Shish-kebab crystals in polyethylene investigated by scanning force microscopy*

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Ultra-thin, highly oriented polyethylene (PE) films drawn from the melt have been investigated using scanning force microscopy (SFM) to study their surface morphology. The results obtained from SFM measurements exhibit the lamellar morphology and evidence for extended chain crystals of the films. Morphological defects, such as structural thickness modulations of lamellae and steps on lamellar crystals of $\leqslant 1$ nm height, were obtained. The fact that the lamellar crystals protrude out of the film surface is explained by a combination of film processing and crystal growth effects. On a molecular scale, high resolution SFM investigations of the crystalline parts of the film show extended PE chains with an intermolecular distance repeat of 0.56 ± 0.1 nm.

(Keywords: polyethylene; oriented films; surface morphology)

INTRODUCTION

During the last few years scanning force microscopy (SFM) has become a well established experimental method for imaging atoms and molecules. Furthermore, SFM is used to image morphological characteristics and structures, e.g. of polymeric materials, on a microscopic scale (10–100 nm). Influencing polymeric morphology and therefore physical properties of polymers in this scale is at the forefront of polymer processing technology. A detailed microscopic study of polymeric morphological features down to the nanometre scale would be of interest, since these features determine many physical properties of a polymeric material, such as mechanical fracture toughness or stiffness. For such SFM studies, no additional surface coating with carbon or metals is required.

Recently, knowledge of the surface morphologies and compositions of thin polymer films has increased[1–5]. The aim of these studies is to correlate the microstructure of these materials with their macroscopic properties. Additional information about these kinds of materials can be obtained by the use of complementary microscopic methods such as SFM and scanning tunnelling microscopy (STM) compared with transmission electron microscopy (TEM). These techniques are well suited to this field of research since they have a unique morphological sensitivity, i.e. the capability to image directly the surface morphology (SFM, STM, TEM with the use of surface coating) or the bulk morphology (TEM).

Particular scientific interest in surfaces of uniaxially oriented, semicrystalline polymer thin films[6] also arises from interfacial and surface effects, e.g. relaxations and reconstructions, which may significantly differ from bulk phenomena because of the very weak intermolecular forces (van der Waals forces). The surface topographic structures of bare polymer films determine the interfacial properties (i.e. adhesion, orientation) in contact with other materials, as for example composite materials[1,7].

Different morphologies of oriented semicrystalline thermoplastic polymer films, such as lamellar crystals (kebabs) in the case of polyethylene (PE)[1,8] and needle crystals (shish) in the case of polypropylene (PP)[1], poly(butene-1) (PB-1)[1,3,9,10] and polystyrene (PS)[11], have been imaged with SFM. Although many lattice defects have been proposed in these macromolecular crystals[12], their direct observation is limited owing to experimental difficulties. In the case of TEM investigations of defects the major problem arises from radiation damage of polymer crystals in the electron beam[13]. Furthermore, the size of the crystals in the range of a few tens of nanometres creates problems in resolving their lattice defects. Nevertheless, several attempts have been made to investigate these defects by TEM[14–16]. Although Petermann and Gohil[14] describe the onset of screw dislocations on lamellae of melt-drawn PE films, investigated by dark-field TEM, a direct imaging of these defects on the nanometre scale has not been reported until now.

SFM investigations down to molecular resolution of ultra-thin melt-drawn PE films having a shish-kebab morphology are presented here. These investigations continue the series[1,3,8–11] of SFM investigations of highly oriented thermoplastic polymer films.

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EXPERIMENTAL

The oriented, semicrystalline polymer substrates were prepared according to the method of Petermann and Gohil[6]: the polymer granulate was dissolved in xylene (0.4% w/w) and some droplets of this solution were then deposited on the smooth surface of a glass slide, where the solution itself dispersed uniformly. On heating the sample to about 420 K, the solvent evaporated. From the resulting melt a highly oriented, ultra-thin film (thickness $\sim 0.1\,\mu$m) was drawn by a motor-driven cylinder (velocity $= 7\,\mathrm{cm\,s^{-1}}$). In general, the morphology and the size of crystalline areas depend on the different types of polymers used as well as on the processing technique[12].

The PE film was deposited onto mica for SFM investigations. A Nanoscope III SFM (Digital Instruments, Santa Barbara, CA, USA) was used for the investigations. Experiments using the repulsive force mode of operation, where the cantilever tip is in permanent contact with the sample surface, were carried out under propanol (spectrophotometric grade). Propanol was chosen to minimize the capillary forces between the cantilever tip and the surface[17] and because it would not cause the polymer to swell or soften. The cantilevers used were supplied by the microscope manufacturer, and had a nominal force constant of $0.06\,\mathrm{N\,m^{-1}}$. The forces applied with the SFM tip were $\leqslant 10^{-9}$ N. The imaging force was adjusted to just above the pull-off point of the cantilever as soon as possible after the first contact in order to reduce the applied force to the minimum possible for stable imaging. From time to time it was checked that the set point was stable and still at the same location of the force curve. No filtering was applied to the feedback signal or the images. All structures shown in the SFM images were reproducible independent of scanning frequency, scanning direction and x–y range.

RESULTS AND DISCUSSION

Earlier TEM investigations have shown that the PE substrate surfaces produced by this technique exhibit a semicrystalline morphology[6]. From the electron diffraction pattern inset in *Figure 1*, the uniaxial orientation of the crystallites and macromolecules caused by the extension of the melt is deducible. The crystalline polymer surface planes of PE substrates are $\{hk0\}$ planes having only the [001] direction (the direction of the molecular orientation) in common. This is known as fibre texture.

The crystalline areas of the PE substrate shown in the TEM image (*Figure 1*) are built up of shish-kebab crystals aligned parallel to the drawing direction of the polymer film. The shish-kebabs are embedded in an amorphous PE matrix. A shish-kebab crystal consists of a needle crystalline core (shish) with extended PE chains, and many epitaxial overgrown lamellar crystals (kebabs) with folded PE chains. The length of the shish-kebab crystals ranges from a few nanometres to several micrometres, while their (core) diameter was found to be 20–35 nm. The thickness of the lamellae was determined to be 40–60 nm. Owing to the bulk sensitivity of our TEM technique, both the needle crystals and the lamellar crystals covering them could be imaged simultaneously.

Typical SFM images of PE substrate surfaces are shown in *Figures 2a* and *b*. The images show an arrangement of close-packed lamellar crystals. The long axes of the lamellae are oriented approximately normal to the drawing direction of the film surface. The thickness of lamellae obtained from SFM measurements was determined to be 40–60 nm. The values for lamellar dimensions fit very well with the values obtained from TEM investigations. Furthermore, an interlocking of lamellae of neighbouring lamellar crystals is deducible from *Figure 2a*. The lamellae show structural modulations along their long axes, presumably owing to local growth defects. Similar structural modulations have been observed with small-angle X-ray scattering[18] for shish crystals.

In *Figure 2a*, groups of lamellae can be seen to have grown centred on common axes (backbones) running parallel to the drawing direction of the film. In some areas of the image, segments of these backbones can be seen elongated along the drawing direction of the film. The typical length of these segments measured parallel to the drawing direction of the film was 10–100 nm,

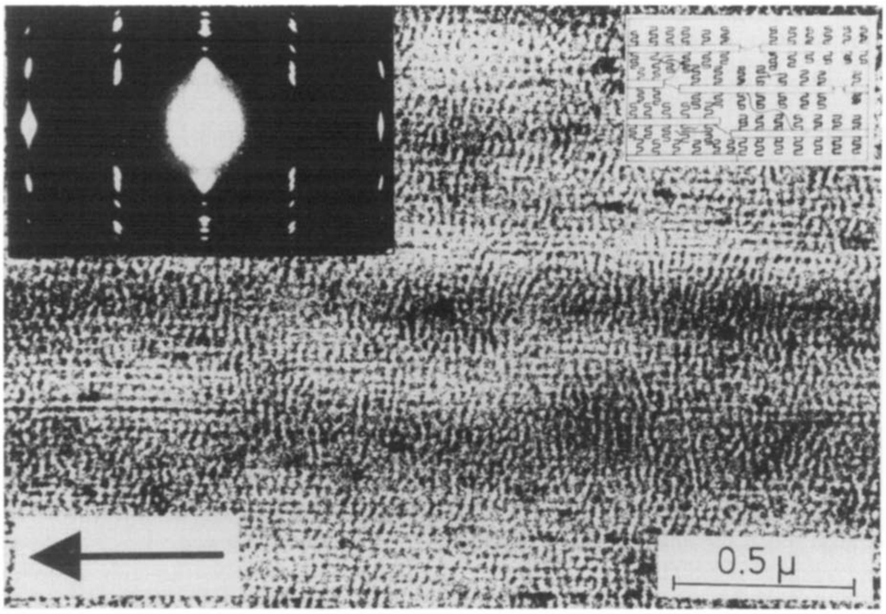

Figure 1 TEM micrograph of a PE film having a shish-kebab morphology. The arrow in the lower left corner indicates the direction of the molecular orientation. An electron diffraction pattern and a sketch of the morphology are shown in the upper left and right corners, respectively

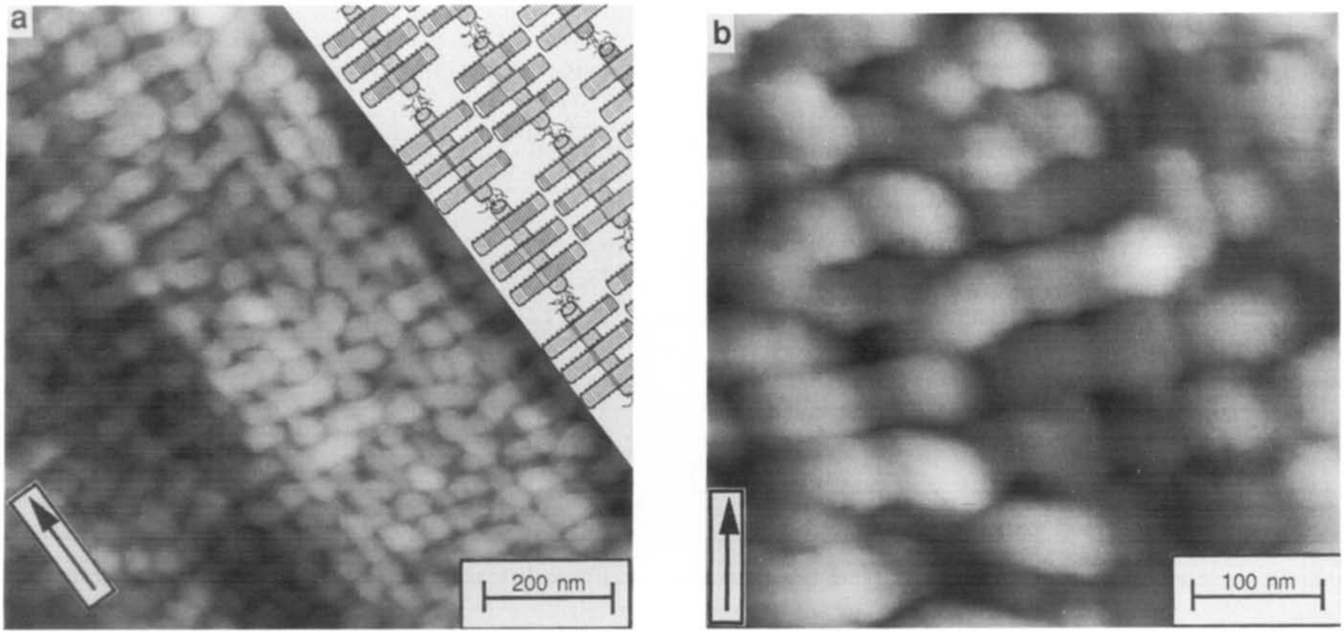

Figure 2 SFM images, at different magnifications, of a PE substrate surface. The surface of the PE substrate shows close-packed lamellar crystals diagonally crossing the scan area. The arrows in the lower left corners of the images indicate the direction of the molecular orientation (drawing direction of the substrate). A sketch of the PE substrate morphology known from TEM investigations is shown in (a). Note that the crystals protrude a few nanometres out of the substrate surface. It is deducible from these SFM images that the lamellae show structural modulations in thickness

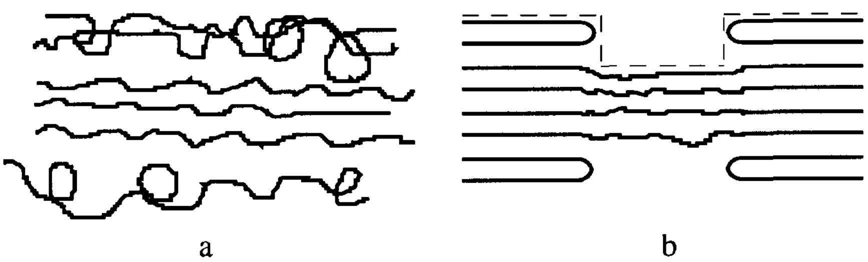

Figure 3 Schematic sketch showing the formation of height differences between crystalline and amorphous surface areas of a PE film. During the film drawing process (a), the molecules in the middle of the film are more stretched than the molecules at the surfaces. This may result in a higher density of chain folds at the surfaces in the case of the processed film (b). The surface profile of the film is indicated by the dashed line in (b). As shown in this sketch, the crystalline surface regions protrude from the amorphous regions

whereas their diameter measured perpendicular to the drawing direction was 40–50 nm. These values fit with results from earlier SFM investigations of polymer needle crystals[11]. Nevertheless, in our SFM investigations direct access of the SFM probe to entire needle crystals is hindered, owing to the close-packed lamellar overgrowth.

Closer analysis of *Figures 2a* and *b* shows that the crystalline parts of the polymer film (shish-kebabs) appear to protrude from the amorphous polymer regions. The height from the amorphous region between the crystals to the top of the crystals was measured to be 0.5–4 nm (local values). This result is consistent with TEM and SFM results obtained earlier from other melt-drawn PE films[1,8]. The fact that the crystalline parts of the film protrude out of the film surface can be explained by a combination of film processing and crystal growth effects, shown schematically in *Figures 3a* and *b*. During the film drawing process, the molecules in the middle of the film are more stretched than the molecules at the surfaces, owing to a different relaxation behaviour of the film surface compared to its centre. The result of this process may be a higher density of chain folds at the surfaces. It is assumed that during the growth process of the crystals, both parts of a chain related to a fold are diffusing into the same growing crystals[19]. Some extended chains in the centre of the film are unable to follow this motion, because they are embedded in two adjacent crystals. This leads to zones of less polymeric material (the lower amorphous areas). In the case of perfectly oriented chains in the centre of the film, extended chain crystals as backbones for the lamellar overgrowth can occur.

Imaging at higher magnification on surfaces of the lamellae revealed the structures shown in *Figures 4a* and *b*. The images show individual lamellar crystals, oriented with their long axes approximately horizontal (*Figure 4a*) and vertical (*Figure 4b*) in the images. In the lower part of the lamellar crystal in *Figure 4b*, five steps on the crystal surface are visible. Additional evidence for the steps was found in numerous line-profile measurements of height in the relevant regions. *Figure 4c* shows a typical line profile obtained for the steps shown in *Figure 4a*. This line profile was taken as a line running approximately perpendicular to the step direction. The height of these steps was determined to be $\leqslant 1$ nm. The same height was measured for the steps on a lamellar crystal, recorded in another region of the PE surface, shown in *Figure 4a*.

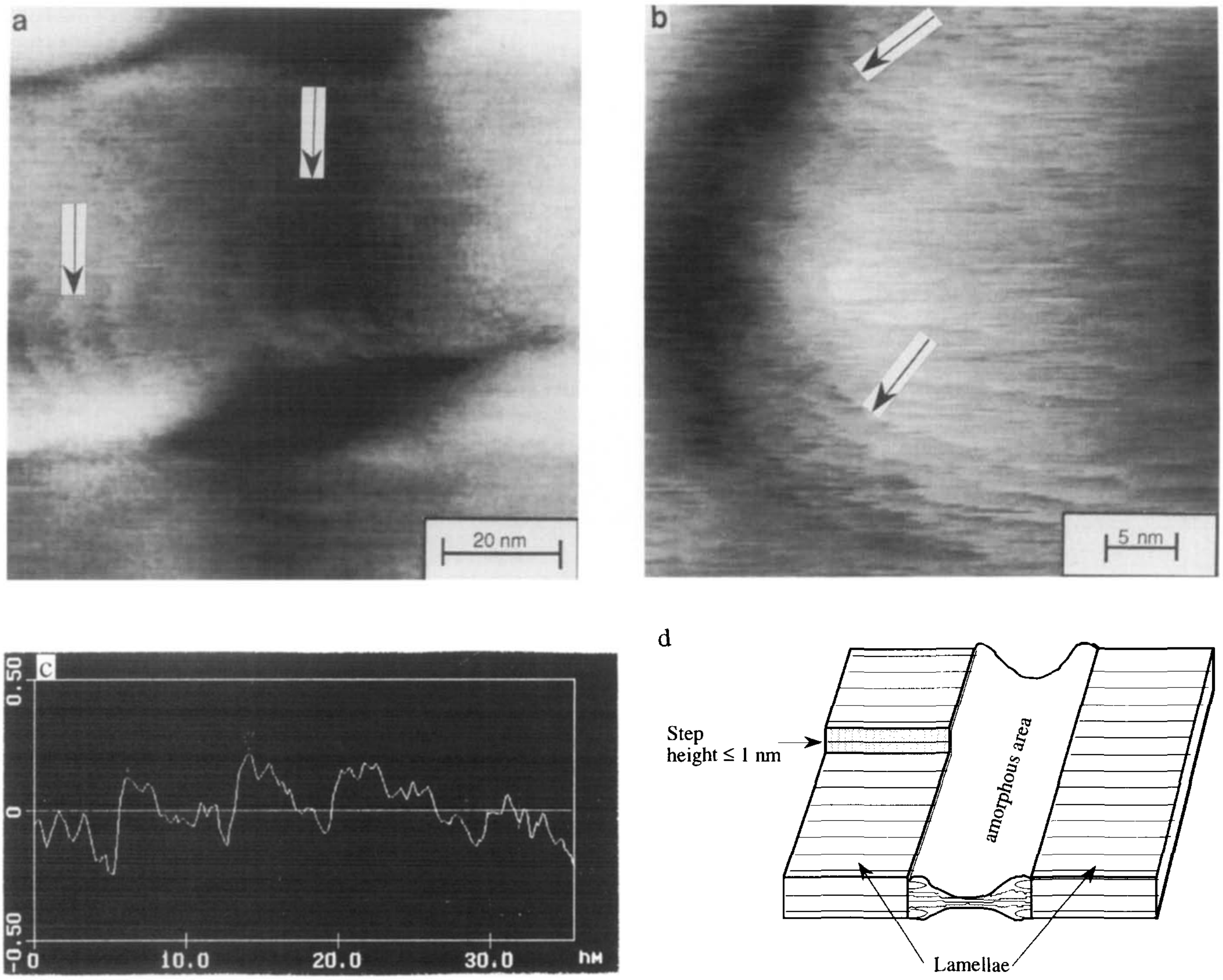

Figure 4 (a) and (b) SFM images of a PE substrate surface, at higher magnifications than the images in *Figures 2a* and *b*. The images obtained in different regions show individual lamellae crossing the image approximately horizontally (a) and vertically (b). The arrows indicate steps on the lamellar crystal of a height ≤ 1 nm. (c) A typical line profile obtained for the steps shown in (a). This line profile was taken at a line running approximately perpendicular to the step direction. Note that the steps appear as peaks in the line profile (indicated by arrows) of the flattened image. (d) A schematic picture of the location of an unbent surface step on a lamellar crystal

Steps of similar height and shape to those shown in *Figures 4a* and *b* were found on most of the investigated lamellae. *Figure 4d* shows a schematic drawing of the location of the steps on a lamellar crystal; for clarity, only unbent steps at the centre of a lamellar crystal are shown.

The steps in *Figures 4a* and *b* are oriented approximately in the drawing direction of the polymer film. In *Figure 4b* curvature of steps at the lamellar edges is visible. The observed steps may result from line dislocations and/or from growth terraces. Uneven thickness of the lamellae in the lateral but also in the chain direction may be compensated by those terraces. If thickness variations are in both directions at a particular place, curved steps can then account for it.

An alternative explanation of the observed steps may be slip traces originating from dislocations which are responsible for a shearing in polymer crystals. Slip traces have been predicted[20] and, in the case of shear parallel to the chain direction, observed by TEM in PE films[14] and PE single crystals[15,16]. In the case of the steps observed with SFM, the glide planes may be $(hk0)$ planes of the crystal with a Burgers vector in $[uv0]$ directions[20]. Such slips would not require a chain kinking, since the glide planes are oriented parallel to the chain direction. It is assumed that thermal stresses are responsible for the observed screw dislocations.

When the magnification was increased to a molecular scale, images such as that in *Figure 5* were readily obtained from oriented lamellar crystals, where the fold surfaces are oriented perpendicular to the observed lateral growth surfaces. The images show structures similar to extended PE macromolecules with an intermolecular distance repeat of 0.56 ± 0.1 nm. This value may be compared to the intermolecular distance obtained from X-ray diffraction of 0.49 nm in the $\{100\}_{\mathrm{PE}}$ planes[21]. The value of intermolecular distance repeat obtained from the SFM measurements is similar to that obtained from the X-ray diffraction measurements, within the error-range of the SFM measurements with the particular tube scanner used. On the other hand, polymer films are known to exhibit a different molecular packing at their outermost surfaces[10]. This surface effect may be caused by the reduced number of neighbouring polymer chains

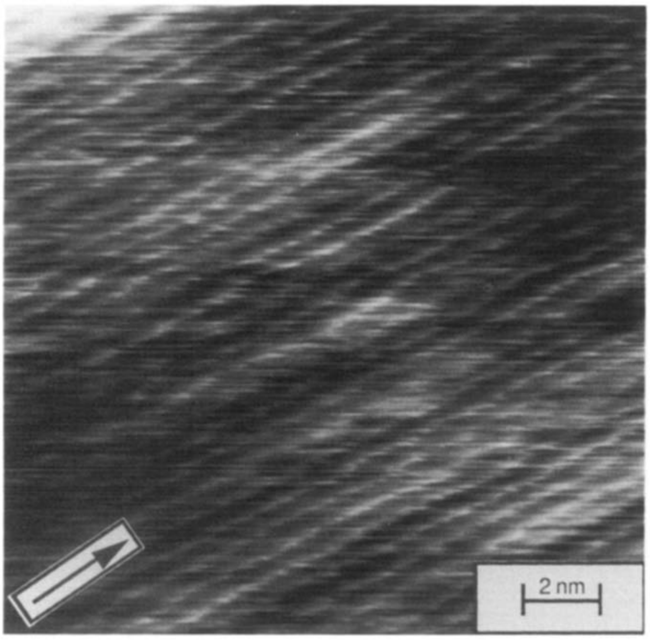

Figure 5 SFM image of a PE substrate surface at higher magnification and with the scanning direction rotated by about 45° compared to *Figure 4a*. The image shows individual PE macromolecules. Normal to the chain direction of the macromolecules, an intermolecular distance repeat of 0.56 ± 0.1 nm was obtained. The arrow in the lower left corner indicates the direction of the molecular orientation

for every individual chain at the surface, resulting in a different binding energy of this chain compared to the bulk.

CONCLUSIONS

A comparison of the TEM and SFM images of the melt-drawn PE films shows the complementary character of these methods. SFM investigations of PE thin film surfaces revealed the close-packed needle crystalline morphology of this substrate. Evidence for shish crystals as backbones of the lamellae (shish-kebab) was found. It has been shown that the lamellar crystals protrude out of the surface for 0.5–4 nm. This phenomenon may be caused by a combination of film processing and crystal growth effects.

Morphological details and defects, such as lamellar interlocking, structural modulations of lamellae and surface steps on lamellar crystals of $\leqslant 1$ nm height, could be obtained. The origin of the steps may be growth terraces or slip traces. Higher magnifications of the crystalline areas of the PE film show PE macromolecules with an intermolecular distance repeat of 0.56 nm. This value may be compared to the intermolecular distance obtained from X-ray diffraction of 0.49 nm in the $\{1\,0\,0\}_{\mathrm{PE}}$ planes.

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