Study of the melting behaviour of ultra-high modulus linear polyethylene using synchrotron radiation

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A study has been made of the melting behaviour of highly drawn linear polyethylene using synchrotron radiation. Previous investigations using differential scanning calorimetry have shown that superheating, an increase in melting temperature with increasing heating rate, was observed in all samples. In order to understand the causes of superheating in these materials two types of melting experiments were performed while observing the wide-angle X-ray scattering. In the first, samples were heated at different constant rates through the melting range. In the second, samples were heated rapidly to a fixed temperature in order to study melting under isothermal conditions. The results of the former have confirmed the presence of superheating while those of the latter indicate different melting times at different temperatures corresponding to the superheating observed. The presence of partial melting, particularly at high draw ratios, has been found indicating the presence of a morphology with a significant degree of crystal continuity. This result is entirely consistent with the results of other investigations into the structure of these materials.

(Keywords: melting behaviour; drawing; polyethylene; synchrotron radiation)

INTRODUCTION

Superheating effects observed in the melting of semicrystalline polymers are associated with an increase in the melting temperature with an increase in heating rate[1]. Although these effects have been mainly observed in extended-chain polymers[2,3], produced by crystallization at elevated pressures and temperatures, they have also been observed in oriented polymers[3–6]. From this superficial resemblance in melting behaviour, it is tempting to interpret the superheating observed in oriented polymers in terms of extended chain crystals being present. In the case of ultra-high modulus linear polyethylene (LPE), this interpretation has considerable attraction since it provides a simple description of the high stiffness and high thermal conductivity of the oriented polymer[7]. However, in oriented polymers, these superheating effects can also be attributed to the entropic restrictions on molecules which connect two or more crystalline regions of the same or different crystals. These entropic effects have been discussed quantitatively previously[8].

In the following, we report on an examination of the superheating of ultra-high modulus LPE employing synchrotron radiation. This technique affords the unique opportunity to record both the wide-angle and small-angle X-ray scattering patterns within a few seconds, thus enabling one to observe rapid changes in the scattering patterns and hence the morphology[9]. In addition, we have examined the melting behaviour of ultra-high modulus LPE under isothermal conditions, in an attempt to shed more light onto the processes which lead to superheating in these materials.

EXPERIMENTAL

Materials

Two polymer samples of low molecular weight and high molecular weight were chosen which previous work has shown to produce drawn products with substantial differences in melting behaviour[10,11].

Details of the samples can be found in *Table 1* where the polymers have been identified by their trade names. Isotropic sheets 0.5 mm thick were prepared by compression moulding at 160°C and quenching in water at room temperature. Sheets of suitable dimensions were cut from these and drawn in an air oven in an Instron tensile testing machine according to procedures described in detail previously[11,12].

Table 1 Details of polymer grades and samples used

Sample	Polymer grade	$\bar{M}_n$	$\bar{M}_w$	Draw temperature	Draw ratios
1	Rigidex 50^a	6180	101450	75	10, 25
2	H020-54P^a	33000	312000	115	10, 25

^{a} BP Chemicals Ltd

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Synchrotron radiation measurements

The scattering measurements were made using a double focusing camera for synchrotron radiation on the polymer beamline at HASYLAB, Hamburg[13]. On this instrument, a bent, triangular monochromator was used for horizontal focusing and a segmented quartz mirror for vertical focusing. The wavelength used was 0.15 nm with a band pass of $\Delta\lambda/\lambda = 5 \times 10^{-3}$. The scattering patterns were recorded using a linear position sensitive detector. The scattering patterns were corrected for fluctuations in the intensity of the primary beam and a background was subtracted.

Specimens were mounted in the synchrotron beam line in the following manner. Small square sections were cut from the drawn sheets and wrapped in aluminium foil. They were then placed in a brass or copper holder, which enabled the position of the specimen to be maintained but which allowed shrinkage on heating.

In order to heat or cool the specimen, the specimen holder was pushed by a piston into a heating block. The heating block consisted of two copper blocks each containing a resistance heating cartridge. Thermal contact was ensured by the thin aluminium foils covering the faces of the sample and by the sample holder being clamped by the copper blocks. The temperature of the sample was determined by a 0.25 mm thick thermocouple embedded in or near the sample. Ancillary electronic controls ensured that temperatures of interest (130–145°C) could be reached in 20 s without overshooting and that programmed constant heating rates could be achieved which were consistent and reproducible.

In previous studies on the melting behaviour of ultra-high modulus LPE, melting temperatures were measured using a Perkin–Elmer DSC-2[3]. With this instrument it is possible to measure melting temperature over a very large range of heating rates, 0.31 to 320°C min^{-1}. In the present investigation the range of heating rates was severely limited. It was not possible to observe changes in the X-ray scattering pattern at heating rates much above 20°C min^{-1} since the temperature change during the finite counting time required to preserve good counting statistics, normally 10 s, made the measurement of temperature highly inaccurate, e.g. at 40°C min^{-1} the temperature change during 10 s is approximately 7°C. This compares very unfavourably with the estimated precision of melting temperatures measured by differential scanning calorimetry (d.s.c.) of ±0.5°C at heating rates up to 80°C min^{-1}. For this reason it was decided to restrict the present investigation to heating rates below 20°C min^{-1}. However, our previous investigation showed that large differences in melting temperature can still be expected in this range[3].

RESULTS

Constant heating rate

The results of the measurements performed at constant heating rate are summarized in *Figures 1a* and *b* for all samples investigated. Also included for reference are the results of melting point measurements by d.s.c. on similar materials for the same range of heating rates.

It is immediately obvious that the values of the melting points measured employing synchrotron radiation are invariably higher than those measured by d.s.c. This systematic difference can be attributed to the different ways in which melting point temperatures are defined and measured in the two experiments. Using synchrotron radiation, the temperature at which discrete scattering disappears was measured, as shown for example in *Figures 2a* and *b*. In d.s.c. on the other hand, peak melting temperatures were measured, as shown schematically in *Figure 3*. The temperature at which discrete scattering disappears can be identified with the end point of the d.s.c. endotherm. It would be preferable to be able to

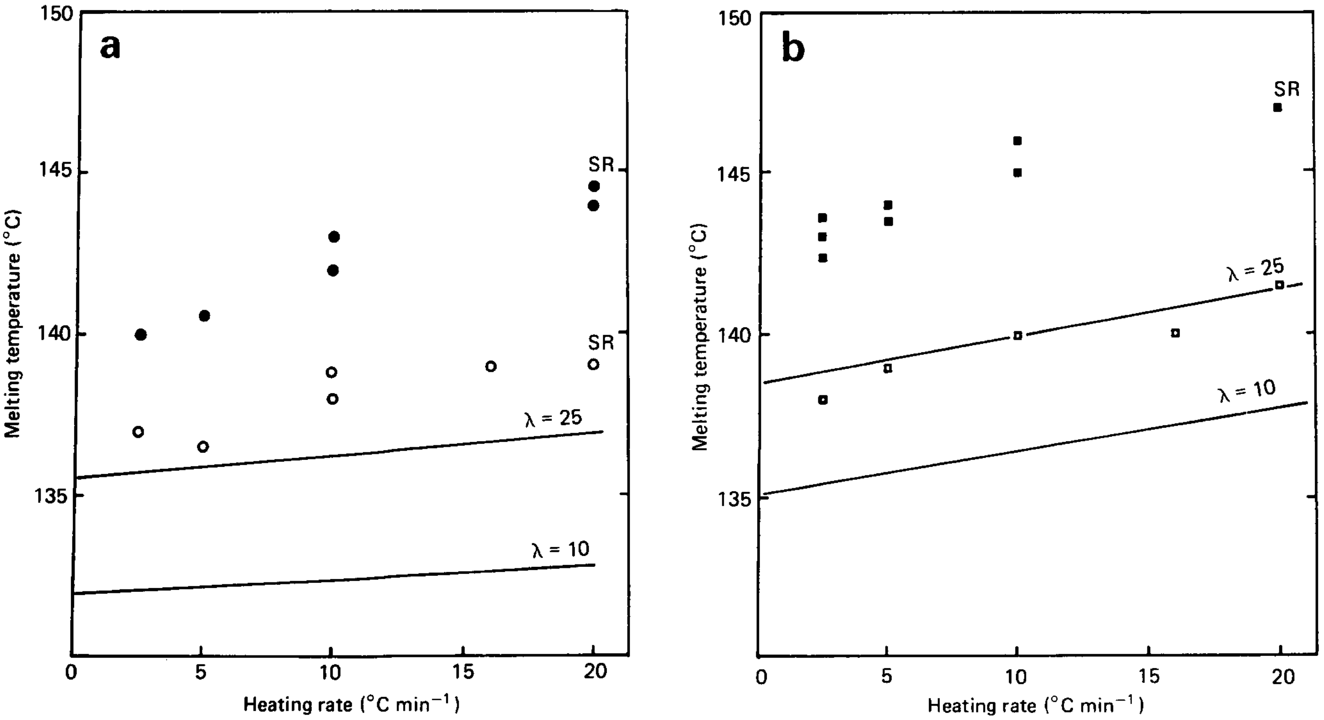

Figure 1 Melting temperature as a function of heating rate, as measured with synchrotron radiation. (a) Sample 1: ○, $\lambda = 10$; ●, $\lambda = 25$. (b) Sample 2: □, $\lambda = 10$; ■, $\lambda = 25$. Solid lines indicate the results of d.s.c. measurements

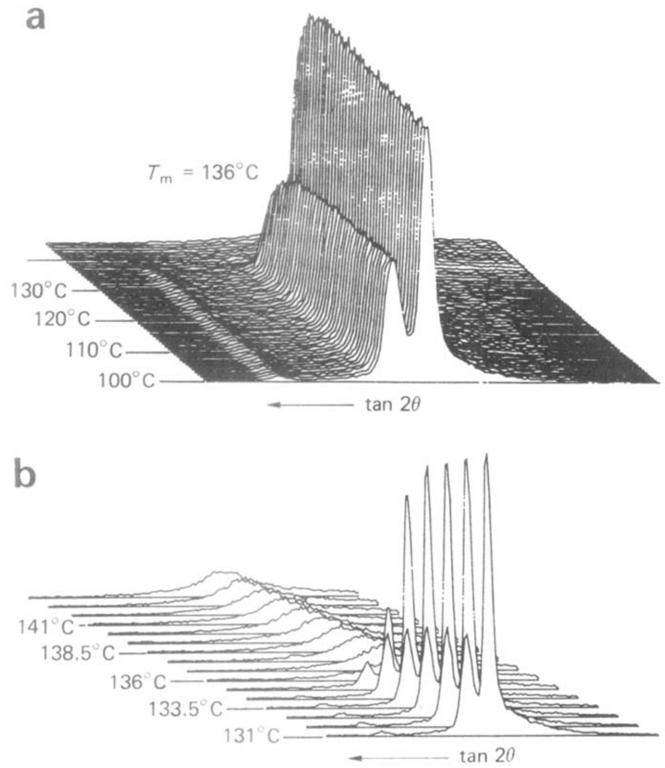

Figure 2 Change of WAXS scattering patterns during heating at a constant rate of 2.5°C min^{-1} for sample 1 ($\lambda = 10$). (a) Patterns for whole temperature range of 100–145°C. (b) Selected patterns showing where discrete scattering disappears

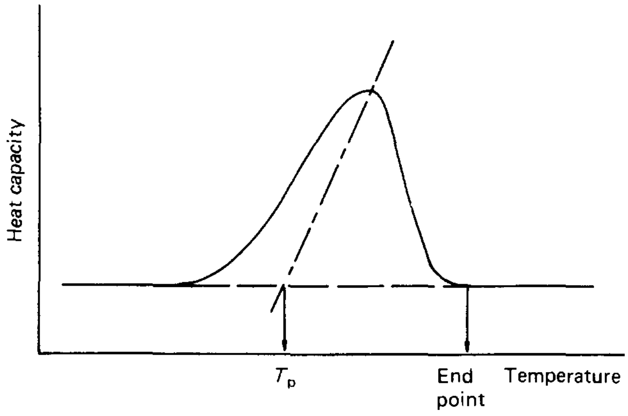

Figure 3 Schematic d.s.c. melting endotherm indicating the peak melting temperature (T_p) and the end point

make a direct comparison between the two experiments, but in d.s.c. the end point of the endotherm depends upon sample mass, and the measurement of such is therefore somewhat arbitrary. However, it is still clear that the presence of superheating in the melting of ultra-high modulus LPE is confirmed by wide-angle scattering measurements employing synchrotron radiation.

Isothermal melting

In this series of experiments, the samples were introduced into the preheated oven, thereby being heated rapidly to a fixed temperature. Although the behaviour of high and low draw ratio specimens is similar, in kind if not in degree, it is convenient to report the results separately.

High draw ratios. At temperatures below the melting range it was found that no significant change in the scattering pattern could be detected, even if the sample was maintained at constant temperature for times exceeding 30 min (*Figure 4a*). At temperatures within the melting range, partial melting was observed (*Figure 4b*), and then no further change in scattering pattern occured. At higher temperatures within the melting range, discrete scattering disappeared in a finite time (*Figure 4c*). The higher the temperature, the shorter the time, until melting occurred effectively instantaneously. Similar results were observed for both high draw ratio samples. In the range of temperatures where partial melting is observed, the degree of partial melting is also dependent upon temperature. In *Figure 5* we have plotted the ratio of final integrated intensity (after partial melting) to the initial integrated intensity (before partial melting) as a function of temperature. All samples show a similar dependence upon temperature, and we note that at temperatures as

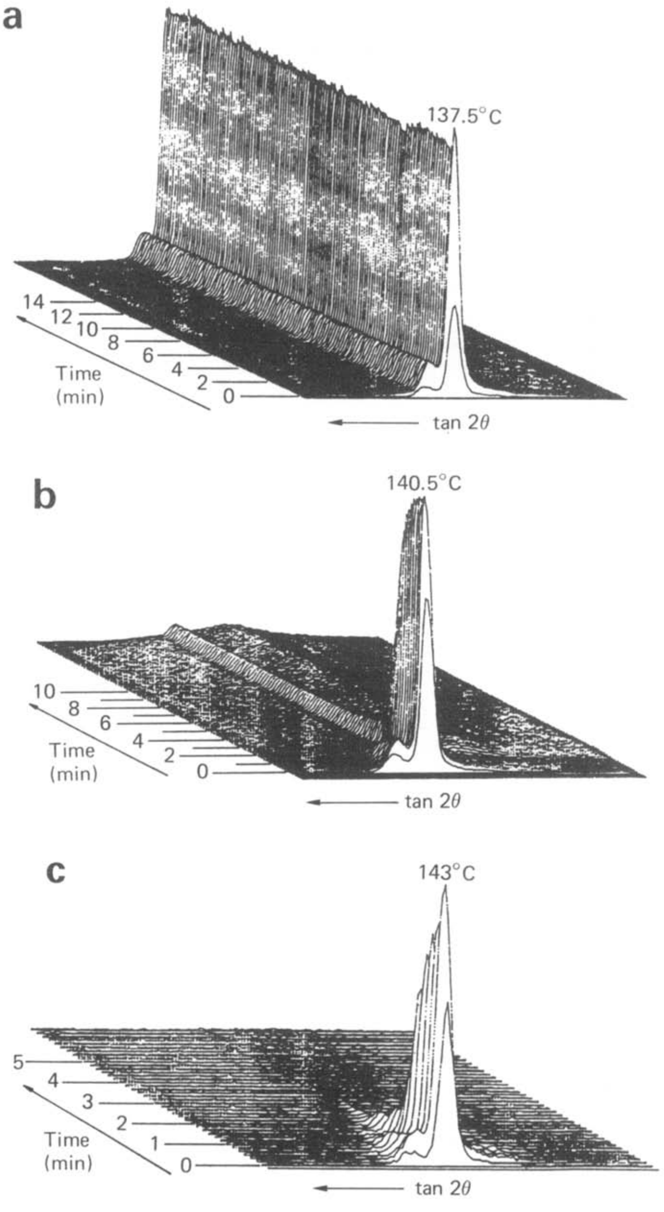

Figure 4 Change in WAXS scattering patterns for sample 2 ($\lambda = 25$) under isothermal conditions. (a) 137.5°C, (b) 140.5°C, (c) 143°C

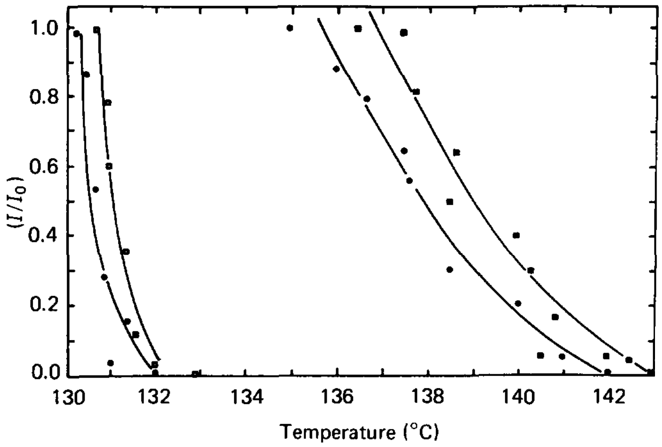

Figure 5 The ratio of the final integrated intensity (after partial melting) to the initial integrated intensity (before partial melting) as a function of temperature for sample 1: ○, $\lambda = 10$; ●, $\lambda = 25$ and for sample 2: □, $\lambda = 10$; ■, $\lambda = 25$

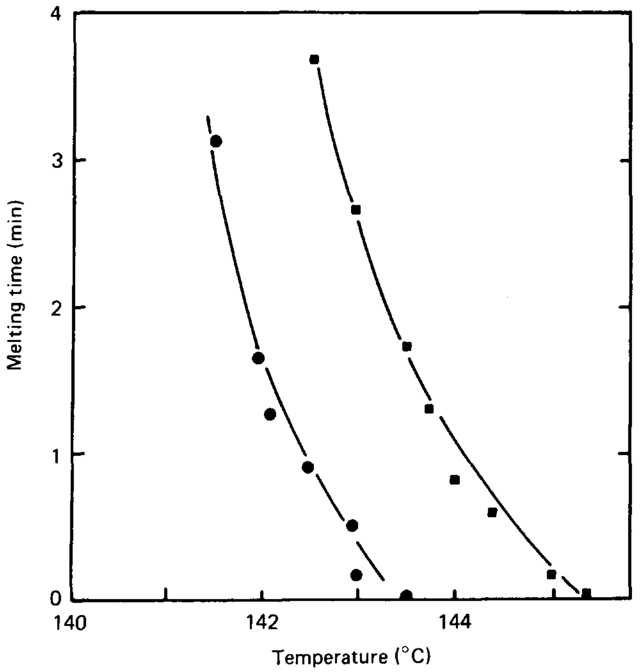

Figure 6 Measured melting times as a function of temperature, under isothermal conditions, for high draw ratio samples. Sample 1: ●, $\lambda = 25$; sample 2: ■, $\lambda = 25$

high as 140°C both samples only melt partially. At higher temperatures, the samples melt completely, as was noted above, and we have summarized the results in *Figure 6*.

Low draw ratios. Low draw ratio samples exhibit a similar behaviour to that observed for high draw ratios. At temperatures below the melting range, no change in scattering patterns was observed. At higher temperatures, partial melting is again observed but the temperature range over which it occurs is greatly reduced (*Figures 7a* and *b*). Again we have plotted the degree of partial melting as a function of temperature and these results are included in *Figure 5*. At higher temperatures, both low draw ratio specimens melt completely in a finite time (*Figures 7c* and *d*). We have summarized these results in *Figure 8*.

DISCUSSION

The results in *Figure 4a* show that no significant change in the scattering patterns are observed below those temperatures at which the onset of partial melting is evident. Extensive structural studies by small and wide-angle X-ray diffraction[14–16] and d.s.c.[3] have shown that no changes detectable by these techniques occur in drawn LPE at temperatures below 90°C. At higher temperatures, however, and certainly above 120°C,

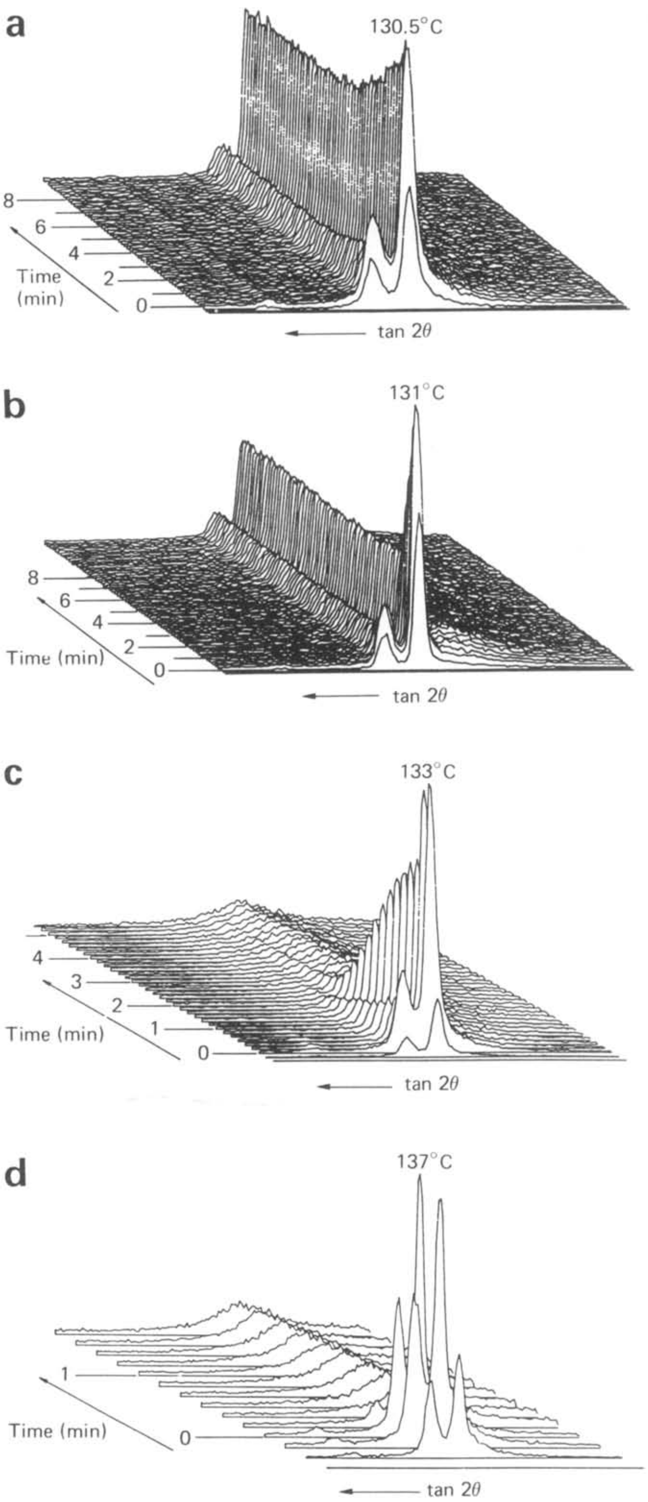

Figure 7 Change in WAXS scattering patterns for sample 1 ($\lambda = 10$) under isothermal conditions. (a) 130.5°C, (b) 131°C, (c) 133°C, (d) 137°C

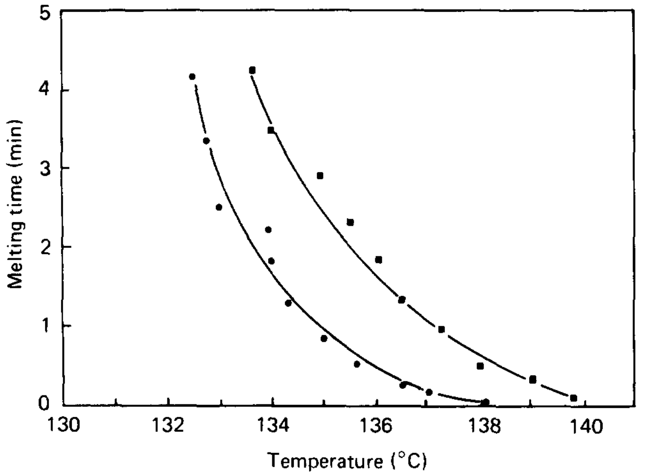

Figure 8 Measured melting times as a function of temperature, under isothermal conditions for low draw ratio samples. Sample 1: ●, $\lambda = 10$; sample 2: ■, $\lambda = 10$

appreciable changes can be observed. It is a little surprising therefore that the present results appear to be insensitive to structural changes which are known to occur at temperatures within the range 120–130°C. It must be remembered, however, that these materials are highly crystalline and that the structural changes that are proposed to take place, e.g. modifications of the surfaces of the lamellae, migration of defects to the interfacial regions and relaxation of the strained amorphous material, will only be seen as minor perturbations and will have little or no effect on the wide-angle X-ray scattering patterns. Most of these changes will result in an increase in crystalline perfection which, due to the low angular resolution of the synchrotron camera will go undetected.

The present investigation into the isothermal melting behaviour of oriented LPE taken together with previous investigations into the annealing behaviour of LPE suggests two distinct regimes must be considered. At high temperature (> 130°C) partial melting takes place. At lower temperatures more subtle reorganization occurs, involving modification and increasing perfection of the crystalline regions.

Previous work by Mead and Porter[17] on oriented LPE rods prepared by extrusion at 134°C shows significant partial melting on annealing at temperatures as low as 126°C. Moreover, on annealing at 130°C, 50% of the crystalline material was observed to melt. Our findings are very different, in that at 130°C only low draw ratio materials partially melt and even those not to such a large extent. The onset of partial melting is not observed in high draw ratio materials until *ca.* 134°C. This can be attributed to the increase in melting temperature with increasing draw ratio seen here and elsewhere[3]. The present results confirm an earlier suggestion that the important parameter in the annealing of ultra-high modulus LPE is ΔT $(= T_p - T_A)$, where T_p is the peak melting temperature and T_A is the annealing temperature[14]. This parameter is also found to be of considerable importance in the shrinkage behaviour[18], in which case T_A is the shrinkage temperature.

The mechanical stiffness of ultra-high modulus LPE has been successfully explained in terms of a structural model where the crystalline blocks characteristic of low draw ratios become increasingly linked by crystalline bridges with increasing draw ratio[19]. The observation that these materials melt only partially over a considerable range of temperatures, and that ultra drawn LPE still displays only partial melting at temperatures as high as 140°C is therefore considered to arise from the enhanced thermal stability given to the structure by the crystalline bridges. At the onset of partial melting it is presumably thinner and/or more highly defective crystals which melt. As the temperature is raised, and melting becomes more progressive, larger and larger crystals will melt. *The fact that the temperature range over which partial melting is observed is very much greater for ultra drawn LPE than it is for low draw ratio samples is due to the significant amounts of crystalline bridges in the higher draw ratio materials.*

In the temperature regions where melting is complete, we observe that this melting takes a finite time, and that the time decreases as the temperature increases. This observation is a direct analogy of superheating.

A statistical analysis of the melting process has been developed[8] and has shown that superheating can be explained on the basis of specific trends in the variation of the average entropy change as melting progresses. Configurational constraints in the early stages of melting lead to very small entropy variations between the solid and molten states. This gives rise to an 'apparent' melting point higher than the equilibrium melting temperature of the crystals. The fact that high draw ratio samples melt at higher temperatures than low draw ratio samples, and that melting time is a function of melting temperature is consistent with the above explanation of superheating, and emphasizes the importance of the increased amount of crystal continuity given by the crystalline bridges.

Conditions for superheating can also occur when stacks of lamellar crystals are connected by strained amorphous material, 'tie molecules'. This interpretation of superheating finds some success in explaining the melting behaviour of oriented polymers which are held under mechanical constraint during melting[3,4,20]. In the case of ultra-high modulus LPE[20], the results suggest that the melting behaviour can be attributed to a highly oriented molecular network, whose junction points are primarily crystalline, but may also include molecular entanglements.

The differences in melting behaviour between low and high molecular weight samples can also be attributed to the development of an oriented molecular network. Recent investigations[21] have shown that the Young's modulus and the degree of crystal continuity only depend on draw ratio, and are largely independent of molecular weight and draw temperature. The large differences in the degree of superheating exhibited by different molecular weight materials cannot therefore be due to differences in crystal continuity. They are presumably due to the presence of a molecular network, which will be more highly developed in higher molecular weight materials.

CONCLUSIONS

Several conclusions can be drawn from this work. First, the presence of superheating upon melting of ultra-high modulus linear polyethylene has been substantiated by employing synchrotron radiation, and observing the changes in the wide-angle X-ray scattering pattern in both constant heating rate and constant temperature melting experiments.

Second, the significant degree of partial melting, particularly at high draw ratios, and the fact that high draw ratio materials melt only partially at temperatures as high as ~ 140°C lends support to our view that there is a significant degree of crystal continuity in these materials, and that the degree increases with increasing draw. The effect of increasing molecular weight can be attributed to the development of a molecular network.

It can be concluded therefore, that the superheating observed in the melting of highly oriented linear polyethylene is due to crystal continuity on the one hand and a highly developed molecular network on the other.

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