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Polymer Chemistry

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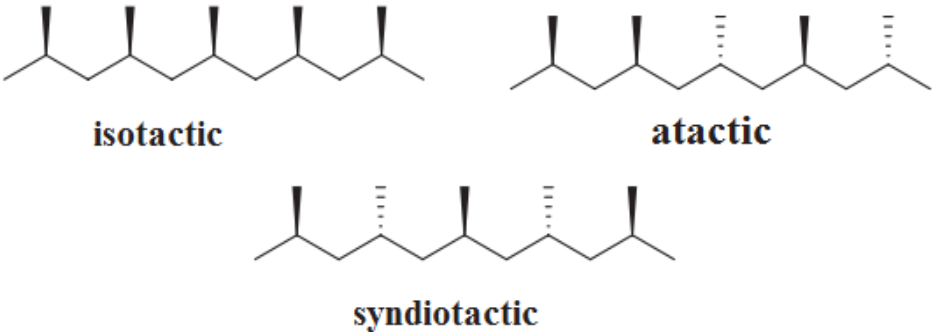
Crystallization and Crystallinity

Lecture Note-5

A. 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 anyone 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 be 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 characterised 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 characterised 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.

B. CRYSTAL STRUCTURES OF POLYMERS

Structural requirements for crystallinity :

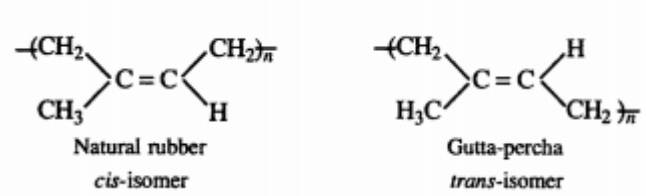
Many polymers, including most fibres, are partially crystalline. The most direct evidence of this fact is provided by X-ray diffraction studies. It is a well known fact that while crystalline substances give sharp and well defined X-ray diffraction patterns, non-crystalline (amorphous) substances give 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 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.

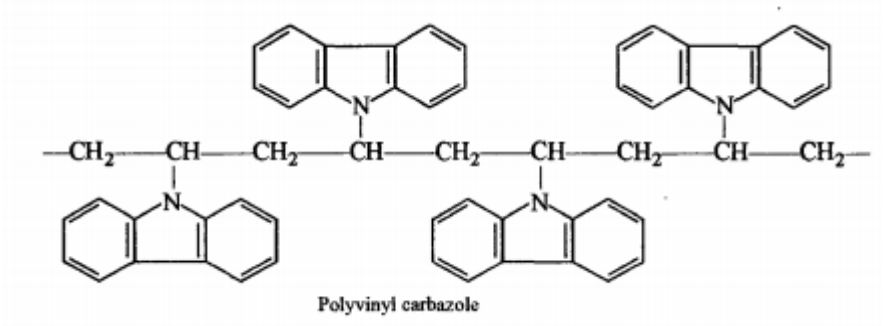
The effect of structural regularity on crystallizability can also be explained by comparing a homopolymer with its copolymer. For example, linear polyethylene is highly crystalline whereas random copolymer of ethylene and propylene is completely non-cryztalline. The reasons is that the random distribution 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 :

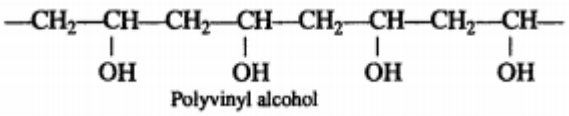
(1) Polarity: Nylon 6, is highly crystalline in nature. This is due to the presence of polar groups in the molecule leading to hydrogen bonding. In Nylon 6, the carbonyl oxygen atoms of one polymer chain forms hydrogen bond with the H-N< groups of another chain. Thus the formation of hydrogen bonds between 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 racking and hence affect crystallizability. For example, poly (vinyl alcohol) can be made to crystallize, although it is derived by hydrolysis from poly (vinylacectate), which has never been crystallized.



Polyvinyl carbazole

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.



Polyvinyl alcohol

Smaller groups like −CHOH−, $-CF_2-$ etc. fit into the crystal lattices despite the stereochemical irregularity of the polymer. On the other hand, the −CHCI− 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.

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 a-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 1a.** This arrangement is found in isotactic polypropylene, polystyrene etc. More bulky side groups require more space, resulting in the formation of looser helices [**Figure 1b-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.

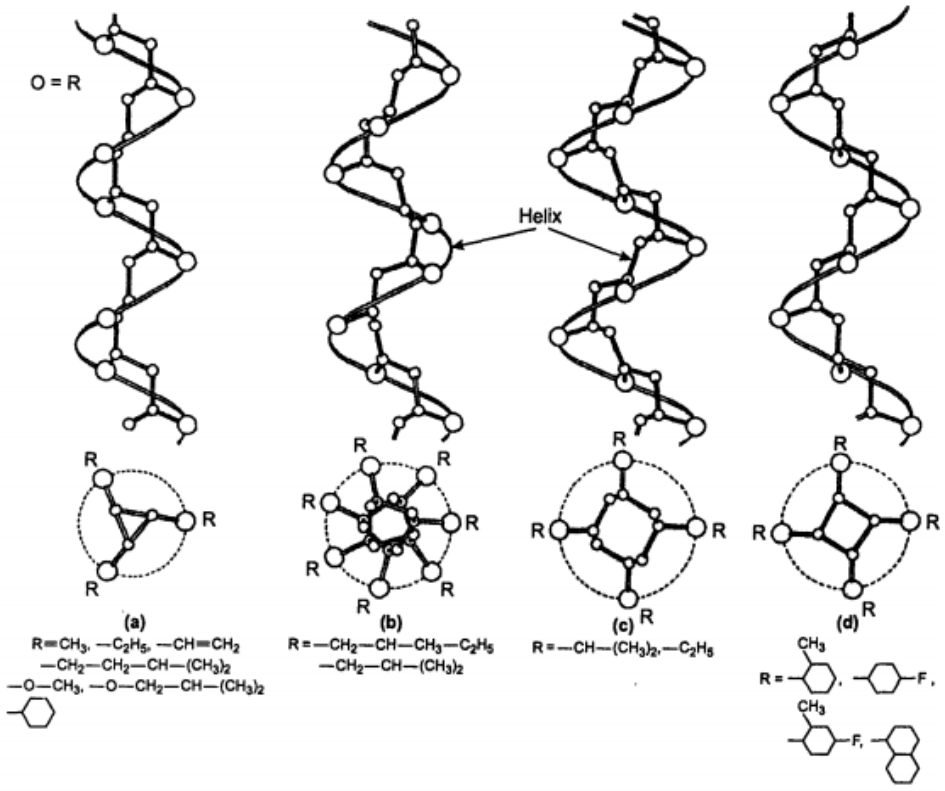


Fig. 1. Helical conformation of Isotactic vinyl polymers.

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.

C. 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.

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 charge. 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.

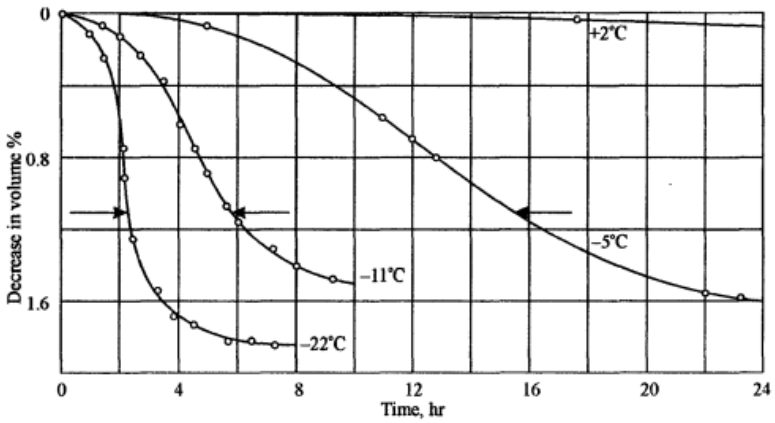


Fig. 2. Volume-time relations during the crystallization of natural rubber. Arrows Indicate points where crystallization is half complete

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 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.

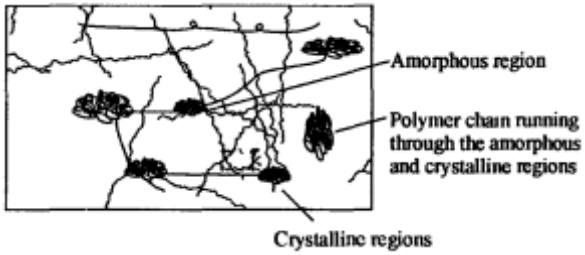


Fig. 3.

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.

D. MORPHOLOGY OF CRYSTALLINE POLYMERS

Polymer single crystals:

Many years ago, the formation of single crystal of polymers was observed. Earlier, it was believed that the single crystals of polymer from their solution were not possible due to entanglement of the molecules. In 1953 Schlesinger, has reported the growth of single crystals. There are many polymers which have been used for single crystals, examples are, polyethylene, polypropylene, gutta-percha, polyamides, poly (α-olefins), polyoxymethylene, cellulose and its derivatives.

Lamellae:

All the single crystals contain same general morphology. They are thin and flat platelets, *i.e.,* lamellae about 100 Å thick. They consist of many micrometers lateral dimensions. They possess spiral growth of additional lamellae and increased into their thickness. A typical lamellar crystal is shown in **Fig. 4.** The shape, size and regularity of crystals depend on their growth conditions. Solvent, temperature and growth rate are important conditions for the crystal growth. Since the molecules in the polymers are at least 1000 Å long and the lamellae are only about 100 Å thick, the chains are folded. This arrangement has been shown to be sterically possible. In the case of polyethylene, the molecule is folded in a way where only about five chain carbon atoms are involved.

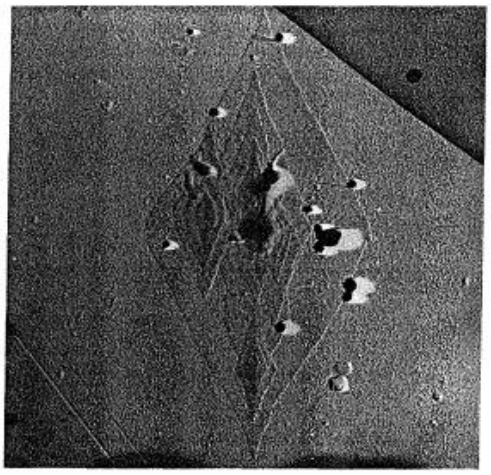


Fig. 4. Electron micrograph of a single crystal of 6-nylon grown by precipitation from dilute glycerine solution (Geil 1960) The lamellae are about 60 Å, thick

Many single crystals show secondary structural features, *e.g.,* corrugation and pleats. Many crystals of polyethylene and few other polymers grow in the form of hollow pyramids.

When solvent is removed during preparation of the crystals for microscopy, surface-tension forces cause the pyramids to collapse.

The hollow pyramidal structure is related to the packing of the folded chains If successive planes of folded molecules are displaced from their neighbors by an Integral (or, with rotation of 180°, by a half-integral) number of repeat distances, a pyramidal structure with a slope of 32° (or 17°) results.

More Complex Structures.

The growth of crystal structures from polymer solutions can result in more complex structures sometimes reminiscent of features found in polymers crystallized from the melt Typical of these are sheaflike arrays corresponding to the nuclei and initial growth habit of spherulites. Each ribbon in the array is composed of a number of lathlike lamellae with the usual 50-100 **Å** thickness. Twinned crystals, dendritic growths, clusters of hollow pyramids, spiral growths, steps, Bragg extinction lines, dislocation networks, moir6 patterns, and epitaxial growths have been described, among others.

Disorder and Nature of the Fold Surfaces.

The major unsolved problem (Keller 1969) in polymer single-crystal studies has for some time centered on the nature of the fold surfaces Although there is strong structural and kinetic evidence favouring regular folding with immediate adjacent recntry of the chain into the crystal, there is even more convincing evidence that considerable molecular disorder exists in polymer single crystals The extent of this disorder appears too great to be compatible with intercrystalline defects and to require some sort of amorphous region or layer at the fold surface. Such a region might involve loose or irregular folds or a more random "switchboard" model as suggested by Flory (1962), and as indicated schematically in **Fig 5.** Although there appears to be agreement that the fold surfaces in polymer single crystals are rather regular and tight, the controversy remains unresolved into the 1980s.

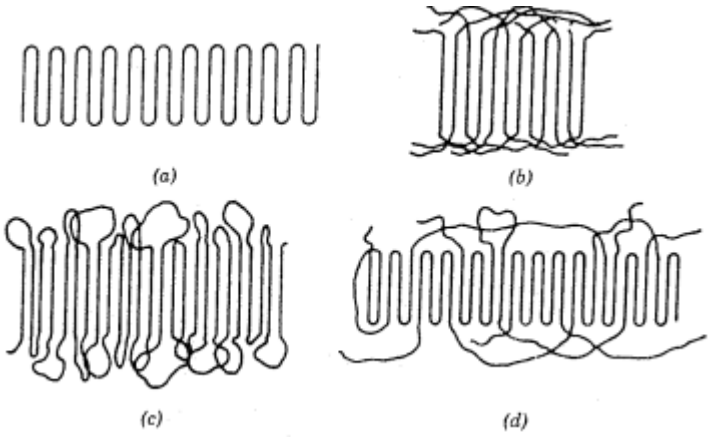


Fig. 5. Schematic two-dimensional representations of models of the fold surface in polymer lamellae (Ingram 1968): (a) sharp folds, (b) "switchboard" model, (c) loose loops with adjacent reentry, (d) a combination of several features

Structure of Polymers Crystallized From the Melt

The Fringed Micelle Concept.

Although x-ray diffraction studies show recognizable crystalline features in some high polymers, the Bragg reflections appear broad and diffuse compared to those from well developed simple crystals. Diffraction theory indicates that this broadening can arise from either small crystallite size or the presence of lattice defects (Bunn 1961), but the diffraction patterns from polymers are usually too weak to permit discrimination between these possibilities Historically, the hypothesis of small crystallite size was selected as more probable.

With this assumption, rough estimates from the width of diffraction rings indicated that crystallite size rarely exceeds a few hundred angstroms. **A** substantial background of diffuse scattering suggested the coexistence of an appreciable amorphous fraction It was suggested that the polymer chains are precisely aligned over distances corresponding to the dimensions of the crystallites, but include more disordered segments that do not crystallize, and hence are included in amorphous regions Since the chains are very long, they were visualized as contributing segments to several crystalline and amorphous regions, leading to a composite single phase structure known as the fringed micelle or fringed crystallite model (**Fig 6.**), the fringes representing transition material between the crystalline and amorphous phases.

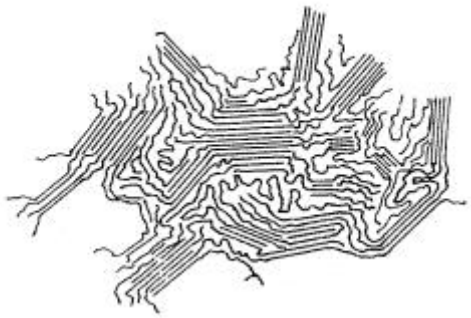


Fig. 6. Fringed micelle model of the crystalline-amorphous structure of polymers (Bryant 1947).

Structure of Spherulites:

It was found that the spherulites are the complex structure of lamellae. It is a spherical aggregate, its size is submicroscopic to millimeters in diameter. Spherulites are recognized by their characteristic appearance in the polarizing microscope; where they are seen as circular birefringent areas consisting of a dark maltese cross pattern.

Relationship of Spherulites with Crystallites:

By examining the polymers, it is stated that in the usual case, spherulites are crystalline, whereas the intermediate non-spherulites are amorphous. The point of initiation of spherulite growth is either its nucleus which may be foreign particle (heterogeneous nucleation) or may arise spontaneously in the melt (homogeneous nucleation).

Morphology of Spherulites:

It is observed by electron-microscope that ·spherulites have lamellar structure in almost all polymers. Crystallization occurs by the growth of individual lamellae. Growth starts from screw dislocations at the nucleus or at spiral growth spreading out as spherulite. When two spherulites meet during crystallization, the lamellae from both extend across the boundary into any uncrystallized material is available. Lamellar structure is found throughout the body of spherulites. Morphology of spherulites (in some polymers) is by the development of ring structure which is due to the periodic twisting of the lamellae.

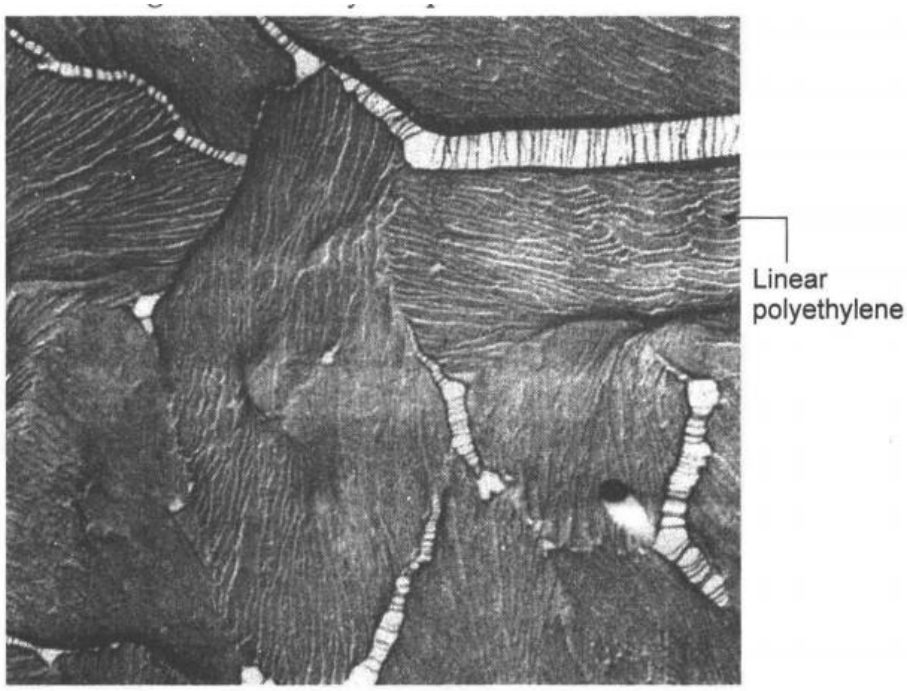


Fig. 7. Electron micrograph of a film of linear polyethylene crystallized by evaporation of the solvent.

Strain-Induced Morphology:

In the absence of any external force, when a polymer is allowed to crystallize from a solution, it forms a single crystal. If the solution is passed through an external-force such as mechanical stirring, again a single crystal is formed but with entirely different morphology.

In the first case when there is no external force, the crystal is formed without any preferred direction along which the polymer chains lie, but in second case, when external stress is subjected on the unoriented crystalline polymer mass, it undergoes a rearrangement of the crystalline material and shows markedly changed physical properties.

Fibrillar Crystallization:

When a dilute solution of polymer is subjected to stirring during crystallization, the crystalline material deposits and forms a central rod like structure with lamellar overgrowths. Such type of morphology of crystal is called as *'shish kebab'* morphology. The *'shish'* (backbone) consists of relatively but not fully extended chains with many defects. The *'kebab'* forms by epitaxial growth using the backbone as a nucleus. The figure is given below.

Cold Drawing:

The 'cold drawing' process is carried out in the fibres of polymer below melting point *(T_m)* but above glass-transition *(T_g)* temperature. In this process when an unoriented fibre is stretched rapidly, it does not become gradually thinner, but suddenly becomes thinner at one point. This is called as *necking down* process.

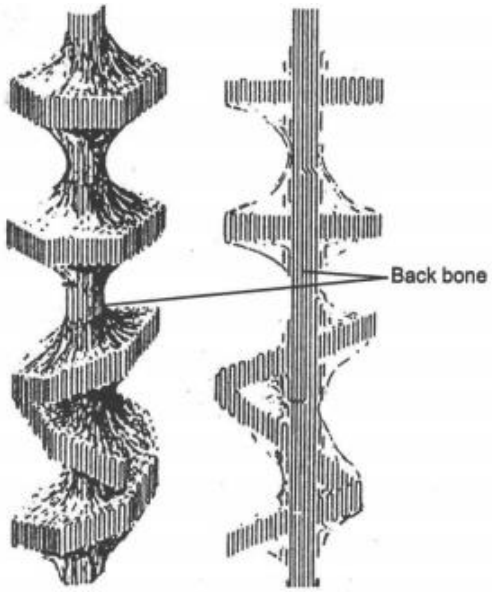


Fig. 8. Model of "shish kebab" morphology formed by crystallizatIon of a stirred polymer solution.

As the·stretching is continued, the thin or drawn section increases in length of the expense of the undrawn portion of the fibre. Throughout the entire process, the diameter of the drawn and undrawn portions remain almost the same. The ratio of the length (draw-ratio) of the drawn fibre to that of the undrawn is about 5 : 1 in most of the branched polymers such as polyethylene, polyesters and polyamides but is more than 10 : 1 in linear polyethylene.

MORPHOLOGY OF POLYMER DURING ORIENTATION

When single crystals of polymer are subjected under induced-stressed, the fibrils are drawn across the break by about 50-100 Å in diameter. This fact is clearly observed in the electron microscope. The fibrils contain many molecules. The sharp discontinuity between the drawn and undrawn material suggests that the molecules are unfolding. In some cases, the

fibrils appear to have a periodicity of 100-400 Å along their length, which is observed by X-ray diffraction. The examination of solution of polymer shows that the lamellae try to rotate toward the drawn direction and or further elongation break up into microlamellae. and finally into submicroscopic units. Since the elongation at break in cold-drawn solution is less than it could be obtained by complete unfolding. It has been suggested that the smallest units are microcrystallites in which the chains remain folded.

Spherulites tend to remain intact during the first stage of drawing. It is often elongating to markdely ellipsoidal shapes. Rupture of the polymer sample usually takes place at spherulite boundaries.

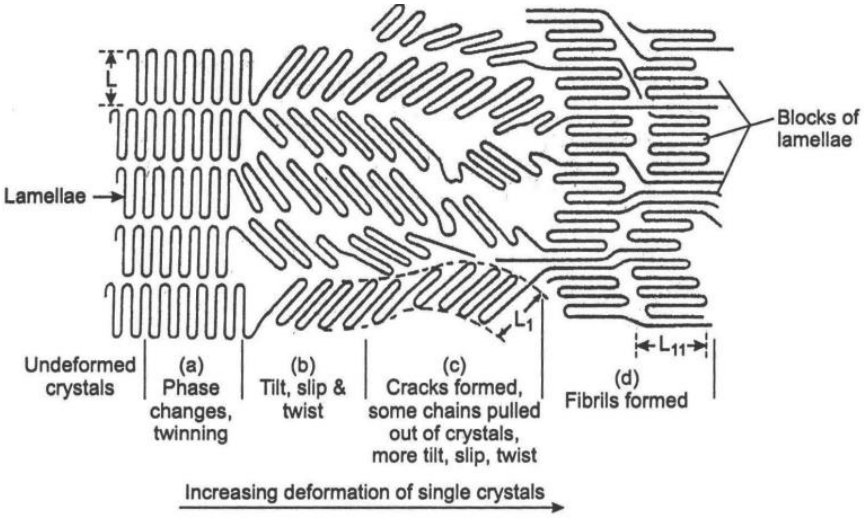


Fig. 7. Presentation of Fibre formation by chain tilting and slipping followed by breaking off of blocks of lamellae.

The fibre structure is still unsettled. X-ray studies show that the molecules are aligned and contain long periodicity. The final stages in the formation of an oriented fibre by drawing can be imagined by Peterlin (1965). A multilayer lamellar crystal is destroyed with tilting and slipping of the chains. At points of concentration of defects, blocks of folded chains break off·and are incorporated alongwith unfolded chains into the new fibre structure. By these processes, the number of chain folds decreases and the number of tie molecules increases. The latter and the partial interpenetration of lamellae increase the mechanical stability, tensile strength, and stiffness of the fibre.

E. THE CRYSTALLINE MELTING POINT :

If we describe the crystalline melting point 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

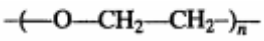
ΔS_m = Change in entropy of fusion

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 engery barriers hindering this rotation range from 0.2 to 1.2 kJ/mole, the same order of magnitude as molecular cohesion forces. It is not surprising therefore that the flexihility of polymer chains is an important factor in determining their melting points.

For high molecular-weight linear polyethylene *Tm* is about 141 °C. Ether units in poly (ethylene oxide)

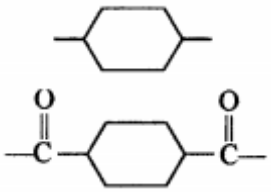


make the structure more flexible than polyethylene, and *Tm* of high-molecular weight versions of the species is only 66 °C. By contrast, poly (p-xylene) is composed of stiff chains and its crystal melting point is 375 °C.

Further polytetra fluoro ethylene *(T_m =327 °C)* melts much higher than polyethylene because of its low entropy of fusion which results from the high stiffness of the polymer chains. Similarly, the high melting point of isotactic polypropylene *(T_m* = 165 *°C*) is attributed to low entropy of fusion arising from stiffening of the chain because of the higher energy barrier of rotation about C-C bonds than in polyethylene.

Stronger intermolecular forces result in great ΔH_m values and an increase in T_m. Polyamides, which are hydrogen bonded. are higher melting that polyolefins with the same degree of polymerisation, and the melting points of polyamides decrease with increasing lengths of hydrocarbon sequences between amide groups. Thus the T_m of nylon-6 and nylon 11 are 225 °*C* and 194 °*C*, respectively.

The substitution of an inflexible group like the p- phenylene group, for six chain CH_2 groups causes a marked rise in the melting point of the polymer. The rise is considerable when the p-phenylene group is connected to CH_2 groups, but greater still when it is connected to carbonyl.



Some examples of this change is shown in the following table:

Repeating Unit	T_m (°C)
—O(CH$_2$)$_2$OCO (CH$_2$)$_6$CO—	45
—O(CH$_2$)$_2$OCO⟨⟩CO—	265
—NH(CH$_2$)$_6$NHCO(CH$_2$)$_6$CO—	235
—NH(CH$_2$)$_6$HNCO⟨⟩CO—	350

Side chain substitution :

In most cases, the substitution of nonpolar groups for hydrogens of a polymer chain leads to a reduction in T_m or possibly complete loss of crystallinity. The crystalline melting point of polyethylene is lowered 20-25 °C on going from the linear to the branched material.

When an alkyl group is regularly substituted into a methylene chain, with the retention of stereoregularity so that crystallization is possible, two effects complete in setting T_m. For example, in the case of isotactic poly (α-olefins), an increase in the length of the side chain results in a looser crystal structure resulting in the lowering of melting point. On the other hand, an increase in the bulkiness of the side chain increases *Tm'* since rotation in the side chain is hindered with consequent decrease in ΔS_m.

sidechain	T_m (°C)
$-CH_3$	165
$-CH_2CH_3$	125
$-CH_2CH_2CH_3$	75
$-CH_2CH_2CH_2CH_3$	55
$-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-CH_3$	196
$-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{\overset{\displaystyle CH_3}{\overset{\vert}{C}}}}-CH_2-CH_3$	350

Replacement of an amide hydrogen with an alkyl group has a much larger effect, since hydrogen bonding is destroyed. Thus, N-methyl nylons melt at least 100 °C lower than their unsubstituted counterparts.

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