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The morphology of isotactic polystyrene crystals grown in thin films: the effect of substrate material

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Thin isotactic polystyrene films (~50 nm thick) have been crystallized from the melt on various substrate materials (carbon, glass, mica, polyimide sheet and silicon). The morphology of the crystals has been examined using atomic force microscopy, and was found to be dependent on the nature of the substrate, with two basic types of crystal forming. Crystals either develop around giant screw dislocations, or around small bundles of lamellae growing perpendicular to the substrate surface. It has further been observed that the number of screw dislocations generated in the lamellae is also dependent on the substrate, as is the growth rate of the spiral terraces. These effects are interpreted in terms of interactions between the molecules in the melt and the substrate surface.

1. Introduction

Many forms of scanning probe microscopy (SPM) [1] now exist; however, for the examination of non-conducting materials, such as polymers, atomic force microscopy (AFM) [2] has proved to be the most widely utilized. Application of AFM to imaging essentially flat, smooth, surfaces, such as molecular monolayers, has produced many notable results. However, when dealing with bulk specimens, the problem of how to reveal the underlying structure is faced. In general, one of the simplest approaches to this problem is to examine fracture surfaces. Nevertheless, for semi-crystalline polymers this technique may produce biased morphological information, with fracture occurring preferentially along certain crystallographic directions [3, 4]. Additionally, fracture surfaces are frequently rough which can cause imaging difficulties when applying scanning probe techniques, and can often lead to tip-imaging artefacts [5]. Recently, Schonherr *et al.* have used permanganic etching to obtain meaningful structural information from bulk isotactic polypropylene samples crystallized over a range of different temperatures [6]. This work has shown that surfaces prepared in this manner do not suffer from the same difficulties as those produced by fracture. Nevertheless, because permanganic etching produces non-specific internal morphological information, namely the crystals are viewed in all orientations, the resultant AFM images can be difficult to interpret.

Crystallization of thin polymeric films provides a convenient method of restricting crystal growth to a desired plane, consequently generating samples that produce more easily interpreted AFM images [7]. However, it has been shown for poly(vinyl fluoride) that restricting crystal growth from the bulk to thin films, affects the resulting crystal morphology [8, 9]. We have shown previously that the morphology of isotactic polystyrene (iPS) crystals grown in thin films (~ 50 nm thick) is not affected grossly by this method of preparation [10]. However, as the thickness of a specimen is reduced (away from the ideal situation of the bulk) the influence of the sample surfaces becomes increasingly important in determining the properties of a thin film. Here we investigate the effect of the polymer/substrate interface on the morphology of iPS crystals grown from the melt in thin films.

We are only aware of a few systematic studies of crystal growth in thin polymer films (e.g. morphology, growth rate, etc.) that have been conducted [9–14]. More generally, the properties and interactions of thin polymer films with their surroundings is an area which has received little attention in the literature. For example, very little quantitative data exist concerning

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the interaction energy between polymeric materials and solid inorganic surfaces. The selective absorption of functionalized polymer chains [15, 16] from dilute solution on to various materials, is wholly reliant on strong interactions between the substrate and certain groups along the polymer chains. Nevertheless, even when weak interactions occur between a thin solid polymer film and its interfaces (i.e. the substrate and the free surface in contact with air), dramatic large-scale effects can occur, e.g. phase separation can be induced in polymer blends simply by reducing the film thickness [17–19]. Keddie *et al.* have studied the dependence of the glass transition temperature, T_g, on film thickness in thin polymeric films [20, 21]. Importantly in the context of this work, they have observed a dependence of T_g on the substrate material employed, and moreover, that T_g can *increase* as the film thickness is reduced. In this paper, we report on variations in the morphology of iPS crystals grown in thin films from the melt caused solely by changes in the substrate material, and hence the interactions between the iPS molecules in the melt and the substrate.

2. Experimental procedure

Thin-film iPS samples (~ 50 nm thick) were prepared using a 0.4% weight by volume solution of iPS ($M_w = 590\,000$ supplied by General Science Corp.) in cyclohexanone. For all substrate types, a drop of iPS solution was pipetted on to a water surface [22]; the partially miscible solvent spreads on the water, evaporating and dissolving into the water, leaving a thin iPS film on the surface. The thickness and uniformity of the cast film was routinely estimated from the interference colours. The cast film was transferred on to the appropriate substrate material by carefully placing the substrate down on to the film; lifting the substrate from the water surface also removes the iPS film which adheres to the substrate. Various substrates have been investigated, including carbon, glass, Kapton (a polyimide film), mica and silicon. Carbon films were prepared by evaporation on to either mica or glass coverslips, mica was freshly cleaved before use, whilst the other materials were used as-supplied. All specimens were crystallized isothermally in a Mettler hot stage at 210 °C for between 2 and 3 h, following melting at 250 °C for 3 min.

AFM measurements were performed using a Nanoscope II operating under standard conditions: images were collected in both force and height mode. Samples for TEM were crystallized on carbon substrates, and stripped from the substrate using polyacrylic acid after first being coated with a thin layer of evaporated carbon. The samples were examined directly without further preparation using a Jeol 100 CX operating at 100 kV.

3. Results and discussion

3.1. Crystal morphology

Two typical forms of morphology have been observed for iPS crystals grown on the different substrates. Fig. 1a shows a force mode image of an iPS crystal grown in a film on mica: the crystal displays a giant screw dislocation at the centre. The other typical morphology observed is shown in Fig. 1b; here the film is on carbon, and the crystal has developed around a bundle of lamellae which grow perpendicular to the plane of the film. The crystal in Fig. 1a is ~ 6 μm across and has grown at a rate of ~ 1.5 μm h^{-1}, about 30% slower than the rate of crystallization in the bulk [10]. Both crystals have a regular hexagonal habit and smooth, flat, lateral facets, the same as iPS lamellae grown in bulk specimens [23, 24].

The largest overgrowth terrace above the mother crystal in Fig. 1a (which was the first to develop) has a regular shape and has developed at approximately the same rate as the mother crystal. The uppermost overgrowth, although regularly hexa-angular, is asymmetric in shape, and seems to lag behind the first overgrowth terrace. Such shapes can be explained by extending the arguments proposed by Mansfield for the curved lamellar profile of polyethylene crystals [25]. As the spiral terrace develops, each additional facet is created at some distinct time. Each successive prior facet will have had longer to grow, and this will ultimately lead to an asymmetric shape. There is, however, an additional factor to consider in the case of these crystals.

The fact that these crystals can be observed by AFM, which is a surface specific technique, necessitates that the crystals are protruding from the surface of the surrounding quenched matrix. Fig. 2 shows clearly that lamellae develop to become thicker than the ~ 50 nm thick film in which they initially start to grow. Each spiral terrace layer is ~ 17 nm thick [26], and as such, after only three crystal layers have developed, the total crystal thickness exceeds that of the original film. Thus, for spiral terraces to continue to develop, once the terrace protrudes from the melt, molecules must diffuse across the basal surfaces to reach the lateral facets of the overgrowth terraces. Under such conditions, the growth of spiral terraces will be affected not only by the supercooling, but by the availability of crystallizable material. It is often observed that overgrowth terraces are elongated towards the nearest facet of the mother crystal, and hence in the direction of the melt, and potentially crystallizable molecules (see Fig. 1b). Thus, any asymmetry observed in the shape of spiral terraces protruding above the level of the melt is probably caused by a combination of factors, namely, the availability of molecules to crystallize, and the ideas proposed by Mansfield.

When iPS films are crystallized on glass or silicon, two different crystal populations develop (Fig. 3a). One group of crystals grows around hollow screw dislocations (similar to crystals grown on mica), whilst the second group displays the other typical morphology, and develop around a bundle of lamellae (akin to those on carbon). The crystals are highly complex with a profusion of screw dislocations resulting in crystals up to 300 nm high. Variability in the lateral size of the crystals shows that sporadic nucleation has occurred, and may indicate that the surfaces of the glass-cover slips are particularly free from heterogeneous nuclei.

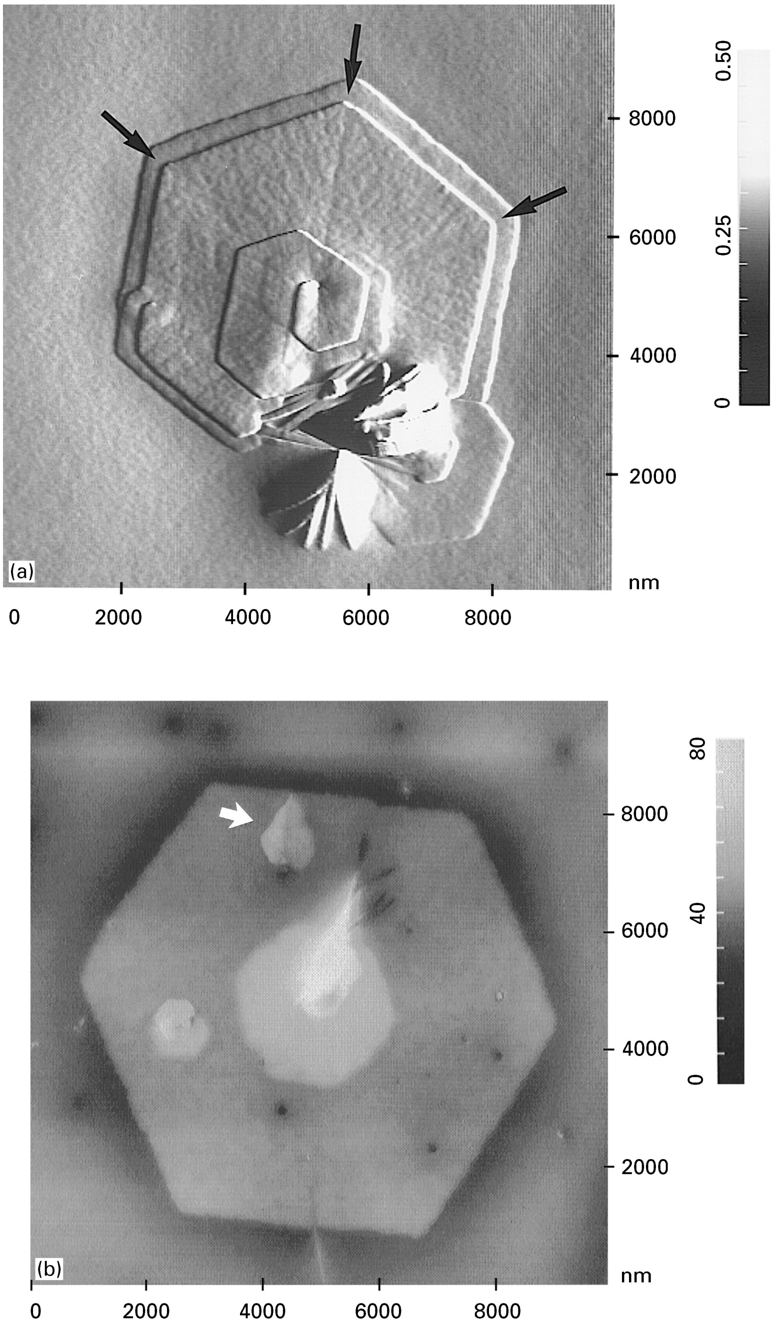

Figure 1 (a) Atomic force micrograph (force mode) of an isotactic polystyrene crystal grown from the melt in a 50 nm thick film at 210 °C on a mica substrate. The arrows indicate sector boundaries. (b) Height mode image of an iPS lamella crystallized under similar conditions on a carbon substrate: the arrow indicates an elongated overgrowth terrace.

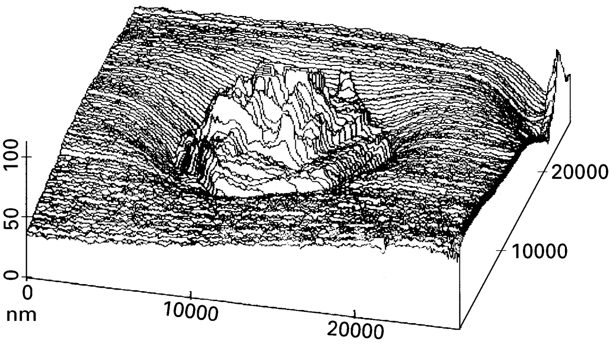

Figure 2 Three-dimensional surface plot of an iPS crystal grown in a thin film. The crystal develops to become thicker than the original film, and consequently protrudes from the film surface.

Lamellae grown in films on Kapton only develop around screw dislocations (Fig. 3b). The morphology of these crystals is very simple, and a number of independent screw dislocations have been introduced into the lamellae at various stages of crystal development, i.e. spiral terraces can be seen at places other than the centre. Comparison with crystals grown on mica and glass substrates (Figs 1a and 3a), shows that the apparent screw dislocation density, i.e. the number of screw dislocations per unit area of crystal basal surface, varies markedly from one substrate material to another. In general, for crystallization in the bulk, the screw dislocation density may be affected by the rate of crystal growth (as determined by the supercooling) [27]; however, all the samples considered here

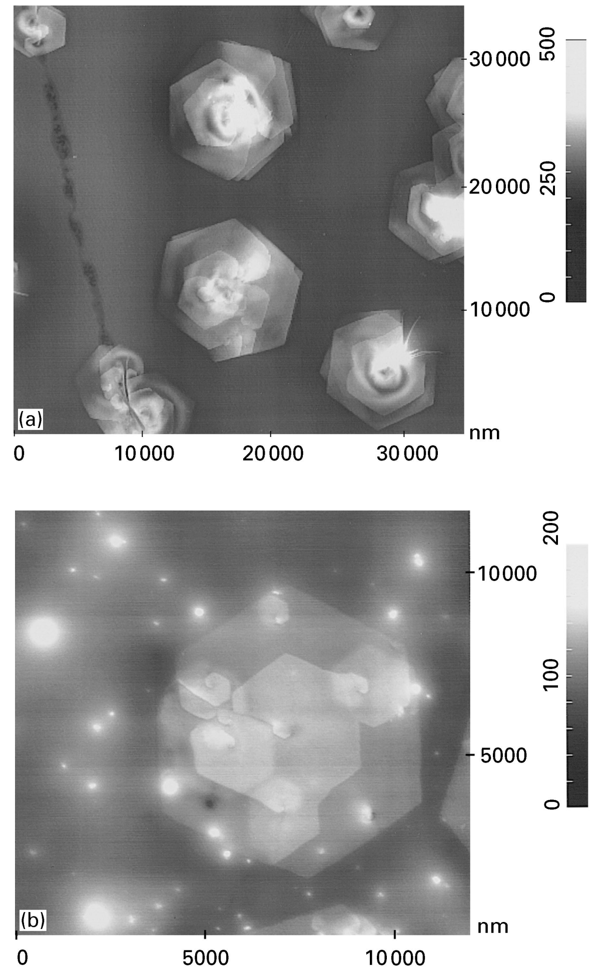

Figure 3 Height mode images of iPS crystals grown in thin films at 210 °C on (a) glass, and (b) Kapton substrates.

have been prepared under identical crystallization conditions, apart from the substrate material. As will be shown, the growth rate of spiral terraces beneath the mother crystal is dependent on the substrate material. However, this variation in growth rate is small, and unlikely to produce such noticeable changes in screw dislocation density. Furthermore, although heterogeneities on a substrate surface could act to distort a developing crystal, thus introducing strain into a lamella, and hence promoting the introduction of screw dislocations, this seems unlikely, and no evidence of this has been found. Moreover, heterogeneities are more likely to act as nucleation sites from which the crystals can develop. Indeed, because two typical crystal morphologies have been identified, which may be distinguished by the nature of the centre of the crystal, i.e. a bundle of lamellae or screw dislocation, it then seems possible that two types of nucleation behaviour are taking place. These may possibly correspond to nucleation on the substrate surface, and in the "body" of the melt, with the relative proportion of each type depending on the interaction between the molten polymer film and the substrate.

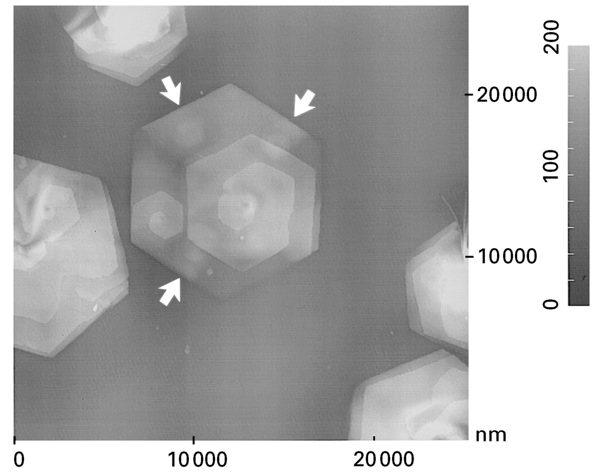

Figure 4 A height mode image of an iPS lamella grown in a thin film at 210 °C on glass, exhibiting spiral terraces (arrowed) beneath the mother crystal.

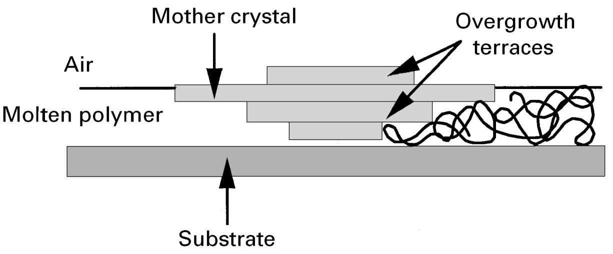

Figure 5 Schematic diagram of an iPS molecule trapped between the mother crystal and the substrate.

3.2. Growth rate of spiral terraces

Overgrowth terraces do not only grow above the plane of the mother crystal, but also below, as indicated by the shadowy outlines in Fig. 4 (arrowed). Compared to overgrowths protruding from the melt, the availability of crystallizable material at the growth front in this case is not a limiting factor in the development of the overgrowths, because the spiral terraces are surrounded by the melt. Nevertheless, the movement of molecules is restricted in the gap between the substrate and the mother crystal; and thus, the molecules can interact with two surfaces (Fig. 5). The effect of this additional interaction with the substrate can be observed as a difference in growth rate between spiral terraces developing above and below the mother crystal. Qualitatively, spiral terraces developing beneath crystals grown in films on carbon substrates grow faster than those above the mother crystal ($G^{\mathrm{C}}_{\mathrm{under}} > G^{\mathrm{C}}_{\mathrm{over}}$) whereas, in contrast, spiral terraces developing beneath crystals grown on mica grow slower than those above the mother crystal ($G^{\mathrm{M}}_{\mathrm{under}} < G^{\mathrm{M}}_{\mathrm{over}}$) (see Fig. 6) [10]. For both substrates, spiral terraces growing above the mother crystal, and thus protruding from the melt, develop at approximately the same rate under similar crystallization conditions ($G^{\mathrm{M}}_{\mathrm{under}} \simeq G^{\mathrm{C}}_{\mathrm{over}}$), and can hence act as a reference. In the case of carbon substrates, the higher growth rate of spiral terraces beneath the mother crystal, and hence in the melt, can simply be attributed to the availability of potentially crystallizable material. However, on mica substrates, spiral terraces beneath the mother crystal grow at a slower rate than those protruding from the melt, despite developing

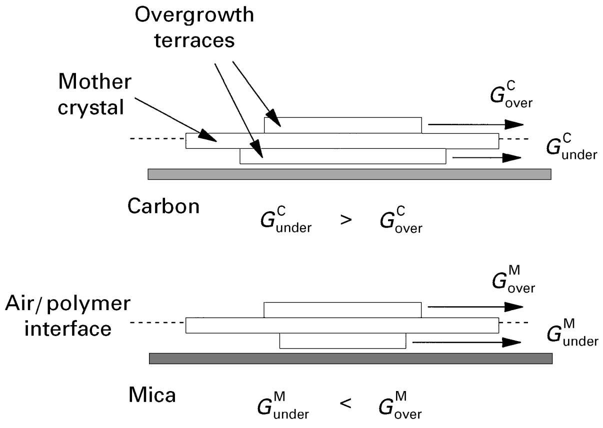

Figure 6 Schematic diagram showing the difference in growth rates of spiral terraces above and below a mother crystal on carbon and mica substrate.

surrounded by more potentially crystallizable material. This demonstrates unequivocally that, under identical crystallization conditions, the growth rate of iPS crystals in thin films is not solely determined by the supercooling, but can be influenced by the nature of the substrate.

Given that the radius of gyration of an iPS molecule ($M_w = 590\,000$) is ~ 25 nm [28], most of the molecules throughout the melt will "feel" the influence of the interface with the substrate, because the film is only ~ 50 nm thick. A simple calculation, assuming no positive interaction between the polymer molecule and the interface [29], shows that under these conditions approximately 0.5% of the molecular segments are within a distance that can conceivably interact with the substrate. If certain segments of the chain become "anchored" to the interface through some strong interaction, there will clearly be an entropic penalty on the system. Hence, the fraction of a polymer chain that experiences an interaction with the substrate will be determined by an equilibrium between the negative absorption energy and the positive entropic penalty. Because it has been claimed that polystyrene interacts only weakly with silicon [30] and mica [31] compared to other more polar polymer molecules, it may be fair to assume that, to a first approximation, we can ignore any entropic constraint on the molecules caused by anchoring. Thus, assuming that molecules diffusing to a growing facet of a spiral terrace beneath the mother crystal must pass through a ~ 17 nm gap, bounded by the mother crystal and substrate (see Fig. 6), then the percentage of molecular segments experiencing the influence of an interface (the substrate or the basal surface of the other crystal) increases to 3%. Although a molecule trapped within this gap would be highly confined, and would have a decreased entropy, it is more likely that only part of any one molecule exists within the gap, and that it passes to the growth front by reptation. Although the fraction of molecular segments which can possibly interact is small, and the interactions are probably weak [30, 31], these data and others [32] show a clear variation in the growth rate of iPS crystals grown in thin films on different substrates.

3.3 Other morphological features

In addition to the variation seen in the morphology of iPS lamellae grown on different substrates, and discussed above, there are other morphological features that deserve some comment. Several sector boundaries are visible in Fig. 1a (arrowed). Height profile traces across the most distinct boundary (which is almost at right angles to the scan direction) show it has a depth of about 2 nm relative to the basal surface. In contrast, for solution-grown polyethylene, polyoxyethylene and polyoxymethylene lamellae, the sector boundaries have been found, in all cases, to stand proud of the lamellar basal surfaces [33]. Whether this difference between the level of the sector boundary relative to the basal surface depends on the nature of the polymer, the manner of crystallization, i.e. from the melt or solution, or the method of sample preparation for AFM, is unclear.

Also observable clearly on the basal surfaces of the crystal in Fig. 1a, and more faintly in Fig. 4, is a lineal texture running at right angles to the lateral facets. Similar striations have been observed in dark-field transmission electron micrographs (TEM) of solution-grown polyoxymethylene and poly(4-methyl pentene-1) crystals [34, 35]. This streaking has been attributed to the non-planarity of these lamellae in solution: sedimentation causing the crystals to flatten, and resulting in shear about the normal to the growth face. Fig. 7 shows a dark-field transmission electron micrograph of an iPS lamella grown isothermally in a thin film on carbon; streaking can be seen in four of the six sectors: the two sectors with growth facets parallel to the diffracting plane do not exhibit

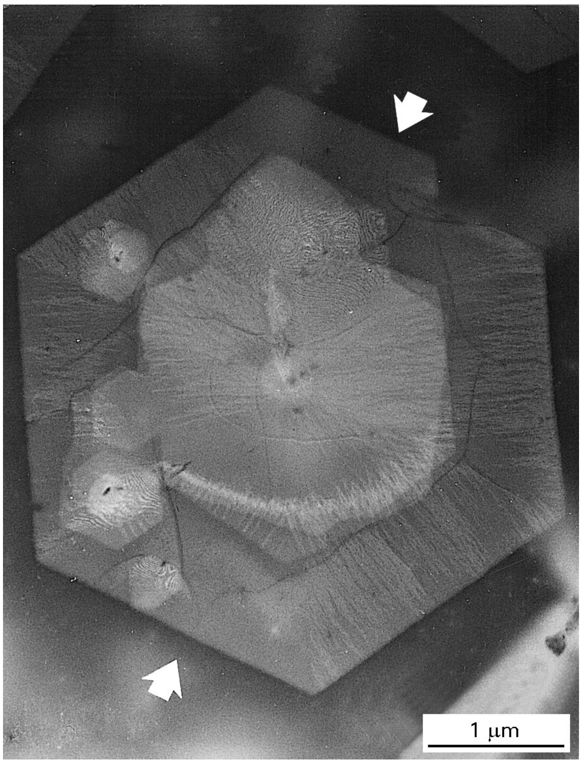

Figure 7 Dark-field transmission electron micrograph of an iPS lamella grown at 210 °C on carbon, exhibiting linear streaking. The two sectors with growth facets parallel to the diffracting plane do not show any streaking (arrowed).

streaking [35]. This would seem to imply that these lamellae are non-planar in the melt, and undergo some form of shear, perhaps when crystallization is terminated by quenching. However, examination of the interior angles of lamellae grown in the bulk gives no evidence to suggest that the crystals are non-planar [13]. Furthermore, bulk iPS specimens crystallized from a quiescent melt, and subsequently exposed to a permanganic etchant, reveal lamellae which exhibit similar streaking on the crystal basal surfaces (see, for example, Fig. 4 in [23]). Clearly, under these growth conditions, collapse and shear cannot have occurred to produce the observed morphology; nevertheless, although unlikely, stresses could be introduced into the melt during quenching. Further investigations into the origin of these features are currently underway, and will be reported in due course.

3.4. Summary

The variation in crystal morphology seen between these nominally identical melt-crystallized thin-film iPS samples is striking. It is only the substrate material that differs between these samples, and consequently, it can only be the affect of the various substrates that gives rise to these changes. Some of these differences may be attributed to the primary nucleation process; either nucleation on the substrate or in the "bulk" of the film, thus producing crystals with screw dislocations or bundles of lamellae at the centre. However, variations in the screw dislocation density, which occur at a later stage of lamellar development, cannot be ascribed simply to the primary nucleation event. It seems improbable that a substrate can influence the introduction of a screw dislocation into a developing crystal with which it is not in direct contact. However, in these thin films a physical connection between a growing lamella and the substrate does exist tenuously, namely through the polystyrene molecules attaching and chainfolding at the growth front. Owing to the thickness of the films, most molecules will "feel" the influence of the substrate and, as such, this may provide some explanation for the variation of screw dislocation density between samples crystallized on different substrates. It has previously been proposed by Keddie *et al.* [20, 21] that interactions between the molecules in a thin polymeric film and a substrate surface affect the mobility of the chains, as evinced by changes in T_g with substrate material. They have further illustrated this by using model polymeric systems, whereby the mobility of the molecules has been intentionally restricted through grafting chains on to the substrate [21]. In the current work, the retardation in growth rate of spiral terraces under the mother crystal on mica substrates, strongly suggests that interactions between iPS molecules in the melt and the substrate can produce significant changes that differ markedly from the "ideal" situation of crystallization in a quiescent bulk specimen.

4. Conclusions

The morphology of iPS lamellae grown in thin films has been shown to be dependent on the nature of the substrate material. Two typical morphologies are observed, either growth around screw dislocations, or bundles of perpendicular lamellae. Furthermore, the number of screw dislocations per unit area of basal crystal surface is also dependent on the type of substrate. Evidence exists to suggest that the rate of crystal growth is not solely determined by the supercooling of the thin-film melt, but is additionally influenced by interactions between the substrate and iPS molecules in the melt.

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