Phase Transitions and Structure
Of Crystalline Polymers

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1. Introduction

Crystalline polymers build up complex structural entities, which blend amorphous and crystalline domains at a very small scale (≈ 10 nm). The coexistence of domains, which are of molecular, dimensions stems from the fact that the chains tend to fold upon crystallisation: this chain folding is a characteristic feature of polymers, and creates an organisational scale which is unique to polymers. It induces a small scale subdivision of the polymer space, and makes it necessary to describe the structure of crystalline polymers at three different length scales: at the level of the unit-cell (characteristic dimensions: fractions of nanometers), at that of the chain-folded lamellae (thickness: 10 nm, lateral dimensions: several µm) and finally, spherulites (from µm to mm).

In view of the small size of polymer crystals, electron microscopy and electron diffraction are very appropriate techniques to visualise and investigate their structure. The present contribution, being essentially descriptive, relies heavily on the possibilities of electron microscopy, which has been the author's main investigation tool in the past years. The recent advent of scanning probe microscopy, and notably Atomic Force Microscopy (AFM) has made it possible to visualise polymers at a sub-molecular level, namely the methyl group. This bias towards imaging techniques should not however undermine the major insights gained through many other diffraction or spectroscopic techniques: X-ray diffraction, NMR and infrared spectroscopies, etc...

Also, it is useful to present first the structure of crystalline polymers in the more general context of phase transitions of bulk polymers. The “spontaneous” structure of crystalline polymers at its different levels, and some ways to alter it, will be analysed next.

2. Phase Transitions in Polymers

Polymers can be divided in two broad classes, depending on their physical properties: amorphous and crystalline. Amorphous polymers have, as a rule, a structure that is irregular, either in terms of its chemistry or stereochemistry. Since stereochemistry is at play, most amorphous polymers contain asymmetric carbons, i.e. bear side-chains, but are atactic (irregular sequence of the configurations).

Crystalline polymers are essentially composed by the class of "linear" polymers, such as polyethylene $(CH_2 - CH_2)_n$ or poly(ethylene oxide) $(CH_2 - CH_2 - O)_n$, as well as polymers bearing side chains provided they are *stereoregular*: isotactic or syndiotactic. The latter class includes in particular most of the polyolefins: isotactic or syndiotactic polypropylene (iPP and sPP), polystyrenes (iPS and sPS), etc...

Phase transitions in bulk polymers are, or may be, complex for two main reasons:

- crystallisation requires an adequate thermal treatment. If the growth rate of a polymer is slower than its possible cooling rate, this polymer can be frozen in as a vitreous polymer by appropriate, fast cooling. Conversely, crystallisation does only proceed for extended stays in appropriate temperature ranges
- Crystalline polymers always have a non-crystalline fraction, which experiences phase transitions characteristic of amorphous systems, and namely the glass transition

The main transitions found in polymers are summarised in a volume-temperature plot (Figure 1), illustrated here for the case of isotactic polystyrene. This polymer crystallises slowly, which makes it possible to generate the different physical states referred to above. The diagram displays various curves, which correspond to different thermal histories and physical states:

- Curve 1: at high temperature, the sample is in equilibrium in the molten state, above its melting temperature T_m (about 250°C). This curve can be followed well below the melting temperature, which indicates that the polymer can be *undercooled* below T_m. Undercooling is a rule for crystalline polymers: it results from the difficulty of the polymer to be nucleated and the slow growth rate. In the lower part of this curve, the viscosity of the polymer increases considerable, and reaches that of rubbers.
- Curve 2: around 100°C, the rubbery, fast quenched iPS is no longer able to contract as a liquid: the structure (as manifested by its volume) is no longer in equilibrium, and departs from strict linearity with the (supercooled) liquid. The sample experiences a so-called glass transition. In this situation, the molecular movements are at the time-scale of the experimentalist. Molecular movements do however take place: the system

slowly contracts and reaches its equilibrium volume, on the extrapolated supercooled liquid curve, but the time scales may become geological. There is no alteration of the chemical structure in the process: the contraction of the glassy polymer corresponds to a true “physical aging”.

- Note that the behaviour described so far is typical of amorphous isotactic polystyrene (aPS). However, aPS experiences *only* the above mentioned transitions, contrary to iPS or sPS, the crystallisation and melting behaviour of which is described now.
- Curve 3: when iPS is maintained for a sufficient time in a temperature interval between T_m and T_g, and preferably around 180°C (i.e. halfway between T_m and T_g, where the crystal growth rate is maximum), the polymer crystallises. Crystallisation results in a volume contraction from the (supercooled) liquid volume v_l to a volume v. The maximum conceivable contraction would bring the volume down to a value v_c located on the extrapolated curve determined from the unit-cell parameters of the crystal, and taking into account its thermal expansion (illustrated by curve 5). However, this stage is never reached in practice. Polymer always crystallise only “partly”, thus the term of “*semi-crystalline*” polymers, and the definition of a crystallinity. The crystallised fraction can be determined by various means (X-ray diffraction, spectroscopic methods, volume, etc). From the curves shown in Figure 1, the crystallinity is expressed by the ratio of the actual volume contraction to the maximum possible contraction (at the crystallisation temperature), thus:

$$x = (v_l - v)/(v_l - v_c)$$

- The semi-crystalline polymer formed in the previous step is thus made of crystalline and amorphous parts, which experience their normal phase transitions upon heating or cooling. If reheated, the crystalline fraction of the polymer (the crystallites) melts at T_m. If cooled below the glass transition temperature, the amorphous fraction *only* becomes a glass.

3. Crystallisation: nucleation and growth

The phase diagram of Figure 1 represents in a condensed form the various, major phase transitions which a crystalline polymer may experience. However, *generation* of crystalline entities is only possible when two conditions are met: germs or seeds must exist in the sample, on which crystallisation starts, and the crystals must grow. These two conditions impose to investigate the *development* of the crystallisation (i.e. the *overall* crystallisation) and to separate the contributions of *nucleation* and *growth* mechanisms (Figure 2).

Nucleation takes place usually on “heterogeneities” of still unknown nature which exist in every sample; these heterogeneities are usually considered to be residues of catalysts, etc... This spontaneous nucleation may be insufficient to reach acceptable crystallisation rates, for example in injection moulding. Nucleation can be enhanced by different processes: by partial melting or, in industrial practice, by addition of so-called “nucleating agents”. Partial melting of the crystalline polymer leaves finely divided crystalline fragments, which on subsequent cooling act as “self-nuclei” for the polymer melt. These self-nuclei are ideal in terms of compatibility with the polymer, crystalline structure and dispersion in the melt. The thermal treatments are however too slow and precise to be transferred to industrial practice. In industry, one relies therefore on the addition of so-called nucleating agents. These are finely divided crystalline powders, very often salts of low molecular weight organic acids (e.g. sodium benzoate): in favourable cases, the nuclei concentration can be increased by a factor of 10^6, typically from 10^6 to $10^{12}/cm^3$. The mode of action of these nucleating agents is via an epitaxial relationship with the polymer: the crystal lattices of polymer and substrates have favourable interactions, often illustrated by a matching of some characteristic distances in the contact planes (*cf.* later).

Growth rates of polymers cannot be modulated to a similar extent. These growth rates are characteristically represented by a “bell shaped curve” as a function of temperature. Growth rates are zero at the glass transition temperature T_g (the molecular movements are too slow to allow crystallisation) and at the melting temperature T_m (equilibrium between the liquid and the crystal: zero growth rate). They are maximum at an intermediate temperature (10µm/hour for the isotactic polystyrene considered here, at 180 °C). For iPS (and for poly(ethylene terephthalate)), these maximum growth rates are relatively slow: when rapidly quenched, the crystallisation process can be bypassed and the sample forms a glass.

Combination of a nucleation process which can be either sporadic in time (usually for nucleation on pre-existing heterogeneities) or simultaneous (in case of enhanced nucleation) and of a growth process which is usually three-dimensional (and creates spherulites) results in a volume contraction which takes the shape of a sigmoïdal curve versus log time. The evolution of the crystallinity is described by the Avrami equation:

$$x = 1 - \log(-Kt^n)$$

in which K is a rate constant and n a factor (normally an integer) which adds the dependence of time of the nucleation step and the dimensionality of the growth process: for sporadic nucleation and three-dimensional growth, n = 4.

CONFORMATION OF SEMI-CRYSTALLINE POLYMERS

The limited size of polymer crystals makes it difficult to solve the crystal structure by single crystal X-ray diffraction and the use of direct methods. Most often, the diffraction data are collected on fibres and the structures are solved by trial and error techniques. Most methods rely on a combination of analysis of the diffraction patterns and model building (conformational analysis). These methods were initially used in the early 1950's to solve the structure of biological polymers and their chemical analogues.

Polymer structure and conformation from the internal coordinates

The conformation of polymers can be described starting from their chemical structure: bond distances, valence angles in the main chain and side-chains, and rotational angles around these bonds. Some domains of the rotational angles are prohibited because they result in steric conflicts between non-bonded atoms (and mostly between atoms in positions 1 and 4). The conformations and corresponding energies can be represented by conformational energy maps Figure 3). The maps may be symmetrical (for achiral polymers) or asymmetrical (for chiral polymers). *Repetition* of any one (allowed) couple of conformational angles generates by necessity a *helix*, the geometrical characteristics of which are fully determined by the internal coordinates considered so far, but which need be determined experimentally.

Structural analysis of helices.

A helix is a spiralling staircase. As such, its geometry is mainly defined by:

- the *height* of one step, h (projected on the axis of the helix)
- the *height* of one helical turn, L, which is equal to the number of steps n times the height of one step: $L = n*h$

The theory of the diffraction by helices has been established by Cochran, Crick and Vand in the early 1950's, just prior to the resolution of the structure of DNA. It can be easily summarised by using optical masks (Figure 4). The projection of a *continuous* helix in a plane parallel to its axis is a sinusoid. Its Fourier transform (FT) is made of a series of diffraction maxima organised on different layers, and with a characteristic form of a cross. These correspond to the different orders of a Bessel function; the zero term is located in the centre of the cross (on the *equator* of the pattern), and successive layers correspond to orders 1, 2, 3, etc... From a geometrical standpoint, the distance *between* layers is important: it is proportional to $1/L$.

A *discontinuous* helix (i.e. made of points, which is the simplest repeat unit) is the product of a continuous helix by a plane function normal to its axis (distance between planes: h). The FT of the discontinuous helix is the convolution of the two FT. In practice, additional crosses are generated in the initial FT of the continuous helix. The centres of these crosses are located on the *meridian* of the diffraction pattern, at a distance $1/h$.

A diffraction pattern of a helical structure provides therefore in a straightforward manner two key data on the geometry of helical structures:

- the height of the first strong layer line indicates the helical turn L
- the height of the first meridional reflection indicates the step or residue height. The ratio of these two quantities corresponds to the number of residues per turn n.

Collection of these data is vividly illustrated by the fibre diffraction pattern represented in Figure , which is an electron (rather than X-ray) diffraction pattern. As such, and because the wavelength of electrons is much shorter than that of X-rays, the diffraction angles are much smaller, and the pattern is virtually undeformed. Figure 5 illustrates the pattern of a poly(γ-benzyl-L-glutamate) which has an α helical structure characteristic of many fibrous proteins. The ratio of the helical turn (≈ 5Å) by the height per residue (≈ 1.5Å) yields the number of residues per turn, i.e. 3.6 (which is equivalent to 18 residues in 5 helical turns, also denoted as a 18_5 helix). Note that this number of 3.6 is not an integer: the α helix is the first example of an irrational helix, in which the number of residues differs from the standard 1, 2, 3, 4 or 6 which, up to the introduction of the α helix by Pauling in the early 1950's (on the basis of model building *alone*), was considered as mandatory, since it corresponds to the standard symmetries in crystallography. Many more examples of irrational helices exist in both natural and synthetic polymers; among them, the helical structures of polytetrafluoroethylene, or PTFE (Teflon®) which has two different helical structures, above and below ≈ 30°C: 15_7 and 13_6, respectively.

Note also in the diffraction pattern a number of discrete reflections on the equator. They characterise the lateral packing of the chains, and can be better assessed by investigating single crystals.

POLYMER SINGLE CRYSTALS.

Crystallisation of dilute solutions of polymers, or thin films at high temperature yields single crystal entities comparable to their low molecular weight counterparts. Single crystals of polymers have become an extraordinary investigation tool, which helped assess the major characteristics of polymer crystallisation, and led in particular to the concept of chain folding, which is a cornerstone in our understanding of polymers. They are also a first rate material in the analysis of the crystal structure at the level of the unit-cell.

Chain folding in polymer crystallisation.

Polymer single crystals produced from dilute solutions have very often a simple geometrical shape, which reflects the geometry of the crystal unit-cell: square for a tetragonal unit-cell, hexagonal for a hexagonal unit-cell, etc... Single crystals of polyethylene (PE) have a lozenge shape, similar to that of paraffin single crystals (Figure 6). The thickness of the crystals is in the vicinity of 10 nm, which is ideal for investigations using optical microscopy (in phase contrast) or electron microscopy and diffraction. The electron diffraction pattern (Figure 6, insert) indicates that the *a* and *b* axes of the unit-cell are parallel to the long and short axis of the lozenge, respectively: the crystal edges are made of (110) planes, which are the most densely populated planes in the unit-cell. All the diffraction spots displayed in Figure 6 are so-called "equatorial" spots in a fibre pattern similar to that shown in Figure 5. This indicates that the electron beam travels parallel to the chain axis in the single crystals. In other words, the chain axis is normal to the large surface areas of the single crystal. However, the thickness of the crystals is only ≈10 nm, whereas the length of the PE chains is usually much larger: it can be 1 µm or more (for PE, the chain length (expressed in nm) is, within 10%, equal to the molecular weight divided by 10). It follows that, in the crystals, the PE molecule must be folded: small crystalline stems ≈ 10 nm long pack side by side, and are linked by folds which must be located in the upper and lower surfaces of the lamella. In other words also, the "single crystals" displayed in Figure 6 have actually a sandwich structure, in which a crystalline core is limited on its top and bottom by more disordered areas in which the chains fold back and forth to re-enter the crystalline core (Figure 7). This concept of "chain folding", introduced by Keller, is the basis of our understanding of the structure of crystalline polymers. In particular, it introduces a structural level intermediate between the unit-cell (organisation at the sub-nanometer scale) and the morphology (in the tens of µm or mm scale): chain folding "divides the polymer space" at the level of 10 nm in crystalline and amorphous regions, which fully justifies the denomination of "semi-crystalline" polymers.

Structural investigations of semi-crystalline polymers has focused on the structure of the lamellae, the impact of chain folding, the organisation of these bi-dimensional lamellae in more complex three-dimensional entities (the spherulites), in the possibility to reduce or eliminate the amorphous zones to reach and exploit the much superior mechanical properties of the crystalline core, etc... Some of these issues (only) are examined now, and illustrated mainly with material gathered from earlier and present investigations performed in our laboratory.

Single crystals as a help in the determination of the unit-cell structure.

Single crystals enable a direct visualisation of polymer chains (in favourable cases) and in any case provide detailed crystallographic information, which is not accessible by standard X-ray diffraction methods.

Direct observation of polymer chains by electron microscopy.

The orientation of chains parallel to the electron beam makes it possible to observe the projection of the chains, and in favourable cases their azimuthal setting. These investigations require however cooling the specimen to 4°K (cryo-specimen stage cooled with liquid helium) and are best performed on polymers that are resistant to the electron beam. The images indicate the spacings and, in several cases, the azimuthal setting of the chains, making it possible to locate and visualise crystal defects.

Unit-cell determination.

Many polymers display a crystalline polymorphism: the chain conformation and/or the packing of chains differs for different crystalline forms. Some of these modifications are unstable to mechanical forces (stretching, etc...) and cannot therefore be produced in the form of fibres: conventional crystal structure analysis by fibre techniques are inoperative. These forms can however be produced under mild growth conditions in the form of single crystals or by epitaxial crystallisation using appropriate substrates (cf. later). The oriented domains are small: typically, a single crystal 1 μm square and 10 nm thick represents 10^{-15} gram of matter. Electrons interact however strongly with matter, and electron diffraction is able to collect sufficient data from such samples to enable (with the help of the tilting stage of the instrument) to allow a structural investigation. Such techniques have been applied to several biopolymers (e.g. an unstable crystal modification of Bombyx mori silk fibroïn) and synthetic polymers (e.g. one of the three crystalline polymorphs of poly(1-butene), and various so-called “frustrated” polymer structures).

Single crystals as a help to investigate chain-folding.

Chain folds, which cover the exposed surface of single crystals, are directly accessible to structural investigation. Investigation of the folds, their organisation and impact on the lamellar shape represents a significant part of past and still present research.

Structure of the folds.

Chain folds are not directly visible by electron microscopy. However, the structure of sharp folds (between adjacent stems) can be investigated by classical X-ray crystallography when using short, cyclic paraffines, in which the organisation of the folds is regular, and indeed part of the crystal structure. Such well-organised loops have also been seen by Atomic Force Microscopy (AFM). On the contrary, the fold surface of polyethylene single crystals is much less regular (due to the presence of longer loops, of cilia, etc...), and is not therefore amenable to such local investigation techniques which, at the present stage of the development of the technique, are just short of seeing such a level of detail in a relatively disordered background (the situation is different for epitaxially crystallised polymers, as seen later). It must indeed be kept in mind that there are roughly 10^8 folds and loops in each fold surface of a PE crystal 10 μm by 10 μm in size, and that, according to Nuclear Magnetic Resonance results, the folds, loops and cilia have some mobility (but less than the “pure” amorphous component) thus the term of “constraint amorphous” part.

Orientation of the folds.

While the structure of individual folds cannot be observed in polymer crystals, it is however possible to determine some average properties, and in particular the orientation of folds. It must be kept in mind that the conformation of a polymer in solution (or the melt) is a random coil. The transformation into a crystalline entity might keep some trace of this initial state: this was indeed the view of Flory, who believed in the fact that the fold surface is probably similar to the old-fashioned switchboard, in which chords link sockets dispersed in a random fashion on the board. This view is however difficult to reconcile with the very "crystallographic" aspect of polymer single crystals. Further indications that polymer folds are oriented come from the observation of dark field images of single crystals (i.e. images which are made with one diffraction spot, i.e. only with electrons that have been scattered by the crystalline core): these images indicate that the different growth sectors of a single crystal have their own identity. Indeed, "nominally" equivalent crystallographic planes scatter the electrons differently depending on whether they are oriented parallel or at an angle to the growth face of the sector (Figure 8). In other words, folds deform the underlying crystal structure in a way that is related to the growth direction: folds must have different orientations in the different growth sectors.

The orientation of the folds, inferred from the above dark field experiments can be assessed at a very local scale (resolution ≈100 nm) with the help of a so-called "polymer decoration" technique. A small amount of PE is heated, partly degraded and vaporised under vacuum. The molecular fragments (about 20 nm long) condense and crystallise on the fold surface of polymer single crystals. Crystallisation is triggered and induced by the short PE molecular segments which exist in the single crystal surface, i.e. by the folds: the deposited fragments align parallel to the folds and loops, and build up small crystalline lamellae which are standing edge-on on the fold surface. The resulting "decoration pattern" is made of small crystalline rods, which are locally oriented *at right angles* to the underlying folds and loops (Figure 9). Furthermore, the decoration pattern is very sensitive to the local structure and organisation of the folds and loops. In particular, it has shown a difference in fold plane structure for crystals in which the chains are tilted, which has bearings on the three-dimensional organisation of spherulites (cf. later).

Single crystals as a means to investigate crystallographic defects.

Crystallographic defects in polymer crystals are essentially of two types: defects that affect the lateral packing of chains *within the lamellae* (twins, edge dislocations, structural disorders of various types, such as e.g. shifts of crystallographic layers), and defects that *generate* new layers, namely screw dislocations. The former category corresponds to relatively local perturbations and can be investigated in quite detail by electron diffraction and analysis of the diffraction patterns. Screw dislocations have a profound impact on the morphology, and are essential in polymer crystal growth.

Twins correspond to the assembly of two crystals along a common plane, usually a dense one. The most frequent twin planes are parallel to the chain axis, i.e. modify the lateral packing of chains. Single crystals are therefore ideally suited to investigate the twin modes of polymers.

Other twin modes are less common. Twin planes may be oriented at an angle to the chain axis; they result automatically in a reorientation of the chain. The kink bands observed in oriented polymers submitted to axial compression may be described as a combination of such twin planes. A most original *rotation twin* exists in the α phase of isotactic polypropylene, and results in a highly unusual *lamellar branching* specific to this polymer and crystal phase (*cf.* Figure 16).

Edge dislocations are created when a crystallographic plane is created (or removed); this is easy in polymers, since it affects only the lateral packing of chains. Edge dislocations are best revealed by Moiré patterns when two crystals are superposed.

Screw dislocations (Figure 10) are of major importance in polymer crystal growth. They induce indeed the generation of extra lamellae from a parent one, and are therefore a major process in the generation of a three-dimensional structure built up of two dimensional lamellae. Screw dislocations of polymer lamellae have original characteristics: their so-called Burgers vector (parallel to the screw axis, and which characterises the displacement induced by the screw) is equal to the *total* thickness of the polymer lamella, including the amorphous fold surfaces, in sharp contrast with other organic or mineral crystals, in which the Burgers vector can be only one unit-cell long. Furthermore, due to the existence of this amorphous component between successive layers, these layers are not crystallographically related through their surface: this relative freedom may result in spectacular rotations of polymer screw dislocations. As already indicated, they are a major feature in the development of polymer spherulites which characterise the development of bulk crystallisation.

SPHERULITE STRUCTURE.

Spherulitic crystallisation is not limited to polymers: it is observed for many systems (inorganic and organic) of high viscosity and/or in the presence of impurity. The major characteristics of the structure of spherulites can be inferred from an examination in a polarising microscope; indeed, most of their characteristics were established (not for polymers!) at the turn of last century on the basis of optical microscopy alone. The birefringence of spherulites confirms their radial symmetry, with the existence of the so-called Maltese cross indicating that the chains are locally parallel or normal to the spherulite radius (cf. Figure 2). The sign of the birefringence (tangential refractive index n_t higher than radial refractive index n_r) indicates that the chains are oriented *parallel* to the spherulite surface, i.e. are tangential. This chain orientation remained a puzzle until the discovery of chain folding. Spherulitic growth is now correctly seen as the development and growth of chain folded lamellae which are oriented radially. Since the chains are normal (or at an angle to) the lamellar surface, they are indeed tangential to the spherulite (Figure 11). Recent techniques of etching of the spherulites has fully confirmed this organisation, and has demonstrated the prominence of screw dislocations in the space filling process associated with spherulitic growth (Figure 12).

While the spherulite structure is correctly summarised by this image of radiating lamellae, it may be more complicated. One common complication, observed for PE, but also for several other polymers (some aliphatic polyamides and polyesters, etc...) is the fact that the radiating lamellae are twisted; this twisting results in a most spectacular periodic banding in the polarising microscope (*cf* Figure 2) and in original concentric surface patterns when growth of the spherulite impinges on the surface of the melt (Figure 13). Various explanations have been given to account for this twisting: one of them rests on the periodic generation of screw dislocations and splaying of the new lamella at the screw centre, which indeed reorients the lamellae. Many electron micrographs of etched crystals and spherulites do indeed display this splaying at the screw dislocation site. Another explanation rests on the existence of stresses in the growing lamellae linked with different fold conformations in the top and bottom fold surfaces of the lamellae (as a result of the chain tilt). Since the stresses are symmetrical in the two lamellar halves, the bending of lamellar halves that are associated is opposite, and can only be compensated by an overall twisting of the whole lamella. It should be noted that experimental support in favour of the two ingredients of this model is provided by investigations of single crystals grown in thin films: the fold surfaces are different, as assessed by their different response to polymer decoration, and half lamellae growing on edge are indeed bent.

MODIFYING POLYMER BULK CRYSTAL STRUCTURE AND MORPHOLOGY.

The complexity of the structure and morphology of crystalline polymers suggests that, in some of its components at least, it can be modified to improve its characteristics to meet specific end uses. Leaving aside the issue of fibre formation, and its more recent evolution, the development of ultra-high modulus fibres by the gel-spinning process, we concentrate here on the alteration of the bulk morphology and structure, and notably the spherulite size, which is a major industrial issue. Reduction of spherulite size is known to impart better impact properties to the materials. Also, for isotactic polypropylene, reduction of the spherulite size to sub-micron dimensions (i.e. in the range of visible light wavelengths) can impart clarity to the material, and open new markets.

In industrial practice, increased nucleation rates are obtained by the addition of foreign particles, which act as nucleating agents. Increased nucleation is manifested by smaller spherulite size, faster overall crystallization, or, for constant cooling rates (as in a DSC), by crystallization peaks located at higher temperatures (Figure 14). These are often minerals (talc, ...) or salts of organic acids (e.g. sodium benzoate), but may be more complex organic molecules: dibenzilidene sorbitol (a gelifying agent, which imparts clarity to isotactic polypropylene), γ-chinacridone, etc... Efficient nucleating agents must (a) be highly dispersed in the material, thus have by themselves small crystal sizes (sodium benzoate), or dissolve and reprecipitate on cooling in the polymer and form a highly dispersed physical gel (dibenzilidene sorbitol) and (b) have a crystal structure which interacts favourably with the polymer.

The interactions are most often of physical nature (always, for non-reactive polymers such as polyolefins), and rest on some form of lattice matching between the crystal faces of the nucleating substrate and the polymer. This matching must be repeated over relatively large distances, i.e. must by necessity be associated with a dimensional concordance of the two lattices. The latter is expressed by a “lattice mismatch factor” which compares the dimensions of corresponding distances in the substrate and the deposit:

Lattice match (in %) = $100\,(d_{deposit} - d_{substrate}) / d_{substrate}$ and which is usually less than 10%.

Investigations of epitaxial relationships between polymer and substrates have indicated that in the vast majority of cases, the chains lie flat-on on the substrate, and that a major lattice matching involves the inter-chain distances in the polymer. The "best" epitaxies involve first-nearest neighbour chains (since this situation corresponds to the highest density of interactions in the contact plane), but second-nearest neighbours are also observed. For helical polymers, the distance between successive turns or helical paths may be involved in the epitaxy. Indeed, for helical polymers, it is only the helical path (and not the helix axis) which is materialised. The helical path orientation depends on the chirality of the helix, i.e. whether the helix is right-handed or left-handed (Figure 15): as a consequence, two different chain orientations are observed for any one epitaxial relationship (Figure 16).

Investigation of epitaxial relationships can also help reach unprecedented detail in the crystal structure analysis and visualisation of crystalline polymers and their polymorphs. Indeed, the epitaxial crystallisation is a "mild" means to orient a polymer. As such, it helps orient polymorphic crystal phases, which are unstable to mechanical orientation means (e.g. fibre spinning or stretching). Also, the contact faces can be exposed by removal of the substrate (by sublimation or dissolution in a solvent). A very ordered crystal face is thus exposed, which can be investigated by modern near-field scanning techniques, and in particular (when dealing with non-conducting materials) with Atomic Force Microscopy. The result of an AFM investigation of the contact face of isotactic polypropylene (in its α phase) is illustrated in Figure 17. It represents one of two potential *ac* contact faces of the α phase, in which methyl groups 0.65 nm apart (the dark dots) are organised in a lozenge shaped pattern, which corresponds indeed to the *ac* face geometry of α iPP, with its monoclinic β angle of 100°: through these preparation and investigation techniques, the crystal structure of polymers can now be investigated at a truly sub-molecular level, since (at least in the present favourable conditions) individual methyl groups can be resolved.

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Legends to Figures

Figure 1.

Volume-Temperature diagram of isotactic Polystyrene. The main transitions are the glass transition T_g and melting or fusion at T_f. Crystallization takes place between these transition temperatures. For the meaning of the different thermal treatments, see text.

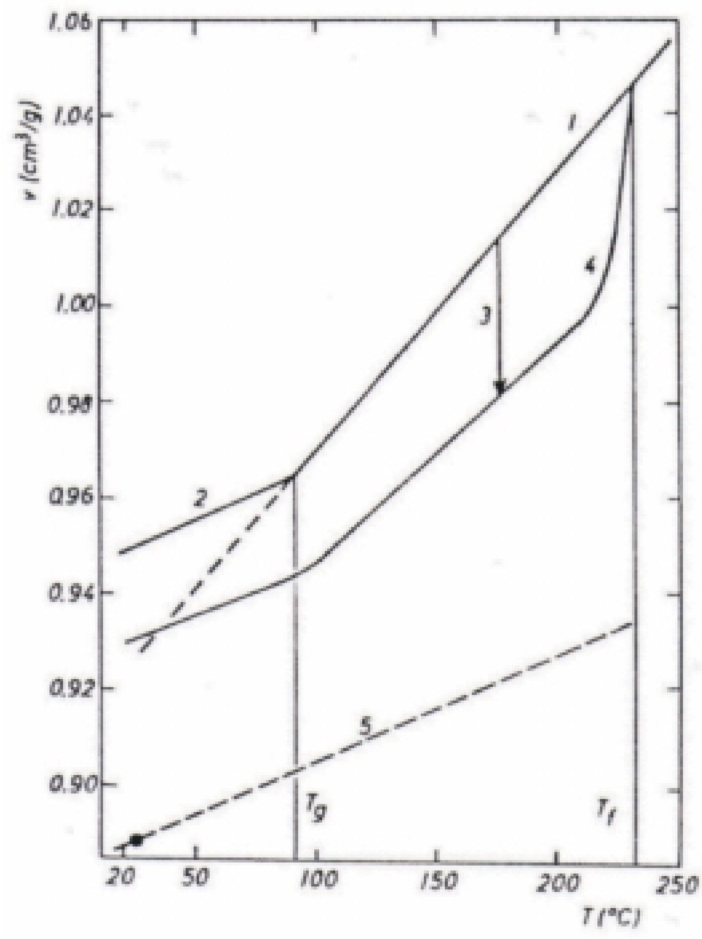

Figure 2.

Spherulitic growth as observed in an optical polarizing microscope during growth (top) and after spherulitic impingment (bottom). Top: poly(ethylene adipate) spherulites. Note the presence of the characteristic Maltese cross (parallel to the polarizer and analyzer) and the regular pattern of concentric rings, indicative of twisting of the radial lamellae. Bottom: spherulites of polyethylene. Larger spherulite size corresponds to earlier nucleation.

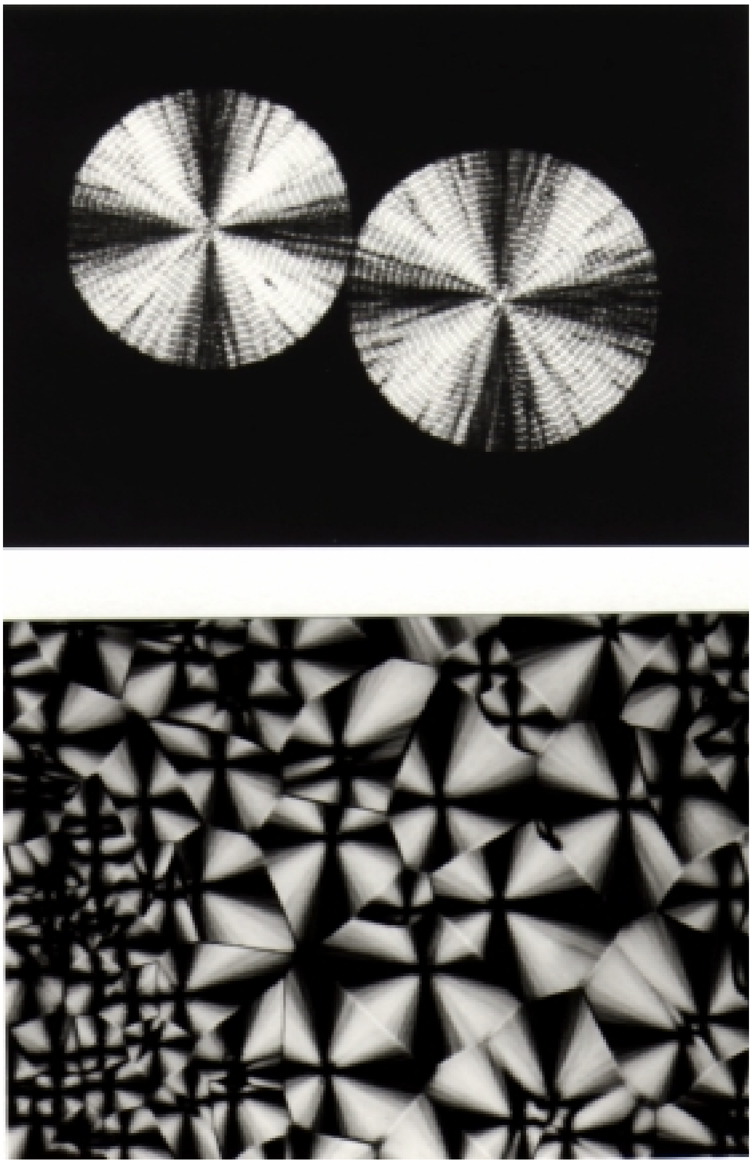

Figure 3.

Conformational energy map of isotactic polypropylene as a function of the two internal rotation angles τ_1 and τ_2. The two lowest energies at (60°-180°) and (180°-300°) correspond to antichiral three-fold helices; a right-handed helix is shown (carbon atoms only, methyl groups shaded, helical path underlined).

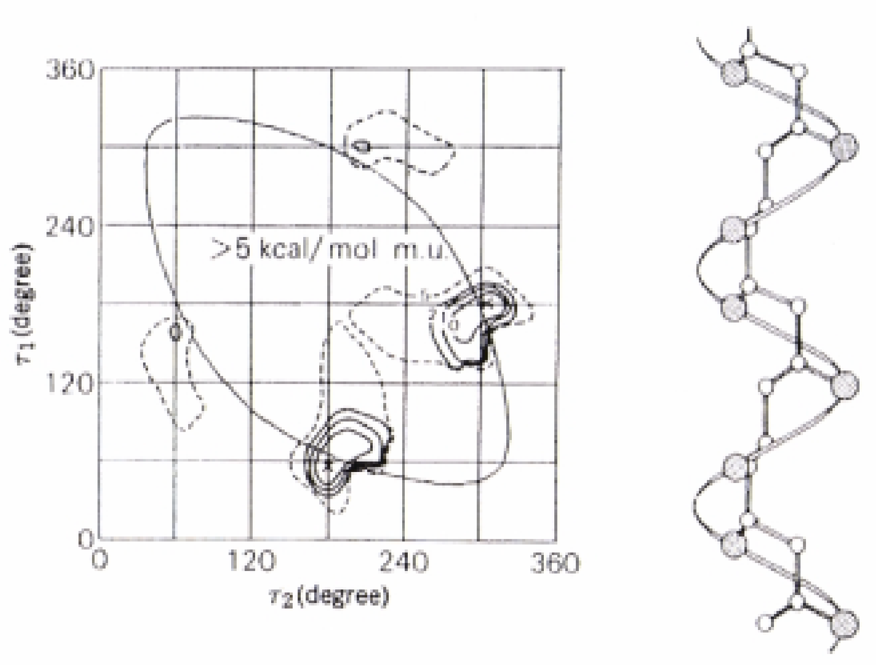

Figure 4.

Optical diffraction by masks of a continuous helx (left) and a discontinuous helix (right).

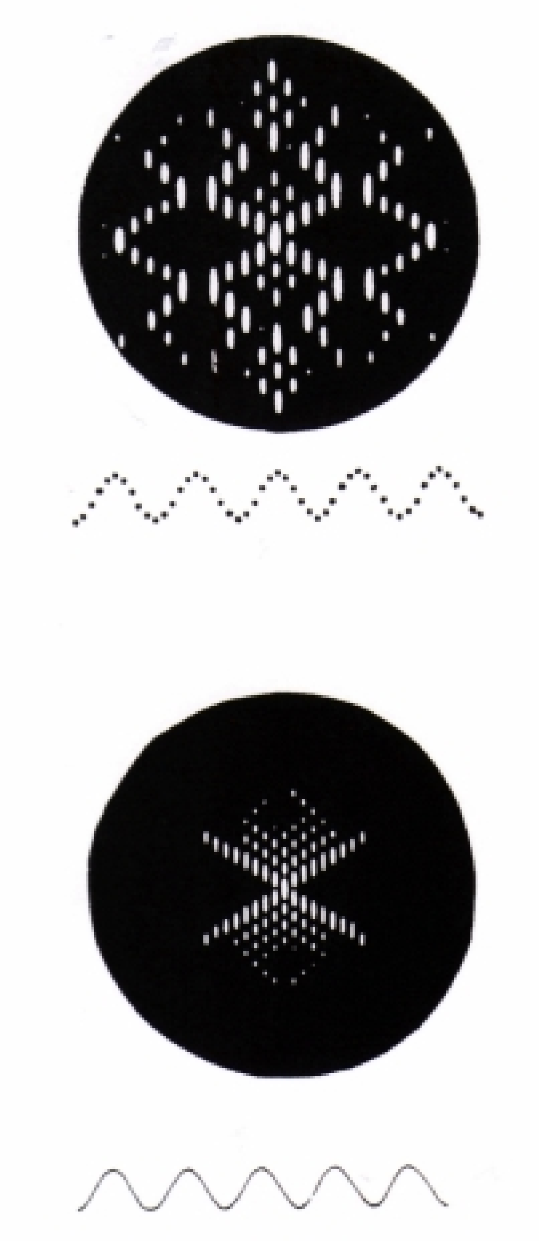

Figure 5.

Schematic drawing of the structure of the α helix of fibrous proteins (right) and its electron diffraction pattern (left).

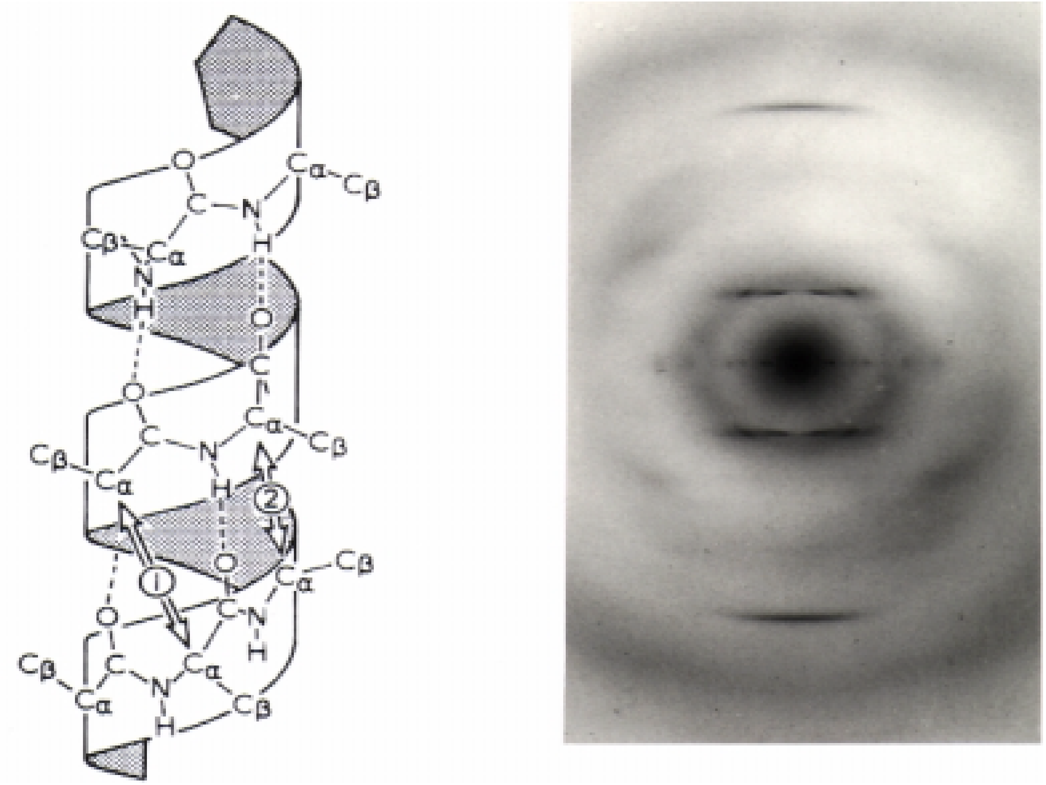

Figure 6.

Single crystals of polyethylene produced in dilute solution, and observed in transmission electron microscopy. Insert: electron diffraction pattern in proper relative orientation with the crystal arrowed. Note the pattern of dark stripes in the single crystals, which underline its sectorization. This is due to the “Bragg contrast” and indicates areas of the crystal, which diffract the electrons. The latter make up the diffraction pattern of the insert and are used to produce the dark field pictures shown in Figure 8.

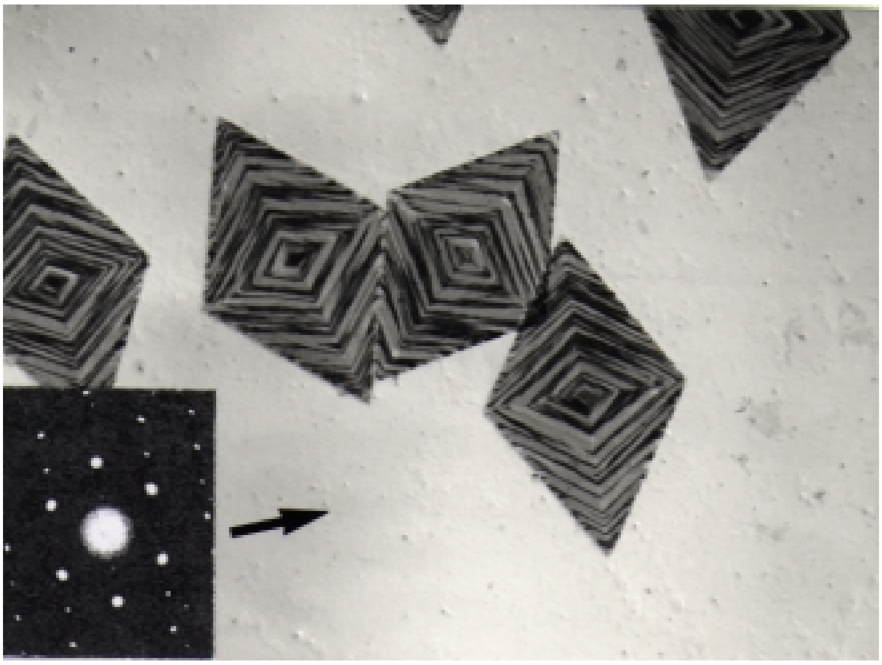

Figure 7.

Schematic representation of the structure of a chain-folded single crystal of polyethylene.

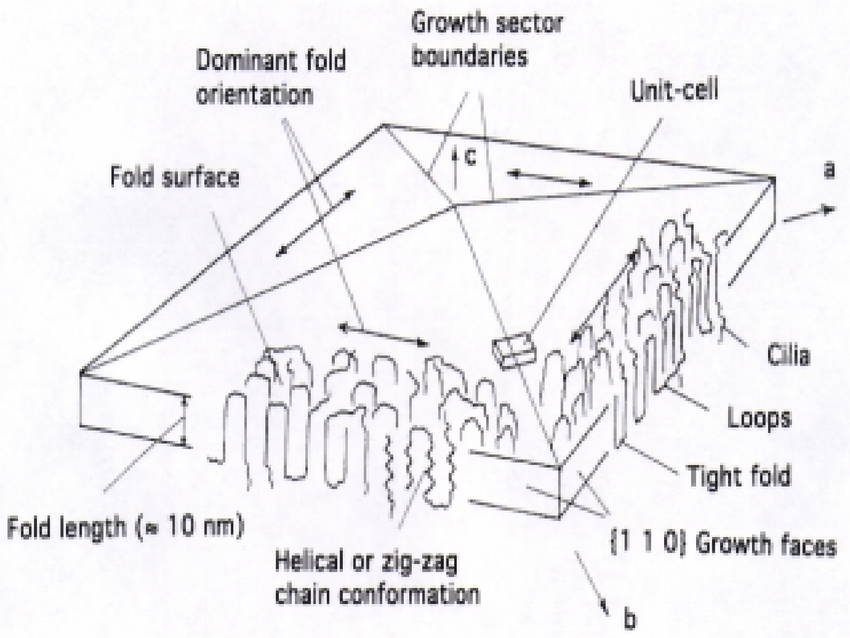

Figure 8.

Dark field imaging of a polyethylene single crystal. The three images are made with the three strongest spots of the diffraction pattern: 110, 020, -110. *a* axis of the unit-cell vertical, *b* axis horizontal.

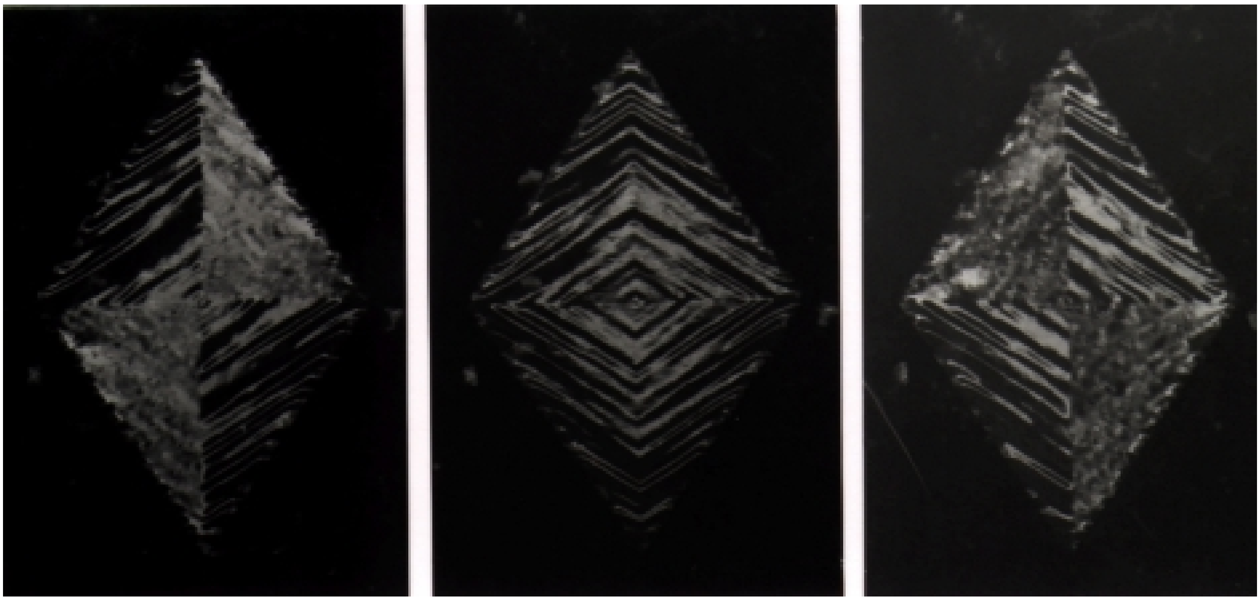

Figure 9.

Polyethylene single crystal decorated by condensation-crystallization of polyethylene vapors. The small rods of the decoration are at right angles to the fold direction, and therefore underline the sectorization of the crystal.

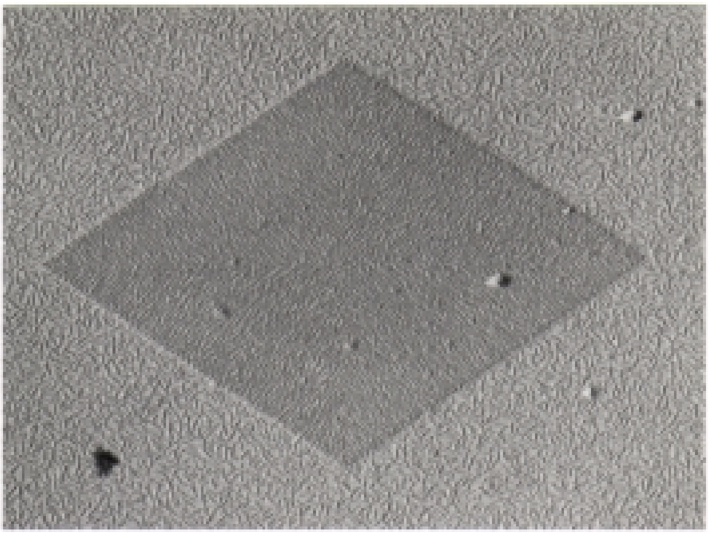

Figure 10.

Screw dislocation (in the present case, double) of a single crystal of poly(ethylene oxide). Note that the successive layers are rotated with respect to the underneath layer, indicating that the crystallographic continuity through the surfaces is shielded by the presence of the amorphous folds surface.

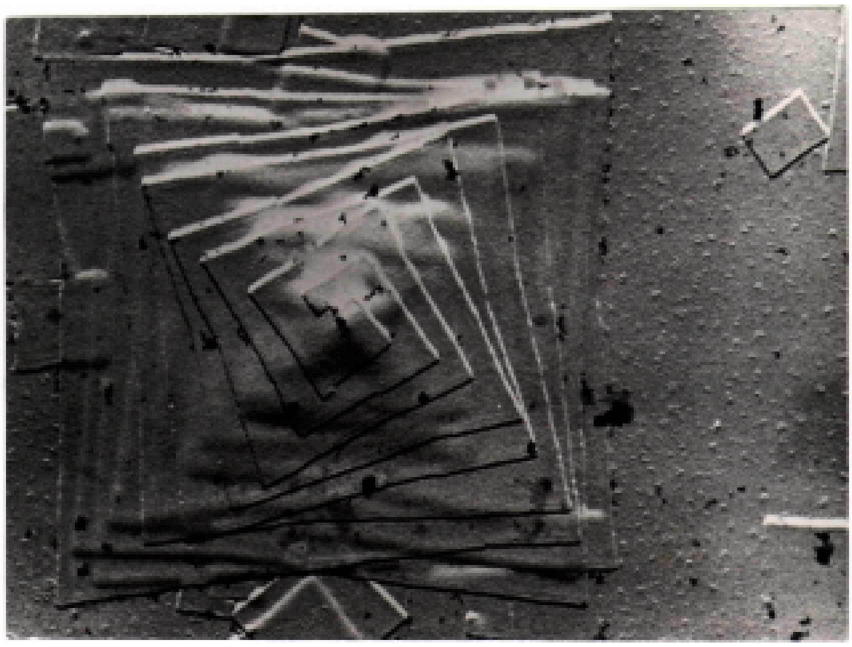

Figure 11.

Schematic representation of the structure of polymer spherulites. The regular twisting shown here for a polyethylene spherulite is not systematic for all polymers. Lamellar branching, mainly via screw dislocations, is an essential ingredient in the space-filling process.

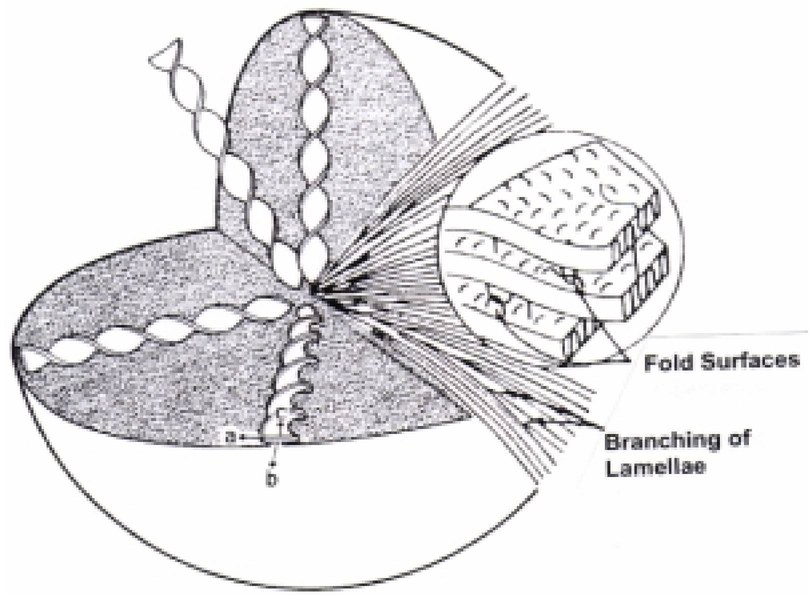

Figure 12.

Internal structure of isotactic polypropylene crystallized from the bulk, as revealed by an etching process. Two crystal phases are revealed by the different lamellar patterns: on the left, part of an α phase spherulite, with a characteristic near-right angle lamellar branching (due to a homoepitaxy specific to this phase); on the right, a β phase spherulite. Note the presence of numerous screw dislocations.

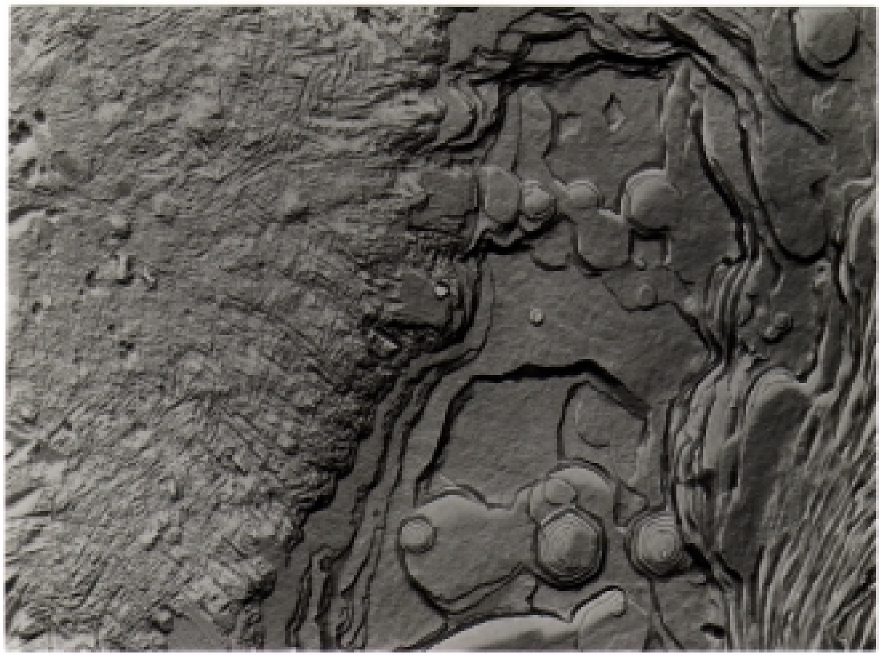

Figure 13.

Surface pattern of concentring rings generated when twisting lamellae impinge at an angle on the polymer melt surface.

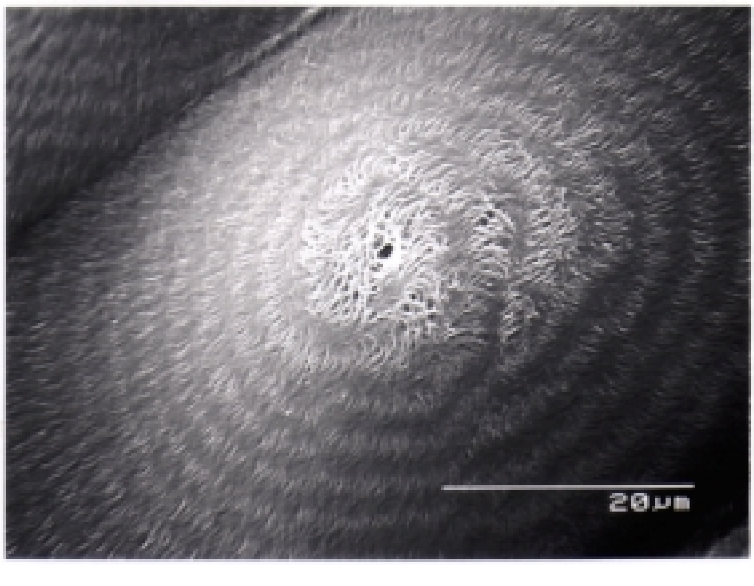

Figure 14.

Impact of the concentration of nuclei on the crystallization process. Crystallization curves of isotactic polypropylene obtained in a differential scanning calorimeter on cooling at 10°C/minute, after partial melting at various annealing temperatures T_s near the melting temperature T_m. For T_s>170°C, only ≈ 10^6 heterogeneous nuclei/cm^3 are left in the material, and the crystallization temperature is 112.5°C (average spherulite diameter: ≈ 100µm). Partial melting at lower and lower temperatures leaves more crystal fragments, which act as nuclei on cooling, and raise the crystallization temperature. For T_s= 166°C, ≈10^{13} nuclei/cm^3 are present, and T_c= 137.4°C (average spherulite diameter: < ≈ 1µm).

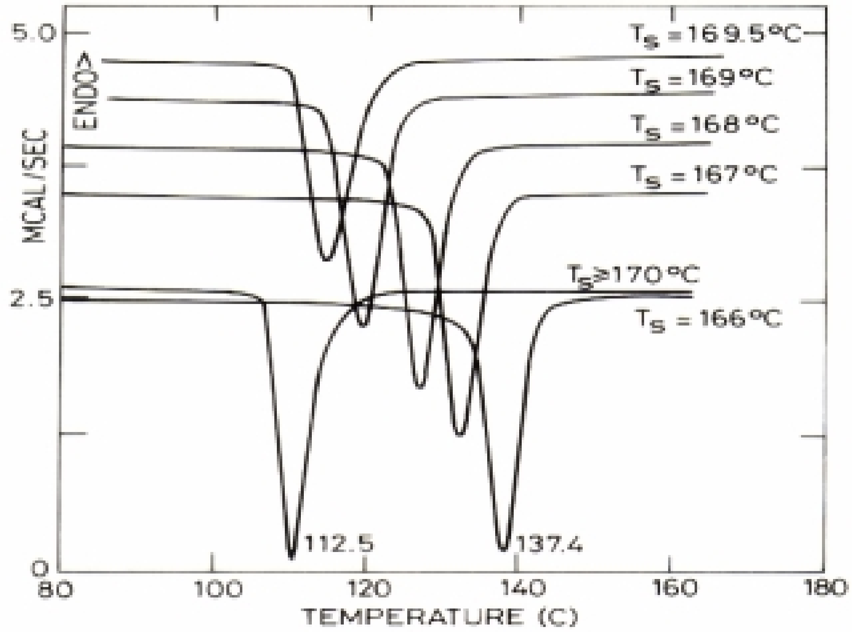

Figure 15.

Dimensional matching of the inter-strand distance of a helical polymer and a substrate periodicity (materialized here by rows of shaded dots). The different orientation of the helical paths relative to the helix axis results in different chain orientations: left-handed helices are tilted to the left, right handed helices to the right.

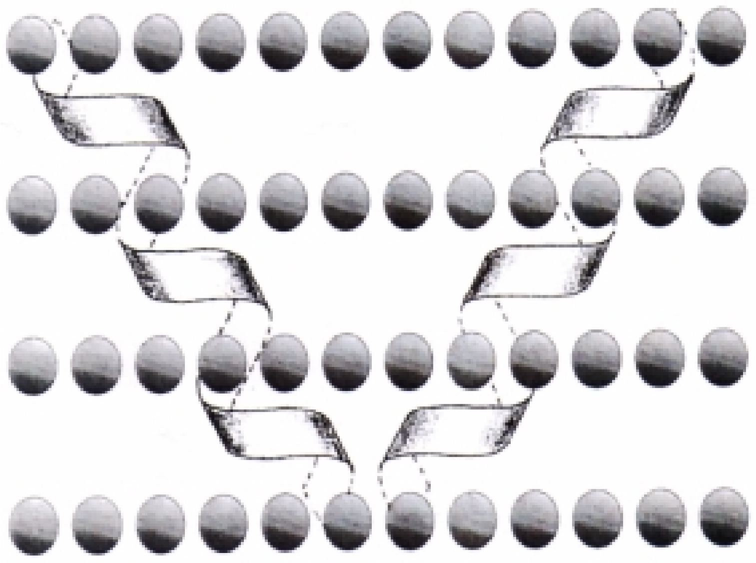

Figure 16.

Generation of two lamellar orientations (of isotactic polypropylene) as a result of the effect illustrated in Figure 15. The face that was in contact with the nucleating agent is exposed: the agent was on top of the polymer film, and has been dissolved away.

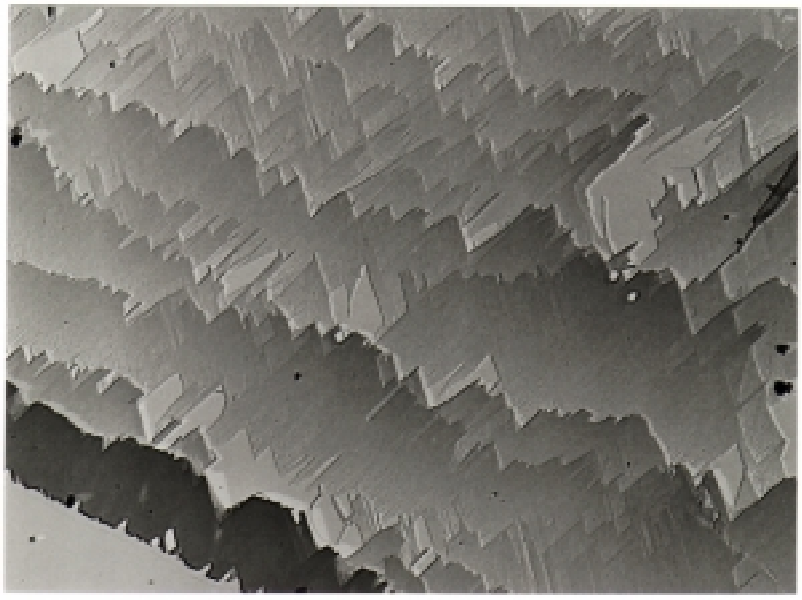

Figure 17.

Investigation by Atomic Force Microscopy of the contact (exposed) face in the lamellae shown in Figure 16. The dark spots correspond to methyl groups. They form a lozenge-shaped array with groups 0.65 nm apart along both the *a* axis and the *c* axis, in agreement with the crystal structure of the α phase of isotactic polypropylene.