Macromolecules **1996,** *29,* 1852−1853

On Spherulitic Growth in a Monodisperse Paraffin

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Received November 16, 1995

Monodisperse long chain paraffins[1,2] offer, for the first time, an opportunity to test a number of fundamental issues associated with the development of spherulites in general and the crystallization of polymers in particular. Their monodisperse nature means that they are completely free of any molecular fraction that could be termed an impurity. Also, since it has been shown that, when crystallized from solution, their lamellar thickness is quantized,[3] the influence of molecular conformations on larger scale morphologies can be investigated. It was with such ideas in mind that we have recently begun a preliminary investigation of melt crystallization of the paraffin $C_{294}H_{590}$ (kindly supplied by Dr. G. M. Brooke, University of Durham, under the auspices of the Engineering and Physical Sciences Research Council of the U.K.), a material that is a monodisperse model for low molar mass polyethylene. In view of long-standing theories concerning the role of impurities in spherulite growth,[4−6] it was by no means obvious, *a priori*, whether spherulites would form in a pure system, nor in one with comparatively short chains. In fact they do but, as will be demonstrated, only when the molecules within the crystals adopt a folded conformation. Then, the resulting morphologies are very similar to the range of spherulitic textures found in polyethylene. When the lamellae contain molecules that are fully extended, the resulting textures are, however, quite different. Under these circumstances, aggregates of crystals develop which have a much coarser overall appearance and in which there is little or no divergence between adjacent lamellae.

Figure 1 shows spherulites of this paraffin viewed between crossed polars in the optical microscope. These may be banded when grown by quenching or normal when crystallization occurs at higher temperatures. The organization of lamellar crystals within such structures has been investigated with the transmission electron microscope, by preparing replicas of film specimens after etching with a permanganic reagent.[7] Figure 2 illustrates the clear difference in organization between chain-folded, spherulitic textures and the extended-chain morphologies that form at higher temperatures. The lamellar texture shown in Figure 2a can be seen to possess the same features recognized as characteristic of polyethylene and other polymeric spherulites.[8] These include the separation and divergence of adjacent individual dominant lamellae, the associated distinction between dominant and subsidiary lamellae, together with branching at giant screw dislocations. Lamellae in this micrograph contain once-folded molecules, as is shown by their thickness and melting point. Conversely, as shown in Figure 2b, chain-extended lamellae are, for the most part, contiguous and do not diverge substantially when additional layers are introduced at screw dislocations.

Samples crystallized in the extended form (at 127 °C) are, however, not devoid of larger scale organization. The early stages of growth are typified by large single crystals, 50 μm or more in length, with curved lateral surfaces and often axially-ridged basal surfaces. These strongly resemble polyethylene lamellae similarly grown at low supercoolings.[9,10] Because of the constraints imposed by crystallization within a thin film, individual lamellae, together with twinned and other multiply-nucleated aggregates, tend to develop parallel to the plane of the specimen. When crystals can be viewed sideways-on, packets of parallel lamellae may be seen diverging, but generally at large angles (see Figure 3). Large deviations differ from the lamellar splay that is so characteristic of spherulitic growth in polymers and are most likely associated with crystallographic processes, such as are known to occur in short-chain paraffins.[11] Possibilities include growth from alternate facets of the ridged basal surfaces or the formation of some other angled twins. In any event, the overall impression is of a very coarse axialitic habit where successive layers are generally parallel with no evidence of the highly localized lamellar divergence associated with the growth of typical spherulites. In summary, the overall pattern of crystallization described above mirrors the quantization of lamellar thickness, and thereby strongly reflects the influence of cilia.

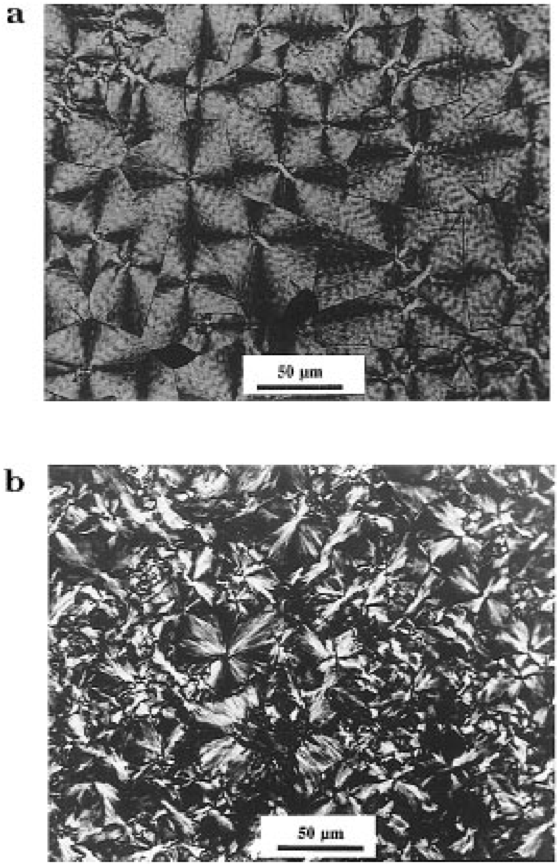

Figure 1. Spherulites in monodisperse $C_{294}H_{590}$ seen optically between crossed polars: (a) banded growth after quenching; (b) the once-folded form grown at 118 °C.

Our findings, therefore, have major implications for the understanding of spherulitic growth, at least in polymers. The system studied is pure, so that neither segregation of “impurities” nor diffusion of molecules to the growing interface can provide an explanation of the observed differences in development. Only the interfaces between the melt and the lamellar crystals’ surfaces remain as possible factors.

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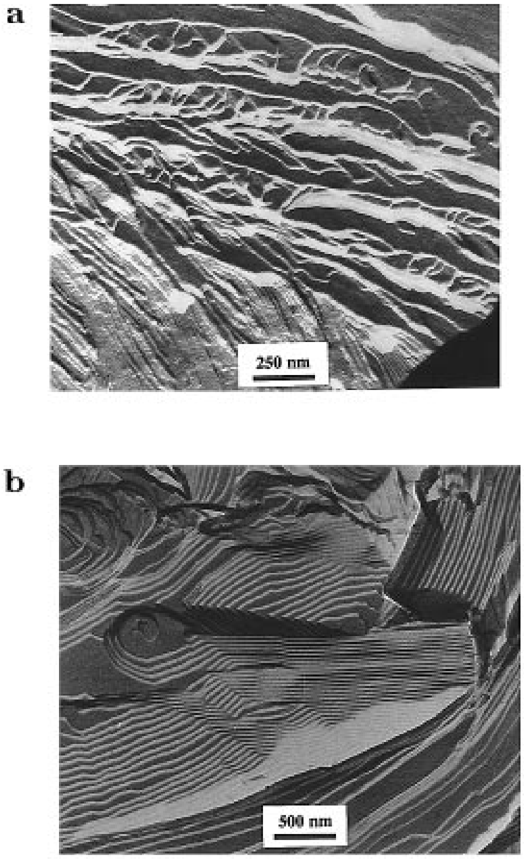

Figure 2. Detail of lamellar structures. The texture of the once-folded form (a) is based on individual dominant lamellae with intervening subsidiaries in contrast to the contiguous parallel lamellae in the extended form (b).

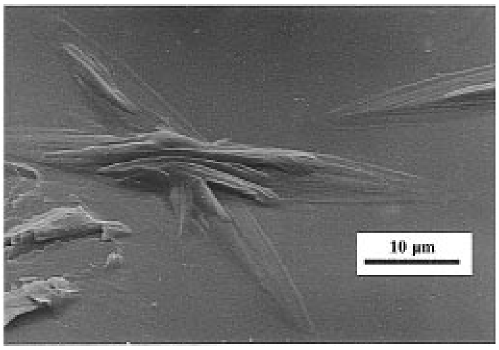

Figure 3. Multilayer crystal of the extended form grown at 127 °C. Note the curved lateral growth faces, the twinned habit, and in the center, the divergence at both small and large angles, of packets of lamellae seen approximately sidways-on.

In this respect, the basal surfaces must be the important ones to consider because the condition of the lateral surfaces would not directly affect lamellar divergence at any given branch point, provided crystallographic continuity is maintained. Differences in surface roughness, such as might result if different kinetic growth regimes[12] were to apply to extended and chain-folded lamellae, might however influence the overall rate of lamellar divergence with radial distance in a spherulite if, for example, more branch points were generated by rougher lateral surfaces.

As for the basal or fold surfaces, in our earlier studies of spherulitic growth in polymers attention has been drawn to the likely responsibility of molecular cilia emerging from them in causing the observed divergence of lamellae[9] (an idea first proposed, to our knowledge, by Frank[13]), and thus the generation of polycrystalline aggregates with a common radial orientation. These latest findings, in which the occurrence of spherulitic growth in a pure system depends critically on whether or not molecules are chain-folded, reinforce the importance of the role of cilia. For an extended chain lamella, kinetic ciliation has been predicted[14] but, at best, it would be small. Conversely, cilia will be large and finite for chain-folded growth. For example, molecules which crystallize in the prevalent once-folded form will have two stems per molecule. Prior to achieving this state they will generally pass through an intermediate condition in which a considerable portion of their length, half on a crude whole stem model of crystallization, will be outside the crystal in the form of a cilium. Ciliation, therefore, offers the basis of an explanation of the morphological phenomena described above, especially the strong divergence of adjacent lamellae. It is this, we suggest, that is the basic cause of spherulitic growth in polymers.

Acknowledgment. S.J.S. wishes to acknowledge financial support from a Royal Society Return Fellowship.

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MA951703H