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Estimation of the linear thermal expansion coefficient in friction-deposited, oriented poly(tetrafluoroethylene) films by temperature-dependent lateral force microscopy

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Summary

Preliminary lateral force microscopy (LFM) results are presented which were obtained at different temperatures on thin films of poly(tetrafluoroethylene) prepared by friction deposition. Chain-chain distances of rodlike poly(tetrafluoroethylene) macromolecules were determined as a function of temperature from LFM images which exhibit molecular resolution. The value of the linear thermal expansion coefficient in the chain-perpendicular direction was estimated to be 3.5×10^{-3} [1/°C] in the temperature range between +10 °C and +40 °C. This value is higher than the literature data quoted for the temperature range between 0 °C and 25 °C. Possible reasons for this deviation are discussed.

Introduction

With the advent of various scanning force microscopy (SFM) techniques in the eighties [1] a new family of microscopes has become available to the scientific community that allows one to image morphological features at polymer surfaces in the micrometer range, as well as to visualize individual macromolecules down to the Angstrom scale, in one experiment [2-4]. At present, the resolution of methyl and methylene groups can be achieved in contact-mode atomic force microscopy (AFM) if the sample surface possesses a two-dimensional translational order at the molecular level [4-6]. A relatively recent addition to SFM, the lateral force microscope (LFM) [7], enables one to perform experiments to map differences in surface frictional characteristics. Dual AFM and LFM scans are useful to simultaneously study topology and friction from the micron to the Angstrom scale. LFM applications include identifying components in multicomponent polymer systems [8], and studies of frictional characteristics at the molecular level (nanotribology) [7], [9]. These studies are extremely helpful to obtain an improved understanding of the atomic dynamics of friction. It was shown first by Mate et al. [7] that frictional force characteristics of graphite on the atomic level have the same periodicity as the "honeycomb"-like atomic structure. Thus LFM images can reflect molecular, or atomic, arrangements and can allow one to image molecular, or atomic, scale features. This is due to a molecular-level stick-slip process. In a recent study we showed that LFM can be successfully used to image oriented poly(tetrafluoroethylene), PTFE, films obtained by friction deposition of oriented macromolecules [10]. In this paper we discussed images with molecular resolution, transfer of PTFE chains to AFM tips, the role of interfacial tension between PTFE and various substrates, and anisotropy of the frictional coefficient that was observed in scans performed at different directions with respect to the macromolecular orientation.

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Oriented thin films of several polymers have been deposited on various substrates by friction transfer [11]. The materials that allow such transfer include linear polyethylene, PTFE, liquid-crystalline aromatic polyesters (Vectra) [11], poly(p-phenylene) and poly(dimethyl silylene) [12]. The technique includes pressing a small block of a solid polymer to preheated smooth substrates (quartz, mica, microscope glass) and sliding it under constant normal load. A thin (2-100 nm) film will form on the substrate by material transfer which consists of polymer chains with a high degree of uniaxially aligned chains. It has been shown that these films induce oriented growth of a variety of materials deposited from solution, melt, or vapor, onto these films. It seems that PTFE films have the best ability to function as substrates in epitaxial crystallization.

Oriented, friction-deposited films of PTFE have been subject of AFM studies [13]. Observations of individual PTFE helices have been reported in these papers with a chain-chain distance of 0.58 nm. In the present paper we focus our attention on LFM imaging with molecular resolution and on the linear thermal expansion coefficient that was obtained from direct-space molecular-level LFM scans performed at different temperatures. Details of the SFM imaging techniques, including contact-mode AFM, LFM and non-contact tapping mode AFM are described in detail in the literature [2] and will not be discussed in the present paper.

Experimental

Dual mode AFM/LFM imaging was performed by a NanoScope III multimode setup (Digital Instruments, Santa Barbara, Ca). The instrument was equipped with an A scanner which was calibrated in x- and y- directions by using images of muscovite mica as described in ref. [14]. All scans were performed in air with Si_3N_4 NanoProbe integrated microcantilevers with a nominal force constant of 0.38 N m^{-1}. The scan rates selected were between 7 and 9 Hz. Scanning was performed at 90° with respect to the direction of the long axis of the cantilever spring, as is usual for LFM/AFM dual imaging. Contact mode AFM measurements were performed in the height mode, while in LFM experiments the twist of the cantilever was measured. This twist is related to the friction force.

The temperature of the samples were controlled in one set of experiments in the following fashion. For a "low temperature" value (10 °C - 15 °C), the scan head was placed in a refrigerator which was purged with dry nitrogen gas. Acoustic shielding was achieved by using a cotton lining in the refrigerator. A temperature above the ambient was obtained by tightly surrounding the scan head with a good thermal insulating foam. The heat released primarily by the piezo head during scanning warmed up the sample compartment to a temperature between 35 °C - 40 °C. Images at room temperature (25 °C - 30 °C) were obtained with free-standing scan heads. The value of the temperature was estimated by a thermocouple placed near the sample.

Results

Friction deposited PTFE films were imaged by performing dual contact-mode AFM and LFM scans. Typical nanographs (scan size: 10 nm x 10 nm) with molecular resolution (raw data) are shown in Figure 1a (AFM) and Figure 1b (LFM), respectively. The scan direction was 56° with respect to the film deposition direction i.e. with respect to the chain direction. The LFM and AFM scans showed aligned, regularly packed, rodlike features which correspond to images of PTFE macromolecules. It is worth mentioning that the observed chain-chain distance on LFM, as well as on AFM images, had a value of 0.58 (± 0.02) nm at 25-30 °C temperature.

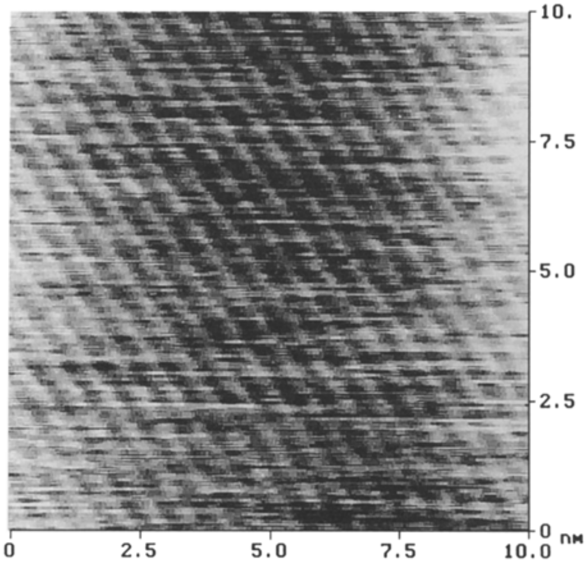

Figure 1a
Contact mode (height) AFM image of oriented PTFE with molecular resolution (retrace).

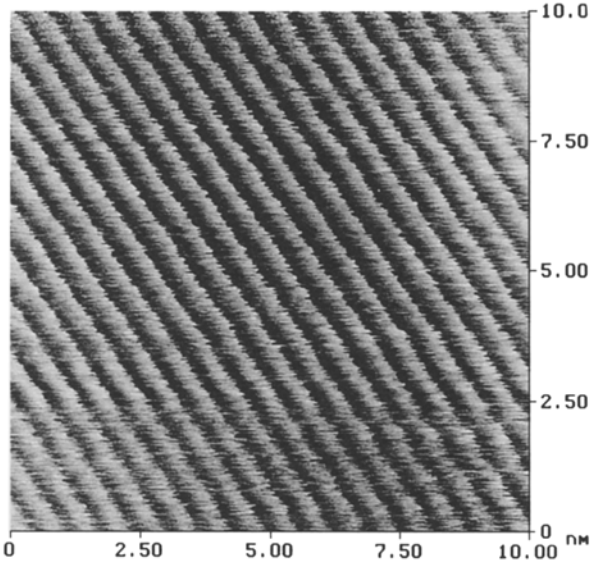

Figure 1b
LFM image of oriented PTFE (same area as depicted in Figure 1a) with molecular resolution (trace).

The features on the AFM image in Figure 1a were captured during retrace experiments in the height mode (i.e. measuring the height of the sample surface in scans from right to left), while the LFM nanograph was obtained during trace (i.e. measuring the twist of the cantilever, which corresponds to friction forces, in scans from left to right). Thus the two images shown in Figures 1a and 1b were obtained by visualizing the same spot at the sample surface. It is obvious that the AFM images of the PTFE chains and the rodlike features observed on the LFM scans are synchronized. Thus one can assume that the rodlike features on the LFM image correspond to actual friction-force images of the PTFE macromolecules. The alternating periodic bright and dark areas on the LFM image correspond to high and low friction forces, respectively (imaging in "trace" scans). The macromolecules in PTFE can be visualized by LFM due to a stick-slip process that occurs during imaging and has the same periodicity as the surface lattice of the chains. Friction forces during trace line scans (i.e. during scans from left to right) twist the cantilever in the clockwise direction. Clearly, during line scans in retrace mode, the cantilever twist would occur in the anticlockwise direction. Trace and retrace signals should essentially be symmetric with respect to zero cantilever twist which corresponds to a frictionless surface (no lateral force). In Figure 2 we show an LFM image which was obtained by scanning in retrace mode from top to bottom between y=10.0 nm and y=4.7 nm vertical distances. At y=4.7 nm we switched from retrace to trace and completed the scan between y=4.7 nm and y=0.0 nm in the trace mode. Clearly, high and low friction (dark and bright tones) changed sign as we switched from retrace to trace.

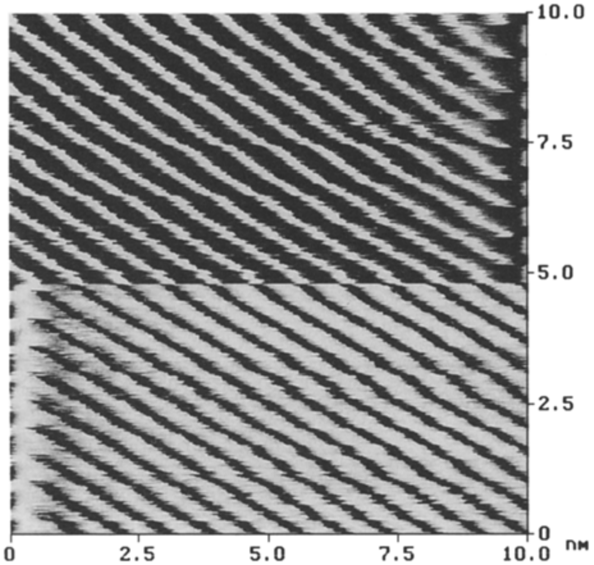

Figure 2
LFM image of oriented PTFE. Top 5.3 nm: retrace. Bottom 4.7 nm: trace.

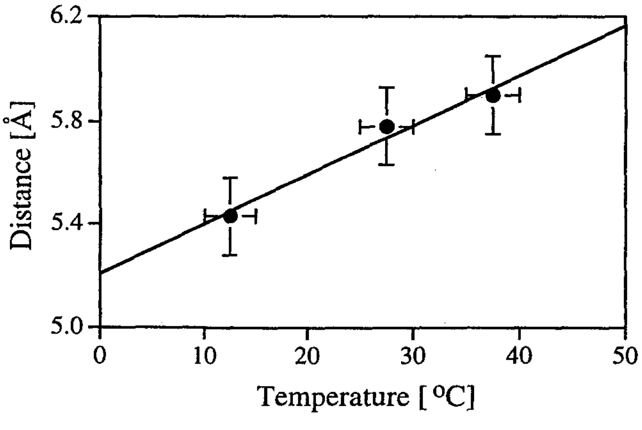

Figure 3
Chain-chain distance of PTFE, obtained from LFM images, as a function of imaging temperature.

It is relatively easy to obtain AFM/LFM images with molecular resolution on the oriented PTFE films used in this work as displayed in Figures 1a and 1b. We used the LFM nanographs to investigate the temperature dependence of the intermolecular spacing. The temperature range covered in this experiment was between +10 °C and + 40 °C. Due to experimental limitations, chain-chain separation values were obtained only in three experiments. The results are shown in Figure 3. A clear trend of an increase in the lattice spacing in the perpendicular direction of the PTFE chains is visible. In the room temperature range, a double structural phase transition is expected for PTFE, centered around 20 °C, and 30 °C, respectively [15]. This set of transitions is related to conformational changes of the PTFE helix. The data shown in Figure 3 allowed us, for the first time, to obtain a rough estimate for the linear thermal expansion coefficient of the crystalline phase of a polymer (PTFE) by scanning force microscopy. A value of $3.5 \pm 2.0 \times 10^{-3}$ [1/°C] was obtained by a linear regression fit. The linear coefficient of thermal expansion of PTFE was investigated and reported in the literature for different temperature ranges [16]. The value of the linear thermal expansion coefficient between 0 ° and 25 ° is 2.0×10^{-4} [1/°C], as quoted in ref. [16]. This value becomes significantly smaller in temperature ranges above and below this temperature interval, as expected, since the phase transitions mentioned earlier occur in the vicinity of room temperature. The value of the linear thermal expansion coefficient obtained in our AFM experiments is significantly higher than the value quoted in the literature. This might be due to several, at this point unknown, reasons. For example, the experimental error in our AFM measurements is quite high, as the temperature control process used was rather simple and inaccurate. The temperature range of our experiments is centered just around the phase transition temperatures of PTFE, while the range where thermal expansion coefficients are given in the literature is somewhat different and is specified for lower temperatures. This might also result in a higher value of the thermal expansion coefficient observed by probe microscopy as opposed to the literature data. The high apparent value obtained by LFM might also reflect a change in the calibration of the microscope with temperature. Work in progress is aimed at the clarification of this and other possible experimental problems. Our value is measured in a well defined crystallographic direction while no direction is specified for the literature value. Thus the literature value corresponds to a directional average which can also result in discrepancies. Finally, there is another, potentially very important, implication of the high thermal expansion coefficient value observed. Scanning force microscopy probes the surface of the material, and the thermal expansion coefficients quoted in the literature are bulk values. Thus the question remains open, whether the values obtained in our work using a surface characterization technique can really be considered as representative data for the bulk. The possible role of temperature-dependent surface reconstruction in PTFE must be addressed in the future.

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