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Polymer Morphology: A Guide to Macromolecular Self-Organization

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Summary: The study of polymer morphology continues to be the principal means of acquiring knowledge and understanding of macromolecular self-organization. Long-standing problems of the nature of melt-crystallized lamellae and spherulitic growth have been resolved, bringing understanding of how characteristic properties such as a broad melting range and spatially-varying mechanical response are inherent in spherulitic morphologies. This reflects the distinctive features of the crystallization of long molecules, i.e. that they impede each other and, for faster growth, form rough basal surfaces. Knowledge of morphology is an essential accompaniment to the informed development of advanced polymeric materials and a full understanding of their structure/property relations.

Keywords: crystallization; fibers; macromolecular self-organization; polymer morphology; structure/property relationships

Introduction

Crystalline polymers are important and successful materials with ever-widening uses, especially polyethylene and polypropylene which are the two in greatest production. Their usefulness is derived not only from their characteristic polymeric properties of low modulus elasticity, easy processability and toughness, but also because these can be substantially enhanced by suitable treatments. This goes beyond simple orientation of the long molecules, as in fibres, and concerns modifications of the internal microstructure. In crystalline polymers this is lamellar with long molecules folded, to a degree, back and forth between the fold surfaces. Contrary to early opinion, properties are not primarily dependent on the degree of crystallinity but upon the way lamellae are organized within a material which, for polymers crystallized from a quiescent melt, is characteristically spherulitic.

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The study of this internal organization, primarily using microscopes – with diffraction techniques used in a complementary role to quantify a defined textural model – is the subject of polymer morphology. This has been and continues to be the principal means of establishing knowledge and understanding of how long molecules self-organize, essentially because the microstructure contains a uniquely detailed record of the history of a polymeric sample, notably its crystallization and deformation, as well as indications of its molecular characteristics. Polymer morphology is key to understanding the fundamental aspects of macromolecular self-organization across the length scales from molecular through lamellar to spherulitic dimensions, and essential for informed control of processing to optimize properties. Following recent advances, the formation of spherulites and melt-crystallized lamellae are now much better understood, although the nature of the molecular networks underlying these entities remains to be well characterized, lying beyond currently achievable resolutions. The value, role and achievements of polymer morphology are the concern of this paper which is complementary to recent reviews.[1-3]

The Morphological Hierarchy

Examination of the interior of a crystalline polymer (of which polyethylene is the archetype, being both the simplest flexible macromolecule and economically the most important) reveals texture at a range of dimensional levels, depending on the magnification and resolution of the imaging technique used. Optical microscopy, the only available means until the advent of modern electron microscopes in the mid 1950s, shows inhomogeneity, at the μm level and above, in the form of spherulites. Literally little spheres, these are polycrystalline with equivalent radii because they contain chainfolded lamellae growing radially outwards.

The discovery of lamellae and their chainfolded constitution in 1957 marked the beginning of modern understanding of macromolecular self-organization. The, then newly synthesized, Ziegler-Natta linear polyethylene forms thin lamellae ~10 nm thick when precipitated from dilute solution in xylene. Electron diffraction showed that the ~1 μm long molecules were transverse within lamellae, whence it was inferred that they must be repetitively folded, back and forth at the basal or fold surfaces.[4] Chainfolded lamellae are a general feature of crystalline polymers, crystallized both from solution and melt, occurring because they are the fastest way in which long chains can crystallize. Their thickness is a physically, rather than chemically, determined quantity, increasing with crystallization temperature. This is to be expected because the gain in volume free energy on crystallization is linear in inverse supercooling, decreasing to zero at the equilibrium melting point.

The presence of fold surfaces increases the free energy of a lamella, making it thermodynamically unstable with respect to an increase of thickness as this decreases the proportion of fold surfaces in the system. Thickening can be accomplished in two ways. The first is by so-called *partial melting* in which the thinnest lamellae in a sample with a range of thicknesses – as would result from non-isothermal crystallization on cooling – melt, then recrystallize on their solid surroundings at an increased thickness due to the higher crystallization temperature. This occurs for solution-crystallized lamellae at temperatures above their crystallization temperature but melt-crystallized lamellae typically show *isothermal lamellar thickening* at their (somewhat higher) crystallization temperatures. In this case, thickening occurs via the strong characteristic longitudinal vibrations. Recent research, discussed below, has shown that thickening of a single polyethylene lamella occurs both at the growing edge, whose thickness increases with radial distance, and in the interior; the latter implies that new material must be incorporated into the lamella behind the growth interface.

The ubiquitous presence of lamellae in crystalline polymers lies behind characteristic properties, first, a reduced and broad melting range, the breadth linked to the spread of lamellar thickness and second, their low modulus. Fold surfaces interrupt the continuous sequence of covalent bonds along the **c** axis of polymeric crystal structures, introducing weaker van der Waals' bonding between lamellae[5, 6]. The actual modulus of a crystalline polymer specimen depends upon the details of the relative arrangement of covalent and van der Waals' bonds. It is least when they are in series and greatest when they are in parallel, with each weak interface both narrow and bridged laterally by a crystallite. Based on these considerations, manipulation of the morphology by suitable processing has produced a number of commercial high-modulus polyethylene fibres with moduli moving towards the theoretical limit ~ 3 Mbar, some 50% above that of steel.

The mutual arrangement and interconnectedness of lamellae is crucial in determining properties. In specimens crystallized from a quiescent melt the texture is characteristically spherulitic. Once it became possible to examine the internal lamellar organization, using chlorosulphonation of polyethylene and permanganic etching of polyolefines and other polymers, it was found that homopolymer spherulites have a dominant/subsidiary microstructure. Individual first-forming or dominant lamellae branch periodically then splay apart, establishing a framework which is filled in by later-forming subsidiary lamellae. Within spherulites, therefore, there is an intrinsic variation in lamellar texture and properties on the scale of the inter-dominant spacing.

This variation may differ considerably. There are differences in orientation between dominant and subsidiary lamellae, giving them different responses to applied stress[7] for an isothermally-crystallized homopolymer of low polydispersity, possibly coupled with small differences in their thickness due to differential isothermal thickening. In more polydisperse homopolymers and, especially, random copolymers, fractional crystallization may place different molecular species in different locations. In the former materials, shorter polyethylene or poorly tactic i-polypropylene molecules, which are prone to crystallize later, may become concentrated between dominant lamellae and/or in inter-spherulite boundaries, promoting brittleness due to concentrations of shorter molecules. Similarly, in random polyethylene copolymers, more-branched molecules (correlated with shorter lengths for Ziegler-Natta synthesis) may concentrate in later-crystallizing regions with comparable consequences.

Copolymers bring additional complexity. Greater concentrations of comonomer lower the equilibrium melting point, reducing the isothermal supercooling and thence the growth rate, an effect which, if sufficiently large, can render growth morphologically unstable with additional microstructural consequences. If, in addition, crystallization is not isothermal, this will increase the supercooling and reduce the thickness of later-crystallizing lamellae, giving them a lower melting point. Spherulitic textures, therefore, go far beyond the evident differences in radial orientation to include systematic variations of lamellar orientation, thickness and molecular composition on the scale of the inter-dominant separation.

Such matters are further complicated when crystallization occurs under applied stress or flow as in industrial processing. Principal of these is the change from effectively point nucleation of spherulites to extended linear nuclei forming the backbone of so-called shish-kebab or, preferably, row structures. Although the growth processes at the crystal/melt interface are presumably the same, linear nucleation does bring significant changes. First, the backbone or linear nucleus, which forms to sustain the applied stress, is higher melting than the thin lamellae which grow from it; in i-polypropylene the difference may be ~50 K. Second, the different geometry means that lamellae encounter different growth conditions to those in spherulites and respond accordingly. These are principally two different conditions. One is that lamellae growing in a close-packed parallel array are unable to thicken uniformly, unlike those which diverge from their nearest neighbours. In practice, those lamellae in such an array which thicken do so at the expense of others which fail to propagate.[8] A striking consequence is that whereas the thickest and highest melting lamellae in spherulites are the oldest, at the centre, polyethylene shish-kebabs melt first not only at the outside of a row but also adjacent to the extended nucleus.[9] The second consequence is that diffusion conditions differ at the growth interface for molecular species segregated during growth. The greater space between lamellae which diverge, compared to those which grow parallel, reduces the local concentration of segregants. If these lower the equilibrium melting point, as in polyethylene random copolymers, the local supercooling will decrease, giving row structures a slower radial growth rate than adjacent spherulites.[9] In turn, if the growth-rate depression becomes sufficiently large, it leads to constitutional supercooling, and the growth interface becomes unstable towards faster-growing protuberances. In row structures this becomes evident by the trace of the interface with the melt, in a section through and parallel to the nucleus, changing from linear to quasi-sinusoidal.[10] Such changes are sensitive to the nature of the segregated species. There are differences, for example, between polyethylene copolymers of the same branching ratio synthesized by Ziegler-Natta means as opposed to the use of single-site or metallocene catalysts.[11]

The spatial variations inherent in spherulitic textures may affect properties in undesirable ways. For example, it is difficult to prepare clear films of i-polypropylene because of light scattering from large spherulites whose size is controlled by the number of primary nuclei. While this is easily increased for polyethylene, achieving clarity in i-polypropylene remains a persistent problem. Internal textures are affected principally by primary nucleation density, molecular constitution and crystallization temperature, variables which offer a limited degree of control.

Spherulitic Growth

The key feature which causes growth to be spherulitic rather than single-crystalline in polymers is that lamellae periodically branch, then diverge. Iteration of this procedure gives spherulites with all radii having the same growth axis, **b** for polyethylene, **a*** for i-polypropylene. Their straight traces show that adjacent lamellae diverge because they are repelled by a short-the next branch. Branching is often, but not necessarily, at giant screw dislocations whose Burgers' vector is the lamellar thickness measured along **c**, the chain axis. It has now been shown in considerable detail for model systems of monodisperse long n-alkanes that the repulsion is due to molecular cilia, both transient and permanent, i.e. uncrystallized portions of molecules partly attached to a lamella. The divergence of adjacent lamellae increases for longer cilia and thinner lamellae.[12] Transient cilia must be present whenever a long molecule adds to a lamella in stages; permanent cilia exist in co-crystallizing binary blends. The effects of transient and permanent ciliation have been separated, with the latter disappearing in blends when the guest molecule is twice as long as the host and crystallizes in a hairpin conformation in a lamella of uniform thickness.[13,14] These studies also revealed a second cause of lamellar divergence, namely surface roughness - a feature associated with rapid crystallization.

Surface Organization and Reorganization

The formation of initially rough surfaces, prone to reorganization, has recently been shown to be characteristic of rapid polymeric crystallization from observations down **b**, the growth direction and radius of polyethylene row structures developing from linear nuclei. These relate to the lamellar habits adopted in different circumstances. In melt-crystallized linear polyethylene, fold surfaces are 201 at low supercoolings, inclined to the chain axis **c** by ~35° but, at ≤~126 °C for typical molecular weight, dominant lamellae viewed down **b**, have S- or C-profiles inclined at $\leq\sim35^{o}$ to **c** in their centres. Dominant lamellae of the second kind are found in banded spherulites; banding and twisted growth does not occur for the first kind of lamellae.

The different profiles come about because at lower temperatures the next molecular layer is added to a lamella before folds in the previous one have had time to attain the preferred 201 packing. Conversely at higher temperatures, with slower growth, there is time for this optimum fold packing to be adopted before the next layer is added.[15] The reason for *inclined* 201, being adopted rather than *perpendicular* 001 fold surfaces (with respect to the chain axis) is that they provide more surface area per fold. Inclined basal surfaces are found not only in polyethylene but also in the n-alkanes, which have the same subcell whose low cross-sectional area per chain militates against too close a packing of bulky end groups or folds. However, the reduction in free energy from fold surface ordering must be small in relation to that from the crystallization of fold stems. Moreover, the latter increases with supercooling whereas the energetic cost of a (disordered) fold surface will be more nearly constant and independent of temperature. It is to be expected, therefore, that faster crystallization will initially give disordered surfaces while ordered surfaces will only occur for slower growth; this is the case even for monodisperse long n-alkanes.

Study of the growth of polyethylene row structures from highly oriented fibres as linear nuclei, has not only given substance to these expectations but also revealed new aspects of macromolecular self-organization. For slower growth, $\geq$ 127 °C for typical linear polymers, lamellae do indeed from inclined on the linear nucleus, the double 201 orientation presenting a chevron appearance viewed down the **b** axis. But, beyond a certain radial distance this gives way to all lamellae lying normal to the nucleating fibre, yet retaining their 201 surfaces. This new phenomenon has been ascribed to the effect of internuclear interference when one molecule is able to crystallize on adjacent lamellae simultaneously.[16] This effect will disappear and allow faster radial growth when lamellae are parallel and sufficiently separated.

By contrast, for faster growth, lamellae form perpendicular to the nucleus, with 001 surfaces. Then, with increasing radial distance, they separate (with some failing to propagate), thicken, and develop S-and C-profiles together with banded growth. The latter two are a consequence of delayed fold-surface ordering within the constraints of an existing lamella to reduce the surface stress of disordered fold packing. The adoption of an inclined profile in the central, oldest region of a lamella will, to maintain integrity, give an S-profile, or a C-profile in narrower, oblique cross-sections.

Confirmation that it is the (partial) relief of fold surface stress which drives banded growth in polymers comes from the development of row structures in random copolymers of polyethylene. Slower growth at higher temperatures begins exactly as for rows of the linear polymer, but in a range now lowered because of the inherently slower growth. Lamellae are inclined, with an initial chevron pattern which gives way to inclined lamellae perpendicular to the nucleus at greater radial distance in combination with isothermal thickening and increase lamellar separation in untwisted growth. However, beyond a certain distance, inferred to be when thickening has brought branches into the fold surface and stressed the surface, growth becomes twisted and dominant lamellar profiles become slightly S-shaped.[17] The band period is reduced by comparison with faster growth conditions with an abrupt decrease of gradient in the plot against crystallization temperature.

Time is of the essence in achieving optimum surface packing: for sufficiently slow growth, there is more time for the system to explore alternative conformations and reach that of lowest accessible free energy. Experiments with centrally-branched monodisperse alkanes have shown that, at the highest crystallization temperature, lamellae spontaneously adopt cylindrical habits, with all branches on the outer, convex, surface demonstrating that the gain from improved surface packing outweighs the cost of straining the lattice in lamellar interiors.

Banded Growth

Although the relief of surface stress is the reason for banded growth, one still has to account for how such asymmetric growth develops and propagates in what are often symmetric systems. In polyethylene the phenomenology is now known. The essential asymmetry is introduced because the axis of S-profiled lamellae does not lie along the **b** axis, as is to be expected because fold placement is not crystallographic. The S-profiles propagate radially and consistently via arrays of isochiral giant screw dislocations lying to one side of the axis of the S where the shear stress for their formation is highest. The increased compliance of a dislocated lamella allows what is effectively an increment of twist to be given to a new lamella inserted at the dislocation.[18]

Towards Improved Properties

The early appreciation that fold surfaces reduced the longitudinal Young's modulus of polyethylene fibres lead to the introduction of different means to produce materials which had higher modulus but were still tough, such as melt spinning, gel spinning and melt kneading. However, the large extensions employed to attain high molecular extension towards this end produced fibres of, say, ~40 μm diameter. An effective means of cementing such fibres together to fabricate specimens of larger size with substantially maintained properties is hot compaction, in which just sufficient polymer is melted from the periphery of lightly compressed fibres to fill the intervening interstices.[19,20] The later development of two-dimensional compactions has since led to the commercial production of polypropylene sheets with exceptional impact properties.

Fibre Structure and Cold Drawing

In addition to morphological studies helping to guide the development of these and related materials, they have also led to significant gains in understanding the organization of macromolecules in highly-oriented fibres and of the cold drawing process.. Examination of the cross-sections of various advanced polyethylene fibres has shown that they share a common internal substructure, though differing in characteristic detail.[21] After etching one sees craters surrounded by high-melting walls on which later and lower-melting growth has nucleated. Linear voids down the centres of etched craters, akin to those often found in melt-crystallized polymer chip, are indicative of a shortage of material to complete crystallization within the defined volume. The walls themselves are presumably generated when the entangled molecular network sustains the applied stress with their differences of detail, particularly scale, reflecting the specific features of the various processing routes. This is new and pertinent information which must underlie a better understanding of structure/property relationships.

Cold drawing is the name given to deformation of an existing structure as opposed to formation of an elongated texture directly from the melt; it is not restricted to ambient temperature but, e.g. for linear polyethylene, can extend above 100 °C. For a long time it was believed, from small angle scattering perpendicular to the draw direction, that the initial morphology was destroyed at high draw ratios. This is not so. Examination of the cross-sections of polyethylene drawn ~50x has shown that a memory of the initial morphology survives.[22,23] This demonstration that the final properties do relate to those of the starting material opens the door to more-informed processing.

Conclusions

The study of polymer morphology continues to be the principal means of acquiring knowledge and understanding of macromolecular self-organization. Long-standing problems of the nature of melt-crystallized lamellae and spherulitic growth have been resolved, bringing understanding of how characteristic properties such as a broad melting range and spatially-dependent mechanical response stem from inherent systematic variations in the internal microstructure of spherulites. These stem from the distinctive features brought to crystallization by long molecules, namely that they impede each other at the growth front and, for faster growth, form rough basal surfaces prone to subsequent reorganization. Morphological knowledge is an essential accompaniment to the informed development of advanced materials and a full understanding of their structure/property relations.

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