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Observations of polyaniline surface morphology modification during doping and de-doping using atomic force microscopy

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Chemically synthesized 30 μm thick polyaniline films were studied during the doping and de-doping process by imaging the polymer surface using *in situ* atomic force microscopy (AFM). The polymer, which was initially in the base non-conducting form, was doped using aqueous solutions of both tosylic acid (pH = 0.2) and HCl (pH = 0.2 and 1.0). De-doping was accomplished by exposing the same doped polymer surface to NH_4OH (pH = 12) base solution. AFM images showed that it was necessary to cycle the polymer surface three times between acid and base before a reproducible surface morphology was established. For the case of doping with tosylic acid, AFM images showed that the polyaniline surface was immediately roughened; the changes in mean roughness for the base and acid conditions were ~ 5.4 and ~ 6.7 nm, respectively. In addition there appeared to be an increase in the size of surface channels and cracks. When doping with HCl (pH = 1.0), no change in surface morphology was observed; however, noticeable surface roughening occurred over 10 min for the case of the lower pH = 0.2 solution; mean roughness changes for the base and acid conditions were ~ 17.9 and 39.2 nm. Radio frequency measurements, which determined the polymer complex permittivity, and d.c. conductivity measurements were used to determine the level of doping in the samples studied by AFM which were exposed to acid solutions.

1. Introduction

Polyaniline (PAn) has been studied extensively since the report of an insulator-to-metal transition upon protonation or oxidative doping of the emeraldine base form to the emeraldine salt form [1]. The preparation of PAn is straightforward and the emeraldine salt (conductive form) is stable in air. Many applications of PAn have been explored including rechargeable batteries [2], displays [3], semiconductor photoelectrode coatings [4] and microelectronic devices [5]. For all of these applications, it is very important to understand the film morphology changes during the doping and de-doping processes, especially for the applications of rechargeable batteries and displays.

The morphology of doped PAn has been investigated using scanning tunneling microscopy [6–10]. However, this technique is limited to conductive substrates and non-conductive layers with thicknesses less than 2 to 3 nm. By contrast, atomic force microscopy has been used to image structures for both conductors [11, 12] and insulators [13], including organic films [14] and polymers [15]. In this report, *in situ* doping and de-doping AFM experiments were performed to observe morphology changes of chemically synthesized PAn.

2. Experimental procedure

Polyaniline was chemically synthesized by oxidation of doubly distilled aniline with ammonium peroxydisulphate in 1.0 M HCl and converted into the base form with ammonium hydroxide as described by Huang *et al.* [16] and MacDiarmid *et al.* [17]. Approximately 30 μm thick films were cast from N-methylpyrrolidone on smooth glass surfaces. Tosylic acid and hydrochloric acid were used at various pH levels to protonate the base material. All reagents were HPLC grade or better and no buffer solutions were used. Chemical structures for the polyaniline base and the two protonated forms are shown in Fig. 1.

The PAn film was cut and mounted in the *in-situ* AFM wet cell. The morphology changes of PAn films were studied during the doping and de-doping processes. The AFM and wet cell used in our studies were of commercially available models (Digital Instruments, Santa Barbara, CA). The AFM probe tip was

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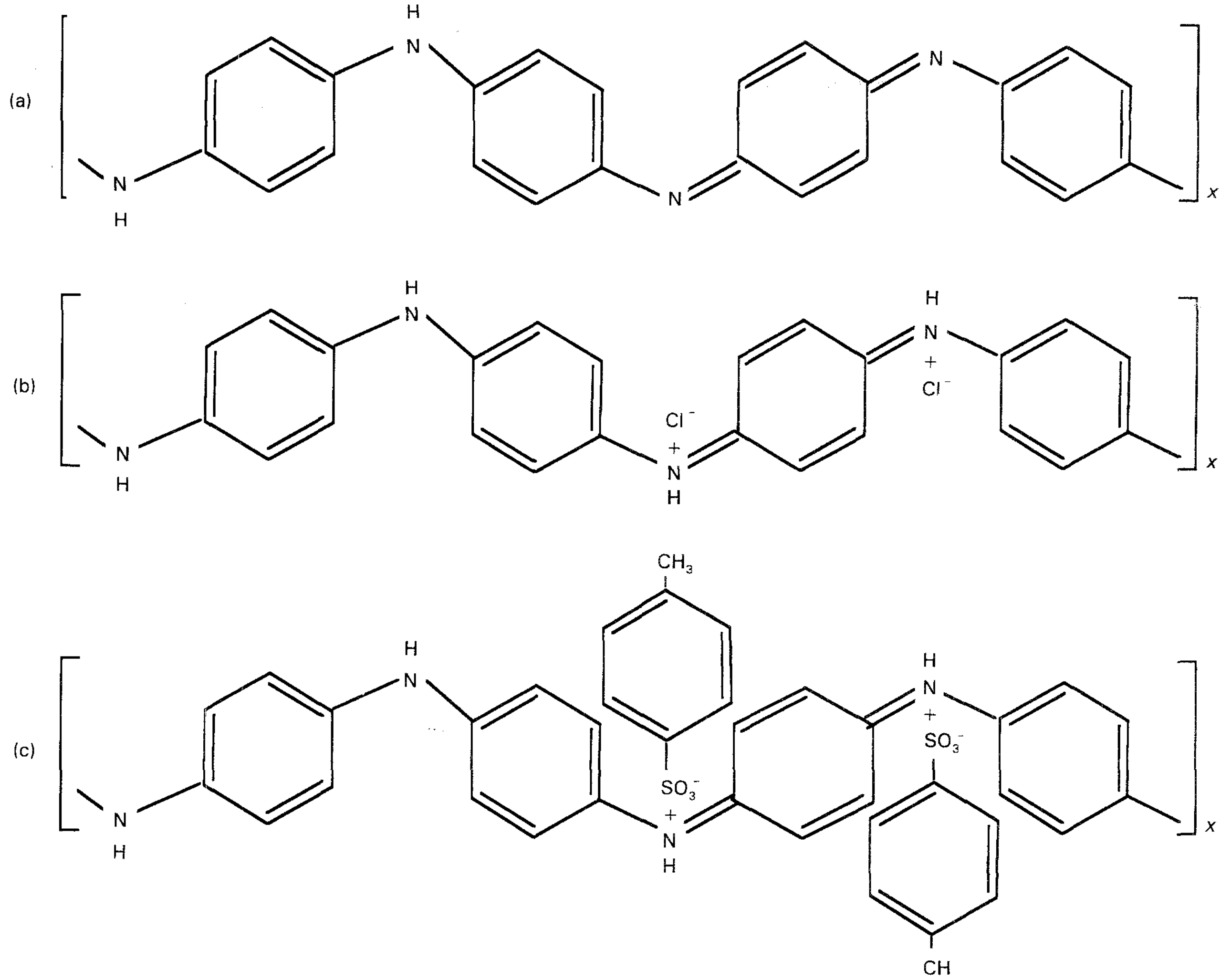

Figure 1 Chemical structures for polyaniline (a) in the base form and doped with (b) HCl and (c) tosylic acid.

attached to an insulating cantilever which had a low spring constant (~ 0.1–1 N m^{-1}) and was deflected in response to the forces between the probe tip and the sample. The deflections of the cantilever in our AFM were monitored using a laser deflection method [18]. All AFM experiments were performed using the contact mode where the force applied between the tip and sample was between 10 and 30 nN.

The electrical behaviour was determined by fitting the samples into a quarter-wavelength R-band waveguide sample holder and measuring the scattering parameters using an HP 8510B network analyser with the millimetre wave option. The scattering data were then used to calculate the complex permittivity. The details of this procedure have been described by Buckley and Dudeck [19].

3. Results and discussion

Two different doping and de-doping cases are reported in this study; one involved doping using a large ion, $C_7H_7SO_3^-$, and the other doping with the much smaller Cl^- ion. The effect of doping and de-doping with these ions on PAn surface morphology, which was observed by *in situ* AFM, is described below.

For the case of tosylic acid (TOS), AFM images were captured just after injecting the cell with TOS (pH = 0.2) which involved protonation of the PAn chains which are also doped with the large $C_7H_7SO_3^-$ ion. The PAn was cycled between the conducting and insulating states using TOS and ammonium hydroxide (NH_4OH; pH = 12), respectively. The surface morphologies for the de-doped and doped states are shown by the AFM images in Fig. 2a and b, respectively. The change in surface morphology was observed to be immediate (changes occurred as soon as the new solution touched the surface of the polymer), as monitored by *in situ* AFM when the TOS or the NH_4OH was injected into the wet cell. The morphology changes were consistent for each state; the sample described here was cycled six times between TOS and NH_4OH, and each time PAn was doped and de-doped the morphology changed in the same way. This is supported by the surface roughness results shown in Table I.

The root mean square of the surface roughness R_{rms} and the mean roughness R_m of the TOS-doped PAn were consistently larger than the surface roughness values for the de-doped state. We believe that the roughening of the surface during doping is a consequence of the large ion rearranging the polymer as it diffuses into and along the chain network. AFM studies also suggested that it takes many hours for the large ions to penetrate the entire thickness of the PAn

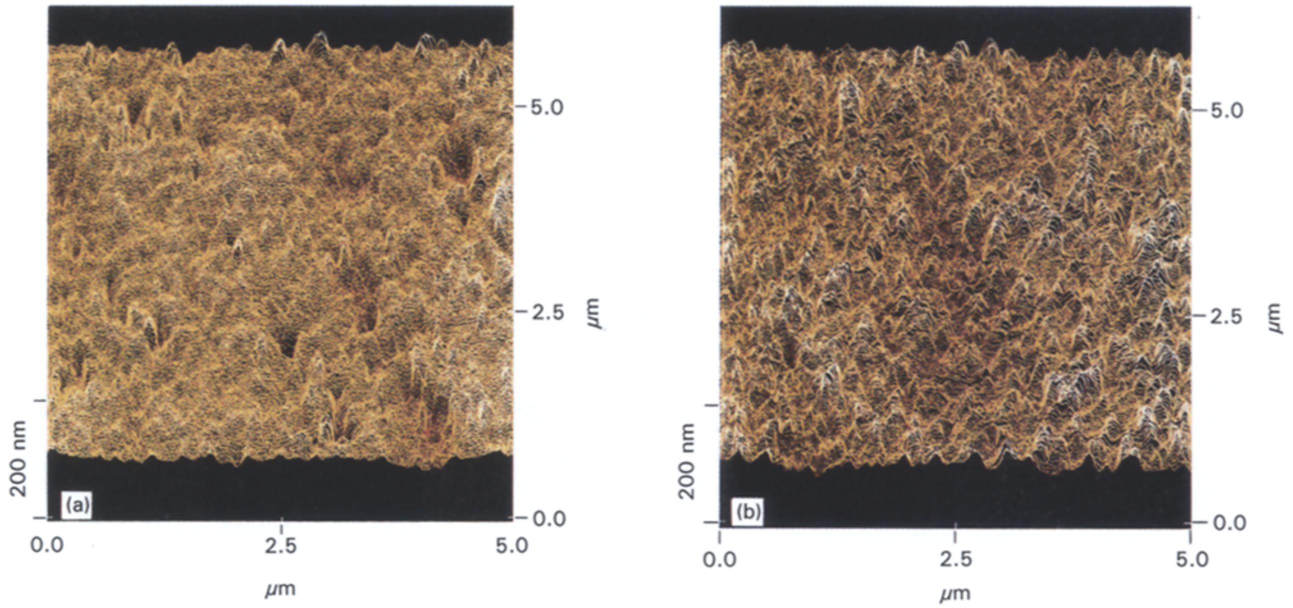

Figure 2 (a) AFM image of the polyaniline surface in the de-doped condition exposed to NH_4OH solution. This is a three-dimensional view at a 60° tilt angle. (b) The same area as in (a), doped during exposure to tosylic acid.

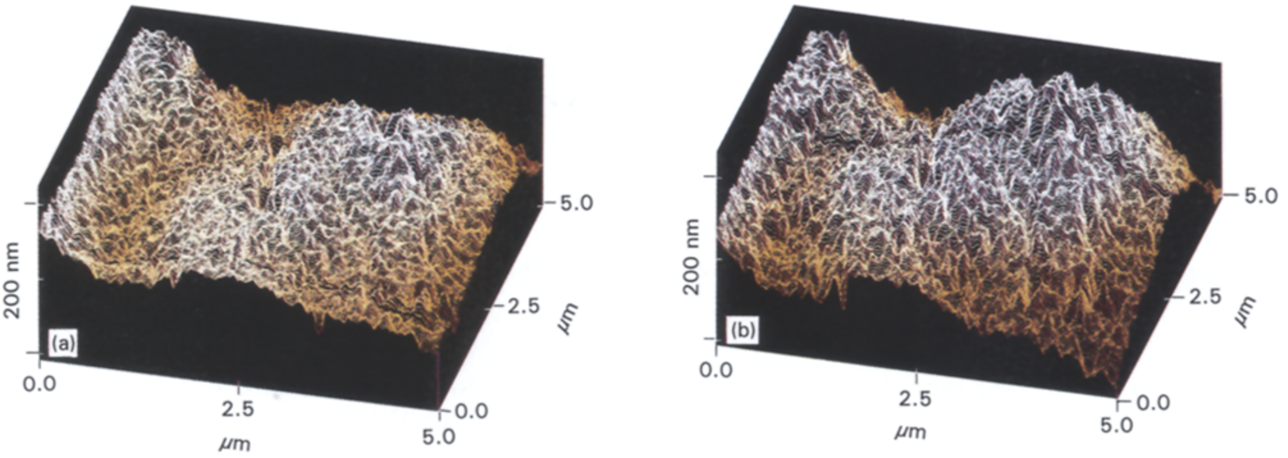

Figure 3 (a) AFM image of polyaniline in the de-doped condition during exposure to NH_4OH solution. This is a three-dimensional view with a 30° tilt angle. (b) The same area as in (a), doped during exposure to HCl solution.

TABLE I The surface roughness of polyaniline doped with tosylic acid

Cycle No.	Solution	Root mean square roughness, R_{rms} (nm)	Mean roughness, R_m (nm)	$\Delta = R_{rms} - R_m$ (nm)
1	Acid	8.1	6.2	1.9
2	Base	7.6	5.9	1.7
3	Acid	8.7	6.9	1.8
4	Base	7.2	5.4	1.8
5	Acid	8.6	6.8	1.8
6	Base	6.9	5.0	1.9

film, i.e. the overall film thickness continued to increase to a final value of ~ 40 μm (a 30% increase) after the polymer was exposed to TOS for ~ 15 h. Overall film PAn thickening was determined by monitoring the change in the amount of mean cantilever deflection during the experiments. The surface morphology AFM studies were repeated on three different samples and were found to give consistently reproducible results.

For the case of the Cl^- ion, AFM experiments were performed to study the effect of a small negative ion on the PAn surface morphology. HCl acid (both pH = 0.2 and pH = 1.0) was used. In this case the PAn chains were doped by Cl ions which are considerably smaller than the large $C_7H_7SO_3$ ions. The PAn was cycled between the conducting and insulating states using HCl and ammonium hydroxide (NH_4OH;pH = 12), respectively. When doping with HCl (pH = 1.0), no noticeable change in surface morphology was observed, although overall film thickening was detected. However, surface roughening along with film thickening occurred after 10 min for the case of the lower pH = 0.2 HCl solution, as shown by the images in Fig. 3a (de-doped condition) and Fig. 3b (doped condition). It can be seen that after doping the grain structure appeared more pronounced. This was accompanied by a general bulging and thickening of

TABLE II The surface roughness of polyaniline doped with HCl

Cycle No.	Solution/pH	Root mean square roughness, R_{rms} (nm)	Mean roughness, R_m (nm)	$\Delta = R_{rms} - R_m$ (nm)
3	Acid/pH = 1.0	18.7	14.2	4.5
4	Base/pH = 12	18.4	13.7	4.7
6	Base/pH = 12	22.8	17.9	4.9
7	Acid/pH = 0.2	39.2	30.5	8.7

the surface, as seen by the growth of the protrusion on the right side of the AFM image in Fig. 3b. The mean roughness for the surfaces before and after doping were ~ 17.9 and 30.5 nm, respectively, as shown by the results in the Table II.

These results combined with the results for tosylic acid doping of PAn suggest that during the doping process both Cl^- and $C_7H_7SO_3^-$ begin to penetrate the surface as soon as contact is made with the solution. The effect of the tosylic acid doping appeared to have a more immediate affect on roughening the surface of the PAn film. This difference appears to be associated with molecular structure reordering in order to accommodate the ions diffusing into the polymer. When the larger $C_7H_7SO_3^-$ ion diffuses into the PAn, a more extensive amount of molecular structure reordering must take place. AFM experiments suggested that the rate of diffusion of the Cl^- ion into the PAn was faster than for the $C_7H_7SO_3^-$ ion at similar concentrations. This assumption was based on AFM results which showed that the overall thickness of the PAn film increased much more rapidly for the case of Cl^-. Overall PAn film thickening occurred as soon as the doping process began for Cl^- (seconds), whereas film thickening for the case of the $C_7H_7SO_3^-$ ion occurred over a time of hours. Consequently, although AFM images show that TOS had an immediate and more rapid effect on PAn surface morphology than did HCl, the rate of diffusion of the negative ions into the bulk of the material appeared to be considerably higher for the smaller Cl^- ion. The physically larger tosylic counterion will not diffuse in or out of the polymer as easily as the chloride ion. This is consistent with the lower d.c. conductivities found for the tosylic acid versus HCl doping of PAn (for equal exposure times), where the large tosylic counterion diffuses more slowly into the polymer [19]. These results emphasize that small ions used for doping and de-doping should lead to faster response times in device applications such as sensors.

The electrical properties of the doped and de-doped PAn were determined by measurements of the complex permittivity in the R-band (26 to 40 GHz). The permittivity data shown in Fig. 4a were determined for a sample studied by AFM which was cycled between the doped and de-doped states using tosylic acid (pH = 0.2) and ammonium hydroxide (pH = 12) and ending with tosylic acid. As shown in Fig. 4b, there was a small increase (ca. 20%) in the dielectric constant along with an order of magnitude increase in the dielectric loss compared to the PAn base material. The d.c. conductivity of this sample was determined to be 0.005 S cm^{-1}. In Fig. 4c the complex permittivity is shown for a similar sample studied by AFM which was cycled in the same manner using HCl (pH = 0.2). The dielectric constant doubled in value along with a two orders of magnitude increase in the dielectric loss. The d.c. conductivity of this sample was found to be 0.02 S cm^{-1}.

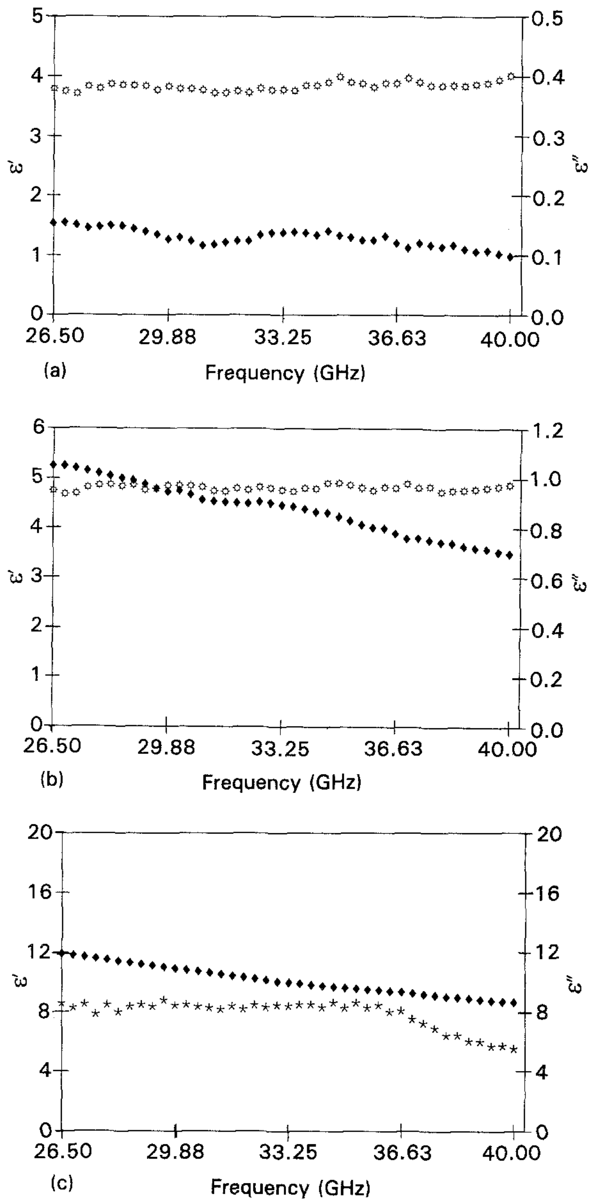

Figure 4 Complex permittivity data for (a) de-doped polyaniline cycled with tosylic acid (pH = 0.2) and NH_4OH (pH = 12), (b) doped polyaniline cycled with tosylic acid (pH = 0.2) and NH_4OH (pH = 12), and (c) doped polyaniline cycled with hydrochloric acid (pH = 0.2) and NH_4OH (pH = 12): (o, *) real part ε′, (◆) imaginary part ε″.

The smaller size of the chloride ion points to a faster and more thorough doping of the PAn material. This was supported by the greater complex permittivity and d.c. conductivity found for the Cl^--doped PAn. From the work of Pouget *et al.* [20] these materials have a partially crystalline structure due to the solvent process that was used to form the films. As determined from our AFM results for PAn, it may take several doping and de-doping cycles to establish a stable and reproducible surface morphology. This could involve a rearrangement of the ordered regions as ions establish pathways in the PAn.

4. Conclusions

We have studied the morphology changes of PAn film during doping and de-doping processes using *in situ* AFM. This work shows that small and large counterions result in dramatically different PAn surface morphologies. For the case of doping with tosylic acid, AFM images showed that the PAn surface was immediately roughened. In addition there appeared to be an increase in the size of surface channels and cracks. When doping with HCl (pH = 1.0), little change in surface morphology was observed; however, noticeable surface roughening occurred after 10 min for the case of the lower pH = 0.2 solution. The tosylic acid doping appeared to have a more immediate affect on roughening the surface of the PAn. This suggests that for the case of TOS a more extensive amount of material structure reordering needs to take place in order to accommodate the considerably larger tosylic ion. AFM experiments also suggested that the rate of diffusion for the Cl^- ion into the PAn was faster than for the $C_7H_7SO_3^-$ ion at similar concentrations. These results emphasize that PAn surface morphologies can be altered significantly depending on the size of the doping ion. This has implications in applications of PAn for devices such as sensors and batteries, where PAn surface stability is essential for reliable device operation.

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