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Mixed electron and proton conductivity of polyaniline films in aqueous solutions of acids: beyond the 1000 S cm^{-1} limit

Jaroslav Stejskal,^{a*} Olga E Bogomolova,^a Natalia V Blinova,^a Miroslava Trchová,^a Ivana Šeděnková,^a Jan Prokeš^b and Irina Sapurina^c

Abstract

BACKGROUND: The application potential of conducting polymers depends on their conductivity. It is generally assumed that the conductivity determined in the dry state is a parameter that unambiguously characterizes them.

RESULTS: The conductivity of polyaniline (PANI) films immersed in aqueous solutions of sulfuric acid may be more than 1000 times higher compared with that obtained by measurement of dry films in air, and is estimated to reach a value exceeding 3300 S cm^{-1} in 1 mol L^{-1} sulfuric acid. This is explained by the reduction of conductivity barriers between conducting PANI islands.

CONCLUSION: The organized polymer chains in the conducting islands of a PANI film are separated by disordered regions of low conductivity in the dry state. The penetration of sulfuric acid solution into the disordered areas increases the overall conductivity of the PANI film by improving the electrical contact between the islands through ionic charge transport. The electronic conductivity of the PANI film in the dry state thus converts to mixed electron–proton conduction in acidic aqueous solutions, electron conductivity being dominant in ordered regions and ionic conductivity in disordered regions separating them. Weakly bound protons are the most important ionic charge carriers hopping along the PANI chains.

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Keywords: polyaniline; conducting polymer; proton conductivity; electron conductivity

INTRODUCTION

Conducting polymers may be electronic or ionic conductors,¹ both types often being regarded as separate groups. Polyaniline (PANI) ranks among the most common and often investigated representatives of the former group.² Some studies suggest that, in addition to electronic conductivity, there is a contribution from ionic conductivity in PANI^{3–10} and this type of conductivity has been associated with the presence of absorbed water in samples.^{6,7} An increase in PANI conductivity with increasing humidity of the ambient atmosphere has often been reported.^{3,4,11–13} It may be anticipated that the potential effect of ionic conductivity will be even more pronounced when a conducting polymer is immersed in a liquid aqueous medium. Several studies suggest that the conductivities of PANI in the dry state and in 'wet' samples after immersion in an aqueous medium are different, the latter always being the higher.^{3,14,15} Indeed, many applications use PANI in aqueous solutions: ion-selective analytical electrodes,^{16,17} electrodes in batteries^{6,7,18} or supercapacitors,¹⁹ electrode materials for electrocatalysis¹⁰ and fuel cells,^{20–22} sensors,²³ electronic devices,^{24,25} corrosion protection,^{26–28} and biomedical engineering²⁹ may serve as examples.

It is usually intuitively assumed that the conductivity of PANI determined in the 'dry' state at ambient atmosphere is a parameter characterizing this polymer. On second thoughts, realizing that the conductivity of PANI may have mixed electronic and ionic

character,^{5,10} the question as to whether this parameter is the same in the dry state and when in contact with aqueous media is pertinent. The charge carriers in PANI salts providing electronic transport are represented by polarons which are produced due to the redistribution of electrons after the reaction of an acid molecule with the imine nitrogen in the PANI base.² The fact that PANI salts are ionic compounds which may dissociate in aqueous media, however, also has to be considered.

The analysis of the mechanism of conduction in PANI has shown that the supramolecular PANI structure is not homogeneous. PANI was proposed, and indeed proved, to be composed of conducting islands embedded in a matrix of low conductivity. The conducting regions are crystalline^{30–35} or comprise highly ordered chains.^{36,37} The overall conductivity is determined by

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the barriers between islands and matrix,³⁸ which have low conductivity due to chain disorder^{31,36} or to a reduced degree of protonation or oxidation.^{3,14,15} The classical concept of metallic conducting islands separated by non-conducting regions is well known from the literature on PANI^{31,39–43} and explains many features of conducting polymers, such as field effect in transistors,¹⁹ ageing,^{41,44,45} dielectric properties⁴⁶ and dynamics of spin relaxation.⁴⁷ The validity of this model has recently been supported both by theoretical calculations⁴⁸ and the direct microscopic observation of conducting islands.³⁵

The present contribution is an attempt to illustrate the effect of an acidic aqueous medium on the conductivity of thin *in situ* polymerized PANI films.^{49,50} It is proposed that the penetration of PANI by an acid solution reduces the barrier resistance between metallic conducting islands due to enhanced proton transport in disordered regions and, consequently, increases the overall conductivity of PANI films.

EXPERIMENTAL

PANI films and their conductivity

Two gold parallel strip electrodes ($5 \times 25 \text{ mm}^2$) were deposited on a $25 \times 25 \text{ mm}^2$ corundum ceramic plate. A PANI film was grown *in situ* over the electrodes and a 15 mm gap between them during the oxidation of 0.2 mol L^{-1} aniline hydrochloride with 0.25 mol L^{-1} ammonium peroxydisulfate started at 20°C .⁴⁹ The supports were well rinsed with 0.1 mol L^{-1} sulfuric acid to remove any adhering precipitate, and the resulting films of PANI sulfate were dried in air. Such films have similarly been deposited on other substrates, such as silicon windows or polystyrene, as needed by specific methods of characterization.

The resistance of the dry ceramic support, R_0 , was first checked (Fig. 1(a)) using a Keithley K6517 electrometer. Its high value, $>0.1 \text{ T}\Omega$, made it possible to neglect its effect on further conductivity measurements. A specified volume of an aqueous acid solution was poured over a ceramic plate placed in a Petri dish (Fig. 1(b)),

and the resistance of the acid solution, R_A , was determined. The same procedure was followed with a ceramic plate holding a PANI film. The resistance of a dry PANI film, $R_{P(\text{dry})}$, was recorded at ambient atmosphere at first (Fig. 1(c)), followed by the resistance, R_{P+A} , in the presence of the same volume of acid solution (Fig. 1(d)) as with the blank ceramic plate. Resistance readings were taken at various acid concentrations, $0\text{--}5 \text{ mol L}^{-1}$, and various voltages, $U = 0.01\text{--}1 \text{ V}$, each being recorded for at least 60 s. The polarity was switched *ca* 3.3 times per second to reduce polarization effects.

Characterization of films

UV-visible spectra were recorded in 1 cm polystyrene spectrophotometric cells with a Lambda 20 spectrometer (Perkin Elmer, UK). The reaction mixture was left to polymerize directly in the cells; the interior was rinsed repeatedly with 0.1 mol L^{-1} sulfuric acid to remove PANI precipitate, leaving PANI films deposited on the cell walls. The spectra of films immersed in 0.1 mol L^{-1} sulfuric acid and of dry films were recorded, a cell without films being used as a reference.

Raman spectra excited with a HeNe laser (633 nm) were collected with a Renishaw inVia Reflex Raman microscope. A research-grade Leica DM LM microscope with an objective magnification $\times 50$ was used to focus the laser beam on the sample placed on an X–Y motorized sample stage. The scattered light was analysed using a spectrograph with a holographic grating of 1800 lines mm^{-1} . A Peltier-cooled CCD detector (576×384 pixels) registered the dispersed light. To avoid degradation of the films by the laser beam, reduced power was always used.

RESULTS

Resistances

PANI film immersed in acid solution has an experimentally determined resistance R_{P+A} . It is composed of two parallel resistors, a PANI film and an aqueous medium (Fig. 1), having

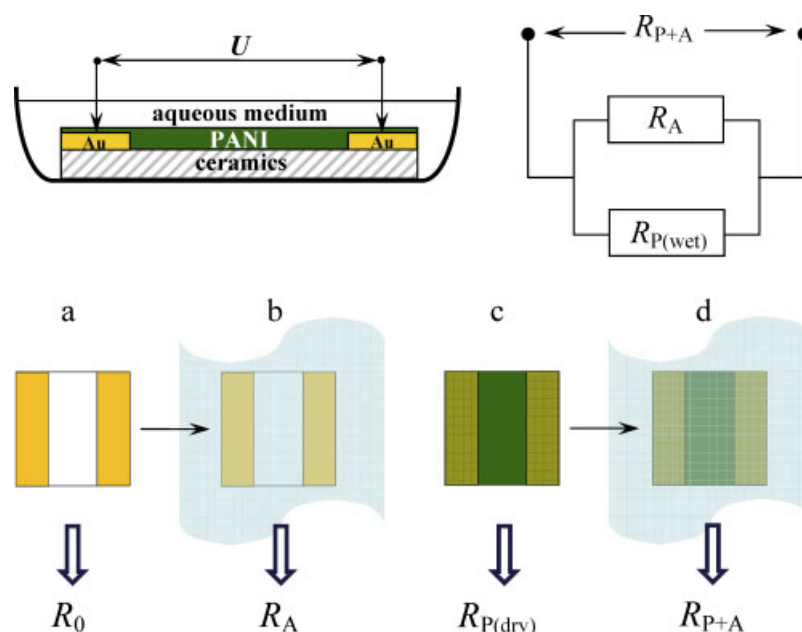


Figure 1. Setup for the conductivity measurements: The ceramic support with two gold electrodes and (a) without or (c) with a deposited PANI film was (b, d) immersed in an aqueous medium, and the resistance between the electrodes was measured at voltage U . For explanations of symbols, see text.

the individual resistances $R_{P(\text{wet})}$ and R_A , respectively. The PANI film has a thickness of about 100 nm,^{49,50} and the solution of sulfuric acid made the layer 0.5 cm in thickness. The resistance of the acid solution R_A is known from separate measurements in the absence of PANI film, and the resistance of immersed PANI film, $R_{P(\text{wet})}$, can be calculated by using, to a first approximation, the relation for two parallel resistors: $1/R_{P(\text{wet})} = 1/R_{P+A} - 1/R_A$. The present experiment should answer the question as to whether the conductivities of PANI films in the dry state, $R_{P(\text{dry})}$, and when immersed in acid solution, $R_{P(\text{wet})}$, are the same, or not. Let us consider an example. The resistance of dry PANI film is 11 170 Ω and the resistance of 1 mol L⁻¹ sulfuric acid in the given experimental setup (Fig. 1) is 21 700 Ω . The combination of these two parallel resistors should yield 7380 Ω , but experiment gives 8.40 Ω (Table 1), a value lower than expected by three orders of magnitude. The relative change in the conductivity of the PANI film after immersion is given by the ratio $\sigma_{P(\text{wet})}/\sigma_{P(\text{dry})} = R_{P(\text{dry})}/R_{P(\text{wet})}$. These values are higher than unity (Table 1), suggesting that the conductivity of the immersed PANI film is higher than the conductivity of the dry film. A similar increase in the conductivity by two orders of magnitude was mentioned in the literature for a compact PANI sample after equilibration with a medium having a pH of 3.5,³ and also in the testing of PANI dispersions.⁵¹

The accumulation of data is illustrated for 0.001 mol L⁻¹ sulfuric acid in Fig. 2. The resistances were recorded for some time until a steady response was obtained; the resistance was then taken as an average of readings taken over 60 s intervals. The resistance of the system composed of PANI film in acid solution is always lower than those of dry PANI film and acid solution alone (Fig. 2). This difference becomes more obvious at higher acid concentrations (Table 1).

When looking at the time dependences in detail (insets in Fig. 2), it can be seen that the resistances measured at various levels of polarity of voltage are somewhat different. For electronic conductors, such as gold, this difference should be negligible. With dry PANI films these changes represent 0.14% of the overall resistance, in good accord with the concept of electronic conductivity in dry PANI. For the acid solution, an ionic conductor, this difference is higher, e.g. 1.06% for 0.001 mol L⁻¹ sulfuric acid, due to concentration gradients caused by relatively slow migration of ions to the electrodes. For PANI film immersed

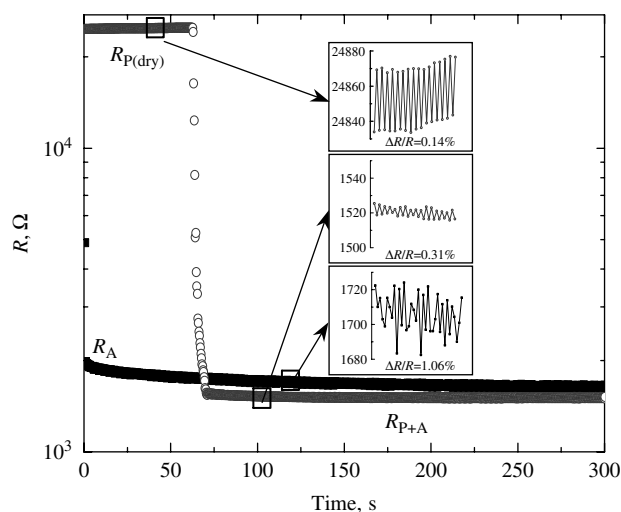


Figure 2. Time dependences of the resistances measured in 0.001 mol L⁻¹ sulfuric acid at $U = 1$ V. Insets illustrate the details. For explanations of symbols, see text.

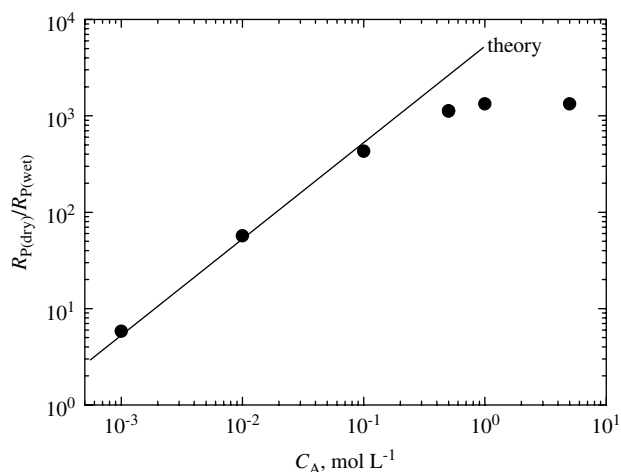


Figure 3. Dependence of the 'wet-to-dry' conductivity ratio of PANI film, $\sigma_{P(\text{wet})}/\sigma_{P(\text{dry})} = R_{P(\text{dry})}/R_{P(\text{wet})}$, on the molar concentration of sulfuric acid, C_A , used for immersion. Measured at $U = 0.1$ V. The straight line has a slope equal to unity.

C_A (mol L ⁻¹)	R_A (Ω)	R_{P+A} (Ω)	$R_{P(\text{wet})}$ (Ω)	$R_{P(\text{dry})}/R_{P(\text{wet})}$
0	1.21×10^6	2 274	2 740	4.07
0.001	78 300	1 540	1 920	5.83
0.01	21 300	195	197	56.8
0.1	20 000	25.9	25.9	429
0.5	23 200	9.92	9.92	1 130
1	21 700	8.40	8.40	1 330
5	122 000	8.39	8.39	1 330

^a Concentration of sulfuric acid, C_A ; resistance of acid solution, R_A ; resistance of the system composed of PANI film immersed in the acid solution, R_{P+A} ; subsequently calculated resistance of PANI film immersed in acid solution, $R_{P(\text{wet})}$; ratio of conductivities of PANI film immersed in acid solution to that in the dry state, $\sigma_{P(\text{wet})}/\sigma_{P(\text{dry})} = R_{P(\text{dry})}/R_{P(\text{wet})}$. The conductivity of a dry PANI film used in these experiments was $R_{P(\text{dry})} = 11\,170 \pm 97$ Ω . Measured at $U = 0.1$ V.

in acid solution, the difference between the resistivity taken at various polarities is 0.31%. This could be interpreted, apart from polarization effects, as an indication of the mixed conductivity of this system, based on both the electronic and ionic types of charge transport.

Acid concentration

The 'wet-to-dry' conductivity ratio, i.e. the conductivity of the PANI film immersed in a solution of sulfuric acid with respect to dry state, increases with increasing acid concentration at low acid contents, approximately in a linear manner when plotted on a double logarithmic scale (Fig. 3). In 1 mol L⁻¹ sulfuric acid, the conductivity of immersed PANI films is more than 1300 times higher (Table 1) compared with the dry state. The conductivity of dry PANI film is typically 2.60 S cm⁻¹.⁴⁹ This means that the conductivity observed in the present case would be 3380 S cm⁻¹.

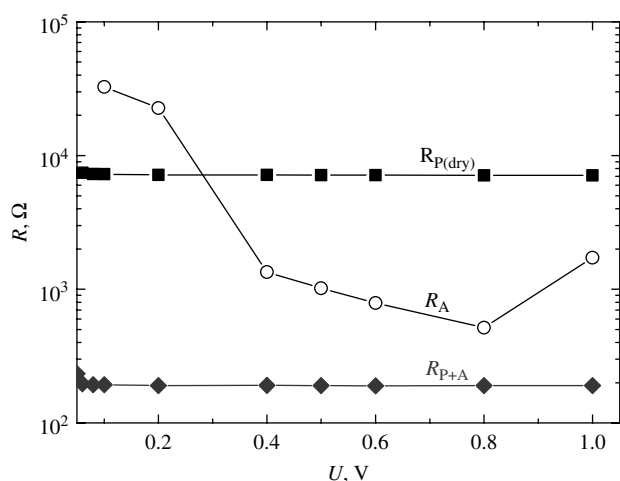


Figure 4. Resistances of dry PANI film, $R_{P(dry)}$ (squares), 0.01 mol L⁻¹ sulfuric acid, R_A (circles), and PANI film in 0.01 mol L⁻¹ sulfuric acid, R_{P+A} (diamonds), determined at various voltages, U .

Voltage

The resistance of dry PANI film is independent of voltage in the tested interval of $U = 0.05\text{--}1$ V (Fig. 4), in accordance with results published in the literature.^{51,52} For the 0.01 mol L⁻¹ sulfuric acid solution, there is a marked decrease in the resistance on increasing the voltage in the low-voltage region. The resistance of PANI film immersed in the acid solution is again virtually independent of the applied voltage.

In addition to dibasic sulfuric acid, the dependences of conductivity enhancement on applied voltage were also tested for monobasic hydrochloric acid and tribasic phosphoric acid (Fig. 5), to check the potential influence of the number of protons afforded by these acids. The results show that the increase in conductivity is less for the tribasic phosphoric acid and comparable for the other two acids (Fig. 5). This is due to the fact that phosphoric acid is weaker than the other two acids. As discussed below, the enhancement of conductivity is thus controlled entirely by the concentration of protons, i.e. by pH, and not by the number of protons associated with a molecule of the individual acid.

DISCUSSION

The conductivity of PANI film immersed in acid solution is considerably higher than that when the film is dry. The observed conductivity of PANI film in 1 mol L⁻¹ sulfuric acid exceeds 10³ S cm⁻¹. The specific conductivity of dry PANI films is only of the order of a few siemens per centimetre.^{2,49,53} A 1 mol L⁻¹ solution of sulfuric acid has an ionic conductivity of 0.36 S cm⁻¹ at 18 °C.⁵⁴ The high conductivity of PANI films thus cannot be explained by the simple combination of the electronic and ionic conductivities of the components¹³ (Table 1). Other concepts based on the intrinsic parameters of PANI film, e.g. its molecular structure or supramolecular chain arrangement, have to be sought.

Molecular structure of PANI in the dry state and in acid solution

Dry protonated PANI (Fig. 6) is green. After immersion in solutions of sulfuric acid, the colour of the film does not change. UV-visible spectra of PANI films determined both in the dry state and when immersed in sulfuric acid are similar to each other, as expected (Fig. 7). The apparent lower absorption of the dry film is caused

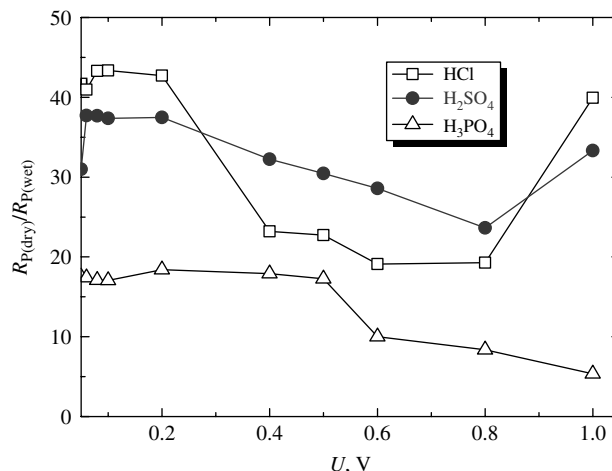


Figure 5. Dependence of the 'wet-to-dry' conductivity ratio of PANI film, $\sigma_{P(wet)}/\sigma_{P(dry)} = R_{P(dry)}/R_{P(wet)}$, immersed in 0.01 mol L⁻¹ solutions of hydrochloric acid (squares), sulfuric acid (circles) or phosphoric acid (triangles) on voltage, U .

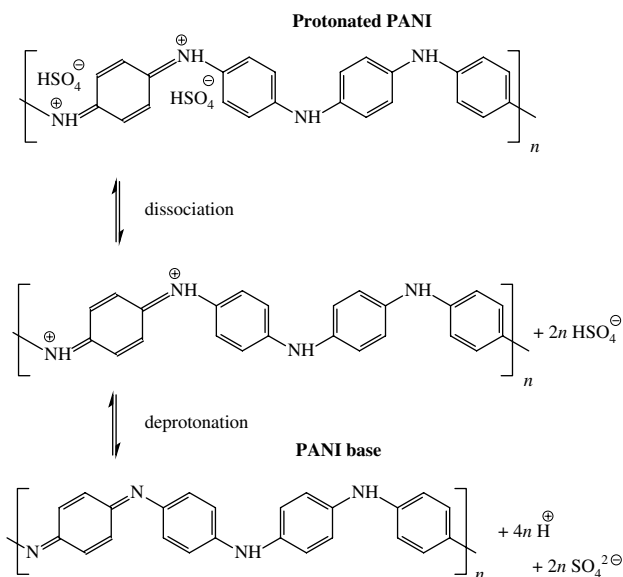


Figure 6. Protonated PANI dissociates in acidic aqueous media. In neutral or alkaline media, the whole acid molecule is separated and the PANI base is produced after deprotonation.

by different reflection of the light beam on the immersed PANI film interface and by the reflection on the solution surface. The position of the absorption maximum at 810 nm remains virtually unchanged. This means that (a) the molecular structure of PANI chains and their conformation have not changed and (b) PANI remains protonated in the acid solution as in the dry state.

Additional evidence is provided by Raman spectroscopy. The Raman spectrum of dry PANI film (Fig. 8(a)) has been described previously.⁵⁵ It exhibits a sharp peak at 1623 cm⁻¹ assigned to the C–C stretching of the benzenoid ring of the protonated form. When the film is immersed in 0.1 mol L⁻¹ sulfuric acid (Fig. 8(c)), the intensity of this peak is lower, but no other apparent changes are observed. After drying the film, its spectrum (Fig. 8(b)) is identical to that of the original film (Fig. 8(a)). The spectrum of completely

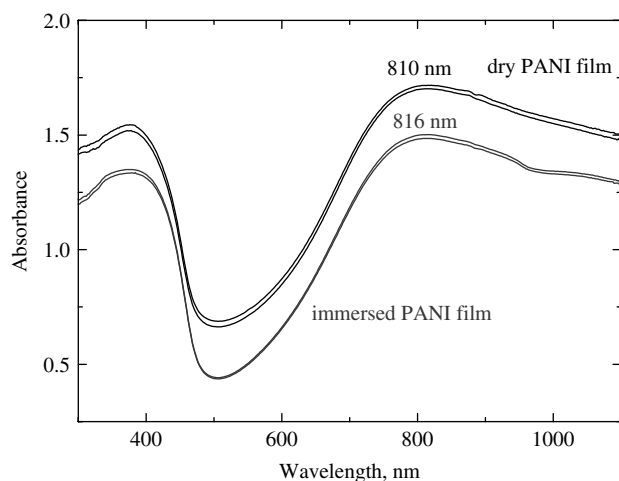


Figure 7. UV-visible spectra of dry PANI film and of the same film immersed in 0.1 mol L⁻¹ sulfuric acid. Two independent preparations and measurements.

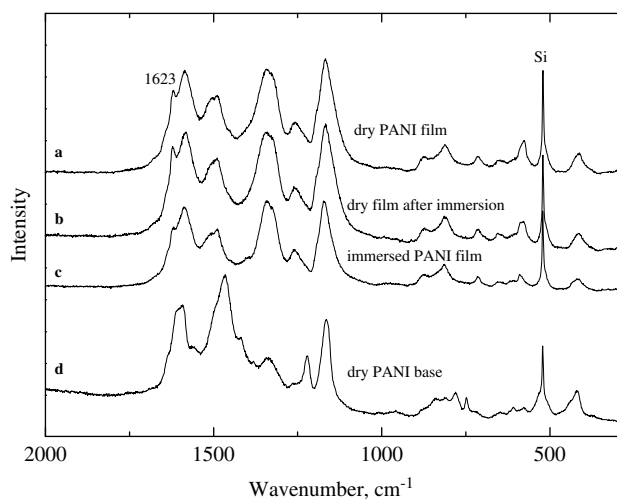


Figure 8. Raman spectra of (a) dry PANI film produced *in situ* on a silicon support, (b) the same film after immersion in 0.1 mol L⁻¹ sulfuric acid and drying, (c) the film immersed in 0.1 mol L⁻¹ sulfuric acid and (d) the dry film of PANI base on a silicon support. Excitation wavelength was 633 nm.

deprotonated film of PANI base (Fig. 8(d)) differs substantially from the spectrum of the immersed film.

We conclude that the molecular structure of PANI chains in the dry state and when immersed in acid solution is the same, except for the localization of counter-ions, which are associated with PANI chains in the former case and may be dissociated in the latter. The differences in the conductivity thus cannot be explained in terms of the molecular structure, and a model based on the supramolecular structure has to be proposed.

PANI as a mixed electron and proton conductor

The conducting form of PANI, an emeraldine salt, is a salt of a weak PANI base with a strong acid, such as sulfuric acid (Fig. 6). The acid protons react with the imine nitrogens and the resulting positive charges on the nitrogen atoms are balanced by negatively charged counter-ions (Fig. 6). The electrons in the protonated PANI structure may become delocalized to produce polarons, which are the charge carriers responsible for the electronic conductivity of

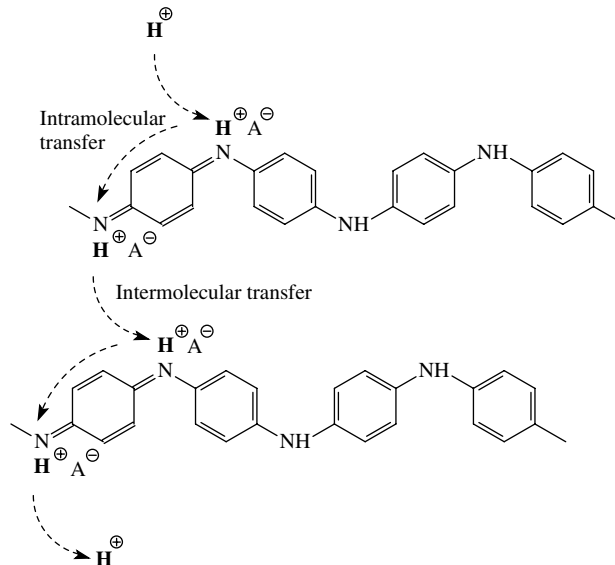


Figure 9. Model of proton conductivity in PANI.

PANI.² At the same time, the chemical structure of a protonated imine site in PANI represents a typical proton-conducting unit.^{56,57} The proton is involved in two types of bonding: a stronger bonding with a nitrogen atom as electron donor and a weaker bonding with an acid anion as acceptor (Fig. 9). This is the typical case of asymmetric hydrogen bonds^{56–58} which participate in proton conductivity. The bonding between protons and imine nitrogens has a non-covalent character, and such protons have been classified as ‘free’ protons.^{59,60}

In the dry state, the acid molecules are firmly associated with PANI chains, and they cannot contribute to potential ionic conductivity. In aqueous media, the acid constituting a PANI salt dissociates. In solutions of acids, protons remain weakly associated with the PANI backbone, and only the counter-ions are released into the aqueous medium (Fig. 6). A high concentration of free protons in the acidic medium suppresses the separation of protons from imine nitrogens, and the PANI remains protonated. In such a case, the weakly bound protons may hop and skip along the PANI structure (Fig. 9). The role of water is not that of a charge-transport medium; the presence of water is needed for reducing the non-covalent bonding of protons to imine nitrogens, thus making them available as charge carriers. Intramolecular, as well as intermolecular, charge transports are possible. The PANI film acts as a macroscopic transport medium, with protons as the charge carriers. This concept resembles the Grotthuss mechanism of proton conductivity in aqueous media,^{56,57} in which the water molecules associated with protons do not migrate with them but are gradually replaced in the proton vicinity by new molecules, only the role of water molecules is taken over by the constitutional PANI units (Fig. 9).

In pure water, whole acid molecules separate from the PANI chains and deprotonation to PANI base takes place (Fig. 6). This is reflected by the conversion of colour from green to blue. Electron and proton charge carriers in PANI disappear, so the PANI converts to a non-conducting form. Only the conductivity afforded by liberated acid may be observed in the surrounding medium. It is marginal due to the low concentration of protons and their solvation, which restricts their mobility.^{56–58}

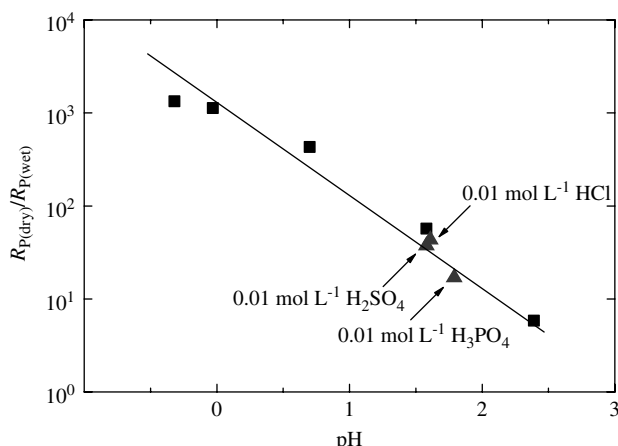


Figure 10. Dependence of the 'wet-to-dry' conductivity ratio of PANI film, $\sigma_{P(wet)}/\sigma_{P(dry)} = R_{P(dry)}/R_{P(wet)}$, on the pH of solutions of sulfuric acid (squares; cf. Fig. 3) and of 0.01 mol L⁻¹ solutions of various acids (triangles) used for immersion. Measured at $U = 0.1$ V. The line has a slope $d[\log(R_{P(dry)}/R_{P(wet)})]/d(pH) = -1$.

The electronic conductivity in PANI salt is always associated with the protonation of PANI, and it depends on the degree of protonation.^{38,61} Mixed electron and proton conductivity or electron-ion coupled charge transports have been discussed in the literature in connection with PANI.^{3,62–64} Due to their high mobility, protons are the dominating ionic charge carriers in any ionic transport in PANI involving strong acids.⁶⁵ For that reason, we prefer to talk about the proton conductivity component^{56,57} in the case of PANI, rather than of more general ionic conductivity, even though both types are always operative simultaneously.

Experimental support for proton conductivity

The role of protons becomes obvious when the conductivity enhancement is plotted against the concentration of sulfuric acid (Fig. 3). To a first approximation, a strong acid such as sulfuric acid may be regarded as completely dissociated in dilute aqueous solutions. The concentration of protons is thus proportional to the acid concentration, $[H^+] = 2C_A$. By recalling the fundamental formula $\sigma = \sum_i n_i \mu_i e$, where the conductivity σ is proportional to the number of charge carriers of type i , n_i , their mobility, μ_i , and the electron charge, e , the number of charge carriers represented by protons is proportional to the proton concentration, $n \sim [H^+] \sim C_A$. Consequently, if protons were charge carriers responsible for conductivity increase and their mobility about constant, a direct proportionality between the logarithm of the conductivity increase, $\log(\sigma_{P(wet)}/\sigma_{P(dry)})$, and the logarithm of the acid concentration, $\log C_A$, having a slope equal to unity, should be observed. This is indeed the case (Fig. 3), and the deviations observed at high acid concentrations can be assigned to incomplete acid dissociation under such conditions.⁶⁶ The conductivity enhancement plotted against pH can be approximated by a straight line (Fig. 10), i.e. such an enhancement is directly proportional to the concentration of protons. If we accept that the fundamental conductivity of PANI is of an electronic nature, then the conductivity increase in solutions of acids is controlled by the protons as ionic charge carriers in PANI.

Conducting islands

It is well known that PANI has a heterogeneous supramolecular structure. The polymer consists of highly conducting regions ('metallic' islands) distributed in a disordered conducting matrix of low conductivity. The conductivity of the metallic islands is expected to be much higher than 10^2 S cm⁻¹,³⁸ and has even been estimated as $ca 10^7$ S cm⁻¹.⁴⁶ The disordered regions constitute barriers and limit the overall conductivity of the material to the observed values of 10^0 S cm⁻¹. If the barriers represented by disordered regions are penetrated by acid solution, they start to be conducting *via* a proton mechanism. Charge transport through them becomes possible, and the overall conductivity of the system increases as a consequence. Neither the molecular structure of PANI nor the mechanism of electronic conduction in the metallic regions changes, only the charge transport between conducting regions assisted by protons is enhanced. This explains why the conductivity increases after the immersion of PANI films in acid solutions. It is not clear, however, if the increased charge transport in disordered regions is of mainly ionic type or if an enhancement of the electronic conductivity is also involved.

In spite of the vast literature on the interpretation of electrical properties in terms of the metallic island model, there are practically no papers explaining *why* such a structure should be present in PANI. It has recently been proposed that hydrophobic phenazine-containing oligomers are generated in the early stages of aniline oxidation⁶⁷ and they strongly agglomerate into nucleates.⁶⁸ The nucleates initiate the subsequent polymer chain growth.^{67,68} When the aggregation of nucleates is random, the star-burst growth of PANI chains takes place. Near the centre of the nucleate, the chains are relatively ordered due to the limited space available and the structure is stabilized by hydrogen bonds and ionic interactions. This ordered structure can be identified with a metallic island. At the peripheries of the grown particles, the ordering of the chains is less and disordered chains merge together at the particle interfaces. These regions have a poor electronic conductivity. The size of the PANI globular particles and the proportions of ordered cores and disordered shells depend on polymerization conditions.⁶⁸

The globular morphology has been observed using electron microscopy,⁶⁴ and high-resolution transmission electron microscopy has also been used to visualize ordered islands.^{32,35} The size of the conducting islands in PANI was proposed to be 8 nm and the barriers between them 1.6 nm.⁴² Other authors use the term metallic strands,^{41,69} and make them comparable with the chain length, or they specify the size range in tens of nanometres: 20–30 nm,^{14,15} 20–50 nm³² or 20–80 nm.^{38,59} The direct observation of conducting islands in poly(*o*-ethoxyaniline) film by transmission electron microscopy gave 7–47 nm as their size.³⁵ PANI films produced *in situ* during the oxidation of aniline have a similar globular structure,^{49,70} which is rendered well visible using AFM (Fig. 11).

CONCLUSIONS

The conductivity of *in-situ* polymerized PANI films immersed in aqueous solutions of acids may be several orders of magnitude higher than the electronic conductivity in the dry state. The conductivity of a dry PANI film increased more than 1300 times after immersion in 1 mol L⁻¹ sulfuric acid, and reached a value exceeding 3300 S cm⁻¹. The classical concept of highly conducting ordered islands separated by disordered areas is used for the interpretation of this effect.

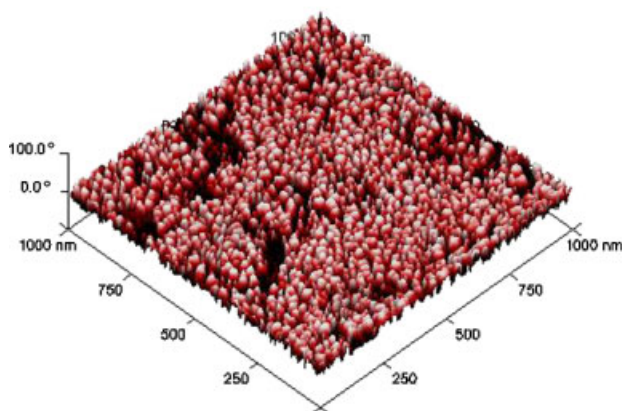
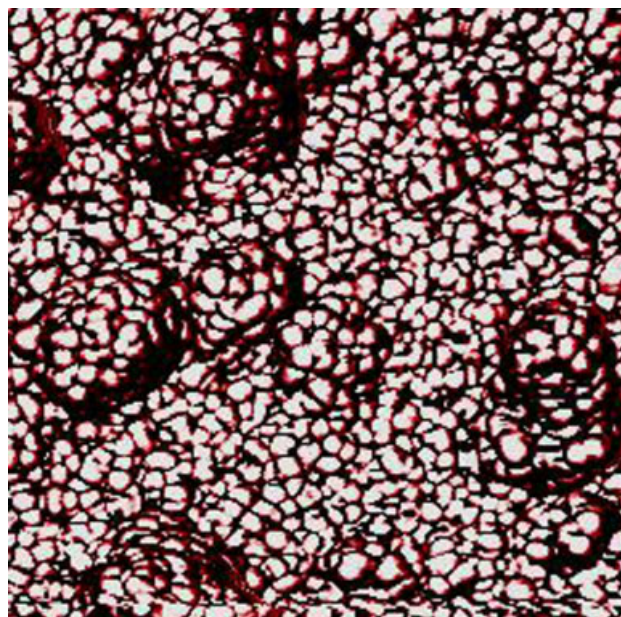


Figure 11. Morphology of PANI film observed using AFM.

In the dry state, ordered electronically conducting islands are separated by disordered less-conducting barriers. The disordered regions become proton-conducting after immersion in acid solutions, the conductivity barriers are reduced and the overall conductivity of the system increases. The proton conductivity in PANI is made possible by weakening the bonding of protons, currently associated with imine nitrogens, in an aqueous medium. The loosely bound protons act as additional carriers in the mixed electron–proton transport of charges. PANI is a heterogeneous material from the structural and, consequently, also from the conductivity point of view. The combination of electronic conductivity in ordered regions with proton conductivity in disordered areas separating them results in the enhancement of the overall conductivity. It is still to be elucidated as to whether the increase in conductivity of disordered regions is of ionic type, or if the electronic conductivity of these regions is also enhanced in the presence of ions.

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