

Letter

Scanning tunnelling microscopy images of polyaniline

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1. Introduction

Polyaniline (PANI) has been recognized recently as an interesting and unusual member of the π -conjugated conducting polymers. Nitrogen atoms are incorporated between phenyl (C_6H_4) rings of the PANI backbone, which is quite different from many other conducting polymers such as polyacetylene, polydiacetylene and polythiophene whose electronic properties are well understood by simply considering the properties of conjugated backbones [1]. Thus the chemical flexibility provided by the nitrogen atoms allows access to several insulating ground states that are distinguished by their oxidation states; reduced leucoemeraldine base (LB), partially oxidized emeraldine base (EB) and fully oxidized pernigraniline base (PNB). Most studies of the PANI system have been focused on the relatively stable emeraldine oxidized state (EB) since it was found that EB could be doped to the emeraldine salt (ES) form by treatment with protonic acids such as HCl. This results in an increase in the conductivity at room temperature by 11 orders of magnitude to about 10 S cm^{-1} [2] and the induction of metallic-like Pauli paramagnetic susceptibility [3]. Chiang and MacDiarmid [4] hypothesized that all nitrogen atoms, all C-N bonds and all C_6H_4 rings are equivalent in the polyemeraldine salt. In their proposed structure all rings 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 charged defects in the polyemeraldine salt are polarons [3, 5-8]. It has also been suggested that these polarons are largely localized on 50% of the nitrogen atoms so that the six-membered rings are largely aromatic [6-9]. In contrast, Hagiwara *et al.* [10] confirmed by analysis of the ^{13}C nuclear magnetic resonance spectra that the chemical structure of the base form of PANI is consistent with that proposed by Chiang and MacDiarmid.

One of us has modified MacDiarmid's proposed molecular structure of polyemeraldine on the basis of the variation in the absorption spectra with the protonation state [11]. Baughman *et al.* [12] concluded that the structure of the highly conducting acceptor-doped polyemeraldine salt is highly delocalized. The rings are of high fractional quinoid character (about 0.5) and the C-N bonds are of high π bond order. As a consequence of the high π bond orders of the C-N bonds, the dihedral angle between neighbouring rings is small, so that conjugation is not interrupted. It can be seen that the detailed molecular structure of the PANI system remains unknown. We believe that scanning tunnelling microscopy (STM), a relatively new technique, could be used to investigate the topography of conducting polymers by measuring the very small force between the STM probe and the sample. Yang *et al.* [13] have reported STM images of polypyrrole tosylate, polypyrrole tetrafluoroborate and polythiophene tetrafluoroborate.

In this letter STM images of polyemeraldine salt films synthesized electrochemically from aqueous HCl are presented and the chain structure of PANI is discussed.

2. Experimental details

A very thin sample of the polyemeraldine salt with chloride counter-ions was prepared by electrochemical deposition on $2.0 \times 3.0\text{ mm}^2$ pieces of freshly cleaved, highly ordered pyrolytic graphite (HOPG) substrates from an aqueous solution of HCl with aniline monomer (about $1.0 \times 10^{-5}\text{ mol l}^{-1}$). The oxidation and polymerization reaction was carried out at constant current densities of $2.0\text{--}0.5\text{ }\mu\text{A cm}^{-2}$. The amount of polymer deposited on the HOPG substrate was controlled by the current passed during the deposition. The charge passed was between 6×10^{-4} and $1 \times 10^{-2}\text{ mC}$ depending on the current and time of deposition. All samples were dried in air after film formation. The STM experiments were performed in air with a home-made STM apparatus [14] using mechanically prepared 80%Pt-20%Ir tips and electrochemically prepared tungsten tips. The scanning tunnelling microscope was run in the constant-current mode with a bias voltage of 98 mV and a tunnelling current of 1.21 nA. All images obtained for this letter are real time photographs taken directly from the computer screen.

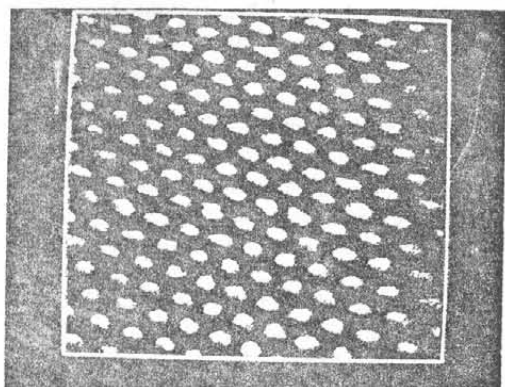


Fig. 1. STM image of HOPG substrate.

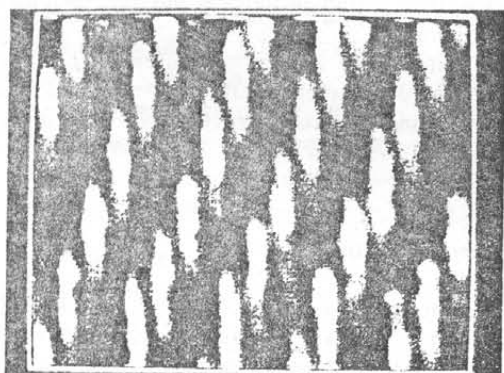


Fig. 2. STM image of polyemeraldine salt with chloride counter-ions.

3. Results and discussion

A typical STM image of the HOPG substrate, consisting of 180×180 points, is shown in Fig. 1. The STM resolution is about 1.0 \AA . A typical STM image of a polyemeraldine salt film with chloride counter-ions is shown in Fig. 2. A periodic structure of the STM image of the polyemeraldine salt with chloride counter-ions was observed along the diagonal line. The neighbouring bright dots along the *a* and *b* directions are separated by distances of 5.02 and 10.76 \AA respectively. According to the results obtained by Baughman *et al.* [12], the N-N distance is about 5.03 \AA , which is reasonably consistent with the value of 4.9 \AA reported by Ginder and Epstein [15]. Therefore the distance between C_6H_4 rings was calculated to be 5.28 and 5.22 \AA according to Baughman *et al.* [12] and Ginder and Epstein [15] respectively. Comparison of the above calculation with our STM observation suggests that the bright dots are C_6H_4 rings since the distance between bright dots along the *a* direction is 5.02 \AA , which is in good agreement

with the results obtained by Baughman *et al.* [12] and Ginder and Epstein [15]. Furthermore, if Baughman *et al.*'s [12] X-ray diffraction results were used and tight interchain contact was assumed, the interchain distance would be about 10.73 \AA , which is also in good agreement with the distance between bright dots along the *b* direction (10.76 \AA). Thus it is reasonable to expect that the periodic arrangement of bright dots along the *a* direction can be considered as the polyemeraldine chain. If the polyemeraldine salt is assumed to be a right chain, *i.e.* the C-N-C angle is zero, the N-N distance along the polymer chain will be about 5.53 \AA . On the other hand, Baughman *et al.* [12] have reported that the polyemeraldine salt chain is not a right chain and that the C-N-C angle is about 131° . Ginder and Epstein [15] suggested that each nitrogen atom possesses two electrons in a P_z orbital perpendicular to the C-N-C plane, while each C_6H_4 ring contributes six P_z electrons. Therefore the calculated C-N-C angle is 152.3° on the basis of the STM observations. According to the above analysis, we propose that the structure of a single chain of polyemeraldine salt is as shown in Fig. 3. It is noted that the bright dots actually consist of three small bright dots of different brightness and that two polyemeraldine chains along the *a* direction are ripped together. This may be due to two single chains overlapping as shown in Fig. 4. According to the structure of a single chain of polyemeraldine salt proposed by us in Fig. 3, the single chain drawn with a dashed line in Fig. 4 is located below the other single chain drawn with a solid line. Thus the brightest dots correspond to C_6H_4 rings while the two dots with lower brightness are related to nitrogen atoms and dopants respectively.

4. Conclusions

A periodic structure of the STM image of a polyemeraldine salt film on an HOPG substrate synthesized electrochemically was observed. The distances between

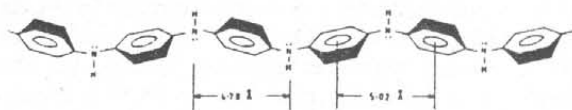


Fig. 3. Single chain of polyemeraldine.



Fig. 4. Two overlapping chains of polyemeraldine.

bright dots along the *a* and *b* directions of STM images are in good agreement with the results obtained by Baughman *et al.* [12] and Ginder and Epstein [15]. A structure for a single chain of polyemeraldine was proposed on the basis of the observations of STM images.

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