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Cylindrical Lamellar Habits in Monodisperse Centrally Branched Alkanes

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Introduction. In his paper inferring molecular chain folding in polyethylene lamellar crystals, Keller[1] refers to paraffin lamellae being curled up into needles or scrolls.[2] Such habits are familiar in these complex systems, appearing at high crystallization temperatures, although their precise nature and the requirements for their formation have remained somewhat unclear.[3] The present work has encountered scrolled, quasi-cylindrical lamellar habits, of constant diameter, in each of two monodisperse centrally branched alkanes at the highest crystallization temperatures. These alkanes have a single central branch which causes molecules to crystallize in hairpin conformation. Branches are located in the fold and, in a scroll, all are on the outside, making opposite basal surfaces of different character. This demonstration that a lamella will distort spontaneously to improve surface packing with opposite basal surfaces distinct is an important, previously unrecognized, morphological principle not just for alkanes but also for crystalline polymers.

Experimental Section. The two monodisperse alkanes investigated were synthesized[4] by Dr. G. M. Brooke and colleagues at the University of Durham under the auspices of EPSRC. They are $C_{96}H_{193}.CHR.C_{94}H_{189}$ with $R = CH_3$ or C_4H_9; henceforth for convenience, they will be denoted as C1 and C4, respectively, referring to the length of the branch.

The results presented here, part of a wider investigation,[5] are confined to transmission electron micrographs. These are of single-stage metal-shadowed carbon replicas of samples etched with a permanganic reagent, following published procedures.[6]

Results. It has previously been demonstrated, by small- and wide-angle X-ray scattering, that both alkanes invariably crystallize with molecules in a hairpin conformation in the usual alkane subcell[7] (and presumably with branches distributed equally but statistically in both basal surfaces). This is in striking contrast to *n*-alkanes of similar length, such as n-$C_{194}H_{390}$, which always crystallize from the melt with molecules fully extended.[5,8] It follows that it is the introduction of central branches which has caused the molecules to fold, with the branches themselves in the folds.

The common habit in both alkanes is lamellar with {201} fold surfaces, i.e., with molecules inclined at 35° to lamellar normals.[7] However, scrolls of unchanged lamellar thickness appear in both C1 and C4 crystallized at 115 °C, the highest crystallization temperature. Figure 1a shows these in C4, lying in the plane of the paper adjacent to a population of conventional lamellae. In the cross section of Figure 1b, the diameter of scrolls in C4 is seen to be rather constant at ~1 μm. They are constructed of rolled layers and, from their geometry, must have crystallized before the matrix with an initially hollow interior, filled by later crystallization. Note in the top center that a lamella which is curved and part of the right-hand side of the scroll then becomes planar and leaves it tangentially on the left. This is a demonstration of the close connection between the two habits of what is the same orthorhombic subcell. Elsewhere, lamellae leaving the scroll are curved but less so than the scroll. The constant lamellar thickness implies that the molecular orientation remains inclined at ~35° to the local lamellar normal.

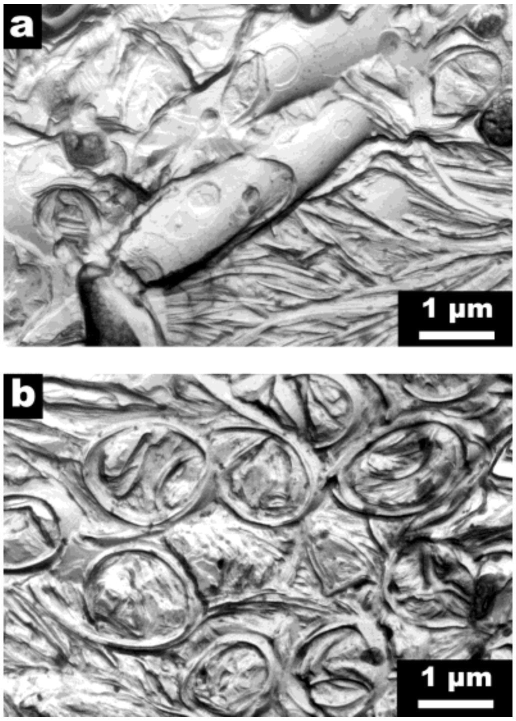

Figure 1. Scrolls and lamellae in C4 branched alkane crystallized at 115 °C. (a) The cylindrical habit of scrolls with conventional lamellae adjacent. (b) In cross section, the scroll diameter is seen to be ~1 μm.

The behavior of C1 is similar to C4 but with a scroll diameter of ~2 μm, twice that of the longer branched alkane. The length of a cylinder is shown in Figure 2a and an area of cross sections in Figure 2b. In the center of Figure 2c a scroll is seen obliquely with part of the same lamella leaving tangentially. In both alkanes the length of the cylinder, which is larger than the scroll perimeter, is inferred to be along **b,** invariably the longest growth direction in *n*-alkanes, from the shape of etch pits and growth spirals.

Discussion. Cylindrical or scrolled crystal habits are by no means unknown outside paraffins; they are found, for example, in chrysotile asbestos based on a cylindrical lattice,[9] in as-polymerized poly(4,4′-oxybibenzoate)[10] and, in melt-crystallized polymers, in the γ phase of poly(vinylidene fluoride) by the curling up of normally planar lamellae.[11,12] All these examples are, however, complex situations; the last is a polar polymer, i.e., inherently asymmetric, for which it has been suggested that electrostatic forces are a factor in the formation of scrolls.[13] In the present case, with very well-defined systems, the packing considerations underlying the

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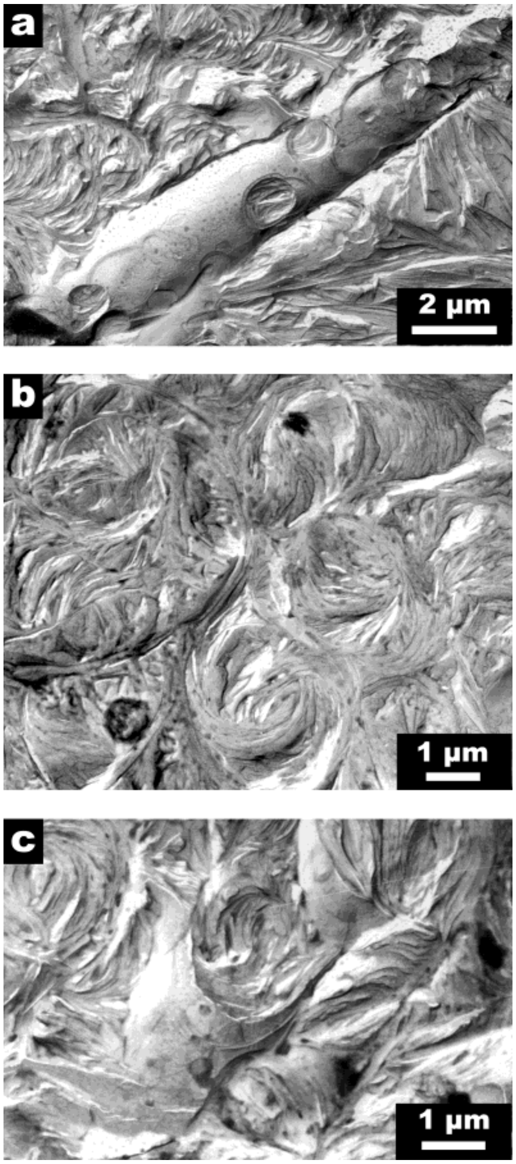

Figure 2. Scrolls and lamellae in C1 branched alkane crystallized at 115 °C. (a) The same cylindrical habit occurs for the shorter branched alkane but with a larger diameter. (b) A cross section shows that the diameter of scrolls is ~2 *μ*m. (c) A continuous lamella is partly on the outside of the central scroll, viewed obliquely, with a planar portion leaving the scroll tangentially.

quasi-cylindrical habit are unambiguous, leading to a new insight into the habits and properties of alkane and polymer lamellae.

The two stable habits, planar and cylindrical, can even be continuous parts of the same lamella, as in Figures 1b and 2c, confirming that they are the same crystalline phase. Whether scrolls form directly from the melt, therefore, or by spontaneous curling up of planar lamellae, it follows that the cylindrical habit, forming only at the highest temperatures, is the more stable. This is an important conclusion, showing that surface packing considerations outweigh the resulting elastic strain in the lattice in this most basic of aliphatic crystal structures.

Whereas the lattice of a planar lamella will be unstrained, this will not be true of a cylindrical one. Here it will be accompanied by a differential strain between the two basal surfaces of l/R, where l is the lamellar thickness and R the radius of curvature, with the outer surface in tension and the inner in compression. Given that lamellae of these alkanes are 10 nm thick,[7] this gives differential surface strains of ~1 and 2% for C1 and C4, respectively. These must arise from the presence of branches predominantly in the outer surface, and with the near constant diameter of scrolls observed for a given alkane, one may safely infer that all branches are then in the outer surface, this being the minimum radius of curvature. It is not possible to decide from present evidence whether regular fold packing is also present though this would be the lowest local minimum of free energy.

The ratio of two between radii of curvature, and thus differential strains, for the two alkanes corresponds not to the length ratio of the respective branches but to its square root. While this may suggest that the butyl branch is spread in the surface of the cylinder, in fact the strain is confined to the cross section of the cylinder, i.e., the *ac* plane (Figures 1a and 2a). Further comment on the significance of the ratio would require information on how branches pack together in the lamellar surface which current molecular modeling may provide.

What is made clear by this work is not only that a cylindrical habit is more stable than a planar alkane lamella but also that, in these precise systems, it results from improved packing of branches in basal surfaces notwithstanding the concomitant elastic strain inside the lamella. It follows that a planar lamella, in which branches will be equally present in both basal surfaces, can become unstable with respect to the adoption of curvature, if branches are able to move to the convex surface. The principle of improved surface packing producing lamellar curvature with opposite basal surfaces of different character is fundamental and can be widened to other causes than the accommodation of branches.

It is always possible, for sufficiently slow growth, for branches to grow directly in the one (convex) surface with others, wrongly presented, being rejected at the crystal/melt interface. Faster growth rates will not allow sufficient time for such selection, and for these, branches must move to the convex surface subsequently as planar lamellae curl up. This agrees not only with direct observations of paraffin wax but also with those lamellae emerging from a scroll which are either planar or less curved than the scroll itself.

In the case of the paraffin waxes, whose molecular masses are ~ 400, with ~10% of branched species,[3] the greater prevalence of scrolls or "needles" in the morphology is to be expected because surface packing will be relatively more important. The scrolls are also of larger diameter[2], ≥~10 *μ*m, so with fewer branches and less curvature the magnitude of differential surface strain is reduced by between 1 and 2 orders of magnitude, even taking the reduced lamellar thickness of ~3 nm into account. Accommodation of branches in basal surfaces will be one relevant factor with a mixture of chain lengths another. In this latter case, a moderate proportion of shorter chains resulting in vacant sites at the surface would reduce surface stress. As a consequence, such surfaces could tend to be on the internal, concave surface of a curved lamella to which all vacancies would eventually move. The consequences of a moderate proportion of longer chains would depend on whether they increased or decreased the stress in their surface.

It appears from the way that lamellae leaving a scroll are either planar or less curved than the scroll itself that initially planar lamellae in these branched alkanes also curl up. The radius of curvature must then decrease progressively as the proportion of branches on the convex surface increases. Whether such a lamella will be able to attain its maximum curvature will depend on the obstacles it encounters. In Figures 1b and 2b internal growths nucleated on a lamella could be a reason for arrest before maximum curvature has been attained. In such a progressive increase of curvature it would be necessary for branches to diffuse through an initially planar lamella to the convex surface, possibly in combination with a stem vacancy, using the characteristic strong longitudinal translational motions.

The ability of the stress associated with bulky defects to move from one basal surface to the other is necessary if a planar lamella, in which such defects would be equally present in both basal surfaces, is to become curved. For these alkanes in which surface stress is due to the presence of branches, movement of branches through a lamella is the only means available, but there are alternatives, discussed below, for polymers in which branches remain outside the lamellar core.

It is to be expected that surface packing considerations will be relevant to polymeric lamellae as well as alkanes. In polyethylene, lamellar thicknesses are typically only 2−3 times more than in the alkanes of this paper, while branches in linear low-density materials are generally much longer than methyl, with hex-1-ene and oct-1-ene common comonomers. The surface energy term can thus remain of comparable magnitude to the elastic energy stored in the lamella which will reflect only van der Waals bonding (and is $Yl^3/16R^2$ per unit area of fold surface for a lamella thickness l, radius of curvature R, and Young's modulus Y), especially so when the radius of curvature is high but finite.

The formation of curved lamellar habits has recently been reported for a linear low-density polyethylene, a random copolymer containing ethyl branches which are known to be substantially excluded from the crystal lattice. This concerns a new phenomenon in which surface stress was created in initially ordered fold surfaces of lamellae undergoing isothermal thickening, causing planar lamellae to adopt curved S-profiles.[14] Once the lamellar thickness increases to the point where it equals the interbranch length of a chain sequence in the crystal, further increase will tend to bury the branch within the surface region as an interstitial surface defect, ISD, with an associated increase in surface stress. There is no requirement that this stress will be the same at both surfaces, and a simple longitudinal chain translation will transfer stress from one surface to the other according to the position of the interstitial branch within the surface region.

A similar explanation may apply to the long-standing, unresolved problem of the cause of consistent curvature, ~20 μm radius, in isotactic polypropylene lamellae of the α modification, present for materials of low tacticity crystallized at high temperatures and increasing from zero as tacticity falls.[15] The curvature presumably reflects an asymmetric concentration, at opposite fold surfaces, of stereo defects in the isotactic chain which require more space as do branches in polyethylene. They, too, could lie on the fold surface or be buried in it as ISDs with increased surface strain after isothermal thickening. While the former would be expected to be laid down more or less equally on both fold surfaces during crystallization, the latter formed once there is lamellar thickening could transfer to the opposite surface, promoting its convexity and leaving a stereo defect behind on the surface. The habit favored would be that observed, namely curving into the acute angle between radial and crosshatched lamellae because of the greater steric interference compared to the obtuse angle.

In summary, the demonstration that a cylindrical habit is stable in two centrally branched alkanes not only reveals the important principle that alkanes will spontaneously adopt a strained lattice to accommodate improved surface packing but also suggests possible explanations for previously inexplicable curved habits in melt-crystallized polymers.

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