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Frictional anisotropy and sectorization in poly(4-methyl-1-pentene) lamellar crystals studied by lateral force microscopy

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Lateral force microscopy (LFM) measurements are performed on solution-grown lamellar crystals of isotactic poly(4-methyl-1-pentene). Fold-domain boundaries are observed to protrude above the surface of the crystals. Within the fold domains the magnitude of the friction signal at a given load was found to depend on the scan direction. Frictional anisotropy is exhibited and is shown to be independent of topography. The observed friction anisotropy is discussed in terms of the structure of the fold surface and ascribed to the presence of an ordered arrangement of folds. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Since the first reported observations of lamellar polymer single crystals[1,2], various aspects of their morphological and physicochemical properties have attracted attention, as summarized in several review articles and monographs[3–8]. It is generally recognized that the polymer chains within a single crystal are organized with the chain direction oriented approximately perpendicular to the large surfaces and folded back on themselves several times[2]. Thus, to a first approximation, a polymer single crystal can be thought of as having a well-ordered crystalline interior and an interfacial region where chain folds occur. The latter is thought to account for much of the amorphous content[8].

There is still some uncertainty about the nature of the fold surface in polymer crystals. For example, are the folds predominantly tight (adjacent re-entry) or loose (random or switchboard model)? As discussed by Hoffman and co-workers in a series of papers[9–12], there are a number of experimental and theoretical results which favour the predominance of tight and regular folding. Conversely, Mandelkern[13] has reviewed several literature reports which suggest otherwise. Presently, there exists no definitive answer to the question of fold arrangement.

The development of atomic force microscopy (AFM)[14] has yielded a highly versatile and powerful tool which has led to greater insight into various aspects of polymer structure. Polymer single crystals were among the earliest systems to be examined by AFM[15,16]. Despite intense research, AFM images exhibiting periodic lattices or images of molecular folds are only rarely obtained[17–19]. Concurrently, the recognition that frictional forces could be measured by lateral force microscopy (LFM) was key to the development of nanotribology[20]. In LFM, frictional properties are examined by measuring the lateral (torsional) twisting of an AFM cantilever as it is scanned across a surface in a raster pattern. In modern AFM instruments, both topographic (conventional AFM) and lateral force measurements can be performed simultaneously. The LFM literature has expanded rapidly since the technique was developed. Several studies into atomic-level stick-slip behaviour have appeared, as summarized in a recent review article[21].

Frictional anisotropy has been observed at the surface of ordered materials such as polymer single crystals[22–24] and friction-deposited polymer films[25,26]. Such anisotropy, in the case of single crystals, arises from the occurrence of sectorization, or fold domains. These are associated with the occurrence of chain-folding preferentially in a plane parallel to a growing crystal face[27]. At the boundary between two sectors, the meeting of distinct fold plains leads to a staggering of the constituent folds, an increase in surface area and frequently the occurrence of a ridge or 'wrinkle'[28]. Frictional anisotropy is by no means unique to polymer systems and has been reported recently in other materials[29,30].

The first investigations of fold-domain boundaries in polymer single crystals by conventional AFM were performed on polyethylene[15] and poly(ethylene oxide)[16]. Subsequently, frictional anisotropy was reported across adjacent sectors in crystals of poly(oxymethylene)[22] and polyethylene[23,24].

The present paper summarizes results obtained of LFM measurements performed on single crystals of isotactic poly(4-methyl-1-pentene), PMP. This polymer forms square-shaped lamellar crystals from a variety of solvents[28,31,32]. The unit cell is tetragonal and the chains adopt a 7_2 helix[33]. This material possesses several polymorphic forms which can be adopted depending on the conditions of crystallization[34–36]. The so-called modification I has unit cell dimensions $a = b = 18.70$ Å, $c = 13.68$ Å, while modification III is characterized by $a = b = 19.44$ Å, $c = 6.8$ Å[35]. The transition III → I can be effected by annealing at 100°C[35]. Modification I is thought to be the more stable one and occurs when crystallization is

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carried out from dilute solution at temperatures above 50°C[35]. This polymer has the interesting property that at room temperature the crystalline density is less than that of the amorphous material[34,37].

PMP was chosen for this study because of the simple and regular geometry of its crystals. Furthermore, it was thought a good choice for such a study since a square crystal, having an optimal 90° change in orientation between fold plains in adjacent sectors, would be expected to yield a high degree of contrast between sectors in LFM if frictional anisotropy is present.

EXPERIMENTAL

Isotactic poly(4-methyl-1-pentene) ('medium molecular weight' according to the supplier) was obtained from Aldrich and used without further purification. Single crystals were grown according to the procedure described by Bassett *et al.*[27]. A 0.01% solution of polymer was prepared in xylenes (isomeric mixture). The solvent had previously been dried for several days over molecular sieves. After refluxing, the clear solution was transferred to an oil bath set at a temperature of 70°C. Pieces of freshly-cleaved mica were added to the solution. After 24 h, the crystals deposited on the mica were washed repeatedly with pure solvent which had been heated up to the crystallization temperature so as to avoid precipitation of dissolved polymer upon cooling. The mica pieces were then removed and dried in a vacuum oven for 24 h.

AFM and LFM measurements were performed on a Digital Instruments NanoScope III, using an E-scanner (permitting a maximum scan size of $14 \times 14 \ \mu m^2$) and NanoProbe Si_3N_4 tips (nominal $k = 0.06$ N m^{-1}). Measurements were performed in contact mode, always minimizing the feedback setpoint. The applied normal force was typically 18 nN, as estimated from the nominal spring constant. All images were obtained, and are displayed, without any filtering. The scan direction in LFM images was 90° with respect to the cantilever axis.

RESULTS AND DISCUSSION

A typical contact mode AFM image of a PMP single crystal is shown in *Figure 1*. This is a height image and represents an actual topographic map of the crystal. It shows a square geometry with sectorization evident from the presence of two intersecting diagonal lines meeting at 90° in the centre. From the height variation it is visible that the fold-domain boundaries represent topographically distinct elements, i.e. they rise above the rest of the crystal surface, as discussed in the literature[28] (see section plot in *Figure 1*). It has been reported that the directions of the *a* and *b* axes of the tetragonal unit cell coincide with the direction of the growth faces[38]. The thickness of the crystal shown in *Figure 1* is approximately 15 nm, in agreement with literature values[27]. The fold-domain boundary protrudes approximately 1 nm above the rest of the crystal.

Before proceeding to the LFM results, it is worth commenting on some fracturing which was observed in several crystals such as that shown in *Figure 2*. This is a so-called deflection image, which provides better lateral contrast than a height image, but at the expense of height information. It can be seen that a portion of the crystal along the bottom sector is 'missing'. It is to be expected that fracture will occur preferentially between successive rows of folds, a row being parallel to the crystal growth face (akin to pulling out the loose end of a knitted square of wool).
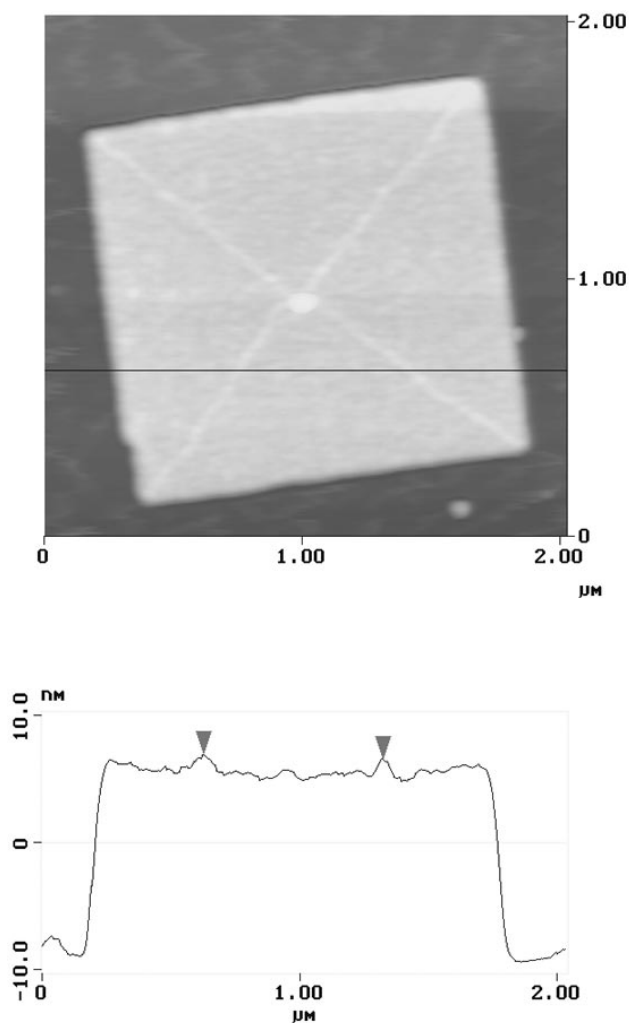

Figure 1 AFM height image and surface profile of poly(4-methyl-1-pentene) single crystal. Vertical scale in image is from 0 to 89 nm (dark to bright)
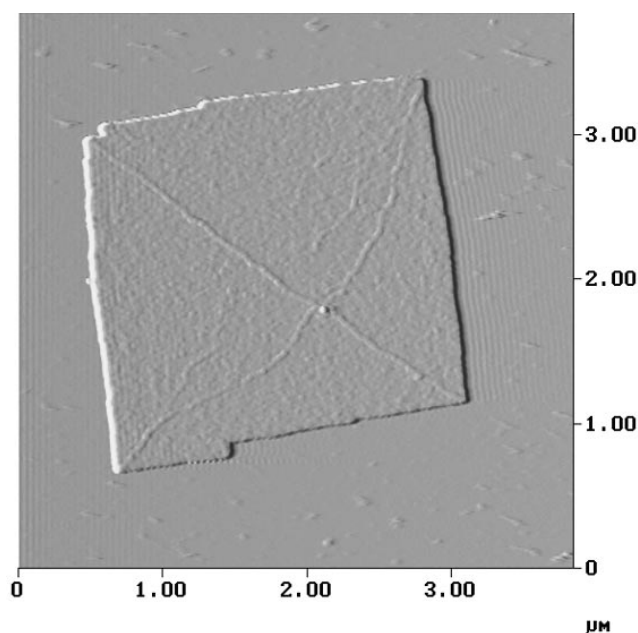

Figure 2 AFM deflection image of poly(4-methyl-1-pentene) single crystal

This has been established several years ago for polyethylene crystals[5,39] and can be ascribed to the ease of overcoming the relatively weak secondary forces which act between adjacent rows of folds, as opposed to the breaking of bonds which would mediate fracture along another direction.

A typical LFM image of a sectorized single crystal of PMP is shown in *Figure 3*. It can be seen that the sectors which are diagonally facing each other have similar frictional signals, distinct from those of the other pair. In this particular image, in which the scan direction was from left to right, areas of light colour (lower right-hand and upper left-hand quadrants) exhibit highest lateral forces, and hence highest frictional forces.

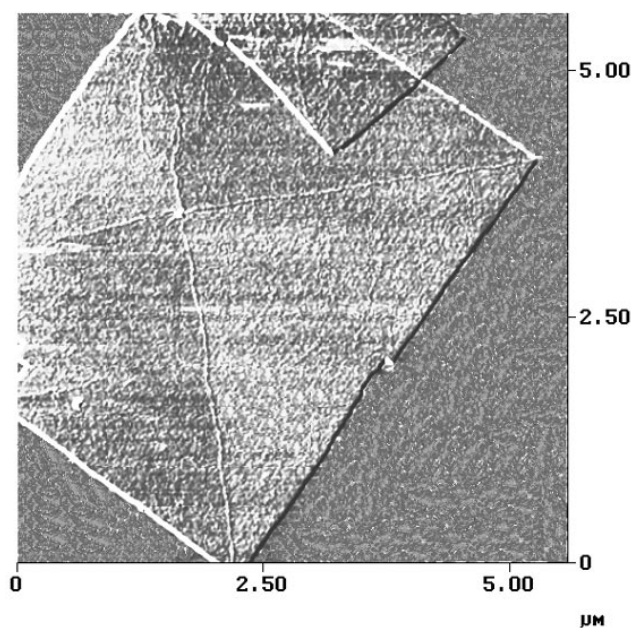*Figure 4* shows a smaller region of the same crystal as in *Figure 3* and emphasizes the lateral force anisotropy inherent in the crystal. Also evident on this scale is the granularity of the surface. Given the large size of the grains (*ca.* 20 nm) it is difficult to assign such a pattern to any atomic-level stick-slip phenomenon. In the case of polyethylene crystals, such a granularity was also reported and ascribed to protrusions of chain stems and loose folds in an otherwise regularly-folded structure[40]. This is a possible explanation for PMP, since, given the bulky iso-butyl side-group, any looseness of folds should result in a 'bumpy' surface as seen for polyethylene. However, more detailed measurements are needed to arrive at a definitive explanation for the granularity observed on crystal surfaces.

An important issue in any study of frictional anisotropy is the influence of topography on the friction signal. As pointed out recently[21], any local surface slope will possess a

Figure 3 Lateral force image of poly(4-methyl-1-pentene) single crystal. Vertical scale is from 0 to 0.4 V (dark to bright)
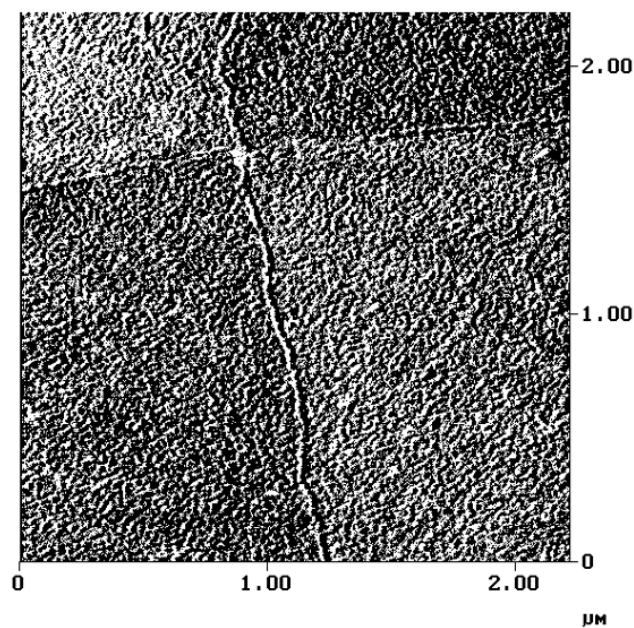

Figure 4 Lateral force image of poly(4-methyl-1-pentene) single crystal from *Figure 3*, smaller area. Vertical scale is from 0 to 0.4 V (dark to bright)
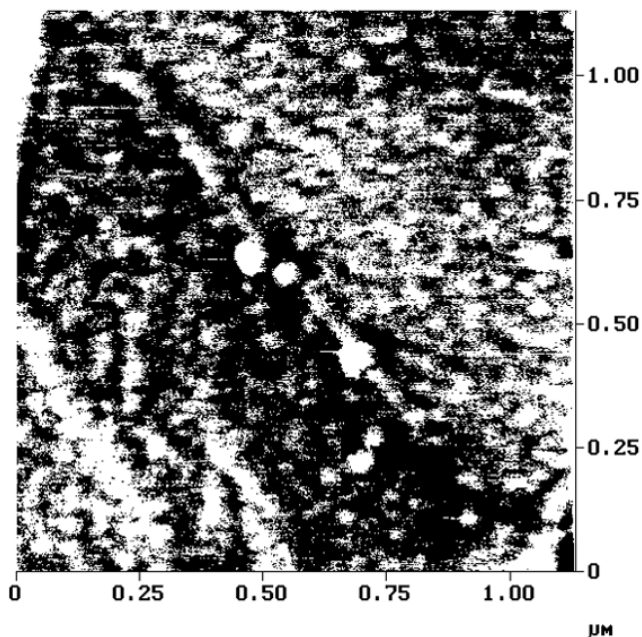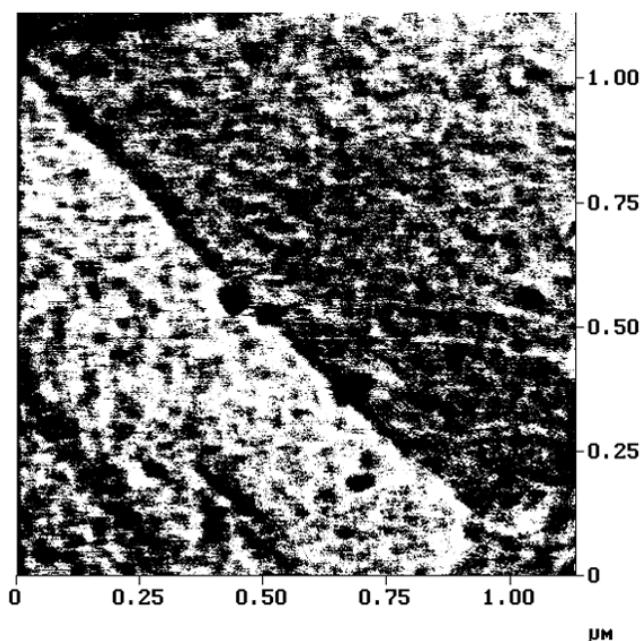

Figure 5 Lateral force image of fold-domain boundary in poly(4-methyl-1-pentene) single crystal: (a) scan direction left-to-right (top); (b) scan direction right-to-left (bottom)

lateral component and result in a lateral force. The fact that the sector boundaries are higher than the remaining crystal surface was a matter of concern. It is possible, for example, that the traversing cantilever tip 'trips over' the sector boundary, giving a false anisotropy between the two adjacent fold sectors.

In order to address the role of topography in our LFM measurements, the effect of scan direction was examined. In *Figure 5a* is shown an image acquired by scanning from left to right (the so-called 'trace' direction). As in *Figure 3*, higher lateral forces are associated with areas of lightest colour (in the area left of the diagonal). In *Figure 5b*, the scan direction was reversed, and the image was acquired while scanning from right to left ('retrace' direction). In this case, largest frictional forces correspond to the dark areas (the inversion of the scale occurs because the sign of the lateral twist of the cantilever changes). It should be noted that there is also an inversion in the image brightness distribution relative to *Figure 5a*, so that the frictional anisotropy is independent of scan direction.

The presence of sectorization in PMP single crystals and the observation of frictional anisotropy which is not a reflection of topography led to the conclusion that this anisotropy must reflect some intrinsic property of the crystal. Since sectorization is a result of the presence of distinct fold plains, it seems reasonable to associate the frictional anisotropy observed with the different fold planes in the four sectors, as has been suggested for poly(oxymethylene) and polyethylene[22–24].

The relationship between frictional anisotropy in single crystals and the regularity of folding is a more tenuous one. It has been suggested that one implies the other, i.e. frictional anisotropy results from 'tight' and regular folding[22–24]. The decoration technique of Wittman and Lotz[41] demonstrates the presence of ordered fold domains on the surfaces of polyethylene, polypropylene and poly(oxymethylene) crystals. However, it is generally accepted that polymer single crystals contain at least some irregularity in their fold structure[4,9]. An obvious question is, therefore, how much irregularity in fold structure can be tolerated before frictional anisotropy disappears? Furthermore, does the presence of distinct domains imply the presence of frictional anisotropy? We hope to address these questions in future work on other polymers.

CONCLUSIONS

Our force microscopy results have demonstrated the presence of frictional anisotropy and sectorization in single crystals of PMP. Furthermore, it is shown that this frictional anisotropy is not due to topography, but instead reflects some fundamental property of the crystal fold surface. It is suggested that it is due to a predominantly regular fold structure.

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