rearrange and pack. Whereas if you give more time, then polymers still have some time to orient themselves or change the conformation and further compact. Hence, generally, if we do cooling faster then we get a slightly higher T_g value compare to a cooling where we do at a slower rate. So for 100% crystalline we only get a T_m, melting temperature, for an amorphous 100% amorphous we only get a glass transition temperature. But unlike the melting point or melting temperature, glass transition temperature actually various depending upon the heating or cooling rate, because this rate of heating/cooling determine the time a polymer molecule can get to reorganize themselves and compact or expand.

The temperature at which the polymer undergoes this transition from rubber to glass is called glass transition temperature or T_g. We will discuss more about this T_g and see actually what is happening in terms of molecular structure. Now in case of semi-crystalline material which have both amorphous phase and crystalline phase, as we decrease the temperature, part of the polymers will actually crystallize. And because there are amorphous regions which do not crystallize then this change will not be as sharp for a 100% crystallized small molecule. So there will be ranger of temperature during which this crystallization take place and we call again like melting temperature. But in this case unlike this case, there will be a range of temperature where these polymers will crystallize. And the lowering of volume will continue till we reach glass transition temperature, below which the contraction becomes much lower compared to higher temp. So this is purely a 100% amorphous material and this is a semi-crystalline material which has partly crystalline domain and partly amorphous domain. This is for semi-crystalline. So crystallizable polymers do not crystallize completely as we discussed earlier.

It crystallizes or melts over a range of temperature, as I just discussed, specially if they are of high molecular weights. The temperature at which the polymer undergoes crystallization and cooling that is called melting temperature or T_m. Now we know what is T_g or glass temperature of a polymer and a melting temperature or T_m of a polymer sample. Remember, here we are telling the temperature at which the polymers undergo crystallization on cooling, but sometimes, because of heating, there could be a crystallization, heating induced crystallization and that may also induce crystallinity, but that is not a melting temperature, that is called T_c or crystallization temperature which is not a true transition in per se. Basically, when we heat an amorphous sample sometimes if the polymer structures are conducive, they can actually form crystal domains at a particular temperature which we call T_c or crystallization temperature.

(Refer Slide Time: 12:10)



The 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

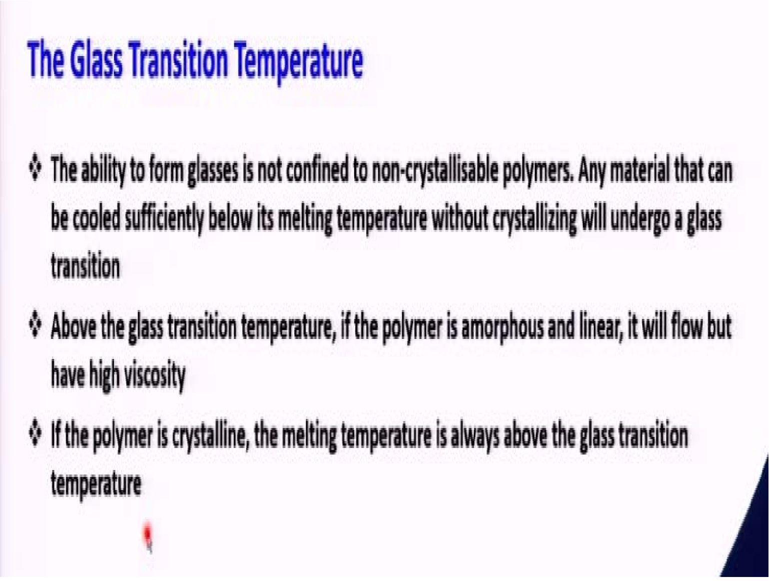
The rubbery state: long-range rotational motion of segments (20-50 atoms) → soft and flexible

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

Now will come back to glass transition temperature, this is the temperature at which the glassy state is change to rubbery state or vice-versa. In glassy state, we have short range vibrational and rotational motion of atoms and it is hard, rigid and brittle state. Whereas in rubbery state, we have long range rotational motion of the segments of about 20 to 50 atoms, and it is soft and flexible. Now when we heat through T_g there are breakdown of Van der Waals forces and on set of large scale molecular motions in polymer molecules. Polymer goes from glassy rigid to rubbery behavior. And for a perfectly amorphous or a completely amorphous material, this is very important because this gives the upper service temperature of the polymer product. So if we talk about a PMMA, polymethyl methacrylate, which is having T_g of 105 °C. This is the highest temperature PMMA is useful, in fact the highest usable temperature for a PMMA is little lower than Tg. For polystyrene, the T_g is 100 °C, the highest useful temperature is probably 90 °C and so on. So Tg is the upper service temperature in amorphous polymer.

(Refer Slide Time: 13:43)

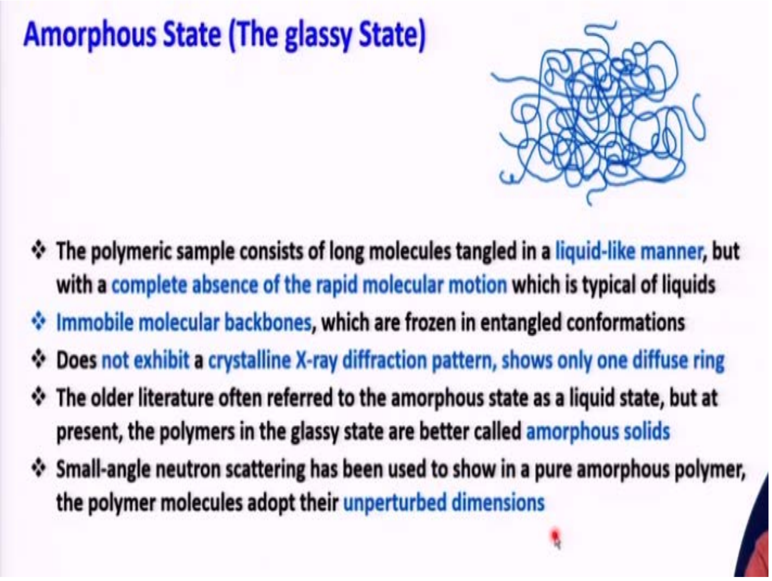


The Glass Transition Temperature

- The ability to form glasses is not confined to non-crystallisable polymers. Any material that can be cooled sufficiently below its melting temperature without crystallizing will undergo a glass transition
- Above the glass transition temperature, if the polymer is amorphous and linear, it will flow but have high viscosity
- If the polymer is crystalline, the melting temperature is always above the glass transition temperature

The ability to form glasses is not confined to non-crystallizable polymers. When we talk about glass transition temperature, this not only restricted to polymers, there are other examples where glass formation takes place like the glass we commonly in our house hold items. They are not polymeric what they are ceramic glasses like silica glass. So, any material that can be cooled sufficiently below its melting temperature without crystallizing it will undergo a glass transition eventually. Above the glass transition temperature if the polymer is amorphous and linear, it will flow but have a high viscosity. If a polymer is crystalline or is partly crystalline, then melting temperature is always above the glass transition temperature of that particular polymer. So if we have a semi crystalline polymer, we have a T_g which is lower than a T_m and in this particular case, the upper service temperature would be the T_m.

(Refer Slide Time: 15:06)

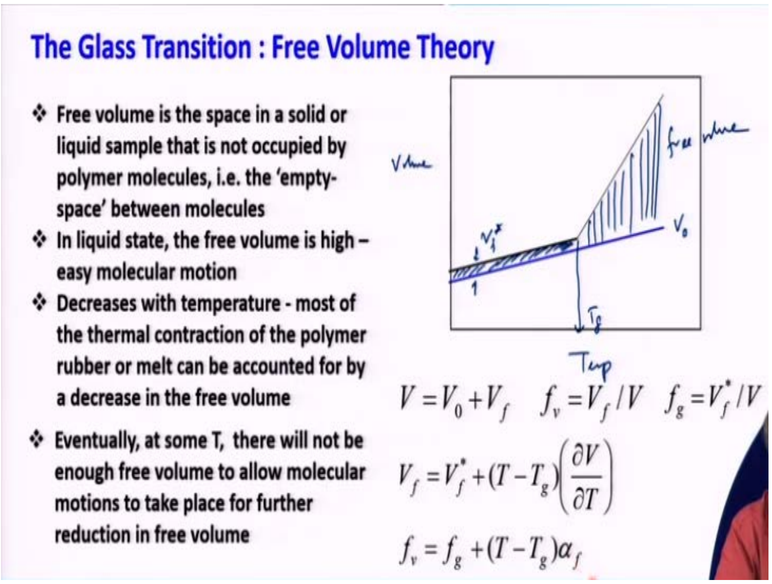


Amorphous State (The glassy State)

- The polymeric sample consists of long molecules tangled in a liquid-like manner, but with a complete absence of the rapid molecular motion which is typical of liquids
- Immobile molecular backbones, which are frozen in entangled conformations
- Does not exhibit a crystalline X-ray diffraction pattern, shows only one diffuse ring
- The older literature often referred to the amorphous state as a liquid state, but at present, the polymers in the glassy state are better called amorphous solids
- Small-angle neutron scattering has been used to show in a pure amorphous polymer, the polymer molecules adopt their unperturbed dimensions

We continue our discussion on amorphous state or glassy state. In this case, the polymer sample consists of long chain polymer molecules entangled with each other like a liquid like manner. There is no long range order in this case but with complete absence of rapid molecular motion, which is typical of a liquid. In case of liquid, we know the molecules are always moving and you have a particular velocity associated with those molecules. But in case of polymer glass or amorphous glass there is no short-range ordering like a typical liquid. There is no rapid molecular motion in this case of polymer glass. So there is a different between a typical liquid and a polymer glass. In true sense polymer glass is probably more like a liquid state but because it has no molecular motion and the viscosity is completely high, in practical from point of view it is actually a solid material. But in molecular point of view it is a liquid material. It has immobile molecular backbones, which are frozen in entangled confirmation. The polymer glass does not exhibit crystalline x-ray diffraction pattern; it only shows a diffuse ring. So unlike a crystalline material which gives a discrete ring and gives a crystalline X-ray diffraction pattern, amorphous material does not give discrete ring, gives only diffuse ring. In older literature amorphous state was often referred to as liquid state. But at present polymers in glassy state are better called amorphous solid. Small angle, this is very important, small angle neutron scattering has been used to show that for a pure amorphous polymer the polymer molecules adopt their unperturbed dimensions. We talked about different dimensions like end to end distance which increase in restriction, and we talked about unperturbed dimension there, which happens for polymers in θ solvent, if you recall, for pure amorphous polymers the size of a polymer will resemble with unperturbed dimension like the dimension in a θ solvent.

(Refer Slide Time: 18:31)



The Glass Transition : Free Volume Theory

- Free volume is the space in a solid or liquid sample that is not occupied by polymer molecules, i.e. the 'empty-space' between molecules
- In liquid state, the free volume is high – easy molecular motion
- Decreases with temperature - most of the thermal contraction of the polymer rubber or melt can be accounted for by a decrease in the free volume
- Eventually, at some T, there will not be enough free volume to allow molecular motions to take place for further reduction in free volume

$$V = V_0 + V_f \quad f_v = V_f / V \quad f_g = V_f^* / V$$

$$V_f = V_f^* + (T - T_g)\left(\frac{\partial V}{\partial T}\right)$$

$$f_v = f_g + (T - T_g)\alpha_f$$

Now the glass tension phenomenon is also described from a free volume theory. Free volume is the space in a polymer solid or a liquid sample that is not occupied by the polymer molecules or is the empty space between the molecules. In liquid state, obviously, the free volume is higher which enables easy molecular motion, and with decrease in temperature, most of the thermal contraction of the polymer sample, rubber, or melt can be accounted by the decrease in the free volume.

With decrease in the temperature, the free volume actually decreases and as a result, the volume of the sample decreases. If we plot volume of a polymer sample with temperature, if we plot temperature here and volume of the sample, and this is V_0 which is the volume of the polymer molecules, which is slightly dependent on the temperature, as the temperature increases the volume goes up.

$$V = V_0 + V_f$$

As we decrease the temperature, the total volume decreases quiet sharply in molten state, and below the glass tension temperature there is no further contraction possible as we discussed because of the frozen molecular motion. Hence, this total volume remains almost same, now this difference between the actual volume and the volume of the polymer molecules are termed as free volume. The free volume below the T_g remains almost constant no matter what is the temperature. Whereas above T_g the free volume increases with temperature. So with decreasing in temperature most of the thermal contractions of the polymer, rubber, melt can be accounted by decrease in free volume. Eventually at T_g, there will be not enough free volume for the molecules to reorient or change the confirmation for further compaction. So if the polymer molecules want to further contract it required some space to rearrange themselves. If the space is not enough, they are entangled, there is no space obviously it cannot further compact. Although thermodynamically it wants to compact, but because there is no free space available, it cannot contract. So at T_g, there will not be enough free volume to allow molecular motions to take place for further reduction in free volume. So, total volume is given by the volume of the polymer molecules plus the free volume and the fraction of free volume is given by the free volume divided by total volume,

$f_v = V_f/V$.

This is the free volume below T_g, so this value, this difference in volume is V_f^*, the free volume below glass transition temperature. The fractional free volume below Tg is given by

$$f_g = {}^{V_f^*}\!/_{V}$$

The total free volume is given by this free volume plus change in temperature and rate of change of volume with temperature.

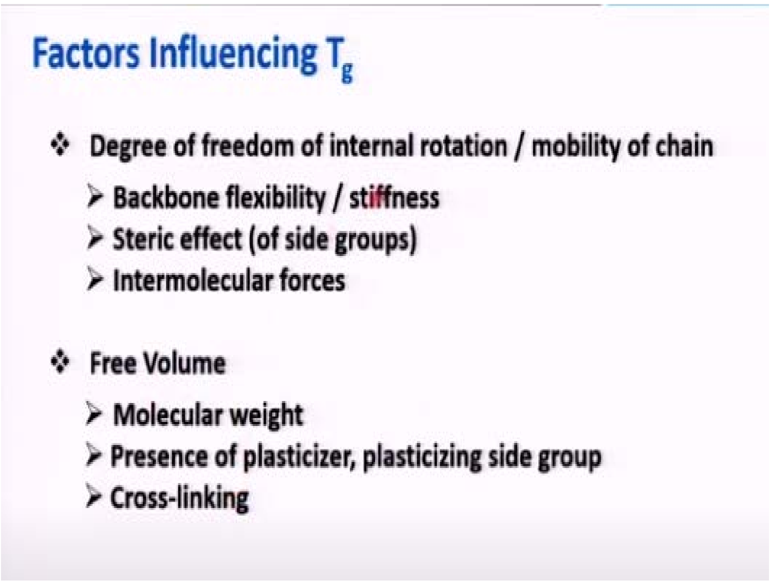
$$V_f = V_f^* + (T - T_g)\left(\frac{\partial v}{\partial t}\right)$$

Because V_f^* does not change much, the fraction of free volume is given by free volume before or below the glass temperature and the thermal coefficient of thermal expansion of free volume.

$$f_v = f_g + (T - T_g)\alpha_f$$

where α_f is expansion coefficient or coefficient of thermal expansion of free volume.

(Refer Slide Time: 24:12)

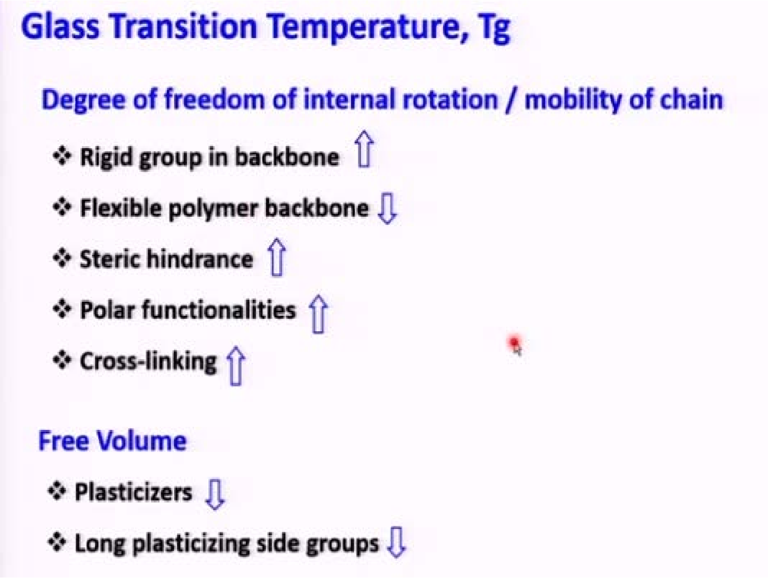


Factors Influencing T_g

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

Now looking at the polymer structure we can actually find out the different factors which influence the value of T_g. Intuitively you can guess that if the back bone structure is more stiff, obviously the mobility or the tendency to rearrange themselves will be lower, as a result T_g will be higher. If the steric effect is higher, which means again the probability of rotation around the single bond will come down, T_g will be higher. If the intermolecular force is higher, obviously, the chains will not be able to rotate more freely, the T_g will be higher. Similarly, the factors, which increase the free volume like decrease in the molecular weight, addition of plasticizer molecule, or long chain side group will increase the free volume, so they increase the value of T_g.

(Refer Slide Time: 25:21)



Glass Transition Temperature, Tg

Degree of freedom of internal rotation / mobility of chain

- Rigid group in backbone ⇧
- Flexible polymer backbone ⇩
- Steric hindrance ⇧
- Polar functionalities ⇧
- Cross-linking ⇧

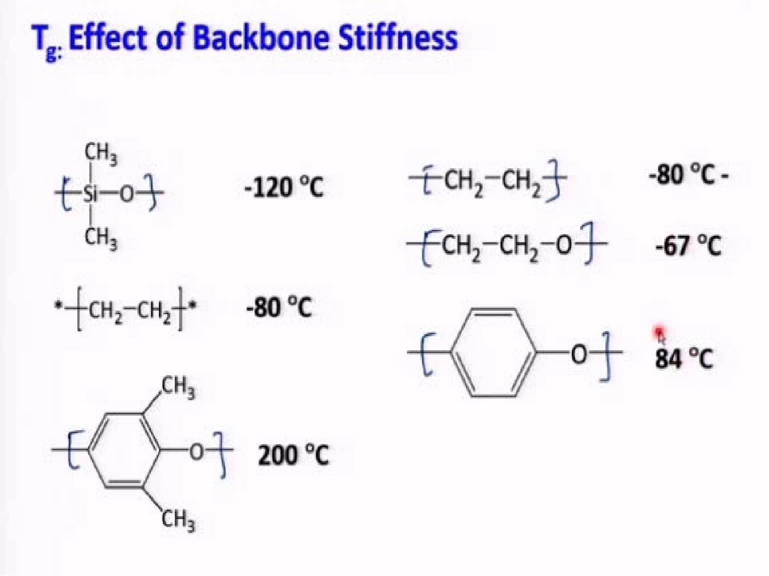
Free Volume

- Plasticizers ⇩
- Long plasticizing side groups ⇩

So, if we increase the number of rigid groups in the backbone then T_g goes up, if we increase the flexibility then T_g goes down. If we increase the steric hindrance, T_g goes up, if we increase the polar functionalities, then T_g goes up. If we increase the cross-linking, the mobility will come down the and T_g will go up. Similarly, in terms of free volume, if we add plasticizer which will increase the free volume, T_g will go down. If we have long plasticizing side groups then also T_g will come down.

I will give some comparative examples to show these trends but you must also remember that it is not always true that a single factor which is in effect. Like if you have different side groups they may actually increase the steric hindrance but decrease the polar interaction, so what I want to say that it is very difficult to completely account for the T_g values by only one single factor, there could be multiple factors which are actually finally responsible for the T_g value of the polymers.

(Refer Slide Time: 26:43)

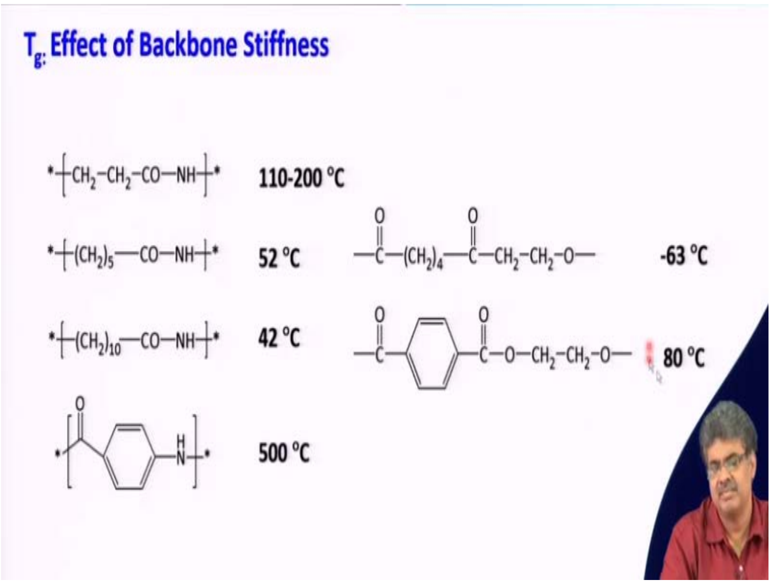


T_g: Effect of Backbone Stiffness

For example, let us compare the T_g values of these three polymers. This Si-O bond is very flexible, even more flexible than a carbon-carbon bond. Similarly, if you have aromatic backbone, obviously, the flexibility is much lower or the stiffness is much higher. Hence, the T_g as you can expect, should be much higher for this. So if we give the values so this will be -120 °C and this will be, for polyethylene the T_g is not a fixed like -80 °C as I mentioned here. This is representative value, the T_g of polyethylene actually depends on various parameters like the molecular weight, crystallinity, branching and so on. But it is having quite low T_g and it has actually a range of T_g, it can be -80 °C or -120 °C, it can be just less than 0 °C and so on. Now as you can see that as the stiffness of the backbone increases, the T_g goes up. Similarly, if we compare these three polymers, as we introduce carbon oxygen bond, this flexibility goes up, hence the T_g expectably go down.

If we increase aromatic group in the backbone, T_g is expected to go down as the stiffness will go up. So if we compare these values, as you can see this is -80 °C, this is -60 °C, in this example this may increase the flexibility but because of the intermolecular interaction is higher because of presence of polar group, the T_g is actually is little higher in this particular case, as I was saying that it will be multiple factors which determine the value of T_g. In this case, because stiffness is higher the T_g is much higher compared to these two polymers.

(Refer Slide Time: 29:13)



$T_{g:}$ Effect of Backbone Stiffness

$*\!-\!\!\left[CH_2-CH_2-CO-NH\right]\!\!-\!*$ 110-200 °C

$*\!-\!\!\left[(CH_2)_5-CO-NH\right]\!\!-\!*$ 52 °C

$*\!-\!\!\left[(CH_2)_{10}-CO-NH\right]\!\!-\!*$ 42 °C

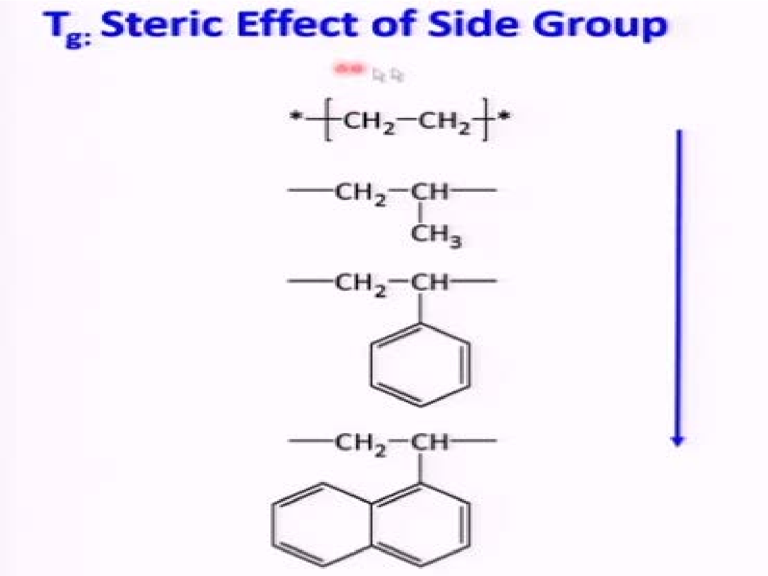
500 °C

$-C(=O)-(CH_2)_4-C(=O)-CH_2-CH_2-O-$ -63 °C

80 °C

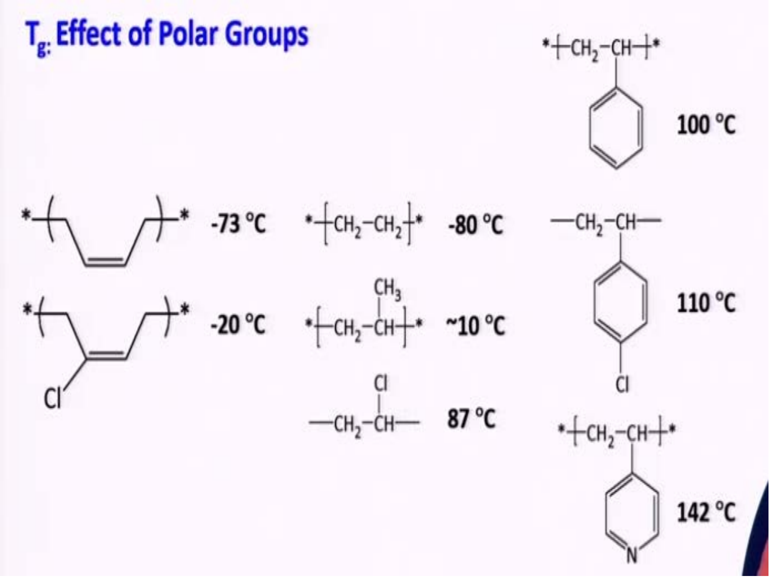
If we compare the T_g of these four, as you can see if we increase these CH_2 groups then the flexibility will be higher, when we have this aromatic group, flexibility or stiffness will be lower and the stiffness will be higher. As you can see this T_g comes down but because of aromatic groups in the backbone the T_g is drastically higher. In this case, if you carefully look that as we increase the CH_2 groups, number of polar groups is decreasing. In fact, in these cases the intermolecular forces actually decrease which should also account for the decrease in this T_g value of this sample. Similarly, if we compare these two, obviously this is much stiffer it should have much higher T_g value compared to this polymer.

(Refer Slide Time: 30:17)


T_g: Steric Effect of Side Group

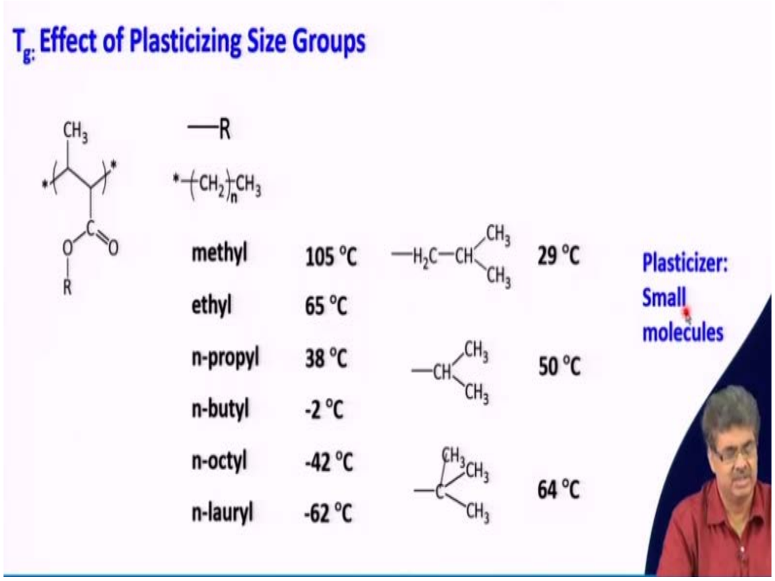
When you compare the steric effect of the side groups you can see that as we increase the size or bulkyness of the side group the steric effect increases and the rotation around this single bond becomes more difficult and stiffness increases, as a result T_g goes up as we increase the size of the side group.

(Refer Slide Time: 30:49)


T_g: Effect of Polar Groups

Similarly, if we have polar groups, obviously intermolecular interaction goes up between polymer chains as a result T_g goes up. If we compare these two, you can see this has higher T_g, and if you compare these three, then obviously presence of chlorine will increase the intermolecular interaction, as a result T_g will go up as it is seen here. Compare to a hydrogen, methyl group will have a higher intermolecular interaction because of higher Van der Waals forces between the polymer chains. As a result we have higher T_g, this also increases the steric hindrance which also contribute to increase in the value of this T_g of this polymer. If you compare these three cases, then as we increase the polar substitution, in these cases the steric effect are almost similar, so the intermolecular forces or the polar effect will be mostly detrimental for value of T_g. If you look at this value, the higher is the polarity higher is the value for T_g for these polymers.

(Refer Slide Time: 32:19)



T_g: Effect of Plasticizing Size Groups

—R

$*\!-\!(CH_2)_n\!-\!CH_3$

methyl	105 °C
ethyl	65 °C
n-propyl	38 °C
n-butyl	-2 °C
n-octyl	-42 °C
n-lauryl	-62 °C

$-H_2C-CH(CH_3)_2$ 29 °C

$-CH(CH_3)_2$ 50 °C

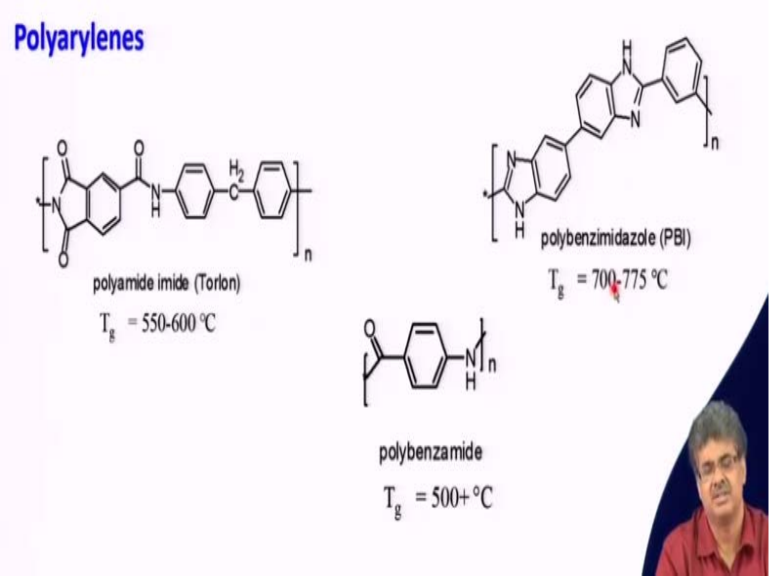
$-C(CH_3)_3$ 64 °C

Plasticizer: Small molecules

Now this is for the contribution from the free plasticizing group or increasing the free volume. In this case of methacrylates, if we increase the size of this R groups, this becomes more flexible and as a result the free volume increases. As the free volume increases, the T_g comes down because, as I explained, as the free volume increases the chains have more space to rearrange itself at a particular temperature, so the T_g can go down further. If you compare this methyl, ethyl, propyl, butyl, you can see that as we increase the chain length the T_g value decreases steadily. When we increase the size of the side group like if you compare a n-propyl and isopropyl group, because this is a linear chain and this is more of a bulkier group, this will have higher T_g. Similarly, from a normal propyl to this propyl group, you have higher T_g.

Similarly, compared to a normal butyl, a tertiary butyl gives a much higher T_g, which means that long linear side chain actually increases the flexibility and increases the free volume. As a result, the T_g goes down. If we had small molecules which are miscible, which gets dissolve in the polymer matrix, actually decrease the free volume quite significantly and this strategy is used for aiding polymer processing process. If the polymer T_g is higher, then these plasticizers are added to decrease the T_g for helping in processing. That happens because on dissolving small molecules the free volume increases.

(Refer Slide Time: 34:44)



Polyarylenes

polyamide imide (Torlon)

T_g = 550-600 °C

polybenzimidazole (PBI)

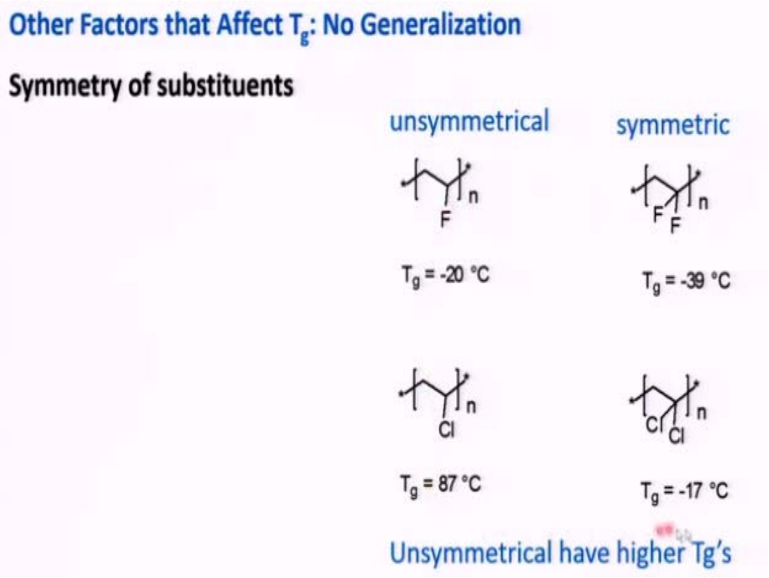
T_g = 700-775 °C

polybenzamide

T_g = 500+ °C

Requirement of very high heat stable polymers is met by, as you can see, imides, which have aromatic groups in the background. So in this case it has very high intermolecular forces and very high rigidity or stiffness in the backbone. As a result, you can see the T_g values are very high and these are used in a very high challenging environment where requirement of heat resistance polymers is very high. Like in space applications where the friction is very high, the polymers need to sustain high temperature heat.

(Refer Slide Time: 35:35)



Other Factors that Affect T_g: No Generalization

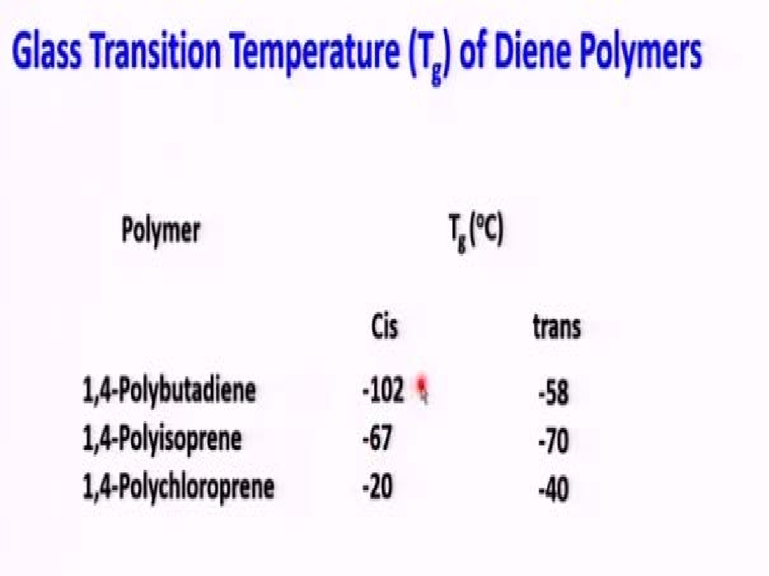
Symmetry of substituents

	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 some other observations about T_g values but there is no generalization for those cases, for example, non-symmetrical substitution has T_g higher values. For example, this has higher value than this and so on. So these are some of the values you need remember or if required, you need to find out from literature. There is no particular trend.

(Refer Slide Time: 35:59)

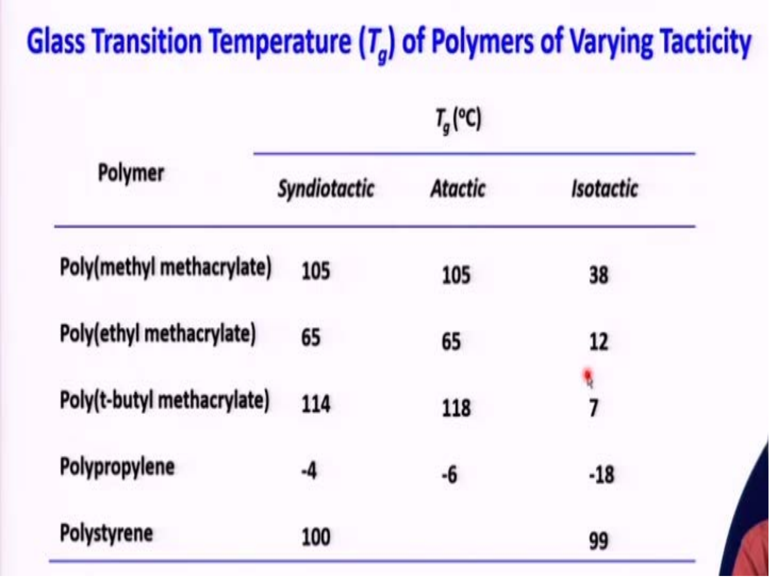


Glass Transition Temperature (T_g) of Diene Polymers

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

Similarly, the glass tension temperature of Diene polymers also is not very predictive it terms of Cis and Trans.

(Refer Slide Time: 36:12)

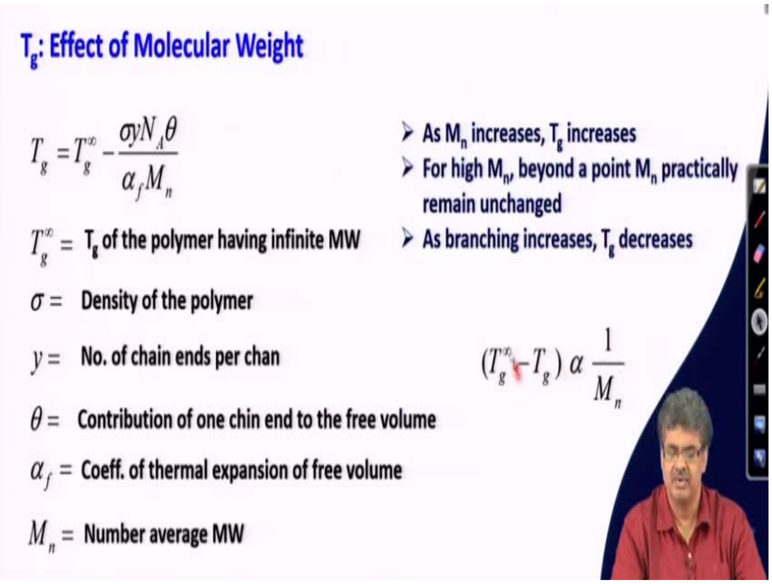


Glass Transition Temperature (T_g) of Polymers of Varying Tacticity

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

Tacticity also change the T_g value, if we have a more ordered structure then packing becomes easier, as the result the T_g value should be lower compared to a situation when there is no particular order in tacticity. For example, isotatic PMMA is having much lower T_g value compared to a syndiotactic. In fact, predicting or explaining this tacticity driven glass transition temperature is quiet complex, hence, it is better to remember the values or at least you should understand or you should appreciate that if we change the tacticity of a polymer, there is a possibility of changing the T_g value as well. So we need to determine the T_g value before we think about an application.

(Refer Slide Time: 37:26)



T_g: Effect of Molecular Weight

$$T_g = T_g^{\infty} - \frac{\sigma y N_A \theta}{\alpha_f M_n}$$

T_g^{∞} = T_g of the polymer having infinite MW

σ = Density of the polymer

y = No. of chain ends per chan

θ = Contribution of one chin end to the free volume

α_f = Coeff. of thermal expansion of free volume

M_n = Number average MW

- As M_n increases, T_g increases
- For high M_n, beyond a point M_n practically remain unchanged
- As branching increases, T_g decreases

$$(T_g^{\infty} - T_g)\ \alpha\ \frac{1}{M_n}$$

There is significant effect of molecular weight on T_g, it is given by this expression.

$$T_g = T_g^{\infty} - \frac{\sigma y N_A \theta}{\alpha_f M_n}$$

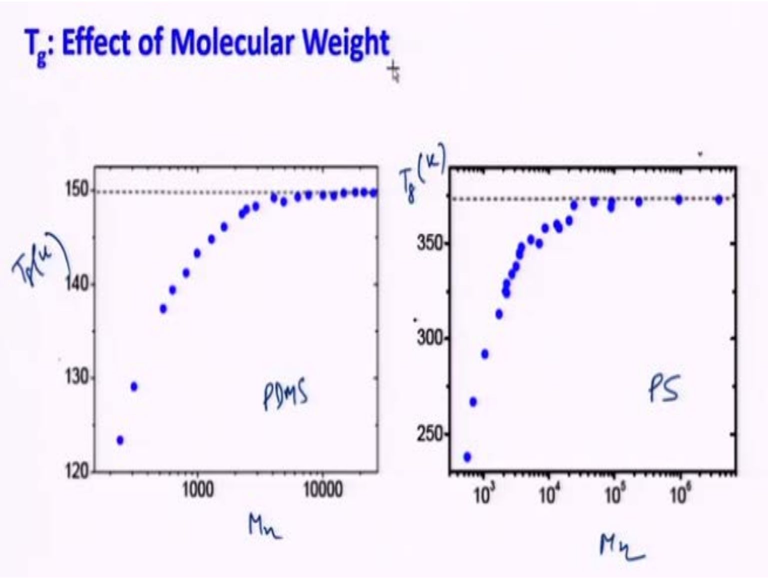
I have shown these terms, you can actually look at the meaning of these parameters, like this is the values for T_g or polymer having infinite molecular weight, this row is a density of the polymer, y is the number of chains or polymer chain, and so on. M_n is the number average molecular weight. Hence, as the molecular weight increases, the T_g value approaches close to a limiting value which is for a polymer having infinite molecular weight.

So as molecular weight increases T_g increases but this increase becomes less important or less significant as you go beyond some particular value of molecular weight. For high molecular weight beyond a particular M_n, practically the value of T_g remain unchanged. As branching increases, the T_g decreases, as we understand, if we have more branches then free volume increases, T_g decreases. So effectively, this difference with the T_g of infinite molecular weight with the particular T_g is inversely proportional to molecular weight.

$$\left(T_g^{\infty} - T_g\right) \propto \frac{1}{M_n}$$

As the molecular weight increases, we approach a limiting value of the T_g which is infinite molecular weight.

(Refer Slide Time: 39:13)



T_g: Effect of Molecular Weight

So if we plot, like in this case, it is shown for PDMS polydimethylsiloxane, and polystyrene. This is a T_g value in Kelvin and this is M_n. As you can see here, as we increase the molecular weight,

T_g goes up, and beyond certain molecular weight it actually levels of, practically there is no change in T_g value. You can see that this value is about say 5000, in this case it is about 10000. And in all practical purposes we deal with the molecular weight above this molecular weight. Hence, when we use for practical purposes the molecular weight range what we typically use, T_g is almost independent of molecular weight. If we go below certain molecular weight like oligomeric range or low molecular weight then T_g actually becomes affected, becomes lower and lower. So with this I will stop today, next I will talk about crystalline state in next class.