Molecular Arrangements and States of Polymers

Prof. Abhijit P Deshpande
Department of Chemical Engineering
Indian Institute of Technology - Madras

Lecture - 17
Amorphous / Crystalline States 1

Hello. You might be wondering that in this course so far we have discussed macromolecular conformations and flexibility and conformations being dynamic and macromolecules changing conformations and so many things and but the plastic objects that you see around you seem to be solid. And so what's the connection? And so, this week and specifically this lecture onwards, we will start looking at the solid states.

But I will again remind you that those macromolecular conformations and flexibility will still come into our discussions. Because how the solid states are formed will depend pretty much on how we processed the materials, how we fabricated the materials and during fabrication segmental mobility or macromolecular conformations are possible. So for example, how fast or slow I cool the material will determine how much flexibility was there, and in the end, what arrangement do I get? So again, no getting away from a single macromolecular picture which is extremely useful. So let's look at this week, the molecular arrangement and different states of polymers. And specifically, let's start looking at amorphous and crystalline states. Our focus will be on learning concepts related to these descriptions of solid states.

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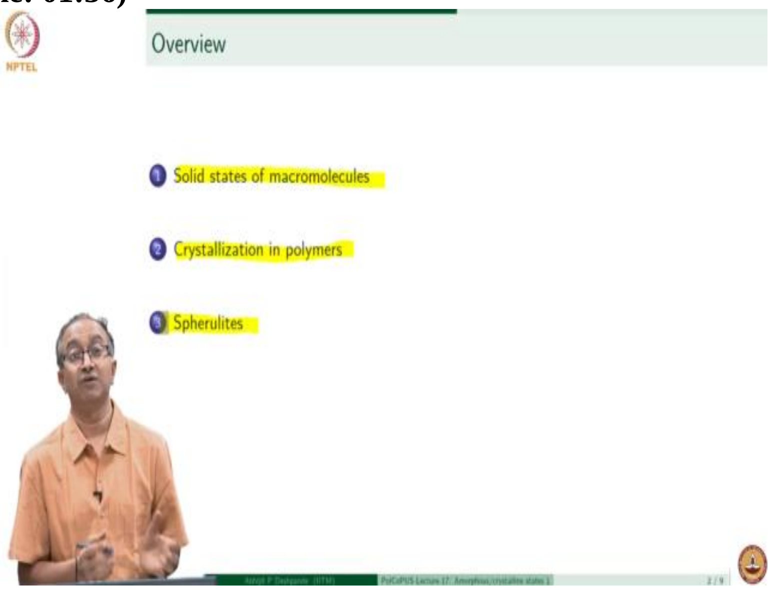

Overview

1. Solid states of macromolecules
2. Crystallization in polymers
3. Spherulites

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And we will do this by first quickly reviewing; which are these amorphous and crystalline states which are possible in macromolecules? And what do we mean when we say crystallization in case of polymers? And the specific arrangement of crystallites in case of polymers, and which is quite often observed in synthetic polymers and plastics which we see around us is spherulites.

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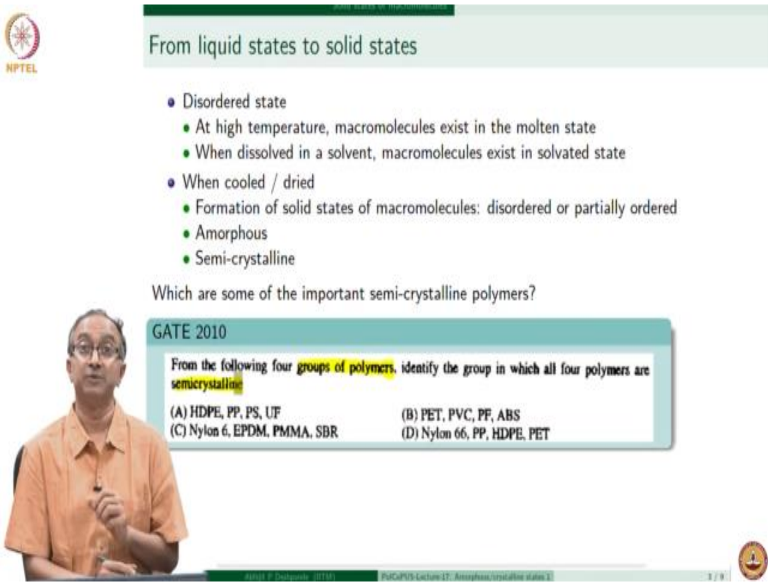

From liquid states to solid states

- Disordered state
  - At high temperature, macromolecules exist in the molten state
  - When dissolved in a solvent, macromolecules exist in solvated state
- When cooled / dried
  - Formation of solid states of macromolecules: disordered or partially ordered
  - Amorphous
  - Semi-crystalline

Which are some of the important semi-crystalline polymers?

GATE 2010

From the following four groups of polymers, identify the group in which all four polymers are semicrystalline

(A) HDPE, PP, PS, UF
(B) PET, PVC, PF, ABS
(C) Nylon 6, EPDM, PMMA, SBR
(D) Nylon 66, PP, HDPE, PET

So, from liquid state to solid state, basically we have the disordered liquid state. And of course, at high temperature macromolecules will exist as molten state where the arrangement of macromolecules is random and macromolecular, segmental flexibility as well as whole macromolecular motion is possible. And of course, this will also be there when we dissolved in a solvent. And in this case, the macromolecules are solvated and by solvation, we mean a significant interaction between a macromolecule and its solvent molecules. And we can picture this by drawing a macromolecule and basically if we depict the solvent, so, basically solvent molecules will have close interactions with the macromolecular chain as opposed to a non-solvated macromolecule where the molecule will be separated from the solvent molecules.

So, again, whenever it is solvated we again have molecular flexibility while in a collapsed state when it’s non-solvated macromolecular flexibility will be less. So, these are liquid like states and then we either cool or dry when we say drying we are removing the solvent and we will reach the solid state of macromolecules which in case of macromolecules are completely disordered, which is what we call amorphous state or partially ordered state which are semi crystalline. We will see because macromolecules are these extremely long molecules to get

100% crystalline states, is not feasible. There are always kinetic limitations to at what rate crystallization can proceed. So, more often than not we only achieve 30, 40, 50% crystallinity and therefore materials are semi crystalline. So, which are some of the important semi crystalline polymers you might ask and to just get you thinking along this direction, what we will do is look at this exam question where we are asked to identify from the group of polymers, semi crystalline polymers. And as I emphasized semi crystalline, because in case of polymers 100% crystallinity is not practically observed in most of the cases. So, while answering this question, you might have a feeling that you know look I need to remember I mean whether PVC is crystalline or not I should remember. But no, what you need to do is to understand carefully, how are crystals formed in polymers which is what we will do in the next lecture, this lecture, next lecture and one more lecture related to crystallization kinetics. And once we understand what is the requirement of crystal formation and how crystals are formed then based on the presence and absence of certain groups, we can make out whether crystallization is feasible in this polymer or not.

So, therefore, judgment is possible in terms of answering this question. So, look at carefully as to what way crystals are formed in case of polymers and you will be able to answer this question.

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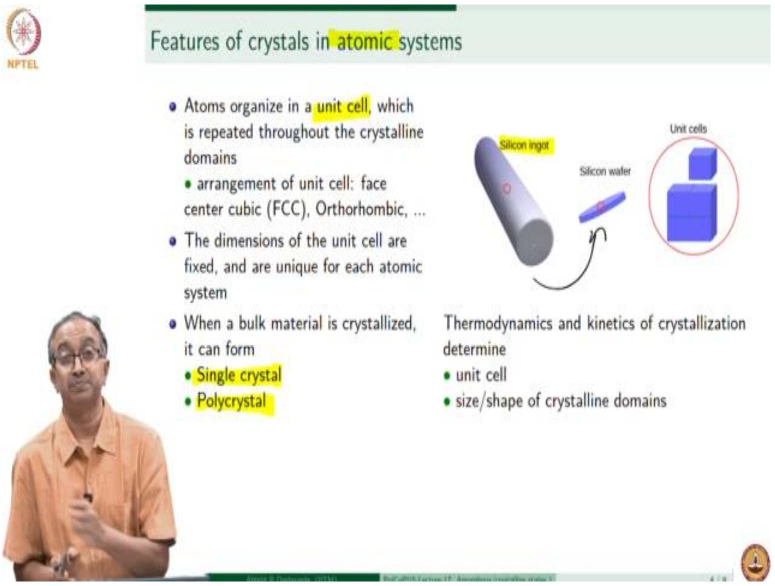

Features of crystals in atomic systems

- Atoms organize in a unit cell, which is repeated throughout the crystalline domains
  - arrangement of unit cell: face center cubic (FCC), Orthorhombic, ...
- The dimensions of the unit cell are fixed, and are unique for each atomic system
- When a bulk material is crystallized, it can form
  - Single crystal
  - Polycrystal

Thermodynamics and kinetics of crystallization determine
- unit cell
- size/shape of crystalline domains

So, let’s just quickly look at features of crystals in atomic systems. This is something you would have learnt in your physical chemistry and basic material science courses. The key aspect of this is a unit cell which repeats itself throughout the crystal and we can have a single crystal or a polycrystal. One prominent example of a single crystal is a silicon ingot from which we actually cut wafer. And in this case, all of the cylinder with it's a few inches of diameter and lengths which is quite longer in terms of meter. So this object has single unit cell, of course, because it's a crystalline material, but the unit cell is exactly repeated with one single crystal. And, so, you can look up some of these concepts associated with atomic crystals, as they will be useful in trying to understand and explain the information for polymeric crystals.

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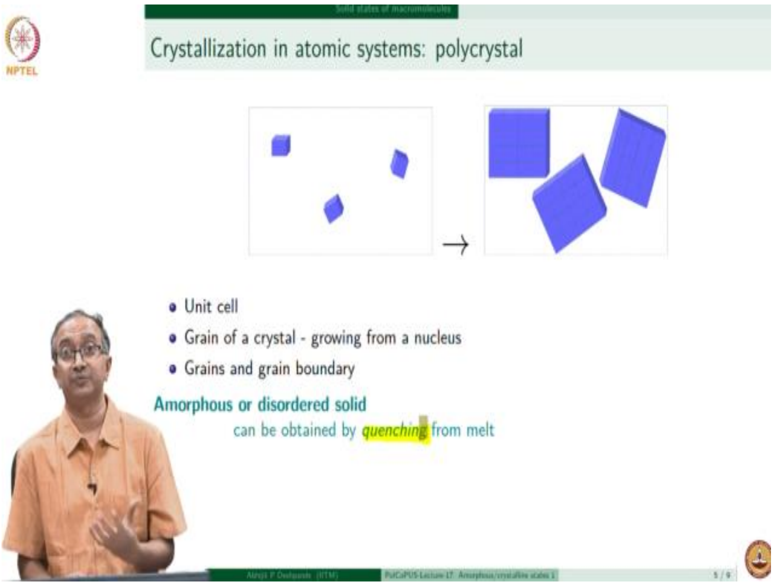

Solid states of macromolecules

Crystallization in atomic systems: polycrystal

- Unit cell
- Grain of a crystal - growing from a nucleus
- Grains and grain boundary

Amorphous or disordered solid

can be obtained by quenching from melt

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So, summarizing again what happens is, if most of the time when crystallization is carried out, this is not how crystallization is carried out for silicon ingot that I mentioned, because that will lead to single crystal. But quite often if you form, you start with a melt and then what happens is few places nucleation happens and then growth takes place of these crystals. And what I have highlighted it here is how unit cell is the same in all of these cases. So, all of these cases, the unit cell is the same, but the orientation of the unit cell is different. So, in this case, for example, this is the orientation in this case. So, all of the cases orientation is different and in the end, all these growth fronts come together and each of them is called a grain. And so, bulk crystalline material has grain and grain boundaries, so this is how crystallization happens and if we prevent this, if we prevent the nucleation formation or if we cool so fast, that the growth is not possible, then we will end up with an amorphous or disordered solid and usually we call very fast cooling a quenching. So if we melt the material and quench it, we can obtain an amorphous material.

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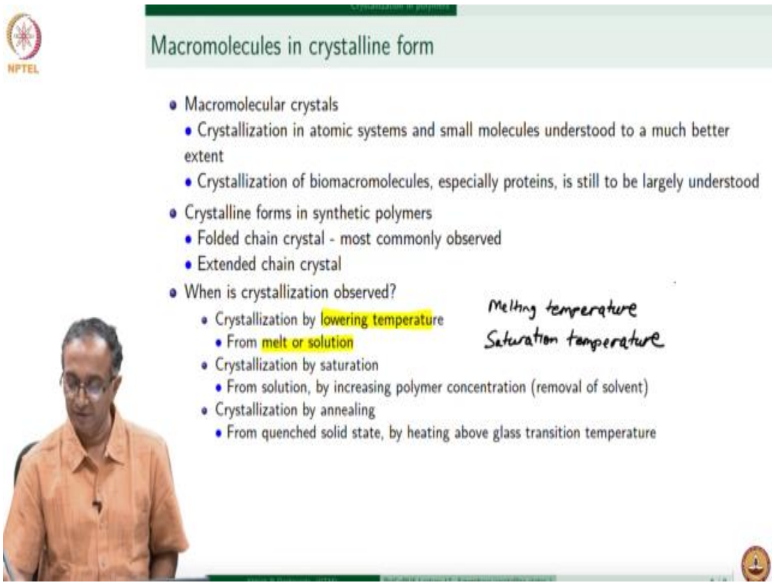

Macromolecules in crystalline form

- Macromolecular crystals
  - Crystallization in atomic systems and small molecules understood to a much better extent
  - Crystallization of biomacromolecules, especially proteins, is still to be largely understood
- Crystalline forms in synthetic polymers
  - Folded chain crystal - most commonly observed
  - Extended chain crystal
- When is crystallization observed?
  - Crystallization by lowering temperature
    - From melt or solution
  - Crystallization by saturation
    - From solution, by increasing polymer concentration (removal of solvent)
  - Crystallization by annealing
    - From quenched solid state, by heating above glass transition temperature

Melting temperature
Saturation temperature

So in macromolecules, how do we form crystals? So, in atomic systems, of course the crystallization is understood much better. In macromolecular systems it’s not understood as well. In case of synthetic polymers and simple polymers such as polyethylene, we have far better understanding. But one of the very big unsolved problem in biology is related to protein crystallization. So, therefore, in general crystallization in macromolecules is not as well understood as small molecular systems. And crystalline form is most commonly observed is called a folded chain. And we are familiar with the polymer chain being a coil like object and if we cool it or if solvent is removed from this, then what happens is, there is a tendency for this chain to align with respect to each other. So, chains which are there can align and this will be called an extended configuration or extended chain. But because of the kinetic factors because this molecule is entangled with another set of molecule, what often happens is the polymer folds itself and starts aligning with itself and this is called a folded chain and this is what is observed most commonly, and that’s why in case of polymers, kinetics, the rate of crystallization plays a far important role compared to small molecular systems.

So, when is crystallization observed in case of polymers? Just to summarize, crystallization is observed when we lower the temperature, we will soon define melting temperature. So when we take the melt below this temperature crystallization can happen or we can also bring it below saturation temperature in case of a solution. The saturation can also be achieved by changing the concentration of solvent by evaporation. And there are in fact a variety of techniques if you look at how solvent is removed, even freeze drying is a method we can remove solvent of course, by heating it, but you can remove solvent by also lowering pressure by vacuum application or freeze drying. So, there are several methods possible. And in macromolecular systems how you do this determines what kind of crystals do you get. Because the rate of crystallization is strongly influenced by the conditions of crystallization. And crystallization in macromolecules can also be done by annealing. What do we mean by that? We can quench the system obtain an amorphous system and then raise the temperature just so that segmental mobility is possible. As soon as segmental mobility is possible, a chain which was randomly organized can start folding and forming crystals.

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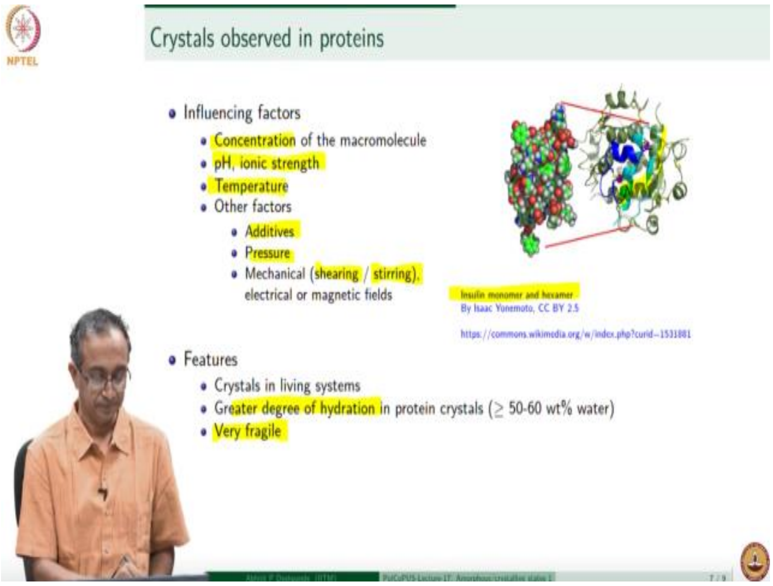

Crystals observed in proteins

- Influencing factors
  - Concentration of the macromolecule
  - pH, ionic strength
  - Temperature
  - Other factors
    - Additives
    - Pressure
    - Mechanical (shearing / stirring), electrical or magnetic fields
- Features
  - Crystals in living systems
  - Greater degree of hydration in protein crystals ($\geq$ 50-60 wt% water)
  - Very fragile

Insulin monomer and hexamer
By Isaac Yonemoto, CC BY 2.5
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So, this is something which we will observe in case of synthetic polymers. Just to summarize before we go ahead and start looking at synthetic polymers and crystals in them, I mentioned already that protein folding and protein crystallization is a very challenging topic, which is very crucial for all biological activities of proteins, but we haven't understood it as well. So, the influencing factor for forming crystals and proteins are many. We can have, what is the amount of proteins which are present? What is the ionic environment which is present? The temperature and of course, several other additives with which this protein is acting and of course, also the mechanical or electrical environment present. Some of these can be used from engineering application point of view also and these crystals are in living systems have a much greater degree of hydration. So, the solvent present even after crystal is formed is much greater, because in biology, presence of water is essential for carrying out variety of biochemical reactions. And therefore, this greater amount of solvent also leads this crystal to be much more fragile than what synthetic crystals that we will talk about. In fact, we will see that presence of crystallinity in synthetic polymeric system will improve its solvent resistant, will it improve its modulus. So, there are very big mechanical advantages, which can be present if we have semi crystalline polymers. And in here I have shown the very complicated structure in which we have helical structures, the sheets, the ribbons, and all of these are present in a complex structure and because of this complex structure protein can serve its function.

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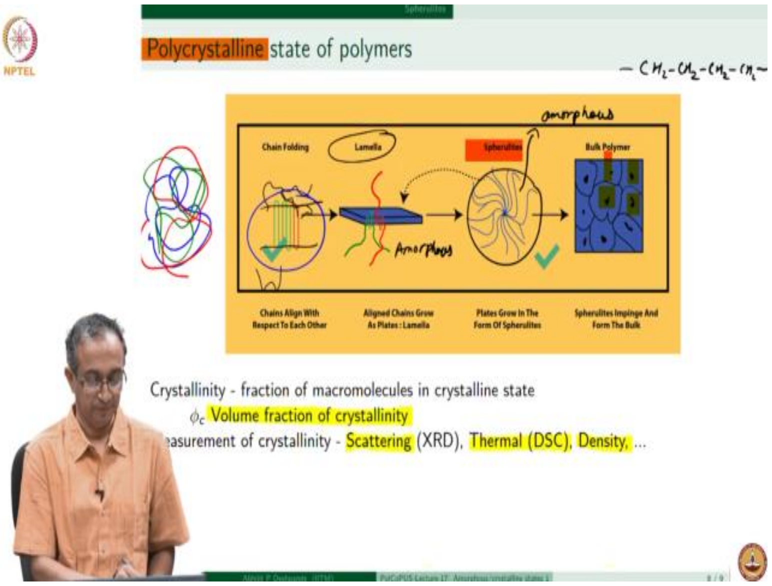

Spherulites

Polycrystalline state of polymers

$— CH_2-CH_2-CH_2-CH_2\sim$

Crystallinity - fraction of macromolecules in crystalline state

ϕ_c Volume fraction of crystallinity

easurement of crystallinity - Scattering (XRD), Thermal (DSC), Density, ...

So, let's look at in summary, what happens in case of polymers when crystal is formed. So, as I have been talking about, we have basically a polymer melt or a solution in which case polymer is present and macromolecules may be entangled with each other. So, with these different molecules which are present, what we have is disorder in the system, but as soon as we lower the temperature or lower the solvent concentration so that saturation is reached, thermodynamic point of view now, Gibbs free energy of a ordered state is favorable. And this is something we will look at in the next lecture, thermodynamic description of crystallization. So, what happens is local segments, of macromolecules can start aligning with each other. Just to understand how this alignment happens, you can also look at how wax forms crystals. Remember wax is nothing but CH2-CH2 repeated throughout, right, which is something very similar to polyethylene. So, a wax molecule which may contain 18 carbon atoms or 27 carbon atoms and so on also forms crystals. So, how are the crystals formed in wax and if you understand wax crystals, then you will be able to understand what this lamella is. So, these chains which are aligning with each other, this grows in 2 dimensions to form what a plate like structure which is called a lamella and these lamellae grow in 3 dimensions in a sphere form and in between there is amorphous region.

So, what happens in each case is a macromolecule starts forming part of this lamella. But then what happens is it goes off and it is part of the amorphous region. Similarly, this because of the entanglements which are present, the macromolecules is there. So, therefore, we will always have amorphous region in between the crystalline platelets and which is what is shown here. So, the blue curves are all the crystalline lamellas which are growing outward in 3 dimension and that's why this is called as spherulitic structure and so, we refer to this as a spherulite. And in case of bulk polymer, we have several spherulites which are impinging on each other, and this is basically the polycrystalline state of a polymer. So, we have semi crystallinity because we have both amorphous and crystalline material, 100% crystallinity is not possible because crystallization starts happening at the rate which it can happen and so, chain start folding locally and start aligning with each other to form a unit cell.

So, in the next lecture, we will also take a look at unit cell in this case. So, in this case, if you look at these chains that is CH2-CH2 going along if it is polyethylene. So, think about it, how will you define a unit cell in case of this kind of crystal. And so, one important characteristic is how much crystallinity is there in the polymer. And how can we measure this crystallinity? Of course, there is thermal possibility because whenever we melt or crystallize heat of enthalpy of crystallization, of enthalpy of melting, enthalpy of fusion is involved. So, therefore, if we measure the heat flow which is in and out of the sample differential scanning calorimetry we can measure the degree of crystallinity. The crystalline portion will then be denser compared to the amorphous portion. So, density of a semi crystalline polymer is a very good indicator of its crystallinity. But, another important feature you can see is whenever there is an order that is present in these systems, there is order at the level of 1 single lamella there is order in terms of how these different platelets are growing and what is the separation between different platelets. So, therefore whenever you have such ordering, I'm sure you can immediately think of scattering. And so, scattering, X ray diffraction is also an important technique to measure the amount of crystallinity in this sample. So, the impinged X ray will get diffracted due to the periodic ordering of atoms and then we can measure the amount of crystallinity.

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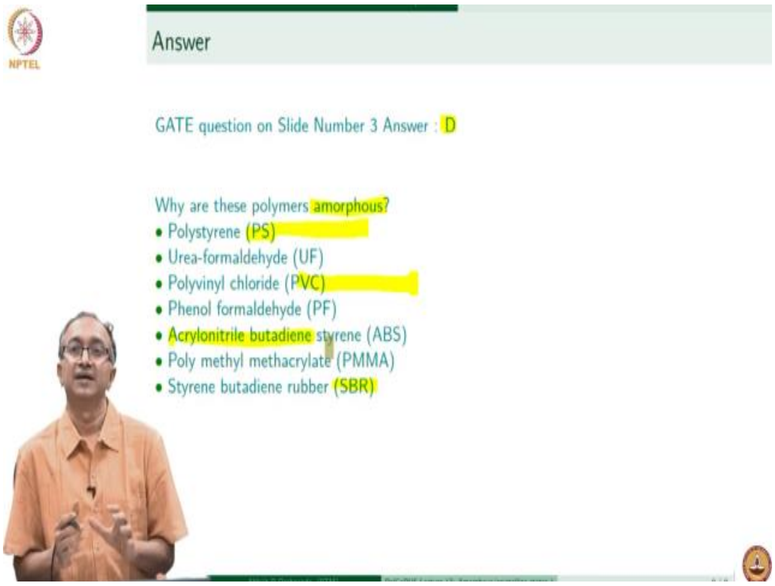

Answer

GATE question on Slide Number 3 Answer : D

Why are these polymers amorphous?
- Polystyrene (PS)
- Urea-formaldehyde (UF)
- Polyvinyl chloride (PVC)
- Phenol formaldehyde (PF)
- Acrylonitrile butadiene styrene (ABS)
- Poly methyl methacrylate (PMMA)
- Styrene butadiene rubber (SBR)

So, with this, just want to end this lecture by looking at the answer to the question which is which group of polymers is semi crystalline set of polymers and you can go back and look and try to see if you could get the answer D. Subsequent question is, you will realize as these are the polymers which are amorphous, from that question all the things which are all the polymers which are mentioned, there are many of them which are not semi crystalline.

So, the question that you ought to ask yourself is why are these polymers amorphous? So, what is about polystyrene that makes it amorphous? What is about polyvinyl chloride that makes it amorphous? Why is a rubber which is a cross link system an amorphous? And if you have looked at how macromolecules fold and form the crystals, as soon as you have crosslink you basically have macromolecules which cannot fold. So, therefore, cross linking is more often than not, it is not observed in case of cross link system. Secondly, whenever you have a bulky group then folding and aligning is not possible. So, if you have chlorine or if you have benzyl group, then folding is not possible. If we have copolymers and blends, then again crystallization is difficult. So, you can go through each of this material, look at the macromolecular structure and in case of cross linking or side groups or blending, you will be able to rationalize why some of these polymer systems cannot form crystals the way we described. So, with this we have finished the introductory aspect of crystallization, we still have 2 more lectures in which we will look at the aspects related to structure and formation of these crystals, the crystallization rate and crystallization kinetics. Thank you.