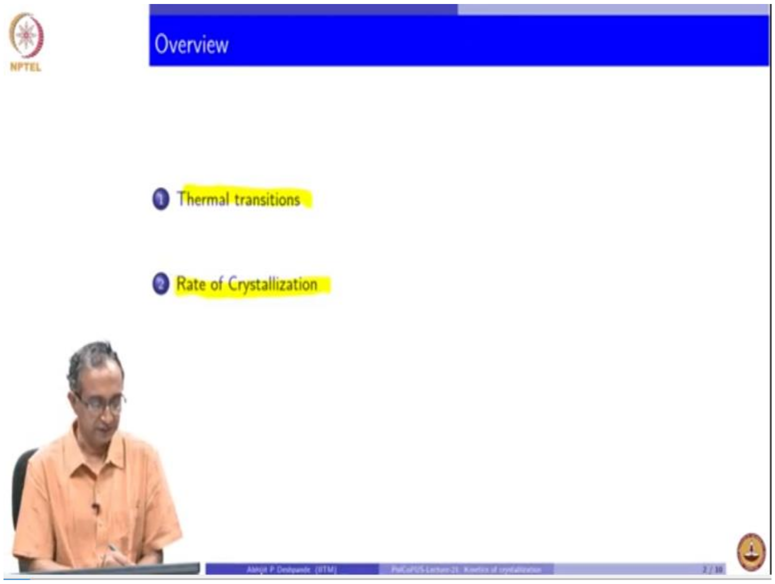
Molecular Arrangements and States of Polymers
Prof. Abhijit P Deshpande
Department of Chemical Engineering
Indian Institute of Technology – Madras

Lecture – 21
Kinetics of Crystallization

Welcome to our journey related to understanding of polymeric systems. In this course, we are looking at the concepts involved in polymers, their properties, the uses and applications and also the overall sustainability aspects. So, in this third week we are focusing on structure. And in this lecture, we will continue looking at the kinetics of crystallization. And, importantly from the point of view of estimating rates and also figuring out practically how kinetics can influence the overall phenomena of crystallization.

(Refer Slide Time: 00:47)

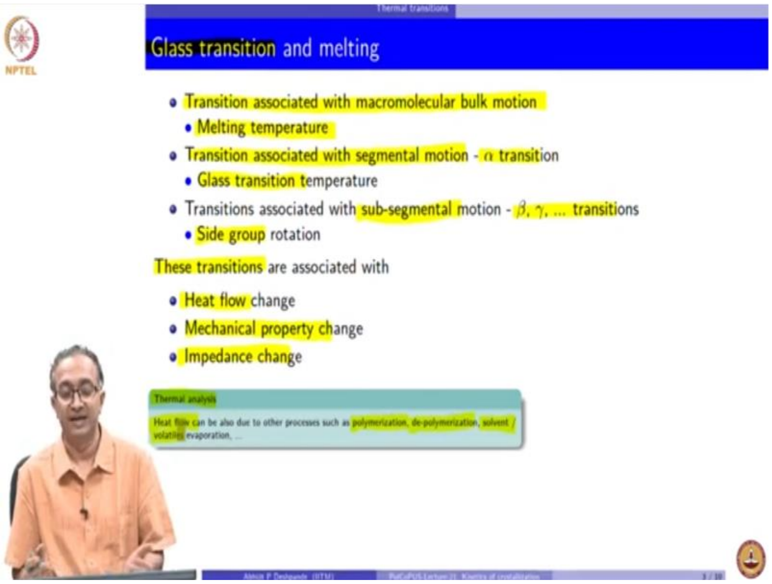


Overview

1. Thermal transitions
2. Rate of Crystallization

And we will do this by first looking at the relevant thermal transitions, because this will determine, in part the rate of crystallization. The thermodynamics driving force given that Gibbs free energy is lower for the crystalline state below certain temperature that drives crystallization, but the other thermal transition related to molecular flexibility imposes restrictions. So, therefore, we need to be aware of other thermal transitions before we look at the kinetics of crystallization. And once having done looking look at thermal transition, then we will see the rate of crystallization.

(Refer Slide Time: 01:23)



Thermal transitions

Glass transition and melting

- Transition associated with macromolecular bulk motion
  - Melting temperature
- Transition associated with segmental motion - α transition
  - Glass transition temperature
- Transitions associated with sub-segmental motion - β, γ, ... transitions
  - Side group rotation

These transitions are associated with

- Heat flow change
- Mechanical property change
- Impedance change

Thermal analysis

Heat flow can be also due to other processes such as polymerization, de-polymerization, solvent / volatiles evaporation, ...

So, the important transition that we need to be aware is called glass transition and the lectures following this, we will discuss glass transition phenomena in greater detail, but right now, what happens is transition associated with the overall bulk motion of the macromolecule, which means the overall macromolecule itself can move around and therefore, above melt temperature the polymer is liquid like. So, if I pour polyethylene at 150 degrees Celsius, the viscosity will be very high, but still I can pour it like a liquid. And so, that transition is melting temperature, because around 120 to 140 degrees Celsius is the melting temperature of polyethylene. But now, when I start reducing the temperature of polyethylene, and I bring it down to room temperature, then we know that it is a solid like material, but it is still flexible.

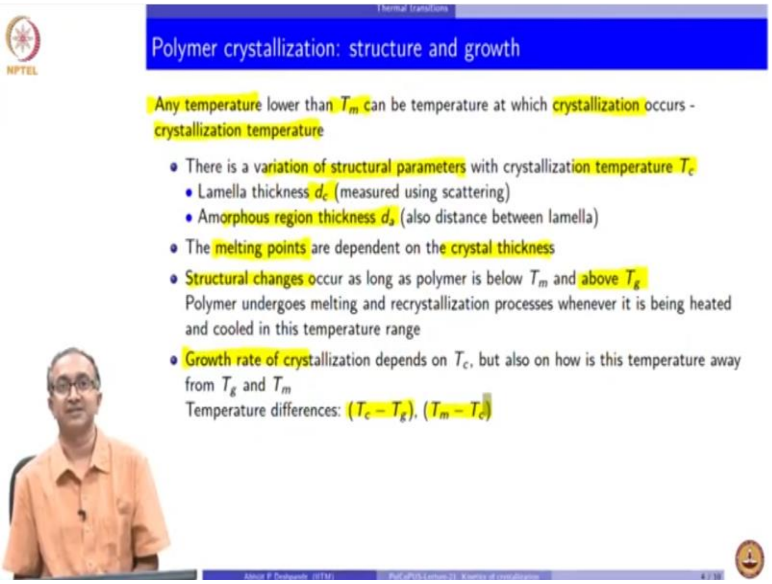
So, therefore, this is where we are still above a transition called the glass transition temperature, where the macromolecular flexibility is there. Sometimes this is also called the alpha transition. Alpha, beta, gamma is just to indicate that you know, there are several mechanisms at the molecular scale and each of them is responsible for one transition. So, therefore, if there are side groups or there are some other conformational changes which are possible, they are associated with the beta, gamma transition and they are necessarily smaller scale compared to segments. So, this is again going back to the idea that we discussed earlier in terms of multiplicity of timescales of response of macromolecular systems. So, there is the whole macromolecule, then segment, and then sub segment and viscoelasticity of macromolecules is very crucially linked to such multi scale response in time as well as length.

So, these transitions are associated, importantly, with some heat flow chain. So, that is a way of measuring also, but that is also an indication if you are trying to use it in some application, we need to know how much does the property change. For example, a mechanical property can change by 3 orders of magnitude across a glass transition. So, if modulus is in G Pas below glass transition, it can become M Pas above glass transition. So, 3 orders of magnitude change, very, very significant change. Similarly, diffusion of small molecules in polymers can also change.

We will also see that electrical properties also change. When we look at impedance, which will be both resistance and capacitance put together, we will see that that also changes when we have all these transitions happening. So, therefore, these changes in properties are important from an application point of view, but equivalently they also become tools for us to measure these transitions. So, one technique for example, is thermal analysis in which case we are looking at the thermal events in the macromolecular system and the signatures associated with it. So therefore, heat flow, for example, in DSC can be a good signature for these transitions. Of course, when we look at a practical polymeric system, there may be other events which are happening, which can also be along with these thermal transitions.

For example, there may be some polymerization, de-polymerization reactions happening, degradation reactions happening, there may be some solvent on small molecules present which may be evaporating. So, real polymers system may have several signatures associated with heat flow and then we might have to delink what is associated with these. Similar is the case with mechanical properties and any other set of properties.

(Refer Slide Time: 05:13)



Thermal transitions

Polymer crystallization: structure and growth

Any temperature lower than T_m can be temperature at which crystallization occurs - crystallization temperature

- There is a variation of structural parameters with crystallization temperature T_c
  - Lamella thickness d_c (measured using scattering)
  - Amorphous region thickness d_a (also distance between lamella)
- The melting points are dependent on the crystal thickness
- Structural changes occur as long as polymer is below T_m and above T_g
  Polymer undergoes melting and recrystallization processes whenever it is being heated and cooled in this temperature range
- Growth rate of crystallization depends on T_c, but also on how is this temperature away from T_g and T_m
  Temperature differences: $(T_c - T_g)$, $(T_m - T_c)$

So, the polymer crystallization both the structure and growth of it, basically is possible when we look at what happens under a given condition. So, when we have any temperature which is lower than the melt temperature, crystallization can happen and that we will refer to as the crystallization temperature. So, if I have polymer above melting temperature no crystallization is possible because their liquid is favored due to lower Gibbs free energy.

When we bring it down below melt temperature, then Gibbs free energy of the ordered crystalline solid is favorable. The only complication in case of polymers is because of entanglements and macromolecular flexibility, 100% crystallinity cannot be obtained and therefore, we obtain folded crystals and spherulite structures. So, therefore, variation of structural parameters is present depending on what is the crystallization temperature.

So, let’s say if PET is taken to 280 degrees Celsius for molding, and then if we bring it down suddenly to 170 degrees Celsius, it will crystallize at 170 degrees Celsius. So, the crystal size that I obtained will be different if I bring it down to 200 degrees Celsius and crystallize it. And so, that can be measured using the thickness of the lamella. What you can notice here is depending on the thermal energy and segmental flexibility, which is there, the polymers, will start folding and the rate at which they fold will depend on the temperature itself. And therefore, the thickness of the fold will also depend on the temperature and naturally therefore, the amorphous region thickness will also be different. So, the melting point of these crystals then are also dependent on crystal thickness. So, this is a complication in case of polymers. Notice what I am saying. There is an equilibrium melting temperature, but that is rarely observed.

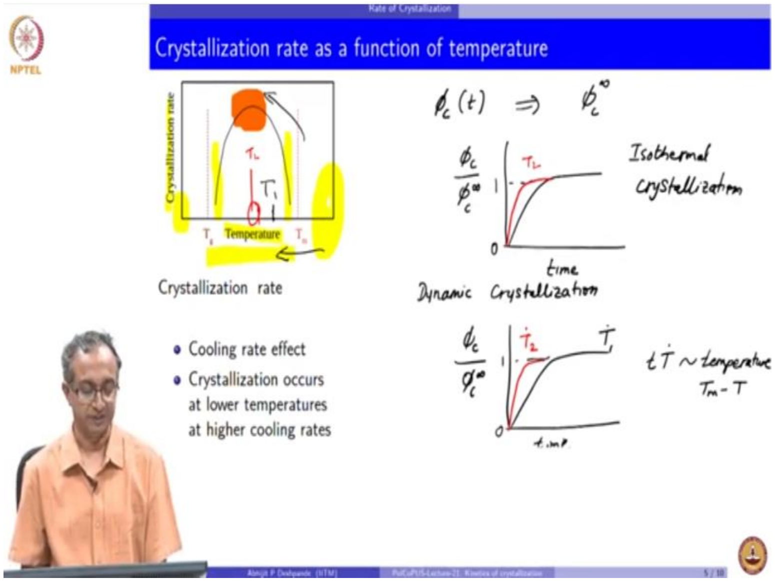
The crystals that are obtained will depend on what temperature crystallization is happening. Now, after these crystals are found, if I melt them, again melting will happen depending on how these crystals are. If crystals are formed at a lower crystallization temperature, they will also melt at lower melting temperature. So, the other complication in case of polymers is as long as segmental flexibility is there, which means we are above the glass transition temperature, structural changes, can happen.

And so, if I am keeping the sample close to melting point or below melting point where segmental mobility is there, crystals can melt and reform, melt and reform. So, if I make the PT crystals at 160 degrees Celsius, and then I heat this sample to 200 degrees Celsius, some of the crystals which are formed at 160 will melt and reform and then I will get a completely different structure at 200 degrees Celsius.

So, therefore, there is a dynamics of crystal formation and melting at any condition which is less than melting point but above glass transition temperature. So, therefore, growth rate under any condition will depend on these 2 temperature differences. So, the crucial temperature differences to keep track are how far away is the crystallization temperature from glass transition temperature, because this determines the segmental flexibility.

As soon as we reach the glass transition temperature segments will be frozen the segmental mobility will go to 0 and therefore, crystallization will not be possible, but if we are away from glass transition and higher, much higher than glass transition then segmental mobility is higher. On the other hand, the temperature difference between the crystallization temperature and the melt temperature is also an important thermodynamic driving force. If we are above melting temperature, of course, no crystallization can take place. So, only when we are lower than melting temperature, then crystallization can take place and this difference between T m and T c tells us how strong is the driving force for crystallization.

(Refer Slide Time: 09:21)



Crystallization rate as a function of temperature

Crystallization rate

- Cooling rate effect
- Crystallization occurs at lower temperatures at higher cooling rates

So, having seen the importance of temperature at which crystallization is happening with respect to the glass transition temperature on one hand or the melting temperature on the other hand, now, let’s look at the crystallization rate a little more closely. If we were to plot the crystallization rate as a function of temperature, what we will notice is that near the melting point, the crystallization rate is lower because the driving force is lower there. And crystallization rate starts increasing as we go to lower and lower temperature. But as we start approaching glass transition temperature, again the crystallization rate drops. So somewhere in between the two transition temperatures, we have the maximum rate of crystal growth. And therefore, it depends on what temperature are the crystals being grown. In case of macromolecular crystallization, the amount of crystallinity that is obtained as well as the structure in terms of the lamella thickness or in terms of spherulite size. So, the morphology or the microstructure of crystalline phase also depends on what temperatures the crystallization is being carried out. Now, one can look at the crystallization in 2 different ways, the way we have been discussing where we do crystallization at a fixed temperature. So, for example, we can bring the material at a temperature which is far higher than melting temperature, and then cool it down. And so, when we cool it down, and to a specific temperature, let us say here, T1. And then what we can do is as soon as we bring it to T1, crystallization will start, we can measure the amount of crystallinity. So, generally, we will define phi c as the fraction of crystallinity which is present in the material at any instant of time.

And, when we are saying that we are looking at kinetics of crystallization, we are interested in tracking how fast or slow this phi c is increasing, eventually, when crystallization is complete, this phi c becomes phi c infinity. So, that is the final value of degree of crystallinity in the sample. So, our interest is in looking at how does this ratio vary? This ratio starts out being 0 at time t is equal to 0 and then at time approaches infinite or very large amount of time, there will be value of 1 as a function of time.

So, in crystallization kinetics, we are interested in following and finding out what is the rate of crystal growth and how fast or slow the crystallization is happening. And I could do this at a different temperature and note the crystallization rate. So, let us say if I do measurement at another temperature, which is T 2 and the rate happens to be faster, and of course, eventually again it will reach some phi c infinity value and therefore, 0 to 1 is the variation.

Now, if I ask you on this graph here, where will T 2 be will it be left off T 1, in the sense will it be lower than T1 or will it be higher than T1? And clearly since the rate at T2 is higher T2 has to be somewhere in this region. So, therefore, this is the region where T2 will be, because the crystallization rate is higher. So, in case of the crystallization rate will be maximum at (T m – T g)/2, somewhere midpoint of the range of temperature from glass transition temperature to the melting point temperature. And if we are interested in practical applications, then what happens is we take the sample to this higher than melting point and then we actually will make the sample flow in a mold or in a cast and so on and, so, the temperature is much higher than the melting temperature and then as soon as mold finishes, then the mold is cooled and so, temperature is decreased at some rate.

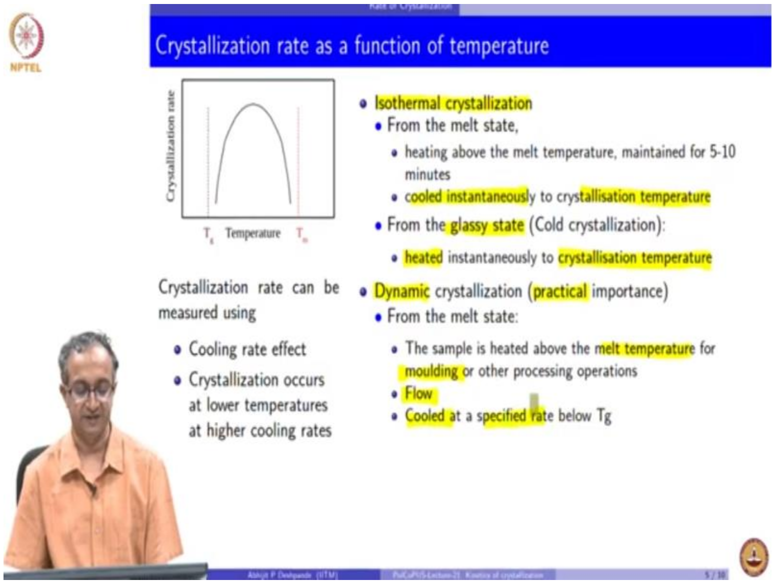
So, in case of practical applications, the crystallization will happen at different temperatures because sample is being cooled as the temperature changes. So, what we had discussed here is an example of isothermal crystallization and practically what is important is dynamic crystallization. So, in this case also the sample starts out with 0 crystallinity and then it goes to eventually crystallinity which is phi c infinity.

And in this case, we could plot this as a function of time or temperature both, and they are related to each other because if we assume let us say there is a constant cooling rate. So, in this case the time into the cooling rate will give us the temperature. In fact, this is going to be let's say T m – T. So, whenever we are at time t is equal to 0, we are temperature T m or higher and then when we start going further and further the temperature will go lower and lower.

So, with this now, the question again will be that, when we do a cooling rate experiment, the crystallization will happen, the degree of crystallinity will go from 0 to 1. Now, the question is at what temperatures is the crystals being formed? One thing that you can realize is if I do extremely high cooling rate, then what happens is the residence time at the temperatures where crystallization is possible is very low.

So, therefore, I can take the sample below glass transition and then have it completely amorphous. But let us say I have cooling rates, which are most practical cases may be 20 degrees Celsius a minute or 15 degrees Celsius a minute or 10 degrees Celsius a minute, then crystallization will happen. And now, the question is what happens at 2 different cooling rates? So, here I have drawn the curve for let us say a cooling rate of T dot 1. Now, if I draw another curve, which is T dot 2, here you can see that crystallization is happening a lot faster, the time required for crystallization is faster. So, let's say that right now we are focusing on x axis as time alone. So, the time that is required is much lower in case of T2 dot. Now, can you think and try to justify whether T1 dot will be greater or T2 dot will be greater, which is the cooling rate which is higher? So, we can you can think about this and towards the end of the lecture, we will look at the governing equation, a simple model and try to again answer this question.

(Refer Slide Time: 17:14)



Crystallization rate as a function of temperature

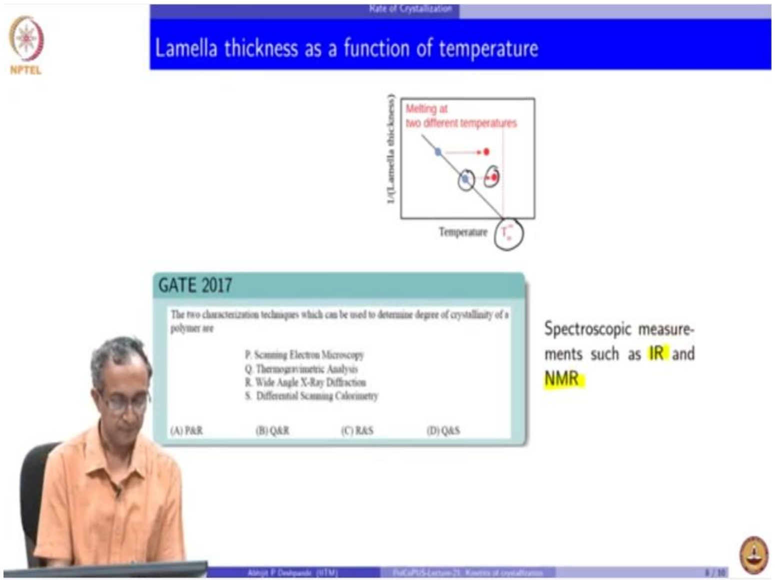
Crystallization rate can be measured using

- Cooling rate effect
- Crystallization occurs at lower temperatures at higher cooling rates

- Isothermal crystallization
  - From the melt state,
    - heating above the melt temperature, maintained for 5-10 minutes
    - cooled instantaneously to crystallisation temperature
  - From the glassy state (Cold crystallization):
    - heated instantaneously to crystallisation temperature
- Dynamic crystallization (practical importance)
  - From the melt state:
    - The sample is heated above the melt temperature for moulding or other processing operations
    - Flow
    - Cooled at a specified rate below Tg

So, just to summarize, we can look at crystallization kinetics under isothermal condition, and here we cool it instantaneously to a temperature and monitor the degree of crystallinity as a function of time. We could do isothermal crystallization by first quenching, so that we go to glassy state and make the material amorphous, then heated to again a crystallization temperature. In case of dynamic crystallization, which is of course, practically very important, we heat the sample above melt temperature so that molding can occur, then we make the material flow and finally cooled it at some specified rate.

(Refer Slide Time: 17:54)



Lamella thickness as a function of temperature

GATE 2017

The two characterization techniques which can be used to determine degree of crystallinity of a polymer are

P. Scanning Electron Microscopy
Q. Thermogravimetric Analysis
R. Wide Angle X-Ray Diffraction
S. Differential Scanning Calorimetry

(A) P&R (B) Q&R (C) R&S (D) Q&S

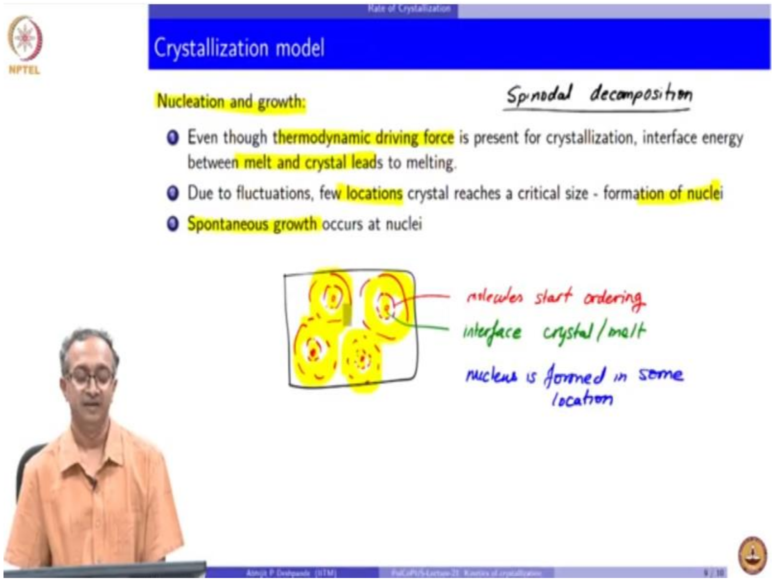
Spectroscopic measurements such as IR and NMR

So, let’s look at what are the consequences of such range of temperatures over which crystallization can happen. And this we have already seen that the lamella thickness depends on the temperature at which the crystallization happens. And somewhere high temperature this is where the equilibrium melting temperature is. So, it is this whole range of temperature where crystallization can happen.

And just to remind you, this is a question based on exam, what are the characterization techniques which can be used to determine the degree of crystallinity? In this lecture, as well as our two lectures earlier when we had discussed the amorphous and crystalline state, we have had a lot of discussion related to order in the material and also related to thermal signatures. So, I am sure you will be quickly able to answer this question.

So, when we come back to this, so, crystallization let us say happened at two different temperatures in the sample and so, at this temperature, the thickness of the crystal is different compared to the thickness of this crystal. So, microstructurally the two crystals are different. Now, if I heat these samples and melt them, again the melting will also be at different temperatures. So, the crystals which are formed at a higher temperature will melt at a slightly higher temperature and only if we do crystallization exceedingly slowly, theoretically, then we can do crystallization at T m infinity and melting also at T m infinity. So, most practical cases there is a range of temperature over crystallization and melting takes place. Another thing to just remind ourselves is given that there is order and disorder in the crystalline and amorphous states, the bonds which are available whether it is a carbon hydrogen bond or carbon oxygen bond or any of the bonds, whether they belong to an ordered structure or disordered structure, they have different spectroscopic signature. So even techniques like IR spectroscopy or NMR spectroscopy can be used to look at the crystallization.

(Refer Slide Time: 20:11)



Rate of Crystallization

Crystallization model

Nucleation and growth:

Spinodal decomposition

- Even though thermodynamic driving force is present for crystallization, interface energy between melt and crystal leads to melting.
- Due to fluctuations, few locations crystal reaches a critical size - formation of nuclei
- Spontaneous growth occurs at nuclei

And so let’s now finish this lecture by looking at a simple set of models. And to do look at this model, we need to quickly again recap as to how we have said is the picture of crystallization. What we have been saying is that crystallization happens where there are a few nuclei form and then growth happens. There is also another mechanism of crystallization, which is important for some material systems.

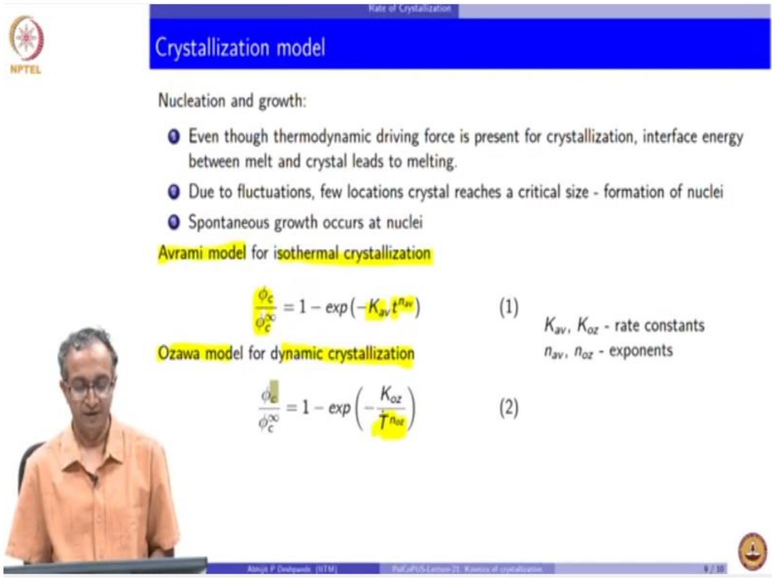
And we will have a chance to discuss this even when we discuss polymer blends. And so, this is generally two different mechanisms of phase transformations in thermodynamics. Nucleation and growth, where some places nuclei are formed, and then growth occurs and then spinodal decomposition where simultaneously throughout the sample structured forms. You can see why this is important when I have described some places nuclei starting and then growing, as opposed to everywhere in the sample spinodal decomposition leading to crystalline and amorphous phases in a co-continuous manner. Now, once these 2 crystallization processes happen, the final material that we get morphology or microstructure is very different. So from an engineering point of view, it’s of interest for us to know which mechanism is followed.

So, let’s look at nucleation and growth which is what happens practically most of the time. We have the thermodynamic driving force for crystallization as soon as sample is brought below the melting temperature. However, whenever we have a sample, and let us say there are a few places where nucleation started or crystal formed, because there is a driving force, so, in these few places, molecules start ordering, which means a crystal starts appearing. However, what happens as soon as a crystal appears is there is now an interface being created a phase boundary being created. So, there is an interface between crystal and melt and this requires energy, there is an interfacial energy associated with it. So, what happens is this ordered crystals again actually go back to the melt. So, this process is a dynamic process and this keeps on happening.

However, few places the crystal goes beyond a certain critical size and then a nucleus is formed. So nucleus formation/ nucleus is formed in some location. You might ask, how do I know what is the density of nuclei formation? And the answer again there is depending on the driving force. The further away from melting point we are, the more will be the number of nuclei and this again will try to give you a picture that if crystallization happens at lower temperature, a lot more nuclei will be there, this spherulitic size will be small.

On the other hand, if we do crystallization, close to melting temperature, then the number of nuclei will be less and spherulitic size will be more. Why am I saying that? Because let's say these are the few places where nuclei have formed and so, what happens is now, growth can happen. So on these nuclei now, crystal starts growing. So, in just to recap, melt and crystal keep on forming and reforming everywhere in the sample. Because of driving force crystallization happens, but because of interfacial energy, the crystal melts, but in few locations, which we call nuclei are formed. And once nuclei are formed, then spontaneous growth can happen. And so now these locations spherulitic structures or whatever may be the morphology of growth that can start. If this drawing was there and the way I am drawing and things basically starting at a point and then growing in space, I do not know if you can recall of a similar situation, this is a month of June here, while I am doing this recording, and monsoon is the time and so, I do not know whether you can correlate this with rain. And if you think closely if you look at a trough of water and if some drops are falling and then waves which are formed and propagate out, the picture I have drawn is very similar to that. And in fact, so, the crystallization kinetics model that was initially proposed was based on the analysis which was done for what is the area being covered by the waves of the raindrops. So, if you start initially, as soon as raindrop falls, it covers very small area, but then the waves propagate out. So, as the time increases, the more and more area of the trough is covered by the waves of the raindrop. So, this is what is happening here also, initially, the area covered is very small, where near the nuclei and then eventually when the growth starts happening, more and more area is covered by the crystallite regions.

(Refer Slide Time: 26:09)



Rate of Crystallization

Crystallization model

Nucleation and growth:

- Even though thermodynamic driving force is present for crystallization, interface energy between melt and crystal leads to melting.
- Due to fluctuations, few locations crystal reaches a critical size - formation of nuclei
- Spontaneous growth occurs at nuclei

Avrami model for isothermal crystallization

$$\frac{\phi_c}{\phi_c^\infty} = 1 - exp(-K_{av} t^{n_{av}}) \qquad (1)$$

K_{av}, K_{oz} - rate constants

n_{av}, n_{oz} - exponents

Ozawa model for dynamic crystallization

$$\frac{\phi_c}{\phi_c^\infty} = 1 - exp\left(-\frac{K_{oz}}{\dot{T}^{n_{oz}}}\right) \qquad (2)$$

Abhijit P Deshpande (IITM)

9 / 10

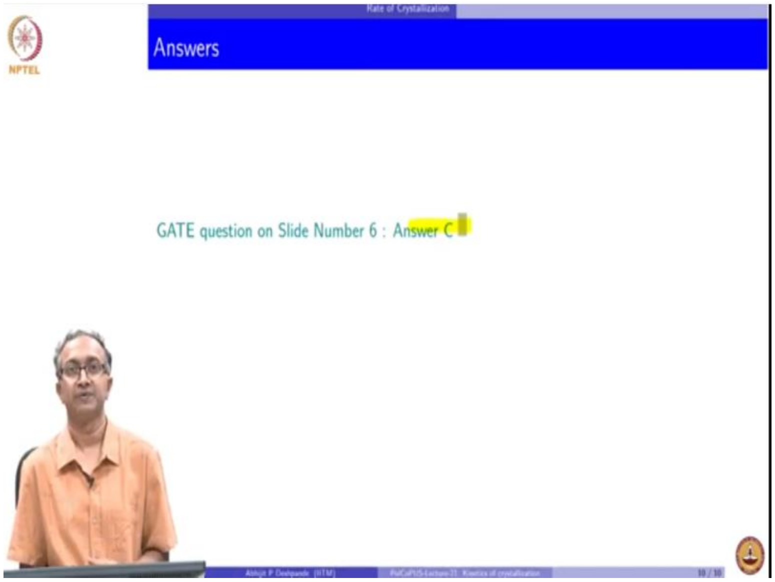
So this model is called the Avrami model. And so this is the Avrami model, which was based on such consideration. And it talks about how ratio of crystallinity from 0 will go to 1 as a function of time. And the important parameters are the rate constant for the process and the exponent, and the exponent depends on what is the nature and geometry of the crystals that are present. And if you look at the model for dynamic crystallization, it is similar based on similar arguments, but instead of time, we have now the cooling rate.

$$\boldsymbol{\frac{\phi_c}{\phi_c^\infty} = 1 - \exp(-K_{av} t^{n_{av}})}$$

And so, if cooling rate is very fast, what happens? If cooling rate is exceedingly slow, what happens if cooling rate is very fast, then what happens? So, if cooling rate is very fast, you can see that this factor will go to 1 and therefore there will be no crystallinity. So, therefore, you can try now, going back to the slide and see if 2 different cooling rates are there, one faster than the other at what you can try to justify and figure out whether the red one was faster cooling rate or the black one was faster cooling rate.

$$\boldsymbol{\frac{\phi_c}{\phi_c^\infty} = 1 - exp(-\left(\frac{K_{oz}}{\dot{T}^{n_{oz}}}\right)}$$

(Refer Slide Time: 27:24)



Rate of Crystallization

Answers

GATE question on Slide Number 6 : Answer C

So with this, we will close this lecture, and I am sure you all have you know the answer to the question, because we have discussed sufficiently that scanning calorimetry, differential scanning calorimetry and X ray scattering and diffraction are the two most important techniques to measure crystallization in samples. So, with this, we have concluded our discussion related to understanding of crystallization in macromolecules.

Now, in next few set of lectures, we will look at glass transition in much more detail, because though we have introduced glass transition, and it seems to be related to segmental mobility of the material, and it prevents crystallization from happening, but what is meant by glass transition and what is this glass transition temperature. So, we will have a discussion related to understanding of glass transition. Thank you.