

## Scanning tunneling microscopic imaging of doped polyaniline

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Scanning tunneling microscopic images of doped polyaniline (PANI) with HCl are presented. Parallel chains with average separation of 0.4 nm are clearly visible, and the measured distance between the nearest two maxima in the polymer chain is about 1.04 nm. Molecular-mechanic calculations were used to optimize the conformation of a model polyaniline chain, and have yielded numerical values which agree well with measurements taken from the STM images.

### 1. Introduction

Polyaniline (PANI) has been the focus of intense study in recent years due to its simple formation, good long-term stability under ambient conditions and high application potential as an electrode material in chemical batteries.

PANI can be distinguished by the oxidation state: reduced leucoemeraldine base (LB), partially oxidized emeraldine base (EB) and fully oxidized pernigraniline base (PNB). MacDiarmid et al. [1] first reported that the conductivity of the emeraldine base form of PANI can be increased by ten orders of magnitude upon the protonation doping. Unlike conventional doping methods used for most conducting polymers, there is no change of the number of electrons in the chain backbone after protonation, although one can change the density of electrons on the chain through control of the oxidation state. Chiang and MacDiarmid [2] hypothesized that all nitrogen atoms, all C-N bonds and all C<sub>6</sub>H<sub>4</sub> rings in the polyemeraldine salt are equivalent. All rings in this proposed structure of PANI are intermediate between

quinoid and benzoid, and all C-N bonds are intermediate between single and double bonds. However, experimental data suggest that the major charge defects in the polyemeraldine salt are polaronic [3]. Hagiwara et al. [4] confirmed by the analysis of the <sup>13</sup>C NMR spectra that the chemical structure of the base form of PANI is consistent with that proposed by Chiang and MacDiarmid. Wan [5] has modified MacDiarmid's proposed molecular structure of PANI based on the variation of the absorption spectra with the protonation state.

PANI is most conveniently produced by the electrochemical polymerization of the aniline monomer directly onto an anode surface. There has been a considerable effort to correlate electrical conductance with growth conditions, chemical composition and structure of the polymers [6]. However, the structural characterization of electropolymerized, doped PANI has been hampered by (1) the amorphous nature of the bulk polymer, and its insolubility in most solvents, and (2) the fact that the chemical composition can show considerable diversity depending upon the electrode-

position conditions. As a consequence of the complexity of this polymer system, no clear picture has yet emerged.

We believe that scanning tunneling microscopy (STM) may provide some information about the molecular structure of PANI. Yang et al. [7] have reported highly resolved STM images of polypyrrole tosylate, polypyrrole tetrafluoroborate and polythiophene tetrafluoroborate.

In this paper, the first STM image of a thin film of polyemeraldine salt synthesized electrochemically from, and the conformation of, PANI obtained by a molecular-mechanics calculation are reported.

## 2. Experiment

Thin films (thickness not determined) of polyemeraldine salt with chloride counterions were synthesized by electrochemical deposition onto 2 mm  $\times$  3 mm pieces of freshly cleaved, highly oriented, pyrolytic graphite (HOPG) substrate from aqueous solution of hydrochloric acid with aniline monomer. The oxidation and polymerization reaction was carried out galvanostatically at current densities of 2.0–0.5  $\mu\text{A}/\text{cm}^2$ . The amount of polymer deposited onto the HOPG substrate was controlled by the current passed during the deposition. The charge passed varied from  $6 \times 10^{-4}$  to  $1 \times 10^{-2}$  mC, depending on the current and time of the deposition. After deposition and removal from solution, all samples were dried in air.

The STM experiments were performed in air with a homemade STM apparatus [8] using mechanically prepared Pt/Ir (80%/20%) tips and electrochemically prepared W tips. The images shown in this report were taken in air from samples prepared previously and stored in air. The STM was run in the constant-current mode with a bias voltage of 98 mV and tunneling current of 1.2 nA. All images obtained for this paper are real-time photographs taken directly from the computer screen. The lateral scaling was determined by calibration of the piezo scanner against a HOPG standard. Measurement errors quoted herein were determined on the basis of measure-

ments taken on four STM images from different scanning areas.

Molecular modelling was performed on a silicon graphics IRIS 4D-20 work station using the interactive molecular graphics program QUANTA and CHARM.

## 3. Results and discussion

Examination of PANI samples by STM showed different structures depending on whether the sample was imaged on the continuous polymer or in the boundary region between the continuous polymer film and native graphite. The STM images taken on the film boundary showed numerous isolated structures, indicating a discontinuous "micro-island" nucleation at the initial growth stages, as was found for polypyrrole [7]. Images taken on the interior region of the film showed no discontinuities on a nanometer scale. Fig. 1 shows a typical STM image taken on the continuous polymer region. The scan dimensions for this image are 3.6 nm along the  $x$ -axis (horizontal) and 3.1 nm along the  $y$ -axis (vertical). At first sight, it appears that the chains have taken on a helical conformation. However, this is most likely

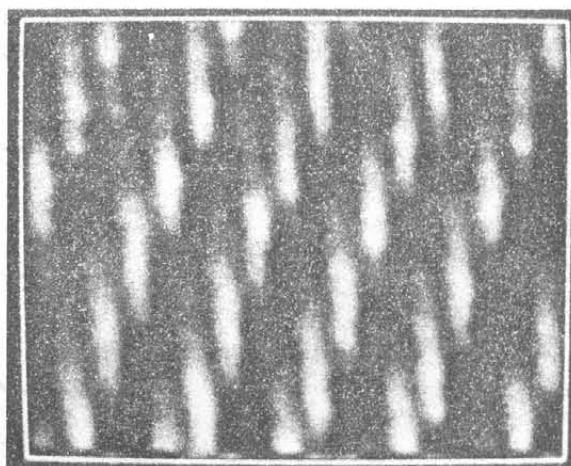


Fig. 1. STM image of electropolymerized, doped polyaniline with a scanning area of 3.6 nm (larger scale of image)  $\times$  3.1 nm (smaller scale of image). The STM was operated with a tip bias of 98 mV and a feedback system maintaining a current of 1.2 nA.



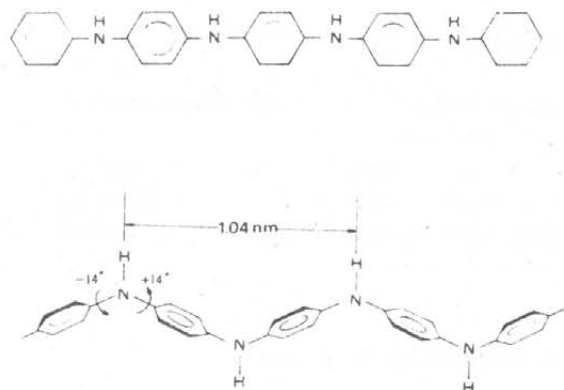


Fig. 2. (a) The model molecule for the theoretical studies. (b) The conformation of the model molecule obtained by the molecular-mechanics calculations.

not the case, as the phenyl rings along a single chain would be forced to overlap in such a manner that the nitrogen-carbon bond angles would be severely strained.

We propose a different interpretation of the two-dimensional structure on the basis of molecular-mechanical calculations which minimized conformational strain energy of a single isolated polyaniline chain. A phenyl-terminated aniline pentamer, shown in fig. 2a, was chosen as the model chain, and the QUANTA package determined the lowest energy conformation obtained from idealized coordinates in terms of bond angles and bond lengths. The optimized conformation is displayed in fig. 2b, showing the phenyl

rings to be alternately rotated  $14^\circ$  above and below the plane of the page. Moreover, the phenyl groups are oriented in a trans-configuration with respect to the nitrogen atoms. The distance between centers of alternate phenyl rings of the idealized molecule was found to be 1.036 nm. The calculated conformation is supported by the X-ray crystallographic results of Baughman et al. [9] on  $\text{ClO}_4^-$  and  $\text{BF}_4^-$  salts of [4-(phenylamino)phenyl]-1,4-benzenediamine, which provide essentially the same conformation although the molecule cut short one  $-\text{NH}-\text{C}_6\text{H}_4$  group compared with the model molecule we used. The van der Waals half-thickness of the molecular chain was determined to be 0.23 nm.

Referring again to fig. 1, it is possible to visualize a lateral stacking arrangement of the chains aligned along an axis tilted towards the upper left quadrant of the image. In this configuration, phenyl rings, represented by the bright maxima, appear to be viewed edge-wise, and are separated by some distance from each other along a given chain. Moreover, they are oriented perpendicular to the substrate, partially overlapping with rings on adjacent chains. We attempted to model this close-packing configuration in fig. 3. Here, idealized PANI chains are shown in a parallel arrangement, with alternating phenyl rings perpendicular to the plane of the page, allowing adjacent rings to incline  $28^\circ$  with respect to the vertical. Assuming this interpretation to be correct, it was possible to measure a distance of  $1.04 \pm 0.03$  nm between maxima whose centers are aligned

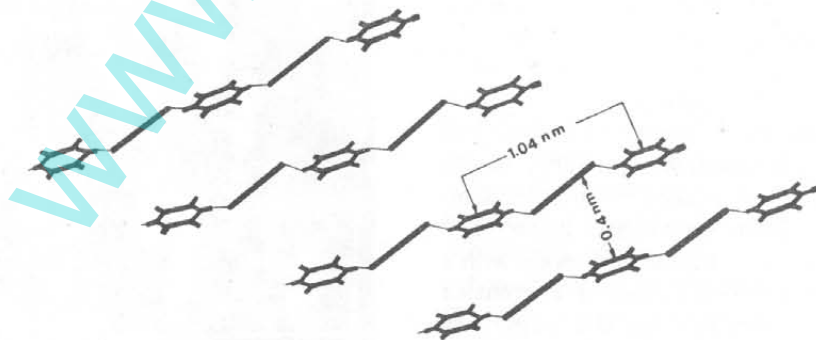


Fig. 3. A proposed model for the polyaniline polymer chains arrangement. The conformation of the single polymer is derived from the molecular-mechanics calculations. Interesting distances are indicated.

along parallel axes tilted at an angle of approximately  $65^\circ$  from the  $x$ -axis of the image (tilted towards the upper left quadrant). The measured interchain distance from the STM images was  $0.4 \pm 0.03$  nm. This value falls short of the theoretical interchain axis-to-axis spacing of 0.46 nm which is based on the calculated van der Waals half-thickness given above for an isolated chain. The fact that the measured interchain distance is less than the sum of the van der Waals half-thicknesses for adjacent chains may be related to the two-dimensional conductive nature of PANI.

Thus, the bright maxima can be assigned to alternate phenyl units along a given chain, whose ring planes are aligned perpendicular to the substrate, and nearly parallel to the  $y$ -axis of the image. Each ring plane is laterally displaced by approximately 0.4 nm from neighboring rings along the same chain. This conformation can be more clearly seen in the schematic shown in fig. 3. These values are in close agreement with corresponding distances determined theoretically for an isolated chain. However, the lack of visibility of the rotated phenyl units cannot be accounted for by this model.

#### 4. Conclusion

From the above discussion, it is evident that highly resolved STM images of electropolymerized PANI can be explained at least in part by the conformational data of an idealized chain obtained by molecular-mechanics calculations. The combination of both approaches provides new insight into the film structure.

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