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The lamellar thickness of melt crystallized isotactic polystyrene as determined by atomic force microscopy

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Atomic force microscopy has been used to investigate the morphology of isotactic polystyrene lamellae growth from the melt in very thin films (~ 50 nm in thickness). It is shown that atomic force microscopy can elucidate the crystal morphology and provide quantitative measurements of the step height (between successive crystal layers of a spiral overgrowth terrace) corresponding to the long spacing, provided suitable procedures are employed. Copyright © 1996 Elsevier Science Ltd.

(Keywords: atomic force microscopy; permanganic etching; lamellar thickness)

Introduction

Microscopy provides a powerful tool to obtain real space information about the size and spatial distribution of particular features in polymeric materials. When these features are large, e.g. spherulites or water trees, then optical microscopy and scanning electron microscopy (SEM) provide a convenient approach, with in many cases simple sample preparation procedures[1–4]. Nevertheless, to examine lamellae in bulk specimens in detail, it has until recently been necessary to utilize transmission electron microscopy (TEM), either on stained thin sections[5,6], replicated etched surfaces[7,8] or fracture surfaces[9,10]. Determining lamellar thicknesses from such micrographs is not always straightforward and resolution may be poor. However, atomic force microscopy (AFM) allows both horizontal and vertical displacements to be measured easily. Nevertheless, obtaining lamellar thickness measurements using this technique, requires that the lamellae are initially in a favourable orientation relative to one of the scan directions. One method by which this can be achieved is crystallization in thin films, so constraining the growth of lamellae to the plane of the film[11–13].

Complementary to real space information, statistical information from scattering experiments is indispensable for understanding the higher order structure of semi-crystalline polymer solids. Small angle X-ray scattering (SAXS) serves as a useful method to obtain the distributions of the crystalline and amorphous thicknesses within a specimen. It has previously been shown that when the thickness distributions are single-modal and symmetric (which should be a reasonable approximation in the case of isothermal crystallization), the SAXS intensities are satisfactorily reproduced in terms of a linear model combined with a Gaussian correlation model[14].

In this paper we report on the use of AFM to measure the thickness of isotactic polystyrene (iPS) lamellae grown from the melt in thin films, and compare the result with SAXS data for a bulk specimen, prepared under similar conditions. However, crystals grown in thin films are covered with a layer of disordered material[15] which obscures detail, and prevents direct unambiguous measurement of the lamellar thickness. It is therefore necessary to devise a method by which this layer can be removed. In this respect, permanganic etching[7,16] provides a potential solution to this problem. It has been proposed that the etchants act by selectively removing disordered material, whilst leaving the crystalline parts of the specimen reasonably unaltered. For routine examination of semi-crystalline polymer this explanation is usually sufficient; however, to be able to measure lamellar thicknesses with any certainty, a better appreciation of exactly how the specimen may be affected by the etchant is required. As well as removing amorphous material from around the crystals, it has been suggested that permanganic etchants can attack and remove the fold surfaces, leaving only the crystalline core[17]. Furthermore, Olley has proposed that molecular stems are not cut or removed from within the crystalline core (which would cause a reduction in crystal core thickness), although entire stems may be removed from the lateral facets of a crystal, so reducing the lateral dimensions.

Experimental

Thin film iPS samples (~ 50 nm thick) were prepared

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*To whom correspondence should be addressed by casting a 0.4% weight by volume solution from cyclohexanone onto a water surface[18]: the resulting films were transferred onto clean glass coverslips. Films prepared in this manner were melted at 260°C for 3 min and then crystallized isothermally in a Mettler hotstage at 210°C for 3 h: this method led to numerous isolated crystals. Bulk specimens for SAXS (∼ 1.5 mm thick) were prepared using the same thermal history as the thin film samples, although crystallization was continued for 15 days under an argon gas atmosphere. Samples prepared in this manner were completely filled with axialites, and no amorphous material was left between the axialites[19]. SAXS experiments were performed at the High Intensity X-ray Laboratory of Kyoto University. A detailed specification of the equipment used and method of data treatment has been given elsewhere[14,20].

Permanganic etching was formed using the method described by Vaughan and Bassett[21]. However since the films were thin and fragile, etching was performed by floating the specimens, still attached to the glass coverslip, on the surface of the etchant for approximately 10 min, before removing the sample and neutralizing the etchant.

AFM measurements were performed using a Nanoscope II (at the Institute for Materials Research, Tohoku University), operating in constant force mode under standard conditions. A high nucleation density of crystals allowed many crystals to be measured ensuring representative results were obtained. Lamellar thicknesses were measured from height profiles across crystals especially chosen on criteria set out in the following section.

Results

Figure 1 shows an AFM image of an iPS crystal grown isothermally in a thin film at 210°C. The crystal displays a hexagonal habit with smooth flat lateral crystal facets (much as seen in the bulk[21]), and has several large overgrowth terraces. The appearance of crystals that have been permanganically etched (*Figure* 2) does not differ significantly from the crystal shown in *Figure* 1. However, the outline of the crystal appears sharper, due to amorphous material around the crystal having been selectively removed by the etchant. This leads to an abrupt step in height between the mother crystal and the surrounding matrix, which results in distinct contrast in the height mode image shown in *Figure* 2a. An increase in the sharpness of the overgrowth terraces can also be observed, caused by the disordered layer covering the crystal surface having been removed by the etchant.

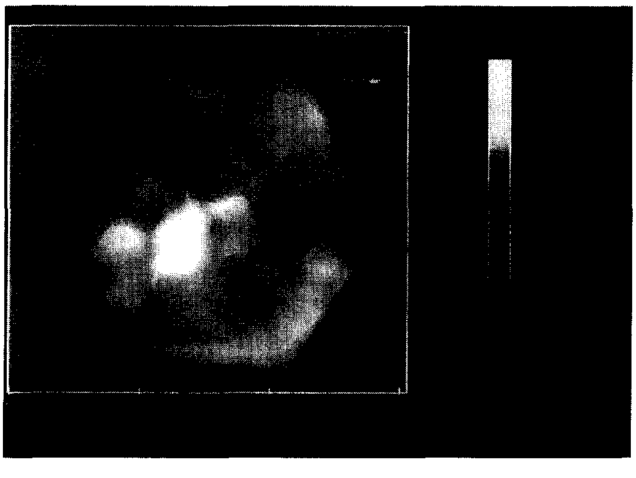

Figure 1 Height mode AFM micrograph of an isotactic polystyrene lamella crystallized on glass at 210°C from a 50 nm thick film

Close examination of the crystal in *Figure* 2a reveals three shadowy objects (arrowed): these features are spiral overgrowth terraces developing beneath the mother crystal. *Figure* 2b shows a surface image of the same crystal; this image shows clearly that the crystal is highly distorted and non-planar. This distortion is caused largely by the growth of spiral terraces trapped between the mother crystal and the substrate. Once these developing overgrowths occupy all the available space, further growth will cause the mother crystal to be forced away from the substrate. Attempting to measure the lamellar thickness from crystals which are as severely distorted as the one shown in *Figure* 2b leads to erroneous results. If truly representative and reproducible measurements are to be obtained using AFM height profiles it is imperative that essentially planar crystals are chosen.

Figure 3 shows a height profile across part of an iPS crystal. The trace shows the mother crystal (*M*) standing

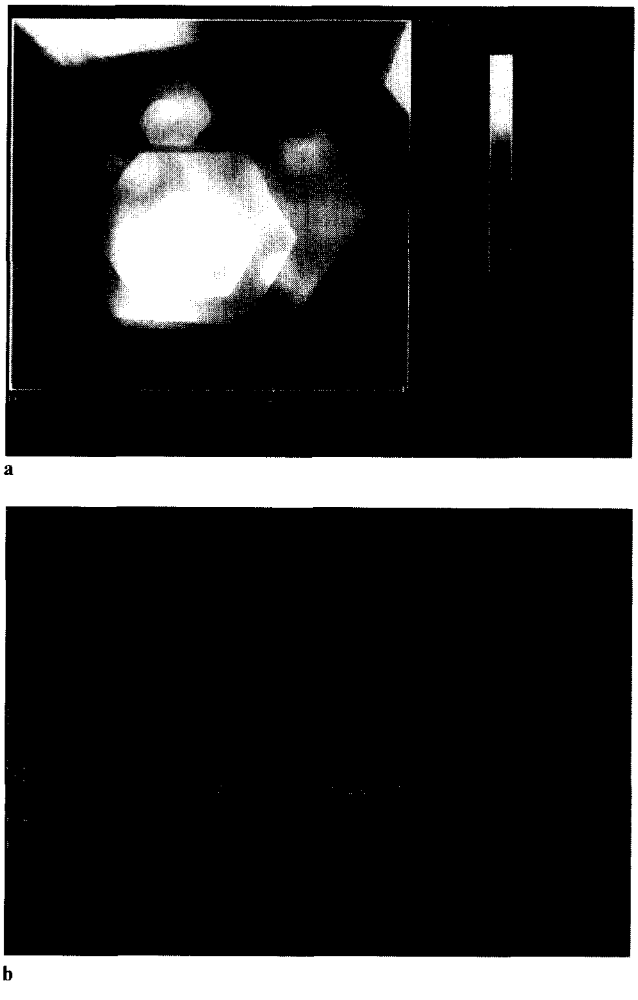

Figure 2 (a) AFM micrograph of an iPS crystal permanganically etched for 10 min. Three spiral terraces can be seen beneath the mother crystal (arrowed). (b) 3D surface plot of the same crystal showing the distortion caused by overgrowth terraces beneath the mother crystal.

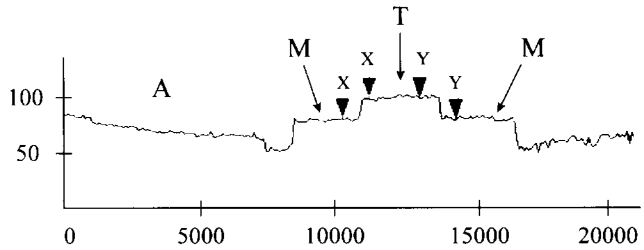

Figure 3 Height profile trace from a permanganically etched iPS crystal. The mother crystal (*M*) has only one overgrowth terrace (*T*) and is surrounded on either side by the amorphous matrix (*A*). The scales are in nanometres

proud of the amorphous matrix (A) by ~ 35 nm. There is only one overgrowth terrace (*T*) in this region of the crystal. The crystal is planar and undistorted, and the surfaces of both the crystal and overgrowth terrace are reasonably flat (the surface roughness is typically less than 0.5 nm). Vertical displacements were measured close to steps (*XX* and *YY*), but sufficiently far away to avoid being influenced by the effect of tip overshoot. Following this approach, step heights (L_{AFM}) were recorded from a number of crystals; the average step height was found to be, 17.4 nm, and the standard deviation, 1.1 nm. This value, however, does not correspond to the crystalline core thickness (L_c) of these crystals (*Figure 4*). During the etching procedure the disordered layer covering the crystals and the exposed fold surfaces are removed. Provided, the permanganic etchant does not penetrate between the crystalline layers, the fold surfaces under each overgrowth terrace will be protected from attack. Thus, the measured step height (L_{AFM}) should correspond to the total lamellar thickness ($L_c + 2L_f$): the long spacing in SAXS. Data obtained using this new method, where abrupt sharp steps are produced in the height profile, are superior to traces acquired from untreated surfaces; such surfaces tend to show extremely rounded height profiles[12], and may lead to spurious results.

Varying the exposure time of samples to the etchant from between 5 and 30 min does not affect the recorded value of L_{AFM}. The lateral dimensions of iPS crystals do however reduce with increasing etching time, indicating that stems have been cut from the lateral facets of the lamellae. Furthermore, although the possibility of both the thickness of a mother crystal and an overgrowth terrace reducing at the same rate exists, the invariance of L_{AFM} to etching period strongly suggests that the permanganic etchant does not attack and diminish the thickness of the crystalline core.

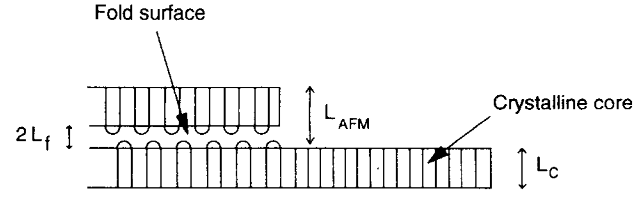

Figure 4 Schematic diagram showing the step height L_{AFM} obtained from permanganically etched crystals

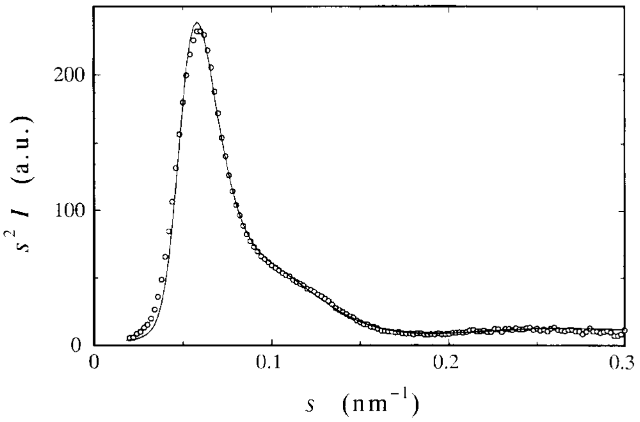

Figure 5 Lorentz-factor corrected SAXS intensity curve from a bulk iPS sample crystallized for 15 days at 210°C. The open circles represent the experimental data, and the solid line shows the calculated fit

Figure 5 shows the SAXS intensity $I(s)$ due to lamellar structure (following the subtraction of corrections for density fluctuations and the foreign particle component to the observed scattering), where the magnitude of scattering vector, S, is given by $S = 2\sin\theta/\lambda$, given that 2θ is the scattering angle, and λ is the incident X-ray wavelength. The intensity $I(s)$ was analysed assuming a two component system (corresponding to the crystalline and amorphous parts of the sample), on the basis of a linear model combined with a Gaussian correlation model[14]. The fitted results are shown by the solid line in *Figure 5*. The obtained structure parameters are as follows: the number average and the standard deviation of the thinner thickness distribution are 5.3 nm and 1.1 nm, respectively, while those of thicker distribution are 9.8 and 3.2 nm. Hence, the number average of the long spacing distribution, $< L >_N$, is therefore 15.1 nm, with a standard deviation (an independent variable in this method), σ_L, of 4.1 nm. These data are consistent with the crystallinity obtained using other techniques, assuming that the thinnest distribution corresponds to the crystalline core thickness[22-24]. If the step height obtained by AFM corresponds to the volume average long spacing $< L >_V$, where $< L >_V$ is given by, $< L >_N + \sigma_L^2 / < L >_N$ and is equal to 16.2 nm, then the AFM result (L_{AFM}) is consistent with the SAXS data, taking account of the width of the distribution.

Notwithstanding the values of the long spacing determined by the two techniques (L_{AFM} and $< L >_V$) agree within the width of the SAXS distribution, it is perhaps surprising that the results agree so precisely. Although both samples were crystallized at 210°C (and should therefore have identical long spacings), lamellae developing in 50 nm thick films grow under conditions where molecular motion is restricted[25]. As such, the introduction of defects during lamellar growth are more likely than in the bulk, and would be expected to have an affect on the measured crystal thickness. For example, cilia trapped between the fold surfaces of an overgrowth terrace will act to increase the step height recorded using AFM. Nevertheless, although probable, this effect is clearly too small to be observed within the current study.

Conclusions

It has been shown that AFM can be used to examine the crystal morphology and lamellar thickness of isotactic polystyrene lamellae growth from the melt in very thin films. Crystals prepared by this method are covered with a thin layer of disordered material which prevents direct lamellar thickness measurement being obtained. This layer however may be removed using a permanganic etchant allowing quantitative values of the step height (corresponding to the long spacing) to be determined provided that suitably undistorted crystals are examined. The step height obtained by AFM for iPS crystals grown at 210°C was found to be 17.4 nm, whereas, the long spacing obtained from SAXS data was 16.2 nm ($< L >_V$), and is consistent taking account of the width of the SAXS distribution.

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