Scanning Force Microscopy of Melt-Crystallized, Metal-Evaporated Poly(butene-1) Ultrathin Films

K. D. Jandt,*,† T. J. McMaster,† M. J. Miles,† and J. Petermann‡

H. H. Wills Physics Laboratory, University of Bristol, Royal Fort, Tyndall Avenue, Bristol BS8 1TL, England, and Fachbereich Chemietechnik, Lehrstuhl für Werkstoffkunde, Universität Dortmund, Emil-Figge-Strasse 66, D-44221 Dortmund, Germany

Received June 23, 1993; Revised Manuscript Received September 7, 1993[⊗]

ABSTRACT: Ultrathin poly(butene-1) (PB-1) films drawn from the melt have been investigated using the scanning force microscope (SFM) to study the surface topography of both bare and tin-evaporated PB-1 films. Two different operating modes of the SFM were used, the repulsive mode and the tapping mode. The results obtained from SFM measurements show structures similar to the PB-1 needle crystalline morphology which agree excellently with recent TEM investigations. On a molecular scale structures similar to PB-1 macromolecules can be resolved with a repeat of 0.7 ± 0.1 nm (the value obtained from X-ray diffraction is 0.65 nm). Attempts to image the tin deposition on the PB-1 film surface using the repulsive mode were hampered as the scanning motion of the probe swept away most of the metal particles. Operation of the SFM in the tapping mode prevented this and allowed the overgrowth of tin on PB-1 films to be observed.

1. Introduction

Thin films are of great interest in technological applications and basic research. Particular scientific interest in surfaces of uniaxially-oriented semicrystalline polymer thin films arises from interfacial and surface effects, e.g., relaxations and reconstructions, which may significantly differ from bulk phenomena because of the very weak intermolecular forces (van der Waals forces). The surface topographic structures of bare polymer films determine the interfacial properties (i.e., adhesion, orientation) in contact with other materials, as, for example, composite materials. Furthermore, various evaporated metals are known to grow crystallographically oriented on semicrystalline polymer thin films.[1] The orientational relationship (epitaxy) between polymer films used as substrates and metals seems to be caused by a graphoepitaxial[2] effect, i.e., orientation induced by nucleation onto oriented topographic features of the substrate.[3]

Recently knowledge of the surface morphology and composition of thermoplastic melt-drawn thin polymer films has increased rapidly. This is due to the use of local scanning probe techniques like the scanning tunneling microscope (STM)[4] and the scanning force microscope (SFM).[5] These instruments are well suited to this field of research since they have a unique surface sensitivity, i.e., the capability to directly image the local electronic structure and the surface morphology.

Different morphologies of semicrystalline thermoplastic polymer films such as lamellar crystals (kebabs) or shish-kebab crystals in the case of polyethylene (PE)[6] and needle crystals (shishs) in the case of polypropylene (PP),[3] poly(butene-1) (PB-1),[7,8] and isotactic polystyrene (iPS)[9] have been imaged with SFM. While STM investigations showed molecular resolution for both PE[10] and PB-1;[11] SFM investigations revealed molecular resolution only for PE.[6]

Owing to the weak adhesion of epitaxially grown metals on polymer films, only very few SFM measurements of these systems have been obtained showing the growth behavior of the metal particles on the polymer sufrace.[3,8] In most cases the metal particles are brushed away from the surface, owing to the frictional interaction between the SFM tip and the scanning motion of the probe.[3,8]

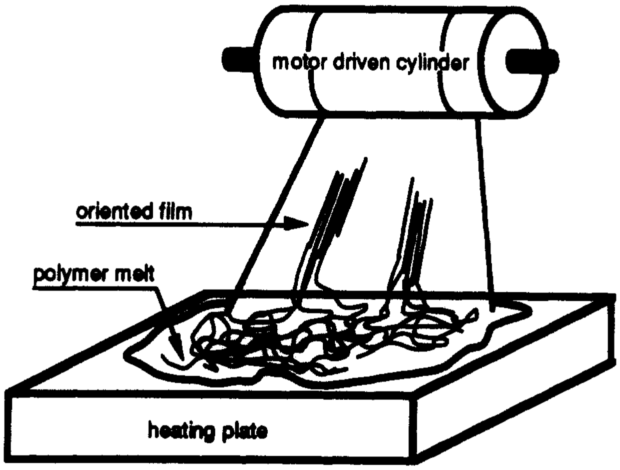

Figure 1. Schematic sketch showing the preparation technique of the ultrathin polymer substrates.

Here we present SFM images of PB-1 needle crystal surfaces showing periodic substructures on a molecular scale and tin-evaporated PB-1 substrate surfaces showing the morphology of epitaxially-grown tin crystallites[3] using the SFM tapping mode. Tapping mode or attractive modes of the SFM appear to result in a lower interaction between the SFM tip and the surface and so offer a more effective way to investigate surfaces of weakly adhering systems.

2. Experimental Methods

The oriented semicrystalline polymer substrates were prepared according to the method of Petermann and Gohil:[12] the polymer granulate was dissolved in xylene (0.4% w/w), and some droplets of this solution were then deposited on the smooth surface of a glass slide where the solution itself dispersed uniformly. On heating the sample to a temperature of about 420 K, the solvent evaporated. From the resulting melt a highly-oriented, ultrathin film (thickness ≈ 0.1 μm) was drawn by a motor-driven cylinder ($v_x \approx 7$ cm/s) (Figure 1). In general, the morphology and the size of crystalline areas depend on the different types of polymers used as well as on the processing technique.[13]

The PB-1 film was deposited onto highly oriented pyrolytic graphite (HOPG) and mica, for STM and SFM investigations. Tin was evaporated on to the ultrathin polymer films in a Balzers BAE 080 evaporation chamber at a pressure of $\sim 5 \times 10^{-5}$ Pa.

---

* To whom correspondence should be addressed.

† University of Bristol.

‡ Universität Dortmund.

⊗ Abstract published in *Advance ACS Abstracts*, October 15, 1993.

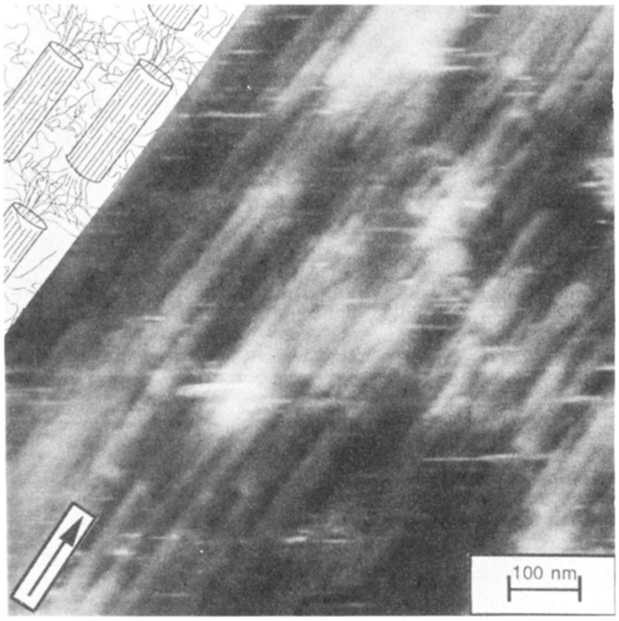

Figure 2. SFM image of a PB-1 substrate surface. The surface of the PB-1 substrate shows close-packed needle crystals diagonally crossing the scan area. The arrow in the lower left corner indicates the direction of the molecular orientation (drawing direction of the substrate). A sketch showing the morphology of the semicrystalline polymer substrate is inserted in the upper left corner (sketch not to scale). Note that the needle crystals protrude a few nanometers out of the substrate surface. The needle crystals are bundled together in groups of a lateral dimension of 60–80 nm. As a result of the scanning process almost all tin crystallites (bright spots) were swept away from the image area.

Deposition was made onto substrates at a temperature of 293 K. Metallic films were deposited to a thickness between 0.5 and 5 nm at a deposition rate between 0.01 and 0.5 nm/s, monitored with a quartz crystal oscillating microbalance.

A Nanoscope III SFM[14] was used for the investigations. Experiments using the repulsive force mode of operation, where the cantilever tip is in permanent contact with the sample surface, were carried out in air and under propanol (spectrophotometric grade). Propanol was chosen to minimize the capillary forces between the cantilever tip and the surface[15] and also because it would not cause the polymer to swell or soften. The cantilevers used were as supplied by the microscope manufacturer and had a nominal force constant of 0.06 N m^{-1}.

The tapping mode, or high-amplitude resonance mode, was used to further reduce the force between tip and sample. Measurements with the tapping mode were made in air using single-member cantilevers of a nominal force constant of 40 N m^{-1} with integral high aspect-ratio tips. In this mode the cantilever is oscillated in a vertical plane at its resonant frequency, typically 300–400 kHz. Intermittent contact, or tapping, of the surface occurs at the lowest point of the cantilever oscillation, which leads to a reduction of the free-space resonance amplitude. It is this reduction in oscillation amplitude that is used as the feedback control signal as the sample topography varies under the cantilever tip. Surfaces of constant reduction of oscillation amplitude are thus obtained, analogous to the constant cantilever deflection (constant force) signal commonly used in the repulsive mode of operation. Tip–sample forces are on the order of 10^{-10} N (manufacturer's estimate), but more significantly the tapping motion may reduce the sideways dragging effect of contact mode SFM. Data were also collected in the tapping mode by using the error signal, i.e., switching off the feedback control on oscillation amplitude and monitoring the variation in amplitude as the tip–sample distance was maintained at a constant value. Simultaneous collection of tapping mode, constant force, and constant height data was performed. The cantilever first traces the topography under feedback control. The cantilever is then scanned at a local fixed height above the sample, and the deflection data are recorded on the retrace scan, using the Nanoscope III "lift" software.

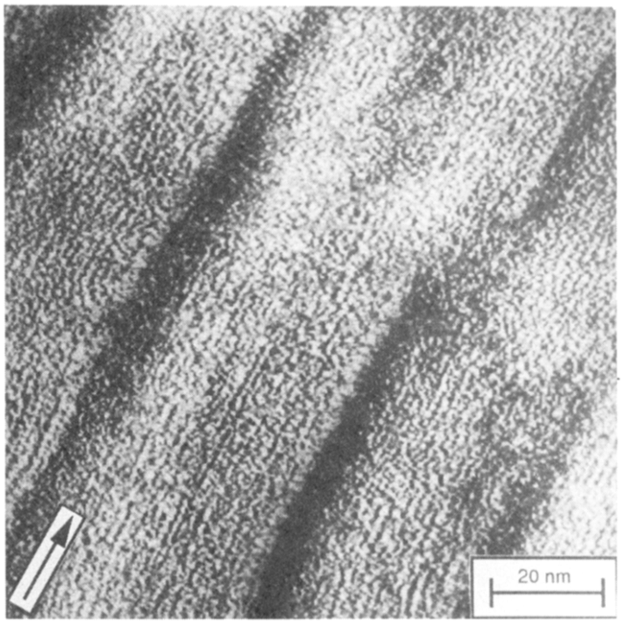

Figure 3. SFM image of a PB-1 substrate surface at higher magnification compared to Figure 2. The image shows four needle crystals arranged parallel to each other diagonally crossing the scan area. The arrow in the lower left corner indicates the direction of the molecular orientation. Note the fine structure of lines arranged parallel to the long axes of the needle crystals.

3. Results and Discussion

Earlier transmission electron microscopic investigations have shown the PB-1 polymer substrate surfaces produced by this technique exhibit a semicrystalline morphology.[3] The crystalline areas of PB-1 substrates are built up of needlelike crystals aligned parallel to the drawing direction of the polymer film. Their lengths range from a few nanometers to some micrometers, while their diameter is found to be 20–35 nm. The polymer surface planes of all considered polymer substrates are $\{hk0\}$ planes having only the [001] direction, the direction of the molecular orientation, in common. This is well-known as fiber texture.

Initially, tin-evaporated PB-1 substrates were investigated using the repulsive mode of the SFM with a force ≤ 2 nN. A typical scanning force microscope image of tin-evaporated PB-1 substrate surfaces in the repulsive mode is shown in Figure 2. This image is typical of those obtained immediately after the first contact of the cantilever onto the polymer surface. The imaging force was adjusted to just above the pull-off point of the cantilever as soon as possible after the first contact in order to reduce the applied force to the minimum possible for stable imaging. From time to time it was checked that the set point is stable and still at the same location of the force curve. The surface of the PB-1 substrate exhibits a regular arrangement similar to close-packed longitudinal needle crystals diagonally crossing the image. All crystals are oriented approximately parallel to the drawing direction. Their length and their average diameter of 20–35 nm agree well with what is known from TEM dark-field investigations of needle crystals. In some cases, the needle crystals are bundled together in groups of a lateral dimension of 60–80 nm. Additionally, the needle crystallike structures protrude out of the surface. The height from the region

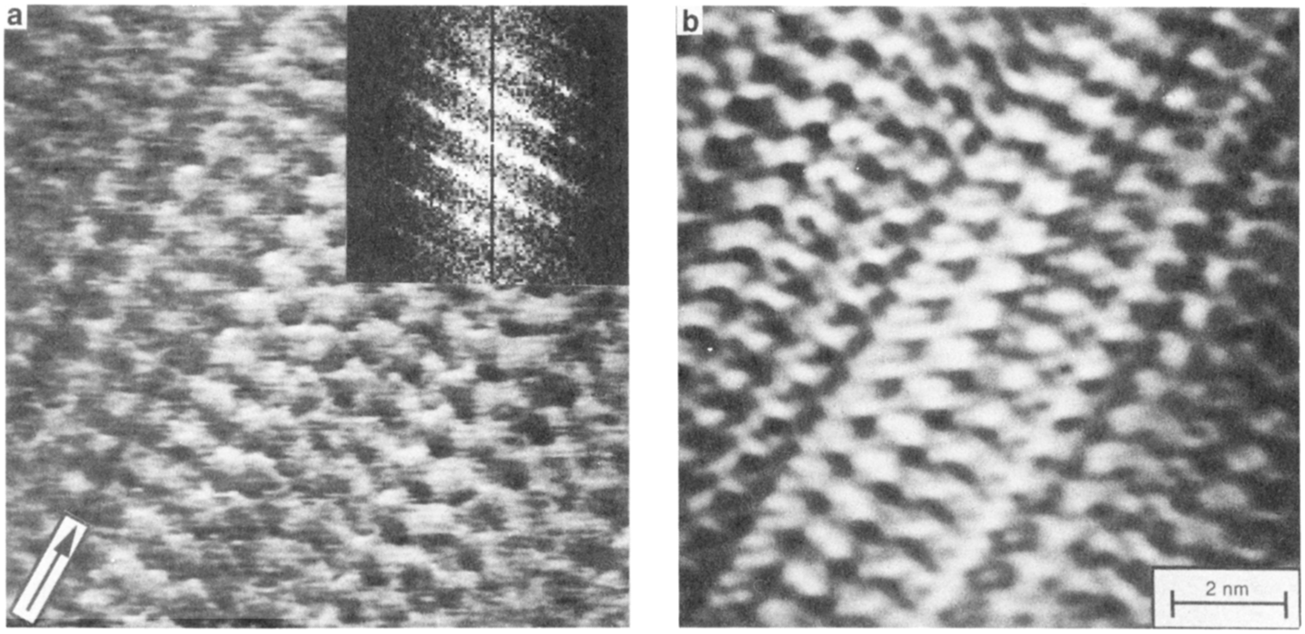

Figure 4. SFM image of a PB-1 substrate surface at higher magnification compared to Figure 3. Part a shows the original image as taken, with a Fourier transform inset; part b shows the Fourier filtered image. The image shows individual PB-1 macromolecules (helices). Along the chain directions of the macromolecules a repeat (pitch height) of 0.7 ± 0.1 nm was obtained. The arrow in the lower left corner indicates the direction of the molecular orientation.

between the crystals to the top of the crystals was measured to be 0.5–4 nm (local values).

Surprisingly, it was possible to obtain SFM images of the tin-free PB-1 surfaces in spite of the tin deposition. It was seen that the tin crystallites were removed from the image areas to their border as a result of the sweeping action of the SFM tip. Frictional and/or capillary forces may be responsible for this tin removal process. Nevertheless a few tin crystallites are discernible as bright spots and clusters on the surface. Further scanning of the PB-1 surface removed all of the tin crystallites. Imaging at higher forces up to 100 nN showed the similar "sweep away" effet for the tin crystallites and showed also the needle crystalline morphology of the PB-1 surface.

Imaging at higher magnification after a period of several minutes revealed structures as seen in Figure 3. The image shows four needle crystals arranged parallel to each other. In the upper part of the middle needle crystal a crystalline branching is visible. The surfaces of the needle crystals exhibit a fine structure of lines arranged parallel to the long axes of the needle crystals and the drawing direction.

When increasing the magnification further to a molecular scale, images like Figure 4 were obtained. The images show structures similar to PB-1 macromolecules (helices) with a repeat (pitch height) of 0.7 ± 0.1 nm along the molecular backbone. This value may be compared with the bulk value from X-ray diffraction data of 0.65 nm.[16] Structures shown in Figure 4 were reproducible independent of scanning frequency, scanning direction, and x–y range.

Although the determination of the pitch height (intramolecular distance) from images like Figure 4 is straightforward, it is more difficult to obtain values for the intermolecular distances in planes parallel to the surface, due to the complex and detailed surface structure. It is assumed that linear uninterrupted structures oriented parallel to the drawing direction in Figure 4 are the backbones of PB-1 macromolecules. The structures between these backbones may originate from interlocking ethyl side groups of the PB-1 macromolecules. A typical value obtained for the intermolecular distance in planes parallel to the surface is 1.2 ± 0.3 nm. This value may be compared with the intermolecular distance in the bulk of a PB-1-crystal: e.g., in the $\{100\}_{\text{PB-1}}$ planes the PB-1 helices are arranged in alternating distances of 0.59 and 1.18 nm.[16] The difference in the observed intermolecular packing with the SFM compared to the bulk value may result from different molecular packing at surfaces and in bulk. Although images like Figure 4 resolve clearly molecular details of the PB-1 surface, it should be mentioned here that such images were obtained from tin-evaporated samples. The interfacial interaction between the tin and the PB-1 may have an influence on the arrangements of the outermost PB-1 layer, e.g., leading to an organometallic surface layer. It is more likely that different surface effects

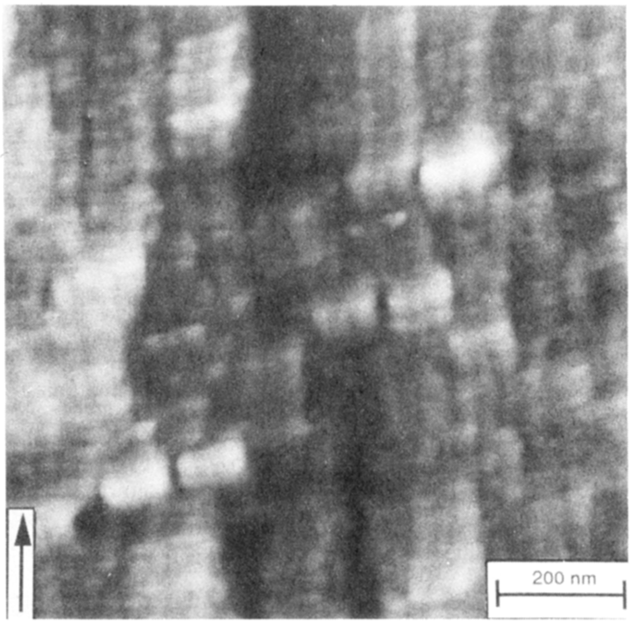

Figure 5. SFM image of a PB-1 substrate surface coated with tin crystallites. The data were collected using the SFM tapping mode. Tin crystallites of 20 nm (smallest size) decorate the needle crystals. The drawing direction is indicated by the arrow in the lower left corner.

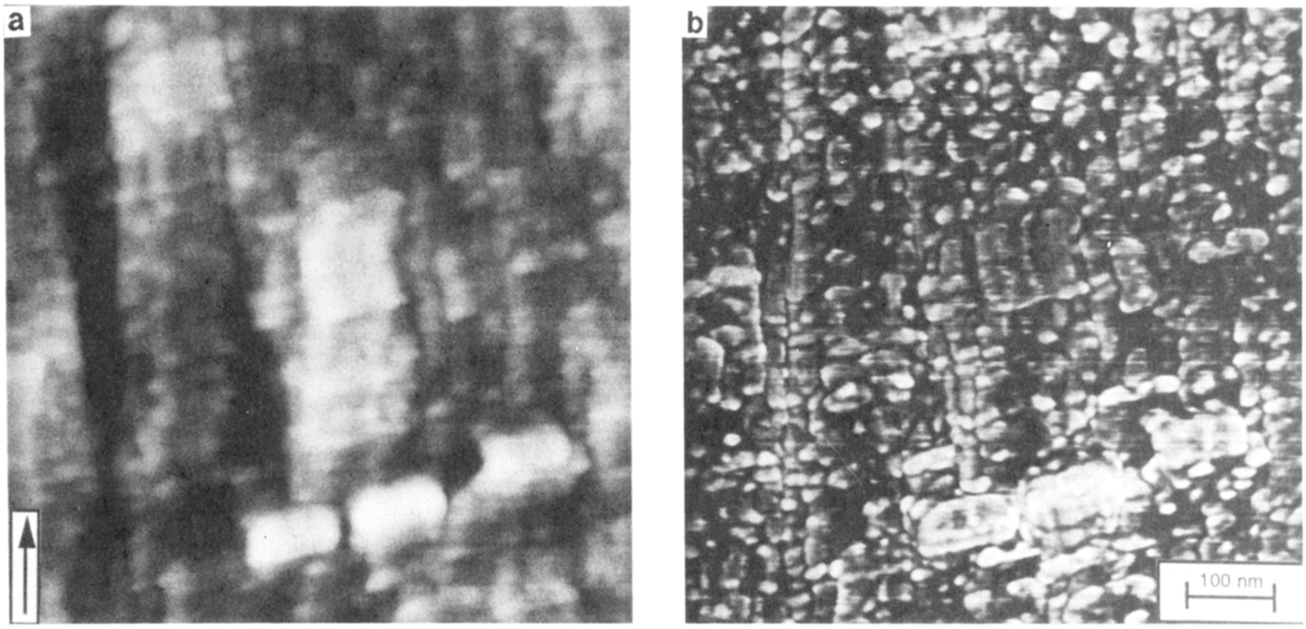

Figure 6. Complementary constant force (a) and deflection (b) images collected from the tapping mode of a different area. The retrace scan was performed at a local fixed height of 3.5 nm above the trace scan. The drawing direction is indicated by the arrow in the lower left corner. The vertically elongated structures in Figure 6b originate from the metal decoration of the underlying elongated polymer needle crystals. This phenomenon is also known from earlier TEM investigations.[3]

like reconstruction and/or relaxation effects may lead to the observed different arrangements of the macromolecules at surfaces compared with bulk arrangements.

Recent scanning tunneling microscopy (STM) investigations of PB-1 thin films fixed on HOPG revealed a drastic change of the molecular arrangement (decrease of molecular pitch height and intermolecular distance).[3,8,11] It was supposed that the helical structure of the PB-1 molecules and the ethyl side groups enables a strong interaction with the graphite, leading to the modification of the molecular arrangement. Furthermore, it is known from Fourier transformation infrared spectrometry (FTIR) measurements[17] that macromolecules are able to turn their side groups toward and/or away from the outermost surface, leading to variation in the pitch and in the close-packing arrangement of the molecules.

Nevertheless, the knowledge of the arrangement of macromolecules at surfaces is sparse. Local probe microscopic methods like STM and SFM in combination with spectrometric methods and molecular modeling methods may lead to a better understanding of these effects.

The removal of tin particles from the PB-1 surface demonstrated in Figure 2 was overcome by using the tapping mode of the SFM operation. Figure 5 shows a 1.07-μm scan of tin particles decorating the PB-1 surface. The smallest size of tin particle that can be observed is about 20 nm, and they are roughly elliptical or spherical in shape. This is in good agreement with recent TEM results.[3]

In many areas of the image it can be seen that the tin particles decorate the needle crystals in vertical rows, parallel to the drawing direction and hence the needle crystal orientation. From TEM investigations it is known that tin evaporated on PB-1 under the conditions used here grows epitaxially with respect to the semicrystalline PB-1 substrate. In certain regions of the image, e.g., the top right quadrant, larger particles of 4–5 times the width of the smaller tin particles "bridge" the structure. These are most likely aggregates of tin particles and may be localized at needle crystal junctions, but this has not yet been determined conclusively. Narrow zones of low relief (dark areas) running down the center of the image may also reflect the underlying polymer surface morphology.

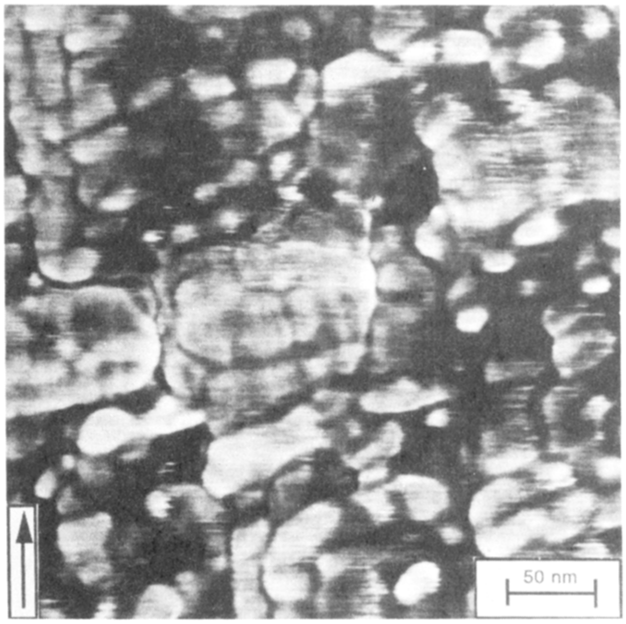

Figure 7. High-resolution scan of part of Figure 6. The data have been collected in the tapping mode as for Figure 6b. The drawing direction is indicated by the arrow in the lower left corner.

Simultaneous collection of constant oscillation amplitude (constant tapping force) and the deflection signal from the same area of the sample is shown in Figure 6. Resolution of the overall surface topography in Figure 6a is enhanced when compared with the corresponding area of the deflection signal image (Figure 6b). However, the edges of structures and particularly the tin particles are much more clearly resolved. A higher resolution scan of part of Figure 6 is shown in Figure 7. Individual tin particles and "bridging" particles are very clearly resolved. The use of the tapping mode is clearly important in not disturbing the tin particle deposition, while the deflection signal information is of great use in defining edge structures.

4. Conclusions

1. SFM investigations of tin-evaporated poly(butene-1) thin film surfaces revealed the close-packed needle crystal morphology of this substrate. It has been shown that the needle crystals protrude out of the surface for 0.5-4 nm.

2. Needle crystalline branching and linear substructures of the needle crystals could be obtained. Higher magnifications of these substructures show PB-1 macromolecules with a repeat along the axes of the PB-1 helix of 0.7 ± 0.1 nm. This value agrees with data obtained from an X-ray diffraction of 0.65 nm.

3. Attempts to image the tin deposition on the PB-1 substrate surface using the SFM repulsive mode were hampered as the scanning motion of the probe swept away most of the metal particles. Operation of the SFM in the tapping mode prevented this and allowed the overgrowth of tin on PB-1 films to be observed.

Acknowledgment. K.D.J. and J.P. gratefully acknowledge the financial support of the Volkswagen Stiftung and the Deutscher Akademischer Austauschdienst (DAAD). T.J.M. and M.J.M. gratefully acknowledge the financial support of the British Council and the AFRC. J.P. acknowledges the financial support of the Fonds der chemischen Industrie (FCI).

References and Notes

(1) Petermann, J.; Broza, G. *J. Mater. Sci.* **1987**, *22*, 1108.

(2) Geis, M. W.; Flanders, D. C.; Smith, H. I. *Appl. Phys. Lett.* **1979**, *35*, 71.

(3) Jandt, K. D. In *Untersuchungen zur Polymer–Metall–Epitaxie in Computersimulation und Experiment*; Fortschr.-Ber. VDI Reihe 5 Nr. 302; VDI-Verlag: Düsseldorf, Germany, 1993.

(4) Binnig, G.; Rohrer, H. *Helv. Phys. Acta* **1982**, *55*, 930.

(5) Binnig, G.; Quate, C. F.; Gerber, C. H. *Phys. Rev. Lett.* **1986**, *56*, 930.

(6) Eng, L. M.; Jandt, K. D.; Fuchs, H.; Petermann, J. *Helv. Phys. Acta* **1992**, *65*, 870.

(7) Eng, L. M.; Fuchs, H.; Jandt, K. D. Petermann, J. In *Scanned Probe Microscopy*; AIP Conference Proceedings Series 241; H. Kumar Wickramasinghe: Santa Barbara, CA, April 1991; p 262.

(8) Eng, L. M.; Fuchs, H.; Jandt, K. D.; Petermann, J. *Ultramicroscopy* **1992**, *42–44*, 989.

(9) Jandt, K. D.; Eng, L. M.; Petermann, J.; Fuchs, H. *Polymer* **1992**, *24*, 5331.

(10) Jandt, K. D.; Buhk, M.; Petermann, J.; Eng, L. M.; Fuchs, H. *Polym. Bull.* **1991**, *27*, 101.

(11) Fuchs, H.; Eng, L. M.; Sander, R.; Petermann, J.; Jandt, K. D.; Hoffmann, T. *Polym. Bull.* **1991**, *26*, 95.

(12) Petermann, J.; Gohil, R. M. *J. Mater. Sci.* **1979**, *14*, 2260.

(13) Wunderlich, B. In *Macromolecular Physics, Vol. 1: Crystal Structure, Morphology, Defects*; Academic Press: New York, London, Toronto, Sydney, San Francisco, 1973.

(14) Digital Instruments, Santa Barbara, CA.

(15) Hansma, H. G.; Vesenka, T.; Siegenst, C.; Keldermann, G.; Momett, H.; Sinsheimer, R. L.; Elings, V.; Bustamante, C.; Hansma, P. K. *Science* **1992**, *256*, 1180.

(16) Natta, G.; Corradini, P.; Bassi, I. W. *Nuovo Cimento* **1960**, *Suppl. 15*, 52.

(17) Elias, H.-G. In *Makromoleküle, Band, 1, Grundlagen*; Hüthig & Wepf Verlag: Basel, Heidelberg, New York, 1990; part 5.