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A comparison of the morphology and crystallization kinetics of two centrally branched monodisperse alkanes with *n*-alkanes of equal and half length

I.L. Hosier, D.C. Bassett*

J.J. Thomson Physical Laboratory, University of Reading, Whiteknights P.O. Box 220, Reading RG6 6AF, UK

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Abstract

The isothermal crystallization kinetics and morphologies of two centrally branched monodisperse alkanes have been studied and compared with two long *n*-alkanes, one of equal and one of half, the molecular length of the branched molecules. The two branched alkanes were $C_{96}H_{193}{\cdot}CHR{\cdot}C_{94}H_{189}$ with R being methyl or butyl, respectively, while the long *n*-alkanes were $C_{194}H_{390}$ and $C_{98}H_{198}$. Both branched molecules invariably crystallize once-folded in contrast to both *n*-alkanes in which molecules are always fully extended in lamellae, demonstrating that branches are excluded and lie in the folds. At high temperatures, both branched systems form scrolls with all folds on the outer convex surface of quasi-cylindrical lamellae. The crystallization range of the branched alkanes is identical to that of *n*-$C_{98}H_{198}$ and the kinetics a little slower, more so for the butyl-branched material; *n*-$C_{194}H_{390}$ crystallizes more slowly and at higher temperatures. It follows that the second fold stem of a branched molecule is laid down much faster than the first, as expected for secondary nucleation, a conclusion which splaying data support. Transient ciliation in these chainfolded systems is sufficiently long-lived to yield the same splaying as permanent cilia do in binary blends of *n*-alkanes and is a pointer to the behavior of polyethylene. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Monodisperse alkanes; Cylindrical lamellae; Crystallization kinetics

1. Introduction

The present paper continues the morphological and kinetic investigation of monodisperse alkanes which, in recent years, has much clarified central and long standing problems of crystallization in polymers. Earlier studies [1–7] have confirmed that ciliation, both transient and permanent, is a major cause of spherulitic growth and assembled considerable evidence that non-parallel packing of initially rough surfaces is a second contributory factor to the divergence of adjacent dominant lamellae which is the underlying morphological requirement. *N*-alkanes, which are models for linear polyethylene, crystallize as expected [8] with quantized thicknesses [9] but only after adjustments from an earlier transient ciliated or non-integrally folded (NIF), state [10]. Dilute binary blends of *n*-alkanes allow the controlled introduction of either permanent cilia or segregating non-crystallizable molecules depending on whether the guest molecule is longer or shorter than the host [5–7]. The contributions of transient and permanent cilia, plus rough surfaces, to spherulitic growth in *n*-alkanes have thereby been shown to be separable in a consistent pattern of splaying which increases linearly with supercooling.

Two monodisperse alkanes of this work, each with a single central branch, were synthesized [11] to explore the effect of branches on crystallization and, in particular, to see whether a methyl branch would be accommodated in the lattice, as it is in polyethylene, while a longer butyl one would be excluded. In fact both sorts of branch are excluded and molecules crystallize in hairpin conformation even though *n*-alkanes of equal length invariably crystallize with fully extended molecules [4,12]. They have, however, revealed the important fact that scrolls form preferentially at high temperatures, with a cylindrical lamellar habit, indicating that surface packing requirements have prevailed over the resulting elastic strain in the lamellar interior. This

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* Corresponding author. Tel.: +44-118-931-8540; fax: +44-118-975-0203.

E-mail address: d.c.bassett@reading.ac.uk (D.C. Bassett).

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has been reported separately in detail [13]; here we report a wider morphological and kinetic investigation in which two centrally branched alkanes $C_{96}H_{193}\cdot CHR\cdot C_{94}H_{189}$ where R is either CH_3 or C_4H_9, referred to hereafter as C1 and C4, respectively, to reflect their branch lengths, have been compared to two monodisperse *n*-alkanes: $C_{194}H_{390}$, of essentially equal extended molecular length to, and $C_{98}H_{198}$, as long as the once-folded length of, the branched alkanes.

One principal outcome is the demonstration that the behavior of both branched alkanes is close to that of *n*-$C_{98}H_{198}$ and significantly different from *n*-$C_{194}H_{390}$, i.e. it is governed by the fold length rather than the molecular length as expected for secondary nucleation. Deposition of the second stem is inferred to be much faster than the first. A second finding, from splaying data, is that ciliation is less temperature dependent for both C1 and C4 than for *n*-$C_{98}H_{198}$ while the contribution of rough surfaces is increased, more so for the longer-branched system, reflecting the longer cilia lengths imposed by the exclusion of branches as the first fold stem is being laid down. The data are quantitatively practically identical, respectively, to those for 5 and 10% binary blends of *n*-$C_{210}H_{422}$ in *n*-$C_{162}H_{326}$ [6] showing that transient ciliation in these folded systems is sufficiently long-lived to emulate permanent ciliation in the *n*-alkane blends.

2. Experimental

2.1. Materials

The four monodisperse alkanes used were synthesized by Dr GM Brooke and colleagues at the University of Durham [11] under the auspices of EPSRC. It is convenient to refer to the two *n*-alkanes as C98 and C194 hereafter.

2.2. Thermal analysis

A Perkin–Elmer DSC-2C differential scanning calorimeter (DSC) was used to examine the crystallization and melting behavior. Prior to use, it was calibrated for temperature in isothermal and scanning runs against pure lead, tin, indium and stearic acid and for enthalpy against synthetic sapphire. For each run about 1–2 mg of the alkane was placed in an aluminum DSC can. The samples were first crystallized by melting at 134 °C for 1 min, then cooled at 40 K min^{-1} to the required crystallization temperature under a nitrogen atmosphere. Following crystallization, samples were removed from the DSC and quenched to room temperature; the melting endotherms of the product were obtained at a heating rate of 20 K min^{-1}. To avoid problems of degradation, a fresh specimen was used after every two crystallization–melting runs.

2.3. Optical microscopy and kinetics

Both kinetic measurements and optical micrographs were obtained using the same samples. Around 5 mg of the alkane was placed between clean cover slip and microscope slide and melted for 1 min on a Kofler WME hot bench to remove any included air. This entire assembly was placed in a Mettler FP82 hot stage (with FP80 controller) held at the melting temperature under a nitrogen atmosphere and was then cooled at 40 K min^{-1}, the highest available cooling rate, to the required crystallization temperature. At the end of crystallization, the sample was quenched on a cold block to room temperature.

In situ observation of growing crystals was performed with the Mettler hot stage mounted on a Vickers Universal microscope fitted with a CCD camera linked to a video recorder and monitor. Kinetic data were obtained by marking on the monitor screen the position of several crystal tips as a function of time and taking the gradient of the curve fitted to these data. In all four materials the radial growth rate was constant until lamellar impingement, consequently only an average figure (from at least 10 crystals) is given. Optical micrographs were taken immediately following crystallization on a Zeiss GFL transmission optical microscope, between crossed polars; magnifications were calibrated using a standard graticule.

2.4. Transmission electron microscopy

Single-stage carbon replicas were prepared of etched surfaces to avoid electron beam damage during observation. The specimens were crystallized on 5 mm diameter gold grids, placed between a clean microscope slide and cover slip in a Mettler FP82 hot stage as described earlier. After quenching, the cover slip was gently removed leaving the grid and alkane adhering to the microscope slide. The combination was etched for 10 min in a pool of etchant (1% $KMnO_4$ in a 10:4:1 mixture of sulphuric acid, phosphoric acid and water, respectively), changing to fresh etchant halfway through. Etching was quenched using a 1:4 mixture of hydrogen peroxide in a 2:7 mixture of sulphuric acid in water, which had been pre-cooled over dry ice beforehand. Subsequently, the sample was washed, by running methanol over the grid, after which the grid was gently lifted from the slide and allowed to dry.

To prepare replicas, tungsten/tantalum metal was evaporated directly on the etched surface of the grids at ~35° to the horizontal, followed by vertical carbon coating. The alkane was then removed from the grids by refluxing in boiling xylene, leaving the replicas ready for examination.

2.5. Splaying angle measurements

Crystal splaying angles were measured as described previously [4–7], using suitable edge on, but distinct, lamellae chosen from TEM micrographs of each material. A

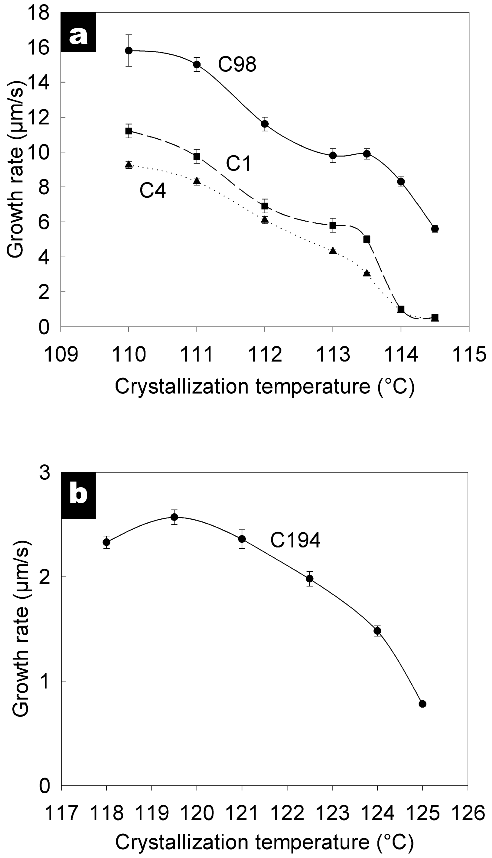

Fig. 1. Average lamellar growth rates of (a) C98, C1 and C4, (b) C194.

total of 30–40 such measurements per point, yields an average value for the angle between adjacent dominant lamellae, which is little biased by any residual tilt of the crystals relative to the viewing plane.

3. Results

3.1. Growth rates

The radial growth rate data for C98, C1 and C4 are very similar and are grouped together in Fig. 1(a). Their accessible isothermal range for crystallization in the hot stage is from ~110 to 114.5 °C, with the growth rate reducing effectively to zero at ~115 °C. At ~113 °C, C98 and C1 show the local minimum for a supercooling of 1–2 K found in other *n*-alkanes [4] and occurring at the onset of lamellar branching. The radial growth rates of the pair of branched materials are a little less than for linear C98, with values for C4 slightly below those for C1. By contrast, C194 (Fig. 1(b)) has a higher accessible range for isothermal crystallization of ~118–125 °C and significantly lower radial growth rates at comparable supercoolings than for C98, C1 and C4.

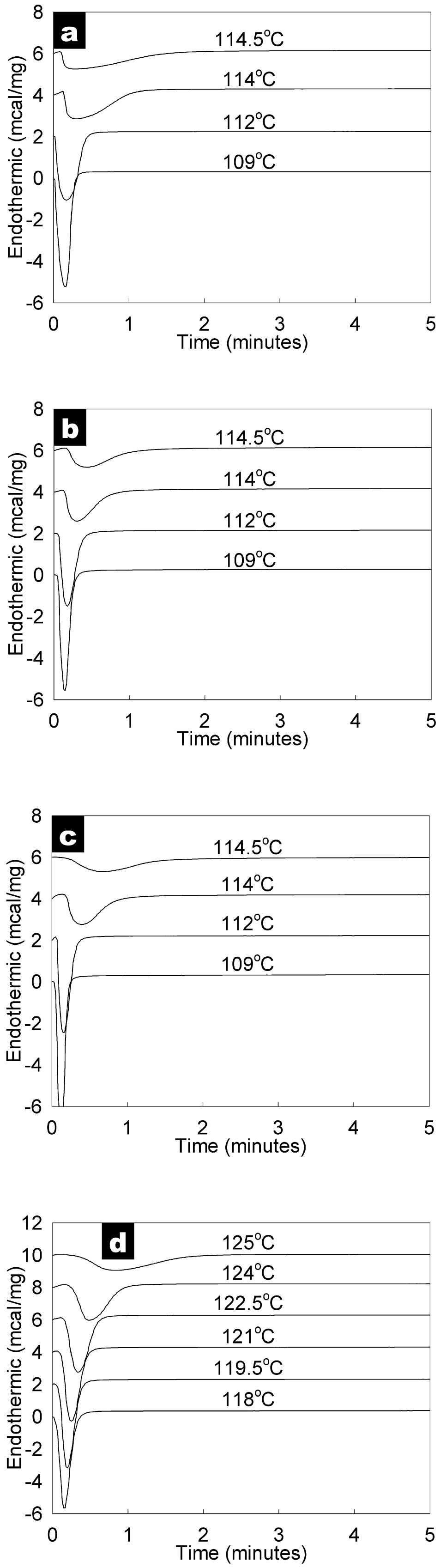

Fig. 2. DSC crystallization exotherms, at the designated temperatures of (a) C98, (b) C1, (c) C4, and (d) C194.

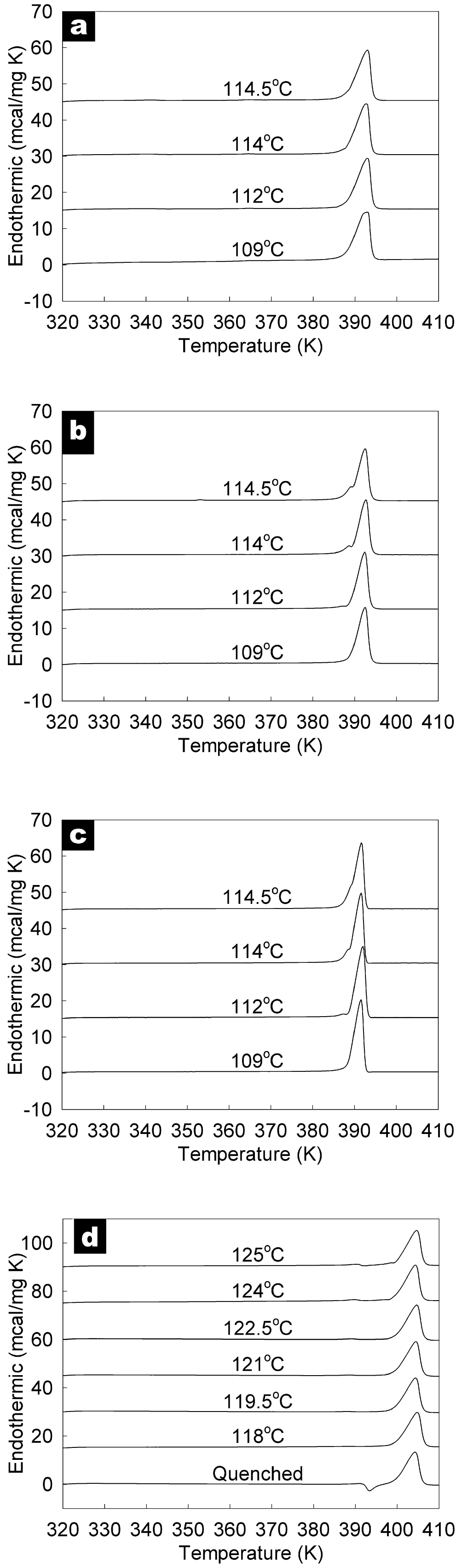

Fig. 3. Melting endotherms, after crystallization at the designated temperatures of (a) C98, (b) C1, (c) C4, and (d) C194.

3.2. Crystallization behavior

Crystallization exotherms for C98, C1, C4 and C194 at the designated temperatures are shown in Fig. 2(a)–(d), respectively. The behavior of the first three alkanes is very similar but totally different to that of C194. The branched alkanes show roughly similar crystallization exotherms to C98, albeit with slightly *reduced* crystallization times. As their radial growth rates are actually reduced, not increased (Fig. 1(a)) one must conclude that the primary nucleation density is enhanced in the branched alkanes; this is confirmed optically below. The average enthalpies of crystallization are less for the branched than the linear alkanes, being 225 ± 10, 175 ± 13 and 185 ± 12 J g^{-1} for C98, C1 and C4, respectively; these values are not significantly dependent on crystallization conditions.

For C194, a direct comparison with C98, C1 or C4 over the same temperature range is not possible but its behavior follows the same pattern as found for other long *n*-alkanes such as *n*-$C_{162}H_{326}$ [4]. The higher average crystallization enthalpy of 250 ± 7 J g^{-1} is in line with these earlier results.

3.3. Melting behavior

Melting endotherms of the four alkanes, crystallized at the temperatures indicated, are shown in Fig. 3(a)–(d) for C98, C1, C4 and C194, respectively. For all crystallization conditions, the first three materials have a peak melting transition at 393 K (120 °C) and an onset at 388 K (115 °C)—which corresponds to the 'cut off' in the growth rate curves in Fig. 1(a), whereas C194 has a melting peak at 405 K (132 °C) and an onset at 399 K (126 °C)—which again corresponds to the higher cut off in the growth rate for this longer *n*-alkane.

The melting point reported for extended chain crystals of C98 is 115 °C [3] and 126 °C that of extended-chain crystals[1] of C194. The melting point of the branched alkanes is identical to C98, not the equally long C194, because of crystallization in the once folded form [12]. There is no evidence of reorganization of either branched alkane into the extended form during the scan as seen, e.g. for C246 crystallized once-folded below 122 °C (cf. Fig. 5(a) in Ref. [7]).

Melting enthalpies are measured to be slightly higher than the crystallization enthalpies, being 241 ± 2, 210 ± 5, 220 ± 6 and 255 ± 2 J g^{-1} for C98, C1, C4 and C194, respectively, reflecting the trends above. The reduced enthalpies of the branched alkanes, seen in both crystallization and melting, can reasonably be ascribed to disorder in the fold surfaces.

C194 manifests the same minor sub-peak of uncertain

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[1] Note that no conclusive evidence for a once-folded form of C194 was detected during this study, even after quenching, while only minor reorganization occurs during the scan itself, Fig. 3(d).

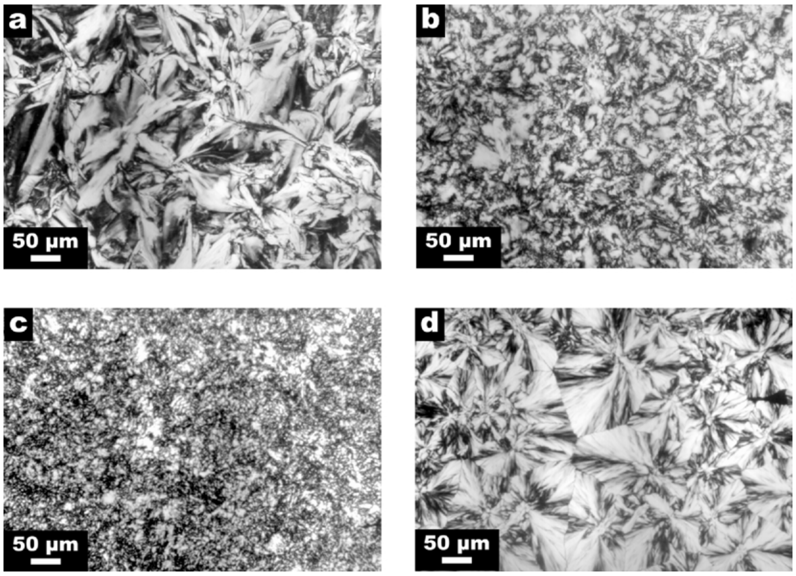

Fig. 4. Optical micrographs between crossed polars of (a) C98 crystallized at 114 °C; (b) C1 crystallized at 114.5 °C; (c) C4 crystallized at 114.5 °C; (d) C194 crystallized at 125 °C.

origin as reported in C246 [4] and then tentatively ascribed to constrained crystallization; here this minor feature is located at 392 K (119 °C) and has an enthalpy (for crystallization at 125 °C) of only 5 J g^{-1}.

3.4. Optical microscopy

C98. Optical examination of C98 between crossed polars shows, as in other *n*-alkanes, objects increasing in size with crystallization temperature and moving away from a spherulitic texture of equivalent radii to one of uniformly extinguishing lamellar packets as in Fig. 4(a).

C1. The texture of this methyl-branched alkane is always finer, with more objects, than C98 at the same temperature confirming its increased primary nucleation but, overall, the morphology varies much less with temperature than C98. After crystallization at 112 °C and above, the morphology appears to have two components with a new granular, if somewhat muddy, texture present between larger and thicker lamellar aggregates. At higher temperatures, the larger crystals become still larger and coarser but the granular matrix becomes generally more prevalent and distinct (Fig. 4(b)). Electron microscopy shows that lamellae and scrolls are present in both regions pointing to primary nucleation as their origin. On melting, a portion of the granular component begins to melt before the larger crystals, corresponding to the low temperature shoulder observed by DSC, but this is too small to represent the whole of this component.

C4. The *n*-alkane with the butyl branch is more heavily nucleated than C1 with an appreciably finer texture. An apparently granular matrix becomes evident after crystallization at 112 °C and, at higher temperatures, can be pervasive (Fig. 4(c)). At any given supercooling, C4 shows a greater proportion of granular material than does C1.

C194. On quenching, C194 exhibits a texture similar to that of C98 appropriate to crystallization in the extended-chain form. Pseudospherulites, whose regions show abrupt extinction as the sample is rotated between crossed polars, and with a finer texture than C98, are always evident after isothermal crystallization increasing in size at higher temperatures (Fig. 4(d)).

3.5. Electron microscopy

C98. Objects formed on quenching (Fig. 5(a)) are composed of individual diverging lamellae. However, after isothermal crystallization at 110 °C (Fig. 5(b)) lamellae are beginning to group together as bundles of near-parallel crystals. At 112 °C lamellar bundles dominate the texture leading to a composite of coarse lamellar stacks of differing orientations (Fig. 5(c)). Finally wide expanses of parallel lamellae are formed for growth at 114.5 °C (Fig. 5(d)).

C1. This alkane, by contrast, shows a more disordered, less distinct arrangement of lamellae. After quenching, less distinct objects are formed which are composed mostly of large, planar lamellae (Fig. 6(a)) with only a single lamellar texture seen. After crystallization at 112 °C and above, a two component texture was found, as shown in Fig. 6(b). To the left of this picture there is an array of broad planar lamellae, but to the right is a region composed of lamellae which are either C shaped or curved into tubes or scrolls of diameter ~2 µm—a feature not seen in C98. At still higher crystallization temperatures, this second component becomes more prevalent and easier to detect in the TEM; the two components are separated in places giving distinctive regions rich in curved lamellae (tubes, Fig. 6(c)) and areas rich in planar lamellae (Fig. 6(d)). The tubes (or scrolls) are unique to the branched alkanes and have

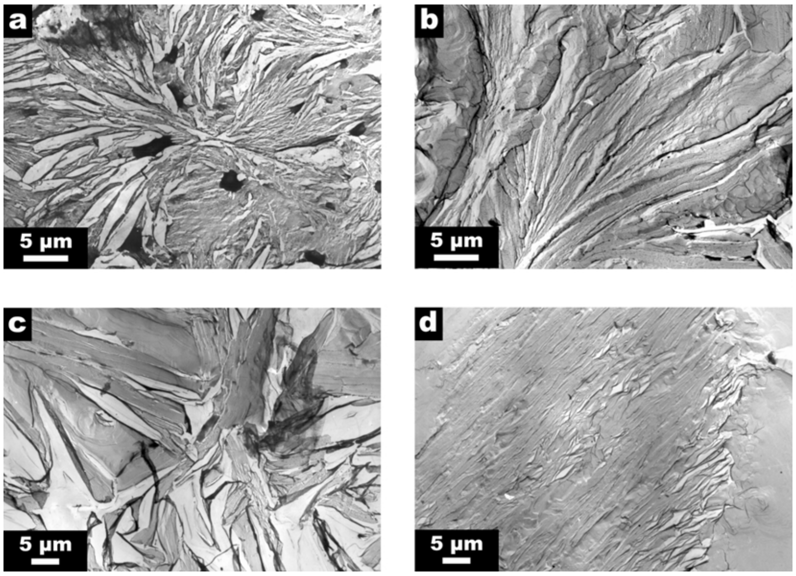

Fig. 5. TEM micrographs of C98 crystallized (a) on quenching; (b) at 110 °C; (c) at 112 °C; and (d) at 114.5 °C.

never been seen previously in blends or any other pure alkane. Their diameter (~2 μm) does not appear to depend significantly on the crystallization conditions.

C4. Some flat-on and edge-on planar lamellae can be seen in Fig. 7(a) between which are curved lamellae, in places forming tubes. These are somewhat tighter than scrolls in C1, having a diameter of ~1 μm. At this low crystallization temperature, the two components are not well demarcated (note the planar edge on lamellae right next to the tubes seen near the center of this figure), and the tubes are relatively difficult to find in the TEM. Similar behavior is noted after crystallization at 112 °C (Fig. 7(b)), however, at this crystallization temperature the tubes become more prominent and easier to detect in the TEM. Notice here the larger dominant edge-on planar lamellae but with regions where lamellae are clearly curved in between. The final two micrographs show examples of this unique texture after crystallization at 114.5 °C when the two components are very distinct. Fig. 7(c) shows tubes, which are edge-on to the direction of view, plus some larger edge-on planar lamellae. In Fig. 7(d) two tubes are now oriented side-on to the direction of view, the bottom one of which is only just exposed by the etchant; all have diameters ~1 μm independent of crystallization temperature, and are tighter than scrolls in C1.

C194. Micrographs from this *n*-alkane are shown in Fig. 8. When quenched, small pseudospherulitic objects form (Fig. 8(a)) having a diameter of ~20 μm with less ordered regions between. After crystallization at 119.5 °C the texture is less spherulitic, i.e. with equivalent radial lamellae

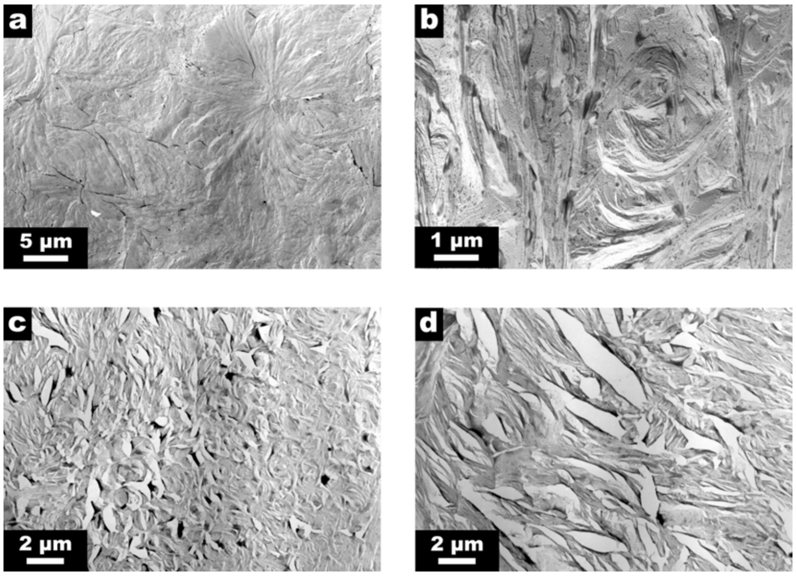

Fig. 6. TEM micrographs of C1 crystallized (a) on quenching; (b) at 112 °C showing mixed planar and curved lamellae; (c) at 114.5 °C—a region rich in tubes; and (d) at 114.5 °C—an adjacent region rich in planar lamellae.

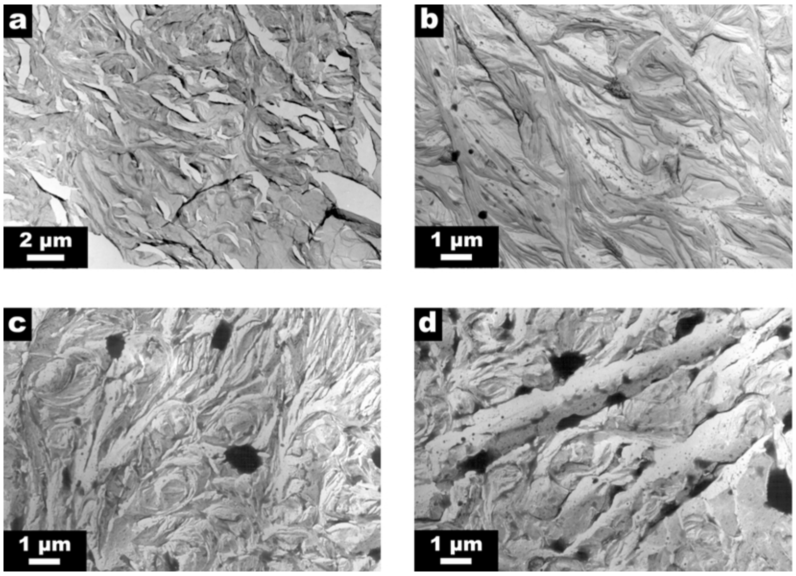

Fig. 7. TEM micrographs of C4 crystallized at (a) 110 °C showing a mixed texture; (b) 112 °C showing planar dominant lamellae and curved subsidiary lamellae; (c) 114.5 °C with tubes seen end on; and (d) 114.5 °C tubes seen from the side.

but is still composed of broad expanses of divergent lamellae (Fig. 8(b)). A similar morphology is observed after crystallization at 122.5 °C (Fig. 8(c)) but with some regions of parallel lamellae and less evidence of spherical symmetry. Finally, after crystallization at 125 °C broad expanses of near parallel groups of lamellae are formed, not usually with a spherical envelope (Fig. 8(d)). This general behavior is consistent with that of C98 and other *n*-alkanes.

3.6. Splaying data

Measured lamellar splaying data as functions of supercooling are shown in Fig. 9. Supercoolings were derived by taking 116 °C as the melting temperature of the branched alkanes with C98, rather than C194, being the more meaningful comparison. For the branched alkanes measurements were made in areas where the lamellae were relatively planar and easy to detect, avoiding areas where tubes were prevalent. Features of note are the reduced gradients for the branched alkanes, more so for C4, coupled with a substantial increase in intercept, ~2°, for C4 and a lesser (almost statistically insignificant) increase for C1. These data are quantitatively very similar to those for dilute binary blends of monodisperse *n*-alkanes with permanent cilia, specifically of *n*-$C_{210}H_{422}$ as guest in *n*-$C_{162}H_{326}$ as host [6].

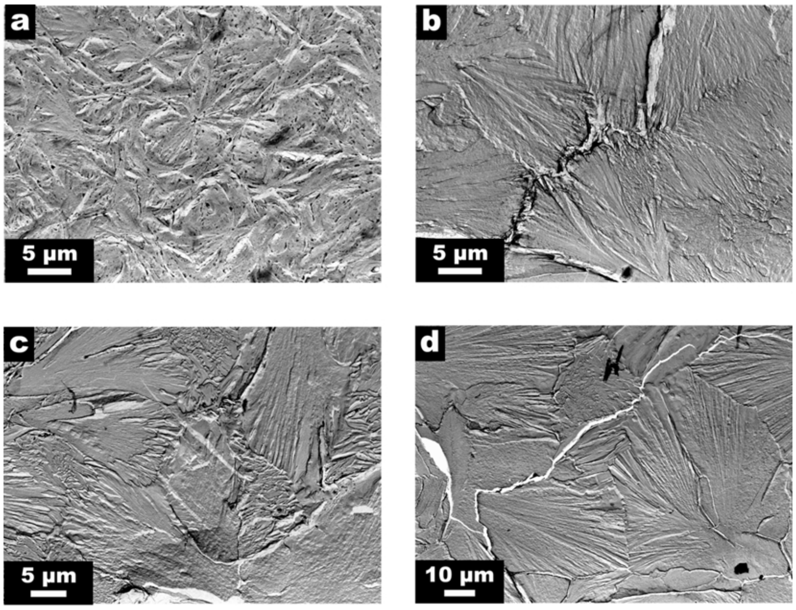

Fig. 8. TEM micrographs of C194 crystallized (a) on quenching; (b) at 119.5 °C; (c) at 122.5 °C; and (d) at 125 °C.

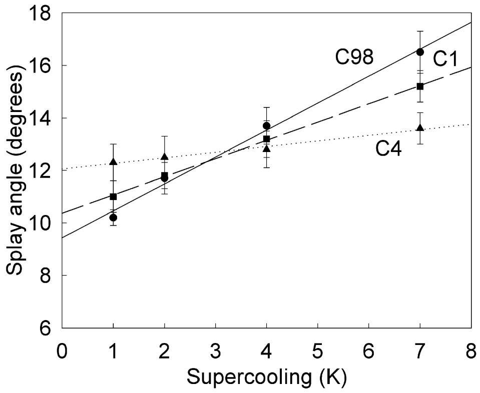

Fig. 9. Measured lamellar splaying angles compared with C98 which has a comparable lamellar thickness.

4. Discussion

The first point to discuss is the similarity of growth rates for C1 and C4 to that of C98, which are much faster than C194 notwithstanding its comparable length. This demonstration that lamellar thickness is a principal determinant of growth rate, is in line with expectations for secondary nucleation (on side surfaces). According to this approach, it is the laying down of the first stem of a new layer which is rate-determining because of the additional side surface free energy then created, in contrast to the addition of all subsequent stems in the same molecular layer. It is to be expected, therefore, that the three alkanes, having the same thickness, will have comparable growth rates, with the two folded systems being somewhat slower because of their higher fold (basal) surface free energies which will include the work of chainfolding. It is also to be expected that C4, with its longer branch, will crystallize more slowly than C1, because of slower transport and possibly also thermodynamic reasons.

Were it possible to crystallize C194 at the same temperatures as the other three alkanes its growth rate would have risen but crystallization of extended-chain lamellae has intervened to prevent such temperatures being reached. Lamellae with fully extended molecules are evidently unstable for these branched alkanes implying that the energetic cost of an interstitial branch is too great even though methyl branches are accommodated within polyethylene lamellae. Thicker lamellae than those encountered here, for which the increase in free energy per unit mass is less, will be required for interstitial methyl branches to be stable.

It follows from the similarity in growth rates that, if stems add sequentially, the second one adds much more quickly than the first, in agreement with the rapid disappearance of the NIF form in X-ray diffraction studies [10]. The theoretical possibility that both stems might add simultaneously in hairpin conformation while the excluded branch remains on the surface is not only unlikely a priori, to have both stems acting in concert but, implying little or no ciliation, is also excluded by splaying data.

The progressively changing textures across the different alkanes are shown in Fig. 4, optically, and with lamellar resolution at different temperatures in Figs. 5–8. A principal feature of these is the increasing divergence of dominant lamellae at higher supercoolings. This element of texture is quantified in Fig. 9 for C1, C4 and C98. It shows that the splaying of dominant lamellae in C1 and C4 fits into the pattern of previous measurements on various alkanes and their binary blends [4,6] even though these are the first inherently folded systems on which measurements have been made. Quantitatively, the data are rather similar to those for certain dilute binary blends with permanent cilia. Those for C4 closely resemble, in extrapolated intercept and slope, data for a blend of 10% of n-$C_{210}H_{422}$ in n-$C_{162}H_{326}$ as host while those for C1 are similar to a 5% blend of the same two constituents [6]. In these blends there are both transient and permanent cilia whereas in both branched alkanes there will be no permanent ciliation (except for excluded branches) but transient ciliation in which half a molecule lies outside the lamella beyond the excluded branch on the fold surface will be a feature. The coincidence of data for the blends and pure branched alkanes implies that, for the latter, the lifetime of transient ciliation exceeds the time over which lamellar divergence is established in the region of branch points. This finding, which indicates the strengthened and less temperature-dependent role of transient ciliation when alkanes are chainfolded, may well be a pointer to chainfolded crystalline polymers for which, with many stems per molecule, ciliation would be expected to be largely independent of temperature.

Finally we comment briefly on the scrolls which form in both branched alkanes at higher crystallization temperatures; a fuller report is published separately [13]. These contain quasi-cylindrical lamellae whose evident strain implies a preponderance of branches in the outer, convex, surface. Moreover as, in each alkane, scrolls have a near-constant (minimum) diameter one can infer that all branches are then on the outer surface. The corresponding differential strains between inner and outer surfaces are ~1% for C1 and ~2% for C4, the factor of two contrasting with the factor of four in branch length. A similar situation applies to the splaying data above for which C1 and C4 match to blends differing in concentration by a factor of two. While this correspondence with the square root of branch length may, at first, 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 making more information on how branches pack together in the lamellar surface necessary for a sufficient explanation of the observed ratio.

At any given supercooling scrolls are generally more apparent in C4 than C1 as might be expected given the greater potential for relief of surface stress. In most cases this novel habit appears to form by the spontaneous rolling up of initially planar lamellae but it might be, and cannot be excluded, that at the slowest growth rates, they would form directly from the melt. In either case, this evidence indicates that scrolls are more stable than planar lamellae signifying that relief of surface stress has outweighed the associated increase in elastic energy of the strained lamella to provide a net reduction in free energy [13]. This is an important attribute of this most important aliphatic subcell structure.

5. Conclusions

The principal conclusions of this work are:

1. Both branched molecules invariably crystallize once-folded in contrast to both *n*-alkanes in which molecules are always fully extended in lamellae, demonstrating that branches are excluded and lie in the folds.
2. At high temperatures, both branched systems form scrolls with all folds and branches on the outer convex surface of quasi-cylindrical lamellae.
3. The crystallization range of the branched alkanes is identical to that of n-$C_{98}H_{198}$ and the kinetics a little slower; n-$C_{194}H_{390}$ crystallizes more slowly and at higher temperatures. This is as expected for secondary nucleation and implies that the second fold stem of a branched molecule is laid down much faster than the first, a conclusion which splaying data support.

Acknowledgements

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