

High-resolution STM-imaging of highly oriented ultra thin poly(ethylene) films

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Abstract

Poly(ethylene) (PE) ultra thin films drawn from the melt have been deposited on highly oriented pyrolytic graphite (HOPG) substrates for an investigation with the scanning tunneling microscope (STM). Similar to earlier examinations of poly(1-butene) (PB-1) ultra thin films (1), the STM investigations exhibited images of PE flakes extending over some hundred nanometers. Their thickness was determined to be much larger than the normal established tunneling distance between the tip and a good conducting (metallic) sample surface. It is supposed that the STM-tip penetrates the film and reduces its thickness by scanning over the film. Thus, a destruction of the film is likely leaving only a monomolecular layer of PE macromolecules on the graphite surface. At higher resolutions an ordered structure pseudomorphic to the simple chain nature of the PE macromolecule is revealed.

Introduction

The crystal structure of poly(ethylene) and many other polymer crystals is well known from X-ray diffraction and TEM investigations (2,3). However, the knowledge about the surface properties of polymeric crystals is less elaborated. These properties influence the interfacial and, therefore, some macroscopic mechanical properties (e.g. in composite materials) (4). What may be observed on such surfaces are effects like relaxations or reconstructions which are not well explored. The surface of uniaxially oriented semicrystalline polymeric thin films is of particular interest, especially for an understanding of interfacial and surface effects, as for example, in the oriented growth of certain metals on polymers (5). To answer some of these questions, the use of a STM (6) is well recommended because of its surface sensitivity, i.e. its capability to directly image the local electronic surface states at an atomic scale. STM will thus be favoured as an excellent complementary method to transmission electron microscopy (TEM) (5) investigations which probes the bulk properties. For good imaging of organic films (7,8,9), an essential premissis is either a sufficiently high electrical conductivity (10) or films

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of such small thickness that the molecules fit spatially into the tunneling gap (11), thereby modulating either the electronic density of states of the substrate material or the tunneling barrier height.

Experimental

The oriented semicrystalline PE substrates are prepared according to the method of Petermann and Gohil (12) : High Density Poly(ethylene) HDPE is dissolved in xylene (~ w. t. 0.4%). Some droplets of this solution are then deposited on the smooth surface of a glass slide where the solution itself disperses uniformly. When heating the sample to a temperature of about 130-140° C, the solvent evaporates. From the resulting melt a highly oriented ultra thin film is drawn (with a thickness below 20 nm) by a motor driven cylinder ($v_x \approx 7$ cm/sec) (Fig. 1). In case of careful preparation, even thinner films can be produced by this technique. The samples were then prepared in two different ways: for TEM investigations, the oriented film was cut into pieces and mounted onto copper grids, while for the STM investigations, the PE film was fixed on a HOPG substrate.

The TEM investigations were performed on a Philips 400 T electron microscope operated at 100 kV. STM investigations were made using a commercial air STM in the constant current mode.

Results and Discussion

Transmission electron microscopic investigations showed that the PE film consists of crystalline and amorphous regions (Fig. 2). The crystalline areas are made of lamellar crystals with dimensions ranging from a few hundred nm to a few μm in length arranged perpendicularly to the drawing direction of the film, and a thickness of a few ten nanometers parallel to the drawing direction. From the electron diffraction pattern of the PE film (inset in Fig. 2), the uniaxial orientation of the crystallites and macromolecules caused by the extension of the melt is deducible. As described above, PE thin films are not of single crystalline order but rather show a lamellar arrangement of individual crystals which have only one crystallographic axis in common, the direction of the molecular orientation (fibre texture). In the crystalline conformations, macromolecules agglomerate parallelly with the linear chains exhibiting an pronounced zigzag-behaviour of a 2.55 Å identity period. The orthorhombic unit cell of PE crystals then measures 4.95 Å x 7.42 Å x 2.55 Å for the a, b, and c axes, respectively (experimental values) (13). For such crystals the smallest distance between two chains is about 4.5 Å. The ratio calculated from the identity period of the PE chain and the smallest distance between two chains thus yields 0.57.

For TEM examinations of the surface topography, the PE ultra thin films were shadowed with platinum. Fig. 2 shows the characteristic surface topography of a film. Parallel to the

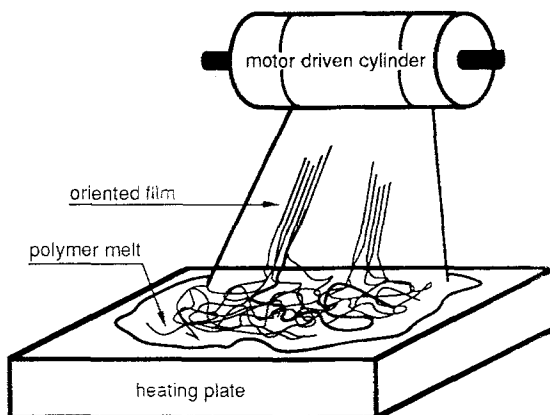


Fig. 1 : Schematic diagram demonstrating the preparation method of oriented PE thin films

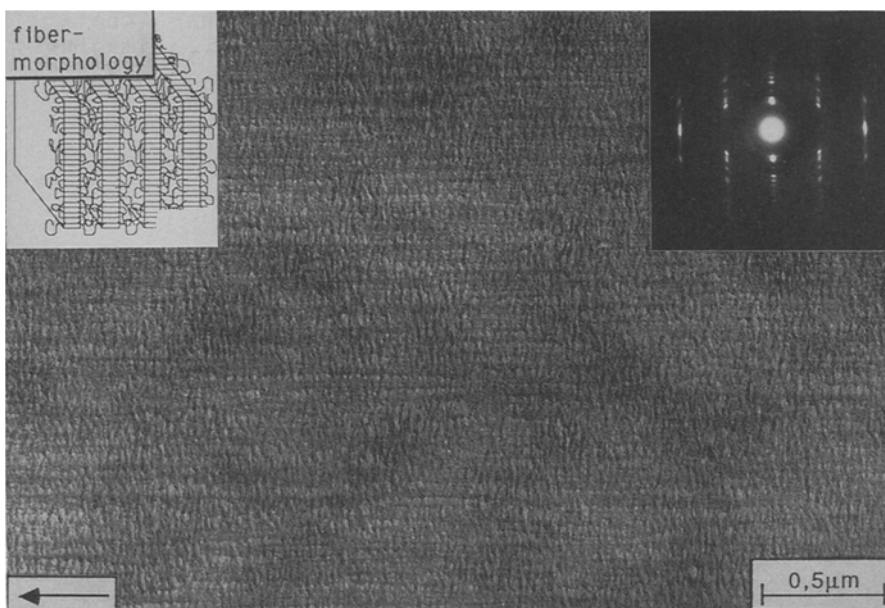


Fig. 2 : TEM picture of a platinum shadowed PE film surface. The arrow in the lower left corner indicates the direction of the molecular orientation. An electron diffraction pattern as well as a sketch showing the morphology are inserted in the upper right and left corners, respectively.

drawing direction of the film a topography originating from the processing technique is visible. Perpendicular to the drawing direction the lamellar crystals protrude from of the surface for a few nanometers.

Fig. 3 depicts a pseudo 3-D-view of the tunneling microscope to a $250 \times 250 \text{ nm}^2$ surface spot revealing the PE polymer film deposited onto HOPG. This image shows some extended PE flakes. There is no evidence for such flakes from TEM investigations consistent with the very first few STM scans on an untouched PE thin film. Therefore, it is supposed that the STM-tip penetrates the film until a finite tunneling current flows. Simultaneous scanning of the tip results in a destruction of the film. The observed polymer film flakes may thus be the result of this destructive process. Surprisingly, it was possible to image these flakes with the STM, although their thickness of about 60 \AA rather implies the insulating character as found in the bulk material (13). The good conductivity thus can only be understood when the top layer of the film is thought to be sufficiently conductive probably due to contamination with H_2O or carbon from the HOPG substrate, or when the high electric field strength locally induces an enhanced mobility of charge carriers along molecular fibrilles of the material. Nevertheless, the surface shown in Fig. 3 provided stable conditions while imaging with STM.

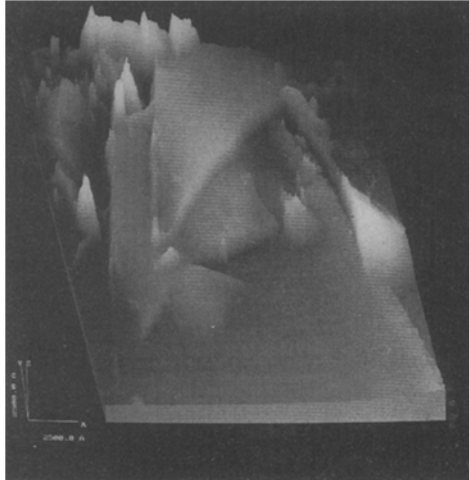


Fig. 3 : Pseudo 3-D-STM image of a PE film deposited onto HOPG. Imaging was done in air over a surface area measuring $250 \times 250 \text{ nm}^2$ in size, with $I_t = 1.0 \text{ nA}$, $V_t = 1000 \text{ mV}$, tip positive. The extended flakes consist of polymeric material.

When imaging thinner parts of the PE film (i.e. closer at the film/substrate interface) at a higher magnification, the STM recorded the fibrillar structure presented in Fig. 4 and Fig. 5. When imaging at even higher magnification on surface spots covered essentially with monolayers of parallelly aligned molecular PE-chains, pictures as presented in Fig. 6 were obtained. In the upper right of Fig. 6, a model of the correspondending molecular PE chain structure is sketched. The intermolecular spacing measured from the mean distance of two chains is 4.7 Å and the pitch height (identity period) of a chain measured from the longitudinal modulation (zigzag) of the molecules 2.5 Å. These values and the ratio measured from the pitch height of the molecules and the mean distance between two molecular chains of 0.56 is in excellent agreement with the PE unit cell parameters of the bulk (13). Earlier STM-investigations of poly(1-butene) thin films showed a much larger misfit of the pitch height and the intermolecular distance. It is supposed that the helical structure and the ethyl side groups of the PB-1 molecules causes a higher interaction with the substrate (1) affecting the lattice parameters drastically. The good agreement of the PE lattice parameters in contrast to the PB-1 investigations, may be the result of the conformational and energetic differences between linear zigzag and helical chains.

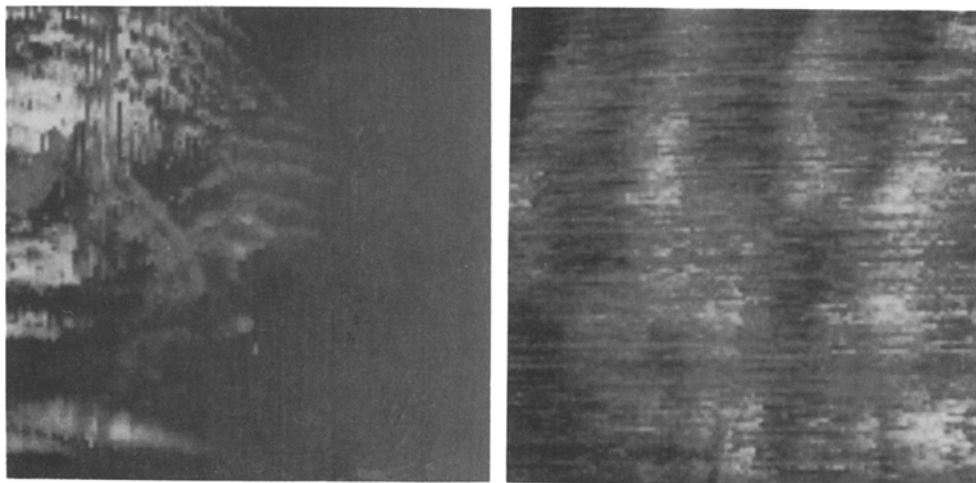


Fig.4,5 : STM image with increased magnification compared to Fig. 3 magnifying the fibrillar structure of the PE film. Images sizes are 100x100 nm² and 20x20 nm², respectively. $I_t = 0.6$ nA, $V_t = 463$ mV, tip positive.

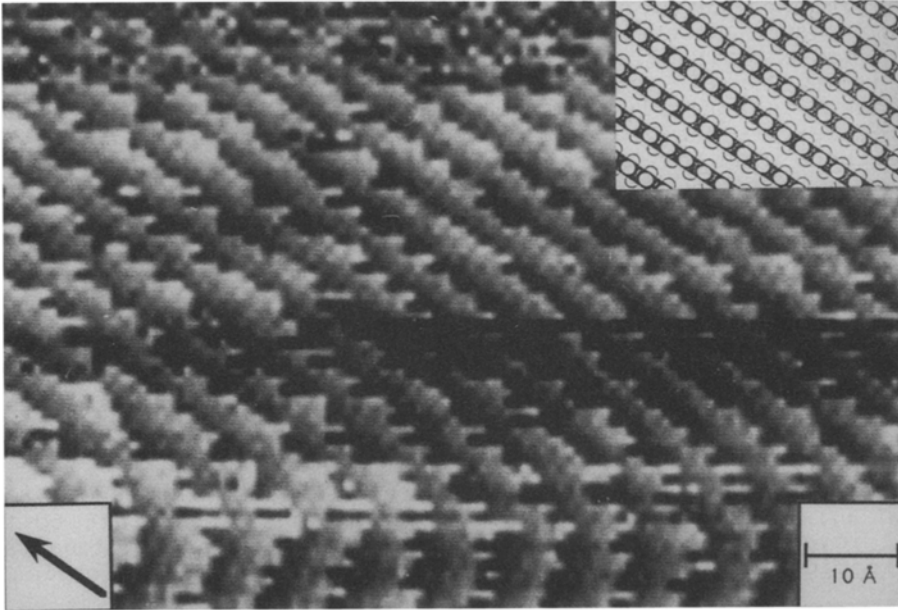


Fig. 6 : High resolution STM picture of a HOPG surface covered with a PE thin film. The linear structure originating from the PE film filaments has a pitch height of $\sim 2.5 \text{ \AA}$. The intermolecular distance measures 4.7 \AA . The arrow in the lower left corner indicates the orientation of the PE chains. The upper right a sketch reveals the expected PE chain configuration. $I_t = 0.6 \text{ nA}$, $V_t = 463 \text{ mV}$, tip positive.

Conclusions

These first STM experiments on melt-drawn PE ultra thin polymer films aimed to investigate the feasibility of structural and electronic surface inspection with the STM as a complementary method to TEM. It is shown that fairly thick parts of the PE films can be imaged, as was also observed on other organic bulk materials. The question of the local electric conductivity of ultra thin films compared to bulk insulators still remains unsolved.

Furthermore, images have been obtained showing the molecular structure of PE, correlating perfectly in pitch height and intermolecular distance with the crystallographic data. A detailed analysis investigating interfacial structural and electronic effects between molecular overlayers and conducting substrates is in progress and will be published elsewhere.

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