

Introduction to Polymer Physics
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Lecture – 17
Crystalline State of Polymers

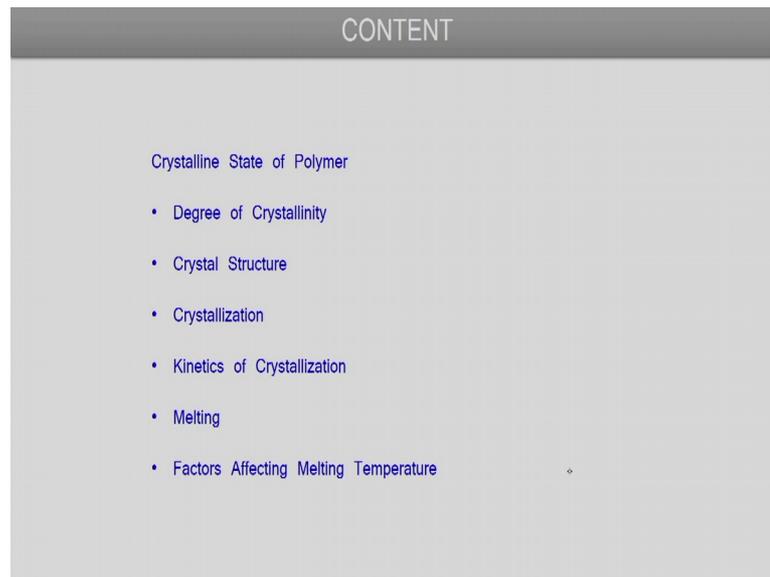
Hello everyone. In the last lecture we talked about the amorphous state of polymers. And we also discussed that most of the polymers are semi crystalline in nature. So, every polymeric material usually contains some crystalline part and some amorphous part.

So, in the previous lecture we looked at the amorphous state. And we discussed specifically an important thermal transition that is characteristic of amorphous state which is the glass transition. So, we noticed that a glass transition is a transition which involves the change in behavior of the polymeric material from a rigid glassy state to rubbery soft state. And this change is because below the glass transition temperature the polymer chains are relatively immobile. They are not able to move around much, because they are pretty much locked in their positions due to the lack of enough free volume for movement to take place.

And above a certain characteristic temperature which is a glass transition temperature. This polymer chains start moving around move, because the free volume increases and at the extra free volume present allows the polymer chains to wriggle about and move about through long segmental motions.

So now in today's class we will be talking about the Crystalline State of Polymer which is the other state of present in the polymeric materials in general. And, we will talk about the fact that the thermal transition important this crystalline state are the crystallization and melting transitions.

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CONTENT	
Crystalline State of Polymer	
• Degree of Crystallinity	
• Crystal Structure	
• Crystallization	
• Kinetics of Crystallization	
• Melting	
• Factors Affecting Melting Temperature	◊

So, for today's lecture the content that we have is we will start with brief discussion on the crystalline state. And we will talk about the degree of in crystallinity of a polymer sample, which characterizes how much crystalline part is a how much crystalline domain is present in the polymer sample.

And then we will also discuss the typical crystal structures that are observed. We will talk about the crystallization phenomenon itself and it is kinetics of crystallization. We will towards the end of the lecture talk a little more about melting in a polymer crystalline polymer samples and also the factors that affect the melting transition.

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CRYSTALLINE STATE OF POLYMER	
	Polymers are rarely fully crystalline; most polymers are semi-crystalline. Examples: Polyethylene, polypropylene etc.
Crystalline State	
Degree of Crystallinity	Polymer chains in the crystalline domains are arranged in an ordered fashion.
Crystal Structure	Chains typically fold to form ordered lamellar structures.
Crystallization	Polymer crystals can exhibit various different crystal structures.
Kinetics of Crystallization	Due to the long chain structure of polymer molecules, their crystallization is a complex process.
Melting	Thermal Transitions:
Factors Affecting Melting	Fully crystalline polymers will exhibit melting transition but not glass transition. Completely amorphous polymers show glass transition but not melting transition. Semi-crystalline polymers can show both glass and melting transitions.

If we talk about the crystalline state one thing to note is that the polymeric materials in general are not fully crystalline. So, almost all the polymeric material that is commonly encountered are not fully crystalline. Most of them may be semi-crystalline. Fully crystalline polymers in some special cases have been prepared. So, for example, by solid state polymerization, but generally the polymer samples that are obtained are only semi-crystalline which have a varying degrees of crystallinity, but will invariably also have some amorphous material present.

On the other hand, completely amorphous polymer samples can be prepared either using a polymeric material which has repeat units which do not allow crystallization to take place. So, for example, polymeric materials like atactic polystyrene, where due to the atactic nature there is no regular order and the amorphous state is the primary state that is observed in such polymeric materials. Or even for polymers which can actually crystallize, if such polymers are molten and then rapidly cooled to below their glass transition temperature. Then they will be trapped in this glassy state and due to the absence of enough free volume they cannot move about and the crystallization cannot take place. So, they will be trapped in this amorphous glassy state.

So, amorphous or almost completely amorphous polymers can be prepared in most cases, but fully crystalline polymers are very rare and through which the specialized techniques like solid state polymerization. One can obtain such materials, but in general

when we say crystalline polymer (Refer Time: 04:39) invariably have some amorphous part and the material will be semi crystalline.

So, the common examples being, let us say polyethylene or polypropylene such kind of polymers are mostly semi crystalline in nature. If we talk about now crystallization of polymers or crystal state of polymers then, this state is characterized by a regular or ordered arrangement of polymer chains. So, we all know that when think of a crystal, then there is a order and long range. So, long range order and some kind of periodicity present in the material.

So, for polymer crystals also the chains are arranged in an ordered fashion. And typically in typical polymer crystals that are encountered the polymer chains actually arranged in the form of or arranged in the form of folds. So, a single polymer chain can fold multiple times to form what are called a planar crystalline structures which are also known as lamellar structures.

So, chains polymers chains can in general fold to form such lamellar structures. And also the when we talked about the polymer crystals; then of course where we will also have some kind of unit cell for these crystals. So, the polymer crystal and crystals can exhibit various different types of crystal structures as tries by the corresponding unit cell. So, one can have a polymer crystals having orthorhombic unit cell a triclinic unit cell monoclinic unit cell. Or the different kinds of crystal systems that are available most of them are observed in one type of polymer crystal or the other.

So, different and types of polymers for crystallize from forming different types of unit cells. And one thing to note about the crystal state of polymeric materials is that polymer chains are macromolecular. So, these are long chain molecules and hence because of this long chain measure the crystallization phenomena itself as well as a crystal structures that are formed these are quite complex.

So, in today's lecture we will try to look at some of the aspects of the crystalline state of polymers as well as the crystallization phenomena and melting phenomena. So, when we talk about the thermal transitions associated with the crystalline state of polymers, then it is important to remember that if polymer is fully crystalline. So, if let us say we have a 100 percent crystalline polymer sample then it will only show melting transition it will not show a glass transition. On the other hand, if you have a fully amorphous polymer

sample where the polymer is 100 percent amorphous and no crystalline domains are present.

Then such a sample will only exhibit a glass transition, but will not show any melting transition. The reason being that since the polymer is amorphous to begin with there is no order present which will basically turn into disorder upon melting. On the other hand glass solution of course, is showing because glass transition is a transition between 2 disordered states as such. So, the glassy hard glassy state below the glass transition is also a disordered state. In the glassy state also the polymer is in a disordered state it has a disordered kind of the chains are in a disordered kind of arrangement only.

And in the rubbery state also we have glass transition the chains are still an amorphous disordered kind of state. So, glass transition will be shown in 100 percent amorphous polymers, but no melting transition. And in most of the cases the polymer samples are semi crystalline. So, they will exhibit both the glass transition and melting transition; so both a glass transition temperature and the melting temperature. So, typically the amorphous domains will show the characteristic glass transition temperature. Whereas, a crystalline domains in a semi crystalline polymer, they will show the melting transition or a corresponding melting temperature.

The next say- let us start by looking at how the amount of crystalline material present in a given polymer sample is usually quantified and how that can be measured experimentally.

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DEGREE OF CRYSTALLINITY

Degree of Crystallinity: A measure of the amount of crystalline part in the sample.

Density Method

Volume Fraction Degree of Crystallinity, ϕ_c :

$$\phi_c = \frac{V_c}{V} = \frac{\rho - \rho_a}{\rho_c - \rho_a}$$

V_c : Volume of crystalline part of sample
 ρ_c : Density of crystalline part of sample
 ρ_a : Density of amorphous part of sample

V : Total volume of the sample
 ρ : Density of semi-crystalline sample

Mass Fraction Degree of Crystallinity, x_c :

$$x_c = \frac{W_c}{W} = \frac{\rho_c V_c}{\rho V} = \frac{\rho_c}{\rho} \left(\frac{\rho - \rho_a}{\rho_c - \rho_a} \right)$$

W_c : Mass of crystalline part of sample
 W : Total mass of the sample

So, degree of crystallinity is quantity which provides a measure of how much crystalline material is present in a given polymer sample. So, if I have polymer sample is semi crystalline the amount of crystalline part present and that is what this degree of crystallinity characterizes. So, now the amount of crystalline part present in a given semi crystalline polymer sample that can be measured using different ways; so one can talk about the volume fraction of the amount of crystalline part present or the weight fraction of the amount of crystalline part present.

So, based on such considerations are different types of degree of crystallinity can also be identified? One of the common methods for measuring this degree of crystallinity of the semi crystalline polymers is through what is called the density method. And in this method the densities of the crystalline and amorphous polymer samples as well as the crystalline, as well as the semi crystalline sample their densities are used to get an estimate of the degree of crystallinity.

If we talk about the volume fraction of crystalline part present in the sample that can be characterized by the volume fraction degree of crystallinity. And that is one can represent that by the symbol phi c and it is defined as V_c by V where V_c of course, is the volume of the crystalline part present in the sample and V is the total volume of our semi crystalline sample. And it can readily be shown just by you doing a kind of a balance a kind of mass balance, where you we say that the total mass of the polymer sample that

we have that will be equal to the mass of the crystalline part present in it plus mass of the amorphous part present in it.

And the corresponding mass we can represent as a density times the corresponding volume. So, using such considerations and just rearranging the atoms one can show that this ratio V_c by V can be given as a ratio of difference in densities. So, here of course, the subscripts a and c denote amorphous and crystalline, and this row here is the actual density of the sample whose degree of crystallinity we are trying to measure

So, the various symbols that I have been used they are defined like this. So, ρ_c as we c is a density of crystalline part of the sample and ρ_a is a density of amorphous part of the sample and ρ itself is a actual density of the total semi crystalline sample that we have.

When we talk about ρ_c ρ_c is will correspond to at the density of the same polymer if it their 100 percent crystalline. Similar ρ_a , is amorphous density. So, if we had that polymer available as a completely amorphous material and if we measure the density of this amorphous polymer then that will correspond to ρ_a . So, ρ_c something that can be readily calculated if we know the crystal detail crystal structure of the polymer, because if you know the details crystal structure we will know the units and dimensions of the polymer as well as how many repeat units are present inside a given unit cell.

So, based on that the total amount number of repeaters present inside unit cell will allow us to calculate the total mass present inside a unit cell, and the dimensions of the unit cell can be used to calculate the volume of the unit cell. So, this mass by volume of the unit cell we will give us the density of the unit cell, which will correspond to the density of a 100 percent crystalline polymer sample. For the amorphous case the couple of these in which one can get the density of a fully amorphous sample. One is that just cooling the molten polymer sample very very rapidly below it is glass transition temperature. So, that the polymer gets trapped in this amorphous glassy state and then just obtaining the density of this amorphous state.

So, that is one-way, but in many cases even rapid cooling does not lead to the formation of the completely amorphous polymer. So for example: if we have polyethylene even, if it is cooled very rapidly crystallization usually takes place because the rate of crystallization is quite high. In such cases one can actually obtain the amorphous density through extrapolation. So, if I know the density of different semi crystalline polymers

having different degrees of crystallinity, then through extrapolation one can obtain the density of the amorphous fully amorphous polymer. Or one can just first start by measuring the density of the polymer melt or the molten polymer and through extrapolation I can try to obtain the density of the solid amorphous polymer.

So, in any case these densities can be obtained. And if we have such densities then one can estimate the degree of sorry; one can estimate the degree of crystallinity of such semi crystalline polymer samples. So, that is the density method, we have defined the volume fraction degree of crystallinity like this.

Similarly, we can also define a degree of crystallinity based on the weight fraction of crystalline part present in the sample. So, if we talk about the mass fraction degree of crystallinity x_c , that simply the mass of the crystalline part W_c divided by the total mass of the sample and of course, mass is the density times volume. So, W_c is just $\rho_c V_c$ and W is just ρV and this ratio V_c by V that we have already mentioned here.

So, substituting that expression for V_c by V we can get the expression for this mass fraction degree of crystallinity. And that is given by this expression which also again contains as a densities of the fully crystalline polymer or fully amorphous polymer and the actual polymer which might be semi crystalline. So, as we discussed a W_c in W represent the mass of the crystal part and the total mass of the sample

So, density method is one way of measuring the degree of crystallinity of polymers; similarly, the other methods available which can also allow and to estimate the degree of crystallinity; so one such method is through the use of X-ray scattering.

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DEGREE OF CRYSTALLINITY

Wide-Angle X-ray Scattering (WAXS)

Crystalline State

Degree of Crystallinity

Crystal Structure

Crystallization

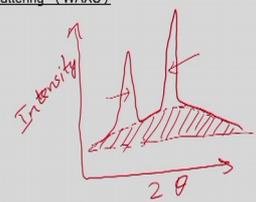
Kinetics of Crystallization

Melting

Factors Affecting Melting

$$x_c = \frac{A_c}{A_c + A_a}$$

A_a : Area under the amorphous halo
 A_c : Area under the crystalline peaks



Differential Scanning Calorimetry (DSC)

$$x_c = \frac{\Delta H_m}{\Delta H_m(x_c = 1)}$$

ΔH_m : Enthalpy change of melting of a semi-crystalline polymer sample
 $\Delta H_m(x_c = 1)$: Enthalpy change of melting of a 100% crystalline polymer sample

So, this wide angle X-ray scattering method can also be used to get an estimator or degree of crystallinity because the X-ray scattering pattern that we get usually of the with through X-ray diffraction, the crystalline part typically shows peaks whereas, the amorphous part will shows kind of what is called an amorphous halo in the scattering pattern that we get.

So, if we can resolve the crystalline peaks as well as amorphous halo then based on the ratio of the corresponding areas one can estimate the degree of crystallinity. So, the X-ray that we are defined earlier that can be written as a A_c by $A_c + A_a$ where A_c is what is A_a is what is called the area under the amorphous halo, and A_c is the area under the crystalline peak of the X-ray scattering pattern that we get.

So, if you just draw a kind of a rough intensity versus 2θ plot ok. So, we will have intensity scattered intensity on the y axis, let us say and we have 2θ here. Then a typical pattern for a semi crystalline polymer may look something like this, where it shows it can show multiple peaks as well as what is called an amorphous halo ok. So, if we subtract whatever background scattering might be there. And if we can identify the part that corresponds to the amorphous polymer, that can be done either by doing X-ray scattering for a completely amorphous polymer, and then using that to identify the amorphous halo.

So, whatever way that is an order by I actually resolving the crystalline peaks and amorphous halo separately. So, whatever way it is done and if we can identify the contribution from the amorphous part as this amorphous halo which let us say we are shading like this. So, this area under this amorphous halo this is what the A_a that we have here. Whereas, the area in under these crystalline peaks this correspond to assemble correspond to A_c . And the degree of crystallinity was will be given by the area and other crystalline peak divided by the area under the crystalline peak plus the area under the corresponding to the amorphous halo ok. So, that is another way to estimate the degree of crystallinity of polymer samples.

One can use other techniques as well. So, there is a technique called a differential scanning calorimetry or DSC which is widely used for studying thermal transitions in polymer samples. So, if you use a differential scanning calorimetry, then quantities like the glass transition temperature or the melting temperature or the temperature at which crystallization takes place. So, such temperatures can be identified using this technique. And apart from that the things like the enthalpy change of melting such quantities can also be estimated. So, it is a very useful technique this DSC for specially when it comes to studying the thermal behavior of thermal properties of polymers.

So, we will not going to the details of the working of DSC it is important to just know that this is a technique which can be used for measuring the different temperatures associated with various thermal transitions in polymers like glass transition melting or crystallization. And also heat effects associated like the enthalpy change of associated with melting or with crystallization.

So, using differential scanning calorimetry, one can actually obtain the enthalpy change of melting. And this degree of crystallization x_c is then defined as the ratio of the enthalpy change of melting of the actual polymer sample to the enthalpy change of melting of a polymer which is 100 percent crystalline. So, this here x_c equal to 1 represents that this ΔH_m is being measured for a fully crystalline polymer.

So, again we know that most of the polymers that we have a not the fully crystalline. So, this quantity actually has to be extrapolated in some way and it is not something which will be directly measurable, but in any case there are ways to estimate and extrapolate this quantity. So, x_c using this DSC technique can also be calculated. So, these are some

of the ways in which one can characterize a polymer by identifying its degree of crystallinity.

Next, we will talk a little bit about the crystal structure. So, what is the structure of the crystalline state inside a polymeric material.

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CRYSTAL STRUCTURE	
	Crystal structure is studied using tools such as X-ray diffraction and electron microscopy.
Crystalline State	Unit cells in polymer crystals contain several repeat units of the polymer chain.
Degree of Crystallinity	Example: Polyethylene unit cell can be orthorhombic or monoclinic, isotactic polystyrene is trigonal etc.
Crystal Structure	Polymer molecules pack into crystals as zig-zags or helices.
Crystallization	Example: Polyethylene adopts planar <u>zig-zag</u> (all trans) conformation, isotactic polypropylene and polystyrene form 3/1 helix
Kinetics of Crystallization	
Melting	Factors determining crystallization and crystal structure:
Factors Affecting Melting	<ul style="list-style-type: none">Linear chainsCopolymerizationTacticity

One can study the structure a crystal structure of a polymer using tools like X-ray diffraction or electron microscopy. Typically, since it is a crystal it will be it will contain a fundamental unit cell. So, let us say polyethylene can have unit cells either of the orthorhombic type or even of the monoclinic type, whereas this isotactic polystyrene has a trigonal kind of unit cell.

The unit cell typically corresponds to the usual crystal structures that are also seen for other materials, but one thing you have to remember about these unit cells is that the unit cells actually contain as form by repeat units of polymer chains. And these repeat units of course, are covalently linked to each other.

So, a single unit cell of a polymer crystal actually contains several repeat units and the number of repeat units was unit cell actually varies a lot between different polymer crystals. And it can be as low as the 4 and it can be actually for some polymer crystals above 10 or even above 20. So, number unit cells in a given number of repeat units in a given unit cell actually there is a lot between different polymer crystals.

Now, the polymer molecules that we have, they of course, the crystal crystals are formed of unit cells, but the how do the polymer molecules are actually are actually arranged in this crystal. So, the polymer chains themselves usually are arranged in a zigzag fashion parallel to each other or they can also be arranged in a helical fashion. So, when we say zigzag fashion typically the it will be a planar zigzag kind of a arrangement of polymer chains where all the torsional angles are in the trans state. So, this when we studied rotational isomeric state in the beginning of this course, then we talked about that in many cases the torsional angles correspond to discrete values which can be either gosh or trans.

So, if all the torsional angles having the trans state then we can get what is called the planar zigzag kind of arrangement, where the entire polymer chain lies in a single plane. And the arrangement of the repeat units is in a kind of zigzag fashion.

So, this planar zigzag arrangement is commonly observed for polyethylene, where there are no bulky side groups present and some other polymers which have side groups present, but the side groups are small then they also can adopt this planar zigzag structure. However, if the side groups present that the pendant or side group present a large and bulky then planar zigzag structure is not the preferable one because it leads to significant steric hindrance and overlap.

So, for such cases such where polymers actually adopt what is called a helical structure. So, polymers like polystyrene specially the isotactic or syndiotactic. These are will be more and often find in kind of a helical structure because of the bulky finial side group which in a planar structure cannot be accommodated easily.

So, polyethylene as we discuss mostly adopts is planar zigzag structure. Isotactic polypropylene polystyrene having some bulky side groups adopt the helix structure more commonly. Something like a vinyl polymer where the pendant or side group is small like a fluorine atoms. So, polyvinyl fluoride that can also adopt a zigzag structure because although it has a pendant group, the pendant group is not very large and the planar zigzag structures can still accommodate the side group without significant steric hindrance.

So, these are some of the features associated with the packing of polymer chain in the polymer crystal. Crystallization of polymers actually is dictated by several factors. So, some of the important factors which determine the crystallization as well as the crystal

structure that is on are the linearity of the chain, whether we have a co polymer and also that tacticity of the polymer.

So, when we talk about linearity of the chain linear chains polymers usually will crystallize more readily presence of branches introduces some imperfections, and the crystallization will become more difficult if branches are present. However, if small number of branches branching is presence small amount of branching is present then in that case crystallization actually can take place all the although the crystal find might not be highly perfect.

Similarly if copolymerization is there; so if we have a copolymer then the presence of other repeat units other type of repeat units can disrupt the crystallization of certain type of repeat units in the copolymer. So, if the amount of repeat unit of the other type is small then that also can be tolerated and crystallization can take place, but if, but if the amount of repeat unit of the other type is large and if we have a random or statistical copolymer mostly it will be amorphous and crystalline crystallization will not take place.

For block copolymers it might happen that one block can crystallize and the other block does not. So, a many different I possibilities are there and it all depends on the type of copolymer as well as the relative proportion of the blocks present in the relative proportion of the different repeat units present in the copolymer.

A very important factor which determines the crystallization as well as the crystal structure is the tacticity of the polymer, but we have discusses that if the polymers are isotactic or syndiotactic there is a regular arrangement and such polymer can crystallize readily, whereas, if the polymer is a tactic where there is no regular arrangement of the side group on either side of the plane containing the polymer backbone.

Then in such cases so, for such atactic polymers the crystallization is usually difficult and in most of the cases the atactic polymer say do not crystallize and from amorphous polymers. However, there can be exceptions. So, if the side group is small ok. So, if the side group is small then in such cases even atactic polymers can form crystalline states. So, if we have something like polyvine vinyl alcohol where the group is quite small. So, it can even atactic PVA can show a crystalline state, but in general the syndiotactic and isotactic those are the ones which will generally crystallize and atactic will usually be usually exist in the amorphous state.

So, a tacticity a polymer is an important factor determining the crystallization as well as a crystal structure. So, again whether the polymer is isotactic or syndiotactic that can dictate what kind of crystal structure the polymer chains should adopt whether they will be in what kind of a helical arrangement will form, that can also differ from an isotactic to a syndiotactic polymer of the same time. So, these factors are the important and determining the crystallization behavior and the crystal structure form.

Next, let us talk about at a talk a little bit more about how are the polymer chains are arranged inside the polymer crystals. So, we talked about the fact that polymer chains can pack in a zigzag a helical fashion and they can form unit cell containing different numbers of repeat units.

But, once a crystal polymer crystal is formed and as we discussed earlier polymer crystals are typically of the lamellar or plate the plate type of crystals. So, for such polymer crystals, how is the arrangement of polymer chains inside the polymer crystal. So, these are some of the aspects that we will discuss next. We have discussed typically polymer crystals are lamellar and structure.

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CRYSTAL STRUCTURE	
Crystalline State	<p>Polymer crystals are typically lamellar (plate-like).</p> <p>Lamellar thickness is typically ~10 nm (for solution-grown crystals).</p> <p>Polymer molecules fold multiple times between the lamellar surface.</p>
Degree of Crystallinity	<p>Folds can be regular and tight or irregular and loose.</p>
Crystal Structure	<p>In concentrated solutions and melts, polymer chains are entangled.</p> <p>Crystallization can result in polymer chains being incorporated in more than one crystal.</p>
Kinetics of Crystallization	<p>In the melt, chains are highly entangled; crystals are more irregular.</p>
Melting	<p><u>Spherulites:</u></p> <p>In melt crystallization, spherulites form by nucleation at different points and then grow.</p> <p>Spherulites consist of many lamellar crystals radiating from the centre.</p> <p>When viewed under polarized light, show characteristic 'Maltese cross' pattern.</p>
Factors Affecting Melting	

So, they have a plate like morphology. So, when we say lamellar denotes the kind of a plane. So, a lamellar structure will basically be kind of a plate like structure.

Lamellar thickness of typically around 10 nanometer we have observed especially for a polymer crystals grown from solutions. Even for melt link polymer crystals the lamellar thickness observed is of the order of a few 10 nanometers or few tens of nanometers ok. So, we have a lamellar crystals which are relatively thin. So, this thickness of this lamellar this is small compared to the lateral dimensions of this plate like lamellars crystal.

And we know that for typical polymer chains, the lengths if we talk about the kind of a control length of a polymer chain not the end to end distance. But, the length measured along the backbone then that length of polymer chains is of the order of 100s of nanometers usually

So, what that leads and believe is that if we have a lamellar crystal polymer crystals like this and it is also been observed that the polymer chain axis is actually perpendicular to this lamellar plane. So, if we talk about the small lamellar plane the polymer chain axis is perpendicular to this lamellar plane.

So, if we take these considerations together then what we can say is that the polymer chains actually are folded perpendicular to the lamellar surface way. If this is the polymer crystal this plate like lamellar then the polymer chains will be folded like this.

So, if you again represent; so if this is the plate like structure of our crystals the and this represents this is the front face and this is the plate like structure we are talking about, in the polymer chain inside this lamellar typically is expected to be folded like this and single chain we can will actually folded multiple times, because it has been observed that the thickness of this lamellar this is of the order of 10 nanometers. And of course, the polymer chain is much much longer than 10 nanometer. So, it polymer chain is to accommodate within this thickness and have it is chain axis perpendicular to the lamellar surface.

Then the polymer chain needs to be folded. So, these are the folds of the polymer chains. And these planes which corresponded lamellar surface are also called the fold planes, which have planes formed by the folds in the polymer chain structure.

So, polymer chains of course, fold multiple times between the surface of the lamellar crystals. And what we have shown here is a kind of folding which is very regular and

tight, but that need not always with the case we can also have a case where the polymer chains again between 2 surfaces might not be folded very tightly, but a bit more kind of irregularly.

So, again here in this arrangement the polymer chains are aligned perpendicular to their lamellar surface, but the folds that are there the folds are more irregular and not as tight. So, the folds are looser in and irregular.

So, such cases can also be there this is a typical kind of arrangement that has been demonstrated to exist in polymer crystals where the morphology is lamellar and the polymer chains are folded multiple times between the lamellar surfaces. The arrangement that we discussed if we let us say grow polymer crystal from dilute polymer solution, then in a dilute polymer solution the polymer crystal polymer chains are pretty much isolated from each other. So, each chain can grow into a separate lamellar crystals which can a lamellar crystal which can precipitate and then later we separated from the solution.

However, if we have a concentrated solution let us say. So, in that case the polymer chains are present in a much higher concentration and the chains will usually not be isolated. They will be entangled with each other, so such entanglements in concentrated polymer solutions as well as melt. So, one can crystallize either from a solution by either cooling the hot solution or by adding a non-solvent to the solution. Or one can a crystallize by a melting cooling a molten polymer. So, if we are talking in a concentrated solution or a molten polymer which is a melt, and V considering crystallization from these. Such kind of systems, then due to the high concentrate concentration of polymer molecules present, chain entangle entanglements will be there. And such chain entangles will lead to the effects which are not seen in crystals come from dilute solutions.

So, even in a melt and concentration solution grown crystals the typical morphology of crystals is still of the lamellar type, but what happens is because of the chain entanglements the polymer actually a single polymer chain can span multiple polymer crystals. So, it might. So, happen that if you have 2 crystals like this again we are just representing the front part of the crystals crystalline lamellar here. And let us say polymer chain is folded here due to the entangling it might happen that the same polymer chain forms part of another crystal.

So, these kind of polymer chain interlinks between different crystals or inter crystalline links of polymer chains can be present if crystals are grown from concentrated solution or polymer melt, because of the entanglement of chains that is that is present. As we discussed the polymer chains can be incorporated in more than one crystal and inter crystalline links can be present. In the melt especially a chains are very highly entangled and the crystals are form will be more irregular.

So, when we talked about the crystalline state initially we said that most of the crystals are a polymer crystals are semi crystalline. And the reason for a semi crystalline nature is that the many in most of the cases the either the folds that we have will not be tight or regular or will have these inter crystalline regions where the polymer chain will exist as in the amorphous state. So, in most of the cases unless the pollination is done very in heavenly controlled veins through solid state polymerization, some amorphous disordered region will always be present along with the crystalline part.

So now when we talk about polymerization from a melt their distinctive crystalline entities that basically grown crystallization takes place from the melt. Such in entities are known as spherulites and in melt crystallization these spherulites are formed by nucleation at different points and then grow. So, these spherulites are spherical kind of entities which when we crystallize a melt by cooling it, where this spherulites from as small nuclei which then grow by the successive addition of polymer chains to this growing nuclei. So, this entity is basically as spherical in nature and they grow as crystallization proceeds and ultimately the growth stops when the growing neighboring spherulites are a growing they contact each other when they impinge upon each other. So, when they touch each other then of course, their spherical radial outward growth will be stopped.

Now this spherulites that we have these spherulites are the spherical growing crystalline kind of entities, but these entities internally are still composed of lamellar crystals of the polymer that constitute the this spherulitic entities.

So, the internal structure of this spherical spherulitic entities is still kind of lamellar crystals of the polymers. And this crystalline lamellae of polymers radiate or originate from the center of the spherulite and radiate radially outwards. And this evidence that the lamellae in this spherulitic entities are actually kind of twisted. So, instead of being

completely flat the lamellae as they radiate from the center to the outer side of the spherulite. They basically get also twisted in some way.

So, at the basic level the crystal crystals are still lamellar in nature in melt crystallization also, but they are basically arranged in the kind of spherical entities which are called spherulites. And these lamellae radiate from the center of the radiate or spherulites outwards.

Another characteristic of say spherulites is that the polymer chains have been absorbed to arranged to be arranged tangentially to the surface of this spherulitic entities. So, if we have this spherulitic sphere like entity that is growing during crystallization. Then the polymer, will basically if we this is the surface of the spherulite, then the polymer chains are arranged parallel to the surface. And there is evidence of the polymer chains which are folded within the lamellae they are folded again parallel to the surface of the spherulite. We have lamellar out grow from the center relating outwards in this spherulite and at the surface the polymer chains in the lamellar are folded in such a way that it is kind of tangential to the spherical surface of the spherulite.

When other characteristic of spherulitic materials is that they show what is called the Maltese cross pattern when they are viewed under polarized light. So, due to the crystalline domains present and the order arrangement inside these spherulitic material entities when viewed under polar polarized light they show what is called a typical Maltese cross kind of pattern. So, kind of a dark cross basically appears on these entities when they are viewed under polarized light. And such crosses such pattern is referred to as a Maltese cross.

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CRYSTALLIZATION

Ordered structure from disordered state. ←

Polymers can crystallize from solution or melt.

Crystalline State

Degree of Crystallinity

Crystal Structure

Crystallization

When polymer melt is cooled to (or below) the melting temperature:

- Tangled molecules in the melt tend to become aligned and form small ordered regions (nuclei)
- The small crystal nuclei grow by addition of more chains

Thus, crystallization takes place through nucleation and growth.

Kinetics of Crystallization

Nucleation:

- **Homogeneous:** Small nuclei form randomly throughout the melt
- **Heterogeneous:** Nuclei formation on foreign bodies (dust particles etc.)

Melting

Factors Affecting Melting

Number of nuclei formed depends on the temperature of crystallization:

- At low undercooling (or supercooling), sporadic nucleation, few large spherulites
- At high undercooling, large number of nuclei form, many smaller spherulites

Now, let me we have talked about crystal structure; let us talk a little bit about the crystallization phenomenon it says ok. So, how just broadly what kind of mechanism is present or is associated with this crystallization phenomeon. So, we know that the crystallization is the appearance of ordered state from a disordered state. So, as we whether we are talking about crystallization from a solution or from molten polymer, initially in the solution the polymer is in a kind of disordered random coil kind of arrangement and as crystallization takes place ordered state emerges.

Similarly, in upon cooling or melt to either up to it melting point or below it is melting point crystallization takes place by where the initially in the melt the polymer chains are in the disordered state. And upon cooling below a certain point the chain start arranging into some order align nuclei which grow and become larger and this larger. This nuclear which are growing or basically polymer crystals where the chains are in an ordered arrangement.

So, as we discuss the crystallization can be from solution or melt and in either case it is basically going from a disorder kind of a state to an ordered arrangement of polymer chains. So, if let us say we focus on crystallization of molten polymers. So, melt crystallization. So, there if the be cool a melt to up to it is melting temperature let us say below in below it is melting temperature. Then the molecules which are in a disorder and

entangle state in the molten in the molten polymer they will start to get aligned as the temperature is brought down to the melting point or below the melting point.

And these aligned polymer molecules are changed several from small ordered regions or domains. And these, small ordered regions are what are referred to as the nuclei and this nuclei will then grow by the successive addition of more polymer chains. And this while growing the nuclei will ultimately growing to larger lamellar kind of polymer crystals. And if it is growing from a melt then typically this lamellar will be arranged in such a way that we get the spherulitic kind of a growth.

So, inside a spherulite the polymer chains will be again arranged in an ordered fashion. And we will get the crystallization of the polymer sample. What we can say is that the crystal nuclear growing by addition of polymer chains and ultimately the mechanism of this crystallization is through nucleation and growth.

So, initially nucleation takes place by alignment of a small number of chains into an ordered region. And then that ordered region ultimately grows and becomes polymer crystals. So, another nucleation that we have the nucleation can be of different types. So, we can have a homogeneous nucleation where the nuclei can form randomly throughout the polymer sample molten polymer sample that we have. Or it can be heterogeneous nucleation where the nuclei actually form at it is on the surface of impurities that are present in the sample.

So, the nuclear formation will not be randomly throughout and uniformly throughout the sample, but it will be on the locations where the impurities are present or let us say on the walls of the container containing the polymer melt. So, nuclei formation takes place on foreign bodies when you heterogeneous nucleation. And homogeneous nucleation the nuclei form randomly and uniformly throughout the melt.

Now, one interesting thing about the number of nuclei that forms is that it depends on the temperature of crystallization. So, as we discuss as we as a temperature of a molten polymer is brought to it is melting point, a crystallization will start taking place. And as a temperature if the temperature is actually brought below the melting point then depending on how much below the melting time we have a come that will also dictate the number of nuclei that has formed that have formed.

If we have a molten polymer and we bring it to a temperature below the melting point of that polymer. Then the amount by which we are below the melting point that represents amount of what is called under cooling or super cooling. So, instead of being at the melting point, we are we have brought the polymer melt below the melting point. So, that is we have super cooled this melt or under cooled this melt.

So, this degree under cooling that is how much below this melting temperature we are that actually dictates how much of this polymer nuclei form. So, if the degree of under cooling is small. So, if you have below the melting temperature, but close to it then a small number of nuclei actually formed and sporadically and that relates to the formation of a few large spherulites. Whereas, if the degree of under cooling is large. So, that we are very below the melting temperature, then when crystallization takes place to a number of nuclei form is quite large. And that is why many spherulitic entities basically grow and form in such in such cases. So far the low under cooling again the few large spherulites are formed and if the under cooling is high a many smallest spherulites are formed because larger number of nuclei are formed.

So, next let us talk about the kinetics of crystallization ok. So, what is the rate at which crystallization takes place and what are the factors that govern it?

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CRYSTALLIZATION KINETICS

Change in linear dimension of growing crystalline entities (at a given T_c) is linear with time (t):

$r = vt$

Crystalline State
 Degree of Crystallinity
 Crystal Structure
 Crystallization

T_c : Temperature of crystallization
 r : Spherulite radius
 v : Growth rate

v is strongly dependent on T_c

Kinetics of Crystallization

Overall Kinetics: Avrami Equation

$$\frac{W_t}{W_0} = \frac{V_t - V_\infty}{V_0 - V_\infty} = e^{-zt^n}$$

W_0 : Total mass of polymer melt initially
 W_t : Mass of liquid remaining after time t
 V_0, V_∞ : Initial and final sample volume respectively
 V_t : Sample volume after time t

n : Avrami exponent
 z : Rate coefficient

$W_0 = W_L + W_S$

$\ln \left[-\ln \left(\frac{W_t}{W_0} \right) \right] = \ln z + n \ln t$

So, it has been observed it is (Refer Time: 45:19) that one crystallization takes place in the change in the linear dimension of the crystalline domain that is actually directly

proportional to time. So, for a given a crystallization temperature T_c linear dimension of the growing crystalline entities that is linearly or directly proportional with time. So, we can write an expression like this r equal to νt where ν is the what is called the growth rate of our crystalline entity, and r in this case we have written as spherulitic radius or spherulite radius. If you are not talking with the spherulite kind of growth pattern lamellar growth in the case of crystallization from a solution or dilute solution then, even in that case similar kind of an expression can apply. The only thing is that instead of r there it will be the lateral dimension of the crystal that is growing.

So, in any case if you focus on crystallization from melt then this r here will be the radius of the spherulite that is forming. And it seem to be linearly proportional to the time that has taken or the time elapsed from the beginning of crystallization process.

So, one thing to note is that this ν of the growth rate is strongly dependent on the crystallization temperature. So, the temperature at which you are crystallization that actually has a strong value to plane residing the growth rate of this crystalline entities or for the melt crystallization which will be spherulites

So, if we let us say try to make a plot of this ν or the growth rate versus the crystallization temperature. So, typically a plot of these 2 looks like this. So, it shows a maximum at a certain crystallization temperature and if we are crystallizing at a higher temperature the growth rate is correspondingly lower than this maximum, and if we are crystallizing at a lower temperature then this point also.

So, if somewhere here again the growth rate will be lower ν ; ν is a strong function of crystallization temperature and it shows a maximum the reason for this maximum can be understood in this way. So, if we crystallization will take place when we are below the melting temperature of course. So, if we are only slightly below the melting temperature then of course, that temperature is high. So, the viscosity of the melt will be a relatively low and the movement of the molecules will also be fast.

So, because of this is one thing that will favor the crystallization rate because the molecules are moving fast, but the driving force for crystallization in this case will not be as much. So, the lower we are compared to the melting temperature the higher the driving force will be for crystallization. So, the more and degree of super cooling or under cooling the greater will be the thermodynamics driving force for crystallization.

So, as we go below the melting temperature initially the thermodynamic driving force for crystallization is a small, because we are only slightly below the T_m . And as we go further down the melting temperature the thermodynamic driving force for crystallization becomes larger. On the other hand, the as temperature is reduced the viscosity of the melt actually will increase; so the movement of chains which through this medium to come and attach to the growing crystal that movement will be hampered.

So, there are 2 competing effects as we go as from the melting temperature we go below this temperature the thermodynamic; thermodynamic driving force for crystallization increases, but the rate at which the molecules can move about and come and attach with a growing crystal that decreases. So, these 2 competing effects actually lead to this kind of a maximum being observing a growth rate, where the 2 competing effects are the best balanced.

And, if we are above this temperature then the thermodynamic driving forces not enough it is a bit low. And if we are believe this temperature then all thorough thermodynamic driving forces high the motion of the molecules to the medium is very slow because of the higher viscosity of the medium and that is why the rate of growth will again be smaller ok. So, these competing effects basically lead to this kind of a maximum in the growth rate with crystallization temperature.

Now, overall a kinetics of crystallization that is something that we can study using this equation which is called Avrami equations. So, this Avrami equation was initially applied developed by a various researches and widely applied by Avrami to study the crystallization kind of behavior. So, here without going to the details of derivation of this equation what we will do is just write down the final expression. And what the Avrami equation states is that the ratio of the weight of the liquid phase that is present at any time compared to the weight of the total polymer melt at the initial point. So, that ratio is equal to exponential of minus $z t$ to the power n .

So, here t that we have t is nothing but the time ok. So, t we have discussed is a time. So, the Avrami equation relates the amount of crystallization that is taking place up to a certain point of time. Here, as we have mentioned the W_{∞} reference a total mass of the polymer melt that is initially present and which has started to crystallize. And as crystallization precedes part of the melt will become solid in the form of spherulites. This

w_s is the mass of the liquid remaining after time t . So, after time t will have some amount of spherulitic entities present which have crystallized; so those will be the solid part and we will also have some multi liquid present.

So, the initial melt present W_0 will can be represented as a some of this w_l the liquid present plus the solid present as the crystallized part of the sample at any time t . And these the corresponding weights of the liquid present in any time t and the in weight of the initial melt present that can be related to the volumes of the present at different times through this kind of an expression ok. So, here V_t is the sample volume after time t V_∞ is the volume of the sample after a long time when all the sample has actually crystallized.

So, V_∞ will correspond to a sample which is entirely solid and which complete crystallization is stating taken place or at least complete solidification as taken place. And V_0 is the volume of the initial polymer melt. So, V_0 volume of the polymer melt and V_∞ is the final volume and this melt has completely solidified and crystallization is complete.

So, Avrami equation relates these ratios to time through this kind of an exponential functionality. And the z and n that we have here this z here and the n here the n is called the Avrami exponent and z is a rate coefficient. And particularly the n that we have in the Avrami equation that is Avrami exponent, it is value has some significance as a respect to the mechanism of crystallization that is taking place. So, a Avrami exponent typically if the crystallization is taking place in such a way that the growth has in all 3 dimensions and the nucleation takes place uniformly at a constant rate throughout the sample, then under these conditions these ideal kind of conditions Avrami exponent values 4.

On the other hand, if the nucleation is almost instantaneous. So, the nuclear appear suddenly compared to the growth rate at which growth is taking place and the growth is still in 3 dimensions and Avrami exponent value will be 3. So, if the nucleation is uniform at a uniform rate and the growth rate is 3; in 3 dimensions then Avrami exponent is 4 for instantaneous nucleation and growth in 3 dimension Avrami equation exponent is 3. If the growth is in less than 3 dimensions if we consider kind of a film growth whether the growth will primarily in 2 dimensions; then in such cases again depending on

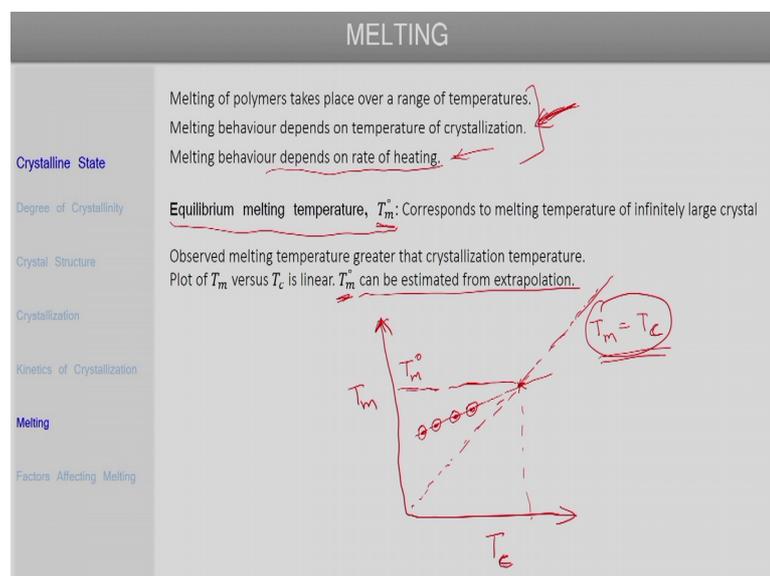
whether the nucleation is instantaneous or whether the nucleation takes place at a constant rate again of Avrami exponent can have a different value.

So, for uniform rate of nucleation for a 2 dimensional growth Avrami exponent will have a value of approximately 3 and of course, for other kind of mechanisms the value of a Avrami exponent can be even lower. So, the value of a Avrami exponent typically ranges between 1 and 4 and the specific value can take give us some idea as to the mechanism of nucleation and the dimensions in which the growth of the crystal is taking place or growth of the spherulite is taking.

So, if we take the natural log of both sides of the one equation 2 times, then we get an expression like this. And if we have this data or alternatively the ratio of the volumes this data available at different times then that the double log of this \ln of minus of \ln of this ratio that can be plotted against \ln of time to obtain the Avrami exponent as the slope if we get a linear kind of relation then the slope of those lines will a line will the that line will be the Avrami exponent.

So, that will graphically one can obtain the Avrami exponent.

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So, the last day topic that we will cover today is related to the melting transition in crystalline polymers. We have discussed that only the crystalline domains in a semi

crystalline polymer can show melting amorphous polymers cannot show melting because they are already in a disordered state.

So, there are some peculiarities about the melting transition of polymeric materials which are not seen in the melting of simple small molecules. So, some of these are listed here. One thing is that the melting many times is not very sharply defining it can take this over a over a kind of a range of temperatures. A melting behavior also depends on the temperature at which crystallization was carried out. So, again that this is a kind of a peculiar phenomenon, where the melting depends on the temperature of crystallization, and melting also depends on the rate of heating.

One of the reason behind this peculiarities is that the polymer crystals actually add quite thin ok. So, if you look at a typical lamellar crystal of polymer the lamellar thicknesses of the order of a 10 nanometer or a few tens of nanometers. Whereas, the other dimension the lateral dimension of the lamellae can be quite large. So, this relatively thin nature of polymer crystal is responsible for many of the peculiarities associated with the melting transition of polymers polymer crystals.

So, what one can do is a define walls what is called a equilibrium melting temperature of such polymer crystals. And this equilibrium melting temperature can be considered as a temperature of melting for infinitely large crystals. So, if we can consider a hypothetical case of crystals which are very large or infinitely large then the temperature at of melting corresponding to such crystals that is what the equilibrium melting temperature T_m not refers to.

So, it is something that of course, cannot be directly measured because usually will not have a crystals of infinitely large dimensions, but it is something that one can obtain from extrapolation. So, what is typically observed for a melting behavior of polymer crystals is that the melting temperature is always above the crystallization temperature. So, if we form a polymer sample by crystallizing it at a certain temperature and then we try to melt it, then the melting temperature is almost always found to be lie above found to lie above the crystallization temperature. So, T_m is always greater than T_c and one other thing that is noted is that if we plot this T_m actual T_m the actual melting temperature versus a corresponding actual crystallization temperature of the sample.

Then they show kind of a linear dependence. So, these kinds of observations can actually be used to obtain the value of the equilibrium melting temperature T_m^0 through the process of extrapolation. So, how we can do that is let us say if we consider a plot of T_m the melting temperature actual melting temperature of a polymer sample against T_c the crystallization temperature. So, the melting temperature depends on the temperature of crystallization and the melting temperature always lies above the crystallization temperature some melting temperature is always higher than the crystallization temperature

And if we draw let us say line here which represents T_m equal to T_c . So, if we have the case of equilibrium melting temperature then that will correspond to the situation where the crystallization temperature and melting temperature actually coincide. So, this line represents the case where the T_m would be equal to T_c . And this is not something that is actually observed, but this line can be used to extrapolate the value of T_m^0 as well T_c .

So, in reality this T_m if we plot T_m against T_c , it might show a behavior like this. So, this T_m will lie above T_c , but the T_m versus T_c curve will also show a kind of linear trend. And if we can extrapolate it all the way up to the point where it crosses this T_m equal to T_c line. So, these are the actual observed points. And if these are extrapolated to cut this T_m equal to T_c line then the point at which this intersection takes place that corresponds to T_m^0 . And as we see at this point T_m^0 the corresponding crystallization temperature will also be the same as the melting temperature.

So, this T_m^0 are the equilibrium melting temperature can be obtained using this kind of an extrapolation approach. So, these are some of the peculiarities associated with to the melting transition of polymer crystals. And next what we will do is try to look at some of the factors which influence the melting temperature of polymer crystals or crystalline polymer state.

The factors affecting melting transition or the factors affecting the melting temperature T_m what has been observed is that the factors that affect T_m and also same and also pretty much the same as the factors that affect the glass transition for an amorphous polymer

sample. And the way in which T_m is affected is also similar to the way in which T_g is affected by these factors

So, in the previous lecture we discuss different factors that affect the glass transition temperature of amorphous polymers. And today, we will look see that similar kind of factors affect the melting temperature of crystalline polymers in a similar way.

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FACTORS AFFECTING THE MELTING TEMPERATURE

<ul style="list-style-type: none"> Crystalline State Degree of Crystallinity Crystal Structure Crystallization Kinetics of Crystallization Melting Factors Affecting Melting 	<ul style="list-style-type: none"> Chemical Structure <ul style="list-style-type: none"> Chain Flexibility: Higher flexibility, lower T_m Polar Groups in Main Chain: Hydrogen bonding within crystal can raise T_m Example: Amide (-CONH-) groups in polyamides such as nylons Nature of Side Groups: Bulky side groups raise T_m Molecular Architecture: Molar Mass and Branching <ul style="list-style-type: none"> Chain ends and branches introduce defects in the crystals. Hence, lower T_m. <p>For linear polymers: $\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_u} \frac{2}{\bar{x}_n}$</p> <p>$\Delta H_u$: Enthalpy of fusion per mole of repeat units. \bar{x}_n: No. avg. degree of polymerization</p> <p>For many homopolymers, T_g lies between $0.5T_m$ and $0.8T_m$ (for temperatures in Kelvins)</p>
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So, if you talk about chemical structure and surfactant T_m , the important thing again is the flexibility of the main chain. So, the backbone polymer backbone has the main polymer chain. If it is flexible, then that will lead to a lower value of T_m and if the backbone is highly a very stiff then the melting temperature will be higher.

Similarly, if we have polar groups in the main chain; so if we have main chain of the polymer containing polar groups like the amide linkage. So, such linkages actually provide opportunity for hydrogen bonding and these polymer chains get along parallel to each other in a polymer crystal.

So, the presence of such a polar groups like the amide linkage in the main polymer chain; they can lead to hydrogen bonding in the polymer crystal. And hence such a presence of such polar groups actually increases the melting temperature. So, these things can such a polar groups can raise the T_m . And an example is the amide groups conh present in polyamide such as nylons. So, in the crystalline state the chains that are arranged parallel

to each other they will form hydrogen bonding between the corresponding co and n h groups. So, the co group of a one of the chains can be aligned next to the n h group of the other chain and they can the n h and co can form hydrogen bond and such hydrogen bonding actually can lead to an increase in the melting temperature.

So, here the nature of the side groups is also important as we discussed in the case of t g. So, in the case of T_m also the nature of side groups is important, and if we have bulky side groups that hinders chain rotation and reduces chain flexibility. So, that can actually raise the melting temperature. So, bulky side groups raise the melting temperature. If we have a side group which is a itself internally flexible. Then that can actually lead to a reduction in melting temperature as well. Or even if it does not lead to reduction melting temperature the internal flexibility of side group will ensure that the melting temperature will not be raised that much compared to if the side group was a bulky rigid kind of a group.

Now apart from the chemical structure, the molecular architecture is also something that plays a part. And we have already seen in the previous lecture that the glass transition is strongly affected by the molecular architecture of the polymer. So, what we will see here today is that the melting temperature is also affected by the molecular architecture of the polymer chains.

So, molecular architecture the factors that we will consider under this molecular architecture is molar mass and branching. So, molar mass typically it seem that the low molar mass polymers will show a lower melting point and the higher molar mass polymers show a higher melting point, but if the molar mass is behind a certain threshold. So, if the molar mass is quite high then further increasing the molar mass does not lead to a significant change in the melting temperature.

So, for low molar mass polymers and polymer crystalline state the melting temperatures are actually low because of the presence of large number of chain ends in such systems. So, chain ends one can think of as a impurities or imperfections present inside the polymer crystal. So, wherever chain ends are present that will lead to some imperfection in the polymer crystal.

Similarly, if branching is present; so branching also constitutes a kind of imperfection the polymer crystals. So, these presence of large number of chain ends which will be there in

low molar mass polymeric materials or the presence of branches as in the case of branch polymers. These will lead to the formation of imperfect crystals and because of these imperfections the melting point of the crystalline state that is formed that will be lower.

So, at lower for low molar mass polymeric materials or for branch polymers typically the melting point will be lower, than the corresponding linear polymer linear and branch polymer. So, the chain ends and low molar mass polymers in the branches and branch polymers they introduce defect in the crystalline cause molar mass cause the melting temperature to decrease.

For linear polymers actually one can relate the degree of polymerization to the melting temperature ok. So, that relation is something like this, where this T_m is a melting temperature of this linear polymer T_m^0 is the equilibrium melting temperature again and which was discussed in the previous slide. This R is a universal gas constant ΔH_u is the enthalpy of fusion per mole of the repeat unit present in the sample and this \bar{x}_n this is the number average degree of polymerization. So, this \bar{x}_n is a number average degree of polymerization number average degree of polymerization.

So, we see that the degree of polymerization is related to T_m . And, if we work through this expression what can be seen is that as a degree of polymerization increases T_m also increases and as \bar{x}_n tends to infinity. So, we have a degree of polymerization which is very large. So, in that case this T_m basically tends to T_m^0 . And this \bar{x}_n of course, is a something that is directly proportional to the molar mass. So, this equation also provides the effect of molar mass on T_m . So, as molar mass increases T_m also increases.

What we have seen here is that the factors that affect melting temperature are similar to the factors that we discussed earlier which affect the glass transition temperature in a amorphous polymers. And the way in which these factors affect T_m and T_g are also similar. So, what it suggests that the regular homopolymer the melting temperature and the glass transition temperature. So, the melting temperature of the crystalline state and the glass transition temperature of the amorphous state of that same polymer they are not independent and they are pretty much related with each other.

And it has been observed that for many homopolymers the glass transition temperature actually lies between $0.5 T_m$ and $0.8 T_m$, if the temperature is taken in the unit of Kelvin. So, normally the glass transition temperature is related to T_m in some way and it is formed to lie between 0.5 and $0.8 T_m$ for regular homopolymers, and what this also suggests that for homopolymers independently the T_g and T_m cannot be manipulated. So, if you have a homopolymer where the due to some modification T_g is changed the corresponding the T_m also might get changed. So, here we see that the glass transition and the melting glass transition temperature and the melting temperature are also related in some way for homo polymers

So, in today's lecture we have talked about the crystalline side of a polymers the crystal structure the arrangement of chains inside the crystals how the crystal chains fold to form lamellar structures and so on. And especially in the case of melt crystallized samples we get these spherical and crystalline entities which are called as spherulites. We also talked about the melting transition in polymers which is they show some peculiar behavior, and also talked about the factors which affect the melting temperature of crystalline state of polymers.

So, with that we will end this lecture here today. And in the next lecture we will focus on the mechanical properties of polymeric materials.

Thank you.