Isothermal lamellar thickening and the distribution of thermal stability in spherulitic isotactic poly(4-methylpentene-1)*

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The thickening of polymer lamellae which occurs when a melt-crystallized sample is heated within its melting range has been investigated for the morphologically simple polymer poly(4-methylpentene-1) using transmission electron microscopy following permanganic etching. It is shown that, even for an isothermally crystallized sample, the lamellar melting point varies repetitively and systematically with position in the spherulitic texture, being highest for dominant lamellae then progressively decreasing because, it is suggested, of increasing constraints during crystallization. Two thickening processes have been distinguished experimentally. At the beginning of the melting range, the least stable lamellae melt and, given time, recrystallize at greater thicknesses. However, the usual interpretation of a doubly peaked melting endotherm in terms of original and transformed lamellae is shown to be oversimplified. At a higher annealing temperature, between the two peaks of the melting endotherm, a population of lamellae forms which is never melted yet increases its average thickness in the solid state logarithmically with time by a second process operative for all lamellae.

(Keywords: poly(4-methylpentene-1); spherulites; annealing)

INTRODUCTION

The properties of crystalline polymers are dominated by the large fold surfaces of their constituent lamellae; in particular, lamellar habits, conferred by crystallization, bring with them inherent metastability with respect to increased thickness because of the associated decrease in fold surface area per unit mass. Phenomena in which average crystal thickness increases at constant temperature are known collectively as isothermal lamellar thickening.

Evidence for lamellar reorganization on heating was discovered in early experiments on solution-grown polymer crystals and their aggregates[1,2]. At least in part the changes observed are a consequence of samples partly melting, then recrystallizing[3]. This can occur because melting points are depressed by the lamellar habit according to the Joule–Thomson equation, made explicit for polymers by Hoffman and Weeks[4]. As polymeric solids generally contain a range of thicknesses and stabilities, melting proceeds in stages and it is then possible for a partly molten sample, given time, to recrystallize as lamellae thicker than those which had melted. A well-known manifestation of this process often occurs progressively during differential scanning calorimetry (d.s.c.) at moderate rates[5].

Lamellar metastability has also been identified by Hoffman and Weeks[4] as being intimately involved in polymeric crystallization from the melt. Because observed melting points exceed those appropriate to the thickness of the secondary nucleus it was inferred that lamellae must have thickened isothermally, by a factor γ, during growth; derived values of γ are typically ca. 3.

The evidence for lamellar thickening has come primarily from low-angle X-ray scattering, supported by differential scanning calorimetry. However, neither of these techniques can identify where, within a sample, lamellar thickening has occurred nor measure lamellar dimensions other than thickness; for this microscopy – usually electron microscopy – is required. Thus early annealing studies on poly(4-methylpentene-1) (P4MP) revealed the influence on sectors[6]; studies on polyethylene also revealed a susceptibility of {200} sectors to transform before {110} sectors in truncated lozenges grown from solution[7], an effect central to a recent formulation of the kinetic theory of polymer crystallization[8]. It is now well known that holes with thickened borders develop when individual lamellae are heated on a substrate but this phenomenon is confined to monolayers so constrained; it is absent from multilayers, whose thickening is cooperative, and from bulk polymer[9].

Knowledge of the morphology of thickening in melt-crystallized systems has been limited by the difficulties, due to radiation damage, of applying transmission electron microscopy directly to these beam-sensitive materials. Nevertheless studies using replication of fracture surfaces, notably on linear polyethylene annealed at 0.5 GPa, have shown all

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lamellar dimensions to increase continuously with the time of treatment[10,11].

The advent of permanganic etching[12] has brought a new ability to study representative internal morphologies to a wide range of polymers[13]. An early preliminary application showed the thickening of S-profiled dominant lamellae in linear polyethylene[9]; a fuller study of this topic is given elsewhere[14]. Such samples were prepared by continuous cooling, so as to accentuate internal textural differences. In this paper we examine an isothermally crystallized polymer of simple habit and do so in a novel way which highlights the differential effects of isothermal annealing in relation to the inherent systematic textural variations within a spherulitic polymer. It is shown that there is a spatially repetitive variation of melting point within an isothermally grown spherulite and two mechanisms of lamellar thickening are identified morphologically: melting followed by recrystallization and solid-state thickening below the melting point.

EXPERIMENTAL

The material of this study is a homopolymer of isotactic poly(4-methylpentene-1) (P4MP) originally supplied by BP and recently measured by the Polymer Supply and Characterization Centre at RAPRA, Shawbury, UK, using gel permeation chromatography, to have a polystyrene-equivalent mass-average molecular mass of 3×10^6 and a polydispersity of 27. The crystallization of this polymer, which is spherulitic, has been described in detail previously[15]. For this study samples were initially films ca. 0.5 mm thick, melted briefly at 270°C and crystallized at 210°C for 3 min, all in an oxygen-free nitrogen atmosphere within the sample pan of a differential scanning calorimeter, then cooled rapidly. At 210°C crystallization is fast, with a radial growth rate[15] of 2 μm s^{-1}; nevertheless, observation on a Mettler hot stage showed directly that growth was not detectable before the temperature had stabilized. That growth was also isothermal in the specimens used is confirmed by the absence of variation in spherulite size and texture through the thickness of the specimen. Samples produced at 210°C, which is the lowest temperature at which isothermal growth is readily attained, have maximum scope for recrystallization at higher temperatures.

Thermal analysis of these specimens gave melting endotherms as shown in *Figure 1*. Such behaviour, first observed for solution-grown polyethylene[5], is widespread in polymers and characteristic of reorganization during measurement: at low heating rates part of the sample melts but has time to recrystallize then remelt during the scan giving a second, higher peak; at high heating rates there is only one peak (associated with the original texture) because of insufficient time for recrystallization but the specimen may also superheat[9] and, as is evident at 80 K min^{-1}, the trace may distort because of instrumental response. Scanning at the commonly used rate of 10 K min^{-1} gives a doubly peaked endotherm with an intervening minimum at 241°C. Annealing experiments have, therefore, been carried out by heating specimens at 10 K min^{-1} to 241°C or lower temperatures as detailed (and calibrated against high purity indium) in the calorimeter (Perkin- Elmer DSC2C), then keeping the temperature constant for times up to 1000 min. Notwithstanding the precaution of an oxygen-free nitrogen atmosphere, evidence based on gradual loss of reproducibility on recrystallization and reduced melting points shows the onset of molecular degradation at the longest annealing time.

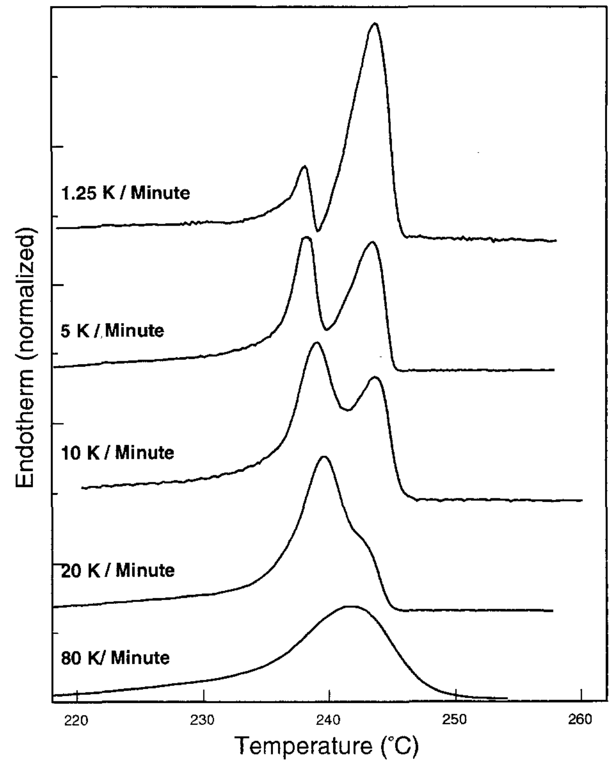

Figure 1 Normalized melting endotherms of the melt-crystallized P4MP as a function of heating rate

All samples, original and annealed, were examined with the transmission electron microscope after permanganic etching. For this they were cut open with a microtome to expose a cross-section through the film, etched for 30 min in a reagent consisting of 1% w/v potassium permanganate in 5/2/2 sulfuric acid/orthophosphoric acid/water, washed according to published procedures[12] then replicated by a standard two-stage process. All photographs are of replicas of such etched surfaces with metal shadowing of the first impression. Where values for lamellar thickness are given, these have been measured directly from photographs when lamellae have been positioned normal to the photograph by appropriate tilting in the microscope.

RESULTS AND DISCUSSION

The starting sample is composed of spherulites, with diameters of ca 20 μm, each constructed from a framework of individual dominant lamellae which branch at, and tend to diverge from, giant screw dislocations[15]. *Figure 2a* shows an area in which lamellae are seen predominantly sideways on, exposing a framework filled in by subsidiary lamellae (of the same intrinsically square habit) within seconds. After etching, dominant lamellae tend to stand proud in the exposed surface (*Figure 2b*), revealing their greater resistance. It is also evident from curved traces etc. that as-grown lamellae are often significantly distorted away from their ideally planar habit.

When this sample is melted at 10 K min^{-1} the two melting peaks shown in *Figure 1* are conventionally interpreted, to a first approximation, as follows: the lower

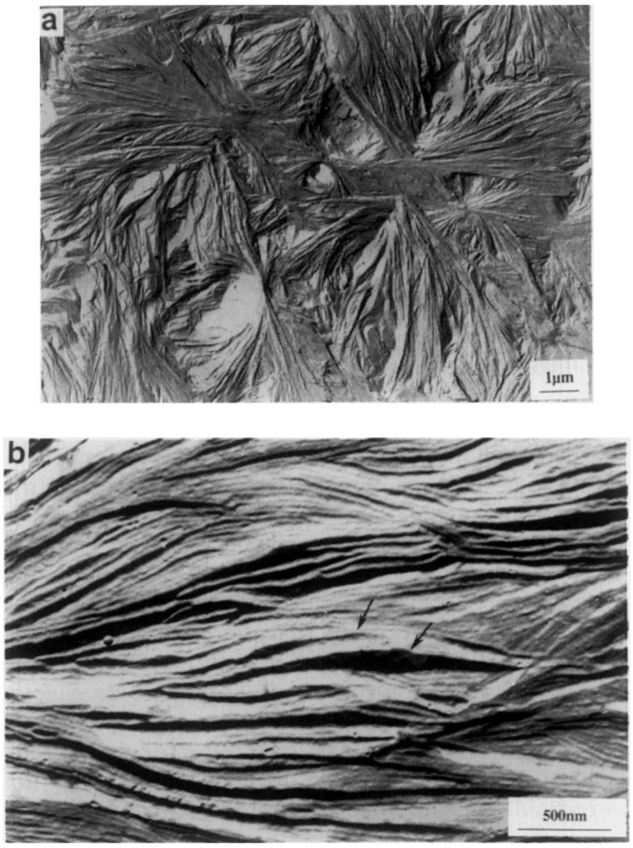

Figure 2 (a) The spherulitic texture of the original material which was crystallized at 210°C for 3 min. (b) Detail showing the variation in relief in an etched surface associated with dominant/subsidiary crystallization; the arrows identify two dominant lamellae

peak represents lamellae originally present, while the upper peak represents new lamellae formed from material which has melted and recrystallized during the scan. This is suggested by the upper peak not being an inherent property of the sample but a consequence of examining it at lower heating rates. The material contributing to this upper peak would accordingly have originally been least stable and melted first during the scan (only to recrystallize as thicker lamellae then melt for the second time), while lamellae of the lower peak would have been the last of those originally present to melt. The question then arises as to the location of these two populations of lamellae in the sample: morphological evidence indicates that the subsidiary lamellae are the first to melt and the dominants last.

This is demonstrated by *Figure 3*, which shows a sample heated only to 239°C at 10 K min^{-1} in the d.s.c., then immediately cooled. At 239°C, according to *Figure 1*, the melting process of the lower peak is incomplete, i.e. some original lamellae will remain whereas the lower-melting lamellae (which would when recrystallized have contributed to the upper peak) will have already melted. With instant cooling there is, therefore, the possibility of affecting recrystallization of this molten portion of the sample by introducing thinner and/or more defective elements into the lamellae it forms, thereby making them more readily etched than the originals. This appears to be the case in *Figure 3*. Not only is the gross texture retained (*Figure 3a*), but also in *Figure 3b* the dominant and neighbouring lamellae remain very evident and at similar lateral intervals as before; however, intervening material is less well formed and more deeply etched. This is consistent with a progressive lowering of the melting point of subsidiary lamellae in the original sample as they are placed further away from the nearest dominant. When, as here, part of the lamellar population is melted, the remainder is seen to include the dominants and their near neighbours. For brevity it will be convenient to refer to this remainder simply as the dominant region.

Differential stability between dominant and subsidiary lamellae is expected even for isothermal growth. It is, for example, in accord with observations on poly(ether ether ketone) (PEEK), for which it was pointed out that whereas dominant lamellae grow in isolation and unhindered, subsidiary lamellae must accommodate to fitting in the intervening space[16]. In consequence their lamellar thickening may be impeded, which would make subsidiary lamellae progressively thinner and lower melting than their surrounding dominants, as is consistent also with the observations of this paper.

Annealing at 241°C

When heating of samples at 10 K min^{-1} is continued up to 241°C, all of the original lamellae will have been melted. That portion giving the upper melting peak in *Figure 1* will have recrystallized and, at 241°C, will remain unmolten. The remainder, which melted as the

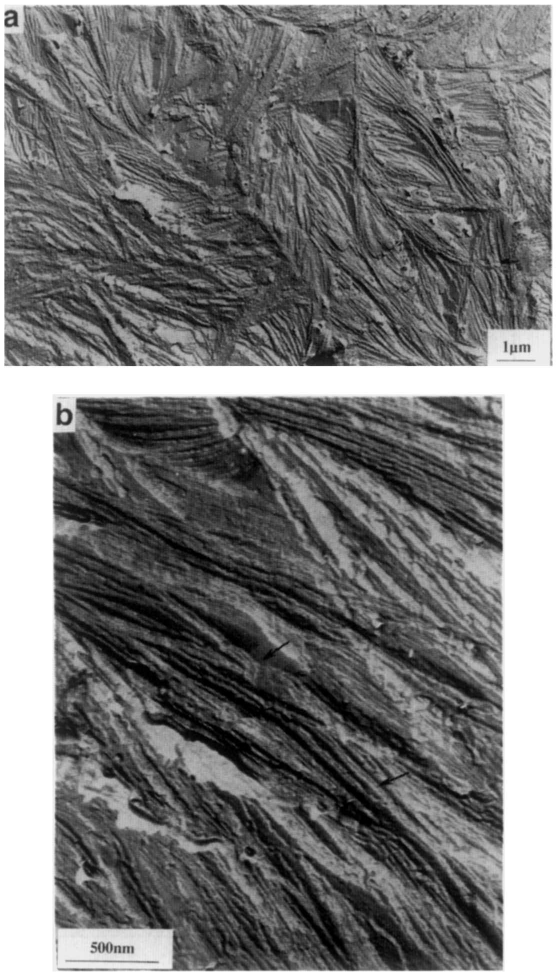

Figure 3 (a) The texture after heating to 239°C then cooling immediately retains the gross spherulitic texture. (b) Detail identifying melted and recrystallized portions (arrowed) of the morphology, lying between the dominant regions

lower melting peak, will now have the opportunity to recrystallize either while holding at 241°C, in which case it will contribute to material melting above 241°C, or on cooling. By maintaining the temperature at 241°C one has, therefore, the opportunity of studying isothermal thickening of lamellae held below their melting point, i.e. by processes which are independent of melting.

The normalized melting endotherms of polymer held at 241°C for various times are shown in *Figure 4*. They show a main peak increasing in size and melting temperature with time and, for 1 and 10 min, clear evidence of lower-melting polymer which would have crystallized on cooling. Lamellar thickness, measured on electron micrographs, increases with the logarithm of annealing time as has generally been found by X-rays for annealed polymers (*Figure 5*). In this instance the morphologies of *Figures 6* to *9* add extra information demonstrating again that the subsidiary regions are lower melting than the adjacent dominants.

In *Figure 6a*, after only 1 min at 241°C, the predominant impression is of a loss of relief in the etched surface; the detail in *Figure 6b* confirms that there are no dominant lamellae standing proud. On the contrary, regions where there would appear to have been dominant lamellae in the initial texture (on the basis of lateral placement and radial extension) have now been etched more deeply than neighbouring areas. Such a reversal of relief is not unexpected for short times when recrystallization of the former dominant and neighbouring lamellae will, as the

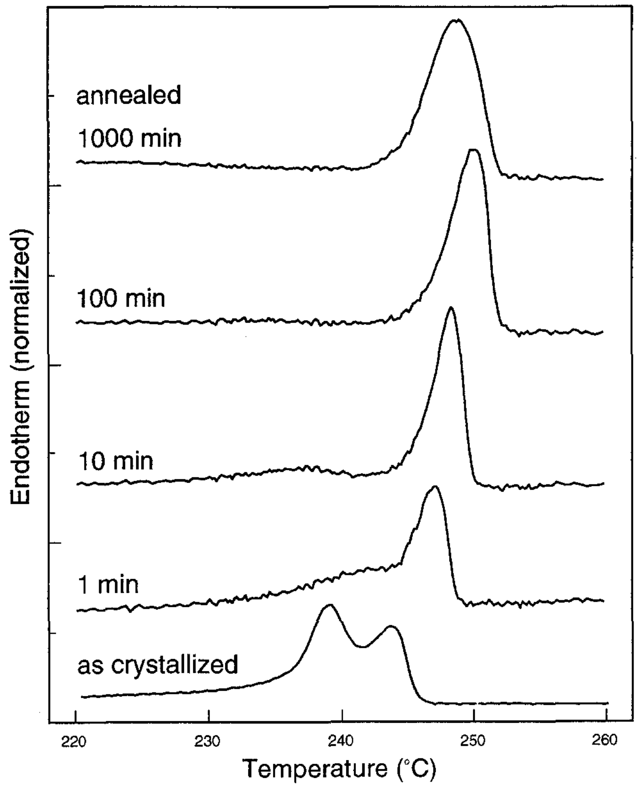

Figure 4 Normalized melting endotherms of the melt-crystallized P4MP measured at 10 K min^{-1} after annealing at 241°C for the specified times

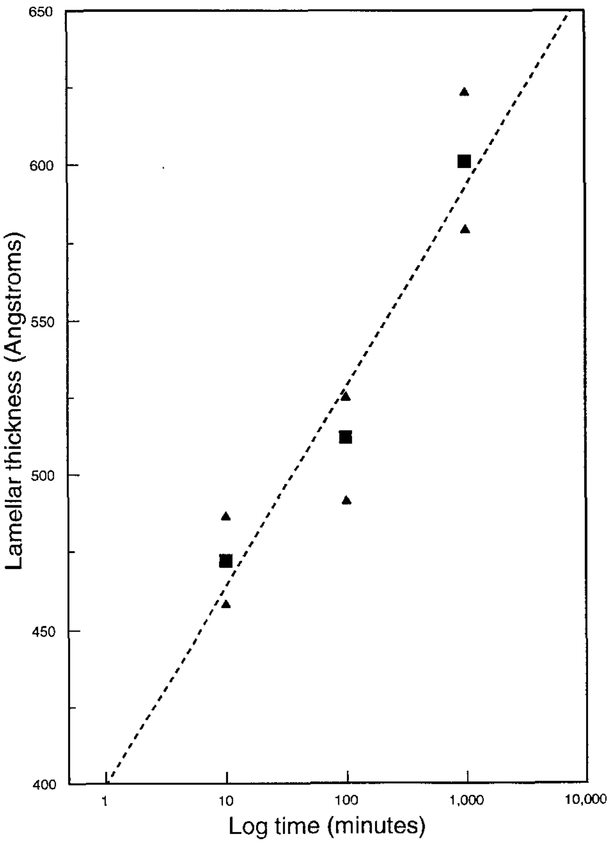

Figure 5 The measured average thickness of the lamellae increases logarithmically with the time of annealing at 241°C: (■) mean; (▲) plus or minus one standard deviation

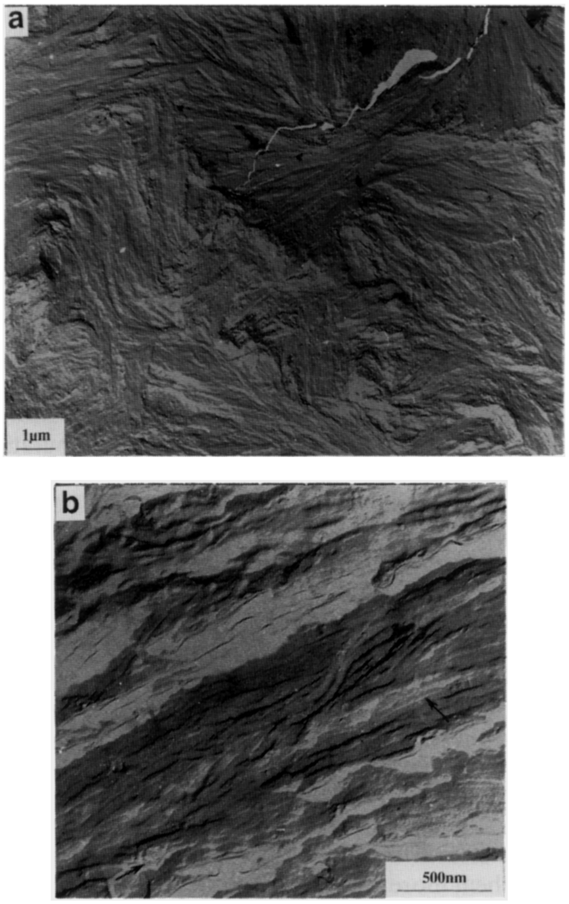

Figure 6 (a) Etched relief is much less after annealing P4MP at 241°C for 1 min. (b) Detail shows a reversal of the normal relief in an etched surface, with the (arrowed) regions surrounding the original dominant lamellae now below the level of the original subsidiary lamellae

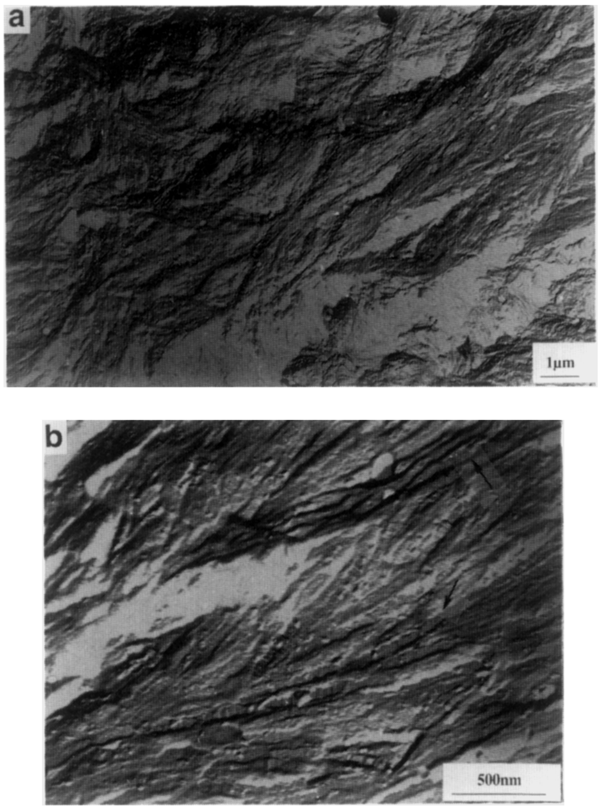

Figure 7 (a) Etched relief increases again after annealing for 10 min at 241°C. (b) Detail shows a reversion to a more familiar contrast with the recrystallized dominant regions, two of which are arrowed, once again standing proud of their neighbours. Note the restricted radial extent

endotherm in *Figure 4* demonstrates, be incomplete (in consequence of a radial growth of ca. 3 nm s^{-1}) when cooling intervenes, thereby tending to make them more prone to etching.

With increasing time, recrystallization of the former dominant regions will be completed and at a higher temperature than that at which the subsidiary lamellae recrystallized. This factor would tend to give thicker lamellae and to restore the relative stability and resistance to etching of the recrystallized dominant regions in relation to the remainder of the sample; on the other hand, the greater annealing time for the recrystallized subsidiary lamellae would have the opposite tendency, but because of the logarithmic time dependence of increasing thickness (*Figure 5*) its magnitude overall would probably be less, so that recrystallized dominants would again be expected to stand proud in an etched surface.

The evidence of *Figure 7* (10 min at 241°C) is of a patchy restoration of 'dominant' relief. At low magnification (*Figure 7a*) proud, recrystallized dominant lamellae are prominent. Higher magnification (*Figure 7b*) shows that there are thick (ca. 50 nm) lamellae in two types of location: in the dominant regions lamellae extend radially for micrometres and more; in between, lamellae tend to be shorter and traverse from one dominant region to the next. On the other hand, 100 min of annealing at 241°C produces a more uniform texture. The distinction between dominants and subsidiaries is still discernible but on different criteria. No strong relief is apparent at low magnification (*Figure 8a*), but higher magnification (*Figure 8b*) differentiates recrystallized dominants from their surroundings both on geometrical placement and on fracture behaviour. Dominants have greater radial extent, often enclosing subsidiaries which, alone, have fractured on replication to reveal the striation parallel to the chain axis familiar for lamellae of enhanced ratio of lamellar thickness to molecular length, notably polyethylene crystallized or annealed at high pressure^{9,17}. Although one must be cautious in interpreting such behaviour, not least because of the importance of the degree of adhesion to the replicating film, in this instance the differential fracture is consistent with longer, more crack resistant molecules being in the dominant lamellae.

Annealing for 1000 min increases lamellar thickness further, sufficiently to render all lamellae prone to brittle fracture during replication (*Figure 9b*). The distinction between recrystallized dominants and subsidiaries, though still discernible in places, is less pronounced. At low magnification (*Figure 9a*) there is depth of relief but on a fine scale. By comparison, crystallization for 1000 min at 241°C produces more clearly defined textural regions at low magnification (*Figure 10a*). Lamellar detail (*Figure 10b*) shows evidence of two lamellar thicknesses – the thinner presumably due to crystallization on cooling – and no indication of fracture during replication. This latter feature in conjunction with *Figure 9b* suggests that, in this melt-crystallized sample, the interlamellar regions are more able to resist cracks

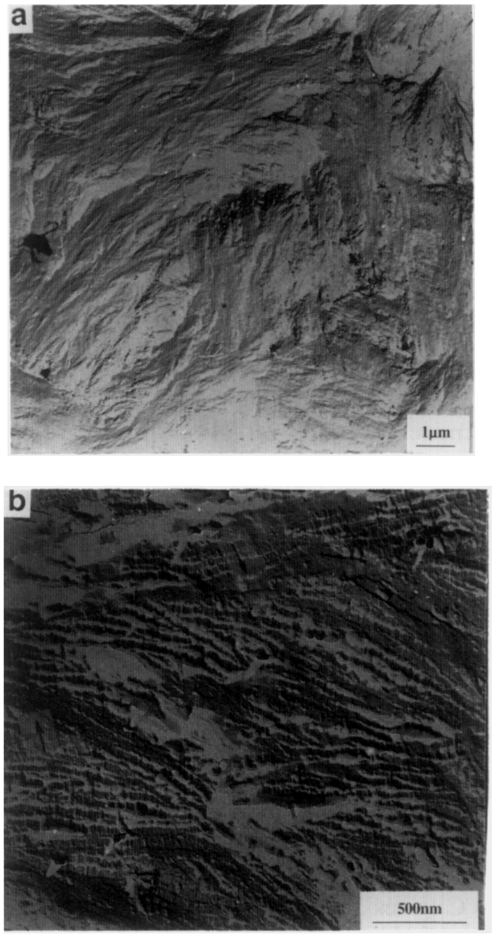

Figure 8 (a) Etched relief after 100 min of annealing at 241°C is on a finer scale. (b) Detail shows the increasing thickness of lamellae and also the tendency of the once-subsidiary regions to fracture during replication in contrast to the dominant regions, two of which are arrowed

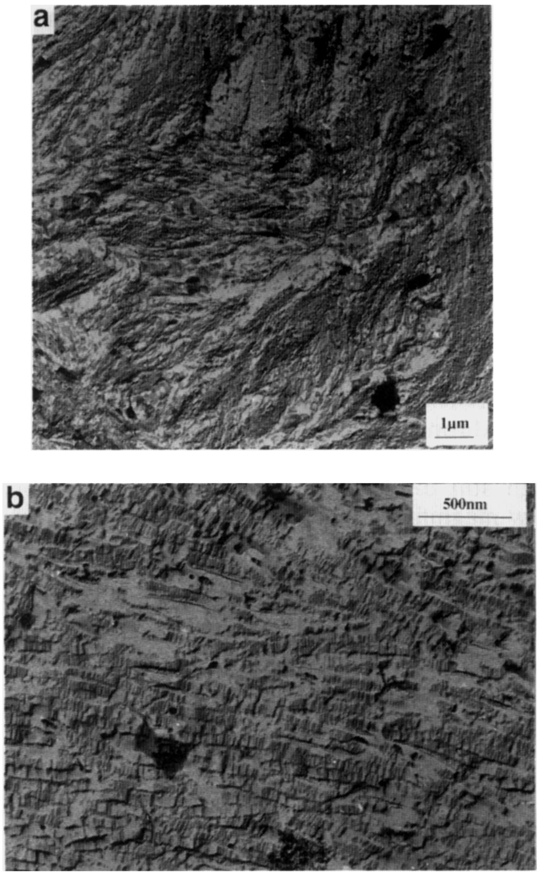

Figure 9 (a) Coarsening of the etched relief, due in part to rougher surface textures, is evident after annealing for 1000 min at 241°C. (b) Detail of lamellae viewed edge-on, showing their increasing thickness, greater widths and general fracture during replication

than in the sample annealed at 241°C for the same time, which would imply that annealing tends to change the nature of the interlamellar regions, possibly by withdrawal of cilia or tightening of loose folds[18].

It is certainly the case that annealing at 241°C for 1000 min roughens the fold surface. The surface texture in *Figure 11* appears to be linear and parallel to the ⟨110⟩ growth direction[15] and to correlate with local variations in thickness. Although radial striations are present in P4MP lamellae crystallized from the melt at such high temperatures[15], the texture in *Figure 11* is rougher than these and also the surfaces of the starting polymer grown at 210°C.

Annealing at 232°C

Further annealing experiments, at 225, 230 and 232°C for times up to 1000 s, serve to emphasize the textural variation of melting point and the role of melting and recrystallization in annealing treatments.

Melting endotherms, at 10 K $\min^{-1}$, of samples annealed at 232°C are illustrated in *Figure 12*. Of principal interest is the great diminution, nearly to zero, of the upper peak in the d.s.c. trace after only 1 min of annealing compared to the original sample. Annealing at 230°C gives a lesser reduction; the effect is still smaller at 225°C. Closer inspection of *Figure 12* shows that the d.s.c. trace after 1 min of annealing contains shoulders above and below the maximum and, in contrast to that for the original sample, is essentially flat below the annealing temperature. The uppermost shoulder, which lies partly above the lower peak for the original sample, must represent polymer which has melted at or below 232°C, then recrystallized as thicker and more stable lamellae at this temperature. That the annealed specimen is now so modified as to be no longer capable of giving the upper peak in the endotherm implies that, in the original sample, this peak derives from polymer melted below 232°C and recrystallized at a higher temperature. One can also infer, from the fact that the lower peak for the original sample has, in part, a greater amplitude than for the specimen annealed for 1 min at

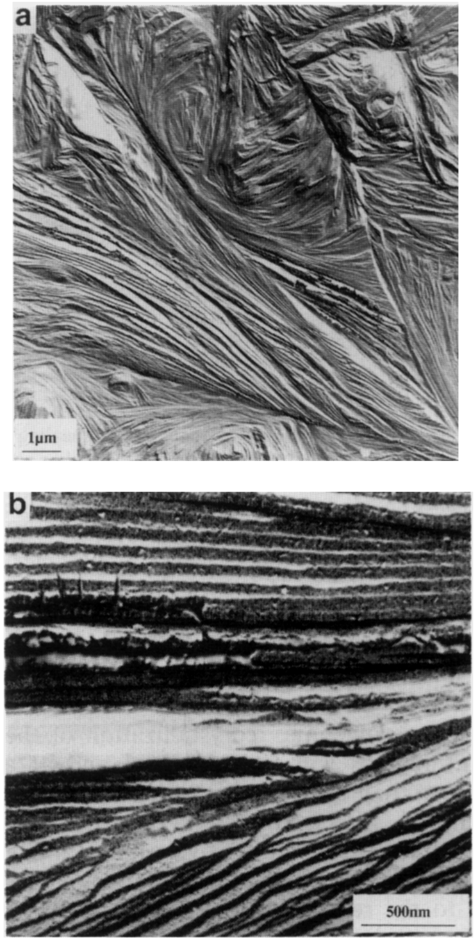

Figure 10 (a) The texture following crystallization of P4MP for 1000 min at 241°C. (b) Detail showing lamellae in two different profiles. Note the more orderly stacking and greater width by comparison with the annealed polymer, and the presence of thinner lamellae occupying the lower right corner

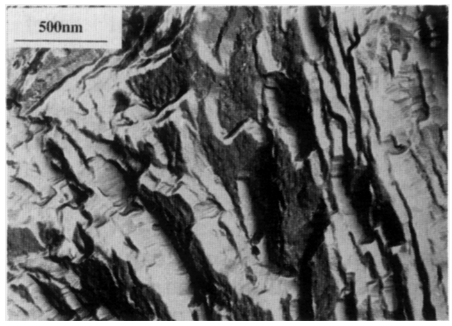

Figure 11 A rough surface texture develops after annealing for 1000 min at 241°C

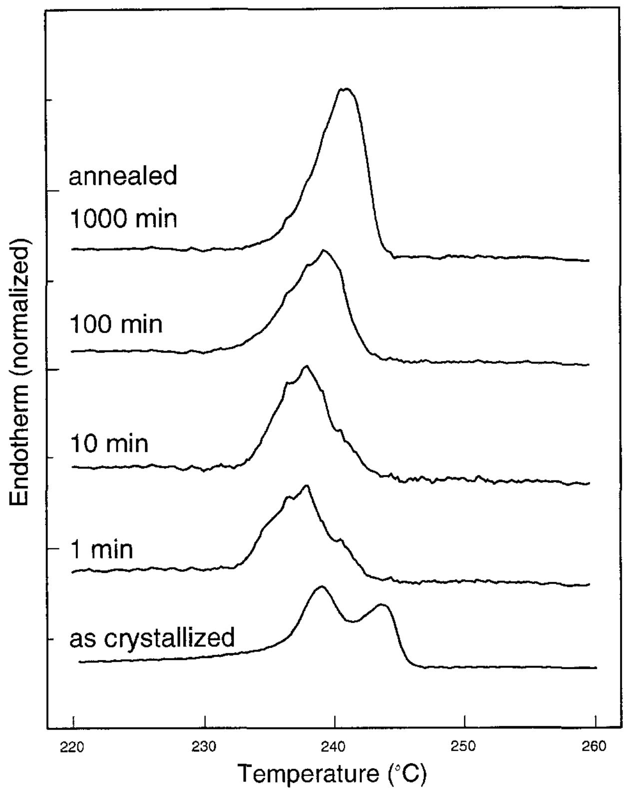

Figure 12 Normalized melting endotherms recorded at $10\,\mathrm{K\,min^{-1}}$ after annealing at 232°C for the specified times

232°C, that it cannot simply represent only residual, higher-melting lamellae in the original sample but must also contain a proportion of recrystallized material.

The morphologies of two samples annealed at 232°C are shown in *Figure 13*. After only 1 min of treatment (*Figure 13a*), etching has produced many small pits, all lying between the original dominants which still stand proud, indicative both of the local scale of melting and how easily the recrystallized regions are attacked, possibly because of the concentration of free volume into microvoids. It is also notable that, after this short treatment, the material exhibits a degree of fracture during replication, probably linked to a degree of fractional crystallization, whereas after longer times the lamellar structure is more uniform and resistant to fracture (*Figure 13b*), consistent with the single d.s.c. peak of slightly higher melting point shown in *Figure 12*.

CONCLUSIONS

This work has substantiated and amplified, using morphological and d.s.c. evidence, three principal conclusions. The first, and arguably the most important, is that the melting point of P4MP lamellae is modulated by spherulitic texture, being highest for the first-forming dominant lamellae and progressively lower for later-forming subsidiary lamellae. It is important to emphasize that this result has been obtained on isothermally grown samples so that the variation of melting point has no contribution from differences of crystallization temperature. The result seems rather to be caused by the increasing difficulties encountered by later-forming lamellae of accommodating to the environment of previously formed neighbours. This concept was proposed earlier for PEEK[16] whose molecular chain is

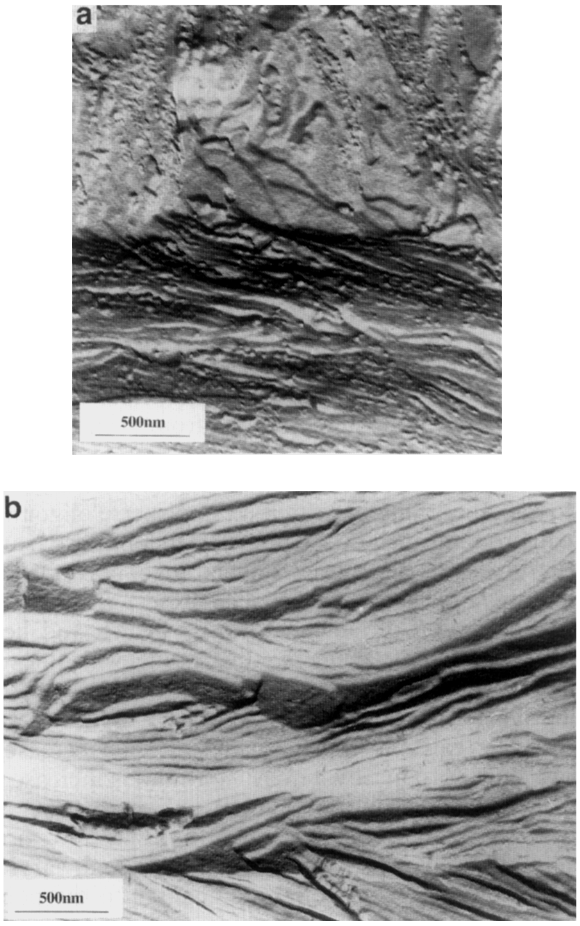

Figure 13 (a) Detail of texture after annealing P4MP at 232°C for 1 min. Note the very localized changes indicating the sites of melting and recrystallization. (b) After 1000 min of annealing at 232°C the structure has substantially healed

comparatively stiff and difficult to fold. Chain stiffness would not be expected to be of comparable significance in P4MP and one would anticipate rather that hindrances to lamellar thickening would be a major contributor to lowered melting points.

The systematic variation of properties with location within a spherulite is now well attested. One sees this, in the first instance, when polymers are etched, when dominant lamellae are invariably found to be more resistant[9,13,15]. This effect can be much amplified, however, by differential deformation during cutting prior to etching[19], an observation which may indirectly reflect how constraints and interlamellar connectivities vary with intraspherulitic location. There is also direct evidence that subsidiary lamellae deform before dominants in macroscopic tensile drawing of banded polyethylene spherulites[20]. The present work extends the spatial variation of response to melting behaviour, a property which is likely to reflect connectivities much less than inherent variations of lamellar thickness*.

The second conclusion is the detailed morphological

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* Systematic variations in melting point have previously been reported for the complicated morphologies of monoclinic polypropylene, whose cross-hatched lamellae melt at lower temperatures than do radial dominants[21,22]. Interpretation is not so straightforward in that complex system

support provided for the widely held hypothesis that melting and recrystallization occur when polymers are heated at slow to moderate rates. Of especial note is the evidence of *Figure 13a* that this begins as a very local phenomenon in agreement with earlier exposition[9]. Nevertheless, it has been shown that the interpretation of a doubly peaked endotherm is more complicated than that usually given.

The third conclusion is the unambiguous morphological demonstration that lamellae will thicken isothermally, approximately as the logarithm of elapsed time, by a process distinct from melting and recrystallization. While it has long been suggested that such processes of solid-state thickening occurred[23–25], one needs to be able to make a clear differentiation from melting and recrystallization phenomena, which the present work has achieved. (It should be mentioned that evidence for solid-state thickening of certain monodisperse oligomers growing from the melt was demonstrated long ago[26], and lamellar thickening during crystallization of polyethylene at high pressure even earlier[17].) The present work shows that a population of lamellae already grown and held near to but below their melting point will thicken continuously and achieve higher stability and melting points. This is achieved not by adding new, thicker lamellae to existing thinner lamellae, so increasing average thickness, but by a quasi-continuous increase of thickness measured on each lamella present.

There have been many suggestions as to how isothermal lamellar thickening may be achieved, varying from the translation of entire fold stems[23] to the point defect of Reneker[27]. The evidence from morphology shows that the major change in lamellar thickness is most often at lamellar edges where it may represent a tapered growth profile most familiar from the crystallization of polyethylene at high pressure[9], but may also reflect surrounding geometrical constraints including the genesis of a spiral terrace (frequently seen to be of only one turn) around a giant screw dislocation[15]. Annealing is clearly seen to increase lateral continuity of lamellae from what may be rather small widths left by recrystallization, but only for the longest times (*Figures 9b* and *10b*) is there evidence of local variations in lamellar thickness, as would be expected from the relative change in free energies. The absence of thinner regions of lamellae from the micrographs in general is evidence for local changes occurring rather suddenly. One lamella can only thicken at the expense of its neighbour, but if that neighbour fluctuates thinner then it will be less stable and more likely to disappear and be consumed quickly.

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REFERENCES

1 Bassett, D. C. and Keller, A. *J. Polym. Sci.* 1959, **40**, 565
2 Statton, W. O. and Geil, P. H. *J. Appl. Polym. Sci.* 1960, **3**, 357
3 Fischer, E. W. and Schmidt, G. F. *Angew. Chem.* 1962, **15**, 551
4 Hoffman, J. D. and Weeks, J. J. *J. Res. Nat. Bur. Stand., Sect. A* 1962, **66**, 13
5 Bair, H. E., Salovey, R. and Huseby, T. W. *Polymer* 1967, **8**, 9
6 Frank, F. C., Keller, A. and O'Connor, A. *Philos. Mag.* 1959, **4**, 200
7 Bassett, D. C., Frank, F. C. and Keller, A. *Nature* 1959, **184**, 810
8 Hoffman, J. D. and Miller, R. L. *Macromolecules* 1989, **22**, 5038
9 Bassett, D. C. 'Principles of Polymer Morphology', Cambridge University Press, Cambridge, 1981, p. 124
10 Bassett, D. C. and Carder, D. R. *Philos. Mag.* 1973, **28**, 513
11 Bassett, D. C., Khalifa, B. A. and Olley, R. H. *Polymer* 1976, **17**, 284
12 Olley, R. H., Hodge, A. M. and Bassett, D. C. *J. Polym. Sci., Polym. Phys. Edn* 1979, **127**, 627
13 Bassett, D. C. in 'Comprehensive Polymer Science' (Eds G. Allen and J. C. Bevington), Vol. 1, Pergamon Press, Oxford, 1989, p. 841
14 Patel, D., Hodge, A. M., Bassett, D. C. and Olley, R. H. in preparation
15 Patel, D. and Bassett, D. C. *Proc. R. Soc. London, Ser. A* in press
16 Bassett, D. C., Olley, R. H. and Al Raheil, I. A. M., *Polymer* 1988, **29**, 1745
17 Rees, D. V. and Bassett, D. C. *J. Polym. Sci. (A-2)* 1971, **9**, 385
18 Witenhafer, D. E. and Koenig, J. L. *J. Appl. Phys.* 1968, **39**, 4982
19 Freedman, A. M., Bassett, D. C., Vaughan, A. S. and Olley, R. H. *Polymer* 1986, **27**, 1163
20 Bassett, D. C. and Freedman, A. M. *Progr. Colloid Polym. Sci.* 1993, **92**, 23
21 Norton, D. R. and Keller, A. *Polymer* 1985, **26**, 704
22 Olley, R. H. and Bassett, D. C. in preparation
23 Peterlin, A. *Polymer* 1965, **6**, 25
24 Gruner, C. L., Wunderlich, B. and Bopp, R. C. *J. Polym. Sci. (A-2)* 1969, **7**, 2099
25 Sanchez, I., Peterlin, A., Eby, R. K. and McCrackin, F. L. *J. Appl. Phys.* 1974, **45**, 4216
26 Kovacs, A. J., Gonthier, A. and Straupe, C. *J. Polym. Sci. (C)* 1975, **50**, 283
27 Reneker, D. H. *J. Polym. Sci.* 1962, **59**, 539