

## The study of conducting polymer interaction with gaseous substances

### IV. The water content influence on polyaniline crystal structure and conductivity

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(Received November 4, 1991; accepted November 12, 1991)

#### **Abstract**

At present the water influence on the polymer crystal structure is poorly studied. Water molecules may interact with the polymer chain active sites during synthesis as well as in the processes of water adsorption from moist air. The thermoprogrammed desorption, conductivity measurement, X-ray phase analysis and high-resolution ESR techniques have been employed to study the interaction of water vapour with an emeraldine form of polyaniline (PANI). It is concluded that water influences the crystal structure of PANI and in this way changes its conductivity.

#### **Introduction**

It was shown earlier [1—5] that adsorbed water exerted influence over the optical, magnetic and transportational PANI properties. In the previous papers [1, 2] we reported on the peculiarities of water adsorption processes on doped and undoped PANI samples and concomitant conductivity changes. In the present paper an attempt is made to follow the mechanism of water action on the PANI properties in connection with crystal structure changes.

#### **Experimental**

Polyaniline samples in emeraldine state were prepared by the chemical oxidative polymerization of 1 M water solution of polyaniline sulfate in the presence of 1.2 M ammonium persulfate at 5 °C. The resultant PANI powder was filtered off and rinsed with distilled water and ethanol, and then treated with 10% ammonia solution to obtain the basic form of PANI (PANI-base).

A part of this as-prepared emeraldine base was washed with ethanol and vacuum dried for 24 h. Another part, after washing, was doped with 1 M sulfuric acid and washed again with ethanol; a 24 h vacuum drying completed the procedure.

X-ray phase analysis of PANI powder samples was carried out with the use of a DRON-3M diffractometer (Cu K $\alpha$  emission with  $\lambda/3$ -filter; 0.5 deg/min scan rate). Diffractometry of doped and undoped dry PANI samples in inert atmosphere, as well as of the same samples subjected to moist air at a 50% humidity level, was performed. A detailed description of conductivity measurements and thermodesorption experiments on PANI samples has been presented elsewhere [1, 2, 6]. X-band ESR spectra were taken on a PC-100.X spectrometer, and those in the 2 mm wavelength band on the ESR5-01 device [7].

## Results and discussion

The starting doped and undoped PANI samples possessed a certain degree of crystallinity (curves 1 in Figs. 1 and 2). The comparative analysis of their diffractograms on the basis of reference [8, 9] data pointed out the fairly noticeable difference in their crystalline structures. The PANI-base diffractogram revealed the broad peaks at the  $2\theta$  angles:  $13^\circ$ ;  $23.7^\circ$  and  $29.5^\circ$  (the mean-weight reduced peak positions) together with a distinct peak at  $19.2^\circ$  (Fig. 1). These peaks belong to the very structure of the PANI-base samples, since all the impurities should have been washed out by the procedure used.

In the previous papers [1, 2, 6] we reported on the water vapour interactions with doped and undoped thin PANI films followed by polymer adsorption capacity and conductivity changes. This paper summarizes the experimental data found and presents a probable picture of the PANI structure evolution in the presence of adsorbed water molecules on the basis of X-ray phase analysis data.

The diffractograms of H $_2$ SO $_4$ -doped PANI samples revealed the same features as in the case [6] of HCl doping, suggesting the pseudo-orthorhombic space group symmetry for both (Fig. 3).

The diffractograms of the starting doped and undoped samples of PANI as well as of the same samples exposed for 5, 60 and 1200 min to moist

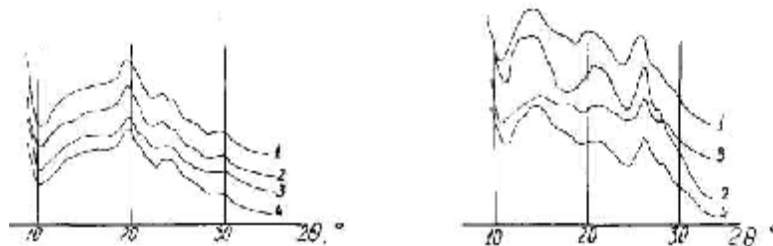


Fig. 1. Diffractograms of an undoped PANI sample exposed to water vapour: (1) a dried sample; (2), (3) and (4) correspond to exposure times of 5, 60 and 1200 min, respectively.

Fig. 2. Diffractograms of a sample of PANI doped with 1 M H $_2$ SO $_4$  exposed to water vapour for: (1) 0 min (dried starting state); (2), (3) and (4) 5, 60 and 1200 min, respectively.

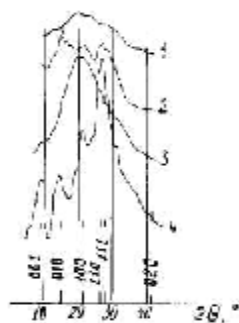


Fig. 3. Diffractograms of PANI samples: (1) in emeraldine state; (2) of emeraldine sulfate; (3) in emeraldine state [7]; (4) of emeraldine chloride [7].

TABLE 1

Interplanar space lengths ( $d$ ) and degree of crystallinity of a doped PANI sample exposed to moist air

Exposure time (min)	$d$ [Å ( $\pm 5\%$ )]			Degree of crystallinity (%)
	$hk\ l=010$	100	111	
0	5.95	4.21	3.33	44
5	6.08	4.04	3.27	49
60	5.63	4.06	3.27	42
1200	5.95	4.10	3.27	51

The degree of crystallinity determined with no account of amorphous and crystal phase extinction quotients.

air are presented in Figs. 1 and 2. The diffractograms of the PANI base showed no significant changes after moist air exposure (Fig. 1). This fact should be related to the negligible water vapour adsorption, in accordance with an effect shown earlier [2]. On the contrary, exposure to moist air of doped PANI samples caused evolutionary changes in the unit cell parameters and in the degree of crystallinity [10] (Fig. 2 and Table 1).

The data of Figs. 1 and 2 and of Table 1 provide evidence for strong distortions of the crystal structure of dried doped PANI samples taking place during the very first minutes of exposure to water vapour, which are exemplified by changes in the parameters  $d^i$ . The subsequent longer exposure results in a new stable structure, quite distinct from the starting one.

The experiments have shown that conductivity of thin PANI films could grow by 1-3 orders of magnitude in the process of their interaction with water vapour, depending on the degree of doping of the starting sample [1, 3].

As the parameter  $d_{100}$  (defining the distance between two neighbouring chains) decreases, the interchain hopping energy of any kind of charge carrier, i.e. solitons, electrons, etc., should presumably diminish in a  $1/r^6$

proportion, as does the dispersion interaction. The existence of a complicated correlation between structure and conductivity is also confirmed by the changes in parameter  $d_{010}$  and degree of crystallinity values.

The ESR data gave additional independent support for the conclusions presented above. In the 3 cm wavelength range, the ESR spectrum of the PANI base gives a symmetric singlet at  $g_{\text{eff}} = 2.0031$ . Its linewidth grows from 2.5 to 9.0 G at saturation of the starting sample with water vapour. Doping of the starting sample with  $\text{H}_2\text{SO}_4$  causes the narrowing of the line to a 1.5 G limit; the saturation of the doped sample broadens the signal to 5.2 G.

The spectra in the 2 mm wavelength range are more informative (Fig. 4). In this ESR range the samples reveal typical spectra of axial symmetry with the effective relaxation time values of about  $3 \times 10^{-7}$  s, which allow us to relate tiny magnetic parameter changes to the introduction of water molecules into the polymer matrix. The water vapour saturation of PANI-base samples causes the broadening of individual ESR lines from 4.6 to 5.9 G sustaining the  $g$ -tensor component values unchanged:  $g_{\perp} = 2.00301$  and  $g_{\parallel} = 2.00249$ .

It is worth emphasizing that doping of the PANI-base samples does not lead to a noticeable change in their magnetic parameters. However, the exposure of doped PANI samples to a wet atmosphere resulted in the narrowing of the individual ESR components from 4.1 to 3.2 G and, moreover, in a change of the spectrum shape (Fig. 4, curve *b*), the  $g$ -tensor components being shifted to  $g_{\perp} = 2.00288$  and  $g_{\parallel} = 2.00271$ . This change in the spectrum shape indicates a significant rearrangement of the close vicinity of the localized on a chain unpaired electron caused by the diffusion of water molecules into the polymer matrix. Since the energy of the excited configuration  $\Delta E \propto (g_{\perp} - g_{\parallel})^{-1}$  [7], the above-mentioned change in the ESR spectrum shape may be explained by the growth of the degree of crystallinity of the doped and saturated samples by the water vapour-exposed PANI sample, in accordance with an analogous conclusion made on the basis of X-ray phase analysis data.

On doping the PANI-base sample the paramagnetic centre concentration increases from  $3.8 \times 10^{19}$  to  $1.1 \times 10^{20}$  spins/g. The concomitant direct current conductivity level constitutes a  $10^6$ -fold value of the initial one. The absence of correlation between electrodynamic and magnetic parameters indicates the localized character of the paramagnetic centres and the non-spin nature

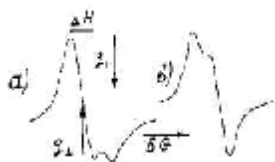


Fig. 4. The 2 mm wavelength range ESR spectra of (a) PANI-base samples in the dried and wet states, as well as of a dry-doped PANI sample; (b) of a wet-doped PANI sample.

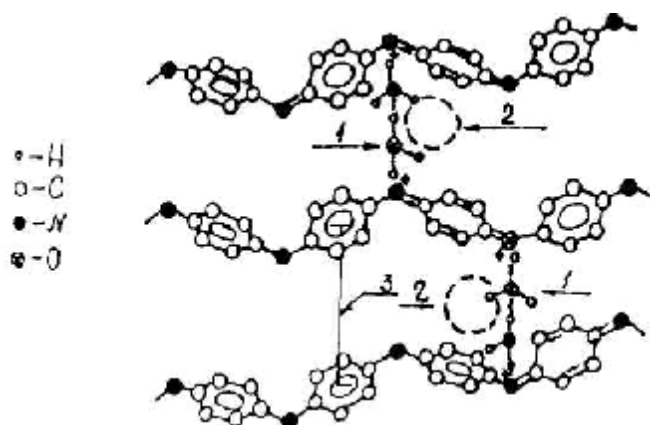


Fig. 5. Schematic spatial presentation of the interaction of water molecules with emeraldine sulfate. Notations in the structure of emeraldine sulfate exposed to water vapour: (1) a fragment of the chain composed from 1—3 water molecules; (2) an anion,  $\text{HSO}_4^-$  (3) the interplanar distance  $d_{100}$ .

of the charge carriers in the systems studied, e.g. bipolarons. This conclusion could be drawn also from the analysis of the ESR lineshapes, presented in Fig. 4, since the charge transfer by spin carriers (polarons) implies the motional averaging of the  $g$ -tensor components [11].

The data above, combined with the known facts [2, 3, 5] on the quantity of reversibly adsorbed water at 5 kcal/mol activation energy level equal to one  $\text{H}_2\text{O}$  molecule per four benzenoid (quinoid) rings, allow us to postulate the following picture of water vapour interaction with PANI (Fig. 5). In the process of protonative doping of the PANI-base samples, positively charged fragments form, containing imino-nitrogen groups [4] which possess an increased tendency to adsorb water. These fragments of closely positioned chains of PANI become hydrated and some kind of interchain bridge forms from water molecules linked by hydrogen bonds.

The changes in interchain distances characterized by the values of interplane space changes in the unit space cell  $d_{hkl}$  (Table 1) reflect, most likely, the process of orientational ordering of benzenoid (quinoid) rings. As a result, compatible with ESR data, the probability of interchain hopping of the non-spin charge carriers increases, causing the huge observable growth in the intrinsic conductivity of PANI films under the action of water vapour.

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