polymer communications

# Molecular resolution of thin, highly oriented poly(tetrafluoroethylene) films with the atomic force microscope

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Thin, highly oriented layers of poly(tetrafluoroethylene) (PTFE, Teflon®) were produced with a simple mechanical deposition technique. Previously, it was shown that these films are exceptionally efficient substrates for oriented growth of a variety of materials. In this communication we report on the structure of the PTFE layers, as revealed with the atomic force microscope (AFM), at a resolution sufficient to distinguish the individual macromolecules. AFM images showed the surface roughness from scan sizes of a few nanometres up to 40 μm. Analysis of damaged films allowed an estimation of the film thickness, which ranges from ~15 to 40 nm thick.

**(Keywords: poly(tetrafluoroethylene); orienting substrates; atomic force microscope)**

*Introduction*

Recently, a new, versatile method for orienting materials has been developed[1]. The technique consists of mechanically depositing a thin, oriented layer of poly(tetrafluoroethylene) (PTFE) onto a smooth counterface such as glass, by dragging the polymer at controlled temperature, pressure and speed against the substrate. Subsequently, the species of interest are deposited onto these PTFE films from the melt or vapour phase or from solution to yield surprisingly well-oriented materials. Electron diffraction of the orientation-inducing films revealed that the macromolecules were oriented parallel along the dragging direction[1]. It was postulated that the PTFE layers were not molecularly smooth, and that their orienting faculty derived, in part, from the multitude of ridges in the film, which presumably provided effective nucleation sites that induced the oriented growth of a great number of materials[‡] deposited onto the PTFE films. However, no direct evidence was available with regard to the structure and topology of the PTFE layer to directly substantiate the proposed mechanism.

This paper reports on the characterization of the thin PTFE films with the atomic force microscope (AFM). The AFM was invented in 1985 by Binning, Quate and Gerber[2,3]. It images surfaces by raster-scanning a sharp tip over the surface at a constant very low force. Under optimum conditions, the resolution of the AFM may be as low as a few angstroms, sufficient to resolve atoms, molecules and polymers[4–9]. Magonov *et al.*[10] have observed oriented polyethylene (PE) at submolecular resolution with the AFM and have detected overlapping fibrils in an extruded PE rod. Patil *et al.*[11] have shown that the AFM is useful for measuring lamellar thicknesses in dendritic crystals of PE.

[‡] In this work we also observed that the present PTFE films effectively induced the ordered growth of a low molecular weight DNA, i.e. a fluorescein-labelled 25-mer

*Methods*

*Preparation of PTFE orienting substrates*[1]. Glass microscope slides used as substrates for PTFE films were cleaned overnight in ethanolic KOH. A solid PTFE (commercial grade Teflon®) bar was moved along the surface of the cleaned glass slide at a rate of 1 mm $s^{-1}$ and a pressure on the order of 1 kg $cm^{-2}$. The temperature of both the PTFE rod and the glass surface was 300°C. The PTFE layers when imaged by cross-polarized light microscopy were barely visible; nevertheless very fine parallel, birefringent rows were detected, which were relatively free of defects.

*AFM imaging*. The PTFE layers were imaged with a NanoScope II from Digital Instruments (Santa Barbara, CA, USA). The image in *Figure 1* was taken using an AFM with a 60 μm 'F' scanner. The image in *Figure 2* was taken with a custom AFM built into a light microscope. This AFM had a 0.6 μm scan range. All imaging was done in air. The silicon nitride cantilevers with integrated tips[12] were 100 μm long with narrow arms.

*Results*

The AFM image of the PTFE layers in *Figure 1* reveals parallel ridges running in the direction in which the Teflon® bar was moved over the microscope slide. Also, a kink band can be seen, about half way across the field and running in a horizontal direction. Defects of this type were uncommon and were probably caused by an abnormal vibration during deposition of the layer.

Heights and spacings of the PTFE ridges were estimated from many AFM images. Measured spacings between ridges ranged from <25 nm to >1 μm. Heights of individual ridges typically ranged from 1 to ~30 nm; ridges as high as 60–70 nm were occasionally seen. The measured heights of individual ridges agreed well with the measurements of overall surface roughness on a

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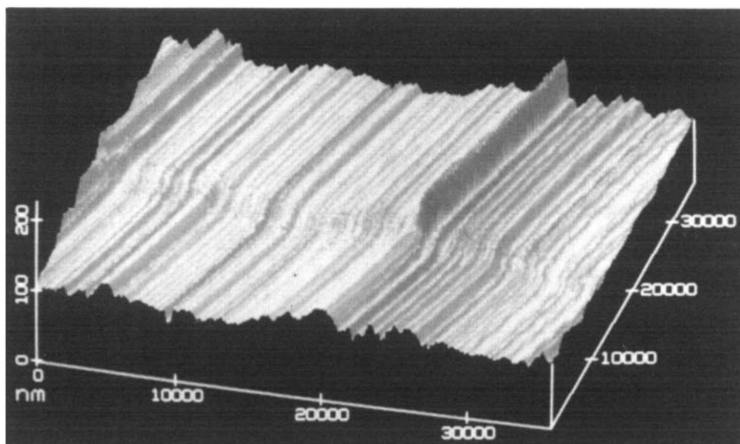


**Figure 1** AFM image of a thin PTFE film. Image area is 36 × 36 $\mu$m. Height scale of 200 nm greatly magnifies the surface roughness. Surface would appear flat if height were plotted on the same scale as length and width. The image has no highpass or lowpass filtering. Note finely spaced PTFE rows running in the direction in which the polymer was laid down; also, a kink band is seen

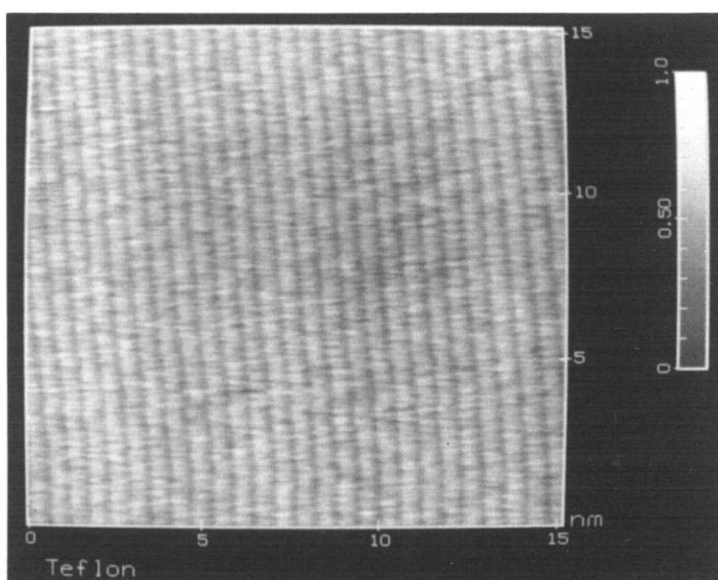


**Figure 2** AFM image of a thin PTFE film showing rows of ~0.5 nm spacing. Image area is 15 × 15 nm. The image was taken with NanoScope II AFM settings of lowpass filter = 1, highpass filter = 4 and was not filtered further. Unfiltered images of the PTFE rows have a similar appearance and identical spacing; the estimated height of PTFE rows in unfiltered images is 0.15 nm

number of samples. The AFM image in *Figure 1*, for example, was of a height of 42 nm, or less, over 96% of the surface; the height of the remaining 4% of the surface reached values as high as 95 nm. It should be noted that the AFM may underestimate the heights of closely spaced peaks, because the AFM tip is pyramidal, with a radius of curvature estimated[12] at 20–40 nm.

A higher magnification AFM image of the PTFE surface unveiled individual molecules (*Figure 2*). The characteristic intermolecular spacing[13] of the PTFE crystal lattice is 0.49 nm, which is not significantly different from the row spacing seen in AFM images of PTFE films. The AFM typically is calibrated by imaging mica, which has a lattice spacing of 0.52 nm. When PTFE and mica were imaged sequentially under the same conditions in the AFM, the spacing of the rows on PTFE was virtually indistinguishable from the spacing in the mica lattice. The molecular weight of the PTFE used was $\sim 10^7$ kg kmol$^{-1}$, which corresponds to a molecular length of $\sim 30\,\mu$m. Thus it is not surprising that no evidence of molecular ends in AFM images of molecular resolution were seen, since such high resolution could only be observed in scans of 40 nm or less. Occasionally, AFM images showed traces of structure along the PTFE rows with the approximate spacing expected for $-CF_2$ groups. Such structure was seen more often when the scan direction was rotated by 90°.

A damaged PTFE film was imaged in the AFM to estimate the thickness of the layer on the glass microscope slide. The average thickness of the PTFE layer deposited under the present conditions varied from 15 to 40 nm on different regions of the film. Interestingly, the PTFE films, unlike many surfaces, could not be damaged with the AFM, even by deliberately increasing the force. The AFM, operating in air, typically scans surfaces with forces[14] of $\sim 10^{-7}$ N. The PTFE layers could, however,

be easily damaged by such actions as touching a plastic pipette tip to the surface.

*Conclusions*

Highly oriented PTFE layers show an unusual ability to orient a wide variety of molecules and have the potential for many practical applications[1]. The AFM was successfully employed to characterize the complex surfaces of PTFE layers on a scale from tens of micrometres to less than a nanometre, thus revealing both molecular features and gross surface topology. The latter information will be of critical importance in developing an understanding of the orienting faculty of the PTFE layers and once more identifies the AFM as an exceptionally powerful tool in materials research.

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