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Isothermal thickening of single crystals of $C_{294}H_{590}$ in dilute solution ☆

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Abstract

Crystals of the long, uniform alkane, $C_{294}H_{590}$ can be grown from dilute solutions in a range of different integer folded forms. At suitable temperatures, folded crystals will thicken from one folded form to another. The morphology of the crystals as they grow depends both on the growth temperature and on the number of folds in the crystal. In this paper we report, for the first time, observations on the morphologies of crystals that have been grown, and allowed to thicken to varying extents, in DSC pans. From the DSC we have precise knowledge of the overall degree of crystallinity and extent of thickening that has occurred over the whole sample.

On thickening from twice-folded to once-folded crystals, the initial crystal shape is lost and a fine, dendritic structure results, in which the thickened regions exist in a surrounding matrix of unthickened material; the thickened regions have a characteristic width of 20–30 nm. It is suggested that this characteristic width is caused by the interplay of solid state diffusion and the lattice strain caused by the reduction in top surface area. At lower temperatures, when thickening occurs from three times folded to twice-folded forms, the initial lozenge shape of the three-times folded crystals is maintained after thickening, forming “picture-frame” crystals, but with a fine web of thickened material within the frame. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: *n*-Alkanes; Isothermal thickening; Crystallization

1. Introduction

Studies of the crystallization of ultra-long alkanes have already provided a wealth of insight into the crystallization of polymers in general and of polyethylene in particular [1–10].

Several groups have studied these and other similar oligomer systems and found generally similar experimental results [1–14], although there has been some disagreement about the interpretation of these results. Nearly all the work on solution crystallized material has shown, from X-ray diffraction, Raman Spectroscopy and even shadow length, that the thickness of crystals formed from exact length alkanes are very close to integral fractions of the overall molecular length. It has been suggested that these materials form preferentially into different (integer folded) states. The actual crystal thickness (or folded state) has been found to depend on the chain length and the crystallization temperature. Many of these studies have involved measuring crystallization rates using thermal and some microscopy techniques [2,3,6–9,11–14], in most cases a minimum in crystallization rate near the transition between different folded states has been observed.

In our opinion, the observations of particular importance are those relating to the crystallization of chains into integer fractions of the chain length [1], the occurrence of a minimum in growth rate as primary crystal growth passes from one crystal form to another [2,3] and the lack of impact of solution concentration on the dissolution temperature at moderate to high dilutions [4].

In this paper we will be dealing with the isothermal thickening of single crystals grown from dilute solution, an issue which may provide insight into the above observations pertaining to uniform alkanes, as well as extending our understanding of crystallization in high polymers. We are concerned with the mechanisms of thickening and have used

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☆ Andrew Keller was closely involved in the work that we report in this paper. Andrew was an inspiration to all of us and the many regular discussions we had together greatly assisted in the formulation of the whole research programme as well as in the specific work described here. We had completed the experimental work contained in this paper shortly before Andrew died and had intended to discuss the implications with him on his return from his skiing holiday. Unfortunately, Andrew died before we could have this general discussion. It is impossible to say whether Andrew would have agreed with the way in which we have presented the data, or indeed whether he would have accepted the conclusions we have drawn. Those who knew Andrew will know that he often held strong views but was always cautious in expressing them in his publications. We have tried to write this paper in a way we believe Andrew would have presented the work, and we must give him full credit for the work, while taking full responsibility for any errors or omissions on ourselves.

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electron microscopy to follow the changes in morphology as the crystals thicken.

In high polymers it is commonly observed that crystalline lamellae grown from the melt thicken after initial crystallization [15]. However, on crystallization from dilute solution it is generally found that the single crystals maintain the thickness with which they originally grew, unless they are annealed above their original crystallization temperature. In contrast, it has been found [16] that ultra long alkanes grown in dilute solution will thicken at the crystallization temperature from an initial (integer) folded form to more stable, thicker, integer folded or to extended forms, given sufficient time. This effect has been extensively studied [16,17] in the case of the isothermal thickening of $C_{198}H_{398}$ between the once folded and extended crystal forms, by use of both DSC and direct observation of the crystals using TEM. However, in these previous studies, from this laboratory, it was found to be necessary to perform different experiments at different solution concentrations because of the contrasting needs of the experimental techniques. In the DSC a relatively high concentration (~3%) was required to obtain an observable signal. However, to prepare isolated crystals for TEM studies generally requires very dilute concentrations, ~0.01%. A further complication arises in that the DSC samples are normally prepared in aluminium pans while those for TEM are prepared in glass tubes. The requirement for different concentrations makes the direct comparison of results from these different methods problematic. In particular, it was not possible to obtain any knowledge of the path taken by an individual crystal, observed using TEM, except by inference from the final morphology. The crystallization history of the sample: when crystallization began; when the initially folded crystals started to transform into a less folded form; how close to completion this transformation was; were all, essentially, unknown. In order to rectify this situation, the present series of studies was undertaken; samples were prepared and characterized in the DSC before subsequent harvesting and examination using TEM. A second motivation for the present work is that previous studies of the morphologies of uniform long alkanes grown in solution have dealt only with $C_{198}H_{398}$. As the longer alkanes undergo thickening processes between more folded forms than conveniently observed with $C_{198}H_{398}$, e.g. three times folded to twice folded, twice folded to once folded, we have endeavoured to identify features of thickening that apply universally to all systems, as well as those which are specific to individual molecular lengths.

In the present work we will deal only with the thickening behaviour of $C_{294}H_{590}$. In a subsequent publication we will present a similar study of the isothermal thickening of $C_{246}H_{492}$ [18]. In parallel work we have used Raman LAM and SAXS to study the lamellar thickness of similarly prepared but more concentrated solutions of alkanes. That study, to be reported elsewhere [19], has allowed us to reaffirm with confidence the existence of exclusively integer folded chains in the ultra-long alkanes studied here when crystallized from dilute solution.

2. Experimental

The materials used in this study were kindly provided by Brooke [20] and the EPSRC.

Two different sample preparation techniques were used for subsequent study by TEM. For most of the morphologies presented here, where comparison with results from DSC was required, samples were prepared in the DSC. A Perkin–Elmer DSC7 was used. For each sample, approximately 0.02mg of $C_{294}H_{590}$ was weighed into an aluminium DSC pan suitable for volatile liquids, approximately 7mg of toluene was added and the pan sealed, to give a sample concentration in the range 0.1–0.4%w/w (all subsequent concentrations quoted will be %w/w). The sample was then heated to 110°C, cooled immediately to 105°C and held for 1 min to ensure that the alkane was completely dissolved; it was then cooled to the selected crystallization temperature, and allowed to crystallize for a given length of time. The sample was then re-heated in the DSC, the resultant melting endotherm allowing the extent of crystallization and the form of the crystals (e.g. once-folded, extended etc.) to be determined in the same manner as has been used previously in this laboratory for the study of crystallization rates [21]. The process was then repeated, but the sample was not heated from the crystallization temperature but rather quenched to room temperature at the maximum cooling rate of the DSC (~40°/min). In some instances a further check was performed, by again re-melting the sample at a heating rate of 20°/min (a rate which has previously been found to prevent most rearrangement of the sample [22]) and observing the melting behaviour, in order to ascertain how much further crystallization occurred on cooling to room temperature. Once the sample was fully characterized and crystallized in the desired form, the DSC pan was removed from the DSC, cut open with a scalpel and shaken vigorously in excess toluene (approximately 0.5ml) in order to remove the crystals from the DSC pan. A drop of the resulting suspension was then placed onto a carbon covered TEM grid, shadowed with platinum palladium and viewed in a Phillips 400 TEM.

At some crystallization temperatures large quantities of crystal were prepared using more standard sample preparation techniques in glassware. Samples of $C_{294}H_{590}$ were placed into glass tubes, toluene added to a concentration of approximately 0.2%w/w and the glass tube flame sealed to prevent escape of toluene during crystallization. The alkane sample was dissolved in toluene in an oil bath at 105°C for 5 min, and then transferred to a second, preheated oil bath at the desired

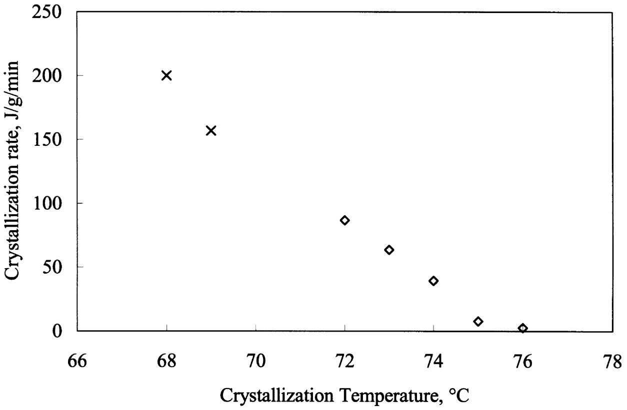

Fig. 1. A graph showing the variation in crystallization rate with crystallization temperature for a 0.18% (w/w) solution on $C_{294}H_{590}$ in toluene over the range of temperatures at which morphologies were studied by TEM. ◇—primary growth in 2F form, ×—primary growth in 3F form. At the temperatures labelled ×, single 3F melting peaks are not observed. Instead a double peak apparently consisting of the melting of 3F and 2F material is seen. It may be that both crystal forms grow simultaneously at the same temperature. However, it seems more likely that the upper peak is due to transformation of material originally grown in the 3F form into the 2F form. In deriving the growth rate at these lower temperatures, we have taken the total area of the 3F and 2F peaks. Although this is not strictly correct—we are including a contribution to the enthalpy change that did not occur during primary growth but during thickening—it is a reasonable approximation when, in the present circumstance, we are only trying to give an indication of the crystallization rate.

crystallization temperature, where it was held isothermally for the desired crystallization time. The tube was then removed from the oil bath, broken open, and the resulting suspension prepared for study by TEM, as described above. It was found that nucleation rates in glassware were considerably slower than those recorded by the DSC, so total crystallization times were not easily comparable. For this reason, as the intention of this study was direct comparison between morphology and DSC data, the majority of samples were prepared in the DSC, even though the glassware technique sometimes gave less damaged morphologies because the method of extracting the suspension from the DSC pan involved vigorous shaking.

It was possible, at higher crystallization temperatures, to calculate the rate of crystallization from the DSC in direct comparison with previous work on $C_{294}H_{590}$ using higher concentrations. The same technique as described in [21] was used, in which a crystallization curve is built up from successive isothermal crystallization and melting runs. The sample is crystallized for a given length of time, melted directly from the crystallization temperature and the area of the resultant endotherm measured. The process is repeated for different lengths of time at the same crystallization temperature until an Avrami type rate curve of endotherm area vs. time has been built up, from which an approximate growth "rate", the tangent to the steepest part of the curve, can be determined. This technique was used for a single sample of $C_{294}H_{590}$ with a concentration of 0.18%w/w, which can be taken as representative of the concentration range under study here. It was only possible to measure rates unambiguously at crystallization temperatures down to 72°C, because below this temperature crystallization was prohibitively fast and the unambiguous identification of the crystal form was not possible from the DSC trace, as further discussed in Section 3. Temperatures above 76°C could not be accessed with the sample used, because the crystallization rate was prohibitively slow. However, a survey of the DSC behaviour was carried out over the entire range of temperatures for which samples were studied using TEM, from 66 to 76°C, using this same sample, even at the lower temperatures where absolute rates could not be obtained with confidence.

3. Results and discussion

We will, first, present the DSC data on crystallization rates and thickening times, in order to provide a background of information before discussing the crystal morphologies observed. In the present study we are interested in the isothermal thickening behaviour of $C_{294}H_{590}$. Using samples of a sufficiently high concentration that they can be characterized by DSC (i.e. greater than 0.1%), we were able to access the thickening behaviour between three times folded (3F) and twice folded (2F) crystals, and between 2F and once-folded (1F) crystals. At these concentrations we were not able to obtain 1F crystals directly from primary growth as the rates of crystallization in that form were prohibitively slow. The alternative, of going to higher concentrations to do the entire study, was rejected because the use of higher concentrations causes large aggregates of crystals to grow, posing serious difficulties for viewing morphologies with TEM and, particularly, making it difficult to be confident that the observed morphologies (from the thin regions) are truly representative.

3.1. DSC data on an example sample

Fig. 1 shows the variation in growth rate with temperature for 2F crystals in the temperature range 68° to 76°C, taken from the enthalpy change on melting vs. crystallization time data. Below 70°C primary crystallization occurs in the 3F form.

Fig. 2a shows a series of DSC melting curves obtained after different crystallization times at 75°C, in which the transformation of 2F (low melting) to 1F (high melting) crystals can be clearly seen. Fig. 2b shows the variation in enthalpy with time for the two crystal forms. As reported previously [22], the total mass of crystal increases rapidly at first, exclusively in the 2F form. A "plateau" region is then reached in which the total mass of crystal only increases very slowly, if at all. Then the 2F crystals start to transform into the 1F form, until eventually the 2F form is entirely replaced by the 1F form.

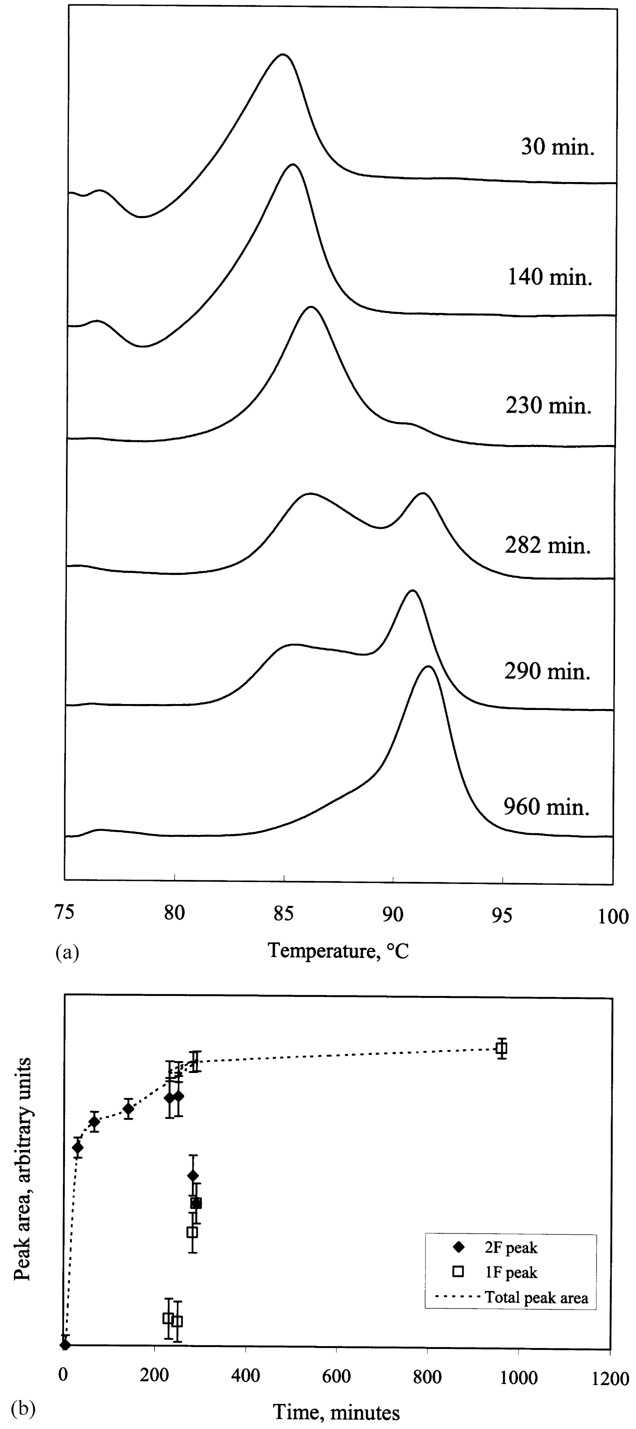

Fig. 2. (a) A series of DSC curves showing the dissolution behaviour of a 0.18% (w/w) solution of $C_{294}H_{590}$ in toluene crystallized for different lengths of time at 75°C. The dips at the beginning of the first two curves are due to slight errors in the subtraction of the baseline, which tend to be accentuated in this region, they are not due to crystallization on heating. The times refer to length of isothermal crystallization. (b) The variation in endotherm area on melting after crystallizing for different lengths of time at 75°C. The dashed line represents the total endotherm area. ◆—2F peak area, ☐—1F peak area. The times refer to length of isothermal crystallization.

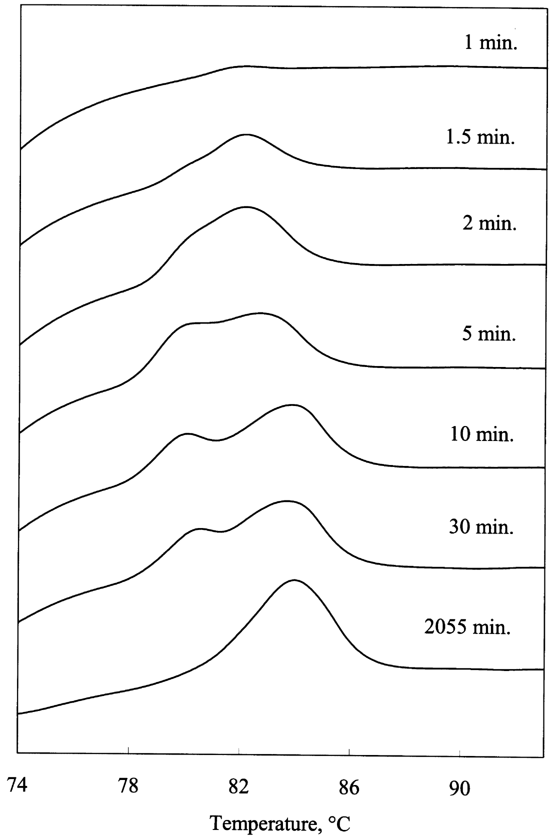

Fig. 3. A series of DSC curves showing the dissolution behaviour of a 0.18% (w/w) solution of $C_{294}H_{590}$ in toluene crystallized for different lengths of time at 68°C.

It appears, from the DSC data, that even after the transformation from the 2F to the 1F state has stopped, a small amount of 2F crystal remains. This is evidenced by the low temperature shoulder on the DSC curve apparent in Fig. 2a (960 min), which is still present even after holding for at least a day after the initial thickening had occurred.

Fig. 3 shows a series of DSC melting curves obtained after crystallization at 68°C for different times. From these curves there appears to be an initial crystal population with a melting point intermediate between the 2F and 3F melting points. As crystallization proceeds this splits into two peaks corresponding to a 2F and a 3F crystal population (at ca 85 and 79°C, respectively). With further crystallization, the area of both of these peaks grows concurrently. After approximately 30 min, the 3F peak starts to become smaller, its melting peak moves to marginally lower values, and the 2F peak becomes larger. Finally, at very long times, the 3F peak has completely disappeared, leaving a single peak corresponding to the 2F material. Similar behaviour was observed for crystallization at 67°C. At higher crystallization temperatures the 3F material was very unstable with respect to 2F material and rapidly transformed into it. At crystallization temperatures below 66°C it was not possible to reach the crystallization temperature before crystallization had initiated. As we are interested primarily in

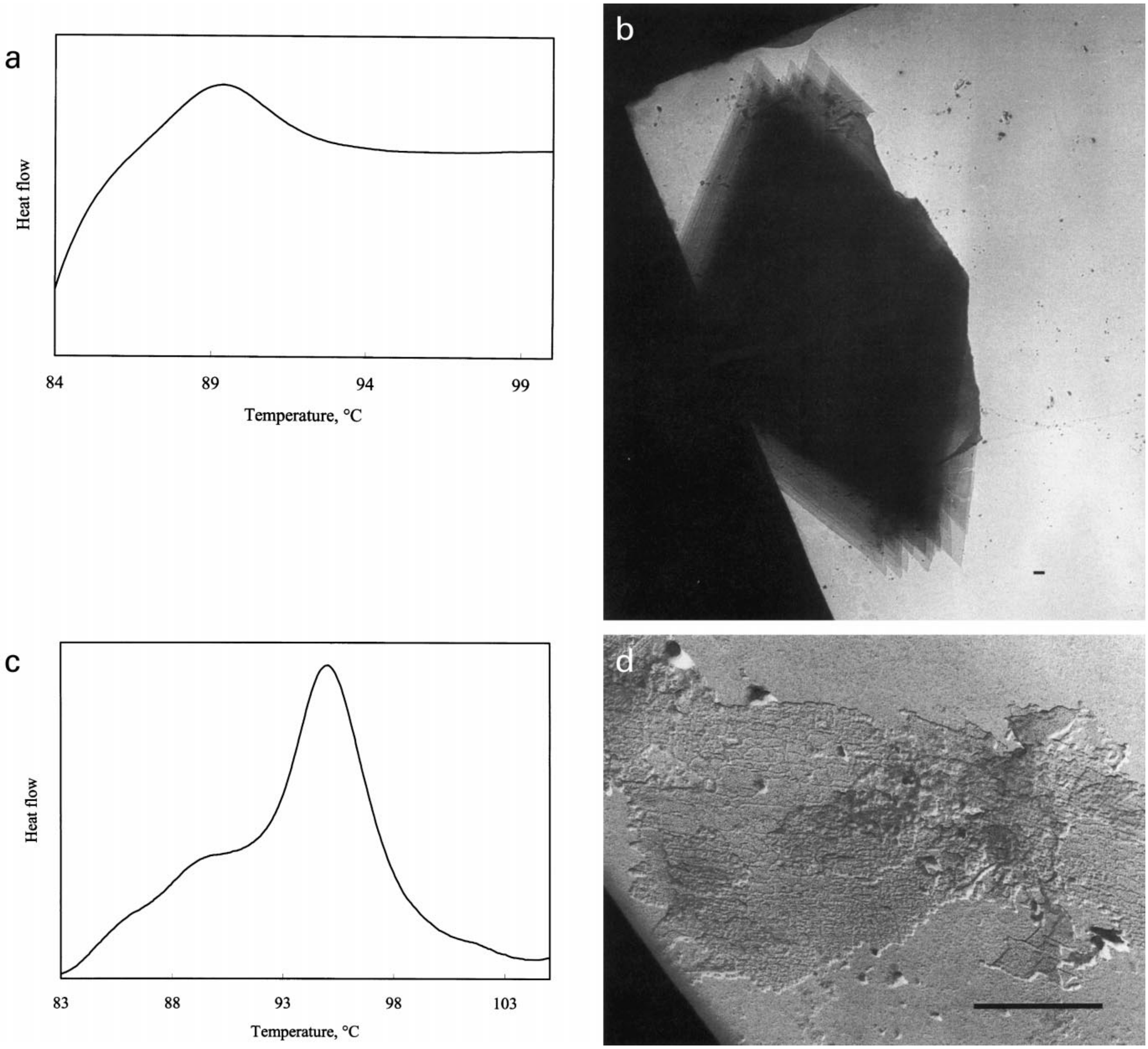

Fig. 4. A series of TEM micrographs and their corresponding DSC traces, illustrating thickening from 2F to 1F $C_{294}H_{590}$: (a) the DSC trace corresponding to (b), the sample was crystallized for 55 min at 78°C; (b) a TEM micrograph showing a large, unthickened aggregate of 2F crystals; (c) the DSC trace corresponding to (d), the sample was crystallized for 26 h at 78°C; (d) a TEM micrograph showing a crystal thickened from the 2F to the 1F crystal form. The scale bars represent 1 μm.

isothermal crystallization, lower temperatures were not studied.

The presence of an intermediate melting point, between that normally observed for 3F and that observed for 2F crystals, at early stages of crystallization could suggest the presence of material that is not integer folded. Works examining crystallization from the melt have often reported crystals that have thickness not corresponding to any integral folded state, these are usually transient states that occur during crystallization, with the fully crystallized materials adopting crystals with thicknesses that correspond to integrally folded states (allowing for any chain tilt that may be present)—although the exactness of the integer folding is still a matter of some debate [8–10]. Indeed recent work [5] using in situ X-ray diffraction experiments suggests that even the apparently non-integrally folded states are in fact integer folded, but with relatively low crystallinity. It therefore seems most likely that the intermediate peak observed at the start of crystallization is due to the transformation of 3F to very imperfect 2F material on heating.

3.2. TEM study of thickening from 2F to 1F

Fig. 4 shows a series of TEM micrographs of $C_{294}H_{590}$ isothermally crystallized for different lengths of time in the temperature region where isothermal thickening from

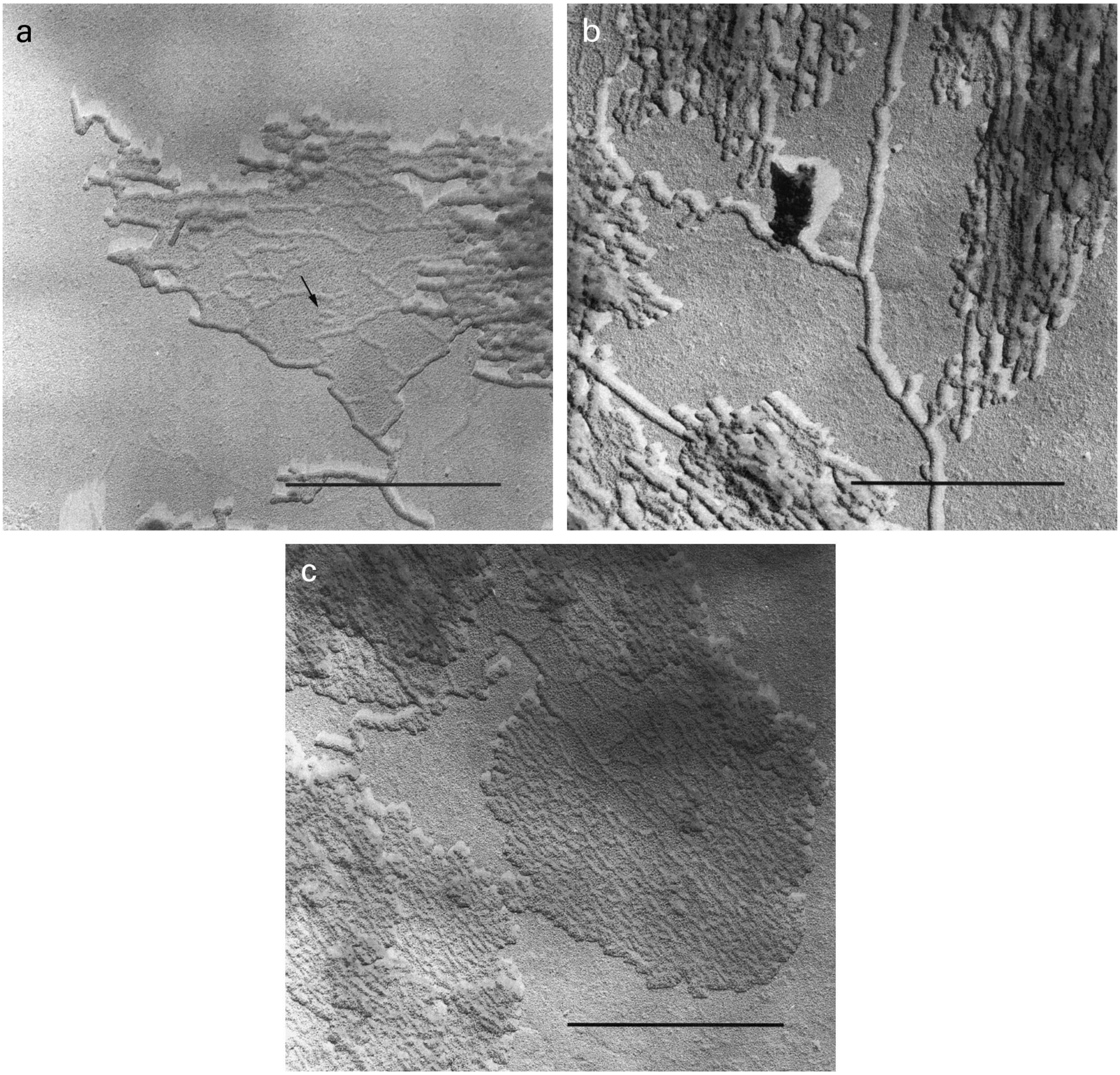

Fig. 5. A series of high magnification TEM micrographs of crystals thickened from the 2F to the 1F crystal form. (a) A lightly thickened region of a crystal. The arrow marks a small region of thickened material surrounded by unthickened material. This sample was crystallized at 74°C for ~65 h. (b) The central region of this micrograph shows a long ribbon of thickened material isolated from unthickened crystal. (c) A densely thickened region of a crystal. (b) and (c) are taken from the same sample as shown in the DSC trace in Fig. 4c. The scale bars represent 1 μm.

the 2F to the 1F form occurs, and their corresponding DSC melting curves.

Fig. 4a shows the DSC trace taken on melting 2F crystals before they had been held for long enough to thicken, with a TEM micrograph of the same sample, prepared in the same manner, shown in Fig. 4b. It is apparent that the material is heavily aggregated, which was generally found to be the case at these crystallization temperatures. The often very large aggregates usually maintain a crystallographic shape, suggesting that there may be register between adjacent chain folded layers. Fig. 4d shows a crystal that has partially thickened from 2F to 1F. Fig. 4c shows the DSC trace corresponding to Fig. 4d. The morphologies that occur on thickening between the 2F and 1F forms are quite varied, so we show a series of higher magnification images in Fig. 5 to illustrate the variety of morphologies we have observed. Fig. 5b and c are from the same preparation as Fig. 4d. Fig. 5a is from a different but similar preparation so the corresponding DSC trace is not shown. In the bottom right hand corner of Fig. 4d an area is shown where the boundary of the crystal briefly follows a flat, apparently crystallographic plane. Such regions are occasionally seen but are not typical. Fig. 5a shows a crystal that still contains large areas of unthickened material. Fig. 5b shows an unusually large

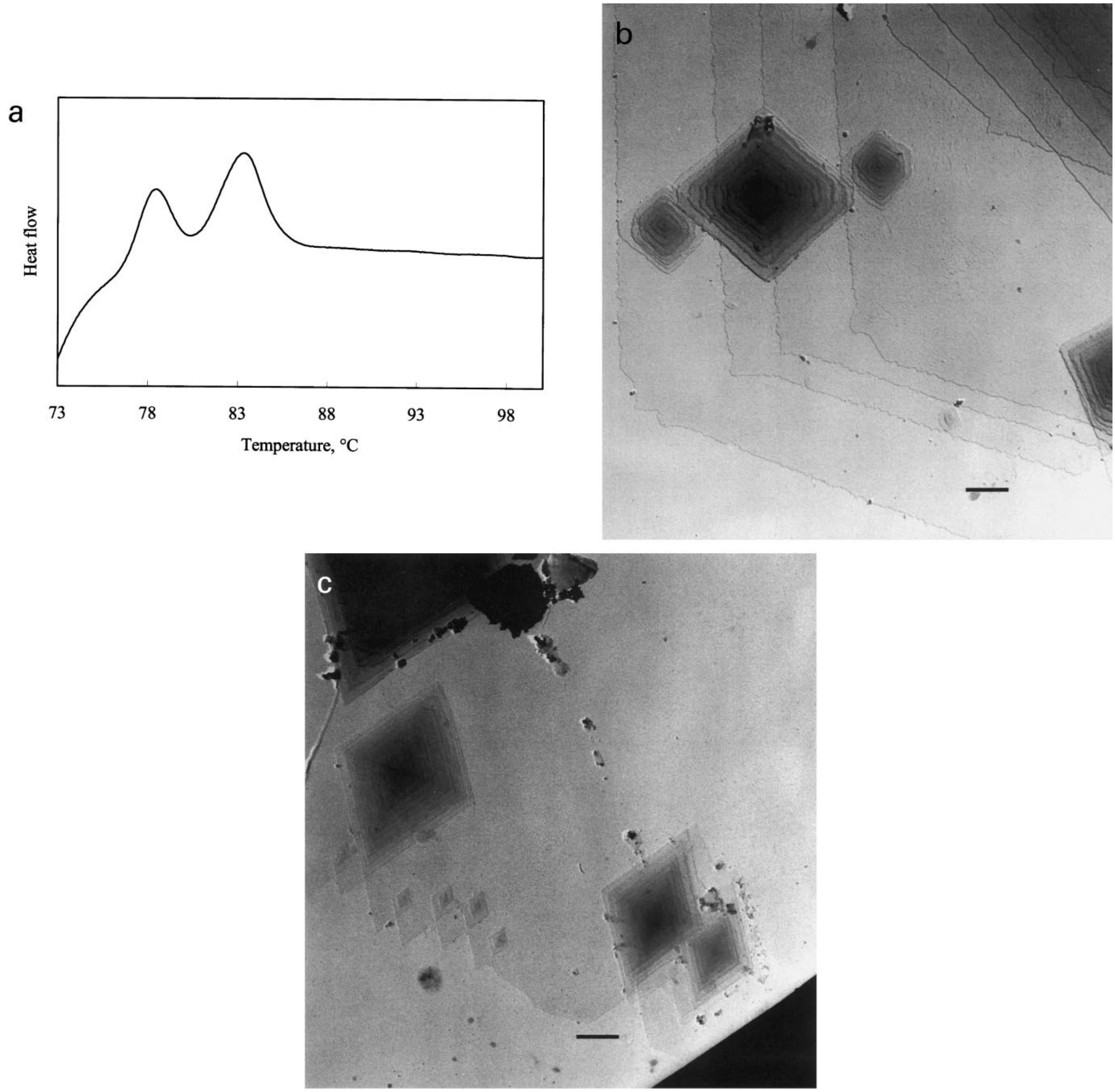

Fig. 6. TEM micrographs, and their corresponding DSC trace, showing unthickened 3F crystals of $C_{294}H_{590}$. The sample was crystallized for 5 min at 66°C. The low region at the start of the DSC trace is due to the instrument settling down at the start of heating. The scale bars represent 1 μm.

piece of thickened material that is not in a matrix of unthickened material. Fig. 5c shows a densely thickened region in which the non-crystallographic, rough nature of the boundary of the crystals is particularly apparent. It was found that, in all cases, small amounts of 2F material were present amongst the thickened material. In the samples which were only partially thickened, some entirely unthickened crystals were also found, although it was not clear if these had formed on quenching or had not yet started to thicken.

From the micrographs of crystals thickened from 2F to 1F, a number of features are apparent. The thickening process has not left any indication of the initial crystal morphology. The initially formed crystals have clearly fallen apart on thickening. In no case were there signs of preferential thickening at the edges of the lozenge shaped 2F crystals. Also, and of particular significance, the final thickened morphology does not consist of large expanses of thickened material with crystallographic faces, as found for the thickening of $C_{198}H_{398}$ [17] in some cases.

The thickened material consists of narrow strips which wander, almost at random, through a matrix of unthickened material. The lateral surfaces of these thickened regions

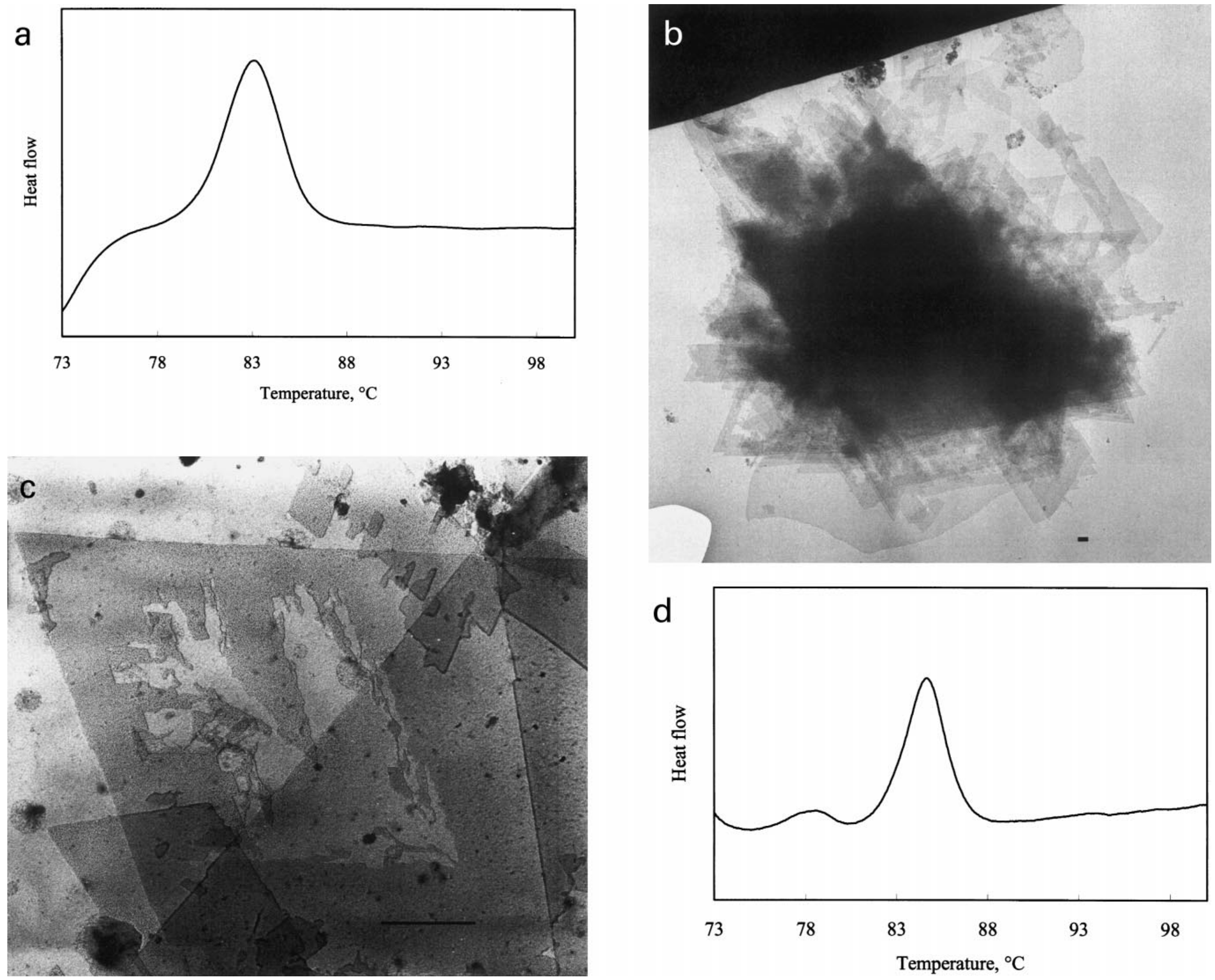

Fig. 7. A series of TEM micrographs, and their corresponding DSC traces, showing $C_{294}H_{590}$ thickened from the 3F to the 2F form: (a) shows the DSC trace corresponding to (b) and (c), the sample was crystallized for 16 h at 66.5°C; (b) shows a large aggregate in which it is clear that the thin layers visible with the TEM have thickened to leave picture frame crystals; (c) shows a close up of a lozenge shaped picture frame crystal; (d) is the DSC trace corresponding to e and f. The sample was crystallized for 16 h at 68°C.

appear rough on a very fine scale. However, it is apparent from, e.g. Fig. 5a and c, that the thickening process can preferentially follow crystallographic planes through the crystal. Also, the thickened regions usually branch at approximately crystallographic angles, suggesting that the barrier to thickening is lower along certain crystal axes.

It is particularly striking that the thickened material consists, in all cases, of very narrow regions separated either by unthickened material or by voids. The width of these thickened regions seems fairly constant (20–30 nm) and no marked impact of the actual thickening rate or crystallization temperature was found. It is worthwhile speculating about the formation of this characteristic width of the thickened material. As the thickened material exists in a matrix of unthickened material, thickening most probably occurs through a solid state process. Once a nucleus of thickened material is formed, presumably through random fluctuations (very probably facilitated by the highly aggregated, multilayered nature of the crystal population), neighbouring chains have a considerably lower barrier to thickening and may start to unfold along the existing 1F surface. New 2F chains are now adjacent to a 1F surface and able to thicken. However, as the 1F crystal is thicker than the 2F crystal, a reduction in the top surface area of the crystal must occur on thickening, leading either to solid state diffusion of the chains towards the thickened region or to considerable build up of strain in the lattice, or most probably, to a combination of both. It may be that, once some critical lattice strain is reached there is no longer any driving force for unfolding, the reduction in free energy, caused by the reduction in the total surface free energy, is balanced by the increase in free energy due to the higher enthalpy of the strained lattice. In that case unfolding might stop until the lattice strain could be relieved by the diffusion of chains

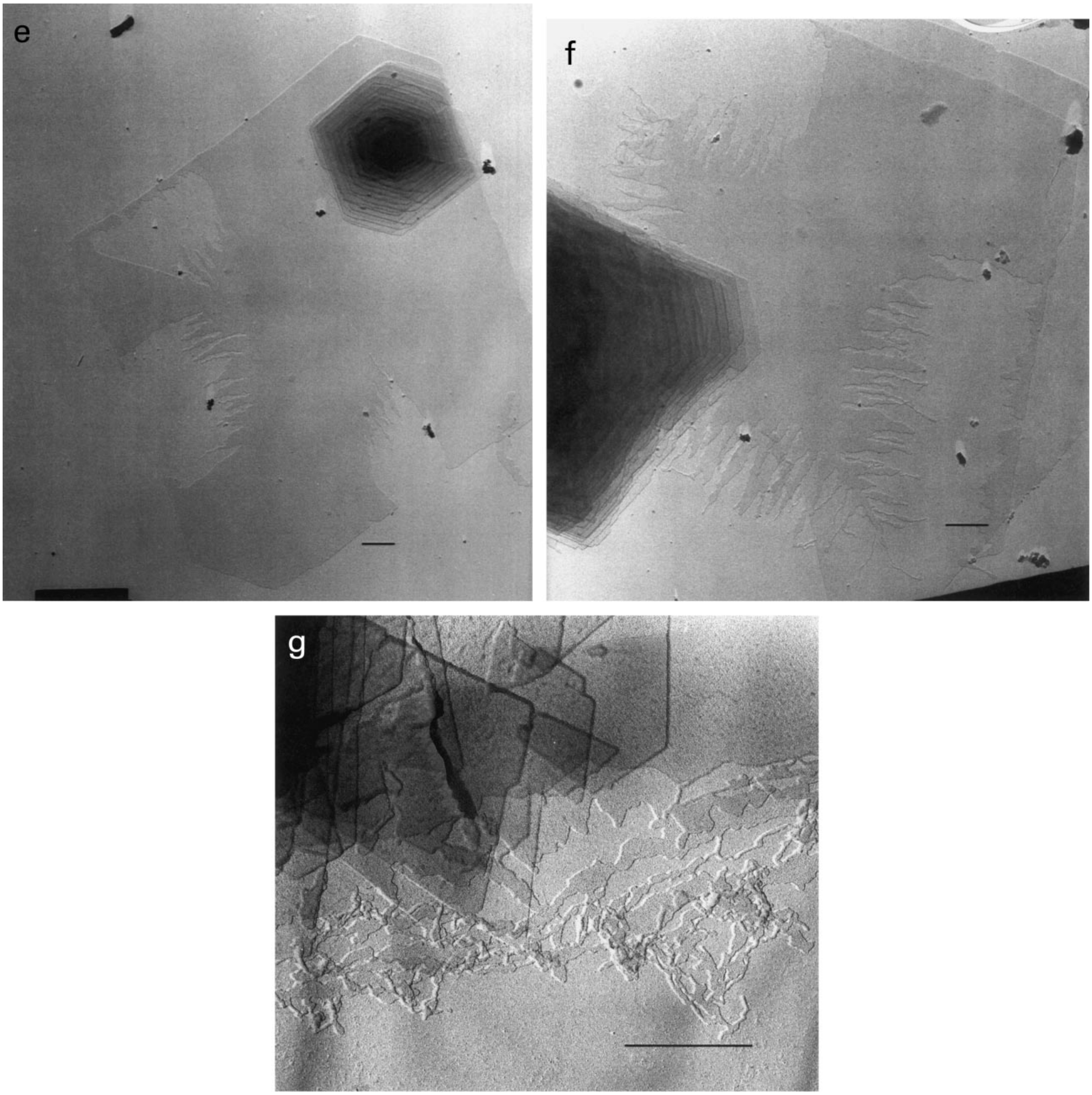

Fig. 7. (e) a thickened truncated lozenge crystal; (f) a slightly higher magnification image of a thickened truncated lozenge crystal in which the dendritic structure of some the thickened material is clearly visible; (g) a higher magnification image showing the dendritic structure of some the thickened material, from a sample crystallized for 16 h at 67°C (the DSC trace is closely similar to that shown in (a)). The scale bars represent 1 μm.

towards the thickened part of the crystal. It might then be easier for a new thickened region to be formed than for the thickening of the initial region to continue in the lateral direction. This would imply that the unfolding is occurring in the planes perpendicular to the thickened lines that we see. From the different angles observed between the thickened regions, it appears that most of the thickening is occurring along 100 planes, and to a lesser extent within 010 and 110 planes. This implies, from the above discussion on the impact of lattice strain on thickening, that chain diffusion within the 100 plane is considerably slower than within the other planes. This may relate to the direction of chain folding, planes containing all the stems of a chain giving a smaller barrier to motion than planes in which adjacent stems usually come from different chains.

One way to approach this problem more rigorously may be to treat it as an example of diffusion limited growth, in which “growth” of the thickened region can only occur by the solid state diffusion of “holes”, i.e. missing stems, away from the thickened nucleus. In this case a dendritic structure might be expected to occur, as is frequently seen in diffusion limited growth, and this would have a characteristic length scale dependent on the coefficient of diffusion. The unthickened crystal matrix will naturally impose a directionality on

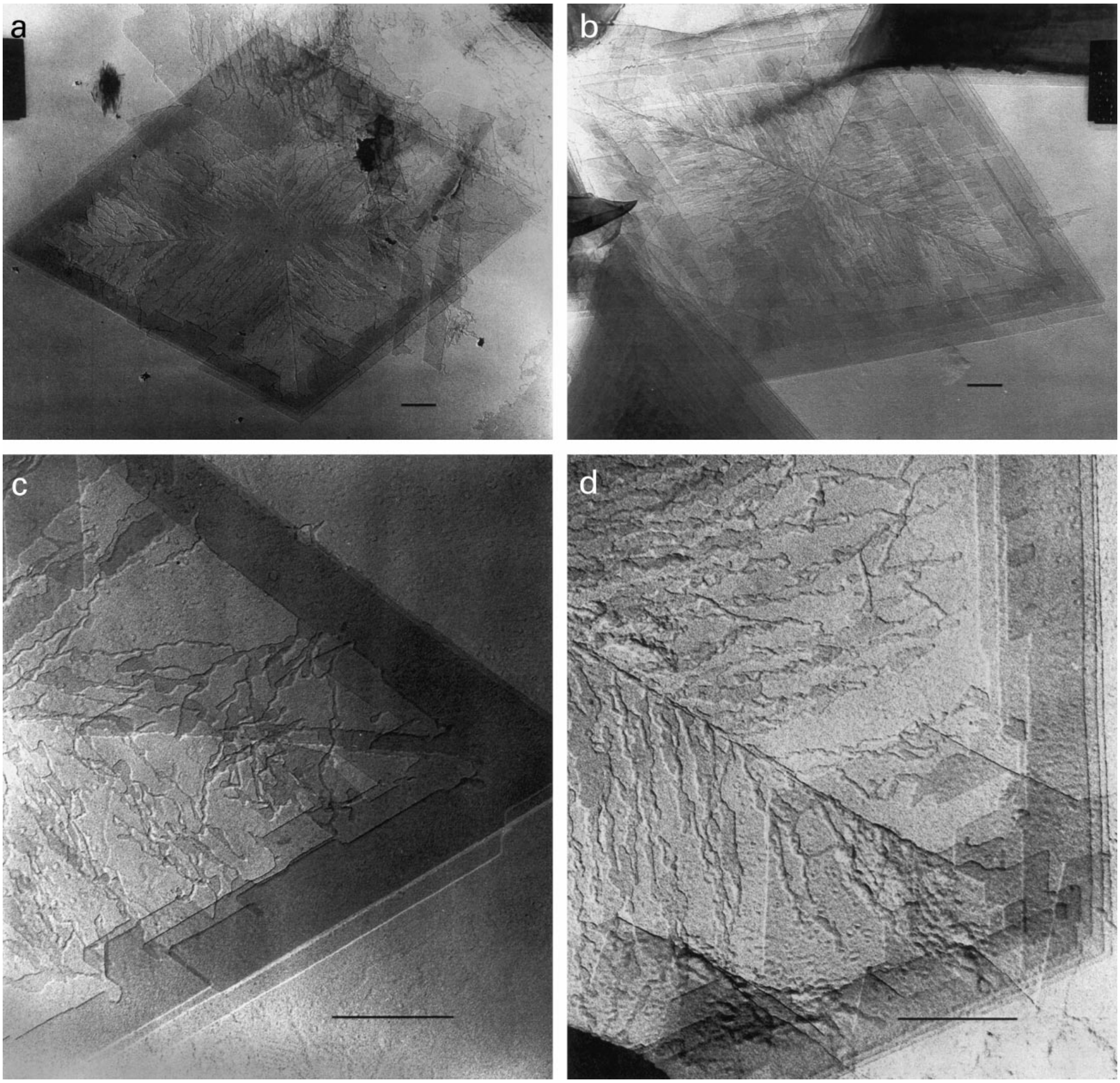

Fig. 8. A series of TEM micrographs showing $C_{294}H_{590}$ crystals thickened from the 3F to the 2F form in glassware. The sample was crystallized at 68°C for 16 h. (a) A thickened lozenge shaped crystal, clearly showing the preferential thickening of the sector boundaries and the "picture-frame" outer rim. (b) Another thickened lozenge shaped crystal, which originally consisted of multiple layers. The preferential thickening of the sector boundaries is again striking. (c) and (d) higher magnification images of parts of thickened lozenge shaped crystals in which both the dendritic structure of the central region and the somewhat irregular, but still crystallographic, structure of the "frame" are clearly visible. The scale bars represent 1 μm.

the diffusion, resulting in the characteristic crystallographic angles observed. However, this explanation might imply a temperature dependent width of the thickened material, as the temperature would strongly influence the diffusion coefficient. This has not been observed. Further work, combining the formalisms of diffusion limited growth with the presence of a crystalline matrix, may prove fruitful in understanding some of the textures observed.

Another important observation regarding the thickening between 2F and 1F forms is that, in a number of cases, small thickened regions entirely surrounded by 2F material are seen. An example is indicated by an arrow in Fig. 5a. This shows that it is possible for the nucleation of a thickened zone to occur away from the edges of the crystal. This is in contrast to the inferences drawn from the thickened morphologies seen for $C_{198}H_{398}$ where it was proposed that thickening initiated at the "tip" of a crystal [17].

In the above we have made the assumption that thickening occurs without the deposition of additional material from the solution. In the case of thickening from 2F to 1F, over the temperature range studied (i.e. several degrees below the temperature at which we believe primary growth to occur in the 1F form), 80–90% of the alkane has crystallized (as measured by the area of the DSC peak on melting) before thickening occurs. After thickening this "crystallinity" increases to 90–95%. We are, at present, doing further work to find if the uncrystallized portion of the 2F material exists as free chains in solution or as dangling cilia, parts of chains the rest of which have crystallized. In either case, the amount of material available to assist in the thickening by crystallizing from the solution is minimal. It is therefore likely that solid state diffusion plays a role in controlling the rate of thickening.

3.3. 3F to 2F thickening

Fig. 6 shows TEM micrographs of 3F (possibly mixed with 2F material that crystallized in that form—see the discussion of the DSC traces above) crystallized in the DSC. Fig. 6a shows the corresponding DSC trace. Fig. 7 shows a set of pictures of thickening between 3F and 2F crystals prepared in the DSC. Fig. 7a shows the DSC trace corresponding to Fig. 7b and c. Fig. 7d shows the DSC trace corresponding to Fig. 7e and f. The crystals shown in Fig. 7e and f have a truncated lozenge form and will be discussed in more detail at the end of Section 3. Fig. 7g shows a close up of a crystal prepared in a similar manner to those shown in Fig. 7e. Fig. 8 shows a series of TEM micrographs illustrating the thickening process observed on transformation from 3F to 2F crystals in glassware. It was found that the morphologies obtained in glassware were considerably clearer than those obtained in the DSC. This was presumably due to the delicate nature of the structures involved (recall that the preparation method for TEM from DSC pans involves vigorous shaking which could disrupt the structure while the preparation method used for glassware does not). In all the samples studied the level of aggregation in the initial crystal population was high, although isolated crystals were occasionally found.

The morphology formed on thickening from the 3F–2F form is strikingly different, in some ways, from that described above for thickening between 2F and 1F forms. It is first worth noting that, in the early stages of growth, thickened crystals were not observed even when both 3F and 2F DSC peaks were present. This implies that the 2F peak was due to thickening on heating although it may be that two crystal populations were present, one of which contained only 3F material and one consisting of 2F material. Secondly, in marked contrast to the 2F–1F case, after thickening no clear case of both 3F and 2F material co-existing in the same crystal was observed. Why this should be is not clear, although we note that the lateral strain induced by 3F–2F thickening is significantly less than that caused by 2F–1F thickening.

The thickened crystals frequently have a very striking morphology, resembling the "picture-frame" crystals found when polyethylene single crystals are allowed to thicken on heating in solution [23,24]. But, in contrast to thickened polyethylene, the centre of the frame contains a dendritic structure resembling the material found on thickening from 2F–1F. This inner dendritic region frequently contains material that has preferentially thickened along the sector boundaries of the parent crystal. Narrow thickened regions can be seen passing from the sector boundaries towards the thickened "frame" roughly following the 110 crystallographic plane. In many cases a characteristic width is apparent, particularly in areas such as that shown in Fig. 8c, again 20–30 nm being typical. However, also in contrast to the 2F–1F case, large expanses of thickened material are present not only in the "frame" regions but also in the central area of many thickened crystals. It may be that the presence of multilayers allows the diffusion of chains not only from within a single lamella but also between adjacent lamellae. This would enable the problems with solid state diffusion limiting lateral dimensions to be overcome. However, a similar level of aggregation was found in the initial population of 2F crystals before thickening to the 1F form, but no large expanses of thickened material were observed without a roughness on the scale of the characteristic width.

Returning to the outer part of the thickened crystal—the "frame"—a number of subsidiary features are apparent. The outer edge of the "frame" is not entirely flat but has frequent steps, sometimes with screw dislocations at the re-entrant corner. The inner edge does not have a consistent nature. In some areas it is flat, in others it resembles the dendritic structure of the central region. The width of the frame varies, which is in marked contrast to the "picture-frame" crystals observed in the non-isothermal thickening of polyethylene in solution [24].

"Picture-frame" crystals have generally been associated with thickening due to a process of melt re-crystallization occurring on heating from the crystallization temperature. Thinner material is thought to dissolve, primarily at the edges of the crystal, although in some cases from the central region [24]. This material is then re-deposited in the more stable, thicker form. The process of dissolution and subsequent re-crystallization continues until the thinner parts of the crystal are entirely replaced. In the case of the alkanes, it is possible that during crystallization, as the concentration is reduced, a sufficiently low concentration is eventually reached such that the 3F crystal form is no longer stable—this was the mechanism suggested to occur in Refs. [16,22]. In this case subsequent growth can only take place in the more extended form. This is, therefore, the isothermal analogy of the non-isothermal situation found in polyethylene. However, this would require the melting temperature to be strongly concentration dependent at low concentrations, which is contrary to our previous observations [4]. This system may be behaving differently from the other alkanes we have studied, but it seems unlikely.

In the present study an alternative mechanism is also possible. As the 3F crystal grows the solution concentration is reduced. After some time a concentration may be reached at which the 3F form is no longer the fastest growing and subsequent growth will be in the 2F form. Growth of the 2F form will then continue in an outwards direction, with further thickening occurring backwards, towards the centre of the crystal, presumably through a solid state mechanism.

Finally, the "picture-frame" morphology may occur as a result of the additional freedom given by the presence of the crystal edge—chains in this area will have considerably more freedom to move, and hence form into energetically favourable crystallographic shapes, giving the flat outer edge observed. From the morphologies alone it is not possible to differentiate between these different possibilities.

3.4. A comment on truncated lozenge shaped crystals

In Figs. 7e, f and 6b we have shown truncated lozenge shaped, three times folded crystals. However, untruncated 2F lozenge shaped crystals are found to grow at higher temperatures, as shown in Fig. 4b. Also, in some cases it appears that it is possible to grow both truncated and untruncated lozenges in the same sample, as seen from comparison of Fig. 6b and c. This is in clear contrast to the behaviour found in polyethylene where the presence of truncated lozenges has been found to be dependent primarily on the absolute crystallization temperature, with progressively larger 100 faces being observed as the crystallization temperature is increased [25]. We have observed similar behaviour in $C_{246}H_{492}$ with truncated lozenges appearing as the temperature of the growth rate minimum between 1F and extended chain crystals is approached. This behaviour is, at first glance, somewhat surprising.

We suggest that the apparently anomalous observation of truncated lozenges may be due to the presence of the growth rate minimum. The temperature dependence of the growth rate of the different crystallographic faces need not be the same—it has been suggested that a difference in the temperature dependence of growth rates on the 100 and 110 faces leads to the observation of 100 faces in polyethylene. It is possible that the exact temperature dependencies and/or depth of the growth rate minimum may be different for the different crystal faces. Hence, as the temperature of the minimum is approached, the growth rate of the 100 face may become slower relative to that of the 110 face until the two growth rates become comparable and both crystal surfaces are seen in the crystal. As the temperature is further increased, and primary growth occurs in the less folded form, the relative growth rates of the different crystal faces may be restored to their previous value and lozenge shaped crystals are again observed.

4. Conclusions

The isothermal thickening of $C_{294}H_{590}$ in dilute solution has been studied by both electron microscopy and DSC. For the electron microscopy study, samples were prepared in DSC pans to allow direct comparison with previous DSC studies and in order to obtain a full understanding of the samples' thermal histories and crystallization behaviour before the morphologies were examined. Although the morphologies were not always as clear as those of crystals prepared using conventional techniques in glassware, it has allowed us to make a rigorous connection between the different experimental techniques.

Different crystal morphologies have been observed when thickening occurs between different folded forms. On thickening from twice-folded to once-folded crystals, the initial crystal shape is lost and a fine, dendritic structure results in which the thickened regions, with a characteristic width of 20–30 nm, exist in a surrounding matrix of unthickened material. We have suggested that the characteristic width is caused by the interplay of solid state diffusion and the lattice strain caused by the reduction in top surface area. At lower temperatures, when thickening occurs from three times folded to twice-folded forms, the initial lozenge shape of the three-times folded crystals is maintained after thickening, "picture-frame" crystals are formed, but with a fine web of thickened material within the frame.

The observation of rough, dendritic type, thickened crystals in both of the cases studied, is in marked contrast to the behaviour found on the thickening of $C_{198}H_{398}$ between once-folded crystals and extended crystals. In that latter case the thickened morphology frequently consisted of aggregates of 110 lozenge type crystals interconnected by narrow regions, usually with straight, crystallographic edges. It has therefore not been possible to draw direct parallels between the different thickened morphologies found in the present work and in the previous study. The relation between the present study and the previous work on $C_{198}H_{398}$ will be discussed in more detail in a subsequent publication in the light of further results on the thickening of $C_{246}H_{492}$ between 1F and extended crystal forms [18].

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References

[1] Ungar G, Steyny J, Keller A, Bidd I, Whiting MC. The crystallization of ultralong normal paraffins: the onset of chain folding. Science 1985;229:386.

[2] Ungar G, Keller A. Inversion of the temperature dependence of crystallization rates due to onset of chain folding. Polymer 1987;28:1899.

[3] Organ SJ, Ungar G, Keller A. Rate minimum in solution crystallization of long paraffins. Macromolecules 1989;22:1995.

[4] Hobbs JK, Hill MJ, Keller A, Barham PJ. Experimentally determined

temperature–concentration phase diagrams of monodisperse alkanes with chains containing between 100 and 200 carbons. J Polym Sci B: Polym Phys 1999;37:3188.

[5] Zeng XB, Ungar G. Lamellar structure of non-integer folded and extended long-chain *n*-alkanes by small-angle X-ray diffraction. Polymer 1998;39(19):4523.

[6] Boda E, Ungar G, Brooke GM, Burnett S, Mohammed S, Proctor D, Whiting MC. Crystallization rate minima in a series of *n*-alkanes from $C_{194}H_{390}$ to $C_{294}H_{590}$. Macromolecules 1997;30(16):4674.

[7] Sutton SJ, Vaughan AS, Bassett DC. On the morphology and crystallization kinetics of monodisperse polyethylene oligomers crystallized from the melt. Polym Commun 1996;37(25):5735.

[8] Alamo RG, Mandelkern L, Stack GM, Kröhnke C, Wegner G. Crystallization kinetics of long-chain *n*-alkanes from the melt and from solution. Macromolecules 1994;27:147.

[9] Stack GM, Mandelkern L, Stack GM, Kröhnke C, Wegner G. Melting and crystallization kinetics of a high molecular weight *n*-alkane: $C_{192}H_{386}$. Macromolecules 1989;22:4351.

[10] Alamo RG, Mandelkern L, Stack GM, Kröhnke C, Wegner G. Isothermal thickening of crystals of high molecular weight *n*-alkanes. Macromolecules 1993;26:2743.

[11] Cheng SZD, Zhang A, Chen J, Heberer DP. Nonintegral and integral folding crystal growth in low-molecular mass poly(ethylene oxide) fractions. I. Isothermal lamellar thickening and thinning. J Polym Sci: Part B: Polym Phys 1991;29:287.

[12] Cheng SZD, Chen J, Zhang A, Heberer DP. Nonintegral and integral folding crystal growth in low-molecular mass poly(ethylene oxide) fractions. II. End-group effect: α,ω-methoxy-poly(ethylene oxide). J Polym Sci: Part B: Polym Phys 1991;29:299.

[13] Cheng SZD, Chen J. Nonintegral and integral folding crystal growth in low-molecular mass poly(ethylene oxide) fractions. III. Linear crystal growth rates and crystal morphology. J Polym Sci: Part B: Polym Phys 1991;29:311.

[14] Buckley CP, Kovacs AJ. Chain folding in polymer crystals: evidence from microscopy and calorimetry of poly(ethylene oxide). In: Hall IH, editor. Structure of crystalline polymers, London: Elsevier, 1984.

[15] Weeks JJ. Melting temperature and change of lamellar thickness with time for bulk polyethylene. J Res Natl Bur Stand US 1963;67A:441.

[16] Ungar G, Organ SJ. Isothermal refolding in crystals of long alkanes in solution 1. Effect of surface self-poisoning. J Polym Sci Part B: Polym Phys 1990;28:2353.

[17] Organ SJ, Ungar G, Keller A. Isothermal refolding in crystals of long alkanes in solution. II. Morphological changes accompanying thickening. J Polym Sci Part B: Polym Phys 1990;28:2365.

[18] Hobbs JK, Hill MJ, Barham PJ. Polymer (submitted for publication).

[19] Hobbs JK, Hill MJ, Barham PJ, Dosière M. In preparation.

[20] Brooke GM, Burnett S, Mohammed S, Proctor D, Whiting MC. Versatile process for the syntheses of very long chain alkanes, functionalised derivatives and some branched chain hydrocarbons. J Chem Soc-Perkin Trans 1 1996;13:1635.

[21] Organ SJ, Barham PJ, Hill MJ, Keller A, Morgan RL. A study of the crystallization of the *n*-alkane $C_{246}H_{494}$ from solution: further manifestations of the inversion of crystallization rates with temperature. J Polym Sci B: Polym Phys 1997;35:1775.

[22] Morgan RL, Barham PJ, Hill MJ, Keller A, Organ SJ. The crystallization of the *n*-alkane $C_{294}H_{590}$ from solution: inversion of crystallization rates, crystal thickening, and effects of supersaturation. J Macromol Sci, Phys 1998;37:319.

[23] Keller A, Bassett DC. Complementary light and electron microscope investigations on the habit and structure of crystals with particular reference to long chain compounds. J R Microsc Soc 1960;79:243.

[24] Blackadder DA, Scheinitz HM. The dissolution and recrystallization of polyethylene crystals suspended in various solvents. Polymer 1966;7:603.

[25] Organ SJ, Keller A. Solution crystallization of polyethylene at high temperatures. Part 1 Lateral crystal habits. J. Mater Sci 1985;20:1571.