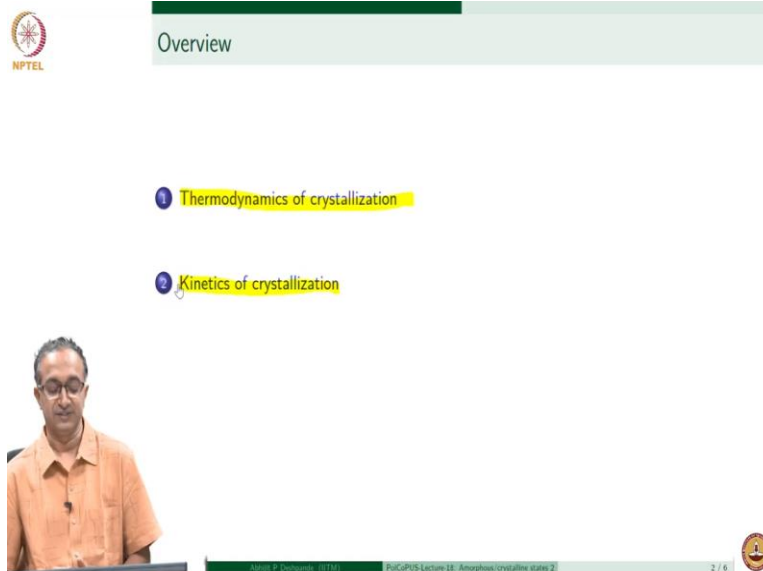**Molecular Arrangements and States of Polymers**
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Lecture - 18
Amorphous / Crystalline States 2

Hello. Welcome to learning on polymers. We are looking at the structure of polymers, in this week. We are looking at the molecular arrangements, as well as states of polymers and the focus is on solid states. In the previous week, we looked at a single macromolecule and the dynamics of a single macromolecule which is very relevant for rubbery and molten states as well as in solutions. And in this particular lecture, we will continue our discussion related to crystallinity in polymers.

We looked at what happens in case of temperature is brought below the melting temperature, where crystallization can happen in polymer and what may be the ways in which a polymer crystal can form. And we also looked at what may be the reasons behind some of the polymers being semi crystalline and some of the polymers being completely amorphous. And the focus in this lecture will be looking at conceptual understanding.

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And we will do this by looking at the thermodynamic description of crystallization in polymers. And we will quickly look at why kinetics is very important. In case of macromolecules, because of

their entanglements; the rate of crystallization is quite significantly different depending on the crystallization conditions. And that also determines the structure of the crystals form as well as the amount of crystallization. And so this is very significant concept to understand because it is very practically relevant. Whenever we make objects out of semi crystalline polymers, how much crystallinity is there depends on what is the crystallization kinetics.

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So, the thermodynamic description is based on description of Gibbs free energy for a material. And these diagrams here are the ones which are routinely used to describe a transition. And crystallization is an example of a first order transition. And it's termed so, because there is a discontinuity in the first derivative of Gibbs free energy. There are first order transitions and second order transitions and the glass transition temperature which we will have a lot of chance to look at in the upcoming lectures.

When you try to describe using some thermodynamic quantities, it appears to have some signatures which are similar to second order transitions, but we will also see that glass transition is not a thermodynamic transition like crystallization temperature or fusion temperature. So, at a given temperature which is denoted here using dashed line, what we have is a demarcation between what is the lowest Gibbs free energy. So, you can read about such diagrams and you can convince

yourself that, in case of higher temperature it is the liquid like state which is more favorable because Gibbs free energy is lower. And in case of solids below a certain temperature, the Gibbs free energy is lower. So, therefore, this transition point denotes a transition from liquid state to solid state. And of course, the liquid state is disordered state while the solid state is ordered state and crystalline.

And so, the transition point here is the melt temperature or the crystallization temperature. When we cool from higher temperature crystallization happens, when we heat from lower temperature melting happens. And one of the important things that we will see in case of polymers, because of its macromolecular nature and crystallization being so dependent on kinetic factors also. The melting temperature and crystallization temperature are in a range, most when we do either processing or when we try to measure these, we will see that these can vary over a range of about 10,20 degrees Celsius or even more, depending on what the polymer is. So, let's continue and look at the thermodynamic description and how is directly relevant, also for measurement of crystallinity. Because there is a volume change in case of the transition we can measure the densities and therefore, we can measure how much crystallinity a sample has. And that can be done by looking at densities of amorphous and crystalline phase and the density of the sample itself. Similarly, using DSC, differential scanning calorimetry, in which case we heat the sample that we are trying to measure along with the reference sample and as we are heating or cooling, we measure the amount of heat that is required to maintain the same temperature in both the samples. So, for example, heat of fusion can also be measured using the differential scanning calorimetry. So, both of these density differences or enthalpy differences are directly relevant in terms of measurement of crystallinity.

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Crystallization of polymers: complexities

- Equilibrium melting temperature ($T_m^\infty = \frac{\Delta H_f}{\Delta S_f}$)

	ΔH_f J/mol	ΔS_f J/(K mol)	T_m^∞ °C
Poly (ethylene)	4017	9.6	145
Polycarbonate	26560	43.5	338

- $T_m < T_m^\infty$
- Effect of finite crystal size (d): Gibbs Thomson equation

$$T_m = T_m^\infty \left[1 - \frac{2\Gamma_{cm} v_m}{d \Delta H_f} \right] \qquad (1)$$

- Effect of diluent

$$\frac{1}{T_m} - \frac{1}{T_m^\infty} = \left(\frac{R}{\Delta H_f} \right) \left(\frac{v_m}{v_s} \right) \left(\phi_s - \chi \phi_s^2 \right) \qquad (2)$$

Γ_{cm} - surface energy of crystal melt interface

v_m molar volume of repeating unit

v_s molar volume of solvent/diluent

Molar mass and molar mass distribution

$\chi \to$ Flory-Huggins interaction parameter

Now, the crystallization in polymers is complex because of the macromolecular nature and at the melting temperature, the change of Gibbs free energy from the liquid to the solid state will be zero or the Gibbs free energy of solid and Gibbs free energy of liquid will be equal to each other or the other way to say this also is chemical potentials of both phases will be equal and in that case, using identity of delta H - T delta S equal to delta G, we can arrive at what is the equilibrium melting temperature; notice the word equilibrium being used. And what in case of polymers what we see is this equilibrium melting temperature is not observed most of the time because of the kinetic factors which are involved. And for polyethylene for example, the delta H is around 4000 and delta S is around 9.6. And therefore, the melting point equilibrium melting point is around 145.

You can see that for polycarbonate, the delta H is very high, implying the interaction between molecules when a crystal is formed is much stronger in case of polycarbonate and that is why the crystal to liquid the delta H the enthalpy change is very high and proportionally so the entropy does not change as significantly. So, whatever side groups are there and the conformational change which is possible in case of a melt, because, segments can move around and macromolecules can move around. When we go to crystalline state that entropy is lost, but that loss is higher compared to polyethylene, but not as high and therefore, the melting point of polycarbonate is much higher.

So, you require to give much more thermal energy to polycarbonate macromolecules for them to disrupt the crystal of polycarbonate. So, as I said most often the melting temperature which is observed will be much less than this and this is due to the crystal size being finite.

So, this equilibrium melting temperature can theoretically be observed if we have the whole macromolecules stretch out and make a crystal which is infinite in size. However, because of the entanglements and because of the chain folding that happens in macromolecules, the crystallization happens at the rate which is most feasible at that condition. And therefore, what we have is finite size of crystals.

And so, one of the factors which is also very important in determining the crystallization in macromolecules as well as other systems is the surface energy which is involved whenever crystal is forming in a sea of molten liquid. Because of this interface what we have is interfacial energy is involved. So, when this interface grows interfacial energy also starts increasing and so, that plays a role in deciding how much is the melting temperature. And it is always the less than therefore, 1 minus a factor and this factor depends on the crystal size is inversely proportional. So, therefore, larger and larger the size eventually this factor will go to 0 and therefore, T m will be equal to T m infinity. The other significant influence is that of smaller molecules present in polymers. This of course, is present in any other substance also freezing point depression, boiling point elevation. These are phenomena that you can read about that when a different molecule is there, it changes the freezing point and boiling point or any other thermodynamic transition of a material. So, in case of polymers also, quite often what we will have is either there may be some residual monomer, there may be some plasticizer which is added or there may be some solvent which is remaining, so, because of these which are called diluents they interact and therefore, decrease the melting point. And in this one of the most important contribution is from the interaction between the solvent or the diluent with the polymer and this is something which we will have a lot of discussion on when we discuss polymer mixing, polymer mixing with solvent or polymer mixing with another polymer in case of blends. This is called the Flory Huggins interaction parameter.

So, there's Flory Huggins theory, which is used for describing mixtures of polymers. So, as part of that theory, this parameter is very useful in determining what sort of interactions are there and

what is the miscibility between 2 different systems. And the other key parameters which are involved in description of the melting point in polymers are related to what is the size of the repeating unit and so, the molar volume and of course, in case of a diluent what is the relative size of the more the repeating unit to the solvent.

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And so, with this, we will close this lecture by pondering on the aspects related to kinetics. The main issue is related to this entangle mass of macromolecules going to a crystal and we have seen that this happens by chains folding locally. So, chain starts folding and then the because of the entanglement, the chain cannot fold and the other chain which stopped, maybe due to entanglement can start folding.

And then this chain also again because of entanglements cannot fold and then there may be another chain, which is free to fold and so, this way, and this is what if you recall from the earlier lecture is the lamella of the crystal. And it is like a sheet of crystal which grows in which all the macromolecules are aligned. And if I zoom into this little closer, and look at this, I can identify a unit cell which is orthorhombic unit cell of a polyethylene.

So, if ethylene is this, then all the ethylene molecules are organized in the thickness direction of the lamella and I can identify a cuboid with the dimensions of this unit cell, which we can find out

using scattering or other methods. So scattering because of the periodic arrangement scattering and deflections are very commonly used to determine crystallinity also. So, the kinetic factors here are the fact that when we lower the temperature and crystallization is favored, the crystallization can happen because of such folding events and where entanglements have to be overcome. And so, therefore, the cooling rate matters quite a lot or the temperature at which crystallization is being done matters quite a lot. For example, if I cool it very suddenly, then what happens is macromolecules do not get any chance to fold and therefore, there may not be any crystallization.

If I bring it to a temperature which is much lower than the melt temperature, the tendency to form crystals is very high, but the molecular flexibility may be low. So, we will see how crystallization rate is affected by the molecular flexibility versus the driving force in terms of being far away from the melting temperature. And so, the rate of crystallization is significantly influenced by entanglements, by chain flexibility and of course, chain flexibility can be manipulated if we do changes of temperature.

If we compare two different polymers, then of course, chain flexibility is different because of the side groups or the backbone bonds and so on. We know polyethylene has C-C single bond. So, therefore, a lot more flexibilities there. We have seen that poly-ether-ether-ketone has benzyl groups in the backbone and therefore, its flexibility is much less than polyethylene. So, therefore, chain flexibility is one factor and then temperature is another factor.

And what is more important in case of polymer is both amount of crystallization which is there as well as what is the structure of those crystals depends on the cooling rate. So, this we will discuss a lot more in detail in an upcoming lecture. And this lecture, we will close by just pondering over certain aspects related to practical application of polymers. When we use these polymers, rarely we will use a single polymer. Quite often there will be additive, so therefore, they will be diluent effects. Quite often we will mix 2 polymers, so, we make a blend of 2 polymers. And then we might also add some reinforcement or fillers. So, what happens to crystallization when we are trying to go from this state to this state? What happens to the ability of macromolecule to crystallize? And you can see that if there is a filler then the filler and polymer interactions will also change how this crystal is formed. Or if we have 2 polymers mixed, and if they are molecularly

mixed with each other, if one polymer has a very large bulky group, and it cannot crystallize, then the other one also cannot crystallize. So crystallization of two polymers is a lot more challenging, because both the polymers have to have similar groups in which chains can fold together of two different polymers. So, therefore, crystallization of polymers for practical systems is actually much more challenging because of the mixtures involved.

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So, in terms of answers that are there, you can basically look at how to calculate density of a sample, given the density of amorphous and crystalline phases, and given the heat of crystallization for 100% crystalline polymer, as opposed to what is measured for a sample. So, with this we will close this discussion on crystallization and amorphous phases, and we will continue in the next lecture. Thank you.