

## **Anisotropic friction on lamellar crystals of polyethylene by lateral force microscopy**

**Paul F. Smith, Rozalia Nisman, Charlene Ng, and G. Julius Vancso\***

University of Toronto, Department of Chemistry, 80 St. George Street, Toronto, Ontario, M5S 1A1 Canada

### **Summary**

Frictional forces are very sensitive to the interface structure and the chemical and atomic structure of surfaces. It has been shown in the late 80's (1) that lateral forces due to friction can be measured by atomic force microscopy (AFM) in the contact mode (2,3). This involves measurements which evoke vertical deflection of the AFM probe and observation of lateral forces which twist the AFM force sensor. A simultaneous detection of vertical deflection and twisting of the microcantilever can be done by using a four-sectored positional sensitive photodetector which measures the change in the deflection of a laser light reflected off the top of the microcantilever. The newest generation of SPM (Scanning Probe Microscope) equipment allows for simultaneous AFM and Lateral Force Microscopy (LFM) scans. There is ample evidence in the literature that contact-mode AFM can be used not only to investigate polymer morphology (4,5), but also to study polymer architecture from a true molecular perspective (6).

### **Introduction**

The mechanism of friction for sliding across smooth surfaces includes forces of adhesion. In LFM for example, the adhesion arises from intermolecular interactions between the surface atoms and the atoms at the apex of the LFM tip. Adhesive forces will reflect the structural symmetry at the surface. Thus it is to be expected that the coefficient of friction will be direction dependent.

One of the first AFM studies involving lateral force measurements to elucidate materials' properties (7) showed that by simultaneous AFM and LFM measurements, information could be obtained about surface topology and identification of the components in phase-separated thin films. We used LFM to study friction at the surface of lamellar crystals of polyoxymethylene (POM) (8). In this study, we reported on the first observations of direction-dependent friction in the different chain folding domains of POM. These results were explained by considering the presence of macromolecular loops at the surface of the crystal arising from chain folds at the folded surface. It is expected that these would be oriented predominantly parallel with the edges of the lamellar crystals in the different chain fold domains (9).

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\*Corresponding author

The questions relating to the nature of chain folding and the structure of the interface of lamellar polymer crystals are practically as old as the first systematic studies of chain-folded lamellar crystals (10). Regular sharp folds in adjacent positions (10), loose loops with adjacent reentry (11), and random folds (switchboard model) (12) have been suggested. In addition, it has been proposed that the existence of physically adsorbed macromolecules on the fold surface of lamellar crystals obtained from dilute solutions could be responsible for the significant amorphous component (13). These models inevitably result in different surface structures at the atomic level. Recent studies on polyethylene lamellar crystals by AFM conclusively showed the presence of adjacent molecular folds (14). Our work on POM (8) by LFM was consistent with directionally ordered folds. Thus, AFM and LFM have the potential to shed light on the old problem of the nature of chain folds by direct-space observation.

## Experimental

### *Crystal Growth*

The linear polyethylene used was obtained from NBS (batch #1475 ) with a weight average molar mass  $M_w=52000 \text{ g mol}^{-1}$  and a polydispersity index  $M_w/M_n = 2.9$ . The lamellar crystals were prepared by isothermal crystallization from xylene. A 0.0033 %w/w solution of polyethylene in xylene (distilled from sodium/benzophenone and filtered using  $0.45 \mu\text{m}$  pore size Sartorius filters) was prepared by dissolving the polymer in the boiling solvent. The solution was boiled for 2 hours and the hot solution was transferred into a crystallization vessel, immersed in an oil bath maintained at the crystallization temperature  $89 \text{ }^\circ\text{C} \pm 1 \text{ }^\circ\text{C}$ . The polyethylene crystallization setup was first described by Keller (15). The apparatus consists of a crystallization vessel, a medium pore sintered glass filter, and a receiver which are connected vertically by ground glass joints. A side arm with a two way tap, connected to the receiving flask, protrudes from the bath. The apparatus was rinsed with filtered acetone ( $0.2 \mu\text{m}$  Sartorius filter), dried thoroughly and kept under dry, filtered nitrogen. When the hot solution is transferred into the crystallization vessel with the side arm tap closed the excess air pressure in the receiving vessel keeps the solution in the top vessel. The crystallization flask contained a stage on which sheets of muscovite mica (which had been cleaved before use) were placed, in order to serve as a substrate for crystal growth. After the desired crystallization time (6 hours) the side arm tap was opened which allowed the solution to flow down to the receiver through the sinter while the crystallization temperature was maintained. The crystals on the mica were immediately washed with filtered xylene at  $89 \text{ }^\circ\text{C}$  to remove any precipitate from their surface.

### *AFM Imaging*

The crystals were imaged using a NanoScope III Multimode SPM instrument (Digital Instruments), equipped with a D scan head. All of the scans were performed at scan rates of less than 3 Hz with NanoProbe Si<sub>3</sub>N<sub>4</sub> microcantilevers having spring constants, specified by the supplier, of 0.38 Nm<sup>-1</sup>. In order to obtain the lateral force images, the sample was scanned at 90 ° to the normal scanning direction so that variations due to the cantilever twisting motion would be recorded as a function of frictional forces between the probe tip and the sample. All of the images were obtained in air at room temperature. No filters were used during imaging.

### **Results and Discussion**

Figure 1 shows a 15 μm x 15 μm scan of a polyethylene crystal (recorded in deflection mode) exhibiting a six sectored truncated hexagonal habit. The crystal exhibits a pleat along its b axis, caused by its collapse from its hollow pyramid form (16, 17). A crystal overgrowth can be clearly seen in the bottom left of the image. A craze which develops as a result of the collapse of the crystal has formed between the two (110) faces on both the defect and the main crystal. As a result of this fracture strands of polymer chains are pulled out of the two sectors and these are also visible in Figure 1.

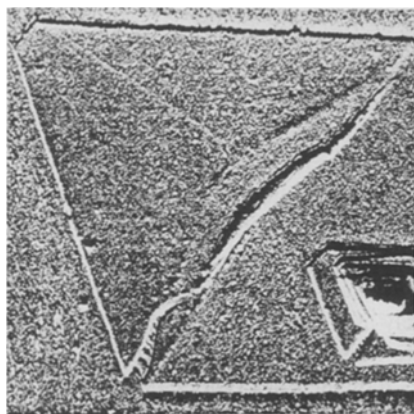


Figure 1. AFM scan of a polyethylene lamellar crystal (deflection mode, scan size 15.0 μm x 15.0 μm).

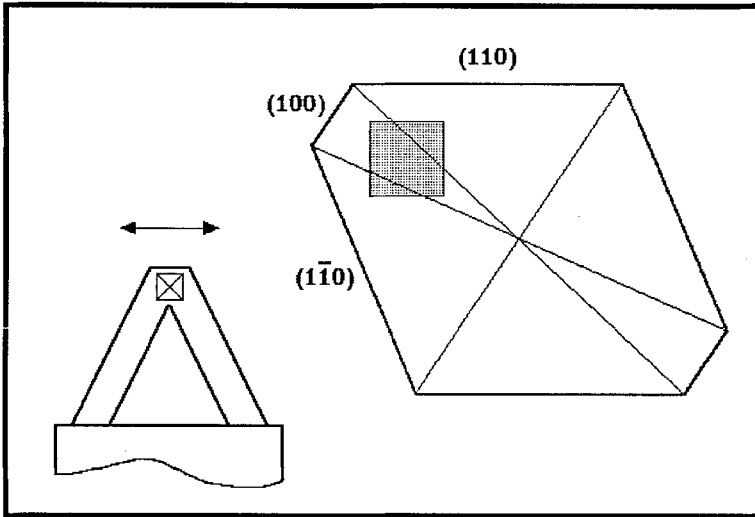


Figure 2. Schematic of the polyethylene crystal. The box indicates the area scanned in Figures 3a and 3b and the arrow above the V-shaped cantilever in the bottom left of the Figure shows the scan direction.

A schematic of the crystal orientation during scanning can be seen in Figure 2. The direction of the scan for the images in Figure 3 is indicated above the cantilever in the lower left corner. The position of the scan is shown by the box. Figures 3a and 3b show dual LFM and AFM images of the polyethylene crystal. The three chain fold domains are clearly seen, with the center, truncated sector positioned at  $-45^\circ$  with respect to the horizontal (at four thirty o'clock). From the height image in figure 3a it can be seen that there is a constant height on the crystal surface in all three of the domains. In the friction image however, there is a lower lateral force (indicated by darker areas) in the top right sector, while the two lower sectors show similar, higher lateral force. Figure 2 shows that during the scan the cantilever was scanning parallel to the edge of the upper (110) sector and at approximately  $45^\circ$  to the (100) and (110) sectors. Since differences in the sectors occur only at the fold surface with the interior of the crystal being continuous throughout, there must be anisotropic friction on the surface of the fold domains. This is very clearly indicated in Figures 4a and 4b. For these images the scan was performed with the cantilever parallel to the (100) face and at approximately  $30^\circ$  to the (110) faces. Figure 4a shows the average height in the sectors to be similar. However, there is a considerable difference in the lateral force, as shown in Figure 4b, with the (100) truncated sector being lower than the two (110) sectors.

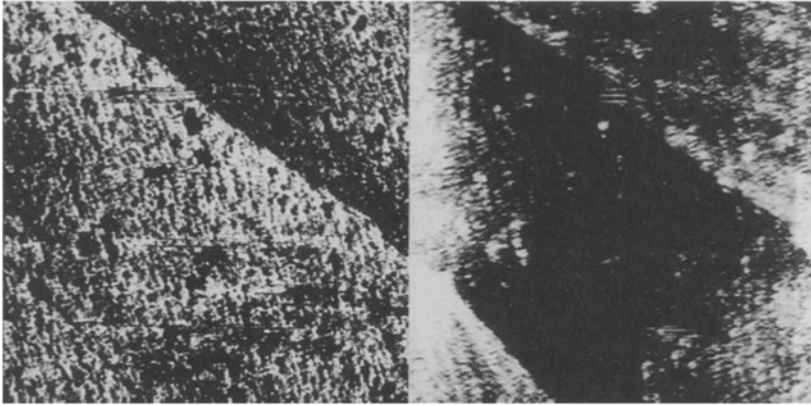


Figure 3a

Figure 3b

Figure 3a. LFM scan (scan size  $3\ \mu\text{m} \times 3\ \mu\text{m}$ ) of the section of the crystal indicated by the box in Figure 2.

Figure 3b. AFM scan (height mode, scan size  $3\ \mu\text{m} \times 3\ \mu\text{m}$ ) of the section of the crystal indicated by the box in Figure 2.

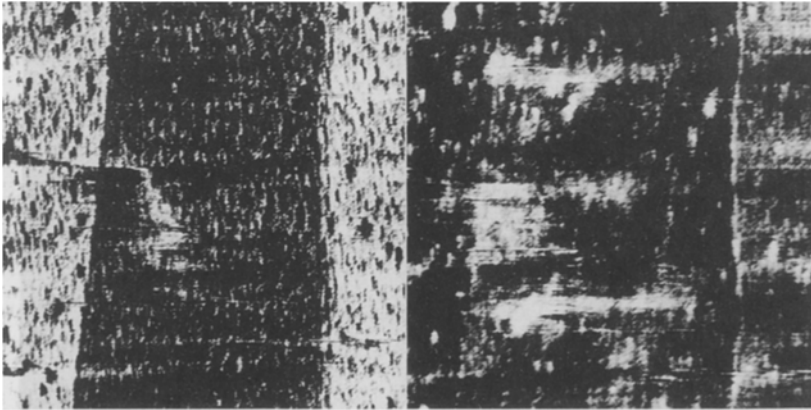


Figure 4a

Figure 4b

Figure 4a. LFM scan (scan size  $3.3\ \mu\text{m} \times 3.3\ \mu\text{m}$ ) of a section of the polyethylene crystal shown in Figure 1, with the scan direction parallel to the (100) face. (The truncated (100) sector runs vertically along the center of the image).

Figure 4b. AFM scan (height mode, scan size  $3.3\ \mu\text{m} \times 3.3\ \mu\text{m}$ ) of a section of the polyethylene crystal shown in Figure 1 with the scan direction parallel to the (100) face. (The truncated, (100) sector runs vertically along the center of the image).

If it is considered that there is a disordered surface on the fold domains with random, irregular chain folds or loose loops then the lateral forces would be isotropic over all of the domains. However, if the folds are formed predominantly parallel to the growing edge of the crystal, then there would be directionally ordered loops on the surface. This would produce two possible cases when scanning, depending on the scan direction. The tip would experience a low lateral force as it "slides" along the loops, when the scan is parallel with the growing edge of the crystal or a higher lateral force when it "bumps" into the loops as it scans against the folds. Therefore the anisotropic friction exhibited in the LFM scans can be explained by considering predominantly ordered folds.

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