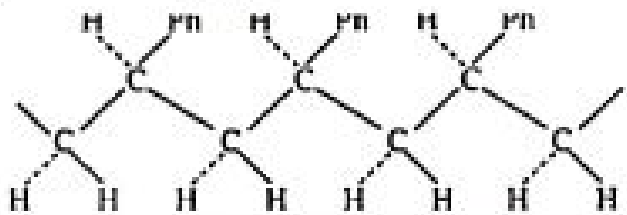
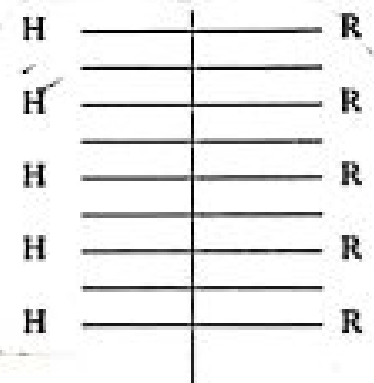


STRUCTURE AND PROPERTIES

1.1. CONFIGURATIONS OF POLYMER CHAINS

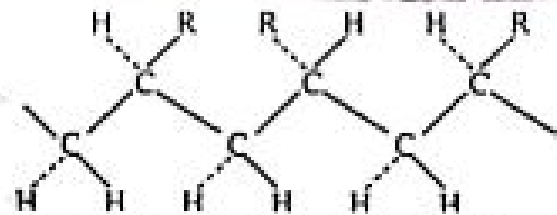
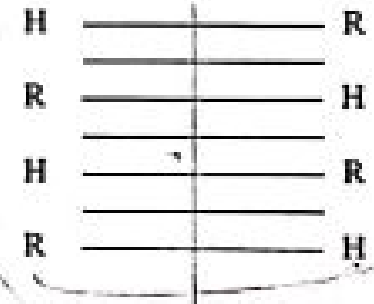
The term configuration relates to those spatial arrangements of the atoms of a molecule that can be changed only by the breaking and making of bonds, whereas the term conformation is used to denote any one of the infinite number of spatial arrangements of the atoms of a molecule that can arise from rotation about a single bond. In other words we can say that the various stereoisomers that differ in configuration can be interconverted only by the breaking and making of bonds whereas the conformational arrangement may be interconverted by rotation of one part of the molecule with respect to the rest of the molecule about a single bond joining these two parts.

Ionic and coordination polymers can provide access to polymers that have a stereoregular structure: Any monomer molecule that possesses an asymmetric centre at a skeletal atom has the capacity to form stereoregular polymers. Three primary possibilities exist with respect to the sequence in which the monomer units enter the chain. These are called isotactic, syndiotactic and atactic polymerisation.



Isotactic polymers are characterized by the presence of only one symmetric type of monomer residue in the chain. One of the characteristic features of isotactic polymers is their ability to crystallize readily. This is a consequence of the fact that the regular disposition of substituent groups along the chain permits the molecule to assume a regular helical conformation and allows adjacent chains to pack together in an ordered manner.

Syndiotactic polymers are characterized by alternating configuration of residues.



Syndiotactic polymers also tend to crystallize readily because of the opportunities that exist for the formation of helices and for efficient chain packing.

Atactic polymers contain no regular sequence of monomer residues along the chain. Because of this, the polymers are characterized by a low tendency for crystallisation.

These three types of polymers have the same chemical structure, but exhibit entirely different properties because of their differing configurations and the resulting geometrical structure. Atactic polymers are for instance, generally low melting and easily soluble, while isotactic and syndiotactic polymers are high melting and less soluble.

Stereoregularity plays an important role in the structures of proteins, nucleic acids and other substances of biological importance. Deoxyribonucleic acid (DNA), for example, has a highly stereoregular double helix structure.

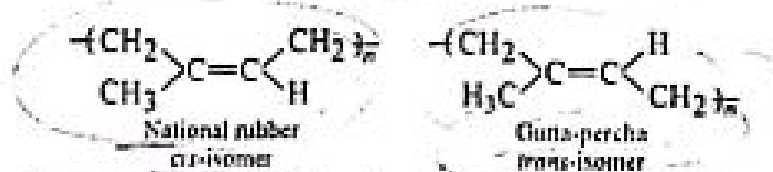
3.2. CRYSTAL STRUCTURES OF POLYMERS

Structural Requirements for Crystallinity : Many polymers, including most fibres, are partially crystalline. The most direct evidence of this fact is provided by X-ray diffraction studies. It is a well known fact that while crystalline substances give sharp and well defined X-ray diffraction patterns, non-crystalline (amorphous) substances give rather diffused and broad patterns. When X-ray crystallographic technique is applied to polymeric solids, it is found that many polymers diffract X-rays like any crystalline substance. On the other hand, many behave like amorphous materials giving very broad and diffused X-rays diffraction patterns.

In fact, polymers contain both crystalline and amorphous regions. That is why, the X-ray diffractions from them are found to be a mixture of sharp as well as diffused patterns.

Regularity of Molecular Structure and Crystallizability : The close relation between regularity of molecular structure and crystallizability has long been recognized. Typical crystalline polymers are those whose molecules are chemically and geometrically regular in structure. By 'Geometry' we mean the configuration of the chain. Stereo-regular polymers i.e., isotactic and syndiotactic, are found to crystallize, whereas atactic ones are unable to do so. Similarly linear polythene has a highly regular configuration and is, therefore, highly crystalline but this high crystallinity drops sharply when there is branching. Branched polyethylenes find it more difficult to crystallize than linear polyethylenes do. Branching imparts irregularity to the molecular structure and reduces the ability of the molecules to get themselves packed closely and hence, their ability to crystallize.

To understand further the effect of geometry on crystallizability, let us take the example of natural rubber and gutta-percha. Both are polyisoprenes. Natural rubber is the cis-isomer whereas Gutta-percha is the trans-isomer.



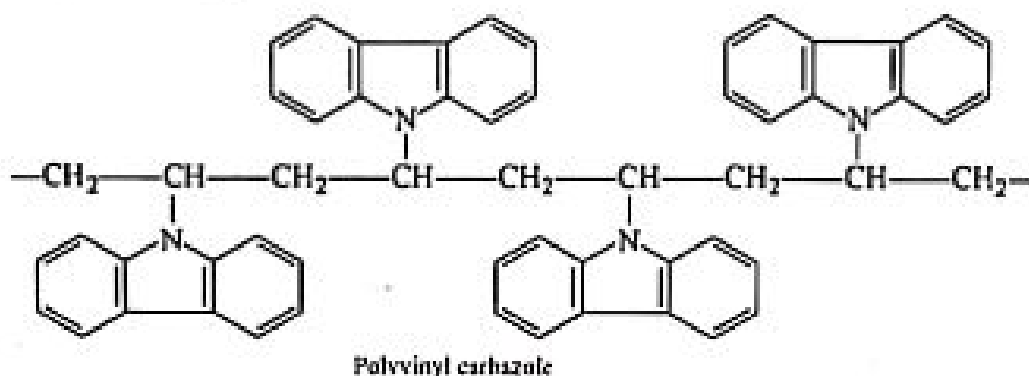
In natural rubber, due to cis-configuration, there is a bending back of the successive isoprene units, giving the molecule a coiled structure. In Gutta-percha, due to trans-configuration, there is a straightening out of the successive isoprene units, giving a rod-like structure to the molecule. A rod-like structure enables gutta-percha molecules to orient themselves in an orderly manner and pack up closely, as compared to the coiled molecules of the natural rubber. Gutta-percha is, therefore, more crystalline.

The effect of structural regularity on crystallizability can also be explained by comparing a homopolymer with its copolymer. For example, linear polyethylene is highly crystalline whereas random copolymer of ethylene and propylene is completely non-crystalline. The reason is that the random distribution of propylene repeat units in the copolymer disturbs the structural regularity of the chain molecule and suppress the tendency to crystallize. That is why, random copolymers do not generally crystallize. Notably, alternating copolymers, where the two repeat units are arranged in a regular alternation, retain the structural regularity and, hence, can show a tendency to crystallize.

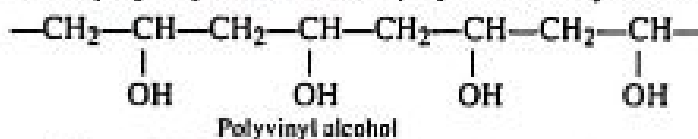
Other Factors Affecting Crystallizability : Apart from structural regularity, there are certain other factors which affect the crystallizability of a polymer :

(1) **Polarity**: Nylon 6, is highly crystalline in nature. This is due to the presence of polar groups in the molecule leading to hydrogen bonding. In Nylon 6, the carbonyl oxygen atoms of one polymer chain forms hydrogen bond with the H—Nc groups of another chain. Thus the formation of hydrogen bonds between two adjacent chains increases the interchain forces of attraction and facilitates tight packing and perfect bonding of the chain elements with each other.

(2) **Effect of bulky groups**: Bulky side groups come in the way of a closer molecular packing and hence affect crystallizability. For example, poly (vinyl alcohol) can be made to crystallize, although it is derived by hydrolysis from poly (vinylacetate), which has never been crystallized.



Polyvinyl carbazole, which has very bulky groups randomly projecting from the chain backbone, is very difficult to crystallize. But on the other hand, if the side groups are relatively small, as in the case of polyvinyl alcohol or polyvinyl fluoride, the polymer can crystallize.



Smaller groups like —CHOH—, —CF₂— etc. fit into the crystal lattices despite the stereochemical irregularity of the polymer. On the other hand, the —CHCl— group is apparently too large, since chlorinated polyethylene is non-crystalline. The absence of crystallinity in poly (vinyl acetate) and similar polymers is due to the combination of their atactic structure and the size of their substituent groups.

3.3. HELICAL STRUCTURES

Polymers with bulky substituents closely spaced along the chain often take on a helical conformation in the crystalline phase, since this allows the substituents to pack closely. Most isotactic polymers, as well as polymers of some 1, 1-disubstituted ethylenes such as isobutylene, fall in this class. Other helical structures of interest are those of polytetrafluoroethylene and the α -keratin structure.

It can be noted from the given figure that in all these conformations the carbon atoms (shown by smaller circles) forming the chain backbone are so arranged that an imaginary line drawn through all the successive substituent groups (shown by bigger circles) attached to the alternate carbon atoms of the chain backbone forms a helix. If the side group is not too bulky, the helix has exactly three units per turn and the arrangement is similar to that in figure (a). This arrangement is found in isotactic polypropylene, polystyrene etc. More bulky side groups require more space, resulting in the formation of looser helices [Figure b-d]. Isotactic poly (methyl methacrylate) forms a helix with five units in two turns, while poly isobutylene forms a helix with eight units in five turns.

Helical structures are of great importance in biological materials. Many polypeptides have, in fact, a helical structure. The DNA structure, for example, is helical. Hydrogen bonding plays an important role in the formation of the double helix of the DNA molecule.

order shown by smaller circles

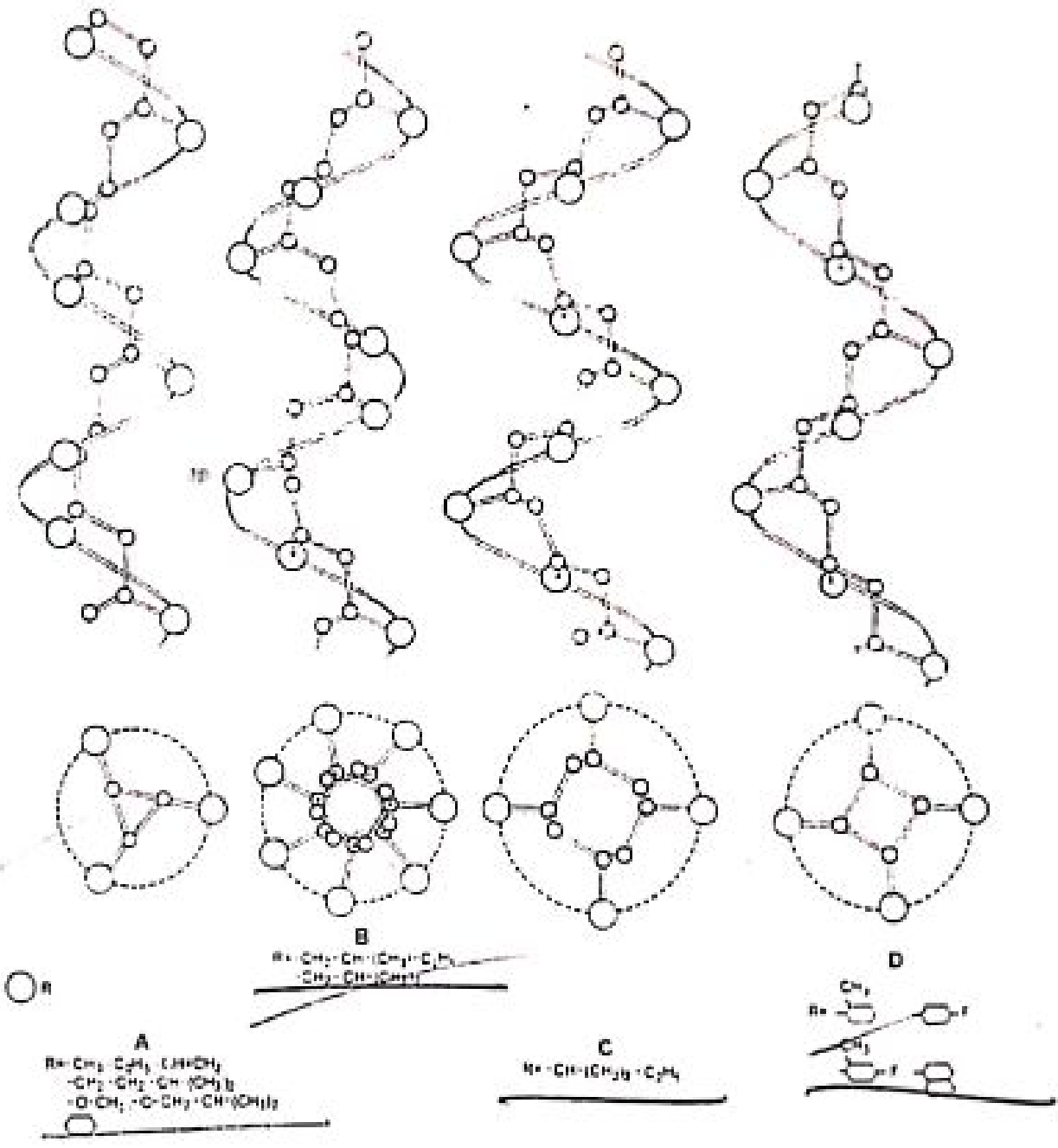


Fig. 1. Helical conformations of isotactic vinyl polymers

Isotactic
vinyl polymer

3.4. MORPHOLOGY OF CRYSTALLINE POLYMERS

The morphology of a crystallizable polymer is a description of the forms that result from crystallization and the aggregation of crystallites.

The term crystallite is used in polymer science to imply a component of an interconnected micro-crystalline structure.

When small molecules crystallize, each granule often has the form of a crystal grown from a single nucleus. Such crystals are relatively free of defects and have well-defined crystal faces and cleavage planes. Their shapes can be related to the geometry of the unit cell of the crystal lattice. Polymers crystallized from the melt are polycrystalline. Their structures are a mass of disordered material and clusters of

crystallites that developed, more or less, simultaneously from the growth of many nuclei. Distinct crystal faces can not be distinguished and the ordered regions in semi-crystalline polymers are generally much smaller than those in more perfectly crystallized micromolecular species. These orderly regions in a polymeric substance are called "crystallites" instead of 'crystals'. Thus crystallites can be visualised as regions composed of imperfect crystal-like chain aggregates. A partially crystalline polymeric material consists of several such crystallites co-existing with amorphous regions of disorderly placed chain segments. X-ray studies show that the highly ordered regions in semicrystalline polymers have dimensions of the order of 10^{-5} - 10^{-6} cm. These domains are held together by "tie molecules" which traverse more than one crystallite. This is what gives a semicrystalline polymer its mechanical strength.

Polymer Single Crystals :

Although the formation of single crystals of polymers was observed during polymerisation many years ago, Schlesingler (1953) and Keller (1957), finally reported the growth of such crystals. The phenomenon has been reported for so many polymers that it appears to be quite general and universal.

Single crystals of various polymers appear similar when viewed under an electron microscope. A polymer single crystal looks as though it consists of many thin, flat platelets (lamellae) kept one over the other in a decreasing order of size. The usual lamellar thickness of the single crystal is around 100Å. The size, shape and regularity of the crystals depend on their growth conditions, such as solvent, temperature etc. Since the molecules in the polymers are at least 1000Å and the lamellae are only about 100Å thick. The question is : How to accommodate the long chain into the narrow lamellae ? The only possible explanation is that the chain folding takes place during the process of crystallization.

Spherulites : Polymers that are crystallized from a melt show some interesting micro structures when observed under a polarising microscope. The most prominent structure on a scale larger than lamellae is the spherulite. It is a spherical aggregate ranging from submicroscopic in size to millimeters in diameter. Spherulites are seen as circular birefringent regions.

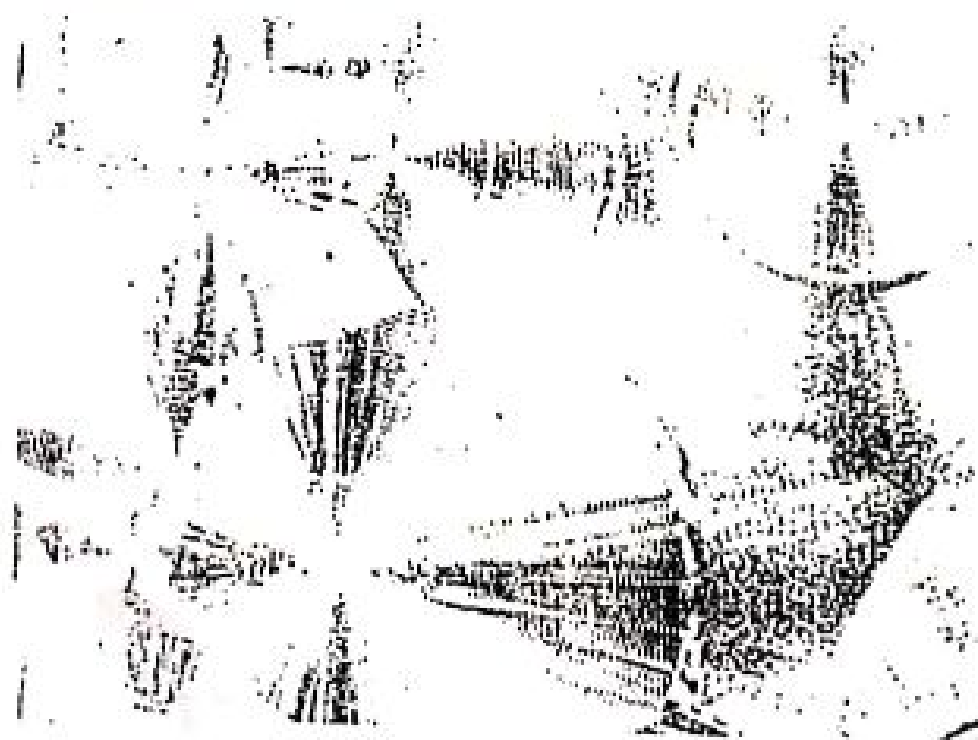


Fig. 2. Ringed spherulites observed in the optical microscope

3.5. CRYSTALLIZATION AND MELTING

Crystallization Kinetics : The development of crystallinity in polymers is studied experimentally by observing the variation of specific volume as a function of time at constant temperature. Specific volume is the property which vary with total amount of crystallinity. The development of crystallinity in polymers is not instantaneous.

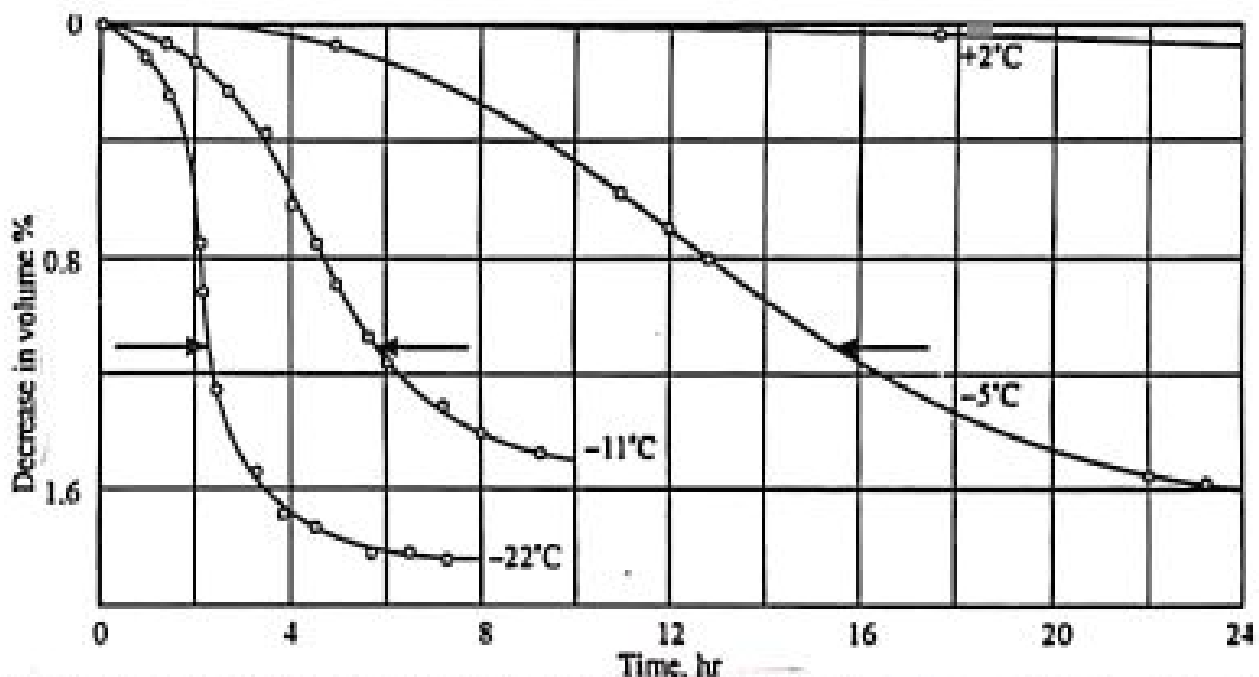


Fig. 3. Volume-time relations during the crystallization of natural rubber. Arrows indicate points where crystallization is half complete.

The graph between volume-time shows that crystallization sometimes can not be considered complete for long periods. Since the time for complete crystallization is somewhat indefinite, it is customary to define the rate of crystallization at a given temperature as the inverse of the time needed to attain one half of the total volume change. The rate so defined is a characteristic function of temperature. As the temperature is lowered the rate increases, goes through a maximum, and then decreases. At temperatures at which the rate is very low, the polymer may be supercooled and maintained in the amorphous state.

If the data for specific volume as a function of time during crystallization, are plotted against time, all the curves have the same shape.

Determination of crystalline melting point (T_m) : Low-molecular-weight molecules melt and crystallize completely over a sharp temperature interval. Crystallizable polymers differ in that they melt over a range of temperatures and do not crystallize completely, especially if they have high molecular weights. Almost all crystallizable polymers are considered to be "semi crystalline" because they contain significant fractions of poorly ordered, amorphous chains. The melting range of a semicrystalline polymer may be very broad. Branched (low-density) polyethylene is an extreme example of this behaviour. Softening is first noticeable at about 75°C although the last traces of crystallinity do not disappear until about 115°C. Other polymers, like nylon 6,6, have much narrower melting ranges.

The disappearance of a polymer crystalline phase at the melting point is accompanied by changes in physical properties. The material becomes a (viscous) liquid with changes in density, refractive index, heat capacity, transparency and other properties. Measurement of any of these properties may be used to detect the crystalline melting point T_m .

Today almost all measurements of T_m are made by differential thermal analysis (DTA). Other methods that could be used to detect T_m are X-ray diffraction, infrared and NMR spectroscopy.

Degree of Crystallinity : Crystallinity of a polymer sample is expressed in terms of that fraction of the sample which is crystalline. In a polymer sample, both crystalline and non-crystalline components coexist. It is for this reason that X-ray diffraction patterns of most polymers show both sharp as well as broad and diffused bands. The sharp bands are due to crystalline regions and the diffused and broad bands are due to non-crystalline (amorphous) regions. These crystalline and amorphous regions, in a polymer sample are held together by long polymer chains which run through them.

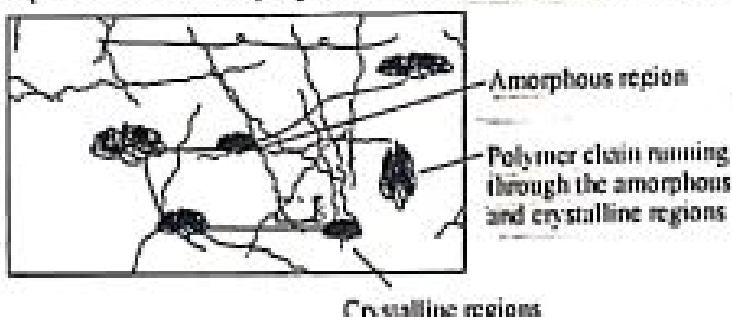


Fig. 4

Further, amorphous components in a polymer are in the liquid phase whereas the crystalline components in the crystalline phase.

The density of the crystalline component is, therefore, higher than that of the amorphous component. For a given polymer a 100% crystalline sample will have the highest density and a 100% amorphous sample will have the lowest. Actually, polymers are only partially crystalline, so its density will naturally be in between those of their crystalline and amorphous components.

From the knowledge of the densities of the crystalline and amorphous components and that of the particular sample, the degree of crystallinity of the sample can be calculated by the equation :

$$X_v = \frac{d - d_a}{d_c - d_a}$$

where X_v is the degree of crystallinity by volume and d , d_a and d_c are the densities of the sample, the fully amorphous and fully crystalline components respectively.

Degree of crystallinity of a polymer sample can also be measured in terms of specific volume.

$$X_m = \frac{V_a - V}{V_a - V_c}$$

where X_m is the degree of crystallinity by mass and V , V_a and V_c are the specific volumes of the sample, the fully amorphous and fully crystalline components respectively.

3.6. STRAIN INDUCED MORPHOLOGY

When a polymer is crystallized from solution in the absence of external forces, crystals are formed, morphology of which we have studied in previous section. If the solution is subjected to an external stress such as stirring, an entirely different morphology can result. The reason is obvious. When a polymer mass is crystallized in the absence of external forces, there is no preferred direction along which the polymer chains lie. If such an unoriented crystalline polymer is subjected to an external stress, it undergoes a rearrangement of the crystalline material. X-ray diffraction pattern suggest that the polymer chain align in the direction of the applied stress. At the same time there is a change in the physical properties of the sample also.

Fibrillar Crystallization : If a dilute (~ 1%) polymer solution is stirred during crystallization, crystalline aggregates consisting of a central rod or ribbon with lamellar overgrowths can be formed.

The morphology has been called the "Shish Kebab" morphology. 'Shish' means 'The backbone' and the 'Kebabs' are the epitaxial growths formed using the backbone as a nucleus. This is perhaps the most spectacular of a number of morphologies produced by crystallization under unusual conditions.

Polymer Structure and Physical Properties :

There are several factors which determine the physical properties of a polymer. The molecular weight, bonding forces, configuration and conformation, and the nature of chain-packing of molecules. These

factors influence the crystallinity of polymers, which in turn, influence such important physical properties as impact and tensile strength, melting point, the viscosity and solution properties of polymers. Polymer structure is also responsible for its unique properties—for example, the elasticity and abrasion resistance of rubbers, the strength and toughness of fibres, and the flexibility and clarity of films.

But one of the most important determinants of polymer properties, is the location in temperature of the major transitions, the glass transition and the crystalline melting point.

If a polymer has a high T_g (say, above 30°C), it will generally be unsuitable for use in applications that require flexibility and rubbery properties. If the material is contemplated for use as an elastomer in a low-temperature environment (e.g., in the arctic or in air craft) it must have a very low T_g and have a low degree of crystallinity. For a polymer to be useful as a textile fibre, it should normally have a T_g that is below its normal operating temperature but a T_m that is above this temperature. A polymer that is to be used as a rigid structural material should have a high T_g (100°C or above). So let us first discuss the relations between molecular structure and T_m and T_g .

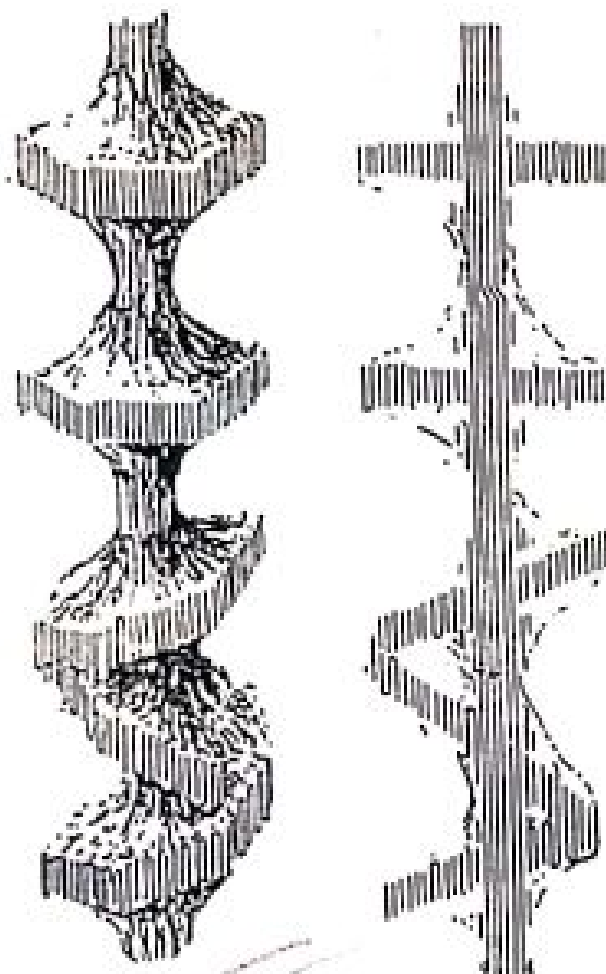


Fig. 5. Schematic model to "shish kebab" morphology formed by crystallization of a stiffed polymer solution

The crystalline melting point : If we describe the crystalline melting point in the thermodynamic terms, melting takes place when the free energy of the process is zero :

$$\Delta G = \Delta H_m - T_m \Delta S_m = 0$$

where ΔG = Gibbs free-energy change

ΔH_m = The heat of fusion per mole of repeating unit

ΔS_m = Change in entropy of fusion

Thus

$$T_m = \frac{\Delta H_m}{\Delta S_m}$$

Melting points of Homologous series and effect of chain flexibility and other steric factors

The flexibility of chain molecules arises from rotation around saturated chain bonds. The potential energy barriers hindering this rotation range from 0.2 to 1.2 kJ/mole, the same order of magnitude as

Side-Chain Substitution

In many polymers, if the non-polar groups are substituted in side chain, it causes reduction in melting point (T_m) or may result for complete loss of crystallinity. If the substitution is random, as in case of branched polyethylene, the initial effect is a reduction in the size and perfection of the crystalline regions usually accompanied by a decrease in the crystallinity. The crystalline melting point of polyethylene is less by 20–25°C from the linear to branched polymer.

If the amide hydrogen is replaced by an alkyl group, it results much greater effect because hydrogen bonding gets destroyed. In another case, such as N-methyl nylons melt at 100°C lower than its unsubstituted material.

In isotactic poly (α -olefins), an increase in the side chain causes an increasingly lower melting point, T_m . On the other hand, an increase in the bulkiness of the side chain increases melting point, since the rotation in the side chain is restricted in the liquid state, with decrease in ΔS_m .

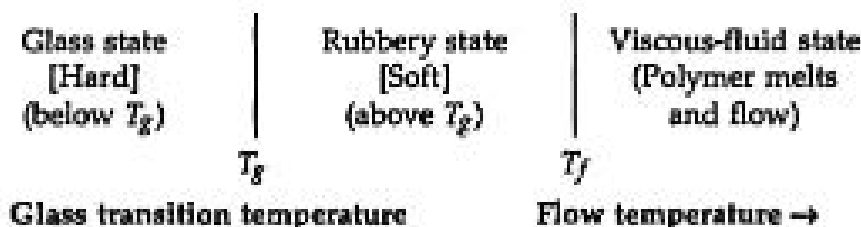
Effect of side chain substitution on the Melting Point of Isotactic Poly (α -olefins)

Side chain	T_m (°C)
—CH ₂ CH ₂ CH ₂ CH ₃	–55
—CH ₂ CH ₂ CH ₃	75
—CH ₂ CH ₃	125
—CH ₃	165
—CH ₂ — CH — CH ₂ — CH ₃ CH ₃ CH ₃ 	196
—CH ₂ — C — CH ₂ — CH ₃ CH ₃	350

▶ GLASS TRANSITION TEMPERATURE

Almost all amorphous polymers and many crystalline polymers possess a *temperature boundary*. Above this temperature the substance remains soft, rubbery and flexible, and below this temperature it becomes hard, glassy and brittle. The temperature, below which a polymer is hard and above which it is soft is called the **glass transition temperature**. The hard, glassy, brittle state is known as the *glassy state* and the soft, rubbery, flexible state is the *rubbery* or *viscoelastic state*. The glass transition temperature is denoted by T_g .

T_f is another term for temperature. When a polymer is heated further, it forms a viscous liquid and starts flowing, this state is known as **viscous-fluid state** and the temperature is termed as **flow temperature** (T_f). The different states with change of temperature are as :



An ordinary natural rubber ball if cooled below -70°C becomes so hard and brittle that it will break into several pieces like a glass ball falling on a hard surface. This happens because there is a temperature boundary for amorphous and many crystalline polymers. The transition from the rubber to the glass-like state is an important feature of polymer behaviour, marking as it does a region where dramatic changes in the physical properties, such as hardness and elasticity, are observed. The changes are completely reversible and the transition from a rubber to a glass is a function of molecular motion, not polymer structure. In the rubber-like state or in the melt the chains are in relatively rapid motion, but as the temperature is lowered the movement becomes progressively slower until the available thermal energy is insufficient to overcome the rotational energy barrier in the chain. At this temperature, T_g , the chains become locked in whichever, the conformation they possessed when T_g was reached. Below T_g , the polymer is in the frozen liquid (glassy) with a completely random structure. It is quite obvious that T_g is an important characteristic property of any polymer as it has an important bearing on the potential application of a polymer.

Experimental Demonstration of T_g

The glass transition temperature is not specific to long chain polymers. Any substance, which can be cooled to a sufficient degree below its melting point without crystallizing, will form a glass. The phenomenon can be conveniently demonstrated using glucose penta-acetate (GPA). A crystalline sample of GPA is melted, then chilled rapidly in ice-water to form a brittle amorphous mass. By working the hard material between one's fingers, the transition from glass to rubber will be felt when the sample is warmed up.

A little perseverance, with further rubbing and pulling, will result in the recrystallization of the rubbery phase, which then crumbles to a powder.

▶ GLASSY SOLIDS AND GLASS TRANSITION

The concepts of glassy solids and glass transition are further understood by knowing the following terms :

(a) States of Aggregation

There are three states of aggregation in low molecular weight compounds (i) solid (ii) liquid (iii) gas.

Polymers are the compounds, possess only two states of aggregation (i) solid (ii) liquid. They never exist in gaseous state, because at the their boiling point, the polymers get decomposed.

In a crystal lattice, low molecular weight solid substance sits in a definite equilibrium position from which it moves only a little space, in a *vibrational motion*. In a crystalline solid,

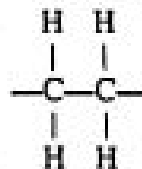
Factor affecting the glass transition temperature

The intermolecular forces determine the magnitude of the molecular aggregates. In the case of hydrocarbon polymers, only vander Waal's forces act on the neighbouring polymer chains and, hence, molecular aggregates are not that strong. Polymer chains can slip past each other easily. Polymer chains containing polar groups like $>C=O$, $>N-H$ etc. are held together by dipolar attraction and intermolecular hydrogen bonding and so are unable to move that easily.

Hindrance to segmental rotation and intermolecular cohesive forces restrict the chain mobility and they are held down to positions of minimum potential energy. The thermal energy of a polymer (which naturally increases with temperature), however, activates thermal vibrations of the chain elements. As the temperature is increased, these vibrations are able to get over the hindrance to segmental rotation and the intermolecular cohesion. When the restrictions are overcome at appropriate temperatures, segmental and molecular motion set in. The onset of these motions determines the T_g as well as the T_m of the polymer. Hence we see that the glass transition temperature and the melting temperature of a polymer depends on chain geometry, chain flexibility and molecular aggregates.

Let us study few examples to confirm above facts.

(1) Polyethylene is made up of the repeating unit



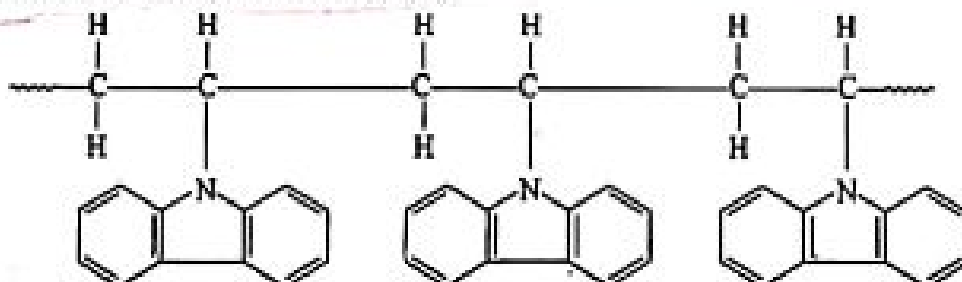
has a T_g value of -125°C . In this case, T_g is quite low because (i) strong intermolecular cohesive forces are absent and (ii) the substituent group on carbon atoms is only hydrogen, which is not bulky at all.

(2) Nylon 6, a polyamide, has a high T_g (50°C). It is due to the presence of a large number of polar groups in the molecules, leading to strong intermolecular hydrogen bonding between $>C=O$ and $>N-H$ groups.

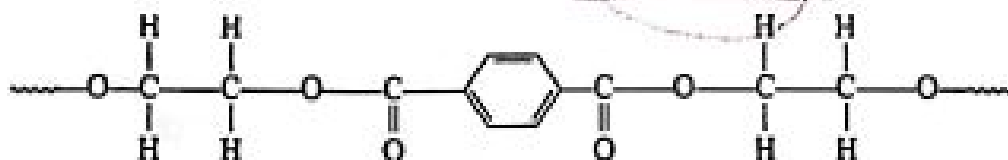
(3) The effect of the side group on chain mobility and hence on glass transition temperature can be studied by taking the examples of polystyrene and polymethyl styrene and also of poly methylacrylate and polymethyl methacrylate.

The presence of $-\text{CH}_3$ groups in poly α -methyl styrene and poly methyl methacrylate, comes in the way of free rotation around $\text{C}-\text{C}$ bond of the chain backbone and, hence, hinders the chain mobility, resulting in an increase of around 70°C and 100°C in their T_g values over polystyrene and polymethylacrylate, respectively.

(4) Polyvinyl carbazole has a high glass transition temperature (150°C) because it contains bulky side groups which hinder the freedom of rotation.



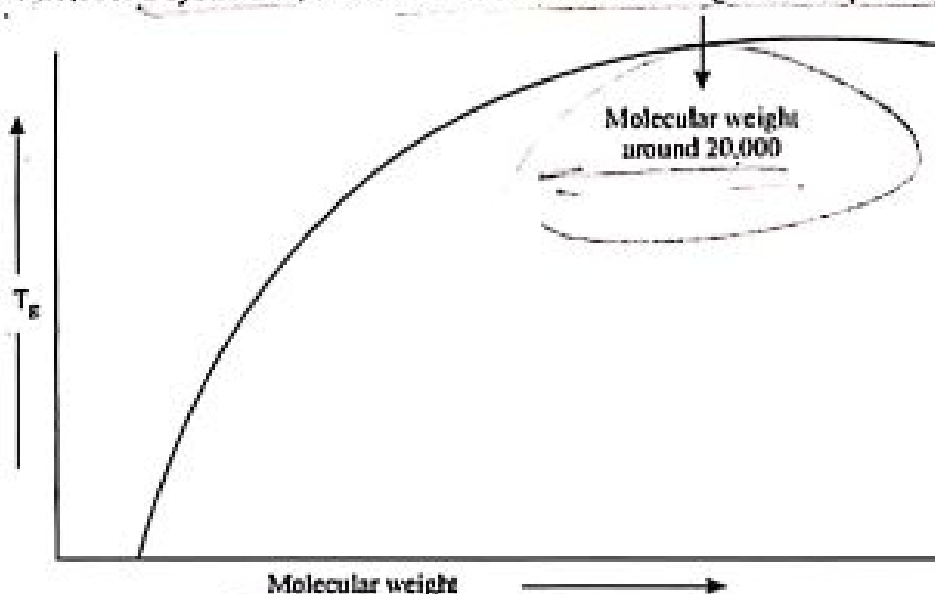
(5) In the case of polyethylene terephthalate the presence of the aromatic rings in the chain backbone increases the inflexibility of the chains and the T_g value is high (69°C).



(6) The higher T_g value for the derivatives of cellulose, such as cellulose nitrate, is largely due to the rigid ring structures in the macromolecular chain.

3.7.1. Glass Transition Temperature and Molecular Weight

The glass transition temperature of a polymer is influenced by its molecular weight, at least up to around a value of 20,000. Beyond this, the effect of the molecular weight is not pronounced.



Following two mathematical relationships have been established between the two :

$$T_g = T_g^\infty - \frac{K}{M_n}$$

$$\frac{1}{T_g} = \frac{1}{T_g^\infty} + \frac{A}{M_n}$$

and

where T_g^∞ is the glass transition temperature at infinite molecular weight and K and A are arbitrary constants.

Now, let us see how the molecular weight can affect the T_g values. We know that polymer chains made of hundreds of monomeric units comprise several segments, each made of a few tens of monomeric units.



It is also well known that the mobility of chain segments influences the glass transition temperature. Now, the segments that are away from the chain ends have a restricted mobility whereas the two end segments containing the chain ends, have more freedom for motion. For a given weight of the polymer, a low molecular weight sample will have more chain end segments than a high molecular weight sample. The larger the number of chain end segments, the larger will be the effective segmental motion. Thus, the T_g value will be lower for low molecular weight polymers.

3.7.2. Glass Transition Temperature and Melting Point :

(Relationship between T_m and T_g)

Many attempts have been made to study the relationship between the glass transition temperature and melting point. Based on experimental observations, T_g and T_m (in degrees Kelvin), have been shown to be related as :

$$T_g = \frac{1}{2} T_m \text{ (for symmetrical polymers)}$$

$$T_g = \frac{2}{3} T_m \text{ (for unsymmetrical polymers)}$$

A combined version of these two equations, irrespective of molecular symmetry can be shown as :

$$\frac{1}{2} < \frac{T_g}{T_m} < \frac{2}{3}$$

3.7.3. Effect of Chemical Structure on T_g

The effects of the nature of the chain repeat units on T_g are pronounced as it is related to intermolecular forces, chain stiffness, and symmetry. Probably the most important factor among these is hindrance to free rotation along the polymer chain due to the presence of bulky side groups. The effect can be visualized by comparing the glass transition temperature of following polymers :

Sidechain	T_m ($^{\circ}\text{C}$)
Poly butadiene	- 85 $^{\circ}\text{C}$
Styrene-butadiene copolymer	- 55 $^{\circ}\text{C}$
Polystyrene	+ 100 $^{\circ}\text{C}$
Poly (α -methyl styrene)	+ 150 $^{\circ}\text{C}$

3.8. PROPERTY REQUIREMENTS AND POLYMER UTILIZATION

We have seen that depending on their ultimate properties, polymeric materials can be classified into three broad categories : Elastomers, Fibres and Plastics. In a simple way, we can say that elastomeric materials exhibit rubber elasticity; fibre-forming materials possess rigidity and stiffness; and plastic materials are generally strong and tough. Now the question arises : what makes them behave differently? And the answer is : It is the chemical and geometrical structure of the individual polymer chains as well as the type of inter-chain arrangement that decide the property of a polymeric substance. Let us discuss the property requirements for elastomers, fibres and plastics.

3.8.1. Elastomers

All substances exhibiting a high degree of rubberlike elasticity contain long chain structures and should comprise of flexible segments capable of attaining free rotation. In the unstrained state, they should tend to take up the more probable randomly coiled conformation such that the entropy factor is highest at its normal state. When strained, the chains should be able to get extended and be brought to more ordered conformations. An ordered arrangement of the chain molecules gives rise to partial crystallinity and also a decrease in the entropy factor. It is thus the decrease in entropy that favours recoiling on release of the force. There should also be sufficient interchain free volume to provide for unhindered segmental mobility during coiling and uncoiling.

In contrast to the high local mobility of chain segments, the gross mobility of chains in elastomers should be low. The motions of chains past one another must be restricted in order that the material can regain its original shape when the stress is released.

This restriction of gross mobility is usually obtained by the introduction of a network of primary bond cross-links in the material. The cross links must be relatively few and widely separated, so that stretching to large extensions can take place without rupture of primary bonds.

The requirement of chain flexibility and segmental mobility can be obtained by selecting repeat units made of the C—C and C—O linkages and by avoiding bulky side groups on the repeat units. By avoiding aromatic and cyclic structures in the chain backbone, chain stiffening can be avoided. In the case of diene polymers, an increase in the *cis*-content will lead to a better chain flexibility.

Branched molecules will provide an increased interchain free volume because such molecules can not have close packing. Interchain cohesive forces can be minimised by avoiding polar groups in the repeat units. Cross-links provided at suitable intervals will hold the molecules together and will not allow them to slip past each other on stretching.

Further, for a polymeric substance to possess the elastomeric property *i.e.*, to behave like a rubber (over a wide range of temperature), its glass transition temperature (T_g) should be as low as possible and the flow temperature (T_f) should be as high as possible. We can push down the T_g by plasticising the material. This can be done by copolymerisation with small quantities of a suitable comonomer.

Copolymerisation lowers the T_g of a polymer. This is internal plasticisation. External plasticisation involves compounding the polymer with a mutually compatible high boiling liquid, called a plasticiser.

It reduces the interchain cohesion in the polymer and favours segmental motion. The elevation of the T_f is done by cross-linking or vulcanization. In a vulcanized material, the T_f is generally so high that the material on heating starts decomposing before its T_f is reached.

3.8.2. Fibres

In contrast to elastomers, fibres exhibit high tensile strength and rigidity or stiffness and undergo irreversible deformation. For obtaining these properties polymer should have symmetry and high cohesive energy associated with a high degree of crystallinity. They should be packed very close to each other in a highly ordered manner and should be held together by strong interchain cohesion forces which resist deformation and do not allow any relative movement between the chains. Thus the selection of a polymer for use as a fibre involves a number of points. First it should be linear polymer with high symmetry and high intermolecular forces resulting from the presence of polar groups. It should have a very high degree of polymerisation. Branching, in the polymer chain disrupts the crystalline lattice, lowers the crystalline melting point and decreases stiffness so it should be avoided. Presence of aromatic and cyclic rings in the chain backbone increases stiffness. Crosslinking between the chain offers strong interchain bonding.

3.8.3. Plastics

In general, the properties of plastics are intermediate between those of fibres and elastomers. Plastic materials possess good tensile strength and rigidity. These can be either fully amorphous or partially crystalline.

Cross-linking of plastic materials, as in the case of elastomers, improves the structural rigidity. When products do not demand high rigidity, uncross-linked systems are used. Polystyrene and polyethylene are examples of such systems. On the other hand, phenol-formaldehyde, urea-formaldehyde and epoxy systems involve cross-linking. Generally the uncross-linked plastic materials are thermoplastic and the cross-linked systems are thermosetting.

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