Nucleation and Growth of Poly(3-methylthiophene) on Indium–Tin Oxide Glass by Scanning Tunneling Microscopy

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Received August 7, 1992. Revised Manuscript Received November 30, 1992

We report here results of a scanning tunneling microscopy (STM) and photogalvanic study of the nucleation and growth of poly(3-methylthiophene) on indium-tin oxide (ITO) electrodes. ITO itself exhibits an irregular surface structure consisting of grains with dimensions of 0.1-0.3 μm, separated by deep recesses. Polymer growth begins as oligomer islets on top of the grains and proceeds to form a thin film. Several polymeric features, like fibrils and large featureless bundles, can be detected during later stages of polymerization. Finally macroscopic growth centers appear on the surface and their evolution determines the structure of a thick film.

Introduction

The study of the chemistry of surfaces has been revolutionized during the recent years by the introduction of scanning probe techniques, especially scanning tunneling microscopy (STM) and atomic force microscopy (AFM).[1,2] In particular, the surface structures of several conductive polymer films have been investigated by these methods.[3-14] The early stages of the electropolymerization process, i.e., nucleation and later growth of the nuclei, are, however, of greatest importance in determining the structure of the resulting film and the understanding of the factors and mechanisms involved is vital for the production of good quality polymer films. The scanning probe techniques show a great promise in studying the morphology and spatial distribution of the initial growth centers on the electrode surface. The STM studies dealing with conductive polymer nucleation have so far concentrated on polymers deposited on very flat electrode surfaces, especially on highly oriented pyrolytic graphite (HOPG)[6,10,15] or smooth metal electrodes.[16,17] The general picture evolving from these studies shows that the nucleation takes place preferentially at small surface irregularities, such as step defects on HOPG. Polymer is deposited in the form of microislands, which are often semicrystalline and may be interconnected by separate polymer strands. The fibrils comprising the microislands have been shown to possess helical structures in case of polypyrrole and polythiophene.[6] The nuclei then grow three-dimensionally, finally coalescing into a uniform film.

Many of the most common electrodes in electrochemistry have, however, a rather rough surface. These include the polished metal electrodes and especially the SnO_2 or indium–tin oxide (ITO) electrodes. In these cases the inherent complexity of the substrate itself introduces difficulties in the interpretation of the STM images. The ITO electrodes are, however, very important in spectroscopic measurements, and we have been using them in several studies dealing with the properties of thin conductive polymer films.[18-20] We have also demonstrated by in situ optical video microscopy that macroscopic surface irregularities, such as scratches, greatly enhance the nucleation on ITO, and that the macroscopic (diameter >10 μm) nuclei grow hemispherically.[21] To be able to study smaller deposits and, therefore, to get closer in time to the beginning of the polymerization process, we have employed STM to study the deposition of poly(3-methylthiophene) on ITO at very low nominal charge densities. Every sample has also been characterized by an independent in situ technique, i.e., by measuring a photogalvanic spectrum of the species attached to the ITO surface.[22] This is, to our knowledge, a first example of such a dual investigation of conductive polymer samples.

Experimental Section

Polymerization was carried out galvanostatically on bare or chemically modified ITO (Planar International, Espoo, Finland; surface resistance *ca.* 20 Ω/□) in 0.1 M solutions of Bu_4NPF_6 and

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3-methylthiophene (both from Aldrich) in dry acetonitrile (<30 ppm H_2O). The current density of deposition was 1 mA/cm^2 in most cases, but some polymerizations were performed with 10 mA/cm^2 and solutions containing CCl_4 (electron accepter in photogalvanic measurements) in a concentration of 0.1 M. No systematic study of the effects of the polymerization conditions was carried out, but in general the differences do not seem to be large. The polymerization apparatus and the cleaning and modification of the ITO electrodes have been described previously.[20,21] The concentration of oligomers in neat monomer was checked spectrophotometrically and was found to be negligible. A photogalvanic spectrum of each sample was measured right after the polymerization at −0.2 V vs Ag pseudoreference electrode (redox potential of the ferrocene/ferricenium couple was +0.63 V under the same conditions), after which the electrodes were rinsed with acetonitrile and dried in air before STM imaging. All the images therefore represent polymer in the neutral (undoped) state. A 450-W xenon lamp (Oriel XBO/2) and a Jobin-Yvon H20 monochromator were used in photogalvanic measurements. Light to the electrode was modulated at a frequency of 25 Hz by a mechanical chopper (Rofin 7506) and the resulting ac current from the cell was amplified using a lock-in amplifier (Princeton Applied Research 128A).

The STM experiments were performed in air using a commercial instrument (Park Scientific Instruments), which was operated in the constant current mode. The electrochemically etched Pt–Ir tip was biased +0.5 V positive to the sample and most of the images were recorded with a scan rate of 0.3–1 Hz and 1-nA current. Some images of ITO were also recorded by AFM using an instrument from the same manufacturer. With each sample surface scans were taken at least at three different locations. Images reported here have been tilted along the *X* and *Y* axes but otherwise appear as recorded, except the three-dimensional illustrations, which have been modified by combining the original image with the calculated curvature and light shaded images.

Results and Discussion

Because of the inherent complexity of the electrode surface itself, a thorough investigation of ITO was considered necessary. Tin-doped indium oxide films can be prepared by a number of techniques, including sputtering and vapor deposition in different atmospheres, spray pyrolysis etc.[23] Scanning electron microscopy shows an irregular nodular surface structure with an average grain size of 0.1–0.5 μm for different kinds of sputtered ITO films, although the actual crystallite size is much smaller.[24-26] On the other hand, we have found only one paper dealing with STM characterization of ITO.[27] This study demonstrates that the average grain size, as determined by transmission electron microscopy, is approximately two-thirds of that obtained by STM, which was attributed to a constant work function across flat grain boundaries.

According to the information from the manufacturer, the ITO specimens used in this work have been prepared by reactive dc sputtering from an In–Sn target having a tin content of *ca.* 5%. Our STM images (Figure 1) reveal that the appearance of the surface varies somewhat from place to place but a nodular texture with an approximate polycrystalline grain size of 0.1–0.3 μm is usually observed, in accordance with previous reports. Very typical features on ITO are deep valleys between the grains and sharp boundaries dividing the grain in two or three domains (Figure 1b). These structures imply that ITO has a columnar structure perpendicular to the film surface, as previously proposed by Smith et al.[26] AFM measurements confirm the nodular surface structure (Figure 1c), but we could not record similar detailed images of the ITO surface as were easily obtained with STM. The same was true also for the polymerized samples, and therefore, we concentrated on tunneling microscopy in the rest of the work.

The nonideal electrode surface necessitates the use of suitable criteria for differentiating between the substrate and the polymer deposits. Figure 1 gives a starting point for composing such recognition criteria. Firstly, ITO surfaces exhibit very little order at any magnification employed and so a clear orientation in an image should be attributed to polymer. The tentative deposits should not have any features typical of a bare ITO surface, e.g., sharp linear depressions attributable to grain boundaries, but, on the other hand, a fine structure with dimensions in accordance with the known structures of conductive polymers[6] could imply polymeric nature. It should also be noted that polymer deposits often appear very bright on the image, possibly because of large height differences. Finally, the polymer surface sometimes produces noisy images when compared to bare ITO, a fact pointed out by several workers[7,13,15,16] and probably due to the tip being buried in the sample.[13] This can be caused by areas of low conductivity, together with relatively large and abrupt height changes on the surface, and result in multiple tunneling contacts. Our set of criteria bears resemblance to that of Everson et al. for polypyrrole on HOPG.[15] They reported their failure to identify the deposits by tunneling spectroscopy, and also our efforts to apply *I–V* spectroscopic measurements did not produce differences large enough to be relied upon. It should be pointed out that the adoption of the above criteria means that some polymeric features on the surface may have been overlooked; however, the features attributed to polymer were clearly distinguishable from those observed on bare ITO surface.

The initial stages of polymerization on bare ITO are rather irreproducible and the polymer deposits corresponding to the same nominal charge densities differ from polymerization to polymerization. Several different polymeric features can also be found on the same electrode. In spite of this a clear trend in the evolution of features is evident. At very low charge densities ($\simeq$0.1 mC/cm^2 corresponding to ca. 0.5 nmol/cm^2 of monomer, approximately equivalent to a hypothetical monolayer coverage by thiophene) STM images do not reveal any clear surface structures attributable to polymerization products. As the deposition charge density is increased to the range of 0.15–1 mC/cm^2 several features not detected on bare ITO begin to appear. One of them is depicted in Figure 2a, which shows patches having a diameter of ca. 100 Å in the vicinity of a typical ITO grain boundary. These spots are clearly distinguishable from the ITO substrate, which typically exhibits a smooth surface at the same magnification (Figure 2b). The spots in Figure 2a are 10–20 Å high and produce somewhat messy images with no detectable fine structure. Also larger areas superficially resembling virgin ITO but exhibiting a noisy surface texture can be found. On the other hand, we know from the photogalvanic measurements of these samples that short oligomers coexist on the surface with long polymer chains, as shown by a photogalvanic signal below 400 nm

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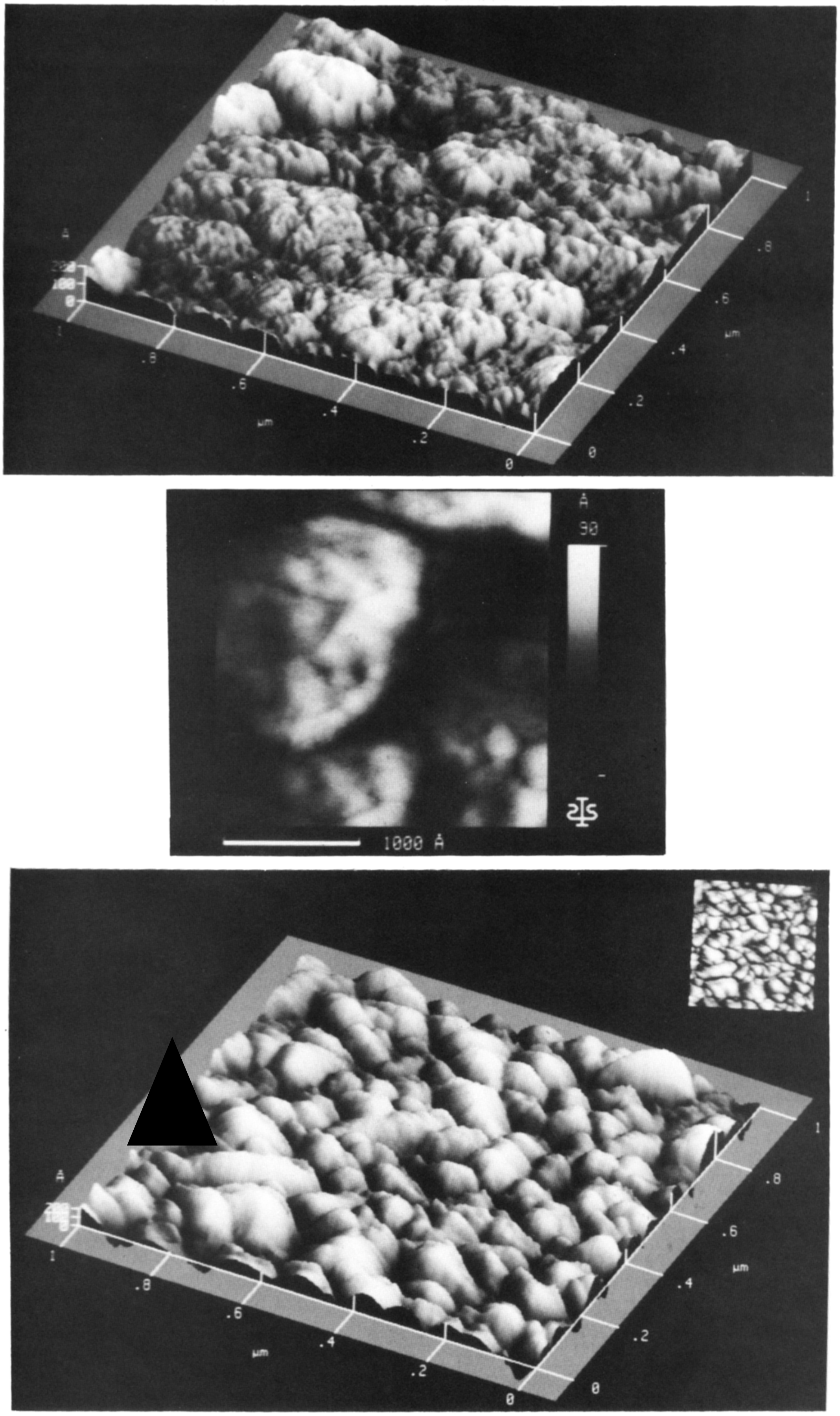

Figure 1. (a, top) STM image of bare ITO surface showing an irregular structure with large polycrystalline grains separated by deep valleys. (b, center) Image taken on top of a grain showing a typical Y-shaped grain boundary, which divides the grain into three domains. Other similar boundaries can be seen close to the lower edge of the image. (c, bottom) AFM image of bare ITO surface.

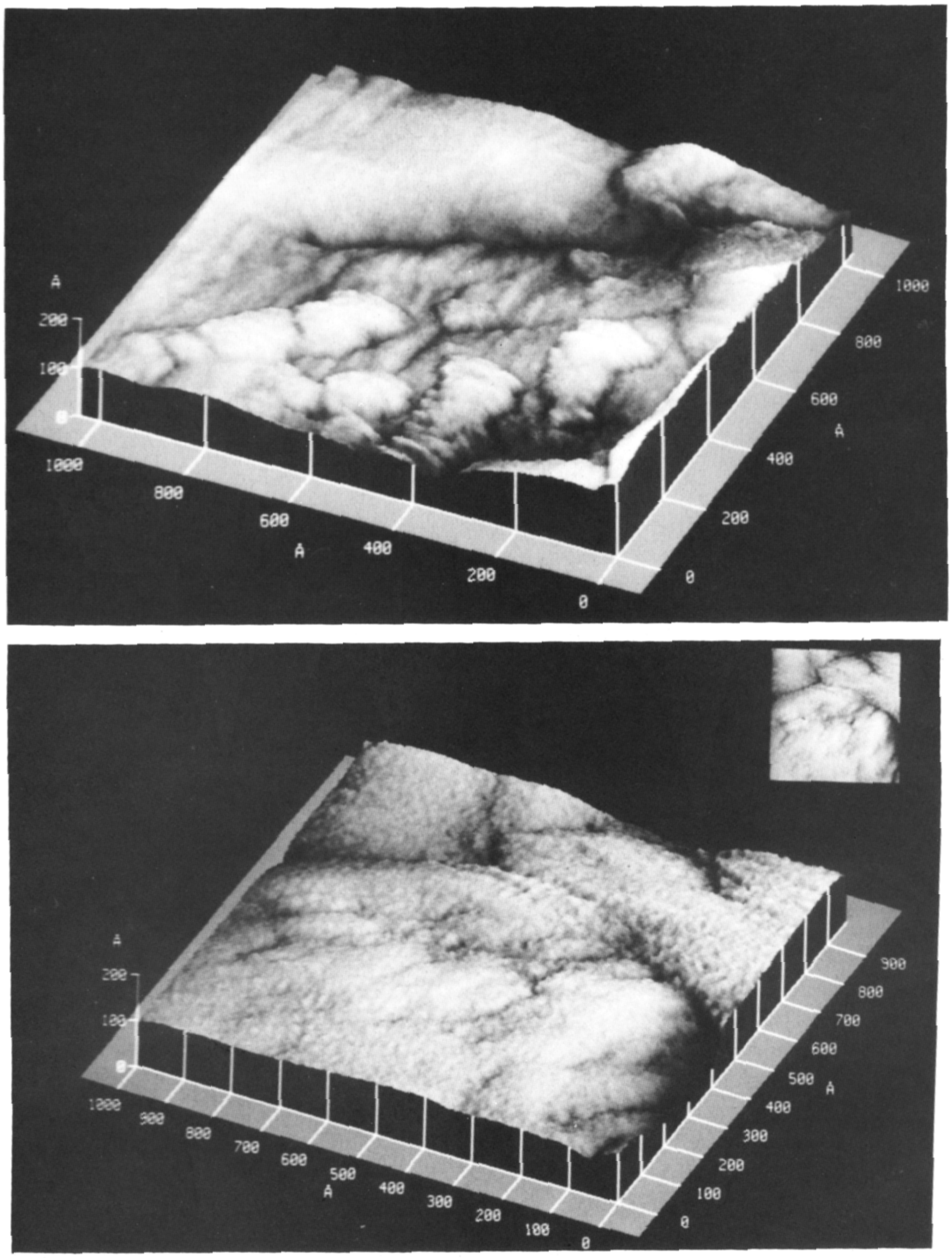

Figure 2. (a, top) Small oligomeric islets with heights of 10–20 Å on ITO surface. The apparent substructure of the islet at the lower margin is a scanning artifact. Notice a typical linear ITO grain boundary in the center (three smallest islets can be seen behind the boundary). Sample prepared with 0.2 mC/cm^2 deposition charge and 1 mA/cm^2 current. (b, bottom) STM image of bare ITO at the same magnification for comparison. The surface is smooth with no abrupt height differences, except for some small cracks.

(Figure 3). These facts, together with the known sizes of the short oligomers (e.g., the length of the 2,2′:5′,2″-terthiophene molecule is ca. 10 Å), lead us to conclude that these fuzzy patches represent the earliest stage of the nucleation, i.e., adsorbed oligomers on the ITO surface. Images of the modified ITO electrodes strongly support this interpretation. Extensive noisy areas were seen on these electrodes, in accordance with their photogalvanic spectra which indicate large amounts of oligomeric species at the surface. The loss of resolution is probably due to the tip ploughing through the chains, as suggested previously.[13]

As polymerization proceeds these patches grow three-dimensionally and begin to coalesce and form structures covering the ITO surface. This process is nicely illustrated in Figure 4a, which shows an ITO electrode with a nominal deposition charge of 0.15 mC/cm^2. The grainy structure of ITO is still clearly discernible (cf. Figure 4b) but thin featureless polymer deposits cover large parts of the grains masking the details of the surface. The deposits seem to be flowing down from the grains suggesting the tops of the grains as the preferential nucleation sites instead of the deep fissures between them. A thin polymer blanket finally also covers the fissures forming a uniform coating, which, however, still reflects the topography of the underlying substrate. At some places, polymerization proceeds further producing large polymer aggregates. These aggregates have the appearance of bundles with

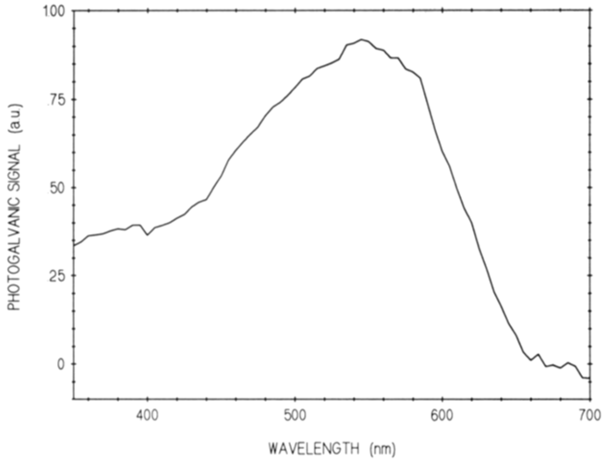

Figure 3. In situ photogalvanic spectrum of the ITO electrode with 0.2 mC/cm^2 deposition charge. The spectrum was recorded at −0.2 V vs Ag with polymer in the neutral state.

lengths and diameters of 1000–3000 and 300–600 Å, respectively (Figure 5). The bundles seem to consist of hemispherical or oval parts, but have no other discernible substructure. On the other hand, they exhibit a clear orientation on areas larger than 1 μm^2, in spite of their relatively large mutual distances. With polypyrrole, polymer tendrils of approximately similar size have been observed to be oriented perpendicular to the steps of the HOPG surface.[15] It is, however, difficult to assign the observed orientation to any similar reason because of the absence of structural order on the ITO surface. Aggregates on top of adjacent grains would, of course, produce linear structures upon coalescence, but in the absence of any driving force their direction with respect to each other would be expected to be more random. Because the bundles lie at angles of ca. 45° with respect to the scan direction and no changes were observed on repeated scans, the orientation is not assumed to be a scanning artifact. In addition, the orientation is limited to an area around that shown in Figure 5. The bundles may simply be oriented by the rinsing solution, which, however, implies that the bundles are continuous structures, probably representing long polymer fibrils lying on the surface. The latter possibility seems to be more feasible an explanation although an unambiguous answer cannot be reached on the basis of the present data. Photogalvanic spectra of these electrodes, however, exhibit a maximum signal around 550 nm. As the absorbance spectra of thick poly(3-methylthiophene) films usually have maxima approximately at 510–540 nm[28], this indicates that chains with conjugation lengths similar to those of mature polymer films are present on electrodes with bundlelike features.

On HOPG, polythiophene and polypyrrole have been shown to form semicrystalline microislands at early stages of polymerization.[6,10] On ITO, on the other hand, polymer deposits exhibiting a semicrystalline structure were found only on top of other polymeric features. A nice example is presented in Figure 6, where small polymer islands consisting of strands running parallel for a couple of hundred angstroms can be seen lying on top of a polymer matrix, as evidenced by the absence of structural details typical of ITO. The strands have a diameter of 25–40 Å, and no clear periodicity was detected within the strands. Two stable conformations have been theoretically predicted for poly(3-methylthiophene), either a rodlike chain or a helix having diameters of 7.2 and 17 Å, respectively.[29] On the other hand, based on X-ray measurements of trifluoromethanesulfonate-doped polythiophene a helical structure with an outer diameter of ca. 20 Å has been proposed.[30] Recently Yang et al. were able to detect two helical structures, one with a pitch and diameter of ca. 8 and ca. 15 Å, respectively, and another having the respective dimensions of 33 and 50–60 Å, both for a BF_4-doped sample of polythiophene.[6] The former is a simple helix while the latter was interpreted as a superhelix, i.e., a helical structure coiled upon itself. The diameter of the chains in Figure 6 is an intermediate between the simple helixes and the superhelixes but is clearly too large for a rodlike structure. On the other hand, the polymer chains

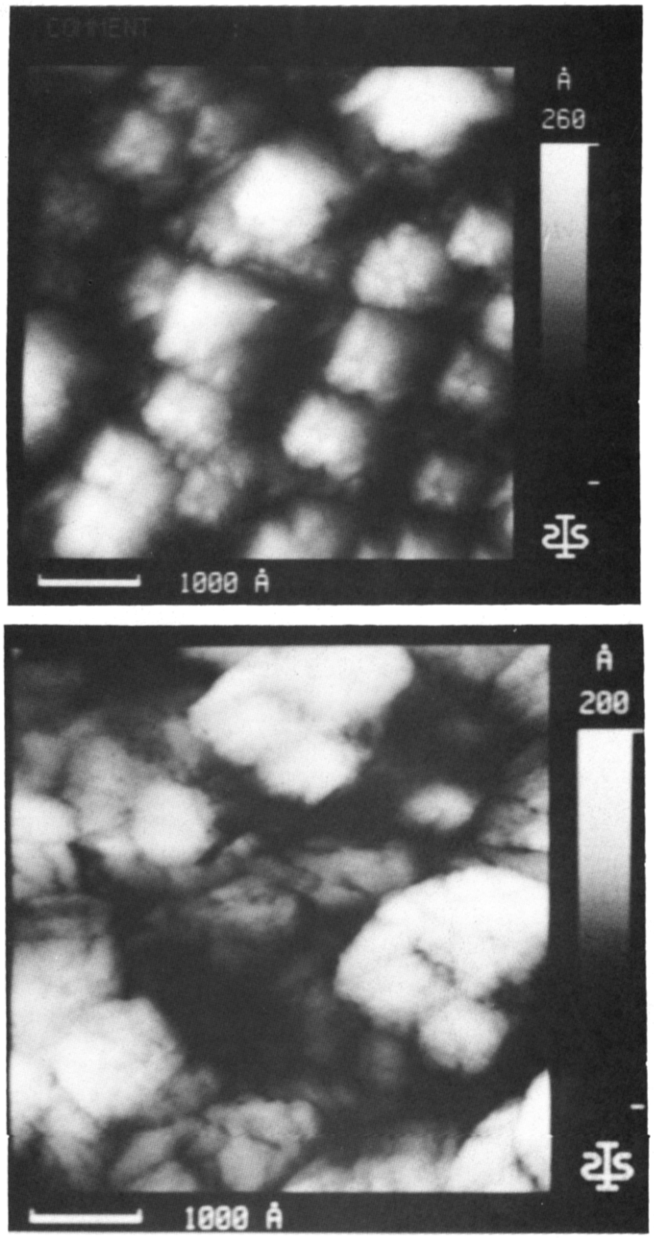

Figure 4. (a, top) Polymer deposits of different shapes on tops of ITO grains. Deposition charge of the sample was 0.15 mC/cm^2 and current 1 mA/cm^2. (b, bottom) STM image of bare ITO at the same magnification for comparison. Notice that the small details of the grain surface are masked in (a).

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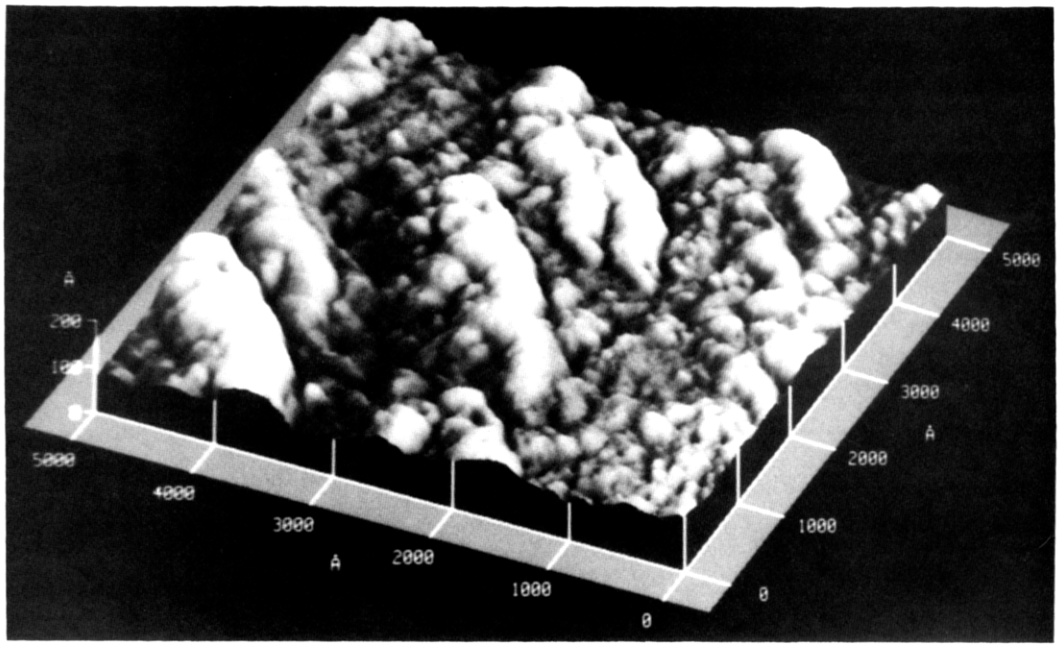

Figure 5. Oriented polymer bundles lying on ITO surface, which is, at least partially, thinly covered by a polymer film. Outside the imaged area the surface has a nonoriented structure. Deposition conditions as in Figure 3.

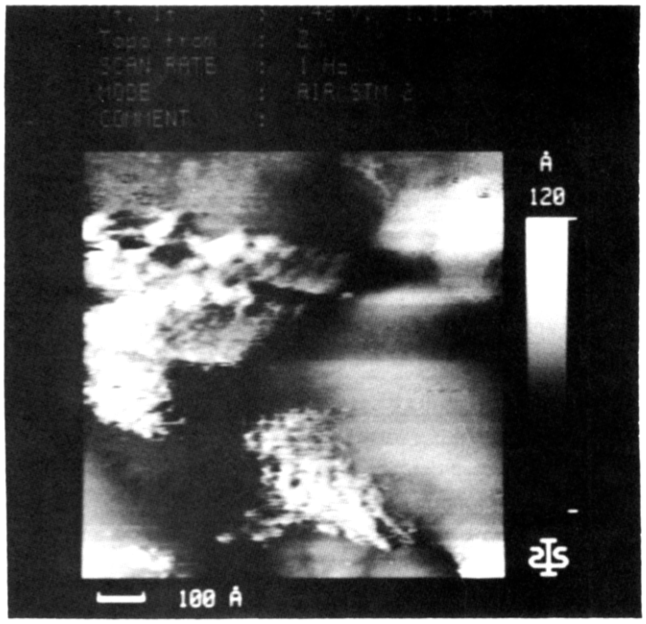

Figure 6. Microislands consisting of parallel polymer fibrils on top of featureless polymer bundles. The polymeric nature of the underlying matrix was evident in images of larger scanning area. Stripes parallel to the X-axis are artifacts caused by scanning. Sample prepared using 0.6 mC/cm^2 deposition charge and 10 mA/cm^2 current in the presence of CCl_4.

appear to shrink upon undoping.[6] We do not, however, believe that the chains in Figure 6 are undoped superhelixes. Caple et al. have reported poly(3-methylthiophene) structures with a diameter close to that predicted for the coil conformation but which have a rather irregular fine structure with several kinks and a zigzag pattern on larger scale[5], a feature in fact detected in some of the strands in Figure 6 (see, e.g., the left edge of the lower island). Similar structural irregularities could explain the apparent variation in the observed chain diameters in Figure 6.

On an electrode surface already covered by a relatively thick film, polymer forms extensive oriented patterns with a diameter of ca. 1500 Å, as shown in Figure 7, and sometimes a wavy structure is observed. Similar wavy features have been observed on the surface of thick emeraldine hydrochloride films.[4] The polymer film in Figure 7 consists of layers of large, seemingly bundlelike structures, many of which exhibit periodic substructure with a pitch of 350 ± 70 Å. However, no periodicity could be observed within their individual sections, and on closer inspection the structure resembles numerous bundles similar to those in Figure 5 lying side by side in several layers. Close to the lower edge of the image this structure borders on a considerably thinner polymer film. The structure in Figure 7 is thought to be related to the macroscopic features previously observed on ITO electrodes because, when the nominal polymerization charge is increased to 1 mC/cm^2 and beyond, the resolution range of the in situ optical video microscopy is reached and spots of polymer visible to the unaided eye begin to appear on ITO.[21] At this stage of polymerization, STM images show that polymer film extends far beyond the visible macroscopic growth centers. At some places the polymer surface appears nodular, as reported for many thick conductive polymer films,[6,10,17] and is found on closer inspection to consist of numerous polymer bundles lying on the surface. In general, large fibril formations effectively covering the surface can be seen far from the visible polymer spots, i.e., at a distance of several spot diameters. The surface of a macroscopically thick polymer layer, as observed in the vicinity of a spot, has a frozen lavalike appearance resembling a thick poly(hydroxyaniline) film (Figure 8).[11] Several domains are discernible, containing oriented polymer bundles with a diameter in the range 250–500 Å, reasonably in accordance with the diameter of poly(3-methylthiophene) fibrils seen in electron microscopic images.[30]

The preceding facts indicate that some sites on the polymer-modified ITO electrode turn into expanding growth centers, the further film development being largely characterized by the three-dimensional growth of these centers.[21] We should point out that our previous estimates on the nucleation density were based on these macroscopic centers[21], and, as evident in the STM images, small polymer

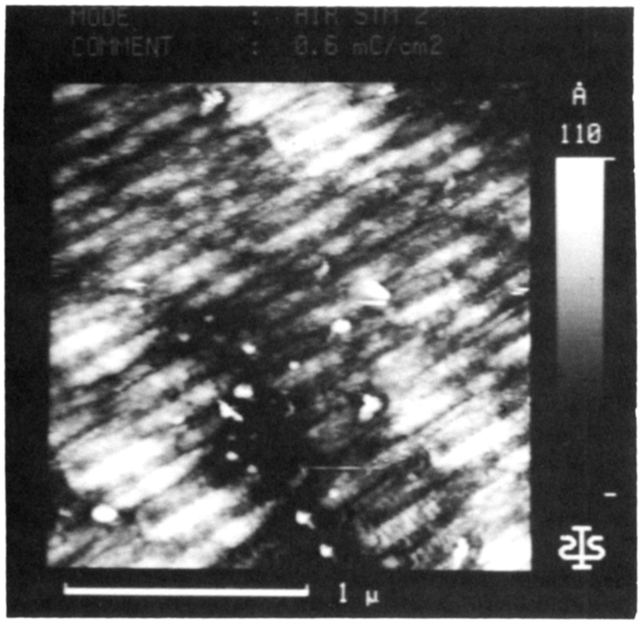

Figure 7. Polymer deposit at different location on the sample in Figure 6. Approximately 1 μm below the image there is a border with a thinner polymer layer and, therefore, the deposit probably represents an embryo of a macroscopic growth center. At higher magnification the apparent periodicity is seen to be due to polymer bundles lying parallel in several layers.

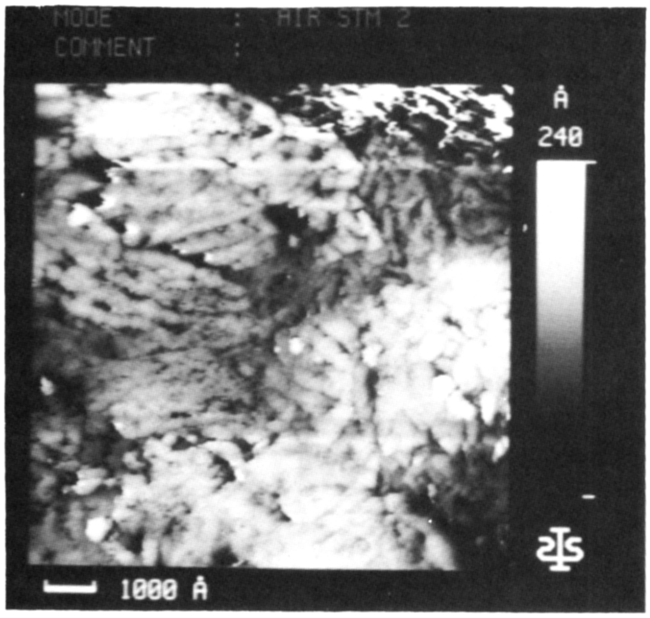

Figure 8. Surface of a rather thick poly(3-methylthiophene) film showing several semiordered domains with fibrillose structure. Image is taken close to a macroscopic growth center.

deposits greatly outnumber them in the very beginning of the electropolymerization. Which factors bring about the formation of these macroscopic nuclei is not known, but it is important to realize that when new centers appear they are not initiated at a virgin, bare ITO surface but that they grow on top of a thick polymer layer. In fact, the structure depicted in Figure 7 may be an embryo of such a center, because below the lower edge of Figure 7 there is a clear border to a thinner polymer film. Preliminary STM investigations of $SiCl_4$–bithiophene-modified ITO electrodes indicate a greatly enhanced fibril formation, in accordance with our previous observations of the nucleation enhancement on these electrodes.

Finally, some general comments on the present work should be added. The electropolymerization of conductive polymers is suggested to take place either through oligomerization in the solution followed by precipitation or preadsorption of the monomers to the electrode surface.[21] This question can not be resolved on the basis of the present data, because we were not able to obtain high enough resolution of the ITO surface to find out whether it contains adsorbed monomers. In addition, all the samples in this work represent dry undoped polymer deposits, and so the images do not depict the polymer nuclei in the nascent state. A growing nucleus probably has oxidized chains projecting from the surface to the solution in a conformation different from those found in the STM images, and some species, e.g., monomers, may have been washed away with the rinsing solution. In spite of these shortcomings polymer growth can be seen to begin preferentially on tops of the ITO grains and then proceed to fill the crevices. This is understandable, because although the theory of metal electrodeposition cannot be straightforwardly applied to electropolymerization, the grains act as small spherical particles, which leads to enhanced diffusion whereas the recesses are largely masked, in analogy with the deposition of metals. This implies that the role of macroscopic surface irregularities in enhancing the polymer growth might also be partly diffusional, although they also provide chemically and physically different environments, probably favoring adsorption. On the other hand, within the grains there may be some preferential sites where the nucleation or adsorption initially takes place, but we could not identify such active sites. They need not correspond to any structures evident in the images but may represent regions having, e.g., higher exchange current density or different atom arrangements, brought about by local variations in charge carrier concentration, crystal structure, or surface chemical composition. On platinum, for example, poly(3-methylthiophene) has been shown to grow preferentially on the Pt(111) crystal facets.[31] On the other hand, at later stages of the polymerization, which are relevant to our previous work by optical microscopy[21], the electropolymerization of 3-methylthiophene on ITO bears resemblance to the island-and-layer mechanism as opposed to the pure layer-by-layer or three-dimensional-islands mechanisms with the lateral growth rate of the film greatly exceeding the growth of the macroscopic centers perpendicular to the surface.[32] What is remarkable, also, is the apparently very high current efficiency at low charge densities. For example, a charge of 0.2 mC/cm^2 corresponds to ca. 1 nmol/cm^2 of monomer (assuming $z = 2$), which is roughly equivalent to 2–3 monolayers of thiophene.[33] In STM images large polymer aggregates can be seen at these low charge densities and a thin polymer film probably covers most of the electrode surface. The representability of the reported images is a problem with STM, of course, because the scanned area always represents only a negligible part of the whole surface, but, on the other hand, images taken at macroscopically different locations and on different electrodes convey the same overall picture. This insinuates the possibility that the polymerization reaction may be catalytic in the sense that the electrochemical oxidation is needed only to initiate

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the polymerization, which may then proceed chemically either on the surface or in the solution, e.g., by a cationic mechanism. The confirmation of this hypothesis, however, requires further studies on the mechanism of the polymerization reaction.

Conclusions

This work represents the first effort to use STM to study the electropolymerization of conductive polymers on such a very rough surface as ITO. For this purpose, a set of recognition criteria for the identification of the polymer deposits on the electrode surface has been composed. This work is also an example of the merits of a dual characterization of the samples imaged, preferably by an in situ technique. The photogalvanic spectra of the electrodes give information on the species attached to the surface, thus facilitating the interpretation of the STM images. In addition, because of the hundreds of photogalvanic measurements carried out we can be sure that our STM samples give a representative picture of the polymerization process.[22] The electropolymerization of 3-methylthiophene starts by formation of small oligomeric islets which grow and combine to form featureless polymer aggregates. Initial polymer growth seems to occur mainly on top of the ITO grains, which act as small spherical electrodes. No semicrystalline microisland formation on bare ITO could be detected, contrary to HOPG, although similar features were found located on top of other polymer deposits. At certain locations on the ITO electrode surface, several layers of polymer bundles are deposited to form macroscopic growth centers. At the stage of polymerization when the macroscopic centers appear, the electrode surface is already extensively covered by a polymer layer. Estimation of the nucleation density in electropolymerization is difficult, because in the course of polymerization different kinds of deposits act as active growth centers, and the assignment of a deposit to an active nucleus is ambiguous. However, the structure of a thick polymer film is largely determined by the appearance and development of the macroscopic growth centers. In addition, the nonuniformity of the polymer film at early stages of polymerization studied in this work implies that the charge–thickness relationships, derived from measurements on thick polymer films,[34] cannot be straightforwardly extrapolated to very low deposition charge densities. Further work with STM and other surface characterization techniques is needed in order to solve the remaining problems, including the mechanism of the growth of the deposits and the polymer chain conformation at different deposits.

Acknowledgment. We are grateful to the Academy of Finland for financial support and to Planar International, Inc., for donation of the ITO samples.

Registry No. 3-Methylthiophene, 616-44-4; 3-methylthiophene (homopolymer), 84928-92-7.

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