Polymer Reaction Engineering
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Lecture – 11
Morphology of Polymers

Welcome to the morphological aspect of a polymeric system under the head of polymer reaction engineering. Now morphology in the polymeric system plays a very vital role whether it is a crystallinity, whether it is any kind of a porosity, etc. Then the morphological aspect plays an important role in deciding the end use of polymer whatever you synthesize in due course of time. So, let us start with the polymer morphological system.

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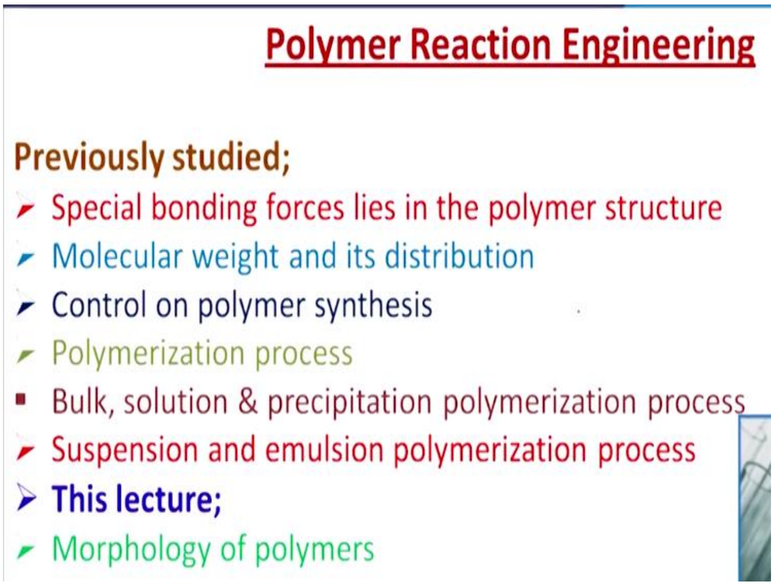

Before we go into this particular lecture let us have that what we have studied about the special bonding forces lies in the polymeric structure. We have talked about the molecular weight and its distribution. We discussed about the various kind of a polymerization process attributed to bulk, solution, precipitation, polymerization, etc. Suspension polymerization emulsion polymerization, etc.

And above all we discussed various kind of a control protocols on the polymer synthesis. So, in this lecture, we are going to discuss about the morphological aspect of polymeric system.

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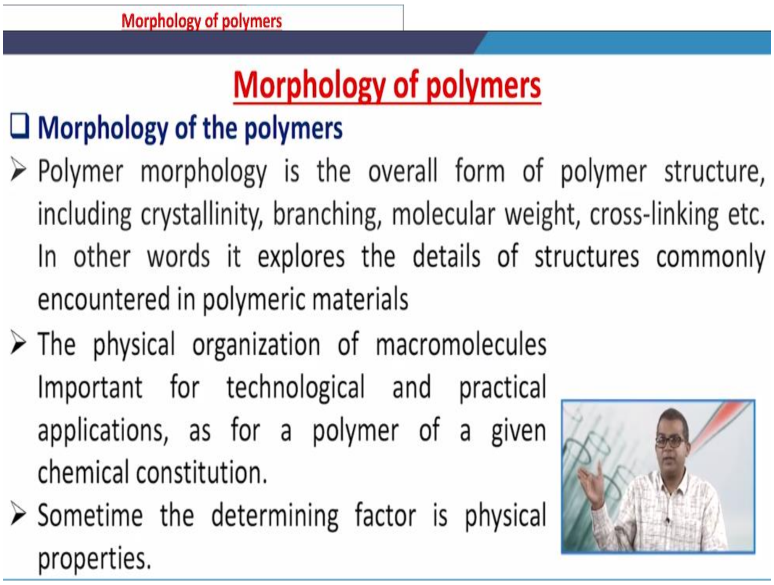

Now let us have a brief outlook about the morphological system of polymers. This is the overall form of a polymer structure. It includes the crystallinity, branching, molecular weight, molecular weight distribution, cross-linking, etc. So, in other word it explores the detail of structure commonly encountered in the polymeric materials and thereby it plays a vital role while the end use of those polymer which you synthesize in due course of time.

Sometimes, it is called as the physical organization of macromolecules or polymer. This is important for technological and a practical application as for a polymer of a given chemical constitution. Now this is again important that the chemical constituent plays a vital role in the structure or architecture of the polymer, ethylene, polyethylene, polypropylene, etc. These are some of the best examples.

Now sometimes, it determines its physical properties too like if you see the cross-linking, cross-linking of polystyrene maybe with the help of diphenyl benzene, etc. it determines the physical property maybe bead like structure, may be film like structure, may be the cross-linking nature, may be stiff or sturdy structure of those polymer. So, you have to manipulate the things to get the desired properties the polymers and that too the morphology is very important.

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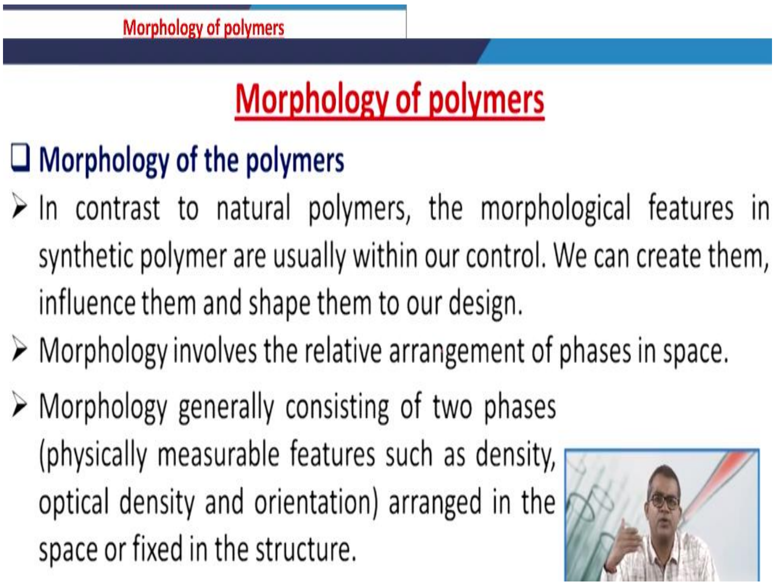

Now sometimes in contrast to natural polymer, the morphological features in the synthetic polymer are usually within our control. Obviously, if you recall the control methodology where you are having an option to change the concentration of solvent, to change the concentration of monomer, to change the concentration of initiator so that you can change the architectural pattern of the polymer.

So, in other words we can create them, influence them, shape them to our design, to our requirement. So, we are the sole controller of the architectural pattern of those polymers. Now this morphology involves the relative arrangement of various phases in space. This generally consists of two phases. Physically measurable features such as density, optical density, orientation, arranged in the space or fixed in the structure.

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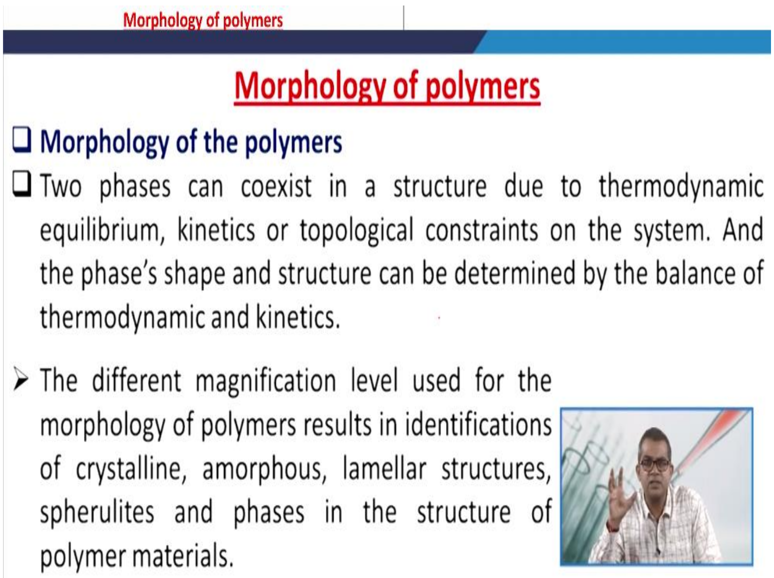

Now these two phases coexist in a structure due to the thermodynamic equilibrium, kinetics, topological constraints on the system. Now the phase's shape and structure it can be determined by the balance of thermodynamic and kinetics. So, by this way you are having the all command in your hand.

Sometimes the different magnification level used for the morphological approach of polymers result in identification of crystalline structure, amorphous, lamellar structure, spherulites and phases in the structure of different type of polymeric materials. So, this is again a very crucial one.

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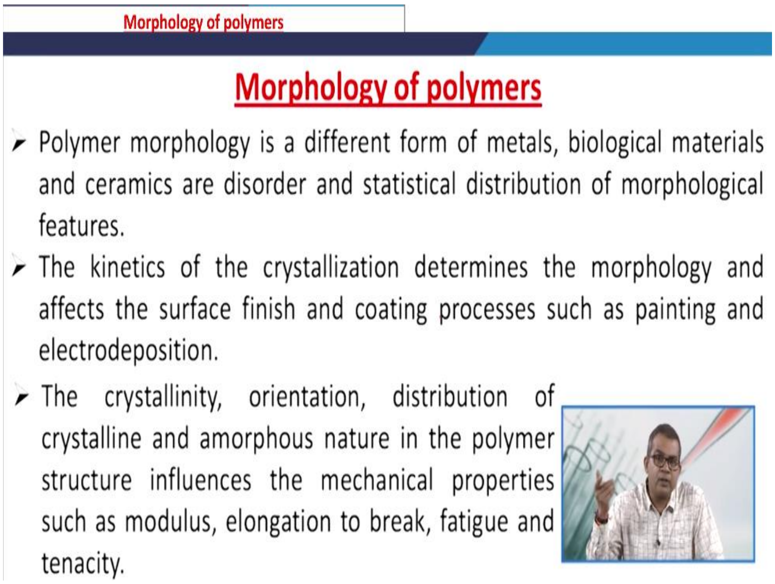

Now polymer morphology is different from whatever you see in the metal, biological materials, sometime the ceramics. Now this is in may be disorder, statistical distribution of morphological features again very important. The kinetics of crystallization sometimes determines the morphology and affects the surface finish, coating process may be like you see in the painting, electrodeposition, sometimes the paper coating, etc.

The crystallinity, orientation, distribution of all kind of crystalline and amorphous nature in the polymer structure influences the mechanical properties such as modulus, elongation to break, fatigue, etc.

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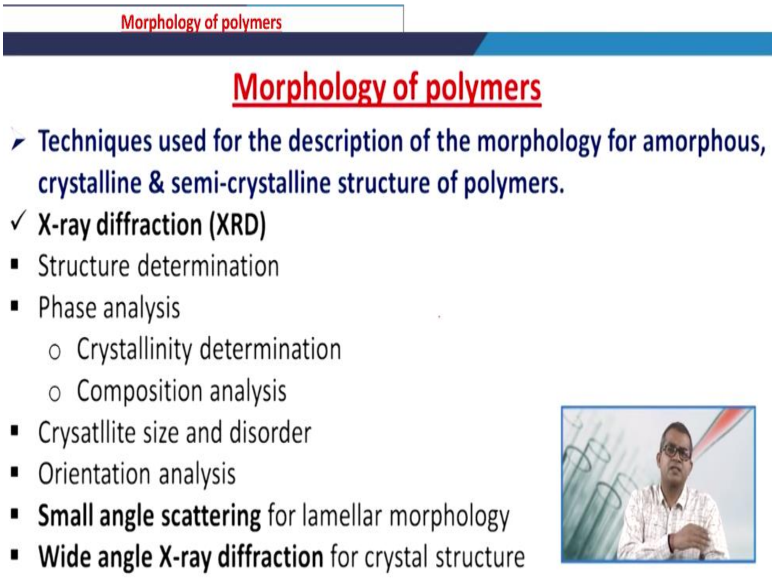

Now there are various techniques used for the description of morphology of amorphous crystalline and semicrystalline structure of polymers. We are going to have some brief overview or you can have a look about the x-ray diffraction. Usually involves the structure determination, phase analysis, may be the crystallinity or determination, composition of analysis, crystallite size and disorder, what kind of a disorder, etc.

Because you see that we had a discussion about the dextro or levo type of isomerization, etc. Then orientation analysis. There are small angle scattering for lamer type of morphology. Wide angle XRD for the crystal structure, etc.

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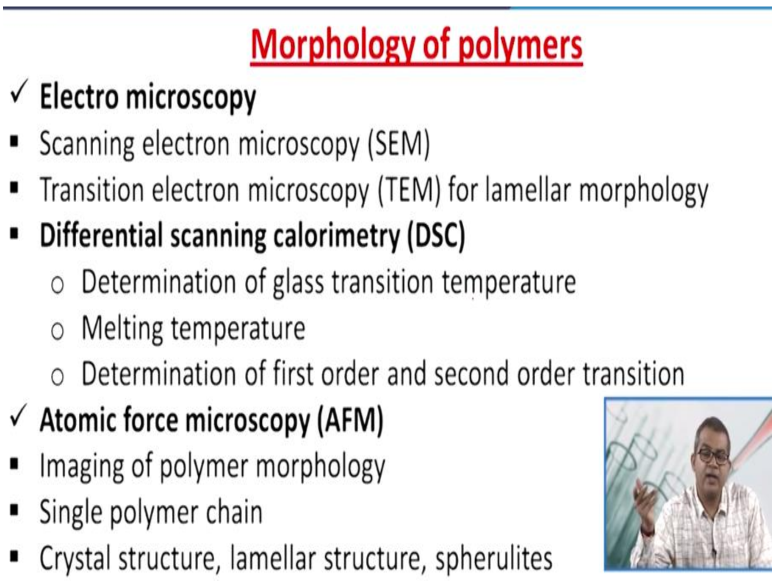

Sometimes, the electron microscopy is being used for the analysis of morphological structure of polymers. There are two type of things. Scanning electron microscopy and transition electron microscopy for the lamellar morphology. Then DSC or differential scanning calorimetry being used for the determination of glass transition temperature, melting temperature because melting temperature is again very important for the processability of the polymer.

Determination of first order, second order transitions, etc. AFM atomic force microscope is again a very vital tool for deciding the fate of a polymer that is imaging the polymer morphology. Single polymer chain you can visualize the crystal structure, lamellar structure, spherulites, etc.

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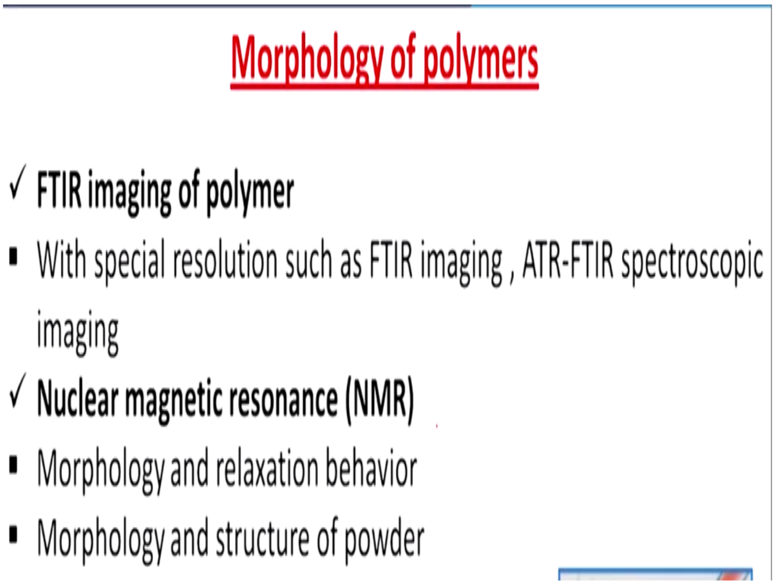

FTIR, in the previous lectures we discussed about the functionality of the polymeric system or polymers. So FTIR, Fourier transform infrared spectroscopy plays a vital role in this aspect with the special resolution as FTI imaging, ATR-FTIR, etc. NMR usually recites the morphological and relaxation behavior of your polymeric chain and morphological and structural aspect of your powder.

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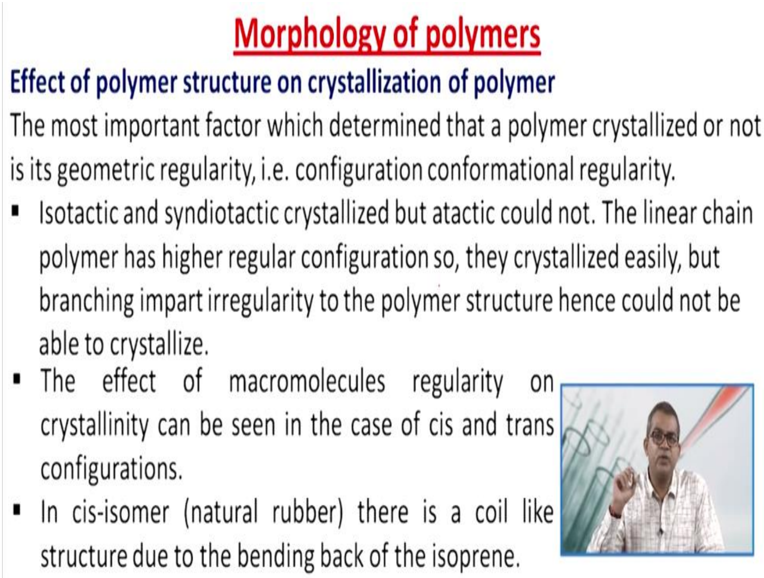

Now just go back to the morphological study of polymeric system. They can be classified in as amorphous and crystalline. Let us have look about the crystalline behavior of polymer first. The atom or molecule they are inbuilt in solid material. They are held together with stabilizing force between them like this such as primary chemical bonds which we discussed in the first lectures metal or ionic, then secondary bonds like van der Waals forces and hydrogen bonding, etc.

We have already discussed this thing prior. These molecules interact with the neighboring molecules in a regular arrangement with minimum total intermolecular energy. Such type of arrangement is usually the crystalline one. These smallest representative groups of atom and molecules they are called unit cells.

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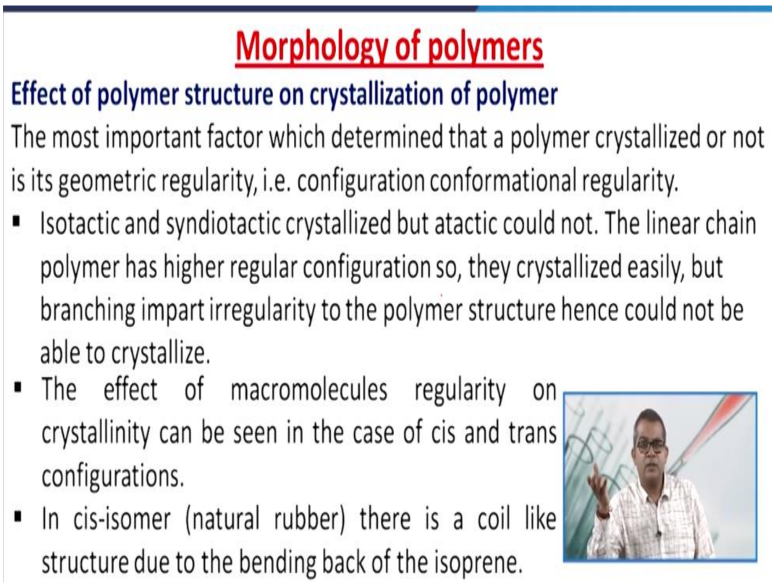

Now there are effect of polymeric structure on crystallinity of the polymer. Now let us have a look about the effect of polymer structure on crystallization of polymer. The most important factor which determined that the polymer crystallized or not is its geometric regularity that is the configuration conformational regularities, etc. of these units. Now isotactic and syndiotactic crystallized but atactic could not.

So, the property of the polymer may become different though the molecular structure and molecular ingredients are same, but sometimes the properties may be entirely different. The linear chain polymer has higher regular configuration. So, they crystallized easily, but branching impart irregularity to the polymer structure hence could not be able to crystallize. Now the effect of molecules regularity on the crystallinity can be seen in case of cis and trans configurations.

We have already discussed the cis and trans isomerization in the previous lectures. Now cis isomer like natural rubber there is a coil like structure due to the bending back of one example is isoprene.

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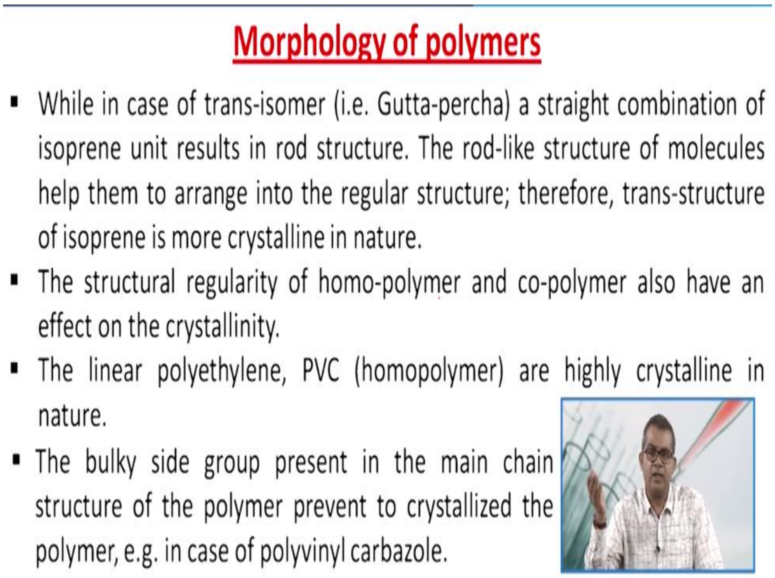

Now if you talk about the case of trans-isomer like gutta-percha, straight combination of isoprene unit results in a rod-like structure as against the bend like structure in the previous one. Now these rod-like structure of molecule help them to arrange into the regular structure. Therefore, transit structure of isoprene is more crystalline in nature. So, this is the difference. See the backbone is same, but this is a difference.

Now the structural regularity in the homo-polymer and a co-polymer also have an issue on the crystallinity. The linear polyethylene that is PVC or sometime homopolymer they are highly crystalline in the nature. So, the bulky side group usually they present in the main chain structure of the polymer. They prevent to crystallize the polymer in case of say polyvinyl carbazole. This is having very wide industrial application in different part of usability.

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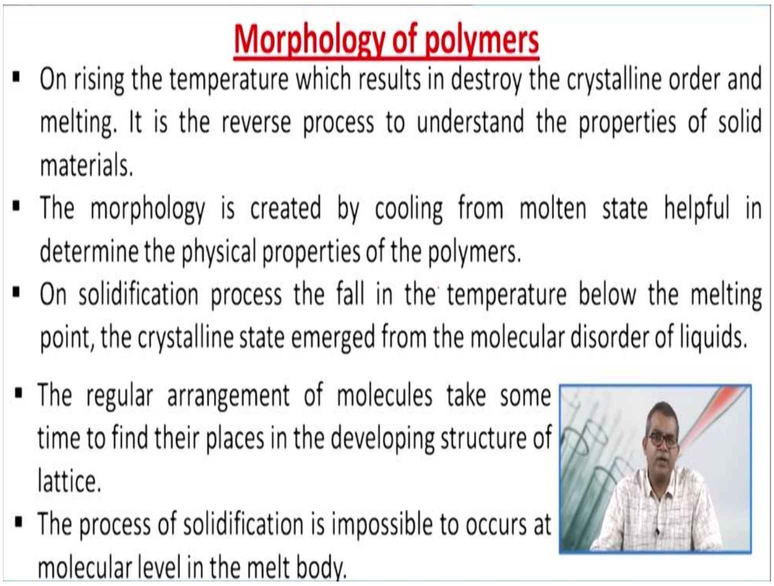

So, there may be certain effects attributed and one more common effect is the temperature. So, on the rising the temperature which may result in the destroy the crystallinity order and melting it. We observed with the help of this particular pen, although the example is bit different. Now it is the reverse process to understand the properties of solid material and sometimes you may see that solid polymer particle may have a tendency to melt.

The morphology morphologies created by cooling from molten state usually helpful in determining the physical properties of the polymers. So, upon solidification process, the fall in temperature below the melting point, the crystalline state emerged from the molecular disorder of liquid. So, there may be an irregular tendency of chain to solidify or to seize its movement may be like this.

Sometimes they may be frittering like this and then if you decrease the temperature then they may be stagnant at any particular level. So that is the issue. Now the regular arrangement of molecules takes some time to find their places in developing the structure of lattice. Now the process of solidification is impossible to occur at molecular level in the melt body.

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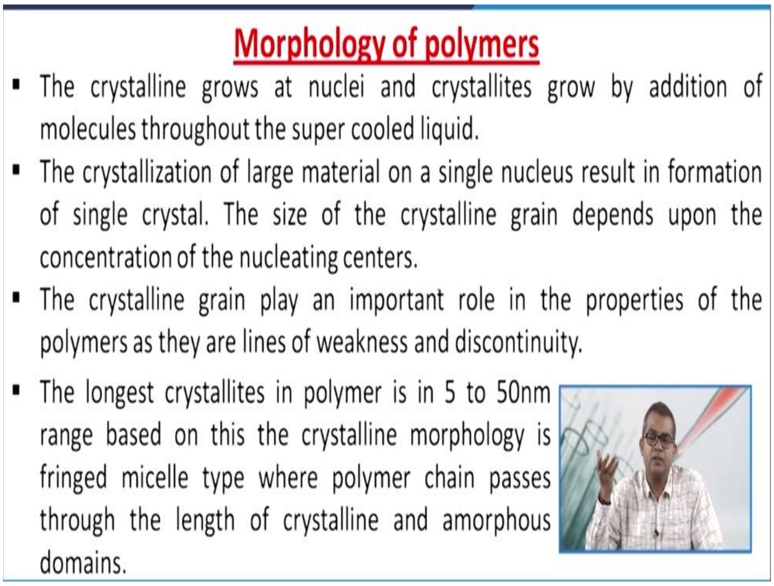

Now the crystalline grows usually, somebody may ask that how this crystalline structure grows. So, usually the crystalline grows at nuclei and crystallite grow by the addition of molecule throughout the super cooled liquid. You know that glass is a super cooled liquid. It is not the solid, it is a super good liquid. So, the crystallization of a large material on the single nucleus sometimes result in the formation of a single crystal.

And the size of that particular crystalline grain depends on the concentration of the nucleating center. So, it may be like this that nuclei and all the things are growing to that particular nucleating center. So crystalline grain plays an important role in the properties of the polymer as the they are lines of a weakness or discontinuity.

So, the longest crystalline polymer is usually in the range of 5 to 50 nanometer range based on this crystalline morphology is fringed micelle type where the polymer chain passes through the length of crystalline and amorphous domain.

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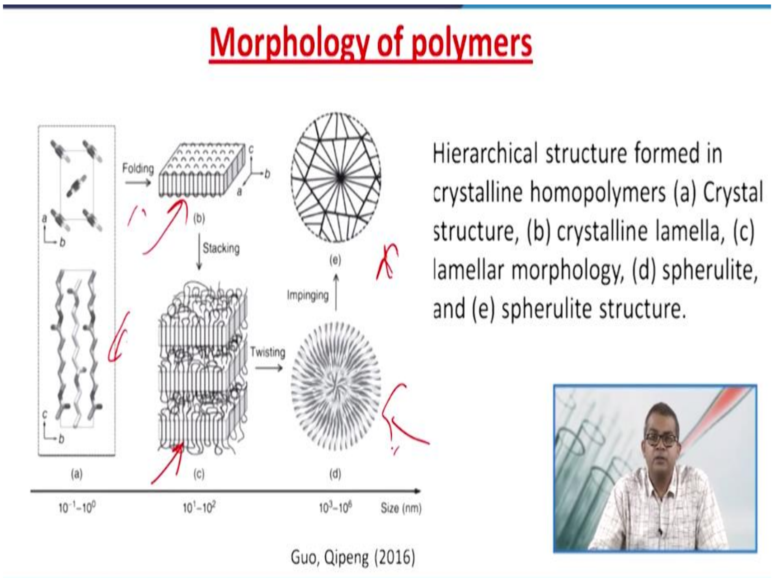

Now this is one particular hierarchical structure usually formed in the crystalline homopolymer. You can see that sometimes these are the crystal structures formed and then this is the crystal lamellae and then this is the lamellar morphology and spherulites you can see over here this is spherulite structures, etc. So, this is you can see just to visualize that what is the impact of different type of morphological approach in polymer system.

Let us have a discussion about the lamellar structure. Now the crystalline domain they are made up of flat ribbon like structure like see you can see in this particular figure.

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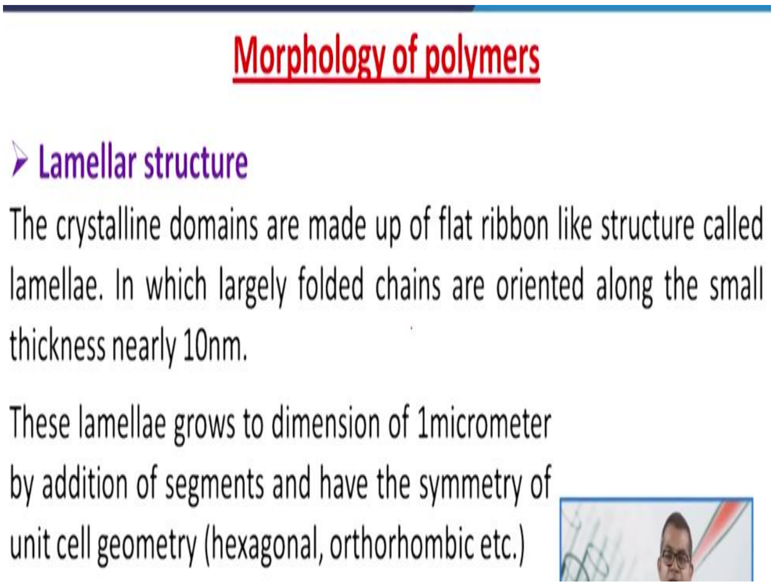

So, they are the flat ribbon like a structure they, are called the lamellae. In which largely folded chains are oriented along the small thickness that is usually 10 nanometers. Now these lamellae grow to dimension of say 1 micrometer by addition of segments and have a symmetry of unit cell geometry, may be hexagonal, may be orthorhombic, etc.

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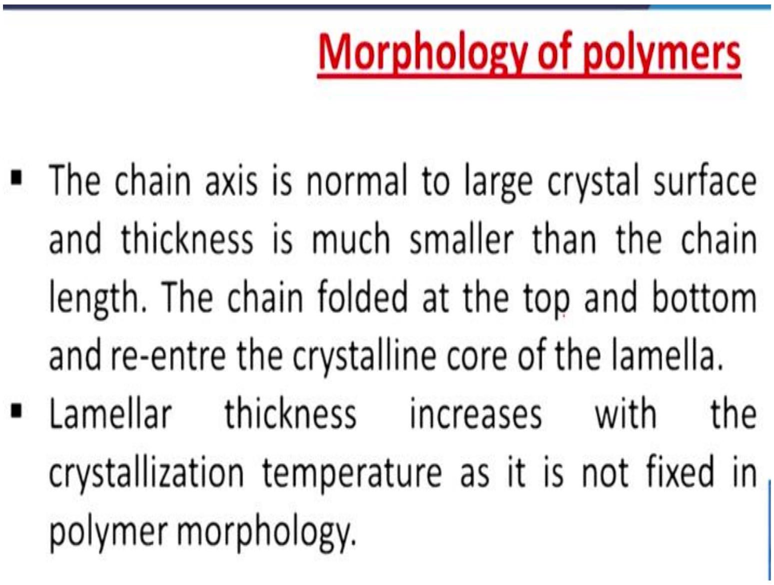

Now this chain axis is normally to large crystal surface and thickness is much smaller than the chain length. So, usually the chain folded at the top like this, bottom and then re-enter into the crystalline core of lamellae. So lamellar thickness increases with the crystallization temperature as it not fixed with the polymer morphology. So, you can visualize the crystallization temperature and then you assess the morphology of that polymer particle.

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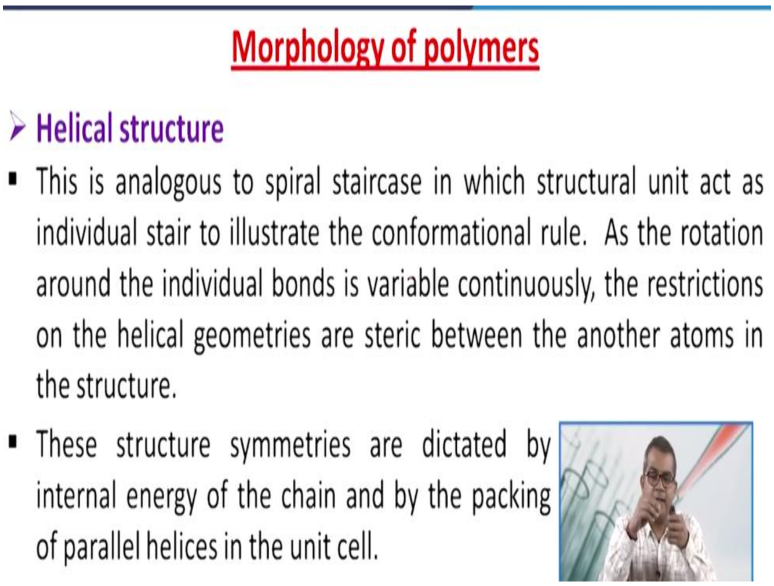

Another important structure is the helical structure. Usually, it is analogous to the spiral staircase in which the structural unit act as individually stair to illustrate the conformational rule. Now as the rotation around the individual bond is variable continuously, the restrictions on the helical geometries are steric between other atoms in the structure. It is just like this one.

Now these structural symmetries are usually dictated by internal energy of the chain, may be attributed to the bond, may be attributed to some other force and the packing of parallel helical in the unit cell.

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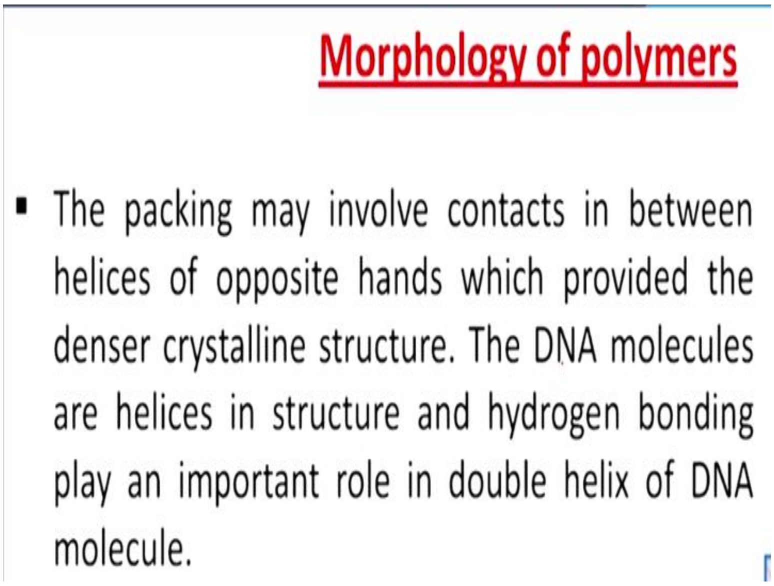

Sometimes these packing may involve contact in between the helices of the opposite hand which provided the denser crystalline structure. One best example is the DNA molecule. The DNA molecules are helix in the structure and hydrogen bonding play an important role in the double helix of DNA molecule.

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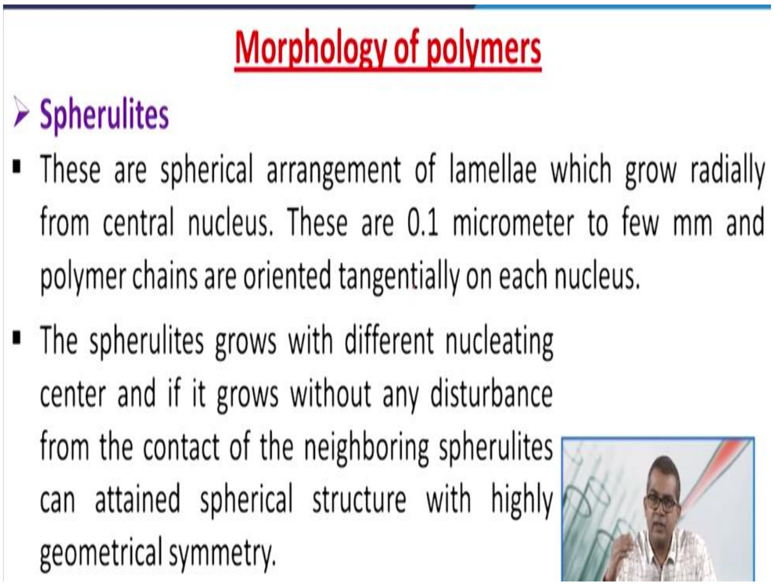

Now, let us have a brief discussion about the spherulites. Now these are the spherical arrangement of lamellae which grow readily from the central nuclei like this. This is your central nuclei and you can grow like this. Now these are 0.1 micrometer or to few millimeters and the polymer chains usually are oriented tangentially to each nucleus like this. Now spherulites grow with a different nucleating center.

Now if it grows without any disturbance from the contact of neighboring spherulites, they can attain the spherical structure with high geometric symmetry.

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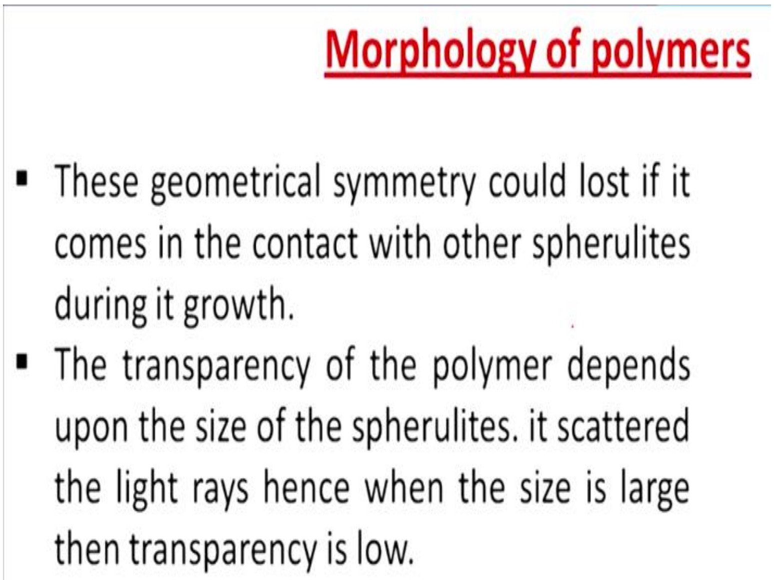

Now this is you can say a very stable structure. Now, these geometrical symmetries could be lost if it comes in contact with other spherulites during its growth. Now the transparency in the polymer usually depends upon the size of spherulites. It scatters light rays, so sometimes the size is larger than the transparency is usually low.

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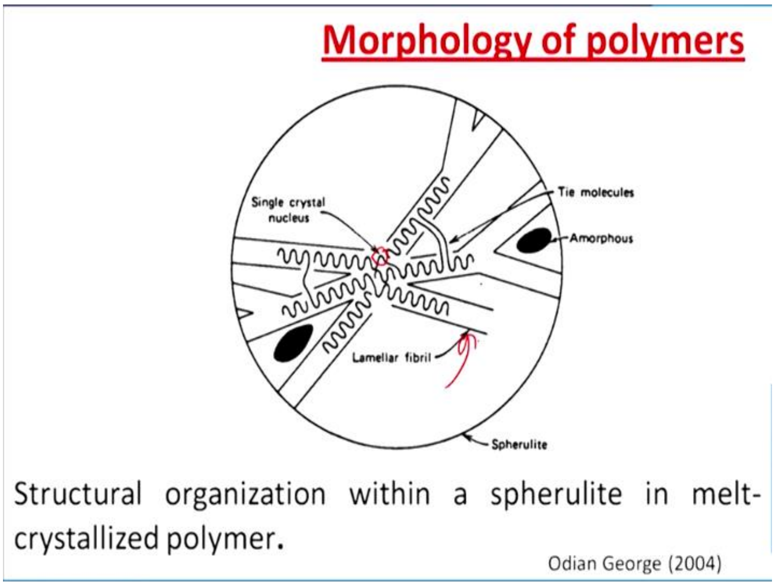

Now you can see this morphology of the spherulite. Now this is you see that the single crystal nucleus and there are various kind of lamellar fibrils like here you can see like this. Now here this is the tie molecules and you see that these are some spheric amorphous sides. So, this the spherical spherulites within the melt crystallized polymer.

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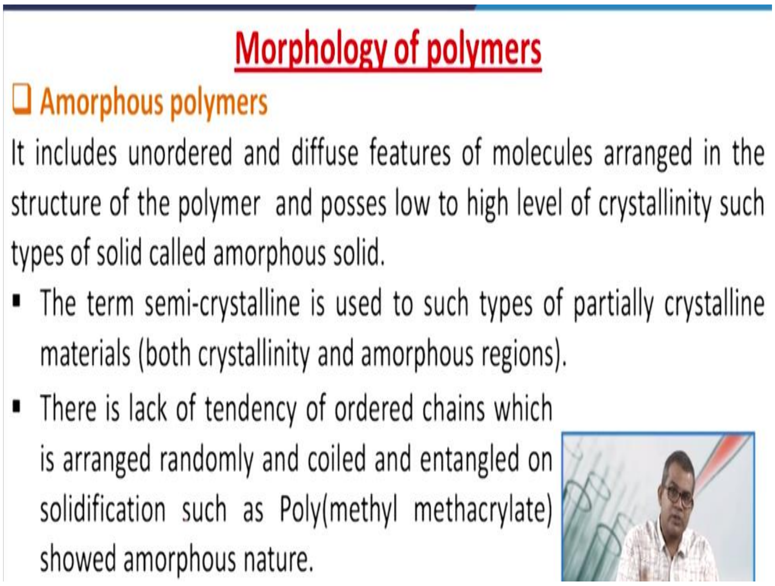

Now last in segment is the amorphous polymers. Now it is an unordered and usually diffuse featured molecule arranged in the structure of a polymer. This possesses a low to high level of crystallinity and this type of the solid structure called the amorphous solid. Now the term semi-crystalline is usually used to have such type of partial crystalline materials, both crystallinity and amorphous regions are common in this nature.

Now there is a lack of tendency of the ordered chain which is arranged randomly coiled and sometimes entangled on the solidification. You may observe this type of phenomenon in polymethyl methacrylate, etc.

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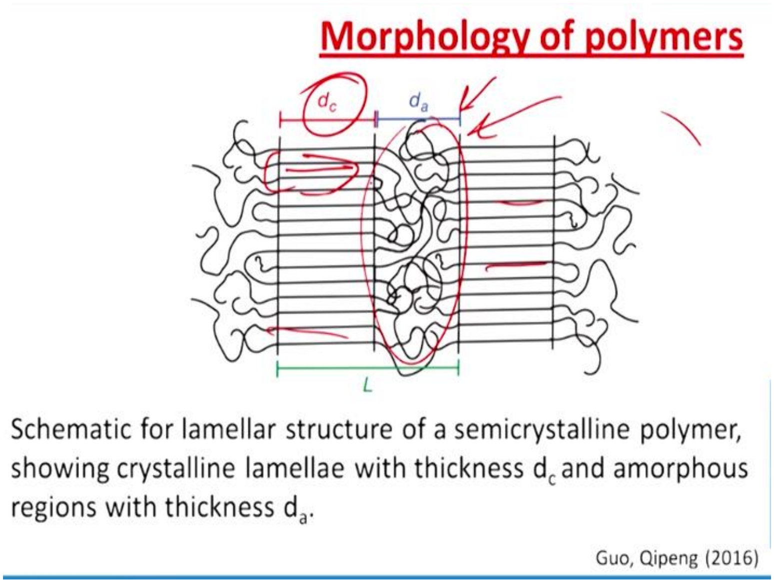

Now here you can see this is the schematic diagram of lamellar structure of semicrystalline polymer. This shows the crystalline lamellae with the thickness of d_c. This is the thickness and amorphous region with the thickness of this one. So, you can see you can visualize the things they are entangled in nature and they are you can see they are having the regular array in this one.

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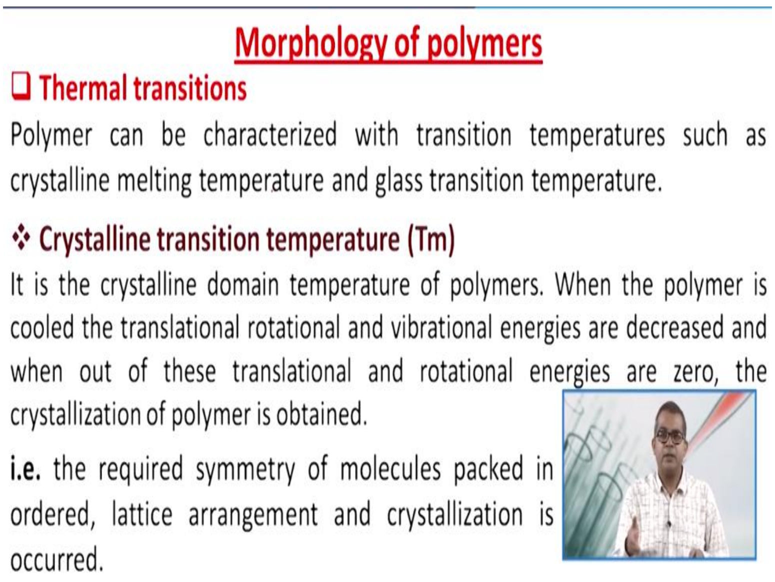

Another aspect which we look into this morphology aspect is the thermal transition. Now this polymer can be characterized with the transition temperature such as crystalline melting temperature or a glass transition temperature. We discussed a brief about this glass transition temperature plays a vital role in deciding the properties of the polymer. Now the crystalline transition temperature it is the crystalline domain temperature of polymer.

When the polymer is cooled the translational rotation and vibrational energy are usually decreased. Now usually when out of these transitional and rotational energies are 0, the crystallinity of the polymer is obtained that is the required symmetry of molecule packed in ordered, lattice arrangement and crystallization is occurred.

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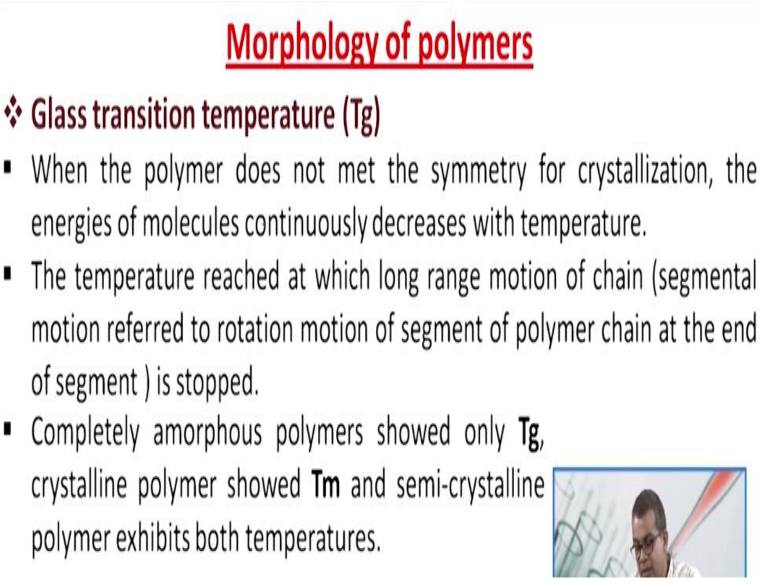

Now the glass transition temperature is very important. Now we have already discussed couple of things related to the glass transition temperature. So, when polymer does not meet the symmetry of crystallization, the energies of molecules continuously decrease with the temperature. So, their motion, their movement are sometimes one stage achieves, then their motions are seized.

So, the temperature reached at which the long-range motion of chain may be segmental motion referred to the rotation motion of segment of polymer chain at the end of segment is stopped. So, it may acquire the condition of a super cooled liquid. So, if you provide certain quantity of heat to this, then this chain segment moment they start movement and then they try to align themselves with respect to the or they try to achieve the more relaxed structure that is the melting.

Now the completely amorphous polymers showed only T_g that is the glass transition temperature, crystalline polymer showed the Tm and a semicrystalline polymer exhibits both the temperature. So, we will discuss this thing and other things.

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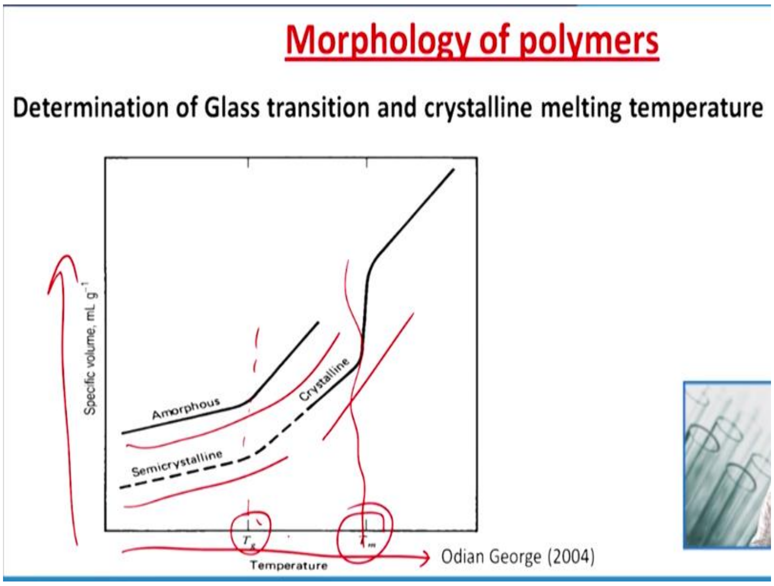

Now here you can see the determination of a glass transition and crystalline melting temperature. Here you see that if you keep on increasing the temperature and specific volume the y axis, you see the behavior of amorphous, semicrystalline and crystalline polymer with respect to this one. And this particular point when they acquire their chain movement starts. That means they acquire the flow character that is called the glass transition temperature and when it takes the drastic change then this is called the T_m.

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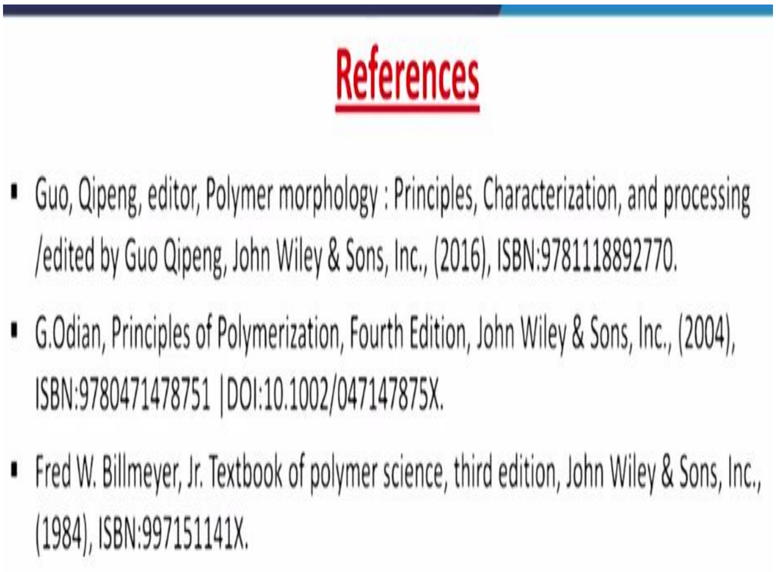

So, in this particular approach or in this particular lecture, we discussed about the morphological issues of polymeric system and we gave major impetus towards the importance of morphological studies in the polymeric system. We discussed about the amorphous crystalline system of polymeric system because they play a very vital role in the further processability of the polymerization process because ultimately our main objective is to get the useful product from those polymerization systems.

Now we discussed about the because see polymeric systems are very vast in nature, sometimes you require some surface properties, sometimes you may require some diffuse properties, etc. so every time the morphology plays a very vital role. We had a brief glimpse about the different type of tools being used to analyze the morphological character of polymer being developed in due course of time.

So, though the morphological study is a very vast field, but we try to give a brief crispy thing related to the morphological study of this system. Now if you wish to have a further study, then you can seek the help of these references which are listed in this particular slide. And the subsequent lectures we will discuss the importance of these morphology in detail because this is the in-situ phenomena of various polymerization processes. Thank you very much.