A Real-Time Wide-Angle X-ray Scattering Study of Crystal Thickening in Ultralong Alkanes

A. E. Terry,[†] T. L. Phillips,[‡] and J. K. Hobbs*,[‡]

European Synchrotron Radiation Facility (ESRF), BP220, F-38043 Grenoble, France, and H.H. Wills Physics Laboratory, University of Bristol, Tyndall Ave., Bristol, UK BS8 1TL

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ABSTRACT: Ultralong alkanes crystallize into lamellae with a thickness that is an integer fraction of the extended chain length. On heating, they unfold or thicken to approach the equilibrium, extended chain form. Using high-resolution in-situ wide-angle X-ray scattering, carried out at the European Synchrotron Radiation Facility (ESRF), Grenoble, it has been shown that this thickening is accompanied by a contraction of the lattice, a contraction accompanying each thickening event between each integer folded crystal thickness. Prior to thickening, there is an increase in disorder, as measured by the change in peak width. In extended chain alkanes with the same crystal thickness the lattice simply expands thermally before melting.

Introduction

Polymer lamellar thickening has been the subject of intensive study, and considerable controversy, since it was first reported in the 1950s.[1,2] In almost all situations polymers crystallize into lamellae with a thickness that is considerably thinner than the equilibrium, extended chain thickness. This thickness is dependent on the crystallization temperature and is due to the kinetics of the crystallization process—the quickest way to consume the available free energy is by the formation of fast growing thin crystals rather than slow growing thick crystals. After crystallization the resulting lamellae are metastable with respect to thicker crystals and will undergo a process of reorganization if this is not prohibited by the constraints placed on them by their environment. In the case of some polymers, such as polyethylene, this reorganization can occur at the initial crystallization temperature, while in other polymers, annealing must be carried out at higher temperatures. In all cases, the higher the annealing temperature, the higher the ultimate thickness that can be obtained. The extent to which the thickening process occurs by solid-state reorganization of the parent crystals, or melting and recrystallization into thicker crystals, is still a matter of discussion and probably depends on the polymer in question and the annealing temperature.

Recent studies have pointed to the possible role of mobile phases, such as the hexagonal phase in polyethylene, in enabling the thickening process to occur.[3] Computer simulations have also been used to address these issues, although this is still hampered by the cooperative nature of the process and therefore the requirement for a large simulation size.

It has been known since the early 1970s[4] that the thickness of polyethylene lamellae can have some influence on the lattice parameters of the unit cell, with a tendency toward higher density at larger crystal thicknesses. Further studies of this effect are hindered in the case of high polymers by the polydispersity of the materials. Polymers are mixtures of chains of different lengths, and this lack of purity is likely to lead to a higher level of defects than would occur in a pure system. This gives a very strong dependence of structure on the age of the crystal and the way in which it was crystallized.

During the past two decades ultralong monodisperse alkanes, with chain lengths up to 390 carbons, have become available.[5,6] These materials, which are model substances for low molecular weight polymers, have provided many new insights into polymer crystallization in general and polyethylene crystallization in particular.[7−12] From the earliest studies[5] it became apparent that, due to the monodispersity of the materials, the thickness of lamellar crystals formed are always an integer fraction of the extended chain length (allowing for any chain tilt), such that the polymers always crystallize in the extended chain form or fold exactly in half (once-folded), or in three (twice-folded), etc. This behavior means that, when the alkanes are crystallized at a particular temperature, the entire lamellar population has very closely the same thickness and stability. The use of such an ultrapure system to study the impact of thickness on lattice parameters removes many of the problems inherent to polymers, while maintaining the most important characteristic of chain length.

In this paper we present a wide-angle X-ray diffraction (WAXD) study using the high-resolution time-resolved capabilities of the ESRF to investigate the effect of chain folding and unfolding on lattice parameters in a series of ultralong alkanes.

Experimental Details

Alkanes were synthesized by Dr. G. Brooke[6] and provided by the Engineering and Physical Sciences Research Council of the UK.

Five alkanes with different chain lengths were studied: $C_{102}H_{206}$, $C_{122}H_{246}$, $C_{198}H_{398}$, $C_{246}H_{494}$, and $C_{294}H_{590}$. Both $C_{102}H_{206}$ and $C_{122}H_{246}$ can only be obtained in the extended chain form under usual crystallization conditions. All the other alkanes undergo chain folding under some crystallization conditions. Samples were prepared in a Perkin-Elmer differential scanning calorimeter (DSC) 7. A small quantity of the alkane was placed in an aluminum DSC pan and toluene added to a concentration in the range 1−5% (the w/w concentration being determined). The sample was then heated in the DSC to

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[†] ESRF.

[‡] University of Bristol.

* Corresponding author: e-mail jamie.hobbs@bristol.ac.uk.

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Table 1. Ideal Crystal Thickness for the Different Alkane Samples Studied, Assuming Six Carbons per Fold

alkane sample	crystal thickness, nm
$C_{102}H_{206}$ extended	13.2
$C_{122}H_{246}$ extended	15.7
$C_{198}H_{398}$ extended	25.4
$C_{198}H_{398}$ once-folded	12.0
$C_{246}H_{494}$ extended	31.52
$C_{246}H_{494}$ once-folded	15.1
$C_{294}H_{590}$ once-folded	18.2
$C_{294}H_{590}$ twice-folded	11.2

dissolve the alkane and cooled to the crystallization temperature. Once crystallization was complete, the sample was reheated and a dissolution endotherm recorded. The temperature at which dissolution occurred was used to determine the thickness of the crystals, in line with previous studies of these materials that have been confirmed through the use of Raman longitudinal acoustic mode (LAM) and small-angle X-ray scattering. The process was then repeated, but rather than redissolving the sample after crystallization, it was cooled to room temperature. Table 1 shows the samples used and the crystal thicknesses assuming six carbons per fold. (These thicknesses agree well with the thicknesses measured on similarly prepared crystals using Raman LAM and small-angle X-ray scattering.)

Each sample was extracted from its DSC pan, the toluene allowed to evaporate at room temperature, and the resulting single-crystal powder transferred into 0.5 mm glass Lindemann tubes. The Lindemann tubes were mounted in a silver block Linkam hot stage and heated from 40 to 140 °C at 2 °C/min. The wide-angle diffraction data were collected at the Materials Science beamline ID11 at the ESRF. The X-ray wavelength was 0.375 Å. The beam size was 300 μm × 300 μm. Data were collected using the Frelon CCD camera attached to an image intensifier. Each frame was collected for 5 s. The sample−detector distance was 0.55 m. The resulting 2-D data were corrected for spatial distortions prior to integration.

The peak positions, full width at half-maximum (fwhm), and total intensity were obtained by fitting a pseudo-Voigt to the 1-dimensional integrated data. The temperature of a thermocouple placed at the end of the Lindemann tube was recorded simultaneously. However, as the melting temperature of the alkanes is well-known from DSC experiments, the actual sample temperature could be calibrated.

The absolute sample−detector distance for the wide-angle data was not calibrated for each individual sample, as it was suspected that mixing a calibrant (such as silicon) with the sample might change the behavior of the alkane when passing through a transition. In particular, if there is melting and recrystallization in the presence of a crystalline calibrant, that calibrant might act as a nucleating site for the alkane through epitaxy, possibly distorting the lattice of the alkane. As no calibrant was used, there could be an error of ±0.5 mm in the sample−detector distance, leading to an error in absolute d spacing of 0.005 Å. This uncertainty leads to difficulty when comparing absolute lattice parameters between different samples. However, within each individual temperature run the sample was not moved, giving a relative accuracy of 0.0001 Å, largely arising from the error in the peak fitting.

Results

Figure 1 shows the variation in the a and b cell parameters with temperature for four extended chain alkanes, as calculated from the positions of the (110) and (200) reflections. The coefficients of thermal expansion derived from these data are, for the a-axis, 4×10^{-3} Å/°C and, for the b-axis, -3×10^{-4} Å/°C. Just prior to melting, the cell parameters drop due to an increase in the error as the peak intensity rapidly drops to zero, reducing the accuracy of the peak-fitting routine.

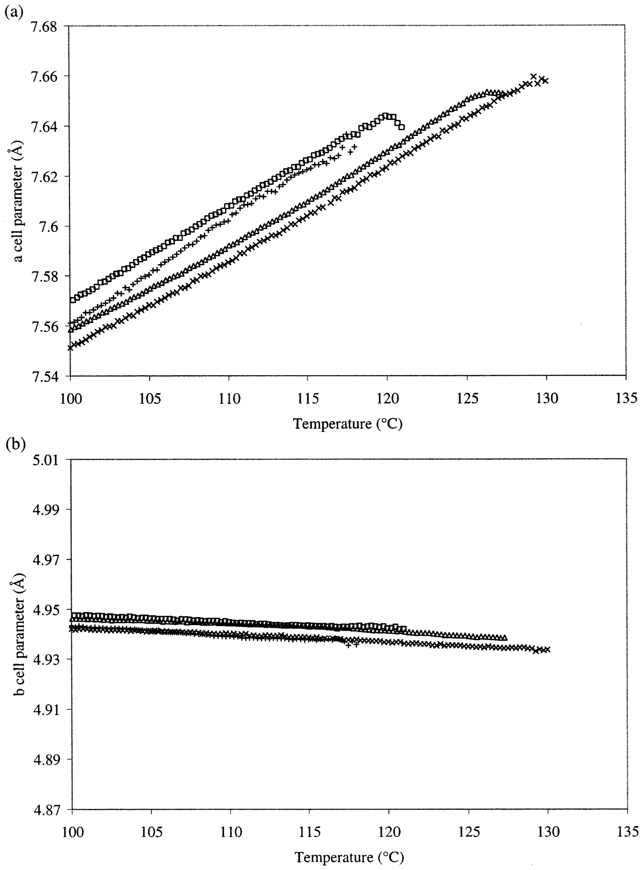

Figure 1. Variation in the (a) a and (b) b cell parameters (as calculated from the positions of the (110) and (200) reflections) with temperature for four extended chain alkanes: +, $C_{102}H_{206}$; □, $C_{122}H_{246}$; △, $C_{198}H_{398}$; ×, $C_{246}H_{494}$.

Figure 2 shows the variation in the cell parameters, again calculated from the (110) and (200) reflections, with temperature for three different once-folded alkanes. In each case there is a sharp transition in which the a cell parameter decreases before the sample melts. We associate this with a transition from once-folded crystals to extended chain crystals.

Figure 3 shows the variation in peak intensity of the (110) reflection with temperature for each of the once-folded samples. For all the samples there is a gradual reduction in intensity over the course of the experiment, most probably associated with a reduction in scattering due to increased thermal motion. For the $C_{198}H_{398}$ there is a slight further reduction in intensity just prior to the transition from once-folded to extended chain crystals, followed by a recovery. Finally, the intensity drops to zero as the sample melts. In the case of $C_{246}H_{494}$ there is a more pronounced drop in intensity prior to the transition, followed by a recovery. For $C_{294}H_{590}$ there is a reduction in intensity of approximately 95% at the temperature of the transition from once-folded to extended crystals, followed by a small recovery in the intensity. We associate the drop in intensity with the partial melting (and partial recrystallization) of the crystal population, although there may also be some reduction in intensity due to an increased disorder in the crystalline lattice. In the case of $C_{294}H_{590}$ there is almost a complete melting of the original crystal population, which contrasts with the $C_{198}H_{398}$ where there is very little melting associated with the transition.

Figure 4 shows the variation in the fwhm of the (110) reflection with temperature as each of the once-folded

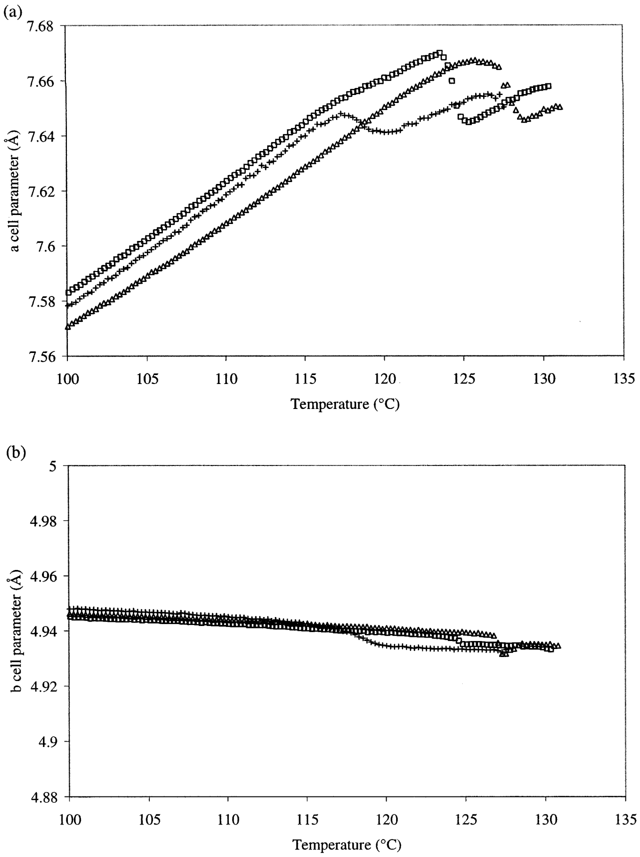

Figure 2. Variation in the (a) *a* and (b) *b* cell parameters with temperature for three once-folded alkanes: +, $C_{198}H_{398}$; □, $C_{246}H_{494}$; △, $C_{294}H_{590}$.

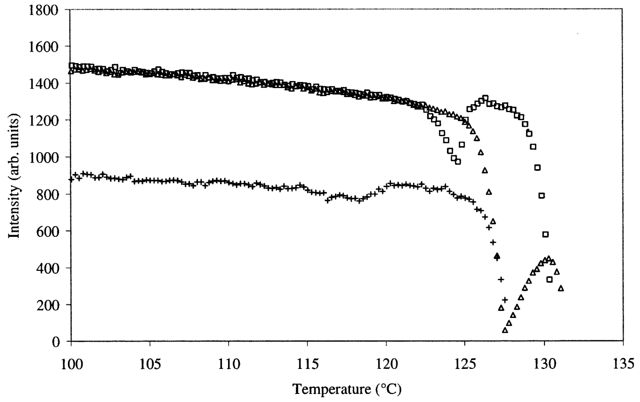

Figure 3. Variation in peak intensity with temperature of the (110) reflection for each of the once-folded samples: +, $C_{198}H_{398}$; □, $C_{246}H_{494}$; △, $C_{294}H_{590}$.

alkanes is heated. In the case of $C_{198}H_{398}$ and $C_{246}H_{494}$ the fwhm increases gradually from approximately 20 °C below the temperature of the transition. At the point at which the lattice contracts, the fwhm drops back to the same value as at lower temperatures. In $C_{294}H_{590}$ the fwhm remains constant until just before the transition temperature, when there is perhaps a small increase. At the point at which the intensity drops, there is a peak in the fwhm, most probably due to an increase in the error in this measurement due to the poor statistics. After the transition, once the intensity has increased somewhat, the fwhm returns to its original value. In the case of the originally extended chain crystals the fwhm remains constant at this same, lower, value (data not shown).

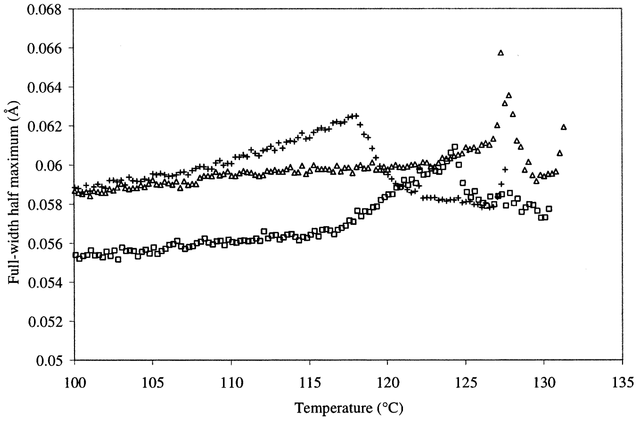

Figure 4. Variation in full width at half-maximum (fwhm) with temperature of the (110) reflection for each of the once-folded alkane crystals: +, $C_{198}H_{398}$; □, $C_{246}H_{494}$; △, $C_{294}H_{590}$.

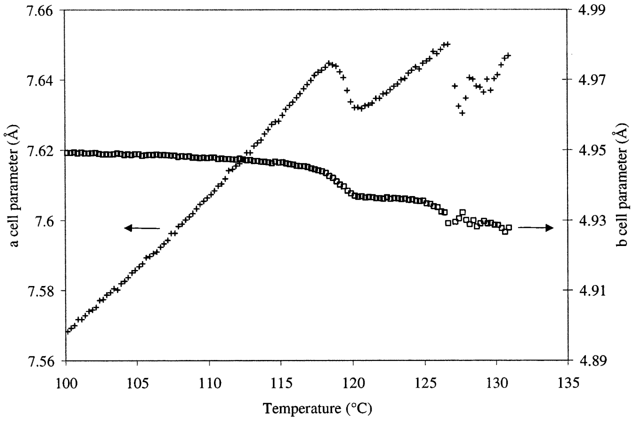

Figure 5. Variation in the *a* and *b* cell parameters for $C_{294}H_{590}$ twice-folded crystals. The left-hand axis refers to the *a* cell parameter and the right-hand axis to the *b* cell parameter. +, $C_{294}H_{590}$ *a*; □, $C_{294}H_{590}$ *b*.

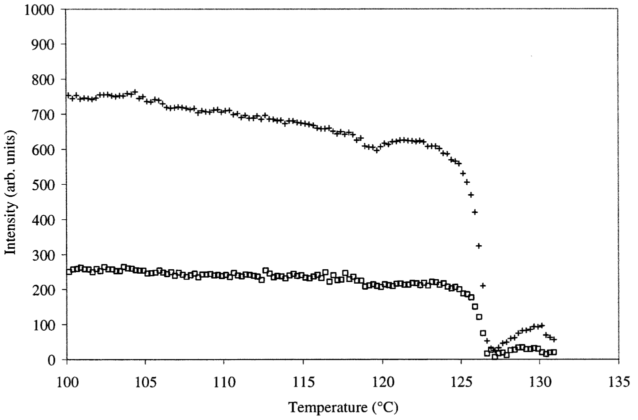

Figure 6. Change in intensity upon heating twice-folded $C_{294}H_{590}$: +, $C_{294}H_{590}$ (110) reflection; □, $C_{294}H_{590}$ (200) reflection.

Figure 5 shows the variation in the cell parameters with temperature for $C_{294}H_{590}$ twice-folded crystals, in which there are two transitions—from twice-folded to once-folded and from once-folded to extended chain crystals.

Figure 6 shows the corresponding change in intensity for the (110) reflection, showing that the intensity remains approximately constant until the transition from once-folded to extended chain crystals, when there is a sharp drop followed by a small recovery, in a manner

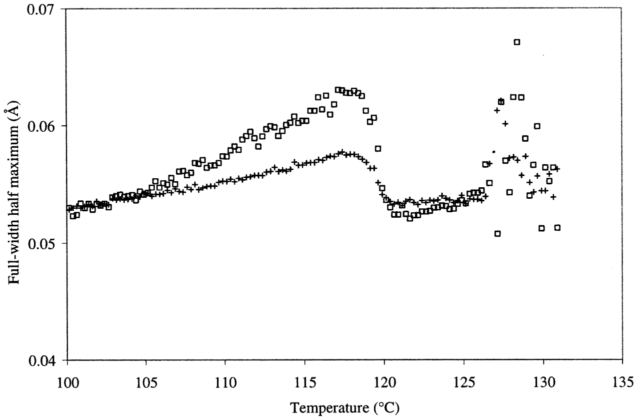

Figure 7. Change in the full width at half-maximum upon heating twice-folded $C_{294}H_{590}$: +, $C_{294}H_{590}$ (110) reflection; □, $C_{294}H_{590}$ (200) reflection.

similar to that seen when the initially once-folded $C_{294}H_{590}$ transformed into extended chain crystals.

Figure 7 shows the change in fwhm for the (110) reflection. Here the transition from twice-folded to once-folded is preceded by a slow increase in the fwhm, similar to that seen when the shorter alkanes thicken from once-folded to extended chain crystals, while on thickening from once-folded to extended chain this proceeds in a manner similar to that seen when the initial crystal population was once-folded.

Discussion

The data presented above provide three separate but interrelated sets of information. First, as expected, the lattice expands on heating due to the increased thermal motion of the chains. In the case of the extended chain crystals, which are already close to equilibrium (at least with respect to size), this is all that happens. Second, if the crystals consist of folded chains, the thickening of these crystals that occurs on heating is accompanied by a contraction in the crystal lattice. This contraction is very striking, particularly in the case of $C_{294}H_{590}$ where it occurs on the transition both from twice-folded to once-folded crystals and at the transition from once-folded to extended chain crystals. This is the first time that such a transition has been followed in real time using WAXD. The contraction of the lattice that accompanies unfolding is superimposed on top of the thermal expansion. Finally, prior to this contraction, there is an increase in the fwhm of each of the crystal Bragg peaks over a temperature range of several degrees, which can be associated with either an increase in local strain in the crystals or a reduction in crystal size in the lateral direction.

The use of different alkanes with different crystal thicknesses and numbers of folds within the crystal enables us to assert with confidence that the contraction in the lattice is due to the thickening process. The fact that the alkanes, due to their strict monodispersity, form crystals with only a few closely defined thicknesses enables this contraction to be seen much more clearly than it is in polyethylene. In polyethylene a range of different crystal thicknesses may be present, and the thickening process generally occurs over a wider range of temperatures, smearing out any steplike effect that may exist.

The principal question, therefore, is why is there a contraction of the lattice on thickening? Two possible reasons for the difference in lattice parameters for crystals of different thicknesses present themselves. One possibility is that the presence of folds at the surface of the crystals expands the lattice either throughout the crystal or else just in the region close to the fold surface. So it is the relatively bulky folds, and the interaction between adjacent folds, that causes the expansion. Another possibility is that it is simply the presence of surfaces that are causing an expansion of the lattice, again either throughout the crystal or else in the surface region only. Indeed, it might be the methyl groups at the end of the chains that are causing the expansion, but this seems unlikely, as the number of methyl groups per unit volume of crystal is always a constant in these monodisperse materials. From the current data set it is not possible to determine between these possibilities as the absolute calibration is not sufficiently good to enable comparison between different samples and therefore between crystals with the same thickness but different numbers of folds. Obtaining such data is the subject of a current research project.

In both of the above possibilities, it could be either the whole of the crystal that has an expanded lattice or just the surface region. Which of these is occurring has some interesting implications for our understanding of polymer crystallization. Polymer crystals are unique in that each molecule is involved in multiple lattice sites as it passes through the thickness of the crystals. Also, a unique direction exists, the chain direction, which is approximately perpendicular to the crystal surface. This means that, although the surface of the crystal might expand, the difference in density between the core of the crystal and the surface can only easily be relieved by introducing defects that pass through the whole crystal. We might envisage a crystal that is made up of bundles of chains like old-fashioned wheat sheaves, in which the chains are closer together in the core than at the surface. For a thicker crystal, the percentage of the lattice sites that are in the more expanded surface region will be smaller than for the thinner crystal, assuming that the important parameter is the proximity of a particular site to the surface. Therefore, the average lattice spacings will become slightly smaller as the crystal becomes thicker. In this case the small energy penalty associated with the expanded lattice in the near surface region can be regarded as being part of the surface energy of the crystal. Some evidence for such a granular structure exists from, for example, AFM data.[13]

Another possibility is that it is not favorable to have a variation in lattice spacing through the thickness of the crystal. Instead, the whole of the crystal is slightly expanded due to the presence of the surface and the connectivity of the chain through the thickness of the crystal. This removes the necessity of having defect lines through the crystal as the “wheat sheaves” pack together—the energy penalty is effectively smeared through the whole crystal. In this case it is unclear whether the increase in free energy associated with the expansion of the lattice (when compared to the equilibrium, extended chain case) should be associated with the surface free energy of the crystal or whether it is a “bulk” effect. This has implications for the interpretation of a Gibbs–Thomson type presentation of thickness vs melting point data, as the splitting of the free energy of the crystal into a bulk and a surface term is not simple when the thickness of the crystal impacts upon the entire lattice structure.

The increase in the fwhm as the unfolding temperature is approached can give us a further insight into what is occurring on a molecular level during unfolding. The fwhm can indicate the extent of the lattice, that is, the crystal size, or it could be an indication of the presence of two crystal populations with slightly different lattice spacings. The increase in fwhm prior to thickening is not due to the superposition of the thickened lattice and the unthickened lattice as this would lead to a gradual shifting in the peak position with increasing temperature, matching the increase in fwhm, rather than the rapid change that is seen. So, if it is due to a superposition of peaks, it is most likely occurring in the same crystal, for instance due to local strains as chain ends are pulled through the lattice. The excursion of chain ends into the crystal is likely to be a thermally activated process, and it is hard to see why this does not occur in the extended chain crystals, despite their ultimate stability, if this is responsible for the change in fwhm.

Morphological studies[14] have shown that alkane single crystals thicken through a nucleation and growth process that appears to be mediated by the presence of side surfaces. Thickening occurs preferentially at edges, and holes move through the crystal, leaving a wake of thickened material behind them.[15] This leads to an initially dendritic thickened crystal structure, with relatively small lateral dimensions. However, if it were this small crystal size effect that was causing the increase in fwhm, a shift in the peak position would be expected at the same time, as the reduction in crystal size accompanies thickening rather than preceding it. The unfolding process is likely to be accompanied by the formation of defects due to the change in thickness but conservation of crystal volume. The crystal structure will be disrupted in the vicinity of the defect, contributing to an increase in the fwhm. We suggest that thickening occurs gradually, over a fairly wide temperature range, but that the lattice contraction only occurs once the majority of the material has thickened, and there are large, continuous expanses of thickened crystal that can then relax into this more perfect structure.

By monitoring the intensity of the peaks as a function of temperature, an insight into the change in crystallinity can be gained. As the samples are heated, there is a gradual reduction in intensity as expected. However, at the temperature of the transition, the effects are much more dramatic. In the case of the unfolding of $C_{198}H_{398}$ from once-folded to extended, and the unfolding of $C_{294}H_{590}$ from twice-folded to once-folded, there is little reduction in intensity, implying that the transition is primarily solid state in nature, or at least any melting is very localized. The other transitions are accompanied by much more pronounced reductions in intensity, showing that there is considerable melting prior to thickening. This difference in behavior most probably reflects the different barrier heights in the different cases due to the different thickness differences (and possibly due to differences in the initial thickness of the crystals, prior to thickening).

Conclusions

A rapid contraction of the crystalline lattice has been shown to occur as ultralong, monodisperse alkanes undergo a transition between different integer folded forms on heating. This contraction of the lattice occurs in all the materials studied, despite apparently different routes being taken between the pre- and post-transition crystal forms. The different lattice parameters can therefore be associated with a particular crystal thickness and fold surface density.

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