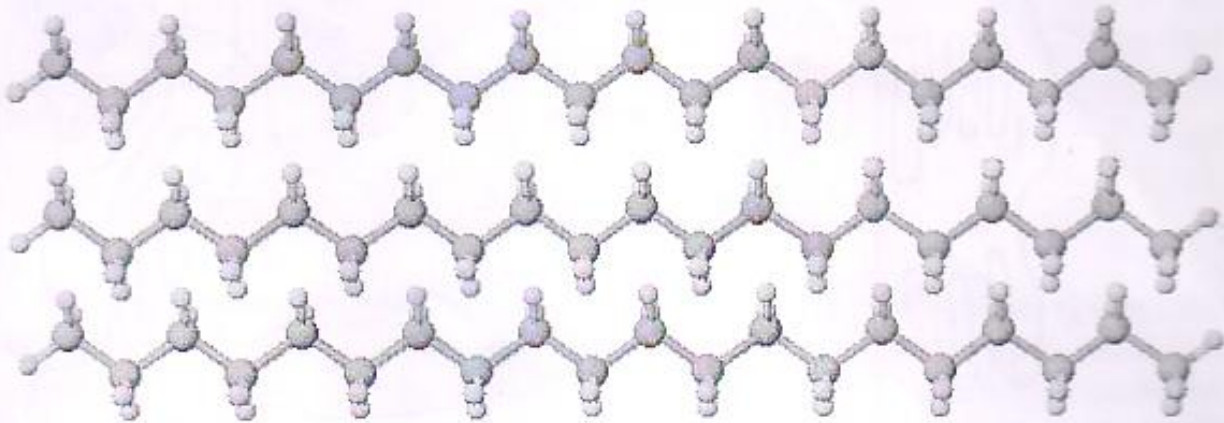


Crystalline and amorphous polymers

To crystallize a polymer chain must be linear, although limited crystallization can take place if a small number of branches are present. Crystallization is favored by a regular arrangement along the polymer chain giving the structure a high degree of symmetry..

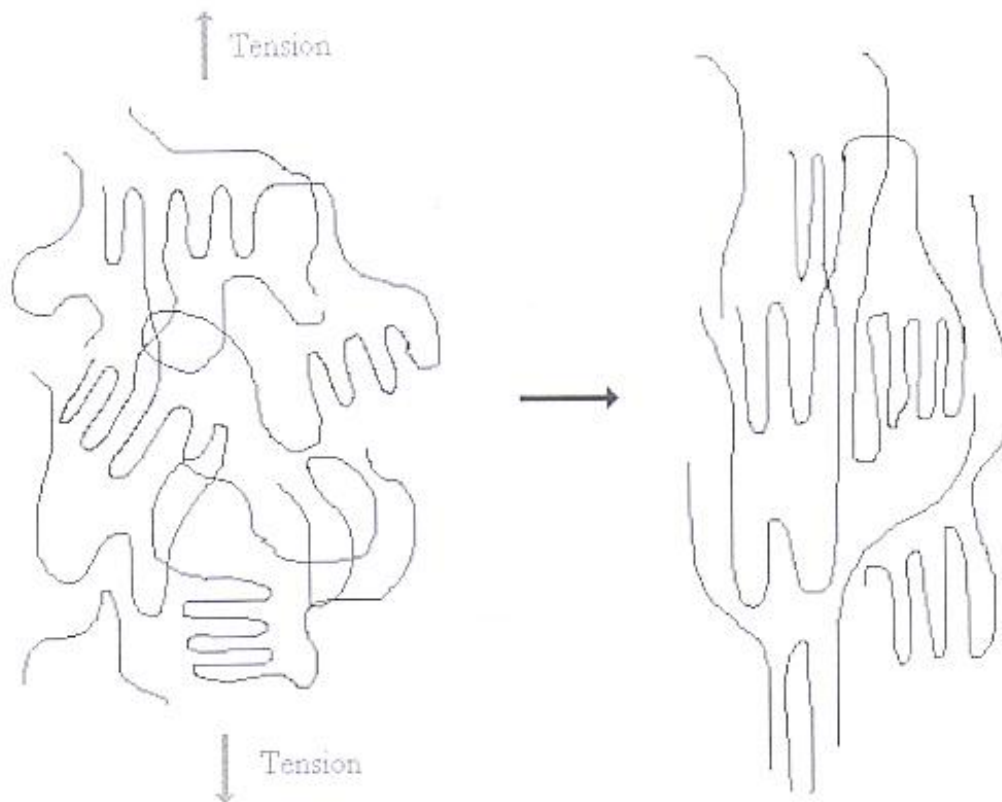


Degree of Polymerization: Relatively short polymer chains form crystals more readily than long chains, because the long chains tend to be more tangled²⁷. High crystallinity generally means a stronger material.

Processing: A major difference between small molecules and polymers is that the morphology of a polymer is dependent on its thermal history. The crystallinity of a polymer can be changed by cooling the polymer melt slowly or quickly.

A. Cooling Rate: When they are processed industrially, polymers often are cooled rapidly from the melt³¹. In this situation, crystallization is controlled by kinetics rather than thermodynamics. There may not be time for the chains, which are entangled in the melt, to separate enough to form crystals, so the amorphous nature of the melt is "frozen into" the solid. A polymer is more likely to have a higher percent crystallinity if it is cooled slowly from the melt.

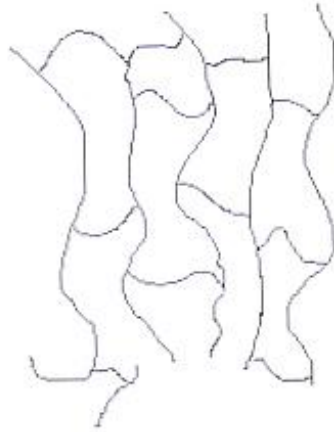
B. Orientation: Crystallinity can be enhanced by pulling the bulk material either when it is synthesized or during its processing²⁶. This is common for both films and fibers. When a film is formed the small crystallites tend to be randomly oriented relative to each other. **Drawing** (stretching) the film pulls the individual chains into a roughly parallel organization as is shown in the schematic diagram ~~at the end~~. Films can either be **uniaxially oriented** (oriented in only one direction) or **biaxially oriented** (oriented in two directions). Fibers normally are drawn so that they are oriented in one direction⁴⁰. Unstretched nylon fibers are brittle, for example.. When the fibers are stretched the oriented fibers are strong and tough.



Thermoplastics: Molecules in a thermoplastic are held together by relatively weak intermolecular forces so that the material softens when exposed to heat and then returns to its original condition when cooled. Thermoplastic polymers can be repeatedly softened by heating and then solidified by cooling - a process similar to the repeated melting and cooling of metals. Most linear and slightly branched polymers are thermoplastic. Thermoplastics have a wide range of applications because they can be formed and reformed in many shapes. Some examples are food packaging, insulation, automobile bumpers, and credit cards.

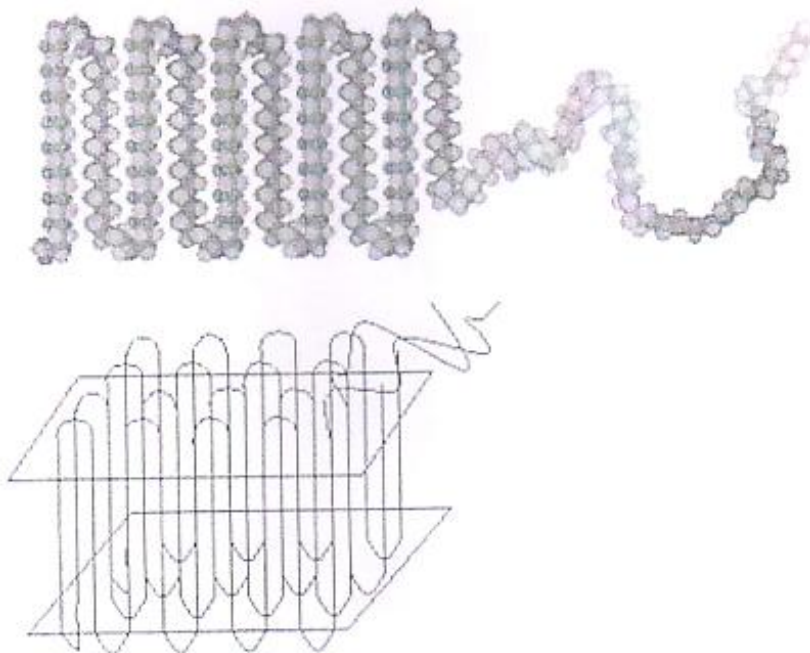
Thermosetting plastic, or thermoset, solidifies or "sets" irreversibly when heated. Thermosets cannot be reshaped by heating. Thermosets usually are three-dimensional networked polymers in which there is a high degree of cross-linking between polymer chains. The cross-linking restricts the motion of the chains and leads to a rigid material. A simulated skeletal structure of a network polymer with a high cross-link density is shown. Thermosets are strong and durable. They primarily are used in automobiles and construction. They also are used to make toys, varnishes, boat hulls, and glues.

An understanding of polymer crystallinity is important because the mechanical properties of crystalline polymers are different from those of amorphous polymers. Polymer crystals are much stiffer and stronger than amorphous regions of polymer. For example, high strength fibres can be produced from polyethylene whereas it is more commonly associated with applications such as carrier bags and plastic cups, where low cost and ease of manufacture are the key considerations in the choice of material. This lecture covers the formation of crystals in polymers, how they can be observed under the optical microscope, and the response of a semicrystalline polymer sample to uniaxial stress.



In ceramics or metals, a crystalline solid comprises repeating unit cells that contain each of the component atoms in the material. Each unit cell is composed of one or more molecular units. In a polymer this is not possible; the molecules are chains containing potentially millions of formula units. There is, however a repeating unit in a polymer - the monomer from which it was made. This must be the basis of both long and short-range order in a polymeric material.

Amorphous polymers are generally found in a random coil conformation and have a disordered chain structure. This is the most common structure of many polymers. Crystalline polymers are predominantly in the all-trans conformation, and the chains are arranged in lamellae, as below:

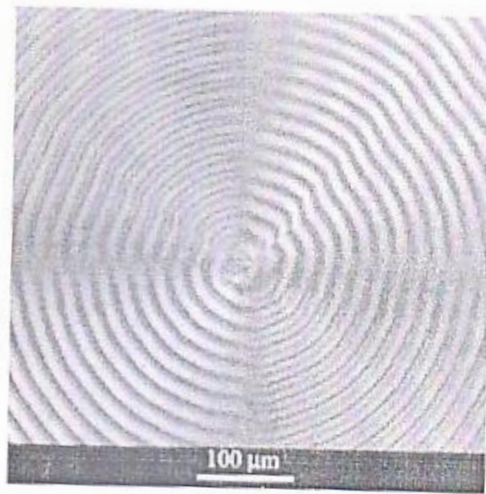


The polymer crystal is made up from one-dimensional chain-folded sequences, shown on the above, where the repeat distance is given by the chain spacing. To the

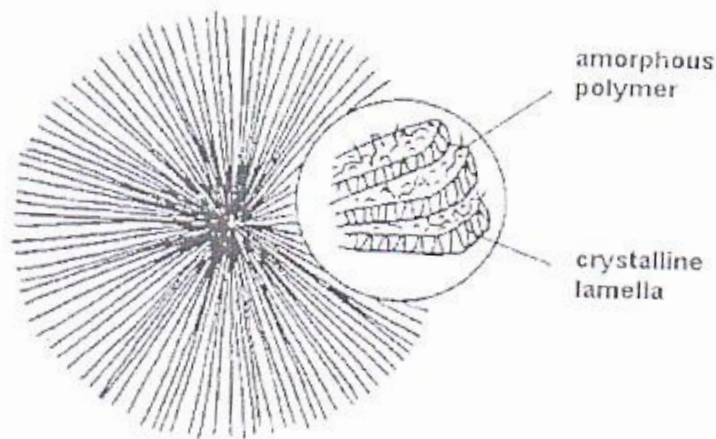
above is shown a schematic arrangement of folded chains into a two-dimensional lamella.

Spherulites and optical properties

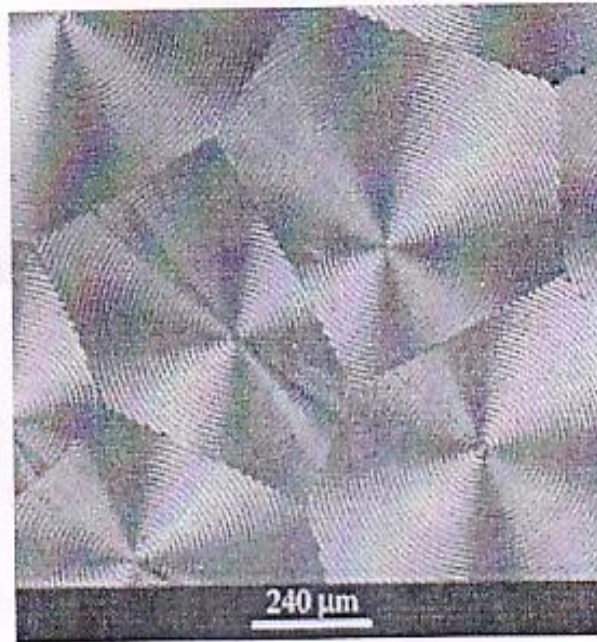
Since crystallisation in polymers follows a different process to that in metals - the laying down of successive lamellar layers of polymer chain - it produces a different structure. After nucleation, growth in most polymers is faster in one preferred direction. The polymer crystals grow in helical strands radiating from a nucleation point. Such growth leads to the formation of structures called spherulites.



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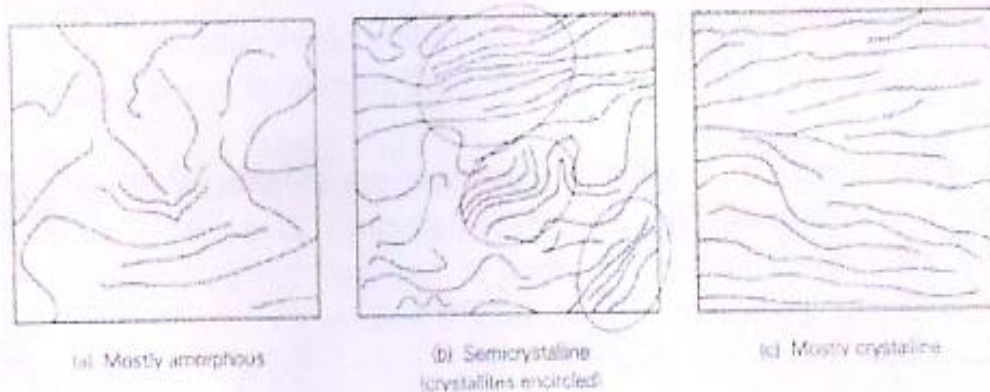


The figure above is a transmitted cross-polarised light micrograph of a spherulite in polyhydroxybutyrate (PHB), where further details of the sample's history can be found. The photograph displays banding and a Maltese cross pattern. These features are characteristic of polymer spherulites viewed with cross-polarised light. The orientations of the polymer chains within a spherulite are shown schematically on the above. Note that the lamella are growing radially, interspersed with amorphous material.



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The image above is an image of PHB spherulites viewed with a transmitted cross-polarised light microscope. A Maltese cross can be seen in each spherulite and each one has a banded appearance. The photograph shows a good example of impingement, which occurs when spherulites growing outwards from single nucleating points meet each other. Due to impingement they are unable to continue growing out radially in all directions. A polygonal microstructure is formed as seen in this photograph.



The morphology of most polymers is semi-crystalline. That is, they form mixtures of small crystals and amorphous material and melt over a range of temperature instead of at a single melting point. The crystalline material shows a high degree of order formed by folding and stacking of the polymer chains. The amorphous or glass-like structure shows no long range order, and the chains are tangled as illustrated below.