

# Investigation of Surface Morphology of Emeraldine Hydrochloride by Scanning Tunneling Microscopy

J. G. MANTOVANI,\* *Department of Physics, University of Tennessee, Knoxville, Tennessee 37996, and Health and Safety Research Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831*, R. J. WARMACK,\* *Health and Safety Research Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831*, B. K. ANNIS,<sup>†</sup> *Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6197*, and A. G. MACDIARMID and E. SCHERR,<sup>‡</sup> *Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104*

## Synopsis

An STM investigation of the surfaces of emeraldine hydrochloride films indicates that the surfaces are characterized by features that are generally fiberlike in appearance. The widths of these structures ranged from 10 to 140 nm, and the apparent heights varied from 0.5 to 70 nm. Fiber lengths of up to 1  $\mu\text{m}$  were observed. In some regions, the fibers appeared to be highly interconnected in a random fashion while in others there was nearly parallel alignment.

## INTRODUCTION

The connection between the macroscopic properties of a material and the arrangement of the constituents at the atomic or molecular level is often obscured by intermediate structural characteristics on the scale of a micron or less. Conducting polymers are a case in point. Although ideal conduction mechanisms for infinitely long 1-dimensional chains are becoming reasonably well understood, the relation to the behavior of a real material composed of finite chains with a variety of configurations is often less apparent. For example, recent investigations of electrical transport processes<sup>1</sup> in emeraldine hydrochloride in the form of films cast originally from aqueous acetic acid solutions imply that there are domains of high conductivity with dimensions of a few tens of nanometers which are separated by considerably smaller insulating regions. Films cast from NMP (*n*-methyl-2-pyrrolidone) solutions exhibit

\* Funding was provided by the ORNL Laboratory Director's R&D Fund and by the Office of Health and Environmental Research, U.S. Department of Energy under Contract DE-AC05-84OR21400 with the Martin Marietta Energy Systems, Inc.

<sup>†</sup> Research sponsored by the Division of Materials Sciences/Office of Basic Energy Sciences, U.S. Department of Energy, under Contract DE-AC05-84OR21400 with the Martin Marietta Energy Systems, Inc.

<sup>‡</sup> Research sponsored by the Defense Advanced Research Projects Agency through a grant monitored by the U.S. Office on Naval Research.

similar conductivities ( $\sim 5 (\Omega \text{ cm})^{-1}$ ) to the above films<sup>2</sup> and to compressed pellets of emeraldine hydrochloride powder.<sup>3</sup>

Scanning electron micrographs<sup>4</sup> of electrochemically polymerized polyanilines have not been particularly helpful in obtaining additional information concerning these domains. Since, to the best of our knowledge, the recently developed tunneling microscope has not been used for studying polyaniline, we have undertaken an investigation of the emeraldine hydrochloride form of this polymer. The samples were prepared by protonating films of emeraldine base, which had been cast from NMP solutions, with aqueous hydrochloric acid.

## EXPERIMENTAL

Films of emeraldine base in NMP were cast on microscope slides as previously described.<sup>2</sup> Solvent was removed in air at  $\sim 70^\circ\text{C}$  during  $\sim 15$  h. After washing with deionized water, the slide with the emeraldine base film still attached was placed in 1 *M* aqueous HCl for  $\sim 15$  h to convert it to the "doped" conducting emeraldine hydrochloride. The resulting film was sandwiched between two pieces of weighing paper and placed in a vacuum desiccator with a glass slide on top to prevent buckling of the film while drying. The desiccator was then evacuated over a period of several hours.

It should be noted that previous experience has shown that the side of the film adjacent to the glass slide during the HCl treatment is frequently less highly protonated than the reverse side.

In order to explore the possibility that the surface morphology observed for these films might have been related to an interaction with the paper used in the drying process, an additional sample was prepared in a different manner. For this case, the emeraldine base was again cast from an NMP solution, but the doping was done using gaseous HCl. The film remained attached to the original substrate and the exposed surface was not contacted by any materials prior to the STM investigation.

## INSTRUMENTATION

Two instruments were used in this work. One was an air-based STM that was constructed at Oak Ridge National Laboratory and which used a cylindrical type of piezoelectric scanner.<sup>5</sup> The second was a NanoScope I (Digital Instruments, Santa Barbara, CA) which also operated in air and was used to collect the majority of the data shown here. The scanning range of both instruments was restricted to about 1  $\mu\text{m}$ , and, in order to investigate different regions of the surface, it was necessary to reposition the samples manually. As a result, it was not possible to follow the full extent of some of the features noted.

Each of the instruments imaged the surface topography in the constant current mode, i.e., the tip position perpendicular to the surface was continually monitored and adjusted by the use of a negative feedback circuit which maintained a constant tunneling current. All the images were taken in air and were obtained with mechanically sharpened platinum-iridium tips. Reproducible images were obtained with tip-sample bias voltages in the range from  $-10$  to  $+10$  V DC. Most of the work was done with a sample bias of  $+0.3$  V (tunneling

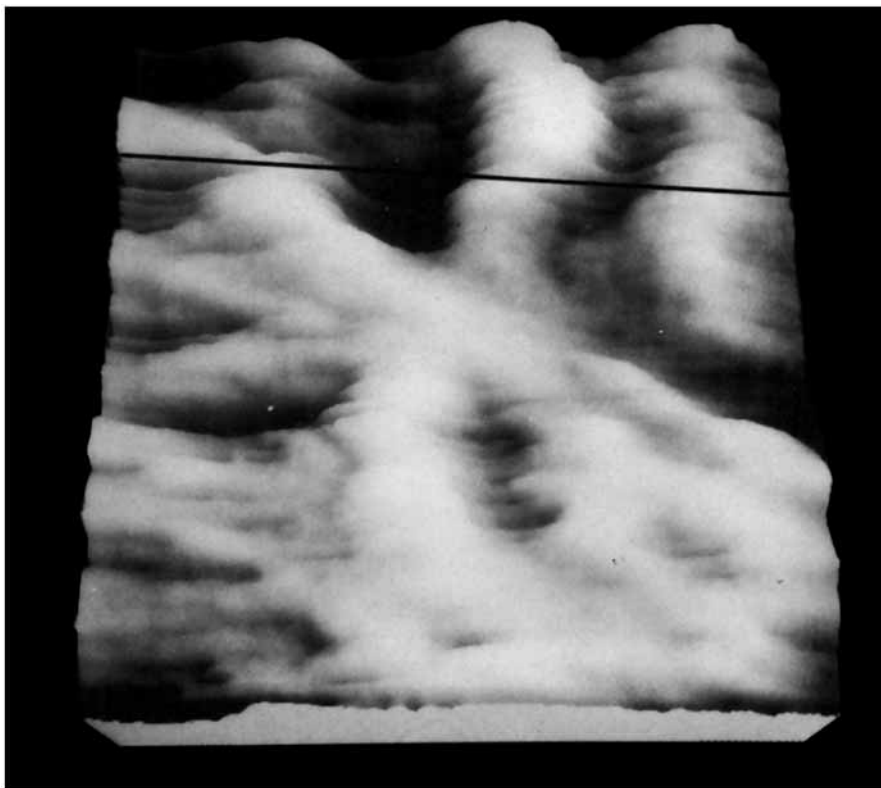


Fig. 1. Area shown is  $500 \times 500$  nm;  $100 \times 100$  point scan. Sample bias, +0.1 V; current, 3 nA.

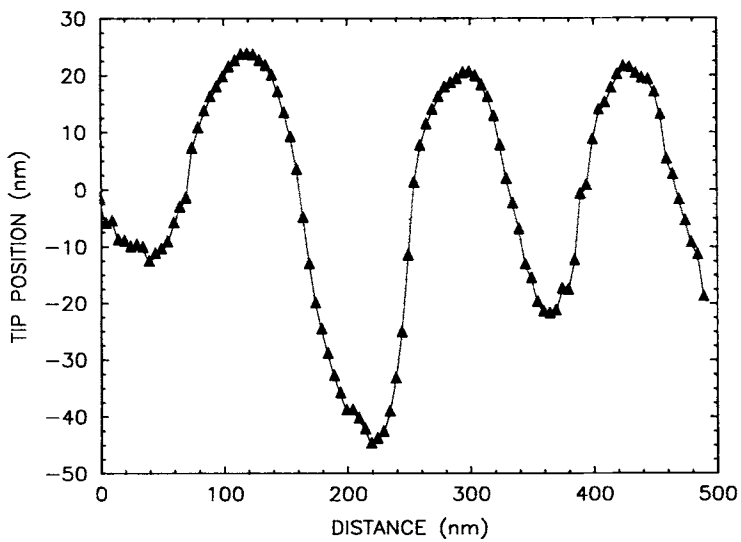


Fig. 2. Profile at position shown by line in Figure 1.

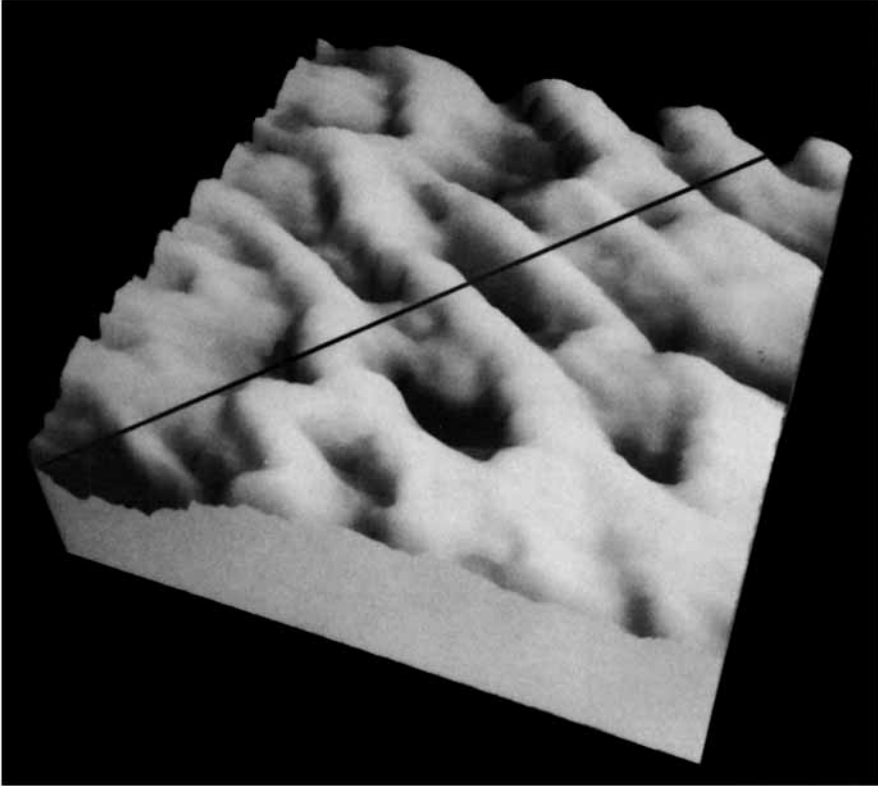


Fig. 3. Area shown is  $1000 \times 1000$  nm;  $100 \times 100$  point scan. Sample bias, +0.1 V; current, 3 nA. Image has been tilted and rotated.

to the sample) and a tunneling current of 1 nA. Both instruments were operated in conjunction with a PC which allowed point by point rather than continuous scanning. Typically the scans involved a  $100 \times 100$  or  $180 \times 180$  point matrix in the plane of the surface. Information concerning the tip position perpendicular to the surface was acquired with an analog to digital converter.

All the images shown in the figures were processed on an IRIS-3020 graphics work station (Silicon Graphics, Mountain View, CA) and were obtained by photographing the video screen. The images were obtained by a combination of height shading and artificial side illumination. In some figures, the images are shown tilted and rotated.

Application of an STM requires a rigid sample surface, and it was necessary to attach the films to a stainless steel substrate with a conducting silver paint (Model No. 14810, E. Fullam, Co., Lathan, NY). Consequently, it was not possible to study exactly equivalent regions on opposite sides of the films. As mentioned earlier, a sample was prepared and left attached to the microscope slide; in this case the sample was examined *in situ*, and silver paint was not used. In principle, it should be possible to shear a film and mount it in such a manner that an edge could be scanned; however, because these samples were only about  $20 \mu\text{m}$  thick, some modifications would be necessary so this procedure was not attempted for the present study.

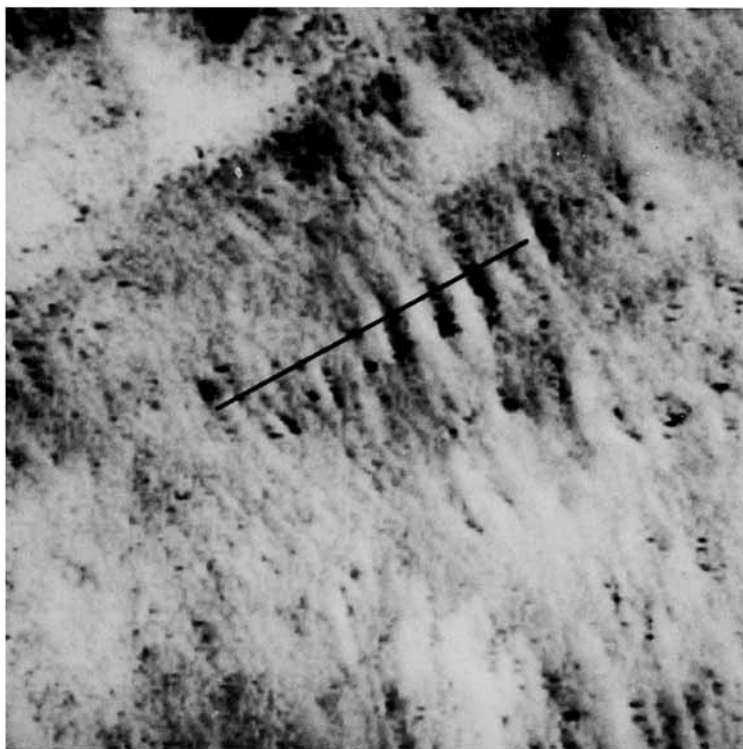


Fig. 4. Area shown is  $1000 \times 1000$  nm;  $180 \times 180$  point scan. Sample bias, +0.3 V; current, 1 nA.

## DISCUSSION

Figures 1 and 3 show the results obtained from different regions on one of the samples with the instrument constructed at ORNL. This particular sample exhibited the largest and most complex features that we observed. Scanning tunneling microscopy provides a measure of the variation in height perpendicular to the surface under investigation, and a profile at the location of the line drawn in Figure 1 is shown in Figure 2. A similar profile at the position shown in Figure 3 was also obtained, and the combination of profiles and images indicate fiberlike structures with widths in the range 100–150 nm and thicknesses of 40–~90 nm. These thicknesses represent minimum values since tunneling from the microscope tip may not be able to accurately track the narrowest regions at the bottoms of the valleys due to the width of the tip. A profile roughly tracing the top of the vertically oriented fiber in Figure 1 indicated a change in height of 40 nm between the point of intersection near the center and the top edge of the image.

An artifact of the scanning and imaging technique may be apparent to the reader in Figure 1. For example, at the left hand end of the line in Figure 1, a small valley centered about 40 nm below the line appears to be intersected by a series of ridges which roughly parallel the line. These should not be construed as a structural feature but are rather due to the relatively coarse scanning steps

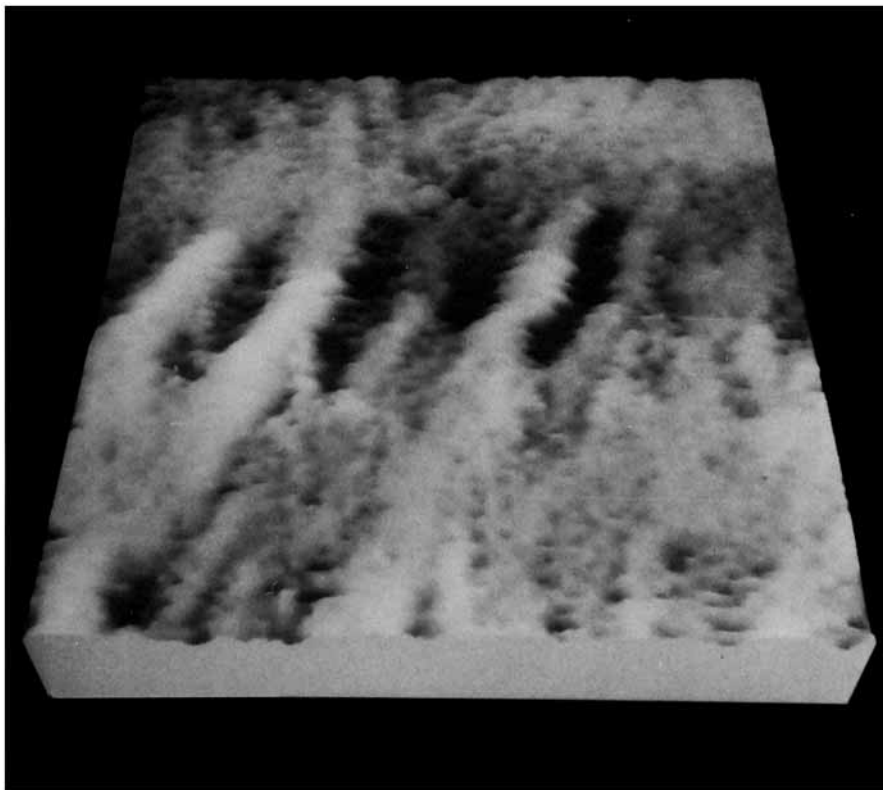


Fig. 5. Area shown is located near the end of the line shown in Figure 4. Area is  $400 \times 400$  nm;  $100 \times 100$  point scan. Actual scan was rotated  $40^\circ$  with respect to that in Figure 4. Sample bias,  $+0.3$  V; current, 1 nA.

used in this case. An interesting aspect of this particular film is that the tunneling process could not be initiated on the reverse side of an adjacent portion of the sample. This may be caused by a smaller level of protonation on this side of the film resulting in lower conductivity as noted previously.

Figures 4, 5, and 6 show a series of images obtained from a second sample with the NanoScope I. In this instance, the sample side was noted and corresponded to the "top" side, this being the side exposed to the air during the removal of the NMP during the casting of the emeraldine base film. The "bottom" side of the film was that in contact with the glass side.

Profiles obtained at the positions indicated by the lines drawn in the figures established that the fibers are smaller (10–60 nm). The images indicate some tendency to parallel alignment. The degree of connectivity is much less, although some examples of branching are apparent. A number of small, roughly horizontal appurtenances to the fibers are also visible. As mentioned in the preceding, these features are likely to be artifacts of the scanning process. However, when a second scan was done at  $90^\circ$  to the first, the principal features remained unchanged. An example of another region on the "top" side of the surface is shown in Figure 7. In this case, one of the fibers appears to split apart and then recombine.

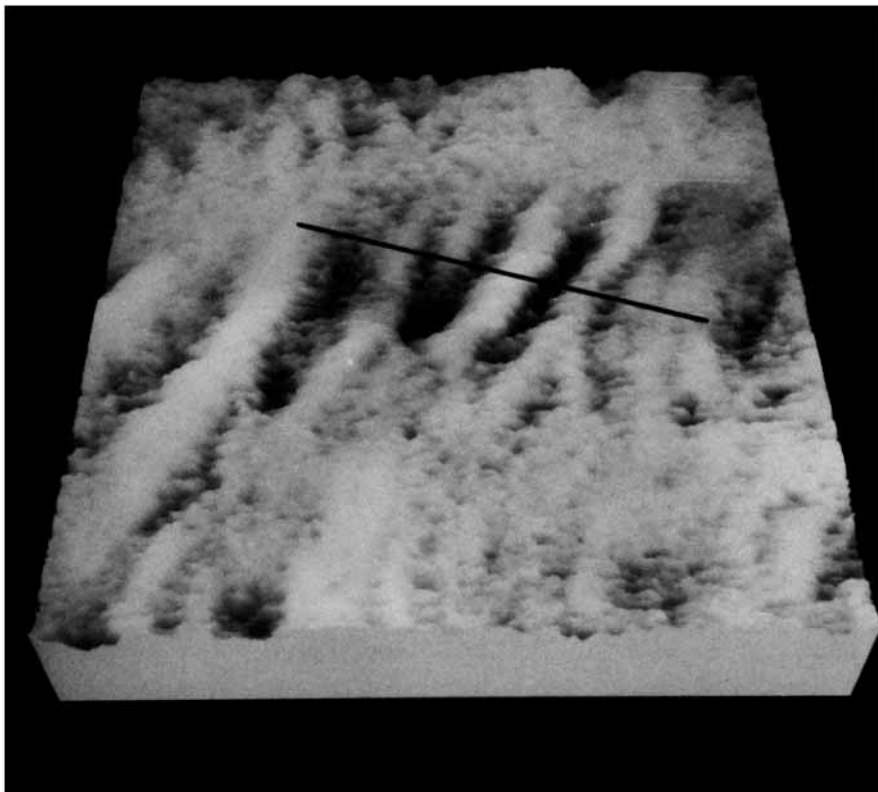


Fig. 6. Area shown is same region as Figure 5 and is  $400 \times 400$  nm;  $180 \times 180$  point scan. Sample bias, +0.3 V; current, 1 nA.

Images obtained from the "bottom" side of an adjacent portion of the film were frequently found to be quite different from those on the "top." Some indication of this is provided by Figure 8. The fiber widths found here were more typically in the 10–20 nm range and a profile at the position of the line drawn in the figure indicated that the heights were only 1–2 nm. Although not present in Figure 8, pits which could be as much as 50 nm in diameter and 10–20 nm deep were also found to be a common feature on this side.

In the case of the sample prepared with gaseous doping, tunneling on the exposed surface was achieved without difficulty and the results were much the same as obtained for the other two samples. Six of the eight areas examined indicated the presence of approximately parallel fibers. The remaining two areas more closely resembled the entangled and interconnected appearance of Figure 3. The fiber widths were in the 10–30 nm range while the peak to valley variations amounted to about 5 nm. These dimensions on the exposed surface are roughly intermediate to those noted previously for the "top" and "bottom."

## CONCLUSION

The surfaces of emeraldine hydrochloride films prepared electrochemically<sup>4</sup> may be fibrillar or relatively featureless depending on experimental conditions,

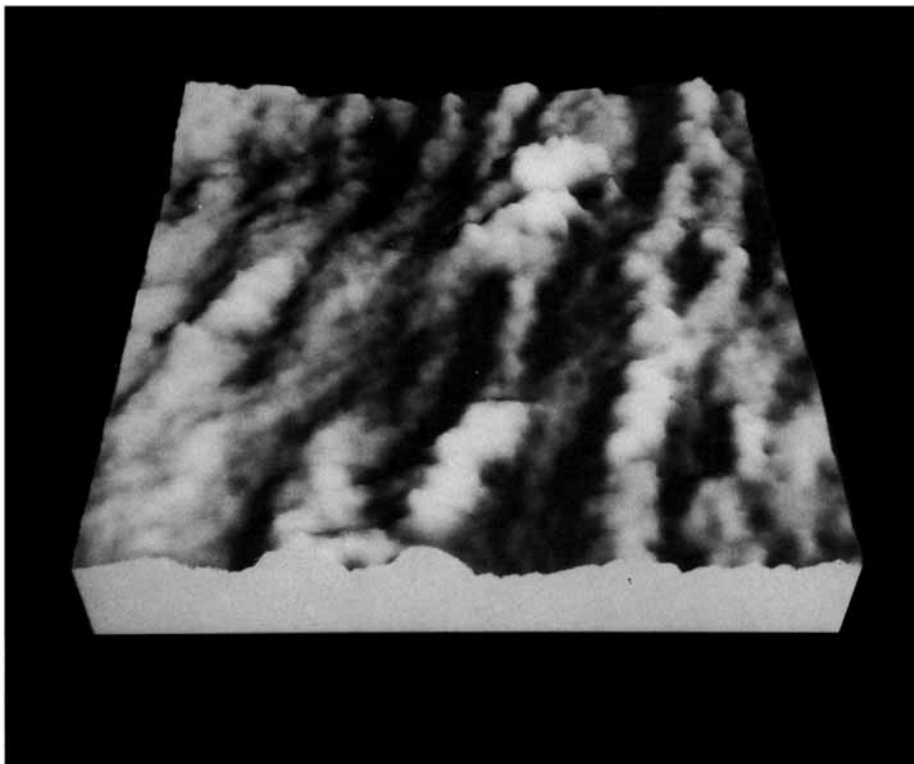


Fig. 7. Area shown is  $200 \times 200$  nm;  $100 \times 100$  point scan. Sample bias, +0.3 V; current, 1 nA.

whereas the solution cast films investigated in this work exhibit a generally fibrillar appearance. No evidence of the nearly spherical particles discussed by Wessling and Volk<sup>6</sup> in connection with another form of polyaniline hydrochloride was found. The structures which we have referred to as fiberlike could in principle be the ends of lamellae extending perpendicularly into the film; however, a parallel investigation of the small angle X-ray scattering (SAXS) from similar films produced the results expected for an amorphous material and give no indication of the lamellae that are readily observable for a material such as polyethylene.

The SAXS work also indicated dense packing, and this suggests that the compact nature of the "bottom" side is more akin to the bulk of the material than are the relatively open networks of Figures 1, 3, and 8.

It is difficult to assess the full potential and/or limitations of the STM as applied to the investigation of conducting polymers on the basis of the present study alone. The highest resolution images shown in the figures correspond to points taken at 2 nm intervals along both the  $x$  and  $y$  direction. Some scans were also made on these samples with 1 nm intervals but did not reveal any additional detail. In the case of the sample doped from the gas phase and left attached to the substrate in the as-cast condition, scans were made with additional intervals of 0.5, 0.25, 0.1, and 0.04 nm. Here also no further insight into the surface details was obtainable. Scanning electron microscopy is gen-



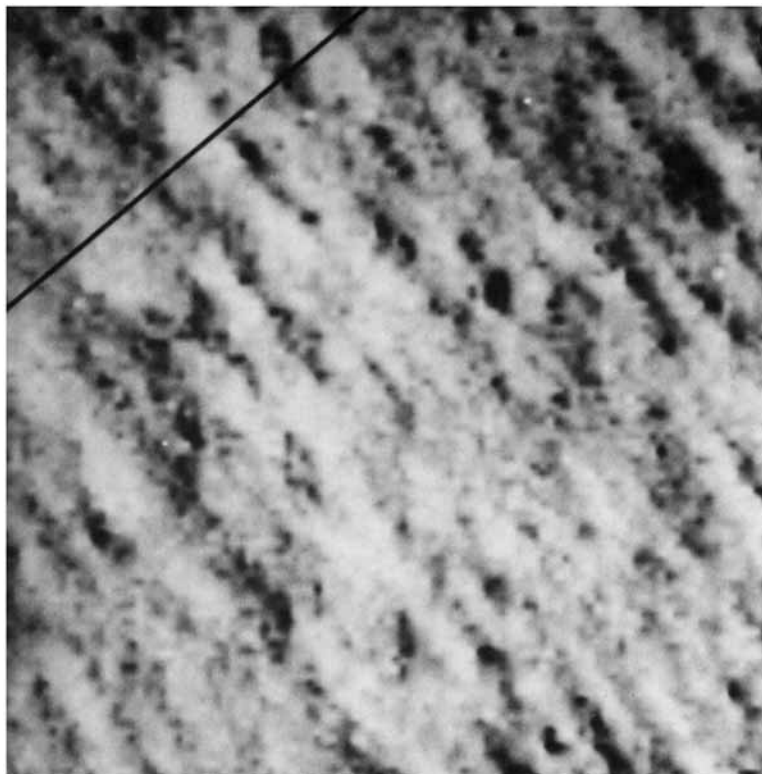


Fig. 8. Area shown is  $200 \times 200$  nm;  $100 \times 100$  point scan. Sample bias, +0.3 V; current, 1 nA.

erally capable of higher resolution in the surface plane than was provided by the STM in this work. However, the SEM does not provide information on the vertical extent of surface features. SEM investigation<sup>7</sup> of portions of the films did not reveal the extensive structure indicated by the STM.

For all the emeraldine hydrochloride samples, it was noted that conductivity fluctuations in the tunneling would occur even when the tip was stationary. Such fluctuations could be due to motions of the surface in response to the tunneling current or from variations in the complex electrical phenomena which govern the tunneling process. In regard to the former, a change in the method of anchoring the film (silver paint vs. as-cast bonding) did not improve the situation. These conductivity fluctuations result in vertical motion of the tip of the order of 1 nm but do not affect the resolution or reproducibility on the size scales shown in the figures. However, these fluctuations do limit resolution, especially on an atomic scale. For example, in the case of graphite surfaces on which atomic resolution was obtained, we observed these fluctuations to give rise to vertical motion of only a few hundredths of a nanometer.

Samples of doped polyacetylene<sup>8</sup> with a conductivity several orders of magnitude greater than that of the polyaniline were also examined in the same fashion with the STM. Here also extensive surface structure was observable, but the ultimate vertical as well as horizontal resolution was not substantially different from that found for the emeraldine hydrochloride.

The authors wish to thank Dr. A. J. Epstein for helpful discussions.

### References

1. F. Zuo, M. Angelopoulos, A. G. MacDiarmid, and A. J. Epstein, *Phys. Rev. B Rapid Commun.*, **36**, 3475 (1987).
2. M. Angelopoulos, G. E. Asturias, S. P. Ermer, A. Ray, E. M. Scherr, A. G. MacDiarmid, M. Akhtar, Z. Kiss, and A. J. Epstein, *Mol. Cryst. Liq. Cryst.*, **160**, 151 (1988).
3. A. G. MacDiarmid, J. C. Chiang, A. F. Richter, N. L. D. Somasiri, and A. J. Epstein, in *Conducting Polymers*, L. Alcácer, Ed., Reidel, Dordrecht, 1987, pp. 105–120.
4. W. S. Huang, B. D. Humphrey, and A. G. MacDiarmid, *J. Chem. Soc. Faraday Trans. 1*, **82**, 2385 (1986); S. A. Chen, and T. S. Lee, *J. Polym. Sci. Polym. Lett. Ed.*, **25**, 455 (1987).
5. G. Binnig and D. P. E. Smith, *Rev. Sci. Instrum.*, **57**, 1688 (1987).
6. B. Wessling and H. Volk, *Synth. Met.*, **18**, 671 (1987).
7. D. C. Joy, private communication.
8. Samples were provided by Dr. N. Theophilou of the Department of Chemistry, University of Pennsylvania.

Received December 19, 1988

Accepted June 21, 1989