Crystalline Polymers in Real Space

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SUMMARY: Recent work has resolved uncertainties as to how polymers develop their melt-crystallized textures and brought a unified context to the subject. Spherulites form because of the long molecular length not because of its polydispersity. When a molecule is only partly attached to a growing lamella the unattached portions will occupy adjacent space and exert a short-range repulsive pressure on any neighbouring lamella at a branch point. This is confirmed by monodisperse long n-alkanes forming spherulites only with chainfolded lamellae not when crystallizing as extended chains. An additional textural element, cellulation, is superposed on regular spherulitic growth beyond a certain radius (in linear-low-density polyethylenes) when there is sufficient fractional crystallization of segregated species which lower the local equilibrium melting temperature and thence the isothermal supercooling and growth rate, the last declining continuously to an asymptotic limit. First results show that both the radius to cellulation and the cell width are effectively independent of growth velocity; neither scales with the diffusion length. A possible explanation is proposed for this novel situation which has no precedent in either polymeric or non-polymeric systems.

Introduction

The length of polymer molecules imposes a mesoscale texture on their crystalline solids which results in the macroscopic mechanical and other important properties differing, usually substantially, from those of the molecules themselves. Knowledge and control of what is a complex internal organization are thus vital to polymer science. As any complex pattern is best appreciated if presented as an image to the eye-brain combination, new microscopies are always of primary interest for their potential use in establishing textural models which other means, such as diffraction techniques, can better quantify. Among current new tools AFM (atomic force microscopy) has proved useful particularly in height measurement but in terms of lateral resolution the transmission electron microscope generally continues to provide the most valuable detailed information. It was not, however, until the problems of radiation damage could be circumvented that the palimpsest which is polymer morphology could first be read routinely to lamellar resolution in melt-crystallized polymers and then the messages it

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contains interpreted. This has not been a straightforward progression but advances have been achieved not merely by examining samples as received but especially by careful choice of system, including special materials, and studying their response to further treatment. Over the last three years uncertainties over how texture is established in polymers crystallizing from a quiescent melt have thereby been resolved and a unified context provided.

The relationship between molecular length, physical microstructure and macroscopic properties is central to polymer science because while the characteristic properties of (thermoplastic) polymers stem ultimately from their inherently long constituent molecules, the macroscopic property depends mostly upon processing conditions i.e. upon the internal molecular organization. As polyethylene is both chemically the simplest synthetic polymer and also economically the most important, scientific and technological interests coincide in their concern with the effect of molecular length on internal organization and thence properties. In polyethylene, as with other crystalline polymers, this is reflected in two basic aspects of self-organization which differ from their low molecular mass or oligomeric counterparts. The first is that polymer crystals are generally not only much thinner than the extended molecular length but also that the chain axis is parallel, or approximately so, to the lamellar normal which, as is well known, brings molecular chainfolding for kinetic reasons. The second is the cause of spherulitic growth which makes texture vary systematically, generally on a sub-micron scale, from point to point within the solid and is a major determinant of properties.

Spherulitic growth is ubiquitous when polymers crystallize from quiescent melts leading to characteristic extinction patterns in the polarizing optical microscope indicative of equivalent radii in mature objects. Tantalizingly the internal microstructure is not fully resolved optically but requires the transmission electron microscope to reveal how chainfolded lamellae are arranged within the larger scale texture. Systematic electron microscopic examination of many systems has shown that polymeric spherulites are constructed on a framework of first-forming or dominant lamellae which diverge at branch points and to which later-forming subsidiary or infilling lamellae must conform. There is divergence even within one crystal for the successive layers of a spiral terrace formed around a giant screw dislocation. Iteration of this divergence at spatially distributed branch points will eventually lead to the eponymous spherical envelope containing equivalent radii. The work of the last three years has not only confirmed our long-standing proposal for the cause of lamellar divergence but also demonstrated morphological instability and cellulation for the first time in an undoped polymer. The outcome is to bring the two mechanisms, each once proposed as the basic cause of spherulitic growth, into a unified context and also to reveal new and unexpected physics of cellulation.

Materials and Experimental

Spherulitic microstructures have been observed in a wide range of polyolefines and other polymers, the former after etching with permanganic reagents, to reveal lamellar textures prior to electron microscopy. All have been constructed upon the same geometrical principles. The illustrations in this paper are of linear-low-density polyethylenes and also monodisperse n-$C_{294}H_{590}$ synthesized by Dr G.M. Brooke and colleagues, under the auspices of EPSRC, at the University of Durham. All these specimens are viewed after permanganic etching. The optical micrographs were recorded with Nomarski differential interference contrast; the electron micrographs are of metal-shadowed two-stage carbon replicas of etched surfaces.

Results and Discussion

Ciliation and Spherulitic Growth

On crystallization in quiescent systems linear polymeric molecules arrange themselves into chainfolded lamellae and these into spherulites which, when mature, grow with all radii equivalent in space. Normally spherulites are constructed on a framework of individual dominant lamellae which diverge at finite angles, typically ~20°, at branch points such as giant screw dislocations so as to maintain a uniform spatial density1). This geometry in all its different aspects is well displayed in Figure 1. Note the lamellar continuity from centre to edge; that new layers are introduced at giant screw dislocations (whose cores have been etched away) and that the (still immature) spherulite is growing into the melt by the advance of individual diverging dominant lamellae at the growth envelope.

The phenomenon creating the spherulitic habit is the iterative divergence of adjacent dominant lamellae. Its cause is indicated by the geometry, in which lamellae show linear traces from shortly beyond their branch point points and successive lamellae diverge at the same angle, to be a short-range repulsive force operating between adjacent lamellae over distances less than

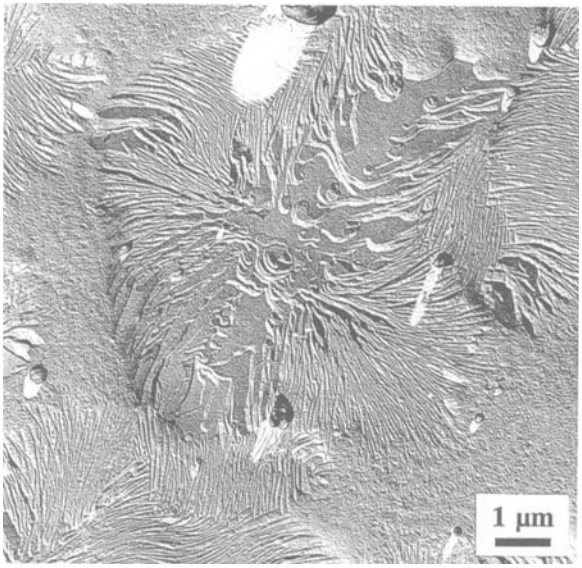

Fig. 1: An embryonic spherulite of linear-low-density polyethylene grown at 124 °C then quenched. Note the separated dominant lamellae, continuity from centre to edge, lamellar widths and branching around giant screw dislocations.

typical molecular lengths. Measurements show that it is related to molecular length and crystallization temperature. As to its origin, the proposal1) first made some fifteen years ago is based upon the following considerations. Until a molecule is able to add completely to a layer, substantial portions (which we term dynamic cilia) will lie outside and adjacent to the fold surfaces. There they will be unable to diffuse away but will occupy space and exert a repulsive pressure, with a weak rubbery modulus, on any competitor for that space. In consequence, adjacent lamellae tend to be forced apart during growth and, given a distribution of branch points in space, iteration will produce the spherical envelope around equivalent radii which constitutes a mature spherulite. One could also readily generalize this mechanism of formation to non-polymeric spherulites if, as is reported for ice2), they form in response to pressure between adjacent crystal arms but very likely the origin of the pressure would vary from case to case.

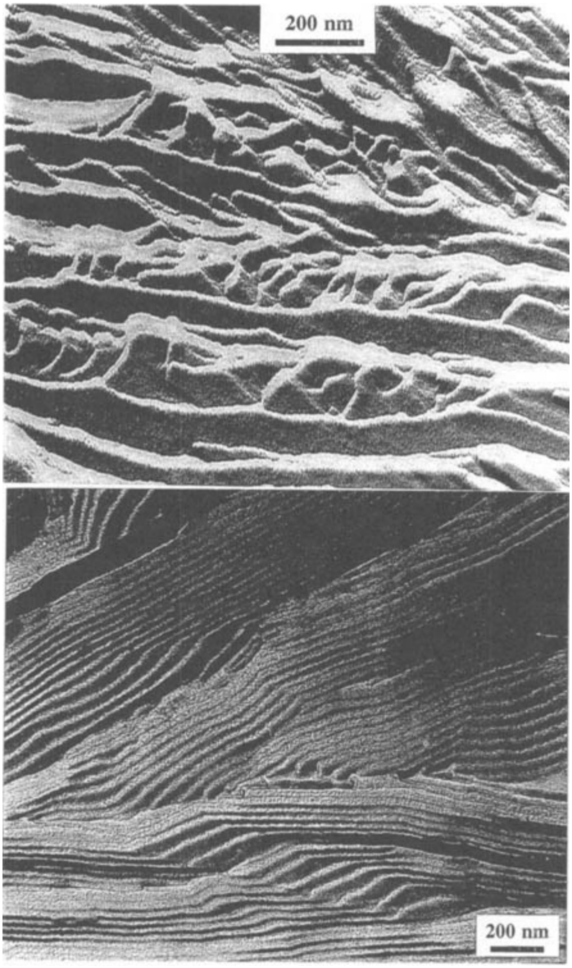

Fig. 2: Comparative microstructures of n-$C_{294}H_{590}$ crystallized from the melt. In the once-folded form (above) the pattern of diverging dominant and infilling subsidiary lamellae is similar to that characteristic of polymer spherulites. In the extended form (below) lamellae are in close contact and have not diverged.

The possibility of making a critical test of this proposal came with the availability of the monodisperse n-alkanes$^{3)}$. These oligomers of polyethylene tend to crystallize from the melt with quantized thicknesses with the molecules either fully extended or once-folded. In the former case they would be expected, on the assumption that stems add to a lamella as discrete units, to have no pendant cilia emerging from the basal surfaces while for the latter, half the molecule will remain in the melt when only the first segment is attached to the crystal. The corresponding prediction is that lamellar divergence and spherulitic growth should be absent for extended chain growth but present for chainfolded growth of the same material. To a first approximation, this is what has been found[4)] for n-$C_{294}H_{590}$. Figure 2 illustrates the difference between the two cases. The microstructure of chainfolded growth (above) is that characteristic of polymer spherulites, composed of wide dominant lamellae whose divergence has allowed subsidiary lamellae to grow in the intervening spaces. By contrast, lamellae of the extended form (below) remain in close contact even when extra layers, associated with a screw dislocation, are inserted. To a second approximation, as growth temperature falls extended chain growth moves towards weakly spherulitic textures, in which lamellar stacks diverge to give a coarse Maltese extinction cross but one which is readily distinguishable from the fine one of typical spherulites. Current research is investigating whether modest ciliation, due to the excess of molecular length over that of the secondary nucleus, is sufficient to account for this modification of the basic pattern of behaviour.

Cellulation

In the early examination of polymer spherulites the problems of radiation damage still limited the application of transmission electron microscopy and systematic morphological examination was confined to optical microscopy. To render what were rather compact textures more amenable for study it was often the practice to add a diluent to open up the morphology. Crystallization of such systems as e.g. isotactic polypropylene with 90% atactic polymer added, produced discrete 'fibres' evidently composed of many chainfolded lamellae, growing radially outwards. Armed with such observations Keith & Padden proposed[5)] that the essential cause of spherulitic growth was cellulation which formed 'fibres' of multiple lamellae as a consequence of fractional crystallization and associated segregation at the growth face. In fact the extrapolation from doped to undoped homopolymers is invalid and cellulation does not occur in these systems. Nevertheless, the first unambiguous observations of cellulation in an undoped copolymer have recently been made in linear-low-density polyethylenes showing that it is a rare phenomenon superposed on regular spherulitic growth in conditions of high segregation[6,7)]. It does not normally occur because there are insufficient concentrations of appropriate segregants present to slow the growth rate and create the necessary conditions.

Cellulation is a response to fractional crystallization and accumulation of rejected species at the growth interface. In the Keith-Padden model5) it was considered that the accumulation of segregants at the interface would slow growth temporarily, making the interface unstable against fibrillation on approximately the lateral scale of the diffusion field, then the rate would be restored as fibres broke through the impurity layer and grew in steady state. In practice, as is detailed below, the growth rate is found to slow continuously towards an asymptotic limit and the characteristic dimensions of cellulation are effectively independent of growth rate so that there is no scaling with the diffusion length7).

To investigate the effects of segregation at the growth interface it is useful to study the growth not just of spherulites but also of rows grown from linear nuclei. The latter have the considerable advantages of being parallel arrays of close-packed lamellae ahead of which segregants can only accumulate and well-defined geometry making for easier examination. The more open structure of diverging dominant lamellae in spherulites, by contrast, allows segregants to diffuse between them so lowering their concentration at the growth front. Provided segregation is effective conditions for cellulation should, therefore, occur first for rows ahead of spherulites in the same sample as has been found to be the case. By effective segregation we mean the ability to slow the growth rate. That this is not always the case and that segregation can be ineffective follows from the observation that in e.g. α polypropylene, both rows and spherulites have the same isothermal growth rate despite their different interfacial conditions. In such circumstances segregation is not affecting the growth rate and is ineffective8).

Effective segregation does occur with linear-low-density polyethylenes because too short inter-branch sequences are unable to crystallize, rejected from the crystal and lower the local equilibrium melting point of the region where they accumulate: isothermal supercoolings are lowered and growth rates slowed, increasingly so as growth proceeds. These effects were found first, both for spherulites and rows9), in a copolymer with 21 butyl branches per 1,000 C atoms, but the former, with their more open texture, always grew the faster. Rows alone, with their higher concentrations of segregants, became morphologically unstable and developed corrugated interfaces. The precise details differ according to the method of catalysis which offers a potentially informative means of investigating differences between various linear-low-density polyethylenes. So far Ziegler-Natta materials alone have nucleated faster growing, essentially spherulitic, protuberances⁹⁾. These have not been found for metallocene polyethylenes which moved smoothly to the final, eventually steady-state¹⁰⁾, condition.

A survey of several different linear-low-density polyethylenes¹¹⁾ then showed that for a metallocene polymer with 28 ethyl branches per 1,000 C atoms, cellulation also occurred in spherulites. So far as we are aware this is the first time cellulation has been unambiguously observed in an undoped polymer. Figure 3 shows that, beyond a certain distance, cellulation is superposed on regular spherulitic growth⁶⁾, identifying it as an additional phenomenon occurring under conditions of exceptional segregation.

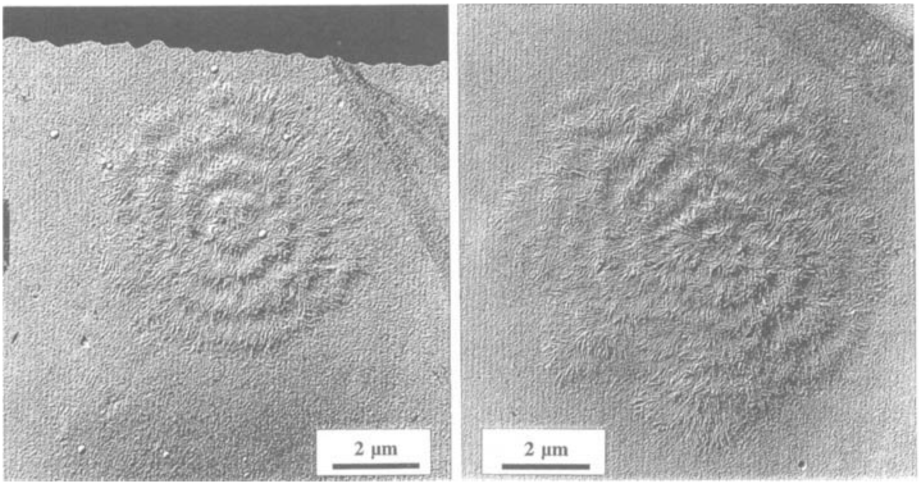

Fig. 3: Morphologies produced in a polyethylene with 28 ethyl branches per 1,000 C atoms, isothermally crystallized at 95 °C. Regular banded growth, on the left, is present after 1 h whereas, on the right, cellulation had set in after 1.5 h.

The most recent results⁷⁾ are of a survey of metallocene polyethylenes with branch contents increasing from 14 to 37 ethyl branches per 1,000 C atoms crystallized under conditions giving ~ 50% segregation. Although spherulitic morphologies of the type once envisaged⁵⁾ do occur, particularly for higher branch contents for which cellulation sets in at smaller radii, the process is different in kind from the original discussion. This follows from the kinetics, Figure 4, which show growth rates decreasing asymptotically towards a steady state, not being restored to the initial value after cellulation. The physics is correspondingly

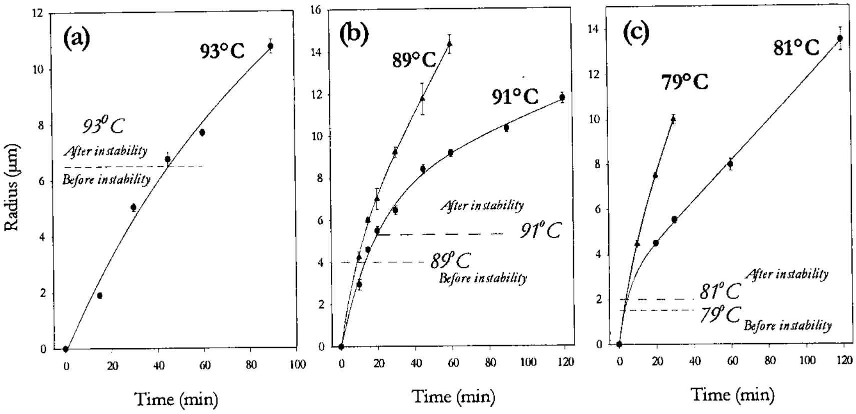

Fig. 4 a, b and c) the radii of spherulites of polymers E, F and G with, respectively, 25, 30 and 37 ethyl branches per 1,000 C atoms, as functions of crystallization time at the temperatures shown;
The observed radius at the onset of cellulation is marked on all figures.

different with the characteristic dimensions of cellulation, namely the radius to its onset and the cell width, both effectively independent of growth rate for the same polymer but decreasing for higher branch content. It follows that there is no scaling with the diffusion length δ = Diffusion coefficient/Growth rate. What appears to be happening, consistent with direct observation of the way a growth front advances, is that segregation slows the growth rate and that once a particular 'fibre' has slowed it becomes liable to be overtaken from the rear by others which are less affected. Cellulation starts when almost the same total quantity of polymer has segregated irrespective of growth rate. Fluctuations in the local segregant concentration then produce greater slowing along certain regions of the growth front than others. Those areas least affected continue to grow, tending to become protuberances ahead of their laggard surroundings. The width of protuberances - in which lamellae diverge away from the centre - is most likely limited by the need to maintain a sufficient component of velocity in the radial direction.

Conclusions

The two mechanisms proposed as the origin of spherulitic growth in polymers have been brought together in a unified context. Dynamic ciliation has been confirmed as the principal cause with cellulation an additional phenomenon occurring in conditions of high segregation.

The first observations of this phenomenon in undoped polymers, in both row structures and spherulites, have revealed it to have novel physics and not to scale with the diffusion length.

Acknowledgements

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