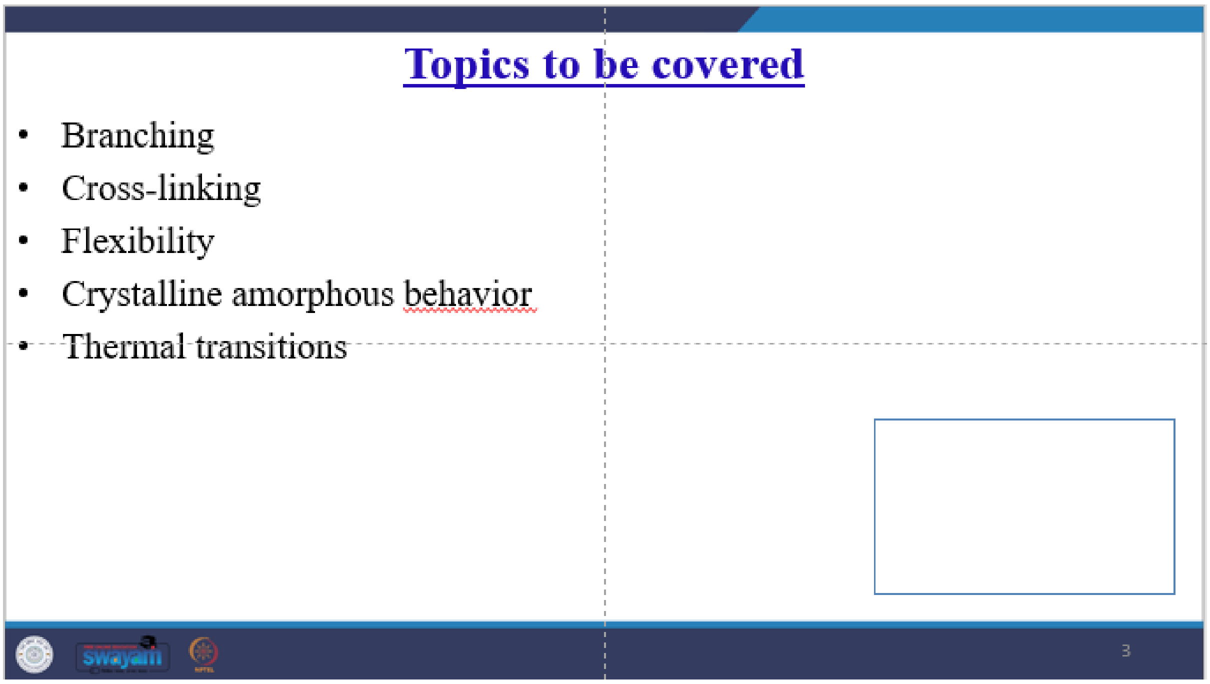
Polymer Process Engineering
Prof. Shishir Sinha
Department of Chemical Engineering
Indian Institute of Technology-Roorkee
Lecture – 04
CHARACTERISTICS OF POLYMERS-II

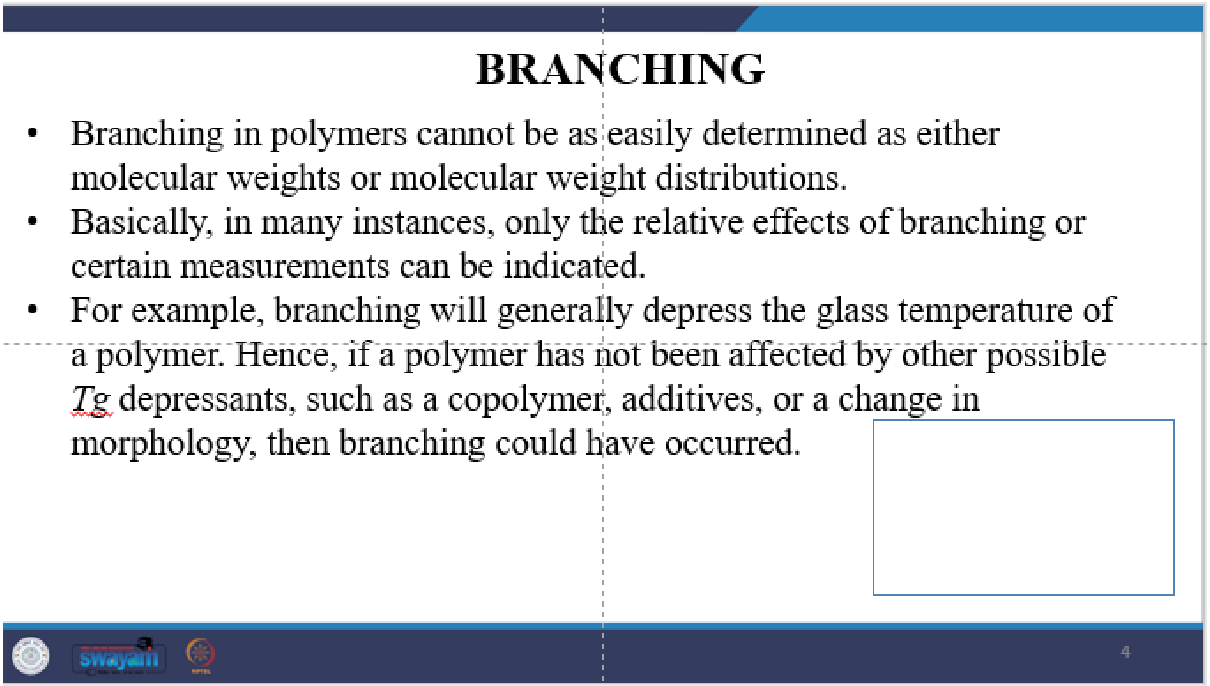
Welcome to another segment of Polymer Process Engineering. Here, we are going to discuss the second part of the characteristics of polymers. You see in the previous lecture we discussed different aspects pertaining to the characteristics of polymers and most importantly we discussed molecular weight which is very integral part of the characteristic determination and molecular weight distribution. In this particular segment, we are going to discuss the branching, cross-linking, crystallinity, crystallinity, and amorphous behaviour of polymers and then thermal transitions. So, let us take the branching. The branching in a polymer cannot be readily determined as either molecular weight or molecular weight distribution.



Topics to be covered

- Branching
- Cross-linking
- Flexibility
- Crystalline amorphous behavior
- Thermal transitions

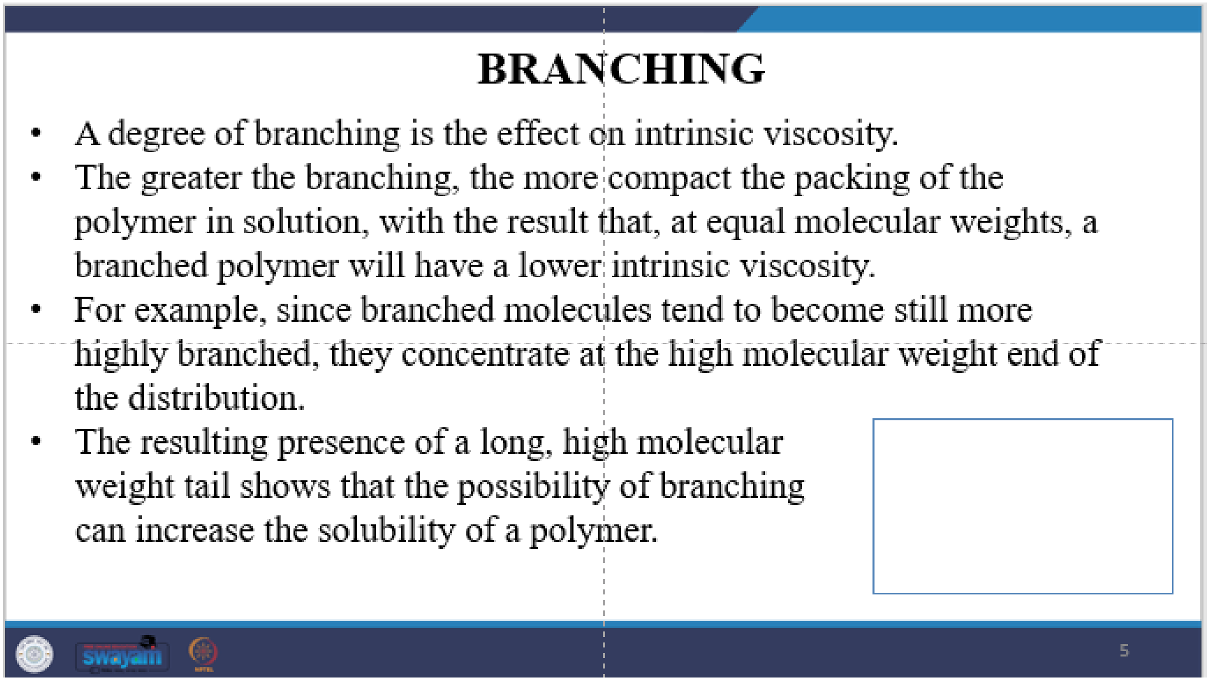
So, basically, in different instances, the relative effect of branching or certain measurements can be indicated. Let us take an example: branching will generally depress the glass transition temperature of a polymer. Now, glass transition temperature is a very important thing where, upon heating, the polymer starts the melt. That is the triggering point and that depends on the molecular weight. So, if a polymer has not been affected by other possible glass transitions in a depressant such as copolymer additive or change in the morphology, the branching could have occurred.



BRANCHING

- Branching in polymers cannot be as easily determined as either molecular weights or molecular weight distributions.
- Basically, in many instances, only the relative effects of branching or certain measurements can be indicated.
- For example, branching will generally depress the glass temperature of a polymer. Hence, if a polymer has not been affected by other possible *Tg* depressants, such as a copolymer, additives, or a change in morphology, then branching could have occurred.

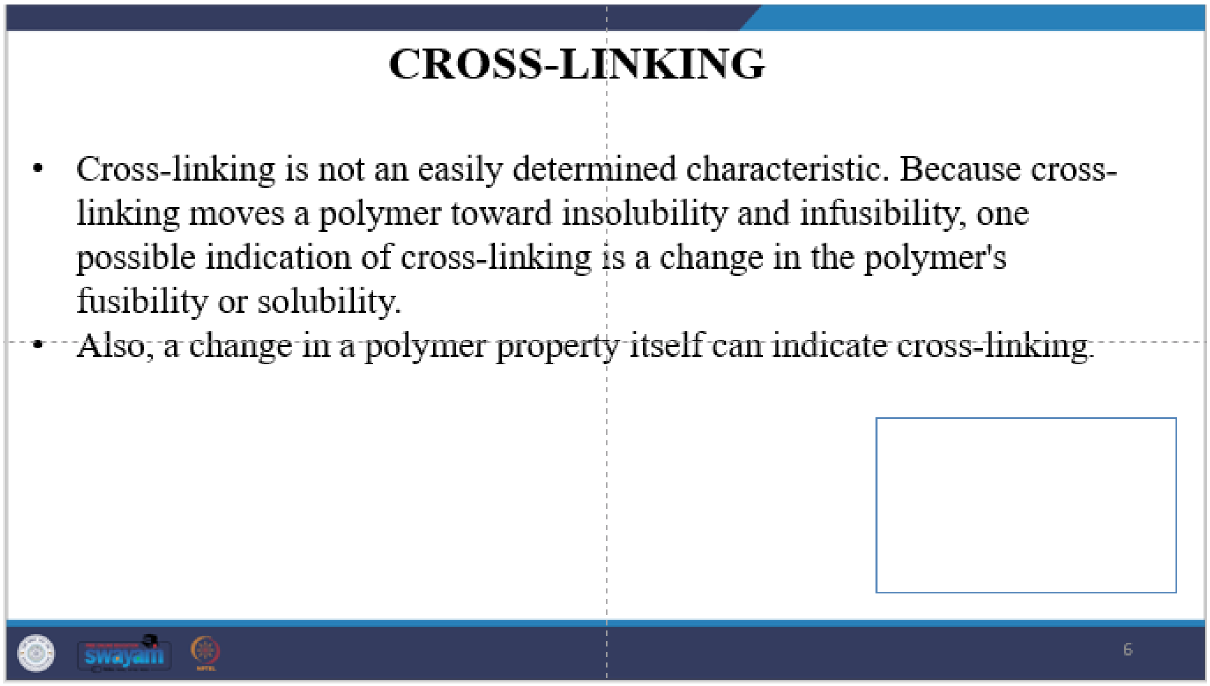
So, the degree of branching is the effect of intrinsic viscosity. Now the greater the branching the more compact the packing of the polymer in the solution. It is like this that we have different chains, and therefore the branching is on them, and the more compact structure would be there, and that results the equal molecular weights. So, branch polymer will have a lower intrinsic viscosity. So, when we determine the molecular weight distribution through the viscometer it plays a vital role.



BRANCHING

- A degree of branching is the effect on intrinsic viscosity.
- The greater the branching, the more compact the packing of the polymer in solution, with the result that, at equal molecular weights, a branched polymer will have a lower intrinsic viscosity.
- For example, since branched molecules tend to become still more highly branched, they concentrate at the high molecular weight end of the distribution.
- The resulting presence of a long, high molecular weight tail shows that the possibility of branching can increase the solubility of a polymer.

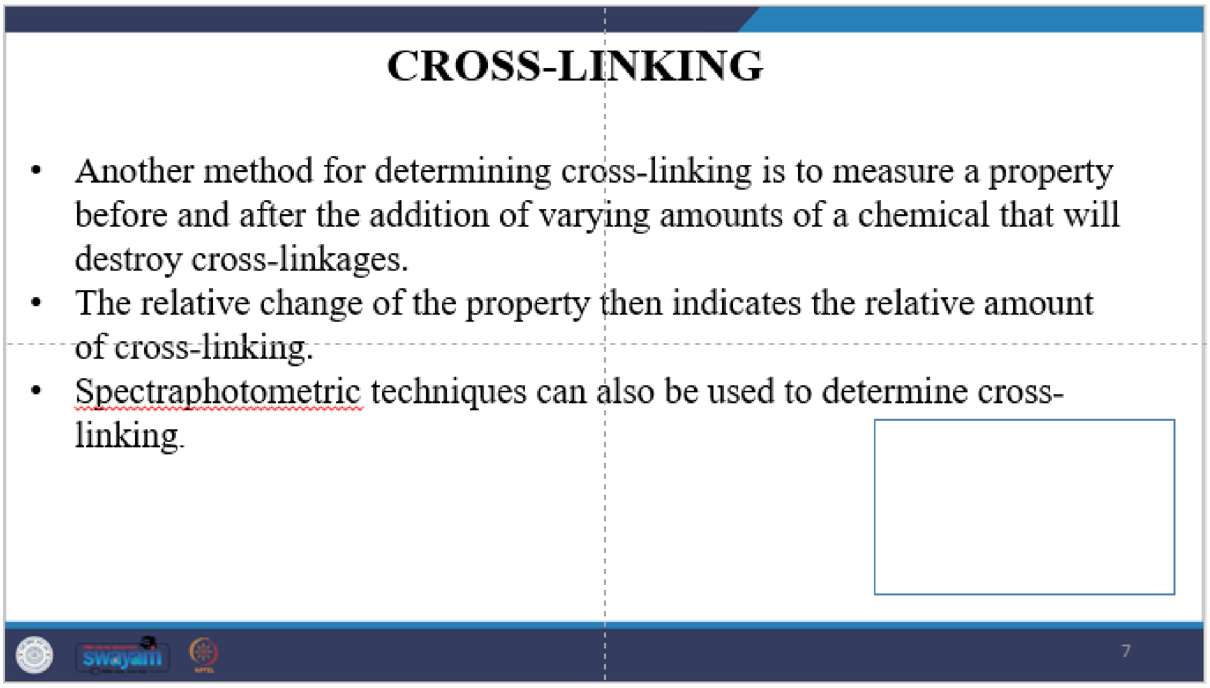
Now let us take an example since the branched molecules tend to become still more highly branched they concentrate at a high molecular weight and of distribution. So, the resulting presence of a long high molecular weight tail reflects the possibility of branching. This can increase the solubility of a polymer. Let us take up the cross-linking. Now, crosslinking is not an easily determined characteristic because crosslinking moves a polymer towards insolubility or infusibility.



CROSS-LINKING

- Cross-linking is not an easily determined characteristic. Because cross-linking moves a polymer toward insolubility and infusibility, one possible indication of cross-linking is a change in the polymer's fusibility or solubility.
- Also, a change in a polymer property itself can indicate cross-linking.

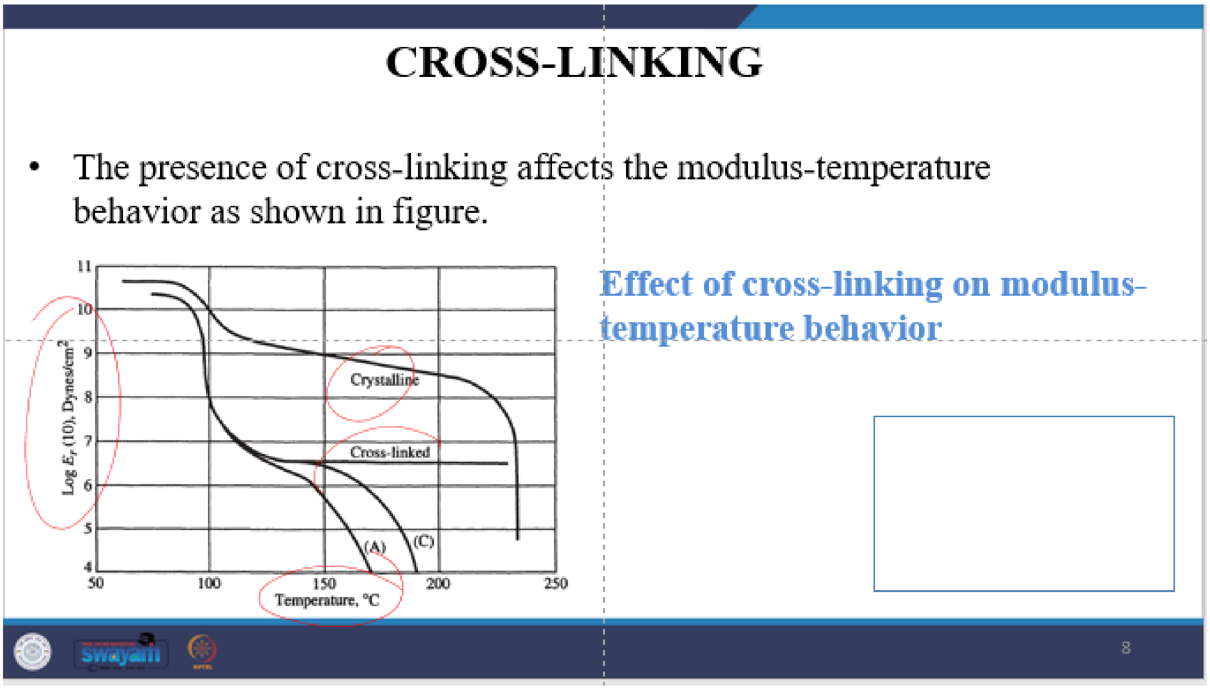
So, because of the presence of a network structure, one possible indication of crosslinking is a change in polymer feasibility or solubility. Now, a change in a polymer property itself can indicate the crosslinking. So, another different method is there for the determination of the crosslinking. One method is to measure a property before and after the addition of varying amounts of chemicals that will destroy the cross-linkage so that they can break this network and then determine. The relative change of property indicates the relative amount of cross-linking.



CROSS-LINKING

- Another method for determining cross-linking is to measure a property before and after the addition of varying amounts of a chemical that will destroy cross-linkages.
- The relative change of the property then indicates the relative amount of cross-linking.
- Spectraphotometric techniques can also be used to determine cross-linking.

Some of the spectrophotometric techniques are available to determine the crosslinking aspects. Now, here you see that different types of crosslinking affect the modulus temperature. Now here, the temperature versus the crystalline crosslinking different type of effects is been discussed in this particular plot. The flexibility, the chain flexibility affects the ability of the polymer to crystallize. The excessive flexibility in a polymer chain, as in the polysiloxanes and natural rubber leads to an inability of the chains to pack.

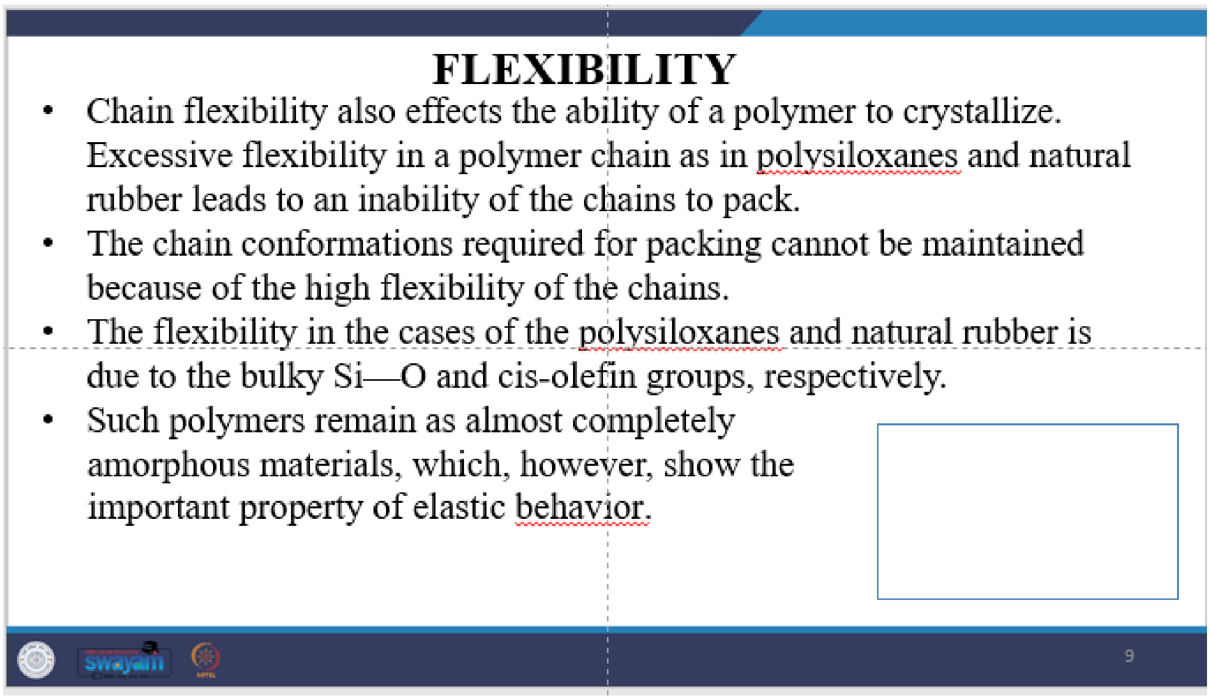


CROSS-LINKING

- The presence of cross-linking affects the modulus-temperature behavior as shown in figure.

Effect of cross-linking on modulus-temperature behavior

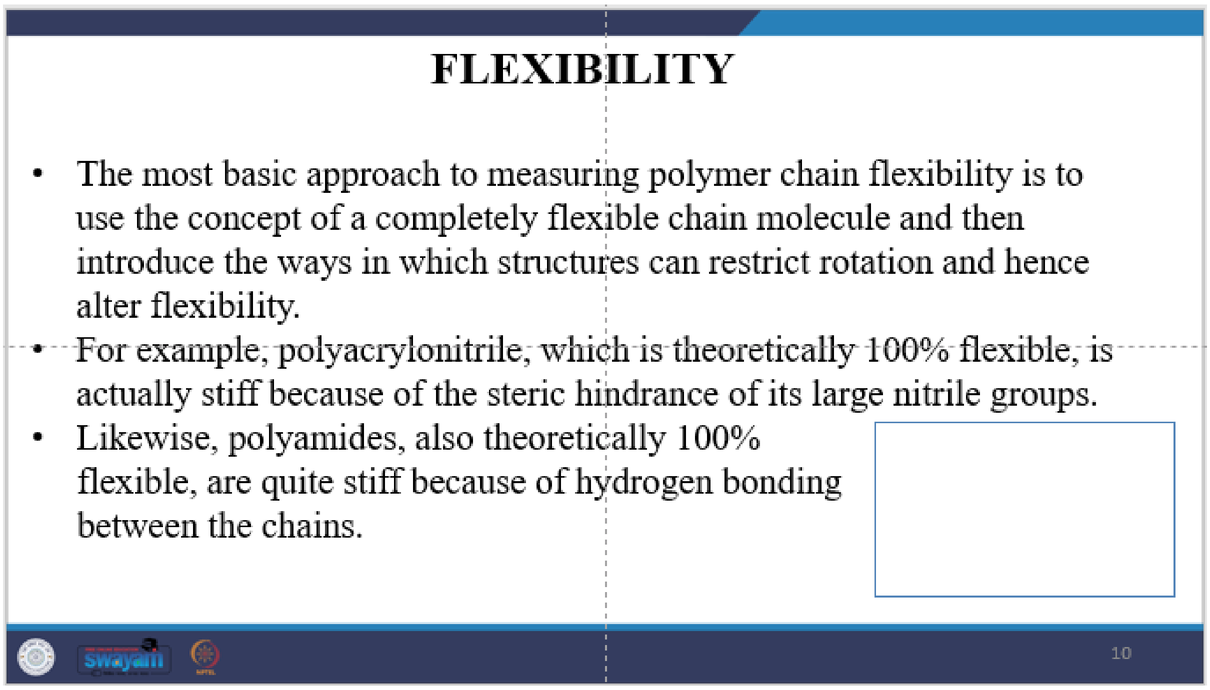
The chain conformation with this may require the packing, which cannot be maintained because of the high flexibility of the chains. The most basic approach to measuring the polymer chain flexibility is to use the concept of a completely flexible chain molecule. Then, introduce the way in which the structure can restrict the rotation and hence alter flexibility. So, we have the say in a hypothetical way: we have the complete flexible system, and then you restrict the flexibility, you restrict the motion of the chains, you restrict the rotation of the chains, and then alter the flexibility, and you measure all these things. Like polyacrylonitrile which is theoretically 100 percent flexible, is actually stiff because of the steric hindrance of its large nitrile groups.



FLEXIBILITY

- Chain flexibility also effects the ability of a polymer to crystallize. Excessive flexibility in a polymer chain as in polysiloxanes and natural rubber leads to an inability of the chains to pack.
- The chain conformations required for packing cannot be maintained because of the high flexibility of the chains.
- The flexibility in the cases of the polysiloxanes and natural rubber is due to the bulky Si—O and cis-olefin groups, respectively.
- Such polymers remain as almost completely amorphous materials, which, however, show the important property of elastic behavior.

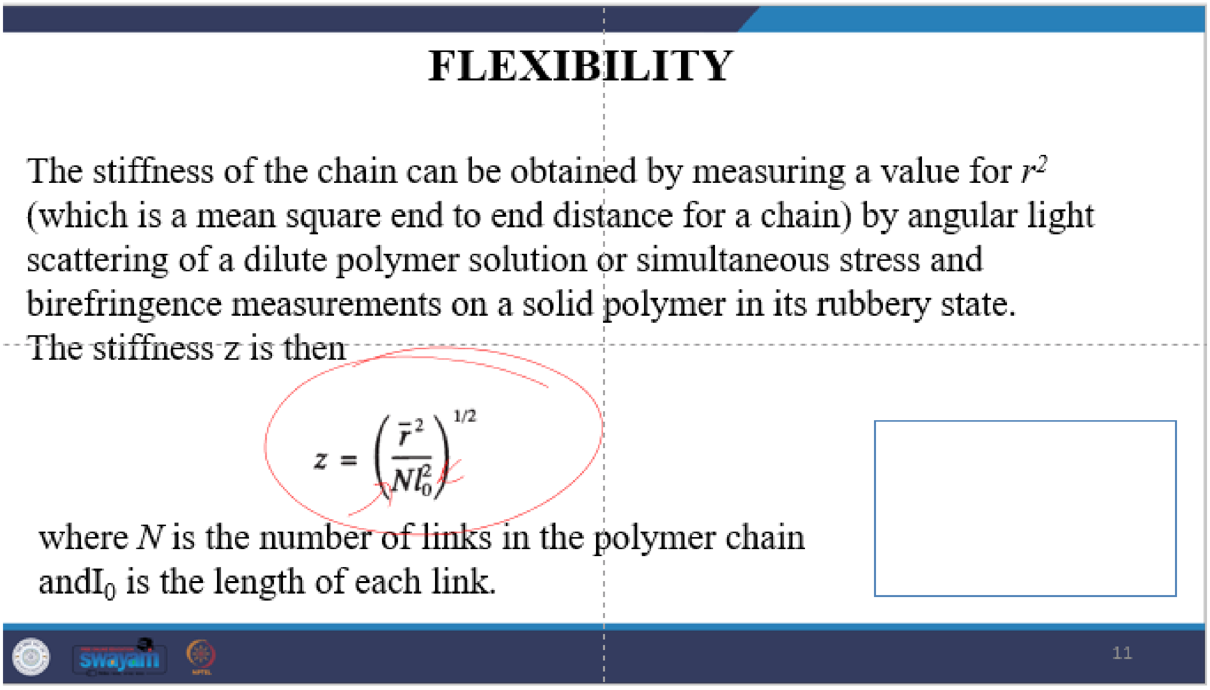
So, steric hindrance causes stiffness. Now polyamides are again theoretically 100 percent flexible but they are quite stiff because of the hydrogen bonding between the chains. So, all these things, so suppose if you make if you wish to make them 100 percent flexible, you need to destroy the hydrogen bonding, or you need to eliminate the steric hindrance. The stiffness of the chain can be obtained by the value of R square, which is the mean square end-to-end distance of a chain. Now, this is by the angular light scattering of a dilute polymer solution or simultaneous stress and then Befringement measurement on a solid polymer in its rubbery stage.



FLEXIBILITY

- The most basic approach to measuring polymer chain flexibility is to use the concept of a completely flexible chain molecule and then introduce the ways in which structures can restrict rotation and hence alter flexibility.
- For example, polyacrylonitrile, which is theoretically 100% flexible, is actually stiff because of the steric hindrance of its large nitrile groups.
- Likewise, polyamides, also theoretically 100% flexible, are quite stiff because of hydrogen bonding between the chains.

So, this is the mathematical representation for the measurement of stiffness. Now here n is the number of links in the polymer chain and l naught, L naught is the length of each link. Another useful method for measuring the flexibility is to use the material's sonic modulus. The sample used should be unoriented and measured below the glass transition temperature. If it is done, the chain stiffness will correlate with the sonic velocity and that is, the grain greater sonic the velocity, the greater the chain stiffness.



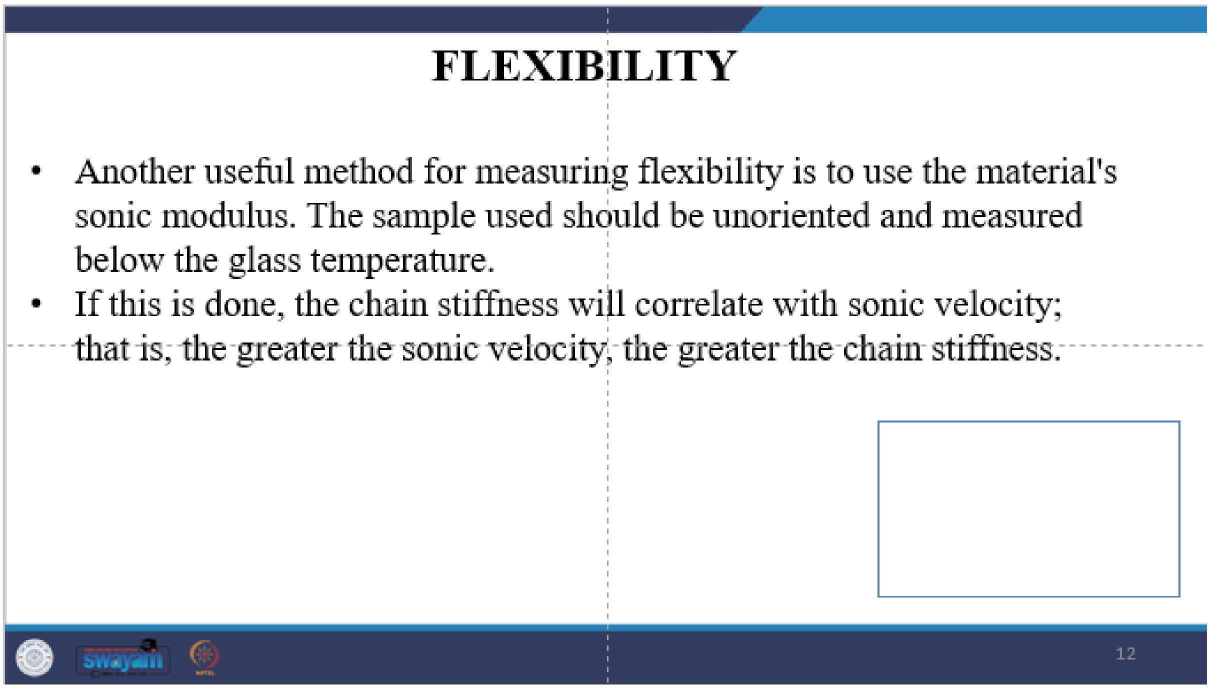
FLEXIBILITY

The stiffness of the chain can be obtained by measuring a value for r^2 (which is a mean square end to end distance for a chain) by angular light scattering of a dilute polymer solution or simultaneous stress and birefringence measurements on a solid polymer in its rubbery state. The stiffness z is then

$$z = \left(\frac{\bar{r}^2}{N l_0^2}\right)^{1/2}$$

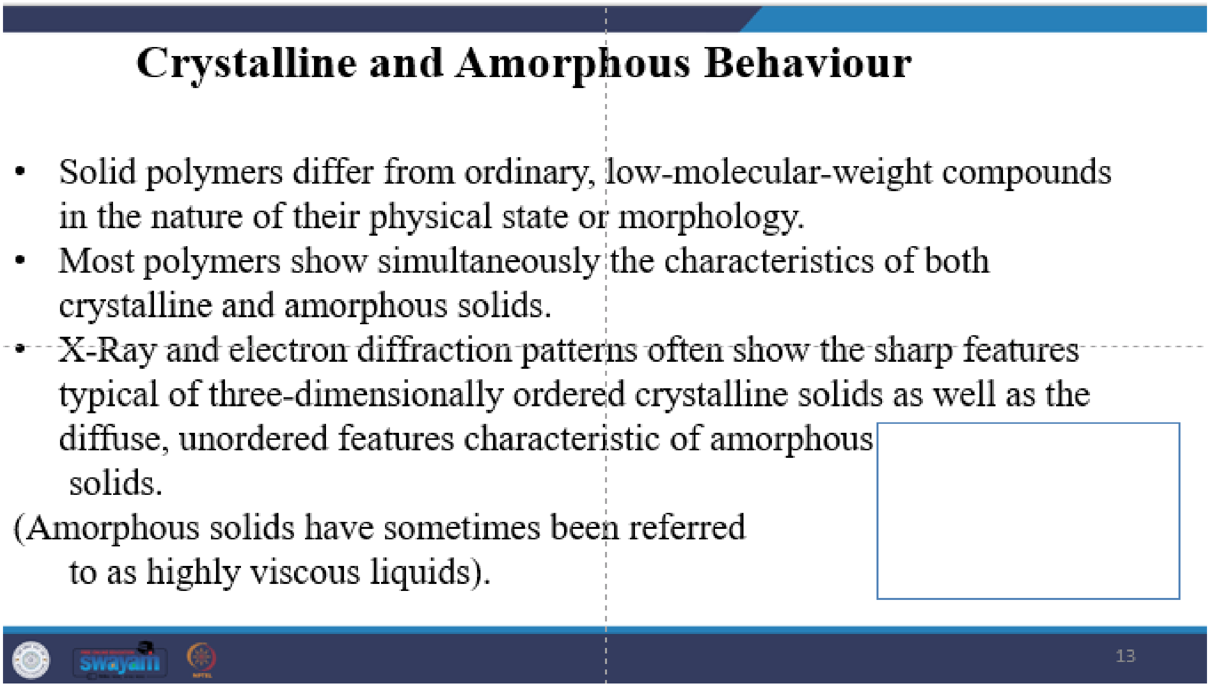
where N is the number of links in the polymer chain andI$_0$ is the length of each link.

So, in this way, you can find out the flexibility. Crystalline and amorphous behavior, the solid polymers differ from ordinary low molecular weight compounds in the nature of their physical state or morphology. So, most polymers show the simultaneous characteristics of both crystallinity and amorphous. X-ray or electron deflection patterns often show the sharp features typical of three-dimensional ordered crystalline solids as well as in the diffuse unordered features characteristics of amorphous solids. The terms crystalline and amorphous are used to indicate the order and unordered polymer region, respectively.



FLEXIBILITY

- Another useful method for measuring flexibility is to use the material's sonic modulus. The sample used should be unoriented and measured below the glass temperature.
- If this is done, the chain stiffness will correlate with sonic velocity; that is, the greater the sonic velocity, the greater the chain stiffness.

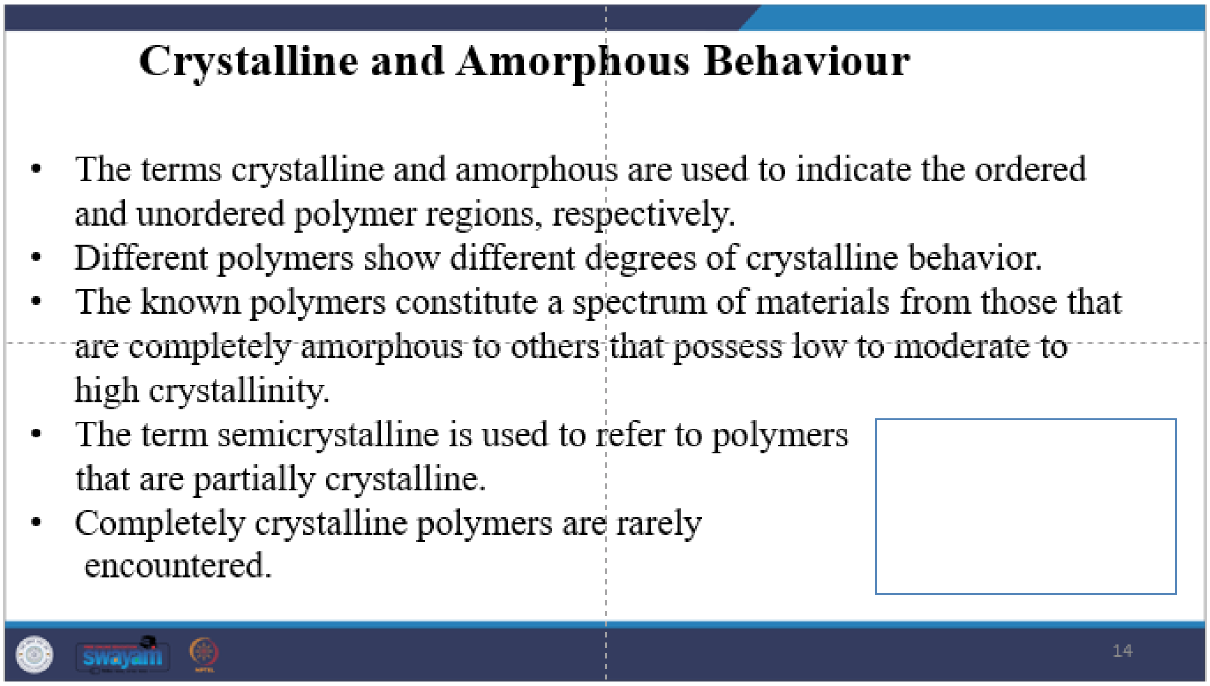


Crystalline and Amorphous Behaviour

- Solid polymers differ from ordinary, low-molecular-weight compounds in the nature of their physical state or morphology.
- Most polymers show simultaneously the characteristics of both crystalline and amorphous solids.
- X-Ray and electron diffraction patterns often show the sharp features typical of three-dimensionally ordered crystalline solids as well as the diffuse, unordered features characteristic of amorphous solids.

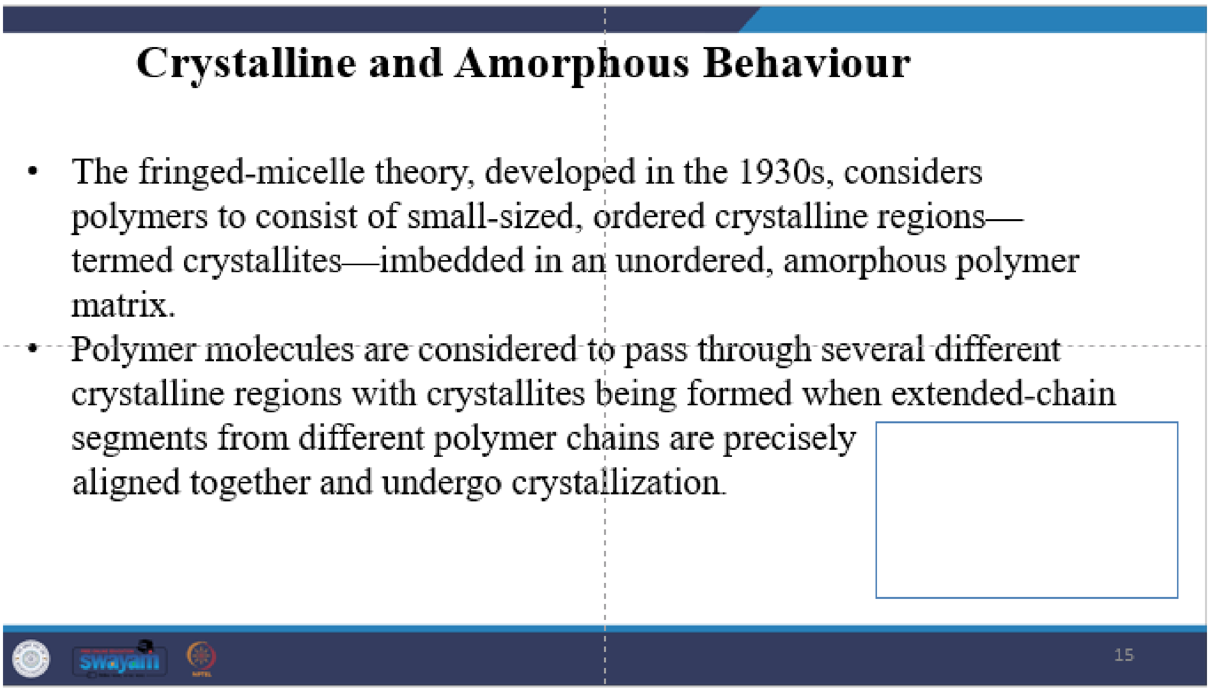
(Amorphous solids have sometimes been referred to as highly viscous liquids).

The different polymers show different degrees of crystalline behavior, and the known polymer constitute a spectrum of materials from those that are completely amorphous to others that possess low to moderate high crystallinity. The Fringe-Micelli theory which was developed way back in 1930, considers the polymer to consist of a small-sized order crystalline region they are termed as crystallites. They are embedded in an unordered amorphous polymer matrix. So, the polymer molecules are considered to pass through several different crystalline regions with the crystallites being formed when extended chain segments from different polymer chains are precisely aligned together and undergo crystallization. Now, each polymer chain can contribute ordered segments to several crystallites.



Crystalline and Amorphous Behaviour

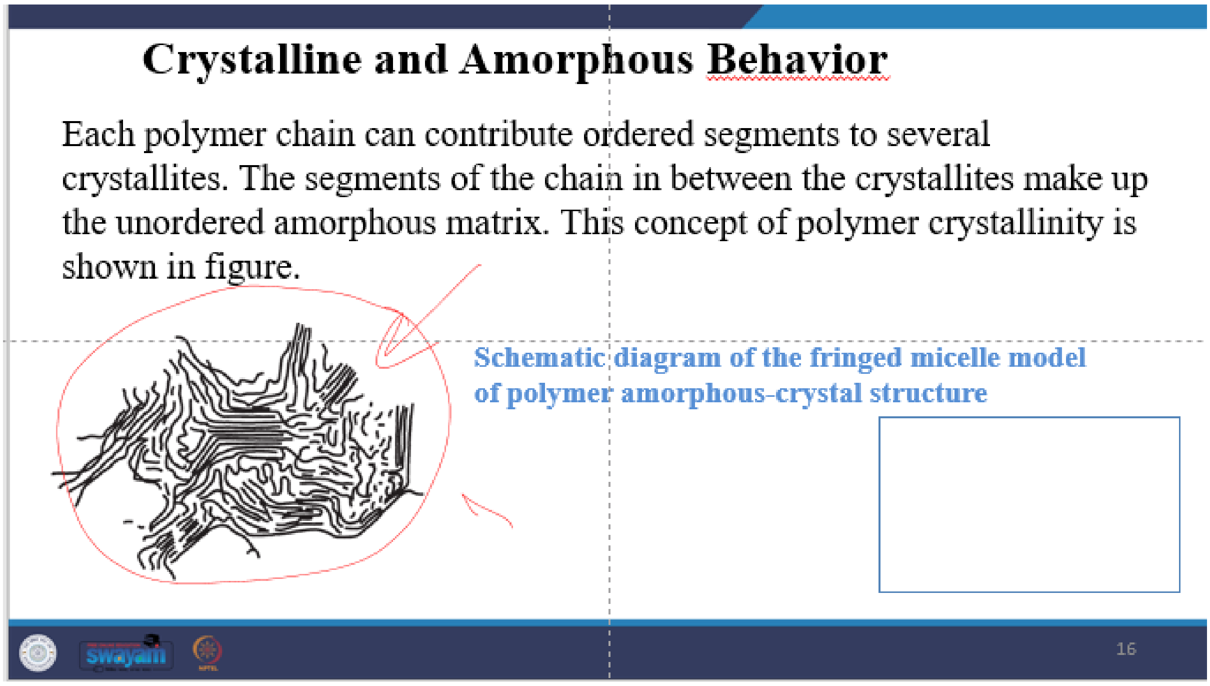
- The terms crystalline and amorphous are used to indicate the ordered and unordered polymer regions, respectively.
- Different polymers show different degrees of crystalline behavior.
- The known polymers constitute a spectrum of materials from those that are completely amorphous to others that possess low to moderate to high crystallinity.
- The term semicrystalline is used to refer to polymers that are partially crystalline.
- Completely crystalline polymers are rarely encountered.



Crystalline and Amorphous Behaviour

- The fringed-micelle theory, developed in the 1930s, considers polymers to consist of small-sized, ordered crystalline regions—termed crystallites—imbedded in an unordered, amorphous polymer matrix.
- Polymer molecules are considered to pass through several different crystalline regions with crystallites being formed when extended-chain segments from different polymer chains are precisely aligned together and undergo crystallization.

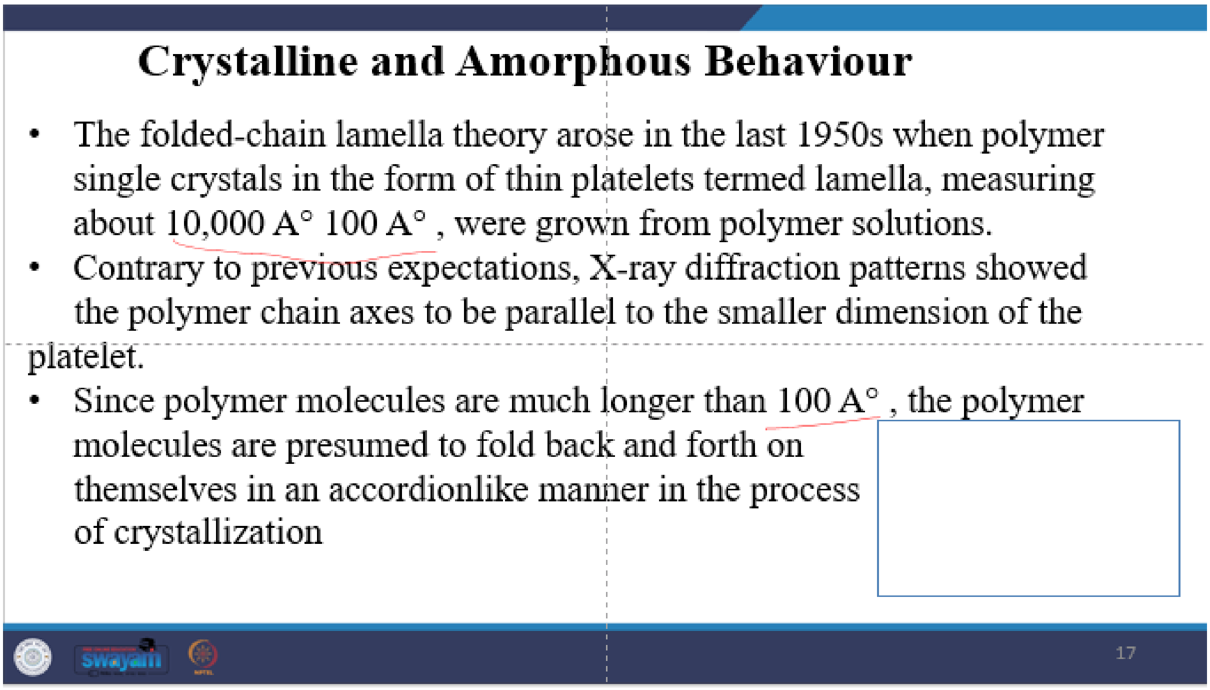
The segment of the chain between the crystallite makes the unordered amorphous matrix. This particular aspect is presented here. This is a schematic diagram of the Fringe-Micelli model of polymer amorphous crystalline structure. The folded chain lamella theory arose way back in 1950 when the polymer single crystals in the form of thin platelets termed lamella measured about 10,000 angstroms to 100 angstroms they were grown from the polymer solution. So, previously people have expected but it was contrary to the x-ray diffraction pattern this shows the polymer chain axis to be parallel to the smaller dimension of the platelet.



Crystalline and Amorphous Behavior

Each polymer chain can contribute ordered segments to several crystallites. The segments of the chain in between the crystallites make up the unordered amorphous matrix. This concept of polymer crystallinity is shown in figure.

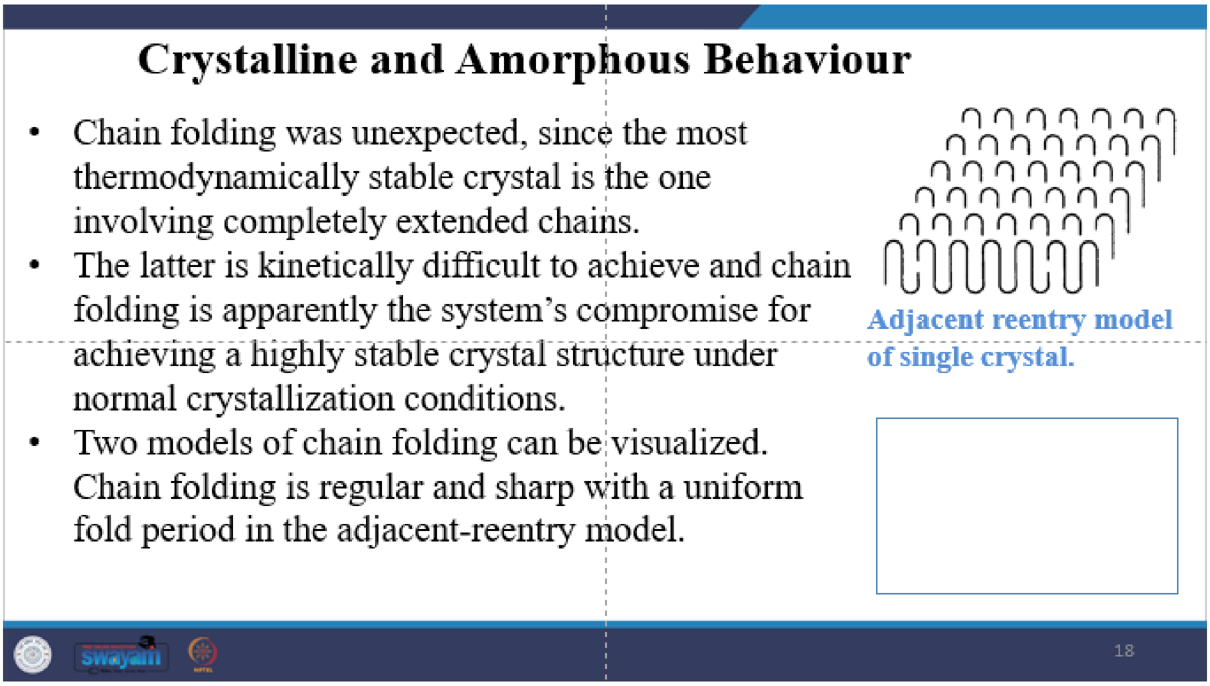
Schematic diagram of the fringed micelle model of polymer amorphous-crystal structure



Crystalline and Amorphous Behaviour

- The folded-chain lamella theory arose in the last 1950s when polymer single crystals in the form of thin platelets termed lamella, measuring about 10,000 A° 100 A° , were grown from polymer solutions.
- Contrary to previous expectations, X-ray diffraction patterns showed the polymer chain axes to be parallel to the smaller dimension of the platelet.
- Since polymer molecules are much longer than 100 A° , the polymer molecules are presumed to fold back and forth on themselves in an accordionlike manner in the process of crystallization

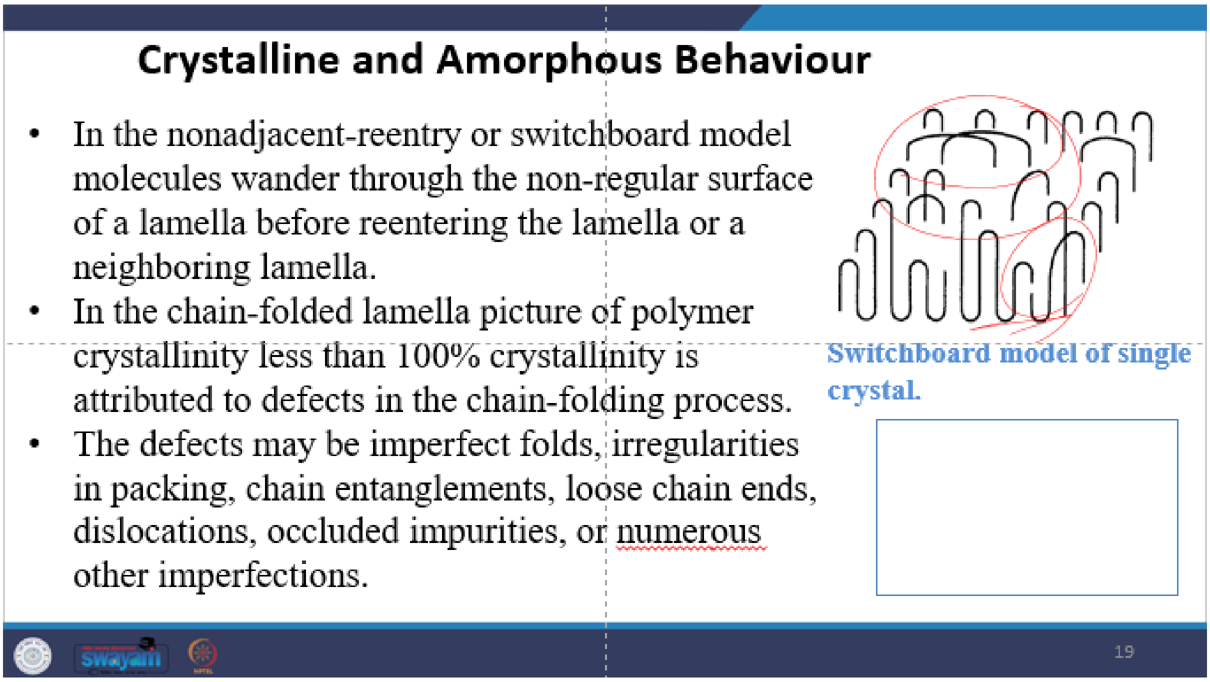
Now, since the polymer molecules are much larger than the 100-angstrom polymer molecules they are presumed to fold back and forth on themselves in an according manner like the process of crystallization. The chain folding was unexpected since the most thermodynamically stable crystals in one involve completely extended chains. So, kinetically it is difficult to achieve the chain folding, which is apparently the system compromise for achieving a highly stable crystal structure under the normal crystallization conditions. Sometimes, the non-adjacent ray tree or switchboard model molecule wanders through the non-regular surface of lamella before re-entering the lamella or a neighboring lamella here you see this particular aspect. In the chain-folded lamella, the picture of polymer crystallinity is less than 100 percent crystallinity is attributed to defects in the chain folding process.



Crystalline and Amorphous Behaviour

- Chain folding was unexpected, since the most thermodynamically stable crystal is the one involving completely extended chains.
- The latter is kinetically difficult to achieve and chain folding is apparently the system's compromise for achieving a highly stable crystal structure under normal crystallization conditions.
- Two models of chain folding can be visualized. Chain folding is regular and sharp with a uniform fold period in the adjacent-reentry model.

Adjacent reentry model of single crystal.

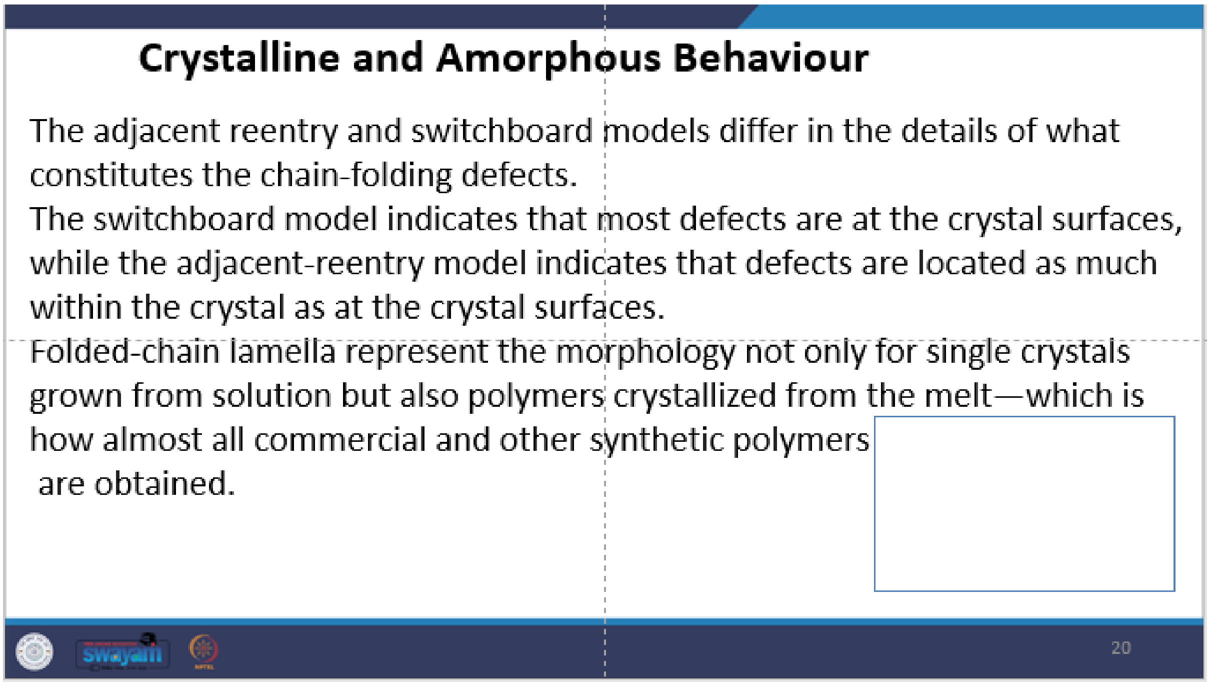


Crystalline and Amorphous Behaviour

- In the nonadjacent-reentry or switchboard model molecules wander through the non-regular surface of a lamella before reentering the lamella or a neighboring lamella.
- In the chain-folded lamella picture of polymer crystallinity less than 100% crystallinity is attributed to defects in the chain-folding process.
- The defects may be imperfect folds, irregularities in packing, chain entanglements, loose chain ends, dislocations, occluded impurities, or numerous other imperfections.

Switchboard model of single crystal.

Now, this defect or their defects may be imperfect folds like irregularities in packing, chain entanglements, loose chain ends, dislocation, occurred impurities, or numerous other imperfections. The adjacent re-entry, like here, and a switchboard model differ in detail of what constitutes the chain folding defects. The switchboard model usually indicates the most defects they are in the crystal surfaces while the adjacent re-entry model indicates the defects that are located as much within the crystals as at the crystal surfaces. Melt-crystallized polymers have the most prominent structural features of the polymer crystals. The chains are oriented particularly to the lamella phase so that the chain folding must occur. Now, chain folding usually is a maximum for a polymer crystal slowly near the crystalline melting temperature.



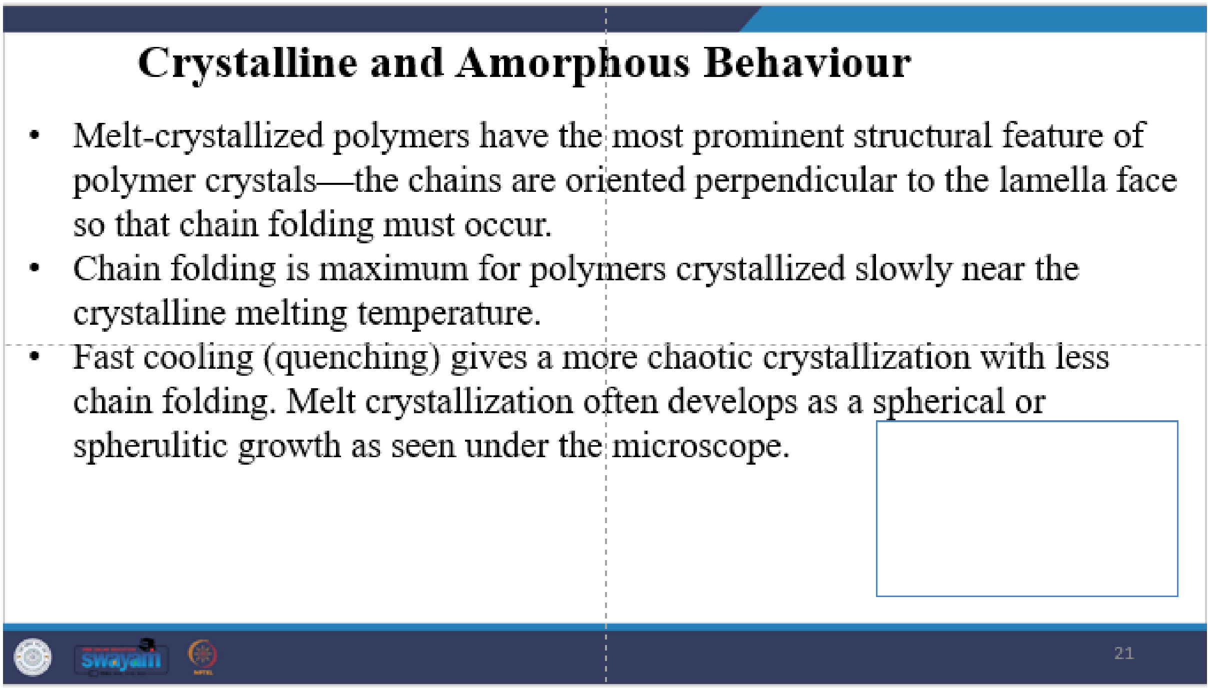
Crystalline and Amorphous Behaviour

The adjacent reentry and switchboard models differ in the details of what constitutes the chain-folding defects.

The switchboard model indicates that most defects are at the crystal surfaces, while the adjacent-reentry model indicates that defects are located as much within the crystal as at the crystal surfaces.

Folded-chain lamella represent the morphology not only for single crystals grown from solution but also polymers crystallized from the melt—which is how almost all commercial and other synthetic polymers are obtained.

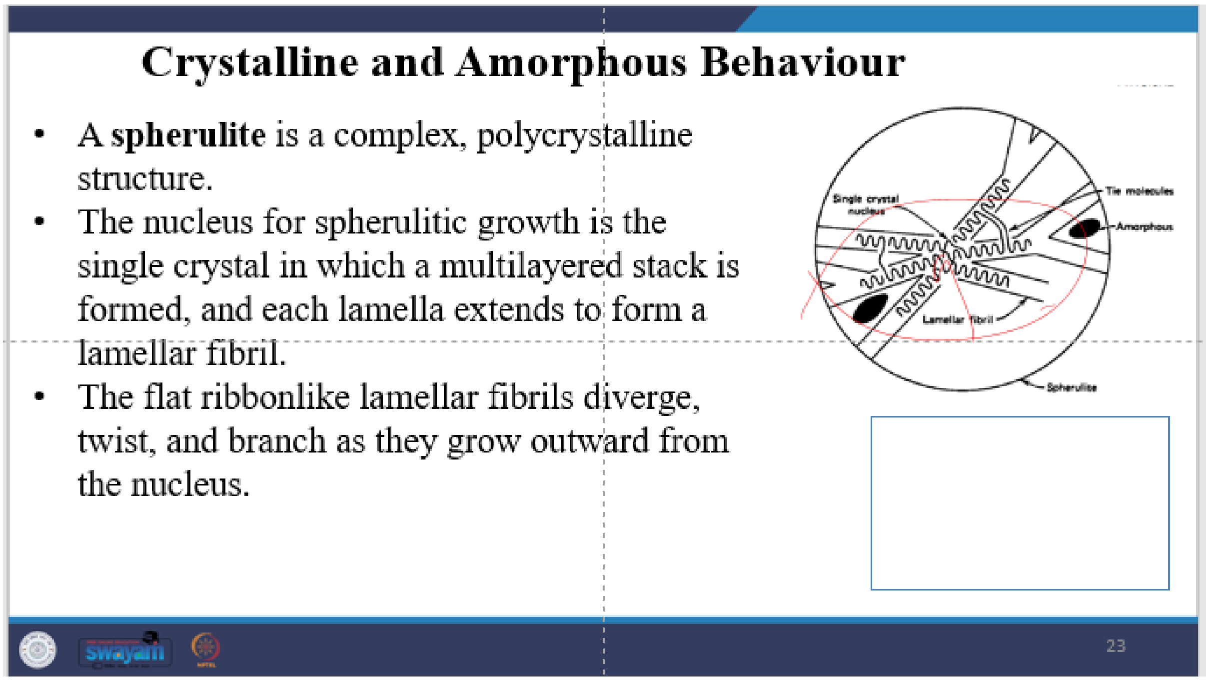
So, the fast cooling sometimes it is sometimes referred to as a quenching this gives the more chaotic crystallization, which is less than the chain folding, and the melt crystallization often develops a spherical spherulitic growth which can be seen under the microscope or only in the microscope. Now the separation of the crystal growth occurs at various nuclei, and crystal growth this proceeds in a radical fashion from each nucleus until the growth from the neighbouring structure impinges on each other. Now, these spherical structures, sometimes termed spherulites completely fill the volume of crystallized polymer samples. Now these spherulities have different sizes and degrees of perfection depending on the specific polymer and crystallization conditions. Spherulite is a complex polycrystalline structure the nucleus of spherulitic growth is the single crystal in which a multi-layered stake is formed and each lamellar extends to form a lamellar fabric.



Crystalline and Amorphous Behaviour

- Melt-crystallized polymers have the most prominent structural feature of polymer crystals—the chains are oriented perpendicular to the lamella face so that chain folding must occur.
- Chain folding is maximum for polymers crystallized slowly near the crystalline melting temperature.
- Fast cooling (quenching) gives a more chaotic crystallization with less chain folding. Melt crystallization often develops as a spherical or spherulitic growth as seen under the microscope.

The flat ribbon-like lamellar like here you see diverge, twist and branch as they grow outward from the nucleus. Now, the growth usually occurs by the chain folding with the polymer chains axis being perpendicular to the length of the lamellar. Now the strength of the polymer indicates that more than Van der Waal forces hold lamellar and these are inter lamellar or inter crystalline fibrils. They are also termed as tie molecules between the lamellar fibrils within the spherulite and between the fibrils of different spherulites. Some of the polymer molecules simultaneously participate in the growth of two or more adjacent lamellae and provide molecular links that reinforce the crystalline structure. So, the chain axis of the tie molecule lies parallel to the long axis of the link each link between the lamellae is an extended chain type of a single crystal.

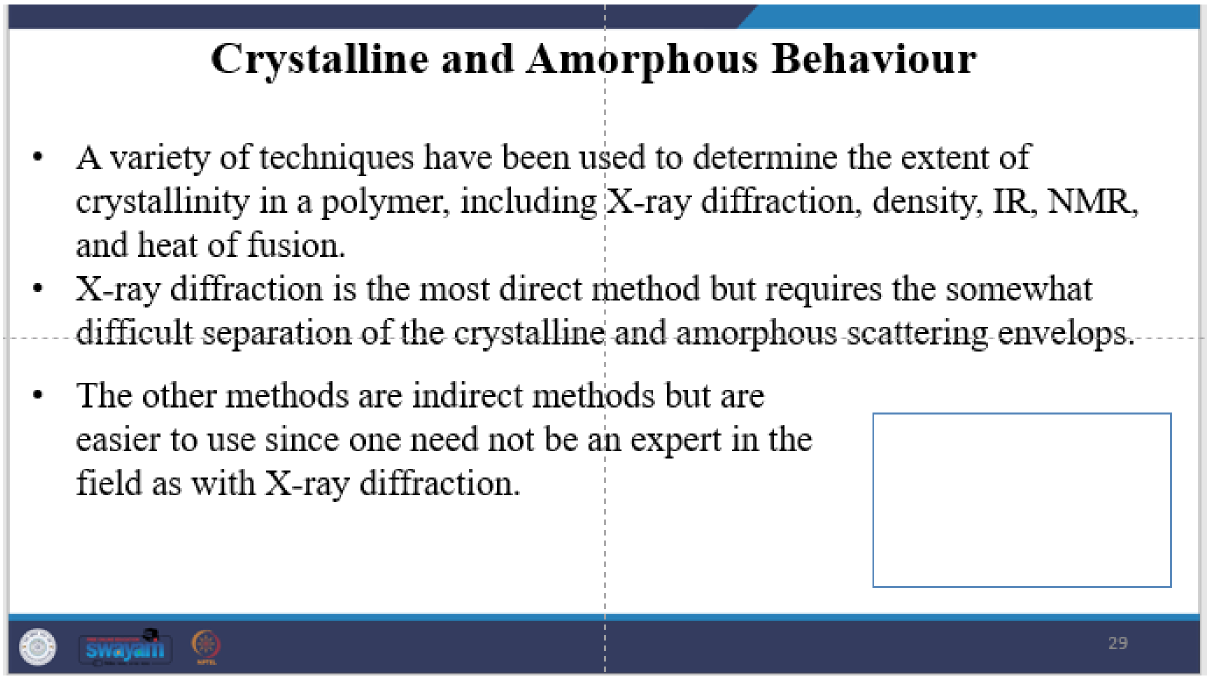


Crystalline and Amorphous Behaviour

- A **spherulite** is a complex, polycrystalline structure.
- The nucleus for spherulitic growth is the single crystal in which a multilayered stack is formed, and each lamella extends to form a lamellar fibril.
- The flat ribbonlike lamellar fibrils diverge, twist, and branch as they grow outward from the nucleus.

The tie molecule is the main component of the modern picture of polymer crystallinity, which is the carryover from the fringed-micelle theory. The amorphous content of semi-crystalline or melt crystallized polymer this sample consists of the defects in the chain folding structure and the tie molecule and the material that either because of the entanglement like this are not included in the growing lamellar fibrils or is rejected from it owing to its unacceptable nature. Some natural polymers like cotton, silk, and cellulose have extended chain morphology, but their morphologies are determined by enzymatically controlled synthesis and crystallization processes. The extended chain morphology is obtained in some of the synthetic polymers under certain circumstances. This includes the crystallization from the melt under pressure or applied stress crystallization of the polymer from the liquid crystalline state.

A variety of techniques have been used to determine the extent of crystallinity in the polymer. XRD or X-ray deflection, density, infrared, NMR, and a heat of fusion. The XRD is the most direct method, but it requires a somewhat different separation of the crystalline and amorphous scattering envelopes. The other method is used, which are indirect method but easier to use since one need not be an expert in the XRD tool. Heat of fusion is probably the most often used method since reliable thermal analysis instruments are commercially available and easy to use.



Crystalline and Amorphous Behaviour

- A variety of techniques have been used to determine the extent of crystallinity in a polymer, including X-ray diffraction, density, IR, NMR, and heat of fusion.
- X-ray diffraction is the most direct method but requires the somewhat difficult separation of the crystalline and amorphous scattering envelops.
- The other methods are indirect methods but are easier to use since one need not be an expert in the field as with X-ray diffraction.

The difficulty in using thermal analysis like DSC differential scanning calorimetry DTA differential thermal analysis, or any other indirect method is uncertainty in the values of the quantity measured for 0 to 100 percent crystalline sample. Since such sample seldom exist, so very rare to find such kind of reference sample. The best technique is to calibrate the method with the sample whose crystallinity is been determined by XRD. Now, how can we determine the polymer crystallinity? This is regardless of the precise picture of order and disorder in polymer, the prime consideration that should be emphasized is that the polymer tends to crystallize. The extent of this crystallization tendency plays a most significant role in the practical way in which the polymer is used.

The consequence of the large effect of crystallinity on thermal, mechanical, and other important properties of the polymer. The different polymers have different properties they are synthesized and used differently because of the varying degrees of crystallinity and, thereby, varying degrees of the processes. The extent of crystallinity developed in a polymer sample is a consequence of both thermodynamic and kinetic factors. So, we will notice the general tendency to crystallize under the moderate crystallization condition which is the condition that extrudes the extremes of time, temperature, and pressure. These three are the most important variables.

Thermodynamically crystallizable polymers generally most crystallize at reasonable rates and if crystallinity is to be employed from a practical viewpoint. Now, the extent to which a polymer crystallizes depends on whether its structure is conducive to packing into the crystalline state and on the magnitude of the secondary attractive forces of the polymer chains. Now packing is facilitated for polymer chains that have structural regularities, compactness, streamlining, and some degree of flexibility. The stronger the secondary attractive forces, the greater will be the driving force for the ordering and crystallization of polymer chains. Now, some polymers are highly crystalline primarily because their structure is conducive to packing, and still, for some polymers and other polymers both factors may be favorable for the crystallization.

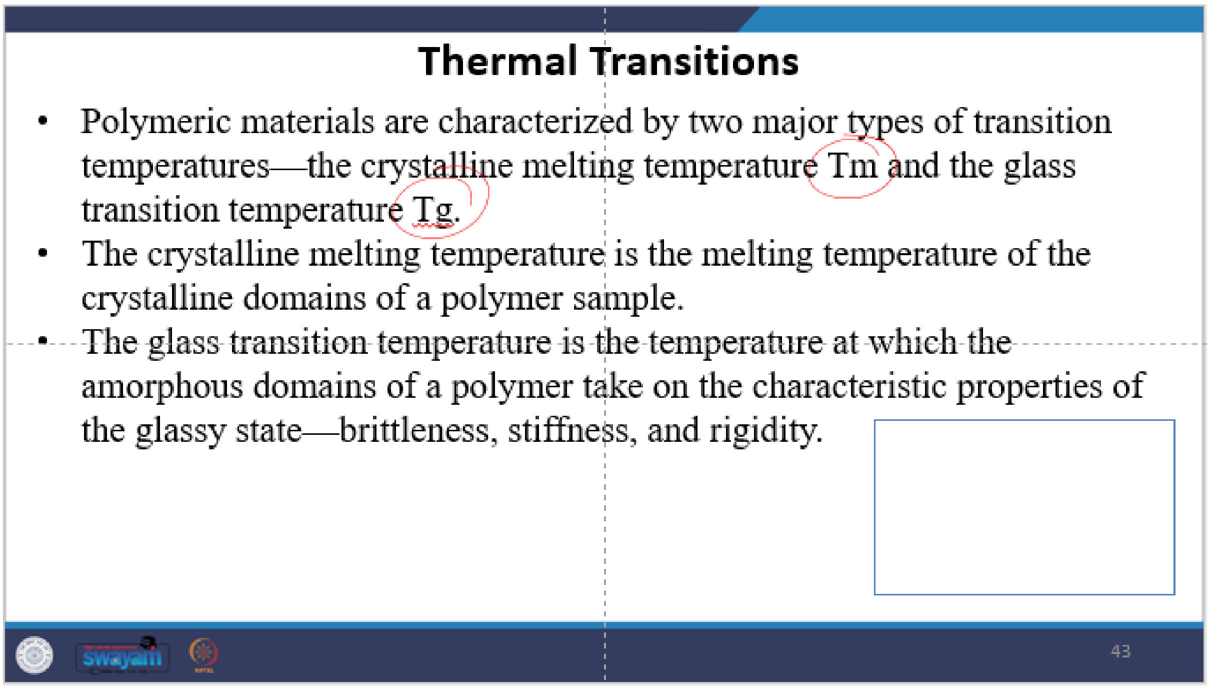
Polyethylene, let us take the example of polyethylene; it is essentially the best structure in terms of its ability to pack into the crystalline state. Its very simple and perfectly regular structure allows the chain to pack tightly and without any restriction as to which segment of one chain needs to line up next to which other segment of the same chain of another chain. The flexibility of the polyethylene chain is also very conducive. This is conducive to the crystallization in the conformation, which may be required for the packing. This can be easily achieved even though the secondary attractive force they are small as forces are smaller. Polyethylene crystallizes easily and to a high degree because of its simple and regular structure, the linear structure The polymers other than the polyethylene have less simple and regular chains.

Polycaprolactam can be considered as a modified polyethylene in which the chain can contain the amide group between every 5 methylene polycaprolactam and other polyamides are highly crystalline polymers. Since the amide group is a poorer one and leads to a much larger secondary attractive force in polyamide, this is due to the hydrogen bonding. The polyamide chains are not simple for polyethylene, and packing requires that the chain segments be brought together so that the amide groups are aligned. This restriction leads to a somewhat lesser degree of crystallization in the polyamides than expected, and that is based only on a consideration of high secondary attractive forces. Now, the crystallinity in the polymer, like polyamide can be significantly increased by mechanically stretching it to facilitate the ordering and alignment of the polymer chain.

So, polymers such as polystyrene, PVC, poly methyl methacrylate, and PMMA show very poor crystallization tendency. So, the loss of structural simplicity this compared to the polyethylene results in a marked decrease in the tendency toward crystallization. Crystalline polymers such as PVF polyvinyl fluoride, polyvinylidene fluoride, or polytetrafluoroethylene are exceptions. These polymers show considerable crystallinity since the small size of fluorine does not preclude packing into the crystalline state or crystalline lattice. The crystallization is also added by the high degree of attractive forces, high secondary attractive forces coupled with symmetry account for the presence of significant crystallinity in polyvinylidene chloride.

Symmetry alone with significant polarity, as in polyisobutylene, is insufficient for the development of crystallinity. The polymers with rigid cyclic structures in the polymer chain as in cellulose or polyethylene -terthalate, are difficult to crystallize. Moderate crystallization does not occur in these cases and as a result of their polar polymer chains. The biosynthesis of cotton proceeds with a geometric ordering of the polymer chain in spite of the rigid polymer chains. So, excess chain rigidity in the polymer this is due to the extensive crosslinking because the crosslinking always hinders the free movement of the chains.

Now this can be reflected in the phenol-formaldehyde and a urea-formaldehyde polymer, and this completely prevents the crystallization. Now, sometimes, the excess chain rigidity is causes several processability problems, which can be reduced by application during application of various additives during the course of processing. Let us talk about the thermal transitions. The polymeric materials are characterized by two major types of transition temperatures. The crystalline melting temperature is Tm and the glass transition temperature is Tg.



Thermal Transitions

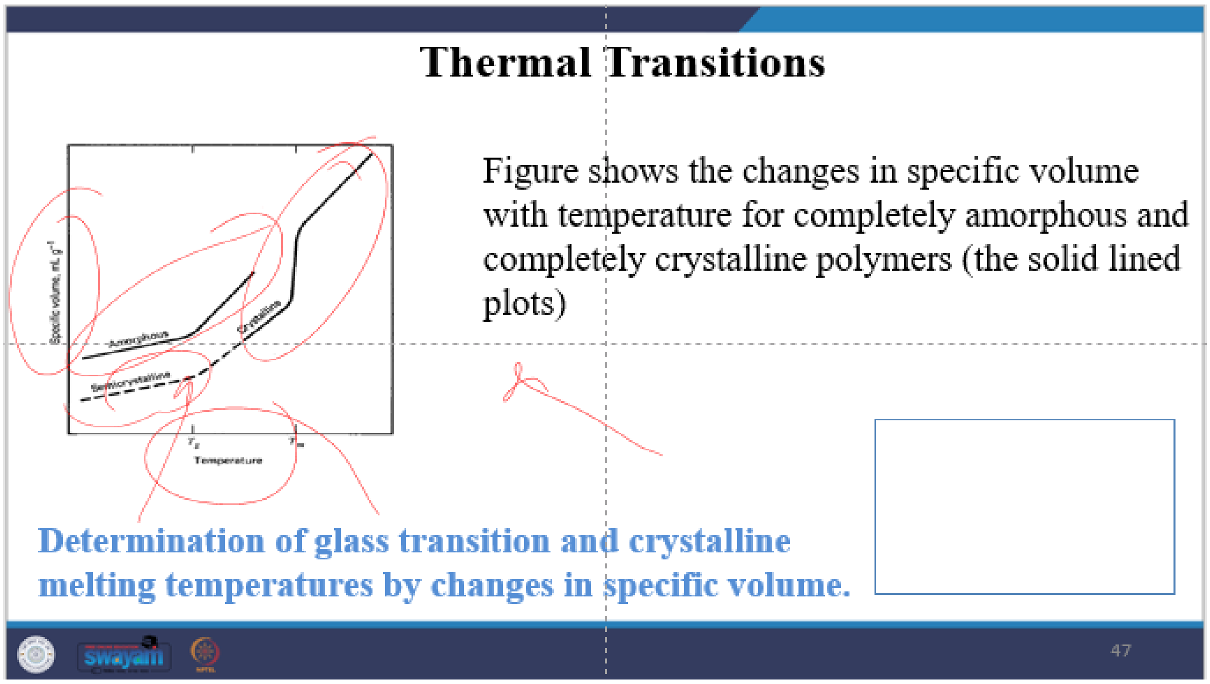
- Polymeric materials are characterized by two major types of transition temperatures—the crystalline melting temperature Tm and the glass transition temperature Tg.
- The crystalline melting temperature is the melting temperature of the crystalline domains of a polymer sample.
- The glass transition temperature is the temperature at which the amorphous domains of a polymer take on the characteristic properties of the glassy state—brittleness, stiffness, and rigidity.

The crystalline melting temperature is the melting temperature of the crystalline domains of a polymer sample. This is the basic definition of Tm. The glass transition temperature is the temperature at which the amorphous domain of a polymer takes on the characteristic properties of the glassy state, brittleness, stiffness, and rigidity. The difference between the two thermal transitions can be explained more clearly by considering the changes that occur in the liquid polymer as it is cooled. So, you heat a liquid polymer polyethylene, and then you observe the behavior during the cooling.

The translational, rotational, and vibrational energies of the polymer molecule decrease on cooling when the total energies of the molecule have fallen to the point where the translational and rotational energies are essentially 0; the crystallization is possible. If certain symmetry requirements are met, the molecule is able to pack into order lattice arrangement, and crystallization occurs. However, not all polymers meet the necessary symmetry requirement for the crystallization. Now, if symmetry requirements are not met, the crystallization does not take place, but the energies of the molecules continue to decrease as the temperature decreases. A temperature is finally reached at the glass transition temperature at which the long-range motion of the polymer chain stops or ceases.

The long-range motion they also referred to as a segmental motion, which refers to the motion of a segment of the polymer chain by concerted rotation of the bond and end of the segment. Whether a polymer sample exhibits both thermal transitions or only one depends on its morphology. Now, if it is a completely amorphous polymer, it shows only tg is a glass transition temperature, and a completely crystalline polymer shows the tm. So, semi-crystalline polymers exhibit both the crystallinity melting and a glass transition temperature, so it is in between. Now, this particular figure shows the changes in the specific volume with respect to the temperature of the completely amorphous and completely crystalline polymers with respect to the temperature and specific volume.

You see that here the structure, the movement of amorphous, and this is the semi-crystalline, and beyond this, this is the crystalline one. Now, tm is the first-order transition with a discontinuous change in the specific volume at the transition temperature, and the glass transition temperature is a second-order transition involving only a change in the temperature coefficient of a specific volume. So, a plot of the temperature coefficient of a specific volume versus temperature this shows the discontinuity. So, if you plot, then you will observe that discontinuity is there. The corresponding plot for the semi-crystalline polymer consists of a plot of crystalline polymer plus a dotted portion of glass transition.



Thermal Transitions

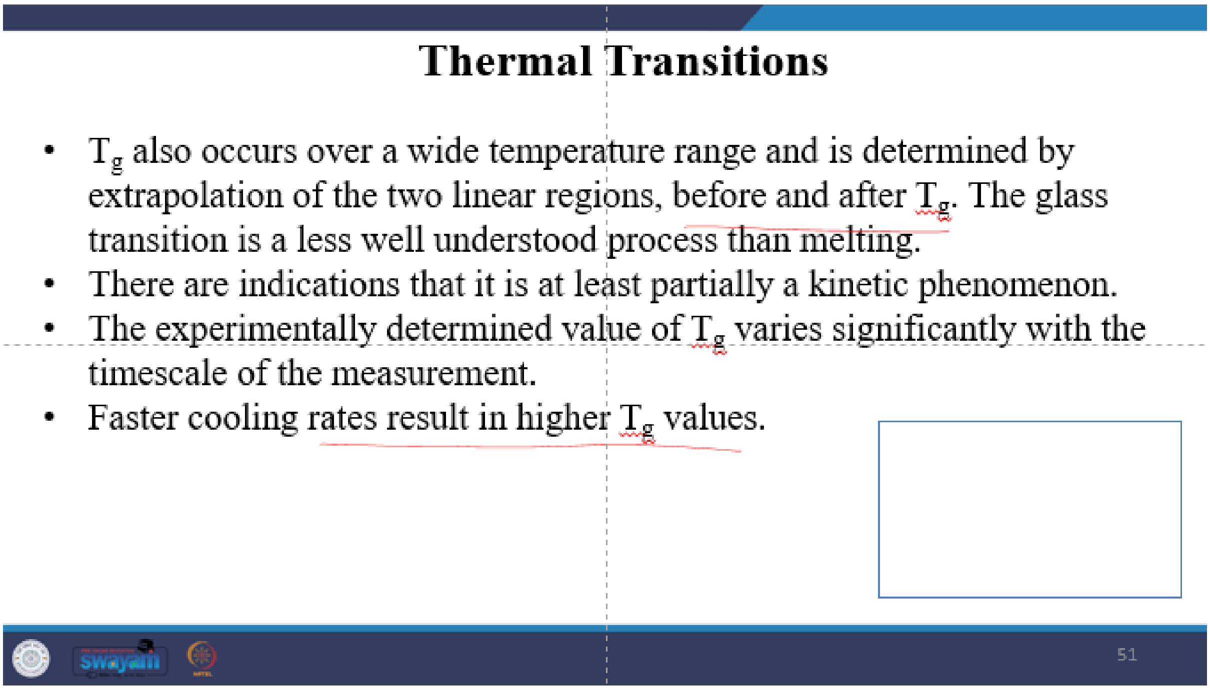
Figure shows the changes in specific volume with temperature for completely amorphous and completely crystalline polymers (the solid lined plots)

Determination of glass transition and crystalline melting temperatures by changes in specific volume.

Here you see. A variety of methods have been used to determine the glass transition temperature and tm, including dilatometry, which is the determination of specific volume, thermal analysis, dynamic mechanical behavior, dielectric loss, broad line NMR, etc., and the most common method is the DST that is the differential scanning calorimetry. This reflects the change in the heat capacity of a sample as a function of temperature by measuring the heat flow required to maintain the zero-temperature differential between an inert reference material and a polymeric material. The melting of a polymer takes place over a wider temperature range than that observed for a small organic molecule such as benzoic acid due to the presence of a different size crystalline region and a more complicated process for melting of a large molecule. Glass transition temperature also occurs over a wide temperature range and determined by extrapolation of two linear regions before and after glass transition.

So, the glass transition is a less well-understood process than melting. Now, there are various indications that it is the least partially a kinetic phenomenon, and experimentally determined values of glass transition temperatures vary significantly with the time scale of measurement. Now faster cooling results the higher glass transition values. Now, significant densification still takes place below the glass transition temperature, where the amount of dependent on the cooling rate. So, the best visualization of glass transition involves the existence of a modest range of temperatures at which there is a cessation of the segmental motions of different polymeric chains.

Now, some polymers may undergo the thermal transition in addition to glass transition and Tm, and this includes a crystal-crystal transition. The values of glass transition and temperature and Tm for polymer affect the mechanical properties at any particular temperature and determine the temperature range in which the polymer can be employed. Let us consider the matter in which the Tg and Tm vary from one polymer to another. One can discuss the two transitions simultaneously since both are affected similarly by consideration of polymer structures. So, the polymers those who are having low glass transition values usually have Low Tm values, and high Tg, and high Tm values are usually found together.

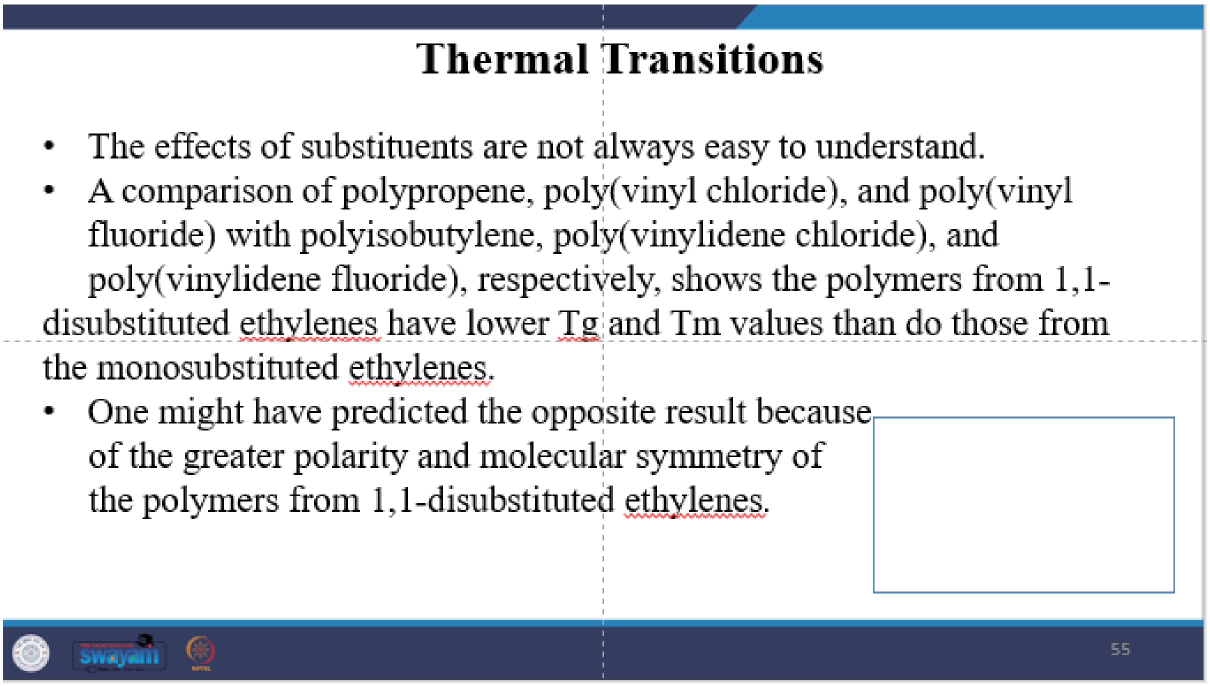


Thermal Transitions

- T_g also occurs over a wide temperature range and is determined by extrapolation of the two linear regions, before and after T_g. The glass transition is a less well understood process than melting.
- There are indications that it is at least partially a kinetic phenomenon.
- The experimentally determined value of T_g varies significantly with the timescale of the measurement.
- Faster cooling rates result in higher T_g values.

Now, the polymer chains that do not easily undergo the bond rotation so as to pass through a glass transition would also be expected to melt with difficulty. The high secondary attractive forces also decrease the mobility of the amorphous polymer chain. So, the movement of the chain is very important. Decreased mobility of the polymer chain increases the chain rigidity, more compact structure, high glass transition temperature, and the Tm value of the crystalline polymer they produced from such rigid chains would also be very high.

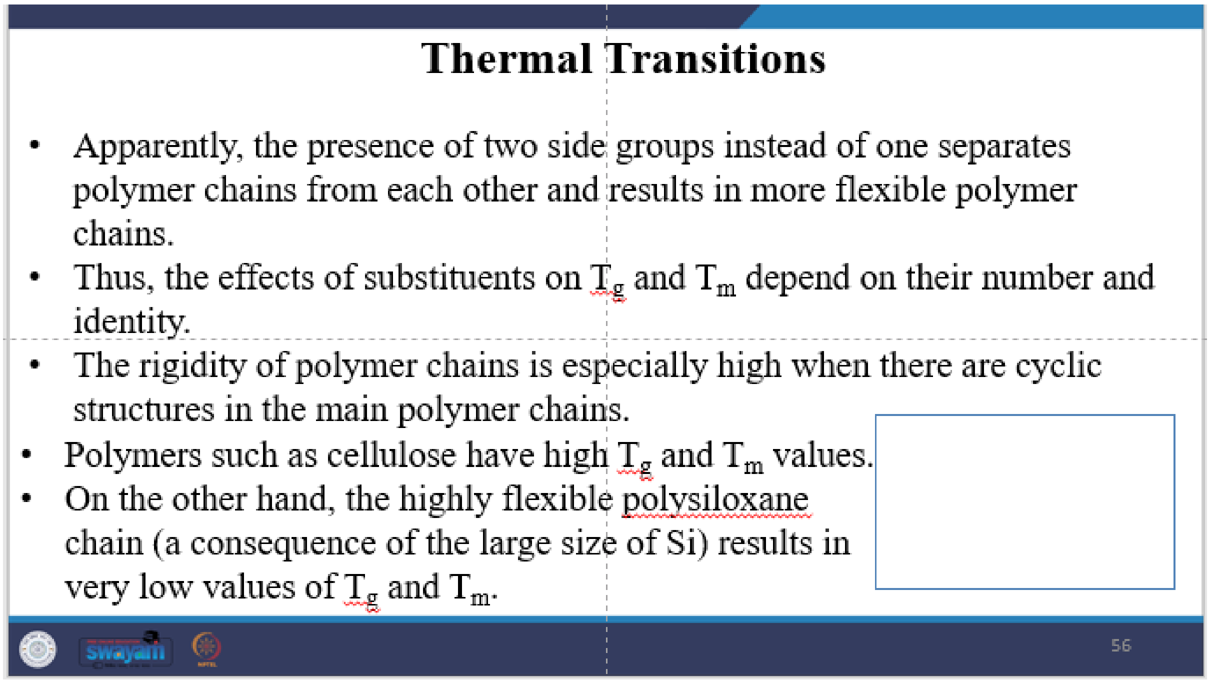
The effects of substituents are not always easy to understand. Usually, the comparison of polypropylene, polyvinyl chloride, polyvinyl fluoride, polyisobutylene, polyvinyl chloride, and polyvinyl chloride they are respectively, shows the polymers from 1 1 distribution of ethylene. They have lower Tg and Tm values than those from the mono-distributed or monosubstituted ethylene. Apparently, the presence of two side groups instead of one separates the polymer chain from each other and results in a more flexible polymer chain. Therefore, the effect of substituents on the glass transition temperature and T_M depends on the number and identity. The rigidity of the polymer chain is especially high when there are cyclic structure in the main polymer chains.



Thermal Transitions

- The effects of substituents are not always easy to understand.
- A comparison of polypropene, poly(vinyl chloride), and poly(vinyl fluoride) with polyisobutylene, poly(vinylidene chloride), and poly(vinylidene fluoride), respectively, shows the polymers from 1,1-disubstituted ethylenes have lower Tg and Tm values than do those from the monosubstituted ethylenes.
- One might have predicted the opposite result because of the greater polarity and molecular symmetry of the polymers from 1,1-disubstituted ethylenes.

Although the glass transition and Tm depends similarly on the molecular structure, the variation in the two-transition temperature do not always quantitatively parallel each other. The Tm values can be seen to generally increase in some same order, but there are many polymers whose Tm values do not follow in the same extend order. Therefore, polyethylene and polyoxymethylene have low glass transition values because of their highly flexible chains. However, their simple and regular structure yields tightly packed crystal structures with high Tm values. So, an empirical consideration of the ratio of glass transition versus Tm is called the Kelvin temperature, sometimes the various polymers at this particular aspect.

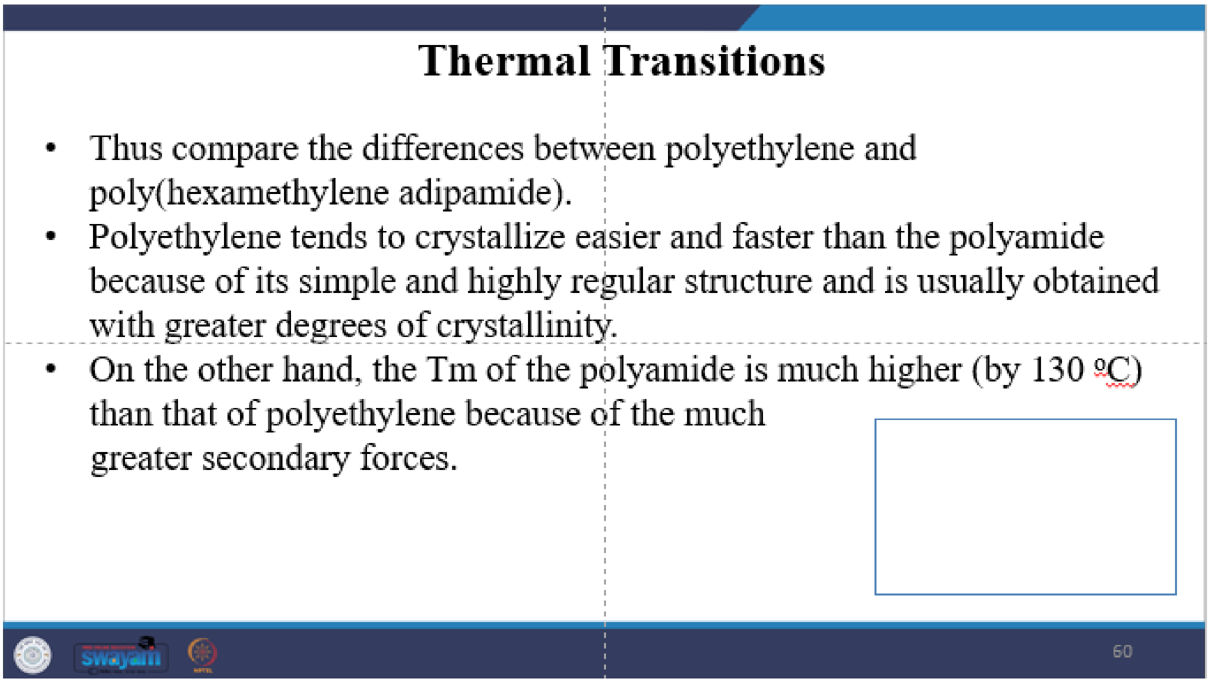


Thermal Transitions

- Apparently, the presence of two side groups instead of one separates polymer chains from each other and results in more flexible polymer chains.
- Thus, the effects of substituents on T_g and T_m depend on their number and identity.
- The rigidity of polymer chains is especially high when there are cyclic structures in the main polymer chains.
- Polymers such as cellulose have high T_g and T_m values.
- On the other hand, the highly flexible polysiloxane chain (a consequence of the large size of Si) results in very low values of T_g and T_m.

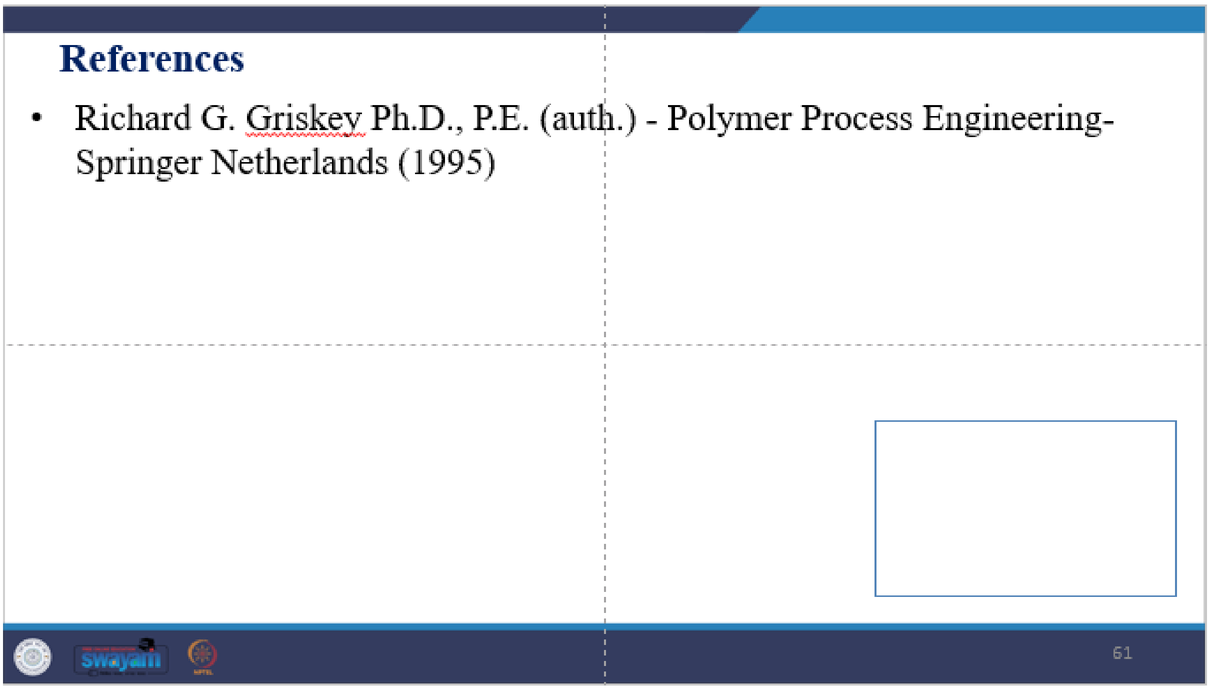
So, when the Tg is equal to the Tm ratio, approximately half of the symmetric polymers, now it should be evident that some of the factors that decrease the crystallization tendency of a polymer also led to an increase in the value of Tm and because Tm is also if Tm is increasing then Tg is will also increase.

So the reason for this is that the extent of crystallinity developed in the polymer is both kinetically and thermodynamically controlled, while the melting temperature is only thermodynamically controlled. The comparative difference between polyethylene and polyhexamethylene adiapamide is that polyethylene tends to crystallize easier and faster than polyimide because of its simple and highly regular structure and is usually obtained with a greater degree of crystallinity. On the other hand, if we talk about the Tm for the polyimide, which is much higher, say by 130 degrees Celsius, than that of the polyethylene because of the much greater secondary forces.



Thermal Transitions

- Thus compare the differences between polyethylene and poly(hexamethylene adipamide).
- Polyethylene tends to crystallize easier and faster than the polyamide because of its simple and highly regular structure and is usually obtained with greater degrees of crystallinity.
- On the other hand, the Tm of the polyamide is much higher (by 130 ºC) than that of polyethylene because of the much greater secondary forces.



References

- Richard G. Griskey Ph.D., P.E. (auth.) - Polymer Process Engineering-Springer Netherlands (1995)

So, dear friends, in this particular segment, we discussed the different behaviors of the polymers, especially the glass transition temperature and melting temperature. We also discussed the different aspects in which we can determine the properties. For your convenience, we included a couple of references. You can utilize those references as and when needed. Thank you very much.