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Dopant dimension influence on polyaniline film structure

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Abstract. The techniques of scanning force microscopy have been successfully used to investigate characterization of the surface structure of polymer films. We obtained AFM/STM images of polyaniline films with molecular resolution. The repeat unit consists of alternating phenyl rings (nitrogen atoms) in polyaniline molecular chains. The results clearly showed characteristic structure in polyaniline films. The molecular chains are separated by dopants with different sizes in the polyaniline films. The distance between molecular chains depends upon the size and geometric shape of dopants, the surface structure of polyaniline films were obviously observed to be also influenced.

Doping processes for conducting polymers always accompany with counterions or counteranions coming in (or out of) polymers. Thus, it is expected that the nature of the dopants employed in the electrochemical or chemical synthesis of conducting polymers can significantly affect the structure and physical and chemical properties of the resulting materials. Wynne et al. [1] and Diaz et al. [2] found that the nature of counterions affects the quality and mechanical properties of the polymer films. Wernet et al. [3] and Yamaura et al. [4] suggested that the counterions employed in the electrochemical preparation have a direct impact on the molecule organization of the resulting films. Warren et al. [5, 6] reported that the structure and morphology of polypyrrole were influenced by the dopant anions.

Recently Bai et al. [7, 8] reported STM images of periodic polyaniline doped with chlorate and perchlorate counterions, and the model of conformation polyaniline chains was obtained from molecular mechanics calculation, which is consistent with X-ray diffraction data reported by Baughman et a1. [9]. These results suggested that STM as a new technique, associated with AFM (contact/tapping) can be used to investigate the topography and microstructure of conducting polymer materials. Therefore, it is very interesting to study further the influence of counterion size on the morphology or the structure of the surface of polyaniline films by STM/AFM techniques.

In this paper, we report high-resolution STM (scanning tunneling microscope)/AFM (atomic force microscope) results of polyaniline films with larger size counterions, and a corresponding model of the films resulting from the molecular mechanics calculation.

1 Experiments

The ultrathin films of polyaniline doped with chlorate, P-toluenesulforic acids (PAN-chlorate, PAN-PTSA) were synthesized by electrochemical deposition on 2.0 mm × 3.0 mm pieces of freshly cleaved HOPG substrates from an aqueous solution of PTSA with aniline monomer according to the method described in [7]. The STM experiments were performed with a home-made apparatus [10], under the following condition: in air, using mechanically prepared Pt/Ir (80%/20%) tips, and constant-current mode, the tunneling current is 1.2 nÅ and the bias voltages are 75 mV and 98 mV, respectively.

The free-standing films of polyaniline doped with perchlorate, camphor sulfuric acid (CSA) counterions were prepared by a coasting solution according to the method described in [11, 12]. The thickness of the films is about 20 μm (50 μm [8]). Studies of the surface structure of the doped polyaniline films were performed using the STM [8] and Nanoscope III (Digital Instruments Inc.) at room temperature in air. The AFM images were obtained in contact mode and recorded in height mode. In these studies we used commercial tips provided by Digital Instruments Inc. The cantilever length is 200 μm with a spring constant of 0.12 N/m.

The molecular models of the doped polyaniline films were obtained using a molecular mechanics calculation in SGI workstation.

2 Results and discussion

By analyzing the microstructure of doped polyaniline films with chlorate, perchlorate, PTSA, and CSA counterions, we find that in the surface of doped polyaniline films the periodic structural units are presented on the polyaniline molecular chain backbone and that the dimensions between polyaniline molecular chains depend on size and geometry of the dopants. They will be discussed in detail as follows.

Investigating the surface structure of polyaniline films doped with chlorate by STM, we obtained images with higher resolution (as shown in Fig. 1a). The scan sizes are 3.6 nm × 3.1 nm. The bright dots represent phenyl rings. The polyaniline molecular chains consist of the phenyl rings in parallel arrangement. The average size of repeat unit in the polyaniline chain backbone is about 1.04 nm. The average interchain distance is measured to be about 0.4 nm.

Figure 1b is a configuration model of the surface structure of doped polyaniline films with chlorate counterions, which is performed using molecular mechanics calculation. The calculated repeat unit size in the chain backbone is about 1.07 nm. Since the chlorate counterions are embedded between adjacent chains, the average size of the interchains is 0.46 nm.

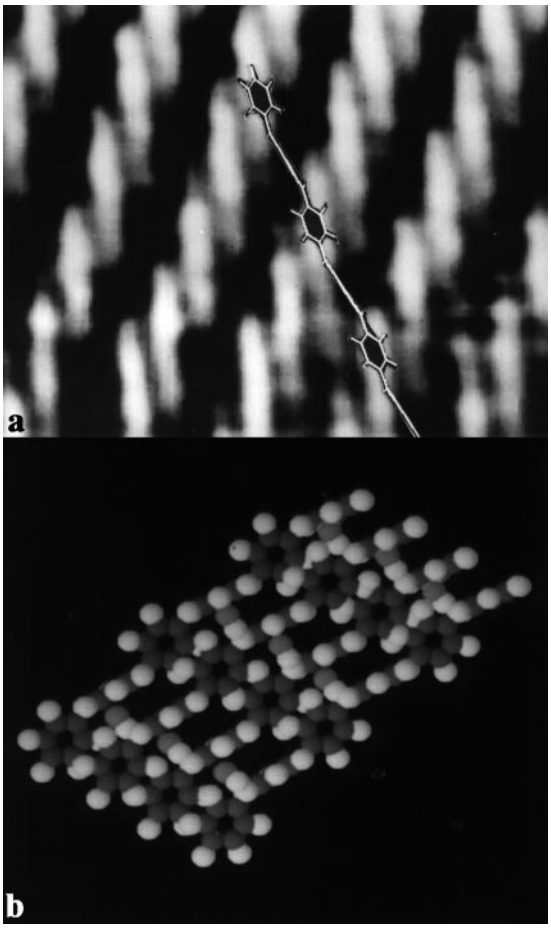

Fig. 1. a STM image of polyaniline film with chlorate counterions, scan size 3.6 nm × 3.1 nm, repeated unit size 1.04 nm, interchain distance 0.4 nm. **b** A monolayer model of polymer chains arranged for the polyaniline film with chlorate counterions. The conformation is from the molecular mechanics calculation

Table 1. Data of doped polyaniline films

Counterion	Interchain distance/nm (Theoretical)	Interchain distance/nm (Experimental)	Dimension of repeat unit /nm (Experimental)
Cl^-	0.35	0.4	1.04
ClO_4^-	0.7	0.6	1.00
PTSA	1.4	1.2	0.90

The theoretical result is basically in agreement with the experiments as listed in Table 1.

Figure 2 shows a STM image of doped polyaniline film with perchlorate counterion. The scan size is 4.0 nm × 4.1 nm. The continuous polymer region is presented. There are many elliptical bright dots in the image. The polyaniline chains are composed of the bright dots and dark holes (these are all known as phenyl rings). The chains are in parallel arrangement along the *y* direction, and the surface structure of polyaniline film is formed. We believed that characteristic configuration showed information of the double-layer films. The schematic of the model of the molecular chain is shown on the image. The chains drawn with a wide line are the first layer of doped polyaniline film, and those drawn with a thin line are the second one. The average distance between the center of the adjacent bright dots within the chains is about 1.0 nm. The average distance between the adjacent chains is about 0.6 nm (interchain distance in the same layer), which is in agreement with Fig. 1.

Fiure 3a is a STM image of doped polyaniline film with counterions PTSA, and the scan size is 6.1 nm × 4.8 nm. The bright dots are known to be phenyl rings. Both the phenyl rings were located on the backbone and sidechains of doped polyaniline films. The backbone of the polyaniline molecular chain is aligned along an axis titled towards the upper left quadrant of the image. The adjacent chains are separated by the PTSA sidechains. The characteristic network structure of the films was formed. The measured dimension of the repeat unit is about 0.9 nm and the distance between both chains is

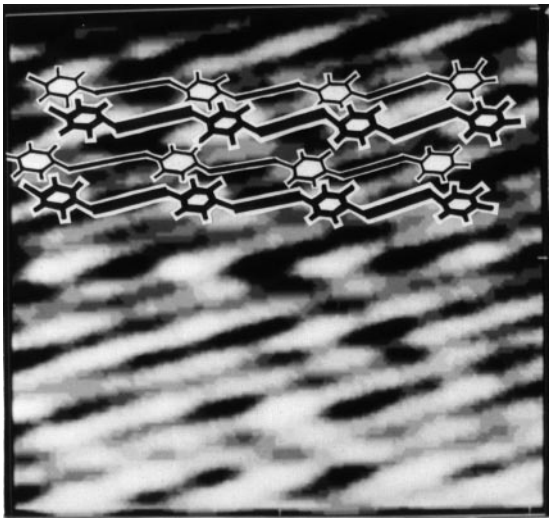

Fig. 2. STM image of polyaniline film with perchlorate counterions, scan size 4.0 nm × 4.1 nm, repeated unit size 1.0 nm, interchain distance 0.6 nm

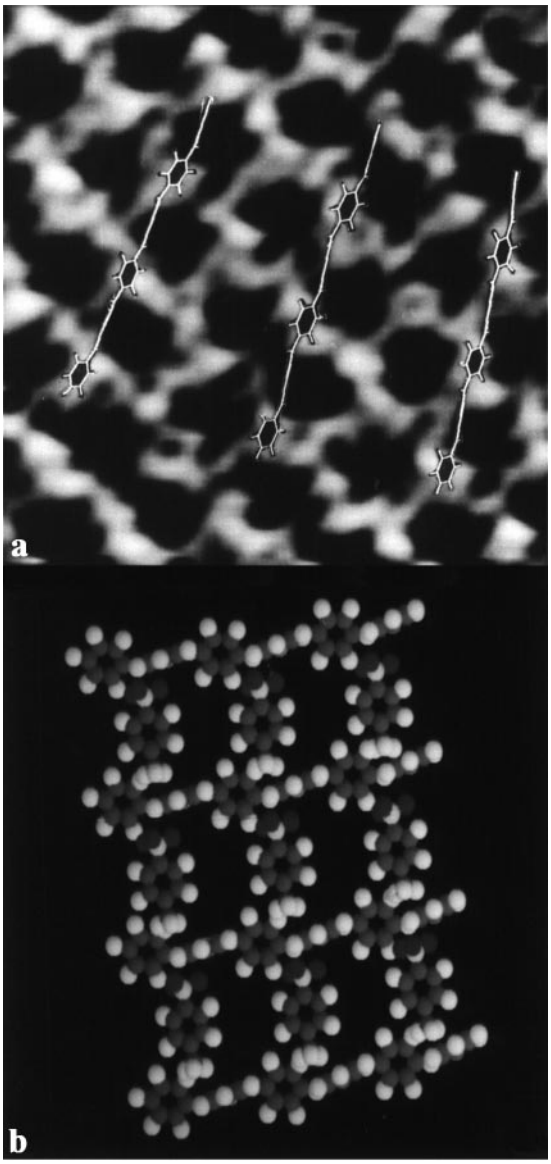

Fig. 3. a STM image of polyaniline film with PTSA counterions, scan size 6.1 nm × 4.8 nm, repeated unit size 0.9 nm, interchain distance 1.23 nm. **b** A monolayer model of polymer chains arrangement for the polyaniline film with PTSA counterions. The conformation is from the molecular mechanics calculation

about 1.23 nm. The results are in agreement with Fig. 1 and Fig. 2.

The structural model of the molecular chains of doped polyaniline film surface with PTSA counterions is illustrated in Fig. 3b. The model of configuration was derived by the molecular mechanics calculation. The characteristic repeat unit consists of the alternating phenyl rings (nitrogen atoms) on polyaniline molecular chains. The average dimension of the configuration is about 1.07 nm, and consistent with the experimental results. The PTSA counterions are located in the domain of alternating nitrogen atoms on the polyaniline molecular chains, and are inlaid between molecular chains. The PTSA counterions are formed because of a phenyl ring connecting with methyl and sulfoions. Thus there is certain geometric shape in the side chain. The side chains are oriented perpendicular to the axis of the polyaniline molecular chains. The average distance between polyaniline molecular chains is about 1.4 nm, which is in agreement with the experimental results.

We have analyzed in detail the effect of three doped counterions (PTSA, perchlorate, and chlorate) in the polyaniline film surface structure (as shown in Table 1). The results suggest that there exists a characteristic chain backbone in the doped polyaniline films. This characteristic structural unit consists of the alternating phenyl rings (nitrogen atoms). The molecular chains are separated because the dopant ions are located in the domain of alternate nitrogen atoms on the polyaniline molecular chain and inlaid between molecular chains. The distance between the chains is correlated with the dimensions of dopants. Obviously, the structures of doped polyaniline film surface are influenced by the dimension and geometric shape of dopants.

The AFM image of the free-standing film with CSA counterions showed a continuous polymer region of the film surface (shown as Fig. 4a). The scan sizes are 6.8 nm × 6.8 nm. There are two different types of bright maxima, which ap-

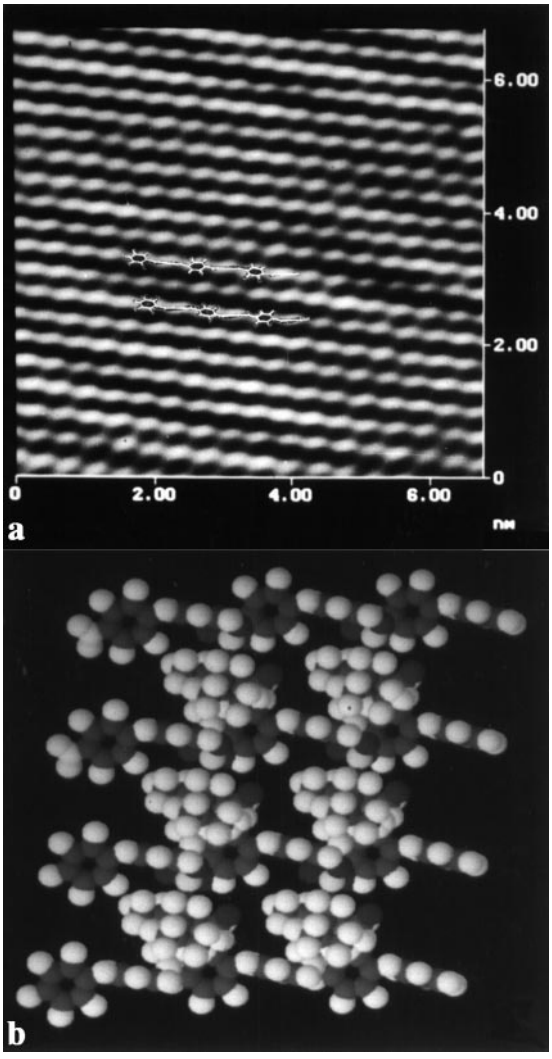

Fig. 4. a AFM image of polyaniline free-standing film with CSA counterions, scan size 6.8 nm × 6.8 nm, repeated unit size 1.06 nm; interchain distance 0.7 nm. **b** The conformation is from the molecular mechanics calculation. Interesting distance of 0.8 nm is indicated

pear to be viewed edge-wise in the image. The bright maxima represent the phenyl rings and CSA counterions. The bright maxima are arranged basically along the x axis of image, and the backbone of polyaniline molecular chain is formed. The schematic data were obtained by molecular mechanics calculation [7, 8] which were placed on the image, and they are consistent with experimental results. The dimensions between the alternating phenyl rings were measured to be about 1.06 nm (as in Fig. 4b). The result is consistent with the investigated results of doped polyaniline films with chlorate, perchlorate, and PTSA counterions, and that is a good evidence for the surface structure of the polyaniline films. The adjacent polyaniline chains are parallel to each other, and those chains are separated by the CSA counterions. The characteristic bright rows are formed by the CSA counterions between both molecular chains, and there is a certain stacked arrangement along an axis of the molecular chain. The distances between the polyaniline molecular chains are measured to be about 0.66 nm (as Fig. 4c). The result is a better evidence for Figs. 1–3.

Figure 4d is the configuration model of the free-standing film surface with CSA counterions, which was derived from molecular mechanics calculation. The distance between the polyaniline chains was indicated clearly. The molecular chains are arranged to be parallel in the plane of the page. The CSA counterions are located in the domain of alternating nitrogen atoms on the polyaniline molecular chain backbone. Because the CSA counterion is a ring-like compound, the atoms and atomic groups are close-stacked. Its dimension is about 0.7 nm. The distance between molecular chains is 0.85 nm, which is in agreement with experimental results.

The above investigated results of the doped polyaniline films with counterions of different size indicated that the repeat units on the backbone of the polyaniline molecular chains were known as the characteristic structure unit on the doped polyaniline films surface structure. The distances between the polyaniline molecular chains are different, due to different dimensions of the dopants in the films. Obviously, there is a certain correlation between interchain distances and dimensions of the dopants. The surface structures of the doped polyaniline films were obviously observed to be also influenced.

3 Conclusion

The experimental and calculated results suggested that repeat units consist of alternating phenyl rings (nitrogen atoms) to form the characteristic structural unit on the backbone of doped polyaniline molecular chains. The distances between both polyaniline molecular chains in doped polyaniline films were highly dependent on the dimensions of dopants. Then the surface structure of the doped polyaniline films were obviously observed to be also influenced. Further investigation is necessary to understand the counterion effect of polyaniline films on the electrical conductivity.

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