Atomic force microscopy of polymer crystals: 1. Chain fold domains in poly(ethylene oxide) lamellae

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Lamellar crystals of poly(ethylene oxide) grown in toluene solutions were investigated by atomic force microscopy (AFM). Typical lamellae had a square habit with a thickness of 12.5 nm and an edge length in the range of 0.01–0.2 mm depending on the crystallization time. On some lamellae large screw dislocations were observed which showed a growth face at the diagonal. When the crystals were exposed to air, the lamellae gradually disintegrated. AFM images of disintegrated regions showed that polymer chains were contracted in bundles which formed tree-like patterns. Diagonal features observed on both dislocation terraces and disintegrated lamellae support the existence of fold domains separated by the diagonals and the chain folding mechanism proposed by Kovacs.

(Keywords: atomic force microscopy; lamella; chain folding; poly(ethylene oxide))

Introduction

The invention of the scanning tunnelling microscope[1] has led to the development of various scanning probe techniques[2], such as atomic force microscopy (AFM)[3–5]. During an AFM experiment the surface of the sample is mapped by measuring the force of interaction between the molecules at the surface and the scanning tip. Recent experiments utilizing AFM have proven the ability of this method to characterize macromolecular structures at polymer interfaces. Results include morphological features on the micrometre scale, such as observations of dendritic polyethylene crystals[6], as well as images with atomic resolution[7,8]. In this communication we report on AFM observations of morphological features on poly(ethylene oxide) (PEO) lamellae.

Experimental

Linear PEO with $\bar{M}_w = 9.08 \times 10^4$ g mol^{-1} was purchased from Polymer Laboratories. Polymer samples were freeze-dried and stored under nitrogen at 0°C prior to crystallization experiments. Toluene (reagent grade) was dried over sodium, freshly distilled and subsequently filtered using a nylon membrane filter (0.2 μm pore size) prior to use. PEO solutions of 0.007 w/w% were prepared at 55°C and then cooled to room temperature (25°C) at a rate of 10°C h^{-1}. The solution was stored at room temperature for at least 5 days to allow crystal growth. AFM experiments were performed on samples which had been obtained by depositing droplets of the crystal-containing solution on glass microscope slides. The solvent was allowed to evaporate at room temperature and the residue was investigated. Samples were first examined by using an Olympus BHSM polarizing microscope equipped with contrast enhancement by the Nomarski differential interference method. A NanoScope II (Digital Instruments, Inc., Santa Barbara, CA, USA) fitted with NanoProbe 200 μm triangular Si_3N_4 cantilevers (Digital Instruments) with wide legs was used to obtain AFM images. Experiments were carried out with a D-type scan head in air at room temperature. The constant force mode was utilized at the lowest possible set point voltage which still maintained tip engagement but kept contact forces between tip and sample low. The habits of the crystals did not change during the first hour following the removal of the samples from the solution. However, characteristic crystal morphology gradually disappeared if samples were stored for longer than 1 h.

Results and discussion

PEO crystals formed in solution consisted of lamellae possessing a predominantly square habit. In a few cases hexagonal and ellipsoidal lamellae were also observed. The morphology of the crystals is equivalent to the characteristics reported in the literature[9]. The edges of the square lamellae were measured by optical microscopy. Typical values were around 50 μm after 1 week of crystallization, while over a crystallization period of 6 weeks the lamellae had grown to ~0.2 mm. Some important morphological details of PEO crystals, which are not accessible for optical microscopy, were readily obtained by AFM. For example, the lamellar thickness was measured by preparing quantitative surface profiles from AFM images across the edge of the lamellae. The step size at the edge, which can be directly determined from the profile, gives the thickness d_0 of PEO crystals. Based on 10 measurements a value of $d_0 = 12.5 \pm 0.5$ nm was obtained which is in good agreement with the results obtained by Arlie *et al.*[10].

In many cases large screw dislocations were observed on the surface of crystals. A good example is shown in *Figure 1*. It is important to mention that close to the geometrical centre of this image, at the dislocation line, the diagonal edge of the growing top layer is clearly visible.

It is interesting to note that a slow disintegration of

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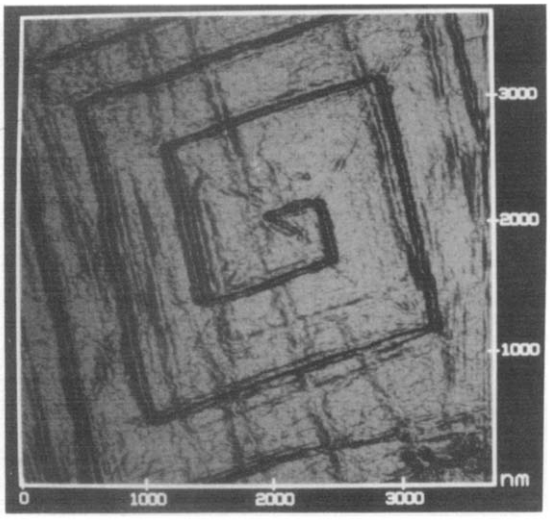

Figure 1 AFM image of a screw dislocation in a PEO lamella

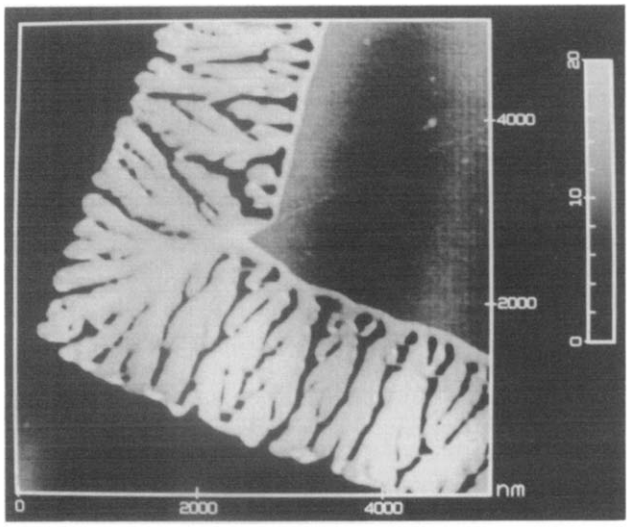

Figure 2 Disintegration of a PEO lamella in air as revealed by AFM. The height (in nm) is indicated by different tones

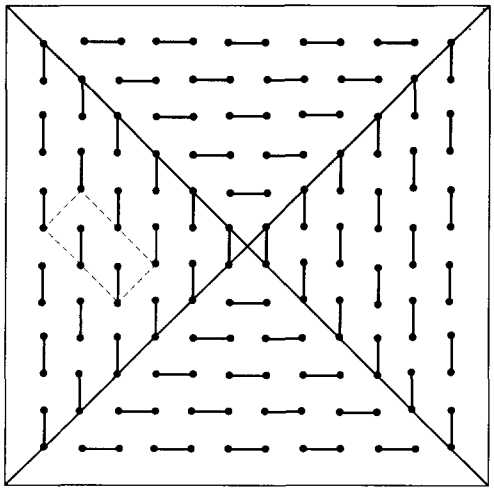

Figure 3 Schematic drawing of chain folding in PEO after Kovacs *et al.*[12]. The rectangle (broken line) corresponds to the projection of a unit cell

the crystal habit was observed in air. During this process the material was contracted in areas which formed irregular, tree-like patterns. An AFM image which captures a typical example for disintegration at a corner of a lamella is shown in *Figure 2*. The thickness of the 'perforated', disintegrated region is typically 5–8 nm greater than the lamella thickness measured prior to decomposition. This suggests that lamella disintegration is accompanied by chain refolding.

Crystal decomposition in the corner region of the lamella depicted in *Figure 2* also shows distinct features associated with the diagonal, i.e. the 'upper' and the 'lower' quarters of the lamella are clearly separated at the diagonal. The size of the 'perforated' regions (degree of decomposition) at the diagonal is also different. The observations of structural features at the diagonal can be explained by assuming the existence of independent chain fold domains which are separated by the diagonal.

Square PEO lamellae with {1 2 0} growth faces and spiral growth have been already reported[11]; and a folding mechanism, which results in square habit, assuming folds parallel to {1 2 0} planes was later proposed by Kovacs *et al.*[12]. *Figure 3* gives a schematic illustration of this model viewed from the (0 0 1) direction. The filled circles mark the axes of the PEO helices grown perpendicular to the plane of the lamella and the lines connecting the filled circles correspond to sharp chain folds on the crystal surface. The existence of fold domains, separated by the (1 0 0) and (0 1 0) diagonals is obvious. Our AFM observations can very well be interpreted assuming this chain folding mechanism.

In conclusion, our results show that AFM can provide images of structural features that help reveal the mechanism of chain folding in polymer single crystals. A detailed discussion of optical microscopy and AFM imaging of PEO will be published in a subsequent paper.

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