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# Lattice imaging of friction deposited PTFE films

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## Summary

Highly oriented poly(tetrafluoroethylene) (PTFE) films were obtained by sliding a bar of a commercial grade PTFE along a strip of mica at a temperature of 300 °C. High resolution transmission electron microscopy was used to image the $10\bar{1}0$ lattice planes of the hexagonal phase IV in suitably oriented regions of the sample, indicating coherent order over distances of the order of at least 0.1 μm both perpendicular and parallel to the chain axis.


## Introduction

It is now well known that highly oriented poly (tetrafluoroethylene) (PTFE) films of a few tens of nm in thickness can be produced simply by sliding a (solid) sample along the surface of a glass or mica substrate at temperatures just below the melting point of PTFE (1). These films are of particular interest as orienting substrates, the orientation being induced either by epitaxy or as a result of supramolecular film structure. Atomic force microscopy (AFM) investigations have shown such films to have ridged surfaces, with the ridges running parallel to the sliding direction and corresponding to thickness variations of roughly 1 to 30 nm, with mean thicknesses of a few tens of nanometres and widths of about 0.1 μm (2,3). High resolution electron microscopy (HREM) has been used in the past to investigate the molecular structure of PTFE single crystals (4). In what follows we describe results obtained by applying the same technique to friction deposited films.

## Experimental

Highly oriented poly(tetrafluoroethylene) (PTFE) films were obtained by sliding a bar of a commercial grade PTFE along a strip of mica at a temperature of 300 °C and at a rate of about 1 $mms^{-1}$ (2). The films were then floated off the mica films onto distilled water, and picked up on carbon coated copper grids for observation in the transmission electron microscope (TEM). For HREM observations a Philips EM 430 ST, equipped with a low dose unit was used, operated at an accelerating voltage of 300 kV (point resolution 0.2 nm)). A plate magnification of 41,000 was used throughout and a defocus of about 100 nm, and the illumination conditions for exposure of the plates were as described by Chanzy *et al.* (4). 512 x 512 and 256 x 256 pixel numerical images were scanned from the negatives for Fourier filtering. Image simulations were Bloch wave calculations carried out using the EMS package (5), based on published structures for the PTFE hexagonal phase IV (6).

## Results and Discussion

Electron diffraction patterns of the thin films showed a very high degree of molecular orientation in the sliding direction, with a quasi-single crystal texture, and edge-on orientation of $10\bar{1}0$ planes of the PTFE hexagonal phase IV locally (with a measured spacing of about 0.48 nm). The $10\bar{1}0$ reflections could be used to form phase contrast images such as shown in Figure 1, which shows fringes extending over distances of the order of 0.1 µm both perpendicular and parallel to the chain direction, with a very high degree of order. The lateral extent of these regions of fringes corresponded to the groove widths as estimated from the mass thickness contrast in highly defocused images, whereas their extent in the direction parallel to the chain axis was possibly more than this: although 0.1 µm represents roughly the upper limit for regions in which the fringes were continuous, patches of fringes with ill-defined edges were observed to be arranged in rows running along the orientation direction over distances of up to several µm. Thus low resolution dark field images formed from the $10\bar{1}0$ reflections showed streaks in intensity, with similar dimensions. The $10\bar{1}0$ reflections increased in intensity when the films were tilted through 30° about the chain axis indicating considerable orientation of the close-packed planes parallel to the film plane, consistent with results obtained by AFM (3), but it was not possible to obtain lattice images in this orientation since the range of available tilts in the EM 300 ST was limited to ± 10°.

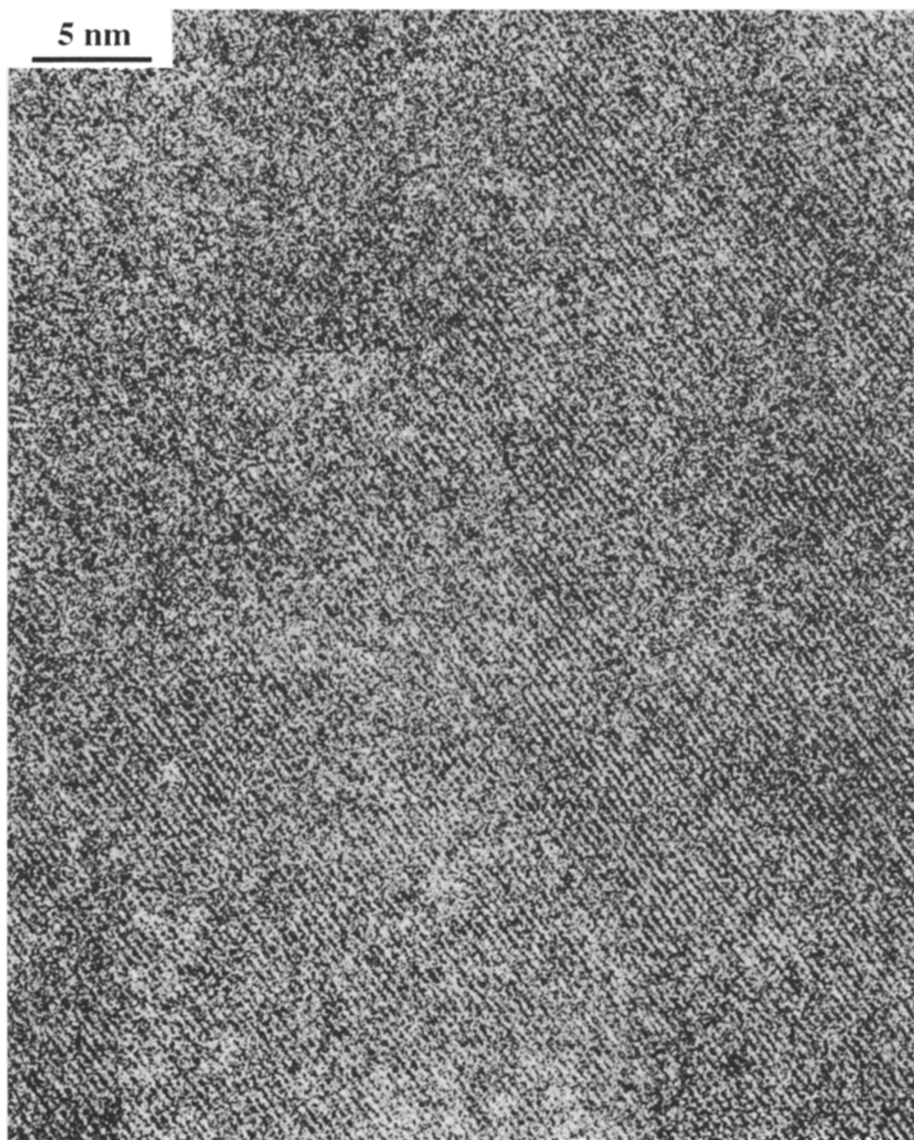


*Figure 1. 10$\bar{1}$0 fringes in an oriented PTFE film, with the sliding direction parallel to the fringe direction (100 nm defocus, original magnification 41,000, no objective aperture).*

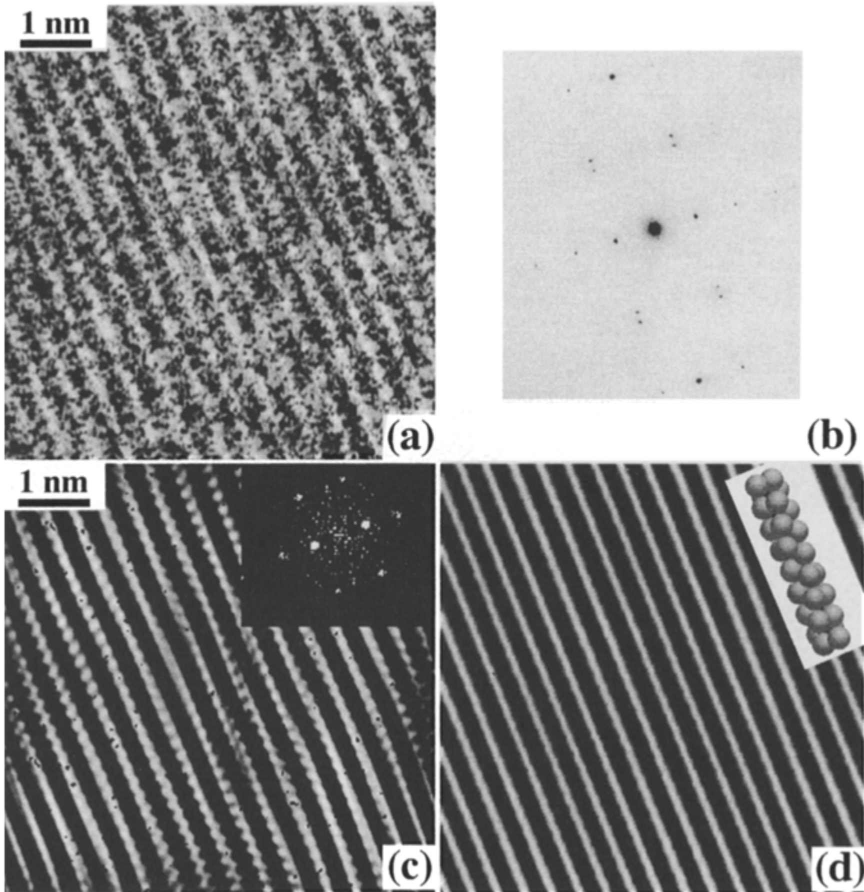


*Figure 2. (a) Selected region of a HREM micrograph (100 nm defocus) and (b) the corresponding microdiffraction pattern; (c) is a Fourier filtered image reconstructed from the fast Fourier transform of (a) (shown in the inset) and (d) is a simulated image for similar operating conditions and an assumed sample thickness of 20 nm (the inset shows the $15_7$ helical conformation used to obtain this image, not to scale).*

The imaging of the $10\bar{1}0$ fringes was relatively straightforward, their spacing of 0.48 nm being well within the resolution of the microscope. In the hexagonal IV phase, the first meridional reflection lies on the $15^{th}$ layer line and the first strong layer line is the $7^{th}$, corresponding to the well known $15_7$ helical chain conformation (see Figure 2(b)). Given a crystallographic repeat distance of 1.95 nm along the helical axis, the $7^{th}$ layer line corresponds to an axial spacing of 0.28 nm and so with the present resolution of 0.2 nm the images should contain information from the strongly diffracting $10\bar{1}7$ planes, and

hence provide some indication of the helical conformation. This proved difficult in practice owing to the beam sensitivity of the samples. Accurate astigmatism correction could not be carried out at the low magnifications necessary to obtain the images, and with the present illumination conditions there was concern over the stability of the $7^{th}$ and $8^{th}$ layer lines, which tended to merge and fade during exposure. Nevertheless, careful searching of the negatives revealed localized regions in which symmetrical peaks corresponding to the positions of the $10\bar{1}7$ reflections were visible in the image power spectrum as shown in Figure 2(a). By first masking these and the $10\bar{1}0$ and the $20\bar{2}0$ spots in order to reconstitute the background noise, and then subtracting this from the original image, we obtained results such as shown in Figure 2(c), in which the main fringes appear slightly corrugated. Also shown for comparison in Figure 2(d) is a Bloch wave image simulation for a 20 nm thick sample at 100 m defocus, showing similar features, each dark "bump" corresponding to the projection of columns of fluorine atoms. Interestingly, the filtered image is also suggestive of twisting about the chain axis on a scale of about 7 of these bumps, but even given our *a priori* knowledge of the chain conformation, we should dismiss as an artefact, particularly since the twisting is poorly correlated, and is not clearly visible in the simulated images.

## Conclusions

We have successfully obtained lattice images of oriented friction deposited PTFE films by HREM, indicating high degrees of ordering, consistent with an extended chain single crystal structure. With Fourier filtering, sub-molecular structure reflecting the helical chain conformations may also be resolvable, although these results should be treated with caution in view of the possibility of artefacts arising from both beam damage and the somewhat subjective nature of Fourier filtering used in this way.

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