Physics of Solid Polymers - Part 5

Morphology of Semicrystalline Polymers on the Micron Scale

Aggregates of Crystals in Bulk Semicrystalline Polymers:
- Spherulites
- Row-structure (Cylindrites)
- Microfibrils

SPHERULITES

These are spherical aggregates, 1 μm to 1 mm in size (typically several μm). They crystallise from a nucleation point and grow radially in 3-d until they impinge (Figure 18). Parallel stacked crystalline lamellae at the centre grow laterally and splay out forming an embryonic spherulite (Figure 23). The lamellae branch out and grow radially to fill the space (Figure 24). Spherical shape is assumed and maintained during growth from the melt (constant growth rate at constant temperature in all directions). Eventually spherulites impinge on each other (Figure 18), ending up being separated by flat interfaces.
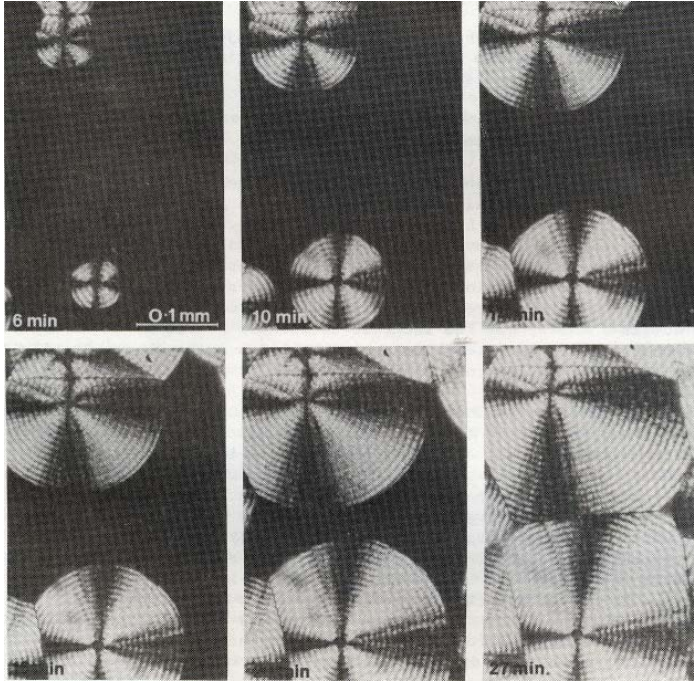

Figure 18 Growth of spherulites in molten i-PP at low supercooling. Viewed by optical microscope between crossed polarizers. Since the sample is a thin film (5 μm), these spherulites are in fact disks.

Spherulites are best viewed in a microscope between two crossed polarizers. The field appears black if no birefringent sample is placed between the polarizers (Figure 19). However, since spherulites are crystalline and optically anisotropic (birefringent), they convert the plane polarized light transmitted by the first polarizer into elliptically polarized light (Figure 20). This now has a component parallel to the second polarizer (analyser) which is allowed through. Spherulites therefore appear bright, with a characteristic black "Maltese cross". The cross is due to the polymer chains in the crystals lying tangentially in a spherulite (lamellae lie radially and chains are perpendicular to the lamellae). The chain direction is usually the optic axis, and the areas where optic axis lies parallel to either the polarizer or the analyser (i.e. within the Maltese cross) appear dark.
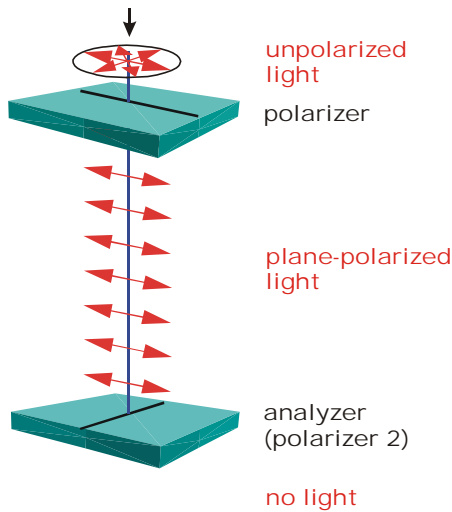
Figure 19 With no birefringent (optically anisotropic) sample between crossed polarizers, no light passes through the second polarizer (analyzer).
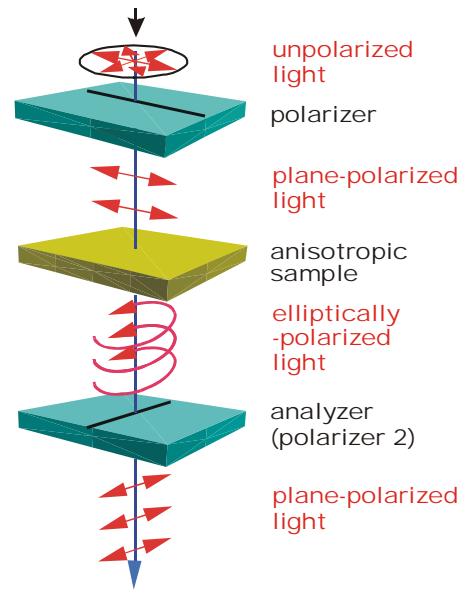

Figure 20 A birefringent (optically anisotropic) sample converts linearly (plane) polarized light into elliptically polarized. A component of it passes through the analyzer.

Sometimes dark concentric rings can be seen in spherulites (Figure 18, Figure 21). This is because as they grow radially the crystalline lamellae also twist around their radial growth axis (Figure 23, Figure 24). The requirement of space filling means that the twist must be synchronised (Figure 22). Hence at a given distance from the nucleus all ribbons must be twisted by the same angle to remain parallel to each other. This gives rise to the concentric circles (actually spheres in 3d).

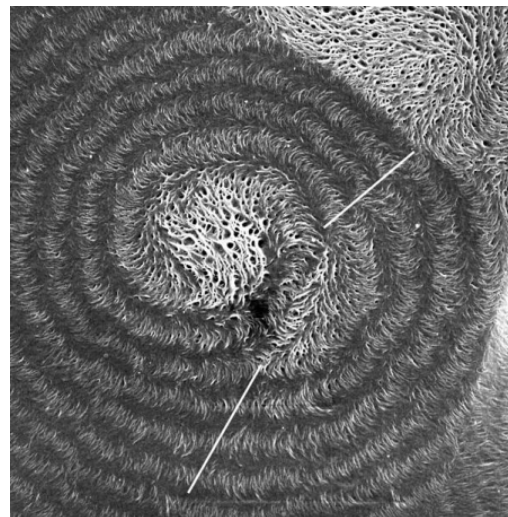**Figure 21** Two impinging banded spherulites between crossed polarizers

Figure 22 SEM image of melt-crystallized PE showing a banded spherulite. The surface was etched with permanganic acid. The white lines show the boundary between two domains with opposite sense of lamellar twist

Spherulite size is determined by the ratio between nucleation and growth rates. Nucleation rate is a steeper function of supercooling than growth rate, so spherulites are more numerous and smaller if grown at lower temperature. Large spherulites degrade mechanical strength because cracks often appear along spherulite boundaries. This is made even worse by

the fact that low molecular weight fraction and impurities are often concentrated in the uncrystallized melt, and thus become concentrated at the spherulite boundaries. To keep spherulites small additives called nucleation agents are sometimes mixed in with the polymer before processing to promote nucleation - e.g. in polypropylene. They are essential in bacterial products like Biopol [poly(hydroxybutyrate)], since these contain no catalyst residues which usually help nucleation in synthetic polymers.
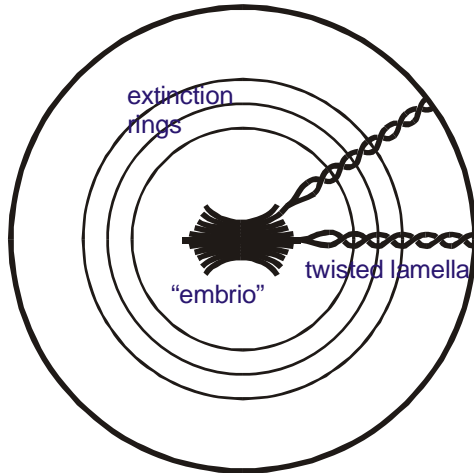

Figure 23 Section through the centre of a spherulite (schematic) with a stack of splaying lamellae at the centre from which twisted lamellae grow radially and branch.

Spherulites are found wherever polymers crystallize from quiescent (static) or slowly flowing melt, such as in compression mouldings or injection mouldings.

If a semicrystalline polymer is to be transparent to light, spherulite size must be less than the wavelength of light. Since spherulites are birefringent objects, they scatter light if their size is $\geq \lambda$. Thus HDPE film is opaque when slowly cooled from melt (large spherulites) but transparent when quenched. Solid polymers (e.g. PET) obtained by "cold crystallization" are usually transparent. LDPE is less crystalline than HDPE, hence is less birefringent and therefore transparent.
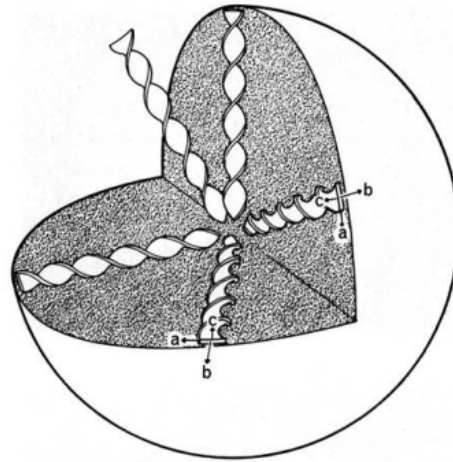

Figure 24 A representation of a a 3-d spherulite

ROW STRUCTURE (CYLINDRITES)

In extrusion processes like melt-spinning of fibres or film blowing, the melt flow creates lines of nuclei, rather than nucleation centres. The reduced entropy of the flowing melt promotes crystallisation, particularly of the longest molecules. Partially aligned molecules have a lower entropy S_l compared to random coil molecules in the melt. Hence $\Delta S_f = S_l - S_c$ is lower and $T_m = \Delta H_f / \Delta S_f$ is higher. Thus at any temperature T the supercooling ΔT is larger for partially aligned molecules and these can form nearly extended chain line nuclei. Subsequently epitaxial chain-folded lamellae grow radially in the plane normal to the flow direction (Figure 25). The result is a 2-dimensional spherulite translationally replicated along the continuous central thread, sometimes called "cylindrite".
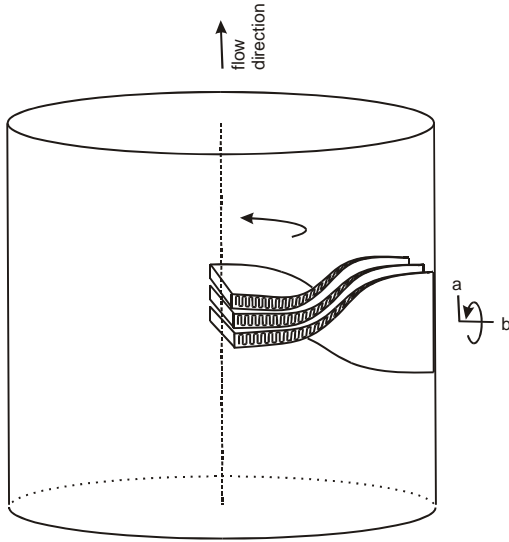
Figure 25 Schematic representation of a section of a cylindrite

central thread has very high Young's modulus. Producing shish-kebabs without chain-folded lamellae was the first instance of producing ultra-high modulus polyethylene fibres. These fibres (Spectra) are now produced commercially from ultra-high molecular weight polyethylene.

Cylindrites in commercial products are usually of 1-2 μm diameter. Lamellae twist around the growth direction, as in spherulites. Row structures have characteristic wide-angle X-ray diffraction patterns.

Row structures have their equivalents in solution-crystallised polymers where the solution had been stirred during crystallisation. The resulting "shish-kebab" structure (Figure 27, Figure 28) consists of an almost extended-chain central thread onto which chain-folded lamellae ("kebabs") grow (Figure 28). The
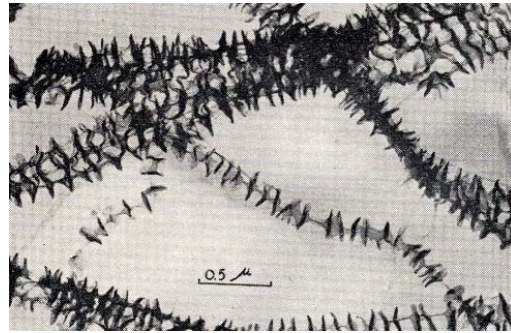

Figure 26 "Shish-kebabs" of polyethylene from stirred solution in xylene (TEM)

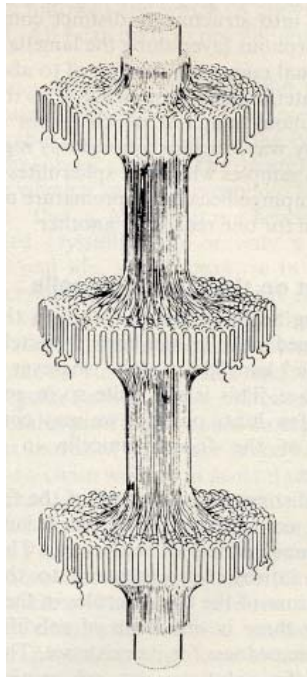**Figure 27** TEM of a single shish-kebab

Figure 28 Structure of a shish-kebab (schematic). (Note that this is not a cylindrite!)

MICROFIBRILS

When spherulitic (or row-structure) polymers are drawn beyond the yield point, oriented fibres are produced, with polymer chains in the crystals lying parallel to the draw direction. The fibre is made up of "microfibrils", 10-20 nm in diameter. These consist of alternating crystalline and amorphous regions, with typically 10-20 nm periodicity. The small crystallites are thus typically 15 nm in width and 15 nm in thickness. They are not lamellar and have a low proportion of chain folds. There are many "tie-molecules" along the microfibril which give the fibre a relatively high axial modulus of a few GPa (compared to a fraction of a GPa in unoriented polymers between their T_m and T_g). Laterally microfibrils are poorly connected and drawn fibres easily fibrillate.