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The essential novelty brought to crystallization by molecular length

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Abstract

There are two key features brought to crystallization by molecular length. First transverse lamellae which, for longer molecules, involves chainfolding and thence spherulitic growth. Second the basal lamellar surfaces; their formation is secondary to the crystallization of stems so that they are only well-defined for slow growth. For faster growth they are increasingly rough, unstable and prone to reorganization towards preferred packing in thicker lamellae. In tightly packed lattices such as polyethylene the associated excess energy drives twisted growth.

Keywords: Crystallization; Molecular length; Fold surface reorganization

1. Introduction

In the fifty years since individual polymer lamellae were first reported and the inference of molecular chainfolding made [1] only relatively recently have the key features been confidently identified which give macromolecular crystallization its special character. These concern particularly the nature of the lamellar surfaces and its time-dependent character.

Polymeric crystallization is lamellar, commonly spherulitic and, in particular systems, twisted as, indeed, also is that of shorter linear molecules or oligomers. There is no real dichotomy in crystallization between the two notwithstanding their different mechanical properties with polymeric toughness related to the presence of interlamellar tie molecules and entanglements which affect quiescent crystallization little. There is continuity in crystallization behaviour reflecting the influence of increasing molecular length rather than a discontinuity possibly related to the onset of chainfolding. Chainfolding enables lamellar crystallization for sufficiently long molecules but necessarily brings with it transient ciliation of partly attached molecules, a major cause of spherulitic growth. The nature of lamellar surfaces depends upon the growth rate and strongly affects higher order morphology, especially on reorganization.

The purpose of this note is to provide a concise summary of this essential physics, with key sources, which has emerged from studies of monodisperse alkanes and polyethylene using linear nucleation. Stressed in particular is the crystallization-rate-dependent nature of fold surfaces and the continuity with oligomers pointing out also that chainfolding does not make polymers essentially different but is an enabling mechanism for their lamellar crystallization.

2. Discussion

2.1. Monodisperse n-alkanes

Macromolecular crystallization has been much clarified by studies of the monodisperse *n*-alkanes, model systems for polyethylene. Being well known to give quantized lamellar thicknesses [2] their crystallization may appear to be governed by the placement of the methyl end groups but not so. The situation is dynamic with the ordering of end groups or folds depending on how fast stems crystallize [3]. When the basal surfaces of lamellae, with or without folds, are poorly defined they are a second contributor to the lamellar divergence underlying spherulitic growth.

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First, with these materials the link between chainfolding and lamellar divergence is shown very clearly. Thus when n-$C_{294}H_{590}$ crystallizes with molecules either fully extended or once-folded at the same temperature and minimum radial growth rate, $\sim$0 002 μm sec^{-1}, lamellae of the former grow in parallel stacks while those of the latter diverge and form spherulites because of transient ciliation [4]. This occurs when molecules fold and are partly attached to the lamella. The unattached portions will occupy space adjacent to the fold surface and repel an adjacent lamella with a rubbery modulus. Chainfolding is thus confirmed to be intrinsically linked to spherulitic growth and transient ciliation a major cause.

The contribution of disordered initial surfaces to lamellar divergence and spherulitic growth is shown clearly in studies of the crystallization of monodisperse n-alkanes with molecules fully extended. With increasing supercooling and radial growth rates $\sim$1 μm sec^{-1}, the morphology changes from divergent groups of parallel lamellae towards more diverging and spherulitic textures [5]. Plots of the divergence of dominant lamellae against supercooling are linear with a finite intercept of $\sim 8°$. Transient cilia, i.e. the unattached portions of a molecule, will here be the excess of its length over the thickness of the secondary nucleus and zero at zero supercooling. The intercept, therefore, registers a second contribution to divergence, shown to be due to surface disorder or roughness, which prevents lamellae from packing parallel, by studies of dilute binary blends and their permanent ciliation.

Permanent cilia are present in co-crystallizing dilute binary blends of monodisperse n-alkanes e.g. 5% n-$C_{194}H_{390}$ in n-$C_{162}H_{326}$. This host crystallizes fully extended so that the composite lamella will possess permanent cilia of maximum length, at one surface, equal to the excess of that of the guest molecule over that of the host. The length of the permanent cilia can be controlled by changing the guest molecule e.g. replacing n-$C_{194}H_{390}$ with n-$C_{246}H_{494}$ and their number by increasing the guest concentration [6]. They can also be reduced to zero when the guest molecule is effectively twice the length of the host and crystallizes once-folded in the extended host as for n-$C_{246}H_{494}$ in n-$C_{122}H_{246}$ [7].

The effects of permanent cilia are supplementary to those of the inferred transient cilia and are revealed in plots of angular divergence (of dominant lamellae) against supercooling. These remain linear when permanent cilia are present but the intercepts increase from the $\sim 8°$ of pure n-alkanes and the slopes of the plots decrease [8]. The extra intercept, i.e. additional splaying, is proportional to the number of permanent cilia and increases with their length but disappears with the permanent cilia and change of slope for the n-$C_{246}H_{494}$ in n-$C_{122}H_{246}$ system when the guest molecules crystallize once-folded in lamellae of fully extended host molecules [7]. This is to be expected because permanent cilia necessarily affect surface condition and, with their presence adding proportionately to the intercept, the intercept is confirmed to be a measure of surface condition.

Regarding the decreasing slopes of the plots, the fall is more for longer pure n-alkanes which have thicker and, therefore, stiffer lamellae [5]. The reduction for binary blends is greater for higher guest concentrations, consistent with a dilution of the transient cilia by the ever-present permanent cilia [8].

SAXS studies of these same monodisperse alkanes, both during and after crystallization, provide complementary evidence, reinforcing these conclusions. On the one hand, when there is folding, quantized ordering occurs at a late stage after lamellae pass through a non-integrally-folded (NIF) stage [3]; crystallization of stems is the primary process. On the other hand, a disordered lamellar interface is present in lamellae with molecules fully extended, revealed as a density deficit, which persists in part even after return to ambient temperature [9]. This pattern of behaviour mirrors rather than contrasts with that found in polymeric crystallization.

2.2. Polymers

Chainfolding enables linear polymers to crystallize in lamellae but two kinds of fold surfaces form depending upon the growth rate. For solution-grown polyethylene lamellae faster growth gives {314} facets; slower growth gives {312} surfaces [10]. Melt-grown polyethylene lamellae have {201} fold surfaces for slower growth (Regime I) but S-profiles when grown quickly in Regime II [11]. This dichotomy reflects a fundamental distinction in the nature of fold surfaces linked to growth rate with consequences for spherulitic and twisted growth.

While transient ciliation occurs whenever chains fold, surface roughness disappears for slower growth. This is the reason for the greater branching and finer textures of polyethylene in Regime II compared to Regime I [12]. In addition, the roughness present for faster growth makes the fold surfaces unstable and polyethylene lamellae liable to twist.

This is shown clearly when the development of polyethylene lamellae during melt growth, from nucleation onwards, is examined down **b**, the growth direction. For slower growth (in Regime I) fold surfaces form and remain {201} whereas for faster growth (Regime II) they initially have rough {001} surfaces which subsequently transform, adopting S-profiles with isothermal thickening and twisted growth [13]. The initial {001} fold surfaces must be stressed because folds are then too close making the surface free energy higher than for {201} and rough to widen contacts where possible, i.e. with a degree of statistical staggering, the more so the faster the growth. Reducing this surface stress by moving towards {201} surfaces with uniform stagger generates S-profiles and twisting as observed in both single lamellae and row structures.

There is a simple explanation of why twisting is confined to faster growth (Regime II) in polyethylene – because in Regime I surfaces are not stressed and twisting would increase, not lower, the free energy. Confirmatory evidence of the link between surface stress and twisting comes from linear-low-density polyethylene where growth in Regime I starts untwisted, with {201} fold surfaces, then starts to twist when isothermal thickening draws excluded branches into surface regions and stresses them [14]. It is also clear that the propensity for twisting in e.g. polyethylene and poly(vinylidene fluoride) relates to their tightly packed lattices whose small cross-section per stem makes it advantageous to increase the basal surface area and the distance between folds by inclining fold surface normals to the chain axis.

The formation of banded spherulites by *n*-$C_{294}H_{590}$ quenched in the once-folded form [4] shows that, in this condition, its basal surfaces are stressed, similarly to polyethylene.

The distinction between slower and faster growth, Regimes I and II for polyethylene, is because in Regime I there is time for fold surfaces to order as molecules attach to the growth interface and adopt their preferred {201} surfaces. In Regime II, by contrast, fold surfaces have insufficient time to order before the next molecular layer is added to the lamella confining them to the interior; the faster the growth rate, the greater the surface disorder. For a given polyethylene the growth rate at which the initial fold surface changes is more or less constant whether crystallized alone or in dilute blends with highly branched polyethylene [15]. When this growth rate is converted into the time to add a 0.5 nm thick molecular strip to the lamella these times are ~50 msec for linear polyethylene of $\sim 10^5$ mass, increasing with molecular length and, for linear-low-density polyethylene, with branch content [15].

2.3. Crystallization and molecular length

Morphological study of polymers and *n*-alkanes has now given a simple basis on which the principal features of crystallization of both can be explained and, generalizing from the archetypal flexible linear chain, the features brought to crystallization by molecular length made clear.

Central is the changing nature of the basal or fold surfaces with growth rate and during crystallization. This is not only a consequence of thermodynamics but has also been demonstrated by SAXS [3].

Crystallization of fold or molecular stems reduces free energy in proportion to their length while surfaces add to it but the latter finite contribution can always be offset by crystallizing long enough stems. The system will crystallize by the fastest means available even if this involves high energy surfaces. Thus, for fast growth, the basal surfaces of monodisperse *n*-alkanes only order after the stems have crystallized [3]. At the opposite extreme very slow growth allows surface ordering to be optimized even at the expense of distorting the lattice. This is the case for centrally branched monodisperse alkanes which form cylindrical scrolls with all excluded branches on the outer surface [16]. Once formed, however, a system will always tend to move towards lower free energy by e.g. improving surface packing (with uniform stagger) and increasing lamellar thickness. The strong longitudinal vibrations present in macromolecular lattices below the melting point facilitate both processes during crystallization from the melt.

Chainfolding enables lamellar crystallization of long molecules but also implies transient ciliation while a molecule is incompletely attached which causes adjacent dominant lamellae to diverge as required for spherulitic growth. For slower growth (Regime I for polyethylene) there will be little or no additional contribution from surface packing as time will have allowed more or less smooth, uniformly staggered, surfaces to form. But when there is insufficient time for fold packing to order before the next molecular layer is added, basal surfaces will be disordered and/or rough, the more so the faster they grow. This leads on one hand to additional lamellar divergence with finer spherulitic textures and on the other to twisted growth partly to relieve the high as-grown surface stress.

There is, however, no requirement that chains should fold other than the relative magnitudes of the free energy of fusion per unit volume and the surface free energy which govern the thermodynamics and thence the growth kinetics. When the former quantity is low as in PTFE and the disordered hexagonal phase of polyethylene, then folding is reduced as thicker lamellae are required to offset the cost of the surfaces.

2.4. Spherulitic growth

Spherulitic growth, typical of melt-crystallized polymers and found in monodisperse *n*-alkanes with folding and, at higher supercoolings also for extended chains, is here a consequence of molecular length. Polymer morphology shows that spherulites develop because dominant lamellae diverge from branch points in a regular way to form the underlying framework which is filled in by later-forming subsidiary lamellae. Lamellae remain planar away from a branch point thereby indicating the presence of a short-range or mesoscopic repulsive force operating over distances no greater than molecular lengths. The responsibility of transient ciliation, i.e. of the unattached portions of partly crystallized molecules, has now been confirmed in detail.

This is true also for the monodisperse *n*-alkanes with and without folding. In the latter case the divergence of dominant lamellae increases with the excess of molecular length over that of the secondary nucleus, i.e. of transient ciliation in this context. It is supplemented by the effect of initial surface roughness (constant for a given system) which gives dominant lamellae an extrapolated finite divergence at zero supercooling. For low supercoolings later-forming lamellae grow in parallel blocks which give way to increasingly diverging morphologies as supercooling and the length of transient cilia increase. In polymers and *n*-alkanes, therefore, molecular length causes spherulitic growth.

Non-polymeric spherulites are neither so well documented as in polymers nor so well characterized morphologically. The systems concerned are usually complex, sometimes incorporating polymers, organic or inorganic such as silicates and difficult to examine at sufficiently high resolution but do show similar embryonic and sheaving geometries to polymeric spherulites. The general responsibility of a mesoscopic repulsion or pressure differential is, therefore, highly probable from the geometry but its precise nature remains to be positively identified in each case. An unidentified pressure differential, for example, has been suggested as responsible for filamentary divergence in ice spherulites growing from water/glycerol [17]. In polymers themselves the responsibility for the differential pressure has been confirmed in much detail to be transient ciliation. While it used to be thought that the occurrence of non-polymeric spherulites required a general explanation for spherulitic growth, independent of a given material, this can no longer be maintained in the face of the very considerable detailed evidence for polymers and the monodisperse *n*-alkanes.

3. Conclusions

There is a continuity, not a dichotomy, in crystallization behaviour from *n*-alkanes to polyethylene which demonstrates that the essential features brought to crystallization by molecular length are as follows.

1. Lamellar growth transverse to molecular chains. For sufficiently long molecules this requires chainfolding but in systems with a low heat of fusion per unit volume such as PTFE and the disordered hexagonal phase of polyethylene the fold period is correspondingly large.

Chainfolding of linear molecules implies transient ciliation adjacent to the growth front which causes lamellae to diverge from branch points and spherulitic growth.

Transient ciliation, of the excess of molecular length over that of the secondary nucleus, causes lamellar divergence and spherulitic growth when *n*-alkanes crystallize with fully extended molecules.

2. The growth rate-dependent nature of the initial basal surfaces. Rough or poorly defined surfaces form for faster growth in both polyethylene and *n*-alkanes when there is insufficient time to achieve optimum packing for all molecular lengths. Such surfaces contribute to lamellar divergence and spherulitic growth by not packing parallel.

The partial relief of associated surface stress, in tightly packed lattices, is liable to drive twisted growth. This is one aspect of their inherent metastability, increasing for faster growth, which renders them prone to reorganization to more ordered packing and to increasing lamellar thickness.

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