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The identification of the initial lamellar thickness of polyethylene crystals grown from the melt using synchrotron X-radiation

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The lamellar thickness of a sharp fraction of linear polyethylene has been monitored during crystallization at 128.5° C at very short crystallization times (30 sec to 30 min) using low angle X-ray diffraction (LAXD) by using the powerful synchrotron source at Daresbury. The observed thickness is much lower than expected and does not change with time. The same sample showed two Raman longitudinal accordion modes (LAM), one corresponding to the lamellar thickness observed by LAXD and the other to a much larger thickness. From these, and further parallel experiments using Raman spectroscopy, differential scanning calorimetry and electron microscopy we deduce that the lamellae as initially formed are much thinner than previously expected, that they first thicken by a single, large step—to the usually reported values for melt crystallized polyethylene—and only then do they exhibit a continuous increase in thickness with time corresponding to the isothermal thickening as reported in previous work.

1. Introduction

In the present paper, fourth of the current set of publications on chain folded crystallization, we shall turn our attention again to the crystallization as occurring in melts, where by abundant past evidence [1, 2] isothermal thickening is prominent, as opposed to crystallization from solutions where, as we have just seen (in Parts 1–3 [3–5]), it is either absent or negligible, and we shall scrutinize the previously obtained values for the unthickened primary fold length. First, however, the background will be briefly recapitulated.

As familiar, the principal entity of a crystalline polymer is the lamella with its associated chain folded structure characterized by the lamellar thickness, l, which in molecular terms is identical with, or closely related to, the fold length. l is determined in the first place by the temperature at which the crystals have formed (T_c), or more precisely by the supercooling ΔT, where $\Delta T = T_m^0 - T_{cr}$, or $T_d^0 - T_{cr}$; where T_m^0 and T_d^0 represent the melting or dissolution temperature of the infinitely extended crystal according to whether crystallization takes place from melts or solutions. It is known further that l can increase after the primary crystallization. In the first and best documented cases such lamellar thickening, and the associated fold length increase on the molecular level, takes place when crystals already formed are heated beyond their original crystallization temperature [6, 8]. This source of lamellar thickening is termed annealing and applies both for lamellae crystallized from the melt and from solution. There is no completely unique description of the time dependence of such lamellar thickening as both sudden jumps, sometimes by a factor close to 2, and steady continuous increases have been reported, the latter continuing indefinitely or stopping at a constant terminal value. Whatever the complete picture there is an essential

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consensus that a continuous logarithmic increase with time, with the rate of increase depending on the annealing temperature, is at least a significant and frequent component of the annealing process. To quote a typical figure for the latter, in the case of polyethylene an increase of l from about 20 to about 50 nm will occur after annealing for a day at about 130° C.

Soon after the recognition of the above annealing phenomenon, fold length increase was recognized also under different circumstances, namely as occurring isothermally during crystallization itself [1,2]. Such "isothermal thickening" has been observed in definitive terms so far only for crystallization from the melt. Its intrinsic interest apart the mere possibility of such isothermal thickening has significant consequences for the studies of chain folded crystallization in view of the fact that it prevents an unambiguous assignment of l_g^* (the primary l value of crystals as formed) to a given T_c or ΔT, as the measurement of any l value on its own does not distinguish between that portion of l which has formed initially (l_g^*) and between that which has arisen through subsequent thickening. In the usual polydisperse material the issue is further obscured by the possibility of segregation during crystallization by molecular weight, there being a different supercooling and hence an l_g^* value and possibly a subsequent isothermal thickening rate for each species.

At this point the following two fold issue arises. First and foremost the knowledge of l_g^* is fundamental for the description and understanding of the chain folding process and its prediction is the prinicipal test of all theories. The assertion that l_g^* depends on T_c or ΔT itself relies on the knowledge of the true l_g^*. For this, any contribution of isothermal thickening to the measured l value, if and when it occurs, has to be identified. Secondly the thickening process in itself is of major interest as being one of the most remarkable features of macromolecular behaviour in general and in determining the final crystal texture (lamellar thickness) of a crystalline polymeric material. A major programme in our laboratory is being devoted to these issues embracing crystallization both from melt and solutions (the subject of three preceding publications [9–11]), in an attempt to place our knowledge on chain folding on a firm basis. The full programme is aimed at unifying our picture of the two hitherto disparate aspects of lamellar crystallization, namely that from the melt and solution. The present paper will be concerned with crystallization from the melt rectifying some recently announced results [9–11] with what we feel are wider reaching consequences.

In the previous works [9–11] which we shall now partly rectify, we announced the attainment for the first time the true l_g^* values in the melt crystallization of polyethylene and this as a function of crystallization temperature (T_c). To accomplish this we had to record l values during crystallization from as early stages as possible in order to minimize and alternatively to identify the contribution of isothermal thickening. This enabled us to extrapolate the measured l values to zero crystallization time which should represent l_g^*. To achieve this we had to obtain substantial amount of crystal at as short crystallization times as possible, so as to ensure detectability and sufficient accuracy in the extrapolation of l. As for a given ΔT, hence T_c, the crystal growth rate is uniquely determined, and thus unalterable, we had to create a large number of nucleating centres in order to have a sufficient amount of crystal after a given short time. This we realized by the newly discovered "enhanced self nucleation technique" relying on a large number of residual nuclei at temperatures only slightly exceeding the optical melting point. These acted as centres for crystallization on subsequent cooling, without however influencing the resultant fold length which remained a function of ΔT appropriate to the chosen crystallization temperature, appropriately modified by isothermal thickening, the subject of our enquiry. The l values themselves were mostly determined by low frequency Raman spectroscopy (LAM mode) after cooling to room temperature. Usually two LAM peaks were observed. One was at high frequency, i.e. corresponding to small l, remaining at a constant frequency but diminishing in intensity in the course of crystallization which was attributed to material which has been molten at the appropriate T_c but crystallized on cooling to room temperature. The other peak was at lower frequencies (higher l value). This latter peak increased in intensity and shifted to still lower frequency after longer crystallization times. It was this latter, larger l value which we considered to correspond to the lamellae formed at T_c and its shift was attibuted to lamellar thickening.

The above works suffered from two shortcomings. First, the samples had a broad molecular weight distribution, the only ones available to us at the time. Secondly, the determination of l was not carried out *in situ* but only after cooling, as the Raman LAM peak is not interpretable (at least in its presently known simple form) near the melting point of the crystals. The only way to achieve the latter would be the application of low angle X-ray scattering, but with the normally available intensities the exposure times are too long to record long spacings in short enough times for the present purpose, even when using the enhanced self seeding technique.

In the work to be reported we have now overcome both the above limitations. We acquired sharp fractions in sufficient quantities for this work, so that the influence of possible molecular weight segregation on the l values can be excluded. Further, we determined l values by using a synchrotron X-ray source which provided sufficient intensity for obtaining l by small angle X-ray scattering (SAX) at the crystallization temperature itself from the early stages of crystallization aided, as before, by the application of the enhanced self nucleation technique. The samples were then examined by LAM after cooling for continuity with the previous work and, as added features, by differential scanning calorimetry (DSC) and by electron microscopy for direct viewing of the morphology (the last of course at room temperature).

The new results obtained in the above manner have led us to change our view expressed previously [10, 11]. There was now only a single diffraction maximum at T_c and the corresponding single lamellar thickness was found to be much thinner than expected from the previous works. This, as we shall show, has led us to the revised picture that on crystallization from the melt, comparatively thin lamellae are formed which then thicken isothermally, first in a single large step and only then in the usually envisaged way logarithmically with time. The previous works [9–11] identified only the latter stage, which means that the initial lamellar thickness obtained by extrapolation form this logarithmic thickening process are significantly in error and do not give the true l_g^* values. Although recognizing this fact, through the present work to be reported here, we leave the correction of the full l_g^* against T_c (or ΔT) dependence for a later paper [12]. In that paper, the last of the 5-Part series, reporting on our comprehensive programme on chain folding we shall also pull together the principal findings on melt and solution crystallization in the light of the new knowledge gained on the true primary l_g^* values.

2. Experimental procedures

2.1. Material and sample preparation

The material of most of the present experiments was a sharp fraction of polyethylene from the National Bureau of Standards, Washington, having a weight average molecular weight of 32 000 of polydispersity $M_w/M_n = 1.14$. We also used for comparison with our earlier work the same Sclair resin ($M_w = 53.6 \times 10^3 : M_n = 9.3 \times 10^3$). In all cases the results were substantially the same for the two polymers.

The samples for examination for long spacings during crystallization were pretreated so as to display enhanced self nucleation in order to yield an abundant amount of crystal in the shortest possible time, even at the highest T_c values [10]. This method, developed in our previous papers [9–11] dramatically increases the nucleation density leading to an increase in overall crystallization rate by several orders of magnitude.

Samples about 100 μm thick were first melted at 160 to 170° C in a Mettler microscope hot stage and then cooled at $\sim 20°\,C\,min^{-1}$ to 125° C, where they were allowed to crystallize in the form of small spherulites. These samples were subsequently reheated in the same Mettler hot stage (except for the samples to be used for DSC work) at $1°\,C\,min^{-1}$ until all birefringence just disappeared when viewed under the polarizing microscope. This occurred typically in the range of 133.8 to 134.4° C. The samples were held at this temperature for about a minute (the exact length of time depending on the particular experiment) before cooling at a rate as fast as possible (typically $20°\,C\,min^{-1}$) to the desired crystallization temperature. At this temperature the spherulites will be seen to reappear by gradual brightening of the whole field rather than by the customary radial growth from their centre. As described by Chivers *et al.* [10] this uniform brightening is the result of the persistence of nuclei throughout the full spherulite volume, the essence of the enhanced self seeding procedure, as opposed to the persistence of a single central growth nucleus in the course of usual crystallization including the simple (i.e. not the enhanced) self seeding experiment. It is through this gradual uniform reappearance of the spherulite that the overall crystallization

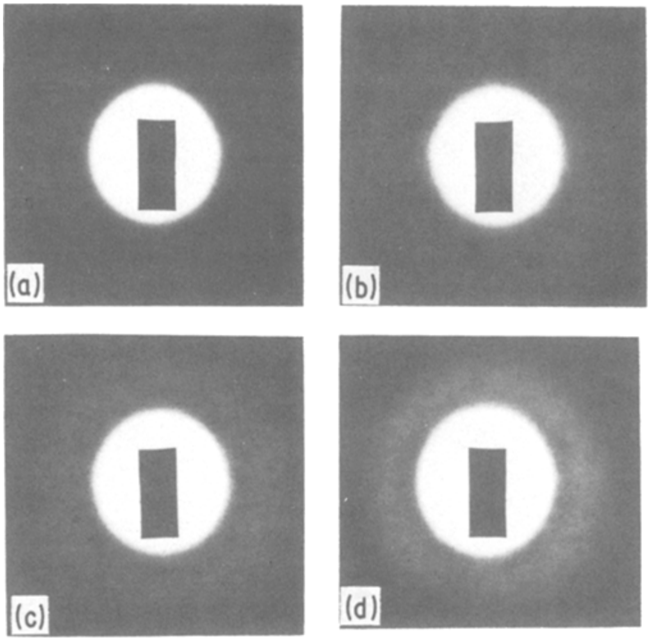

Figure 1 A sequence of low angle diffraction patterns taken during crystallization. Each exposure was for 30 sec starting after (a) 30 sec, (b) 150 sec, (c) 590 sec, (d) 1080 sec.

proceeds much faster than through radial growth from the same number of spherulite centres.

2.2. X-ray diffraction using the synchrotron source

The crystallization corresponding to the gradual emergence of the spherulites as produced by the enhanced self seeding procedure was followed *in situ* by low angle X-ray scattering.

2.2.1. Experimental procedures

The high intensity radiation of the Daresbury synchrotron source was utilized. The sample was held between a pair of aluminium plates in a Mettler hot stage (normally used for optical microscopy). The hot stage was modifed for use in the X-ray beam by cutting a slot ≈ 0.15 × 0.4 mm in the heating plates and removing the glass heat shields to allow X-rays to pass through. These modifications affect the precision of temperature control; typically with a specimen inside the Mettler stage the temperature is accurate to ± 0.2° C at the centre of the aperture but increases by up to 1.5° C towards the edges of the slit. The temperatures we quote here are those we expect at the centre of the aperture. Experiments were carried out in the low angle region using a specimen to film distance of 2.28 m. The film was changed using a carousel film changer which allowed exposures every 60 sec. The sample was heated to its optical melting point (134° C) and a 30 sec exposure taken. The sample was then cooled to 128.5° C and 30 sec exposures taken after 30, 90, 150, 270, 590, 600 and 1080 sec. The sample was then cooled to room temperature (after 20 min at 128.5° C) and subsequently reheated to 128.5° C and a further 30 sec exposure taken.

2.2.2. Results

None of the exposures taken at 134° C showed any low angle scattering indicating that the sample was molten. For the exposures taken at 128.5° C after about 1 min a low angle peak appears. The intensity of this peak increased up to 10 mins and then remained constant within experimental error; the position of the peak was unchanged within experimental error during the experiment. We illustrate this in Fig. 1 with some of the films. There is clearly a peak corresponding to a Bragg spacing of approximately 19.0 ± 5 nm. The exposure taken after cooling to room temperature and then reheating to 128° C shows no change from the exposures taken during crystallization at 128.5° C after 10 and 18 min.

2.2.3. *Implications*

The above described experimental series was the only one we had the opportunity to perform with the aid of the synchrotron source. Nevertheless, scarce as this experimental material may be, its implications were decisive for the subject in question and have enabled new conventional experiments to be performed and/or re-evaluated with notable consequences.

As already stated, at 134° C the material was and remained molten by the SAX evidence. Crystallization could be observed on cooling to 128.5° C where by the new SAX evidence this is completed in 10 min in our specially nucleated samples. The appearance of a discrete spacing suggests that the lamellae are adequately stacked to produce a sharply defined peak even at very short times, yet by the corresponding Bragg spacings the lamellae must be unusually thin for such a high crystallization temperature (19 nm) where by past experience minimum thicknesses of 30 nm would be expected even from our own previous works where we believed that the influence of lamellar thickening following primary crystallization was eliminated. Further, the results suggest that no isothermal thickening of these lamellae takes place on a time scale of 20 min.

2.3. Raman spectroscopy

2.3.1. *Experimental procedure and results*

In addition to measuring lamellar thickness by X-ray diffraction it is possible to measure the length of chains within crystalline lamellae using the longitudinal accordion mode (LAM) Raman scattering which occurs at low wavenumber shifts [13]. Indeed in our previous papers [3–5, 9–11] this has been the principle tool for measurement of lamellar thickness. However, presently we are limited to investigations at room temperature or below, since the LAM peaks are not resolvable or quantifiable at higher temperatures. Thus we cannot with this technique distinguish between material crystallized at the crystallization temperature and with any which crystallized on subsequent cooling. However, we are confident from both the X-ray work already reported and from our DSC work described in the next section that for samples crystallized at about 128.5° C crystallization is complete within 10 to 15 min.

We examined first the same sample which had been crystallized in the synchrotron X-ray beam at Daresbury, and then a series of samples crystallized separately for various times using the same experimental conditions but with better temperature controls: in this case we used an unmodified Mettler hot stage ensuring uniformity and precision of temperature within 0.1° C. The fold lengths, l, we quote here were calculated from the frequency shift, $\Delta\nu$ using

$$l = 316.9/\Delta\nu \, \mathrm{nm} \qquad (1)$$

where $\Delta\nu$ is in cm^{-1}. The sample used in the X-ray work shows two LAM peaks. We reproduce in Fig. 2a the actual trace and in Fig. 2b the data after appropriate corrections [14] have been applied to the intensitites. The effect of these corrections is principally to increase the relative intensity of peaks at higher frequency shifts. In the uncorrected data after background subtraction we see peaks at 42 and at 23 nm, while after correction the peaks are at 40.6 and 24.0 nm.

Using samples prepared at the same temperature as in the X-ray experiment (128.5° C) but in an unmodified hot stage we were able to investigate the variation in intensity, and position of the two LAM peaks with crystallization time. We found that the peak corresponding to the shorter fold length always occurred at a frequency shift of $15.7 \pm 0.3\,\mathrm{cm}^{-1}$, i.e. at 18.8 ± 0.5 nm, while the other peak moved consistently to lower wave numbers (i.e. longer fold lengths). After 3 min crystallization this peak was at $10.2\,\mathrm{cm}^{-1}$ while after 30 min it was at $8.5\,\mathrm{cm}^{-1}$ (i.e. a change from 31.1 to 37.3 nm). The intensities of the peaks after correction were also measured and the results are plotted in Fig. 3. The intensity of the peak corresponding to the short fold length starts to decrease after 5 min crystallization and the peak can no longer be detected after 120 min crystallization. The intensity of the peak corresponding to the larger fold length increases over the same period.

2.3.2. *Implications of the Raman results*

We can deduce that two populations of lamellae exist, thin ones and thick ones. The polymer first crystallizes with thin lamellae and these slowly but through a discontinuous step transform into thick lamellae. The thick lamellae themselves become thicker with increasing time.

We may explain the differences in position of the peaks between the sample used for X-ray work, and the set of samples specially prepared for Raman work through the temperature gradient

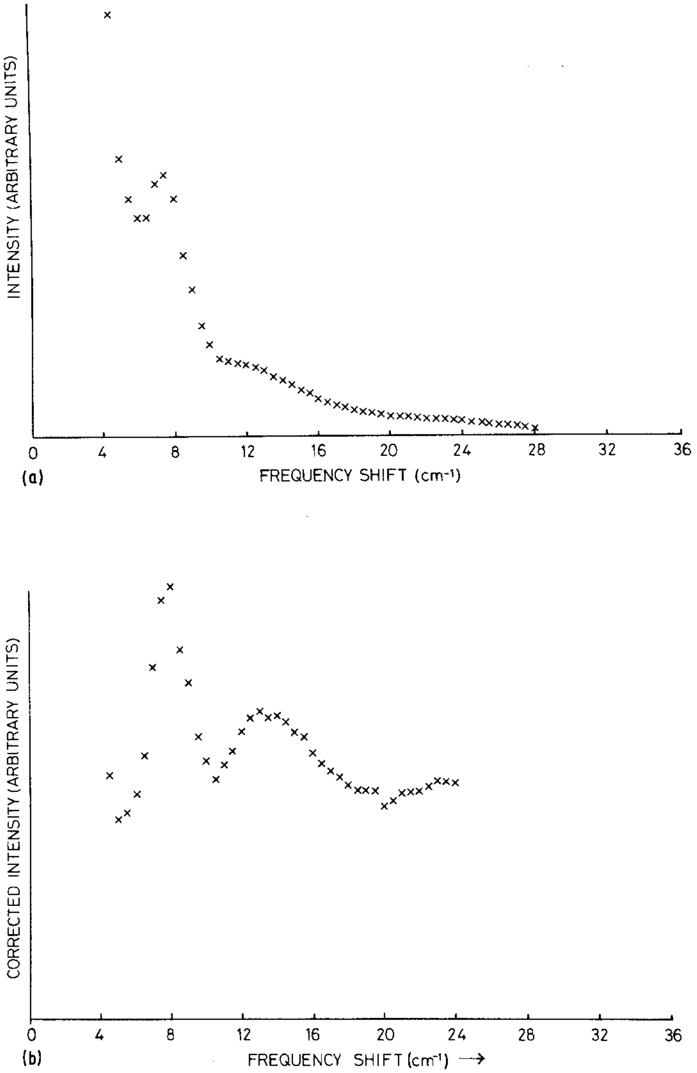

Figure 2 (a) Original trace from Raman spectroscopy of the sample crystallized in the X-ray beam of the synchrotron source. (b) The same data after applying appropriate temperature correction [14].

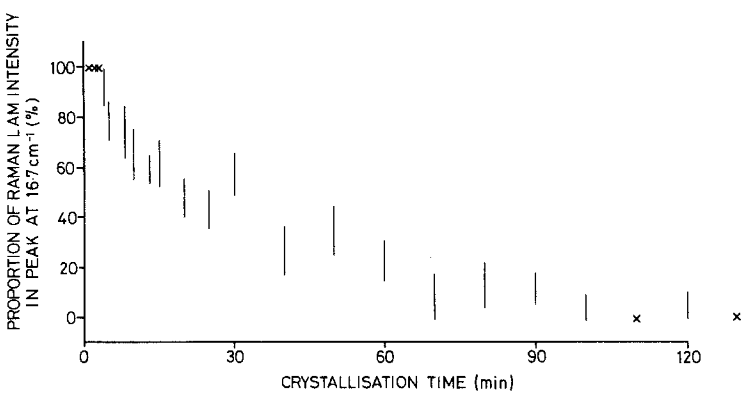

Figure 3 A graph showing the intensity of the Raman peak at 16.7 cm^{-1}, as a percentage of the total LAM Raman intensity (after corrections as in Fig. 2), as a function of the time of crystallization at 128.5°C prior to quenching to room temperature.

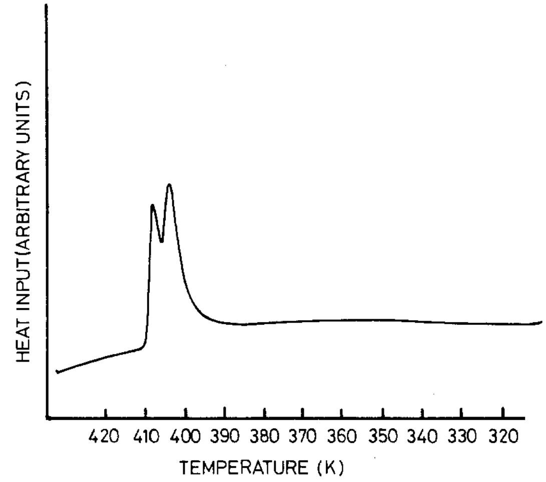

Figure 4 DSC trace form the sample crystallized in the X-ray beam of the synchrotron source. Heating rate 10° C min^{-1}.

which existed across the sample crystallized in the X-ray beam so that the particular area we examined using Raman spectroscopy may have been crystallized at a temperature higher than 128.5° C. The intensities of the Raman peaks suggest that the amount of thick, and thin lamellae were approximately equal in the sample crystallized in the X-ray beam.

2.4. Calorimetry

2.4.1. Experimental procedure and results

The proportion of material with thick, and thin lamellae may be assessed more directly by melting. On heating in the DSC (at 10° C min^{-1}) the sample used for X-ray diffraction work at Daresbury shows two distinct melting peaks (as shown in Fig. 4) one at about 135° C the other at about 131° C. The areas under these peaks suggest that 40% of the material contributes to the higher temperature peak. This would indicate about 40% thick and 60% thin lamellae in this sample.

We have also prepared samples directly in the DSC by first melting at 134° C, cooling (60° C min^{-1}) to 128.5° C and holding there for some time. In this way not only can we observe the recrystallization at 128.5° C but by reheating the sample we can also observe how the areas of the two melting peaks change with time. In order to establish how far our Raman samples had crystallized we studied the crystallization of such samples at 128.5° C. We simply measured the heat liberated by the sample as a function of time and from this deduced the proportion of material that had crystallized. We found that 95% of the crystallizable material had crystallized within 10 min in all our experiments. On heating samples (at 5° C min^{-1}) immediately after they had fully crystallized (i.e. after 8 to 15 min at 128.5° C) we always found two peaks, one at about 131° C and the other at about 134° C with 30 to 40% of the material contributing to the higher melting peak. In a separate set of experiments we tested the validity of our Raman intensity measurements by allowing recrystallization at 128.5° C for various times before reheating. We could then see how the area of the two melting peaks changed with crystallization time. Except for samples crystallized for less than 2 min (or more than 100 min) we always saw two melting peaks one at 131° C the other at 134 to 136° C, the temperature being higher for longer crystallization times. At short times only the 131° C peak was seen and at long times only the 136° C peak. We show in Fig. 5 how the proportion of material contributing to the 131° C peak decreases with increasing time.

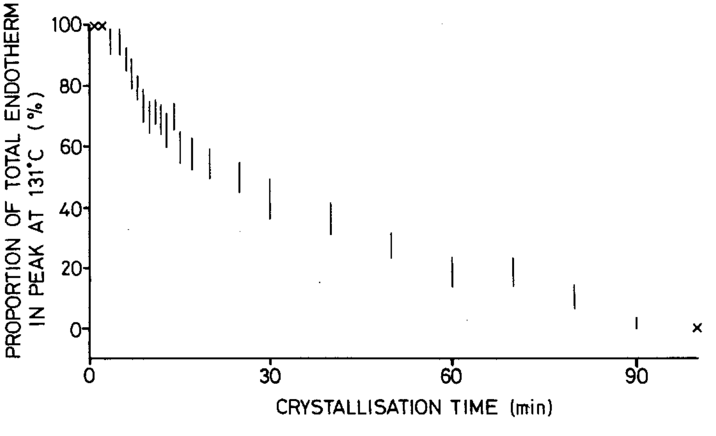

Figure 5 A graph showing the percentage of the total amount of material melting at 131° C as a function of crystallization time 128.5° C.

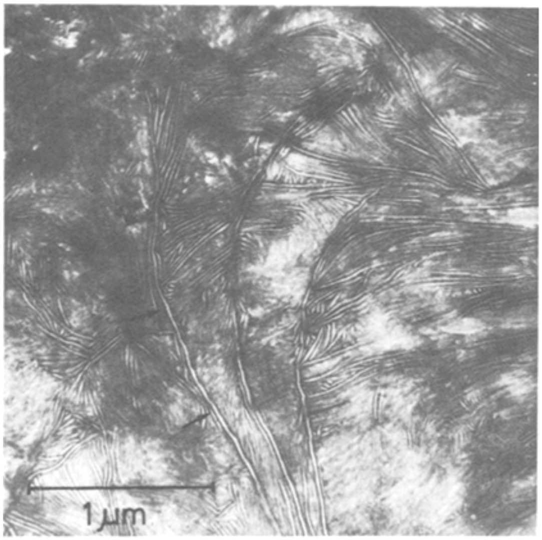

Figure 6 Electron micrograph of the sample crystallized in the synchrotron source. The staining technique is described in the text. Two populations of lamellae are present. There are a few long lamellae running approximately vertically, these are the radial lamellae referred to in the text. The remaining lamellae which are stacked together and fill the spaces between the dominant radial axes have a reduced thickness. The arrows indicate one of the radial lamellae which, on close inspection is seen to be segmented in thick and thin parts as described in the text.

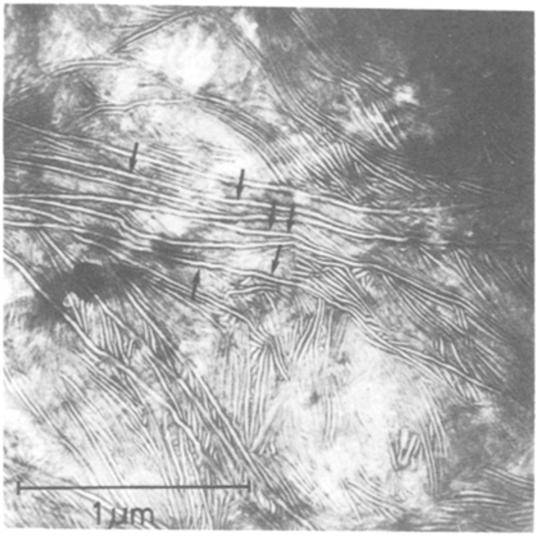

Figure 7 Electron micrograph of the same sample as in Fig. 6. Here the dominant radial lamellae are running approximately horizontally and in this area they are more common; those marked with arrows can be seen to taper and have long lengths of both thicker and thinner parts. The remaining, well stacked lamellae are the "in filling" lamellae referred to in the text.

2.4.2. Implications of the DSC results

The DSC results support the X-ray and Raman work. We can safely conclude that the X-ray sample was substantially crystallized within the 20 min of the experiment from our results on crystallization in the DSC. By heating the samples from the crystallization temperature and observing first one peak at 131° C and at longer crystallization times 2 peaks, at 131 and 134 to 136° C, we may deduce that the thin lamellae are definitely formed at the crystallization temperature and that the thick ones arise by transformation from the thin ones.

2.5. Electron microscopy

2.5.1. Experimental procedure and results

A part of the sample used for X-ray work was also examined in the electron microscope. It was first etched with chlorosulphonic acid at 60° C for 16 h and then stained with uranyl acetate for 45 min at room temperature before being sectioned for electron microscopy. Some typical micrographs are shown in Figs. 6 and 7. The prominent features are bright bands separated by dark narrower zones, which by past experience are associated with the cross sectional view of stained lamellae. Several features are worthy of particular note. It is clear from all the micrographs that there are two populations of lamellae; thin ones which are packed regularly together in stacks and isolated thick ones. The unstrained regions of the thin lamellae have a thickness of about 10 nm and a periodicity (including the stained regions) of about 20 nm. The thick lamellae have an unstained core of about 20 nm which allowing 10 nm for the stain as in the thin lamellae, gives an overall thickness of about 30 nm.

The thick lamellae tend to be arranged radially within a spherulite while the thin ones have no particular orientation; they appear to have grown in spaces between the thick ones. On occasions (e.g. in Fig. 6) the radiating, normally thick, lamellae appear segmented with thin portions located between the thick ones. Occasionally (e.g. in Fig. 7) there are radiating lamellae which appear tapered so that they have long lengths of thickened portions. That neither of these effects is due to twisting can be seen by rotating the sample.

2.5.2. Implications of electron microscopy

We can clearly see that we have two populations of lamellae. We can also see why only the thin lamellae contribute to the X-ray signal while both sets are observed in the Raman experiment. This is because only the thin lamellae are regularly stacked and hence only they give a discrete diffraction signal.

The observations also allow us to hypothesise about the origin of the enhanced self nucleation process. If a few thick crystals survive melting then these will act as nucleation sites on recrystallization. Further, if the orientation of these crystals is preserved then on renewed growth they will form lamellae which are radial within the original spherulite. We would of course expect the new growth to have a lower lamellar thickness than the nuclei. The presence of the original thick nucleus may then provide a ready site where isothermal thickening could start*. Thus we would expect that it is these radial lamellae which thicken first. Indeed in this sample most of the radial lamellae are seen to be thick, while only few of the "in filling" lamellae have yet started to thicken. Occasionally, however, we do see parts of the radial lamellae where thickening has not yet occurred. Although in this sample we do not see much direct evidence for the thickening of the thin regularly packed lamellae, such effects have been seen previously in samples of fractions crystallized for a long time [15].

3. Summary and conclusions

A single experiment using the synchrotron source in combination with our enhanced self nucleation technique, which allowed us to observe the low angle diffraction at very short crystallization times backed up by Raman, DSC and electron microscopy has radically changed our view of isothermal thickening in polyethylene. We can now see that initially the lamellae are crystallized with a much lower lamellar thickness than previously envisaged and that the first step of thickening consists of a jump to a considerably larger thickness. The exact amount of this jump is not known at present but it may be by approximately a factor of two. The implications of this recognition for our earlier studies, in which we attempted to assess the initial lamellar thickness in polyethylene, are far reaching as will be apparent from the paper to follow where, amongst others, the newly obtained data for l_g^* will be compared with corresponding values for crystals grown from solution.

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*It is commonly believed that annealing, and hence by implication isothermal thickening, begins with the formation of a small patch of thicker material within a lamella. This thickened patch then acts as a nucleus for the thickening of the surrounding material.