Molecular mechanics calculation and scanning tunneling microscopic research of polyaniline doped with perchlorate

C. Bai, C. F. Zhu, P. C. Zhang, and T. Yu
Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

F. S. Wang
Chinese Academy of Sciences, Beijing 100086, China

(Received 8 August 1993; accepted 14 December 1993)

On the basis of the molecular mechanics method, using a minimized conformational strain energy calculation, several models have been proposed for chains with six repeat units of aniline. First, a model of a single isolated polyaniline chain is set up. Second, according to the interaction between the two adjacent polyaniline chains, a monolayer film model of parallel chains is presented. Third, a model of double layers of polyaniline chains is presented based on the interaction among three chains located in the different layers. Polyaniline film doped with perchlorate was investigated by a scanning tunneling microscope (STM). STM data are basically in agreement with the above molecular mechanics calculated models.

I. 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 leuoemeraldine 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 in 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_6H_4 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 ^{13}C nuclear magnetic resonance (NMR) spectra that the chemical structure of the base form of PANI is consistent with that proposed by Chiang and MacDiarmid.

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 polymers.[5] However, the structural characterization of doped PANI has been hampered by the amorphous nature of the bulk polymer, and its insolubility in most solvents. As a consequence of the complexity of this polymer system, no clear picture has yet emerged.

We believe that scanning tunneling microscope (STM) may provide some information about the molecular structure of PANI. Yang *et al.*[6] have reported highly resolved STM images of polypyrole tosylate, polypyrrole tetrafluoroborate, and polythiophene tetrafluoroborate.

Here, STM images of polyaniline doped with HCl and a corresponding polyaniline chain model obtained by molecular mechanics calculation was reported by Bai *et al.*[7]

In this paper, we further propose models of single and double layers of polyaniline. They are compared with STM images of polyaniline doped with perchlorate.

II. EXPERIMENT

The instrument used in the experiments is a home-made STM.[8] The tip used in the experiments was obtained by electrochemically etched tungsten wire (diameter = 0.5 mm). Using the constant current mode, the tunneling current was 1.20 nA and the bias voltage was 75 mV.

The studied polyaniline doped with a perchlorate acid free-standing film was prepared by a casting solution. A 2.0 g pure polyaniline powder was first placed in a 250 ml bottle, then 60 ml mixture of *N*-methylpyrrolidon (NMP) and *N,N*-dimethylformamide (DMF) was poured into the above bottle. The solution was stirred for 24 h, then filtered by a G_4 funnel. A dark blue polyaniline solution was obtained. We extracted 10 ml of the above solution, slowly dropped on a 15 × 15 cm^2 glass plate, and heated by a infrared lamp. A procedure of volatilization took place. At the end of the procedure, we put it into a 1.0 N perchlorate acid aqueous solution for more than 24 h. The obtained sample was then soaked in distilled water for about 5 min. After that, the film was dried in a vacuum for more than 96 h. Finally, we obtained the polyaniline free-standing film with perchlorate ions. On a SGI 4D/310 work station, the molecular models were calculated.

III. RESULTS AND DISCUSSION

Using energy minimization calculations, we can propose models in the following steps.

First step: A phenyl-terminated aniline hexamer, shown in Fig. 1(a), is chosen as the model of a single isolated chain, and the BIOSYM-DISCOVER package determines the low-

 0734-211X/94/12(3)/1927/3/$1.00

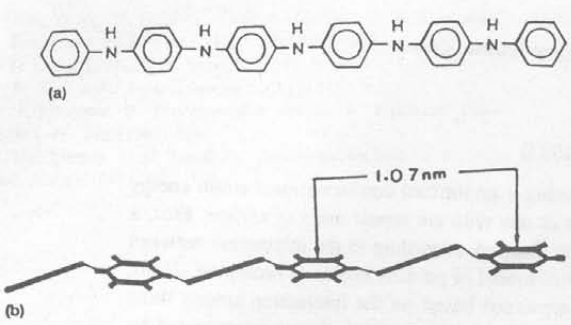

FIG. 1. (a) The model single isolated chain for the theoretical studies. The chain consists of six phenyl-terminated aniline. (b) Aniline hexamer conformation obtained by using the energy minimization calculation.

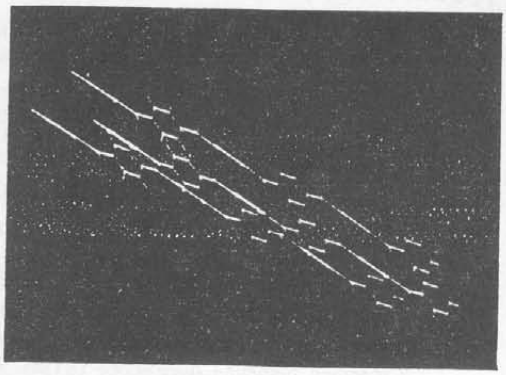

FIG. 3. The double layers model of polyaniline molecule is optimized by energy minimization.

est energy conformation obtained from idealized coordinates in terms of bond angles and lengths. We used 200 steps of the "steepest" method, 1000 steps of the "conjugate" method, and 500 steps of the "VA09A" method to fulfill the energy minimization calculation. Root-mean-square (rms) deviations of the derivative was less than 0.001. The energy was decreased from 409.8216 to 288.5875 kcal/mol. Figure 1(b) shows the conformation of aniline hexamer obtained by using the energy minimization calculation. The distance between the centers of alternate phenyl rings of the idealized molecule was found to be 1.07 nm. The phenyl rings are alternately rotated 14° above and below the plane of the page.

Second step: In order to propose a monolayer model for the polyaniline chains arrangement, we carried out a molecular mechanics calculation for a system containing two aniline hexamer chains. After 1000 steps of the "conjugate gradient" method of energy minimization, an arrangement of aniline hexamer chains is shown in Fig. 2. Nearest interchain distance of N atoms in the monolayer of this ideal model was found to be 0.38 nm.

Third step: Based upon the monolayer model in step 2, we hypothesize that two aniline chains lie parallel in the same layer. The third single isolated aniline hexamer chain is placed in the adjacent layer. This third chain is displaced and compared with two other chains. These three chains could form a primary double layer model. After this model is optimized by energy minimization, the obtained double layer is shown in Fig. 3.

Investigating the surface structure of polyaniline doped with perchlorate by a scanning tunnel microscope, we achieved a STM image shown as Fig. 4. The scan area is 4.0 $\times$ 4.1 nm^2. In the figure, we can see many elliptical bright dots and dark holes. The bright dots and holes are well arranged that they form structures of many chains. The chains are oriented in a horizontal direction. Elliptical bright dots are believed to be the reflection of surface electronic density of states. We propose that the bright dots in the figure stand

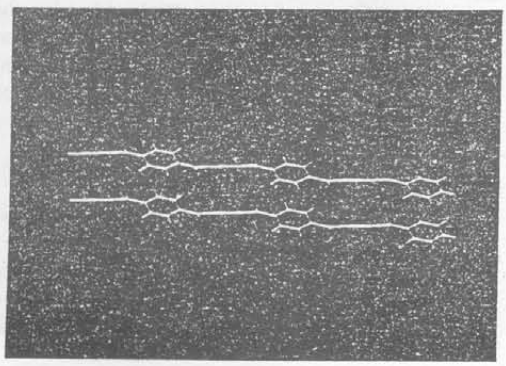

FIG. 2. A monolayer model for the polyaniline polymer chains arrangement. Two aniline hexamer chains were chosen to propose the model.

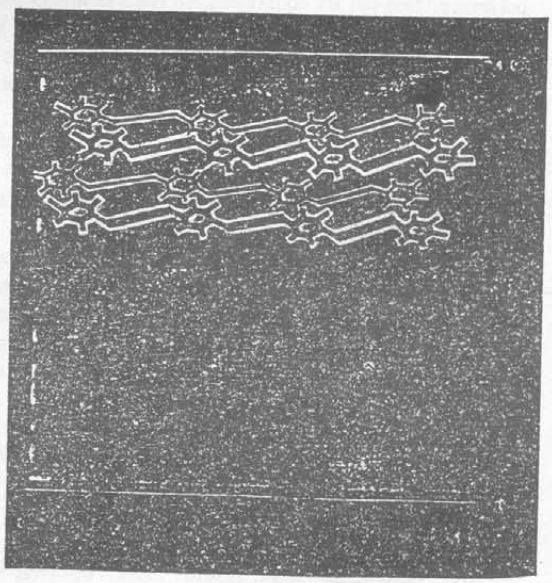

FIG. 4. STM image of perchlorate-doped polyaniline free-standing film, with a scanning area of 4.0 $\times$ 4.1 nm^2. The STM image was obtained with a tip bias of 75 mV and tunneling current of 1.20 nA.

for phenyl rings, which exist in the chains of polyaniline doped with perchlorate. The polymer chains are parallel to each other, forming part of the free-standing film. In the STM image, we believe surface structures of a double layer can be revealed. This is drawn in Fig. 4. The chains drawn with a heavy line are the first layer of doped polyaniline, and the part of the chains drawn with a light line is the second one. As we can see, this STM image contains both an electronic structure and topography.

In order to explain the image of STM, we compare the data in Fig. 4 with the models set up before. In the STM image, the average distance between the centers of the adjacent bright dots within the chain is about 1.0 nm. The average distance between the centers of every other adjacent chain (interchain distance in the same layer) in Fig. 4 is about 0.6 nm. In the model of Fig. 1(b), the distance between the centers of alternate phenyl rings is found to be 1.07 nm. This is about the same as the data in the STM image. Note that the model represents undoped polyaniline chain and the STM image was achieved with a doped polyaniline. It demonstrates that backbones of polyaniline do not change with a doped ion.

In the model of Fig. 2, we find the nearest interchain distance in the same layer is 0.38 nm. This is much smaller than the measured distance (0.6 nm) in the STM image. The model was set up for an undoped polyaniline chain. If we consider the size of perchlorate ion effects on the model, the interchain distance will be changed. We think that the perchlorate ion could be alternately inserted into the position near the nitrogen atom between two adjacent chains. Acid characteristics of perchlorate and alkaline characteristics of nitrogen are easier to bind together. Insertion of this perchlorate ion will lead to an increase of interchain distance. Suppose that interchain distance of polyaniline doped with a perchlorate free-standing film is simply the addition of the size of undoped polyaniline, and the molecular diameter of perchloratic acid, then the model of double chains containing perchlorate can be built. If the model is superimposed into the STM image, as shown in Fig. 4, we can find that the STM image is in agreement with the model we have presented. Interchain distance of the model is 0.586 nm, comparable to that of the measured results. This demonstrates that the interchain distance depends on polyaniline structures, the size of doped ion, and geometry of the sample.

IV. CONCLUSIONS

In summary, based on the models we proposed, the distance between the centers of alternate phenyl rings and the interchain distance are in agreement with the STM data. So, the molecular mechanics method is helpful for elucidation of molecular structures of polyaniline from the STM image.

[1]A. G. MacDiarmid, J. C. Chiang, M. Halpern, W. S. Huang, S. L. Mu, N. L. D. Somasiri, W. Q. Wu, and S. I. Yaniger, Mol. Cryst. Liq. Cryst. 121, 173 (1985).
[2]J. C. Chiang and A. G. MacDiarmid, Synth. Metals 13, 193 (1986).
[3]A. J. Epstein, J. M. Ginder, F. Zuo, R. W. Bigelow, H. S. Woo, D. B. Tanner, A. F. Richter, W. S. Huang, and A. G. MacDiarmid, Synth. Metals 18, 303 (1987).
[4]T Hagiwara, M. Yamaura, and K. Iwata, Synth. Metals 26, 195 (1988).
[5]M. Wan, Synth. Metals 31, 51 (1989).
[6]R. Yang, K. M. Dalsin, D. F. Evans, L. Christensen, and W. A. Hendrickson, J. Phys. Chem. 93, 511 (1989).
[7]C. Bai, C. F. Zhu, G. Z. Huang, J. Yang, M. X. Wan, and R. S. Chen, Ultramicroscopy 42–44, 1079 (1992).
[8]C. Bai, Chin. Sci. Bull. 34, 1318 (1989).