ELSEVIER

S0032-3861(96)00252-2

Polymer Vol. 37 No. 22, pp. 4993–4997, 1996

0032-3861/96/$15.00 + 0.00

On chain conformations and spherulitic growth in monodisperse n-$C_{294}H_{590}$

D. C. Bassett*, R. H. Olley, S. J. Sutton and A. S. Vaughan
J.J. Thomson Physical Laboratory, University of Reading, Reading RG6 6AF, UK
(Received 7 November 1995; revised 5 January 1996)

The morphology of the melt-crystallized monodisperse long-chain paraffin n-$C_{294}H_{590}$ has been investigated by optical and electron microscopy. Spherulites form in this material, notwithstanding the absence of impurities, but only when the constituent lamellae contain chainfolded molecules, not when there is extended-chain crystallization. The optical distinction carries through to the lamellar microstructure with the observation that spherulites are constructed with a dominant/subsidiary framework. As chainfolding implies the existence of molecular cilia during growth while extended-chain crystallization does not, these conditions on the formation of spherulites provide strong support for the previously postulated central role of pressure from molecular cilia in the development of spherulitic growth. Copyright © 1996 Elsevier Science Ltd.

(Keywords: monodisperse long-chain paraffins; spherulites; melt-crystallized polymers)

INTRODUCTION

Since their first synthesis a decade ago[1,2], the precisely monodisperse paraffins have provided model systems giving valuable insights into the crystallization mechanisms of long-chain molecules[3]. Of particular interest is that these paraffins form lamellae of quantised thickness. Molecules of length L adopt stem lengths L/n, with n a positive integer ≥ 1, i.e. they are either extended or integrally folded, with end groups located on the large basal surfaces.

This dichotomy between folded and extended chain conformations has prompted us to examine the morphology of such long-chain paraffins after melt-crystallization to test a previous proposal that spherulitic crystallization in polymers results because the pressure of uncrystallized molecular cilia emerging from basal surfaces causes adjacent dominant lamellae to diverge[4–6]. Cilia should, to a first approximation, be present in monodisperse paraffins when molecules are folded but otherwise absent. It would follow that major differences in morphology should occur between the two conditions. The results strongly support this suggestion in that spherulites do form but in n-$C_{294}H_{590}$ only when there is chainfolding, not for extended-chain crystals. Moreover, that spherulites form at all in a pure system with no detectable impurity confirms unequivocally that the presence of impurities is not essential to spherulitic growth.

EXPERIMENTAL

Monodisperse n-$C_{294}H_{590}$ was kindly provided by Dr G. M. Brooke, University of Durham, under the auspices of EPSRC. This crystallizes from the melt as lamellae containing molecules which are either extended or once-folded for growth temperatures above and below 124.5°C as indicated by the growth rate data plotted in *Figure 1*. These were calculated using successive images in a polarizing microscope, recorded with either TV or optical cameras, from the maximum dimension of selected spherulites or axialites as functions of time. The assignment of once-folded or extended conformations is supported by the sequence of melting, recrystallization and final melting in the d.s.c. endotherm of a sample of the former, also shown in *Figure 1* and by thicknesses of lamellae observed in the electron microscope. In this paper we use *Figure 1* only to indicate the temperature ranges within which each form may be crystallized. We do, however, note in passing that the growth rate of the extended form does pass through a maximum with decreasing temperature in accordance with previous reports[7].

Unless stated otherwise, samples were crystallized between slide and cover slip. For isothermal conditions this was under oxygen-free nitrogen, in a Mettler hot stage, after rapid transference from an adjacent stage where they had undergone brief melting. There is no evidence to suggest that they suffered any degradation during the crystallization procedure, e.g. of inhomogeneity at the edge of the cover slip; specimens appear to have retained their integrity as supplied.

Permanganic etching was used to develop detail prior to electron microscopy. A typical treatment would be 10 min at room temperature in a mixture of 0.7% $KMnO_4$ in 2/1 H_2SO_4/H_3PO_4, followed by standard washing procedures[8]. The resulting topography was monitored by Nomarski reflection optics after which the etched surfaces were viewed either directly, after gold coating, in a scanning electron microscope or, for best

---

*To whom correspondence should be addressed

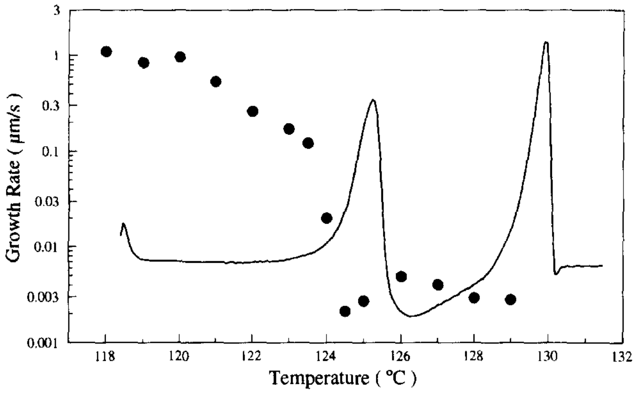
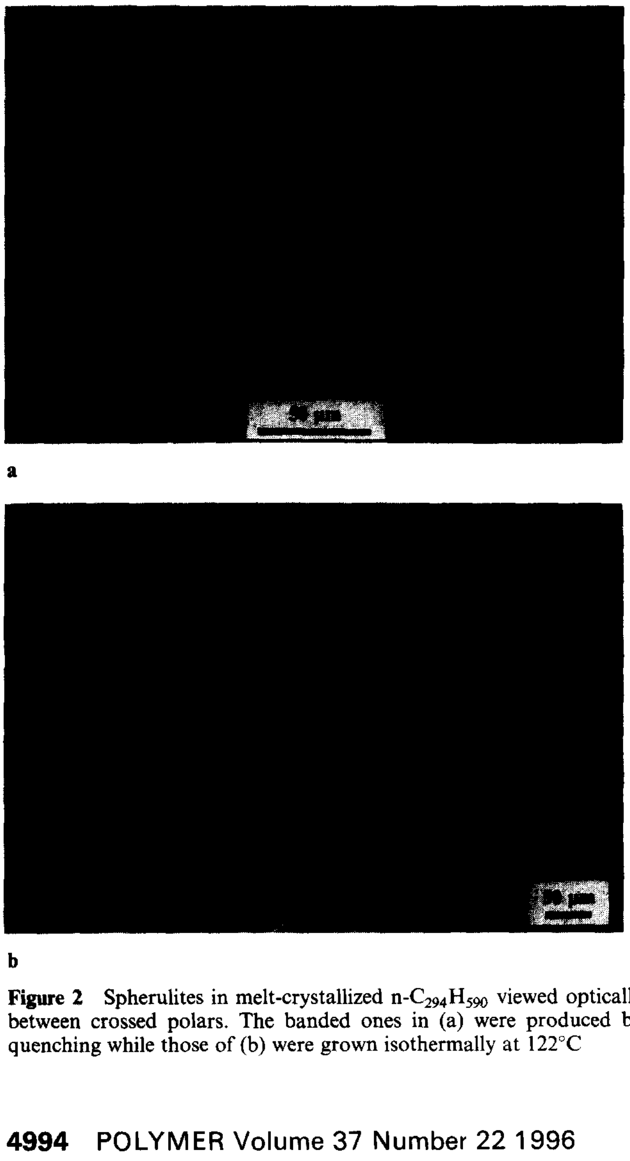


Figure 1 Growth rate data superimposed on a melting endotherm of once-folded n-$C_{294}H_{590}$

detail, after single-stage replication in the transmission electron microscope.

RESULTS

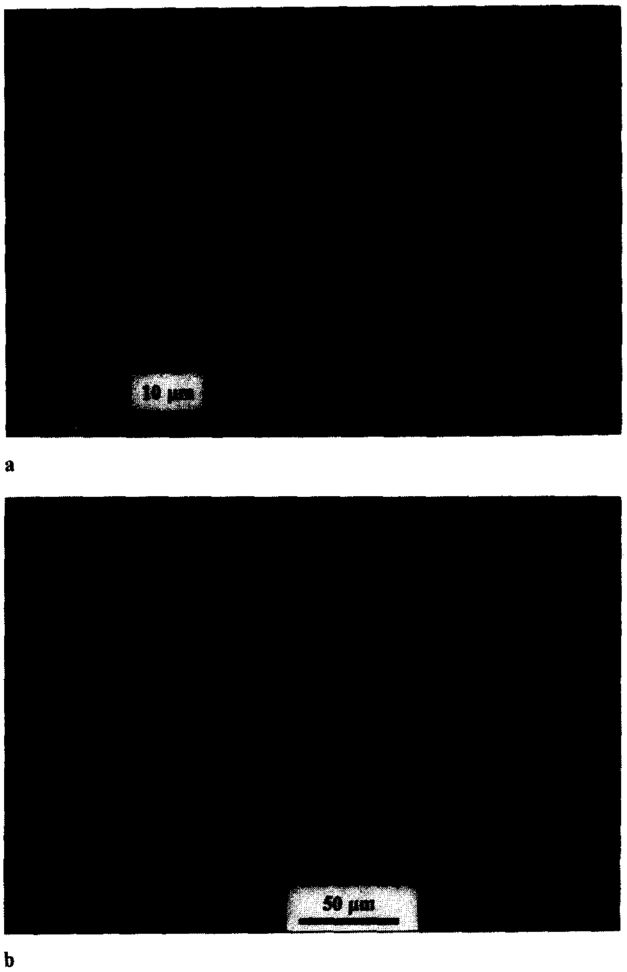
Examination with the polarizing optical microscope shows that spherulites do form in this long-chain paraffin notwithstanding the fact that it is monodisperse with no detectable impurity. *Figure 2a* shows banded spherulites formed by rapid quenching from the melt and *Figure 2b* unbanded spherulites crystallized isothermally at 122°C.



a

b

Figure 2 Spherulites in melt-crystallized n-$C_{294}H_{590}$ viewed optically between crossed polars. The banded ones in (a) were produced by quenching while those of (b) were grown isothermally at 122°C



a

b

Figure 3 (a) Extended chain crystals of n-$C_{294}H_{590}$ crystallized at 127°C from the melt (scanning electron micrograph) and (b) a multilayer extended chain crystal at 127°C within a quenched spherulitic matrix of once-folded molecules (Normarski reflection optics)

By contrast *Figure 3a* shows crystallization of the extended form firstly in unetched discrete islands produced by melting the original powdered specimen on a slide then recrystallization at 127°C. Crystals produced in this way are long with curved prism surfaces closely resembling the habit of individual polyethylene lamellae grown at high temperatures[6] and commonly twinned. *Figure 3b*, on the other hand, shows a continuous film containing both forms side by side. In this instance the background is of spherulites of the once-folded modification crystallized on quenching surrounding a multilayer extended chain crystal grown at 127°C and seen sideways on. The appearance is of a coarse axialite within which pockets of lamellae have begun to splay apart. At this stage we note only that the habits of the once-folded and extended forms are quite different at the optical level and readily identifiable by inspection. The former is undoubtedly spherulitic in contrast to the latter.

This distinction between the two morphologies carried through to their lamellar textures seen with the transmission electron microscope. Those within spherulites (of the once-folded form) have a dominant/subsidiary arrangement very similar to those found to be typical of polymeric spherulites in general[9,10], whereas extended chain crystals form stacks of contiguous lamellae. A general view of spherulitic growth within the interior of a sample crystallized at 124.5°C is shown

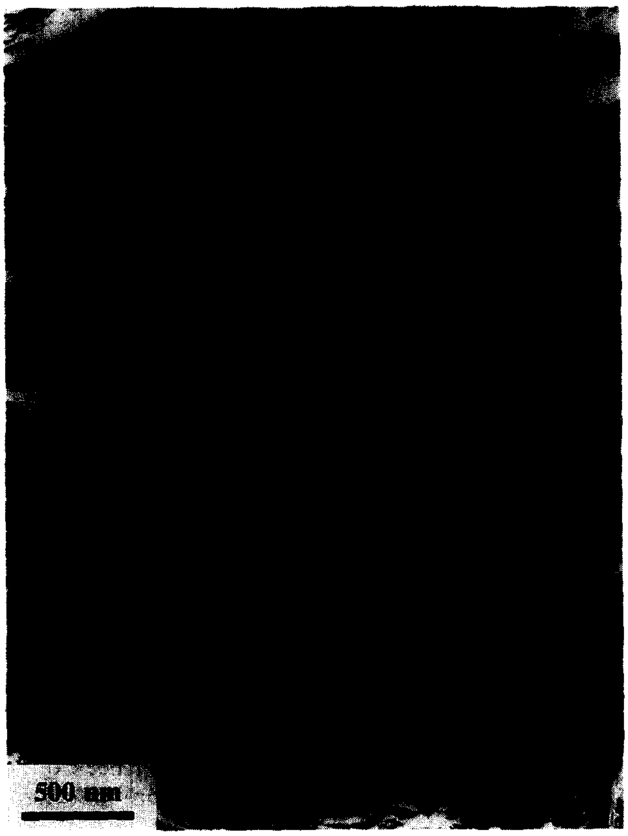


Figure 4 A general view of texture within a spherulite of n-$C_{294}H_{590}$ grown at 124.5°C

in *Figure 4*. At the top is a wide region of flat-on lamellae edged by an array of (etched out) screw dislocations. Below this is a region of diverging radii which, from the presence of faceted tips and radial crests and troughs of ridged lamellae, can be inferred to lie along the *b* axis paralleling the behaviour of polyethylene[9]. When one finds the edge of a growth front, as in *Figure 5* (where one is advancing across an underlying lamella) the parallel with polymers is again evident in that it contains individual dominant lamellae separated from one another with the intervening regions having crystallized later. The intersecting facets at the growth tip to the right of A show once more that the *b* axis in the direction of radial, i.e. fastest, growth in these long-chain paraffins as it is for polyethylene. Essentially the same dominant/subsidiary construction, but at a later stage of development, is seen especially clearly in *Figure 6* and in three different perspectives. In its central portion (A) are wide dominant lamellae between which are sandwiched many subsidiary layers with inclined traces. This geometry mirrors that of polyethylene for surfaces normal to the *b* axis which, as details of facet tips confirm, is effectively the case in this region. Extensive flat-on dominant lamellae are seen at the bottom of the photograph (B) whose normals will be inclined to *c* by ~35°. Finally, at the top of the figure (C) lamellae are being viewed more or less sideways on i.e. approximately down *a*, a direction from which the dominant/subsidiary pattern is effectively concealed.

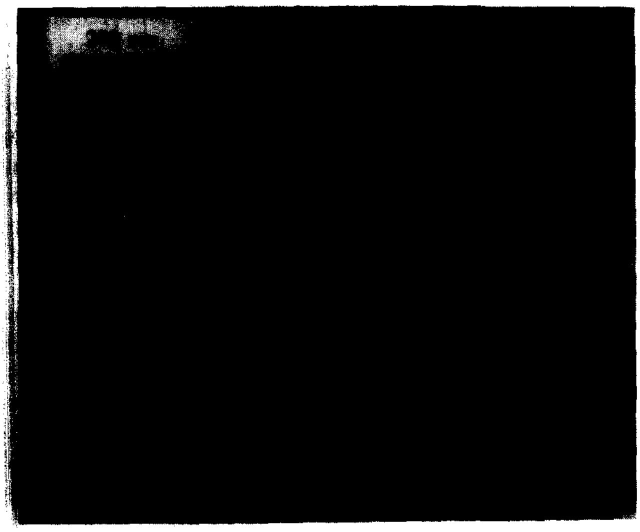


Figure 5 The edge of a growth front in n-$C_{294}H_{590}$ showing the dominant/subsidiary construction of spherulites grown at 124.5°C

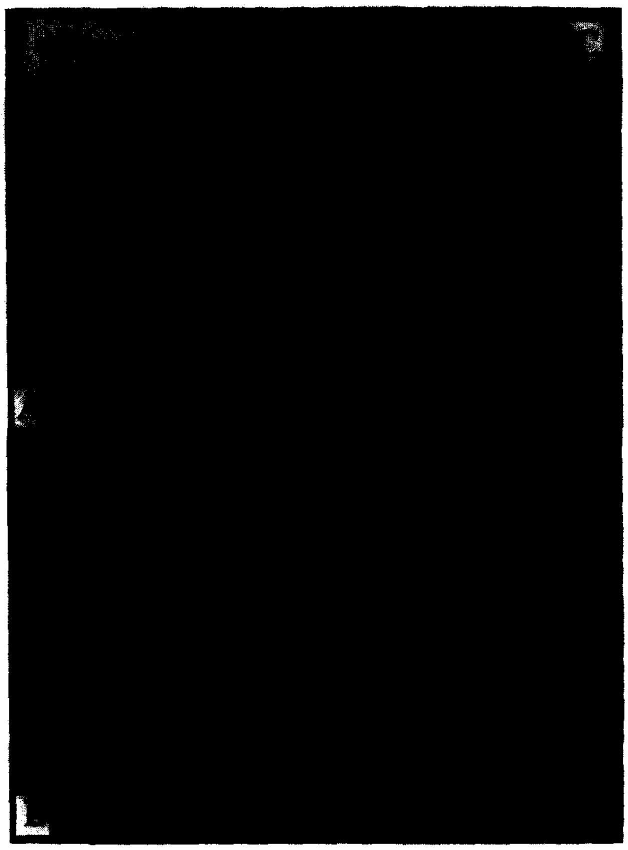


Figure 6 Dominant/subsidiary organization seen in spherulites of n-$C_{294}H_{590}$ grown at 124.5°C

The relationship between dominant and subsidiary lamellae is usually difficult to ascertain from a single etched surface but in *Figure 7* the position is clear. Here one sees a two-dimensional array of spiral terraces around giant screw dislocations, in which additional subsidiary layers are generated from the underlying dominant lamella. Each terrace is ridged along the *b* axis with one side—the lower in the photograph—parallel to the underlying basal layer but the upper side substantially inclined to it. As was also the case for *Figure 6*, this inclination of subsidiary layers to the dominants, will be visible when viewed down the *b* axis but not readily so for

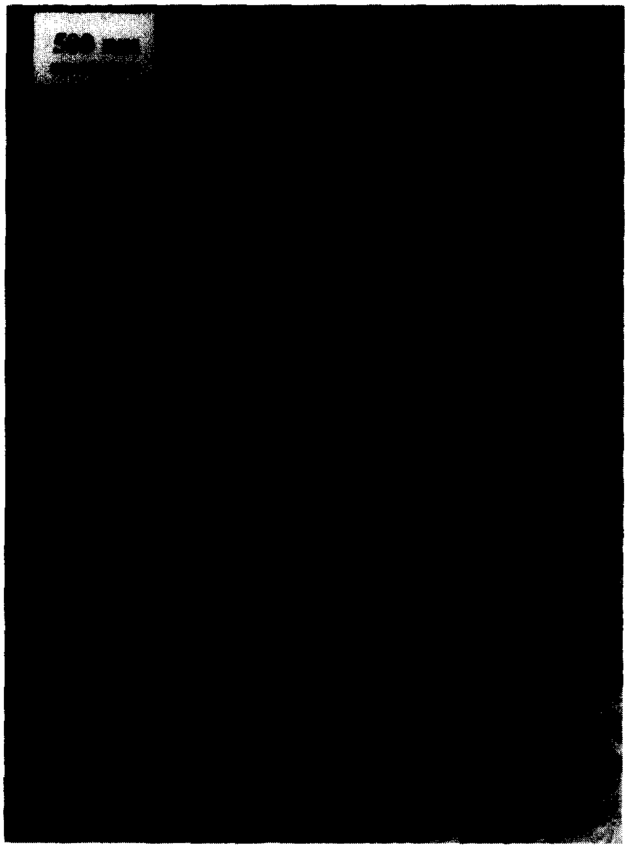


Figure 7 Isochiral spiral terraces of subsidiary lamellae associated with twist boundaries and developing from an underlying dominant grown at 124.5°C

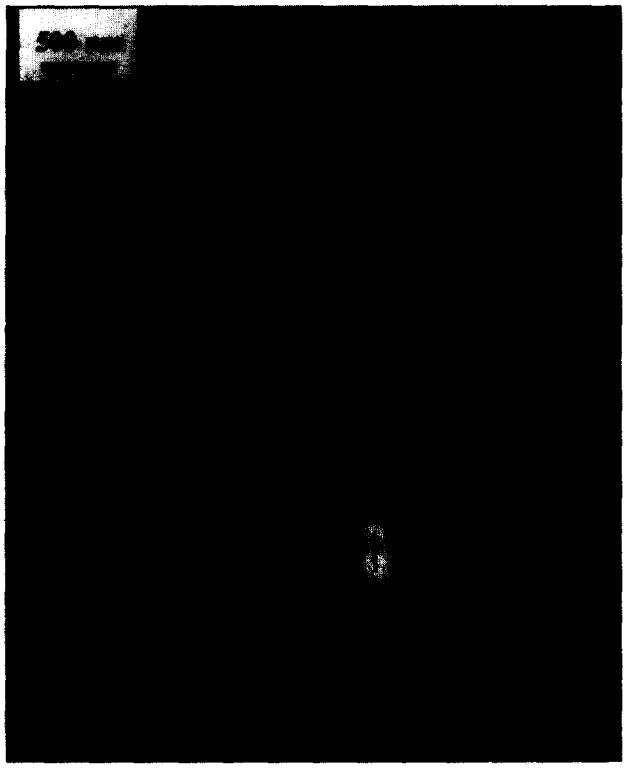


Figure 8 Internal microstructure of extended-chain material formed at 128°C consisting of blocks of parallel contiguous lamellae. The arrow indicates where an extra layer has been inserted

examination down *a*. One notes also that spiral terraces are isochiral and tend to be lined up, at about 30° to the vertical on the page, in a direction approximately normal to {110}; this interesting feature constitues a series of twist boundaries but its significance is beyond the scope of this paper.

The lamellar microstructure in the extended form has a quite different appearance. Internally such materials consist, as shown in *Figure 8*, of parallel stacks of equal contiguous lamellae. There is no spatial divergence of the growth direction as was present in *Figure 3* for spherulitic growth. Even when new layers are injected as arrowed, this does not lead to a persistent long-range divergence of lamellar traces but merely a local disturbance. This characteristic morphology implies the absence of the dominant/subsidiary morphology typically present in polymeric spherulites.

DISCUSSION

Two principal points emerge from this work. The first is confirmation in an unequivocal way that the presence of impurities is not essential to the formation of spherulites here in oligomers and, by implication, in crystalline polymers. Although this necessity has long been questioned, especially since the demonstration that well-purified systems crystallize in this manner[11], nevertheless a recent review[12] did conclude that the prevalent opinion was still that impurities were essential to the formation of polymeric spherulites. This view can no longer be sustained. While there is no question that the presence of non-crystallizable or polydisperse molecular species affects spherulitic growth, sometimes coarsening textures very pronouncedly, our findings confirm that it is not the prime cause.

The topic of spherulitic growth is central to polymer science because with it, even in embryonic form, comes an internal spatial variation of important properties, notably thermal, mechanical and chemical[13]. Their control lies at the heart of the study of structure/property relationships. It is, however, only with the advent of techniques, especially permanganic etching, which have allowed systematic electron microscopy of the internal lamellar organization of crystalline polymers, that the essential feature of spherulitic architectures requiring explanation have been properly appreciated. One now knows that spherulites are built around a framework of individual branching and diverging dominant lamellae to which later-forming subsidiary and infilling layers must conform[9,10]. Such a geometry is incompatible with the role hypothesized for impurities, especially cellulation linked to diffusion fields[14,15]. Instead one needs to account for the repetitive branching and divergence of the dominant lamellae.

In our previous work we have shown that there is an innate tendency of adjacent layers of the same spiral terrace in one melt-grown polymer crystal to splay apart which, given an array of branch points is geometrically sufficient to create the observed spherulitic framework[6]. Because successive layers have also been observed to diverge at constant increments of angle but thereafter retain linear traces, i.e. display the characteristics of a short-range force operative close to the branch point, it has been suggested that it is pressure of molecular cilia which is responsible for the divergence[4–6]. By cilia we mean those portions of molecules which are partly attached to a growing lamella but are outside it and occupy space which would be required if the next lamella were to form in contact with the first one. While it may happen that such cilia are incorporated within the next lamella it must also be the case that they may not be, in which case there will be a pressure, typically of a weak rubbery modulus, acting to make adjacent lamellae splay apart[13]. The phenomenon will be a dynamic one and reflect the instantaneous conformations of molecules which are not necessarily those in the final morphology. Our second point is that the conditions under which spherulites form are those when cilia will be present. When cilia are effectively absent, in extended chain crystallization, spherulites are not formed in this long-chain paraffin.

The expectations concerning cilia are as follows. On the crude approximation that molecules add to lamellae as integral stems then evidently a once-folded molecule will generally pass through a condition in which only one stem is attached to a lamella with the other remaining in the melt as a cilium. On the same assumption, an extended molecule would not be expected to show significant ciliation. More realistically, theories do envisage that molecules attach progressively along a stem. While this does not change the essential situation for folded molecules, it does affect that for extended-chain crystallization and it has been suggested that a moderate degree of kinetic ciliation occurs during extended-chain crystallization[16]. Although this would blur the simplistic distinction between folded and extended growth one would nevertheless expect a significant difference between the level of ciliation in the two cases with corresponding consequences for spherulitic growth. This is what we have found. Moreover, because of the nature of the system other tentative explanations for the distinction, e.g. involving diffusion, are effectively excluded. There is a clear difference between the packets of equal contiguous lamellae in *Figure 8* and the dominant/subsidiary microstructure of spherulites shown in *Figure 6*. This carries through to the distinction at the optical level between spherulites and axialites. Overall, the demonstration that the molecular conformation in the solid has a major influence on whether or not crystallization develops spherulitically is strong support for the view that the essential cause of spherulitic crystallization here in monodisperse paraffins, and by extension, in crystalline polymers is the pressure from molecular cilia. There is also quantitative support for this model in other work from this laboratory, namely a detailed study of lamellae and their association in α polypropylene grown on a linear nucleus[17].

CONCLUSIONS

The two principal conclusions of this work are:

(1) that spherulites do form in thin pure monodisperse paraffin but only when lamellae contain chainfolded molecules and not for extended chains;
(2) the presence of molecular cilia is the underlying cause of the development of spherulites in long chain paraffins and crystalline polymers.

ACKNOWLEDGEMENTS

SJS is in receipt of a Royal Society Fellowship. The authors would like to thank G. M. Brooke, S. Burnett, S. Mohammed, D. Proctor and M. Whiting for the supply of n-alkanes under the auspices of EPSRC.

REFERENCES

1 Paynter, O. I., Simmonds, D. J. and Whiting, M. C. *J. Chem. Soc., Chem. Commun.* 1982, 1165
2 Bidd, I., Holdup, D. W. and Whiting, M. C. *J. Chem. Soc., Perkin Trans. 1* 1987, 2455
3 Ungar, G., Stejny, J., Keller, A., Bidd, I. and Whiting, M. C. *Science* 1985, **229**, 386
4 Bassett, D. C. and Olley, R. H. *Polymer* 1984, **25**, 935
5 Bassett, D. C. and Vaughan, A. S. *Polymer* 1985, **26**, 717
6 Bassett, D. C., Olley, R. H. and al Raheil, I. A. M. *Polymer* 1988, **29**, 1539
7 Ungar, G. and Keller, A. *Polymer* 1987, **28**, 1899
8 Olley, R. H., Hodge, A. M. and Bassett, D. C. *J. Polym. Sci. Phys. Edn* 1979, **17**, 627
9 Bassett, D. C. and Hodge, A. M. *Proc. Roy. Soc. Lond. A* 1978, **359**, 121
10 Bassett, D. C. *Crit. Rev. Solid State Mater. Sci.* 1984, **12**, 97
11 Magill, J. H. and Plazek, D. J. *J. Chem. Phys.* 1967, **46**, 3757
12 Phillips, P. J. '*Bulk Crystal Growth*' (Ed. D. T. J. Hurle), North Holland, 1993, Chap. 18
13 Bassett, D. C. *Phil. Trans. Roy. Soc. Lond. A* 1994, **348**, 29
14 Patel, D. and Bassett, D. C. *Proc. Roy. Soc. Lond. A* 1994, **445**, 577
15 Keith, H. D. and Padden, F. J. *J. Polym. Sci. Part B Polym. Phys.* 1987, **25**, 229
16 Hoffman, J. D. *Polymer* 1991, **32**, 2828
17 White, H. M. *PhD Thesis*, University of Reading, 1995