

Crystallinity in Polymers

Polymers are widely used materials. Their versatility makes them suitable for a whole range of applications, and comes from the capability of manufacturers to tailor microstructures and therefore properties through control of the processing conditions.

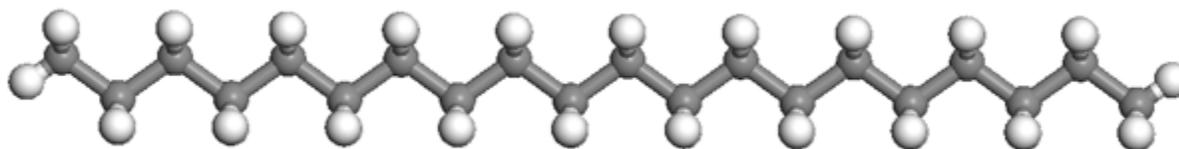
An understanding of polymer crystallinity is important because the mechanical properties of crystalline polymers are different from those of amorphous polymers. Polymer crystals are much stiffer and stronger than amorphous regions of polymer.

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 TLP 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.

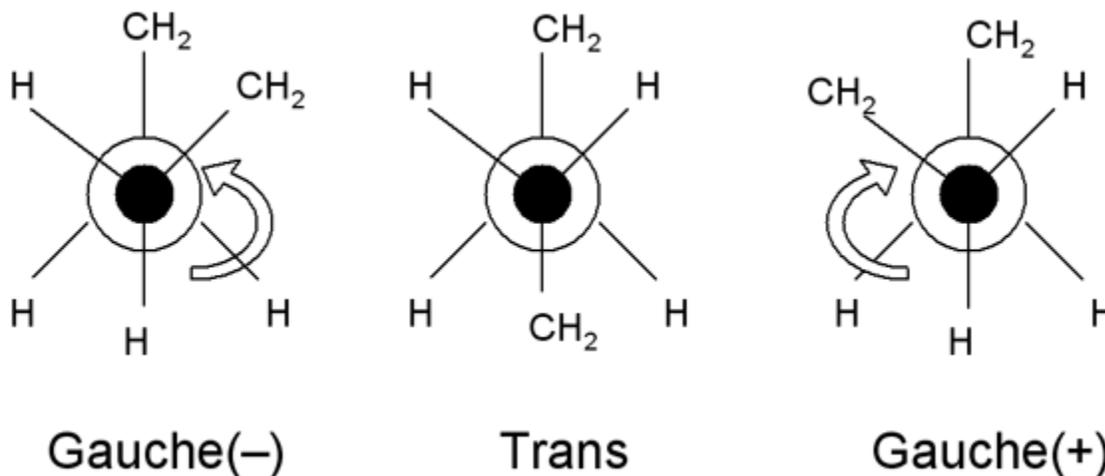
Crystalline and amorphous polymers :

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.

For example, a short section of linear poly(ethylene) looks like this:



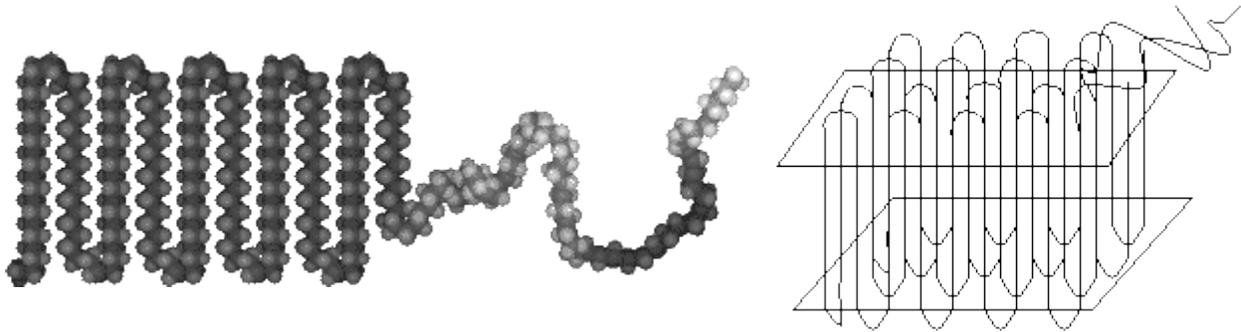
However, the conformation of the bonds around each carbon atom can be represented schematically as follows:



These diagrams are called Newman projections. The circle is a single C-H bond; and this diagram represents a projection along it. These two structures thus represent one half of the backbone continuing on either side of a C-C bond (trans), or both halves on the same side (gauche). Note that there are two possible gauche states, labelled gauche (-) and gauche (+).

Whilst the trans conformation has a lower energy (since it's easier to position the hydrogen atoms on the carbon backbone further apart), an all-trans conformation would be a considerably more ordered structure than a random one - that is, it has a much lower entropy.

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 left, where the repeat distance is given by the chain spacing. To the above right is shown a schematic arrangement of folded chains into a two-dimensional lamella.

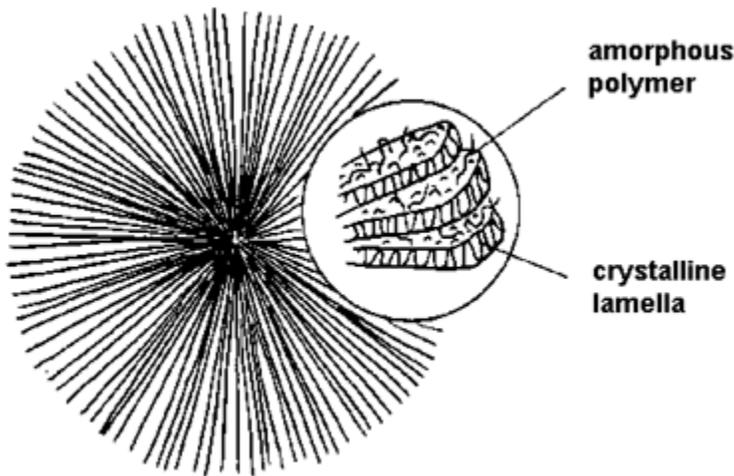
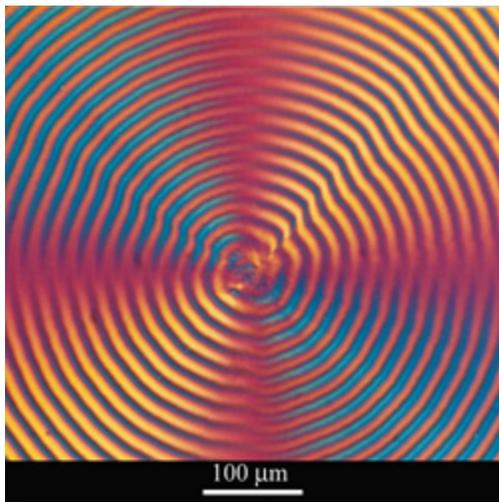
An amorphous polymer has the maximum entropy conformation (given by the Boltzmann distribution), and the chains are arrayed randomly throughout the material, making atomic positions quasi-random as in any other glassy material.

As a result of the difference between the amorphous and crystalline arrangements of polymer chains, the X-ray diffraction patterns of the two phases are very different. The amorphous phase contains no long-range order, meaning that there are no regular crystalline planes to diffract X-rays. Thus the incident X-rays are scattered randomly and there are no sharp peaks in the diffraction pattern. In the crystalline phase, the repeating lamellar chains provide a regular structure, thus the diffraction pattern will contain sharp, prominent signature peaks, the position of which depends on the exact spacing between chains.

As the degree of crystallinity of a polymer affects its properties, accurately determining it is important. X-ray diffraction can be used to determine the degree of crystallinity of a sample. Thermal analysis techniques such as [differential scanning calorimetry](#) (DSC) can also be used. The two determinations may not necessarily be in agreement, and the reasons for this are complex.

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. By convention this is called the b-axis. The other two axes (the c- and a-axes) grow at the same speed, and have no set direction provided they are orthogonal to the b-axis. Thus they are free to rotate. This means that polymer crystals grow in helical strands radiating from a nucleation point. Such growth leads to the formation of structures called spherulites.

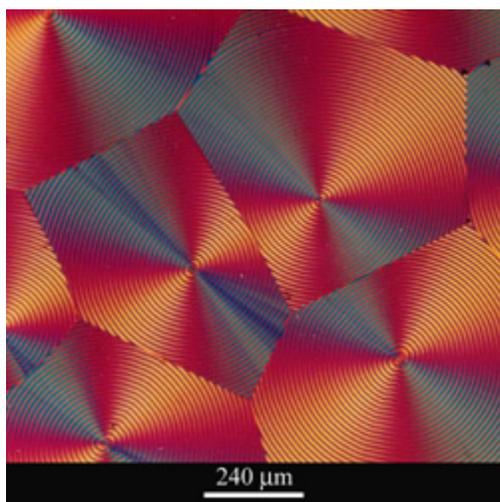


On the left is a transmitted cross-polarised light micrograph of a spherulite in polyhydroxybutyrate (PHB), [micrograph no 600 in the DoITPoMS Micrograph Library](#), where further details of the sample's history can be found. The photograph displays banding and a Maltese cross pattern. These features 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 right. Note that the lamella are growing radially, interspersed with amorphous material.

The Maltese cross is seen because polymers are birefringent. Polarised light cannot travel through a crystalline polymer if the direction of the polarisation of the light is perpendicular to the direction of carbon chain in the polymer. As a result, when a sample is studied under crossed polars, only those polymer chains perpendicular to neither polariser nor the analyser are visible - these are at approximately 45° to each polaroid. The [Introduction to Photoelasticity](#) TLP goes into more depth on the subject of birefringence.

The banded appearance of the image is also a consequence of birefringence. Due to a regular helical twist of the lamellae growing radially there are regions in which the polymer chain will be orthogonal to the polarisation of the light in the x-z plane, even if it is running at 45° to it in the x-y plane. These positions will occur at periodic intervals, once every full 360° rotation of the polymer chain. This translates to a given length outwards along each strand. This is then observed under crossed polars as alternating dark and light areas.



The image above is [micrograph 601 in the DoITPoMS Micrograph Library](#). It 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

Source: <http://www.doitpoms.ac.uk/tlplib/polymers/index.php>