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ON THE NATURE OF THE CONDUCTING STATE OF POLYANILINE

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ABSTRACT

The role of disorder in the polyaniline properties is emphasized. Evidences are given against a true metallic state: the presence of two types of acidic functions is not compatible with a regular periodic lattice ; the spin dynamics behavior reflects incoherent carrier motion. Pulse and CW ESR data are consistent with high spin concentration clusters (conducting islands), and it is concluded that a conducting island just consists of a single conducting polymer chain.

INTRODUCTION

Polyaniline (PANI) has emerged as a particularly interesting and complex material. Actually, the most fascinating property of this compound lies in the Insulator-to-Conductor transition which occurs as a function of the protonation level. Conductivity increases by ten orders of magnitude upon treatment in acidic solution, while the number of electrons on the polymer chains remains constant [1-4]. Furthermore, protonation -i.e. simply addition of protons- results in large increase in spin susceptibility [3,5]. Part of this spin susceptibility has been shown recently to be of Pauli type, giving evidence for finite density of states at the Fermi level [5]. It is thus tempting to describe the conducting behavior of PANI as a metallic state, as proposed by Epstein et al. in terms of a polaron lattice model. However, other data, such as the poor value of the conductivity, its hopping characteristic temperature dependence,

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and the large relative number of Curie spins are evidence for localization, and suggest a Fermi glass [6]. In order to reconcile the hopping features of the conductivity with the idea of a metallic state it has been proposed that instead of homogeneous protonation there exist fully protonated domains (metallic islands) embedded in unprotonated regions (insulating) [5,7]. This picture is consistent with the observation that the Pauli susceptibility is almost proportional to the protonation rate, y. It is also in agreement with a theoretical model considering commensurability effects [8].

In the present work we report recent experimental results and we discuss the nature of the conducting rate.

RESULTS AND DISCUSSION

Spin susceptibility in the conducting state

We first concentrate our attention on the factors which controle the spin susceptibility, χ_s, in the conducting state. The χ_s data are given in Fig.1 as a function of the sample potential versus SCE, in 1M HCl aqueous solution. Data have been obtained using in situ ESR experiments in an electrochemical cell. Measurements have been performed on electrochemical films of different thicknesses, as well as on a sample obtained by chemical polymerization (prepared 1M HCl aqueous solution with $(NH_4)_2S_2O_8$ as oxidant). The general

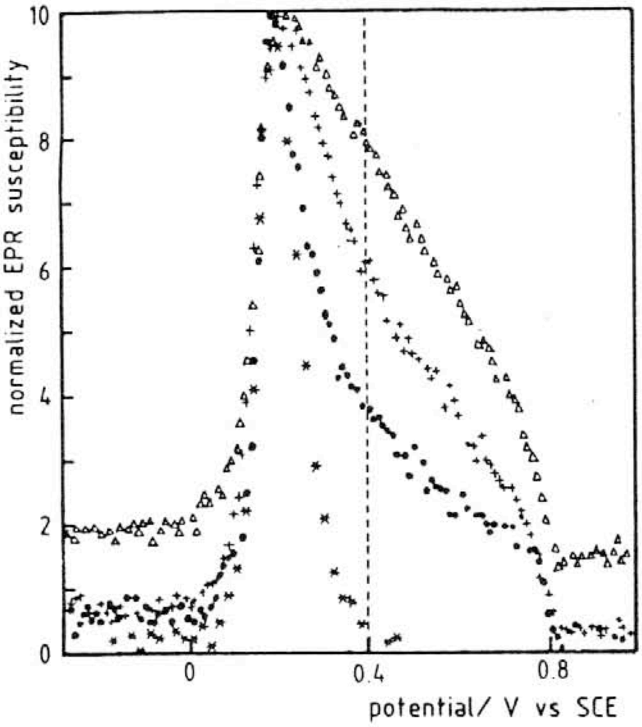


Fig. 1. In situ ESR susceptibility vs potential of electrochemical films of different thicknesses : 1000 A (*), 2000 A (•), 7000 A (+), and chemical powder sample (Δ). The dashed line at 0.4 V indicates the potential of as prepared chemical samples.

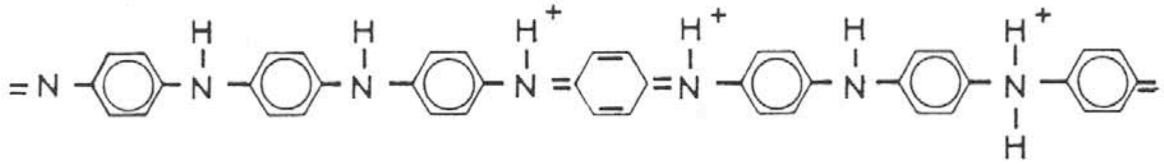
variation of χ_s versus V is similar to the behavior also observed in other conducting polymers. This has been discussed in previous papers and interpreted in terms of polaron and bipolaron populations in thermal equilibrium [9-11]. At high doping level this model should be improved to take into account band formation, at least in the case of PANI, as evidenced by the presence of Pauli susceptibility (χ_p). However, considering the decay of χ_s with increasing V in the high doping region, it seems that the conclusion that only bipolarons remain at full charge should be still valid. This statement is not in agreement with the polaron lattice model. We note that theoretical studies support the polaron lattice model [12], while another one concludes in favor of bipolaron formation [13]. The χ_s data usually reported in literature refer to chemical samples, for which a potential of 0.35 to 0.4 V vs SCE is measured. Although the χ_s data from different authors are generally in good agreement, it appears that χ_s can vary in a large extent :

a) As a function of the potential. Among others for the chemical samples χ_s can be lowered well below the as-prepared sample value if one completes the oxidation by increasing the potential above 0.4 V. This result gives evidence that the χ_s data usually considered for oxidized PANI are not an intrinsic value.

b) With the sample preparation conditions. Data obtained with electrochemical films are also presented in Fig.1. The films were deposited on a Pt wire by cyclic potential scanning in a solution of aniline in the eutectic mixture NH_4F,2.35 HF. One sees in Fig.1 that for the thinnest film χ_s at 0.4V is very low. Thus, at least in this case, it seems clear that bipolarons are the basic charged species in the oxidized state. Similar results have been reported by other groups [14]. It is noteworthy, as evidenced in Fig.1, that intermediate behaviors between thin electrochemical film and chemical powder are observed as a function of the film thickness. What could be the reason for the difference between chemical and electrochemical samples, and for the film thickness dependence ? We believe that the leading parameter is some kind of disorder in the material. Disorder is expected to be stronger in chemical powder that in electrochemical films. Furthermore, it has been shown that the growth of PANI films during electropolymerization gives rise to fractal surface, which could explain the thickness dependence of the mean disorder [15].

Acidic functions

A study of the acidic functions in PANI has been achieved using titration technique [16]. We, here, summarize the main results. In reduced PANI a well defined acidic function at pK $\simeq$ 3, with concentration per ring $C = 0.25$, is evidenced corresponding to amine groups. In the oxidized state two types of acidic functions are present : one type at pK around 6 ($C = 0.32$) corresponds to imine groups, as expected. But in addition acidic functions of amine type (pK $\simeq$ 3, $C = 0.14$) are still present. An estimate shows that about 25% of the amine groups can have two protons : $-NH_2^+-$. The PANI structure in the conducting state can be represented as follows :



The doubly protonated nitrogen sites, which appear for pH < 3, can be thought either as regularly spaced in a superlattice, and then opening a gap at the Fermi level, or randomly distributed, and then introducing disorder. In both cases their presence is not consistent with the proposed structure for a polaron lattice.

Conductivity and magnetism versus protonation

The dc conductivity (σ), and χ_s of chemical PANI samples equilibrated in HCl aqueous solutions of different pH are shown in Fig.2 a) and b), respectively.

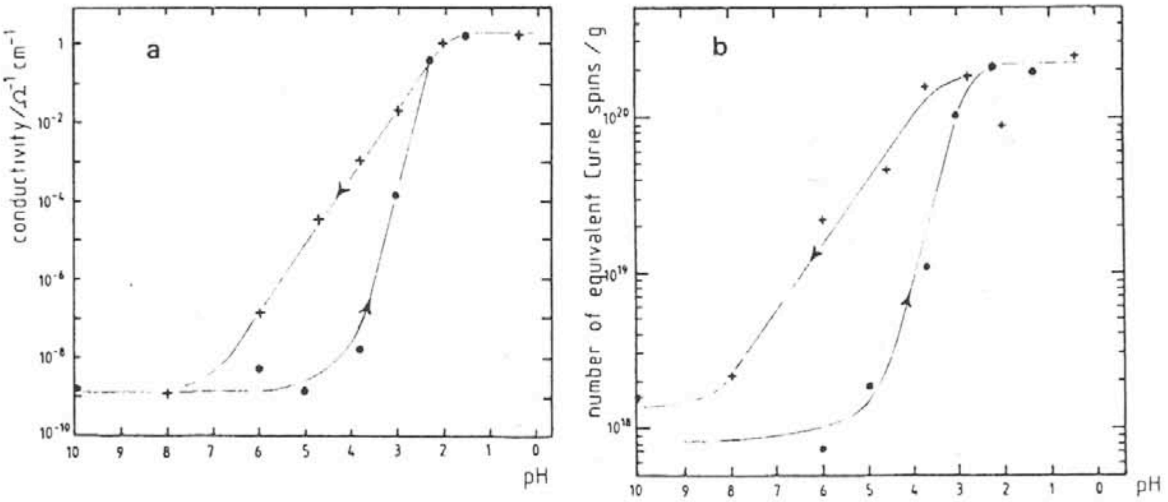


Fig. 2. Conductivity (a), and susceptibility (b) of PANI vs (•) decreasing, and (+) increasing equilibration pH

Equilibration times as long as 40 hours have been used. We notice a clear hysteresis effect, depending on whether the pH has been obtained from increasing, or decreasing values. However, if they are plotted as a function of **y** the data superpose, which indicates that the hysteresis concerns the protonation process itself. The protonation rate is, thus, the relevant parameter.

In Fig.3, σ and spin susceptibility (Pauli : χ_p, Curie : χ_c) are given as a function of **y**. Measurements have been performed with a SQUID susceptometer. A linear scale has been chosen for σ, instead of the log plot usually used.

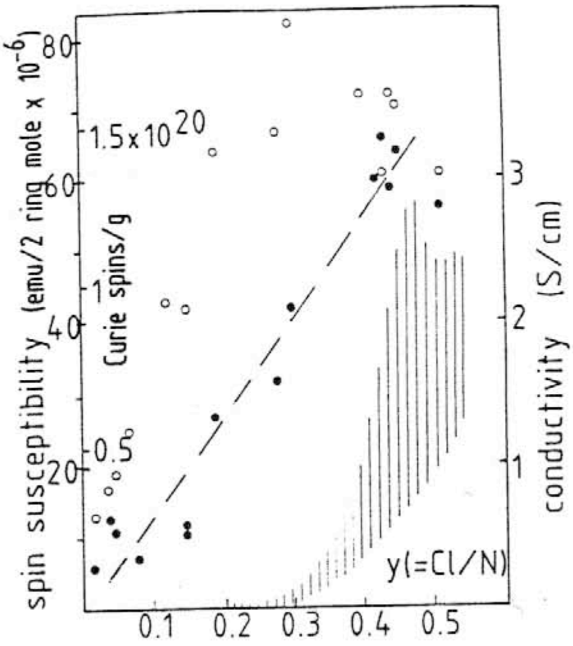


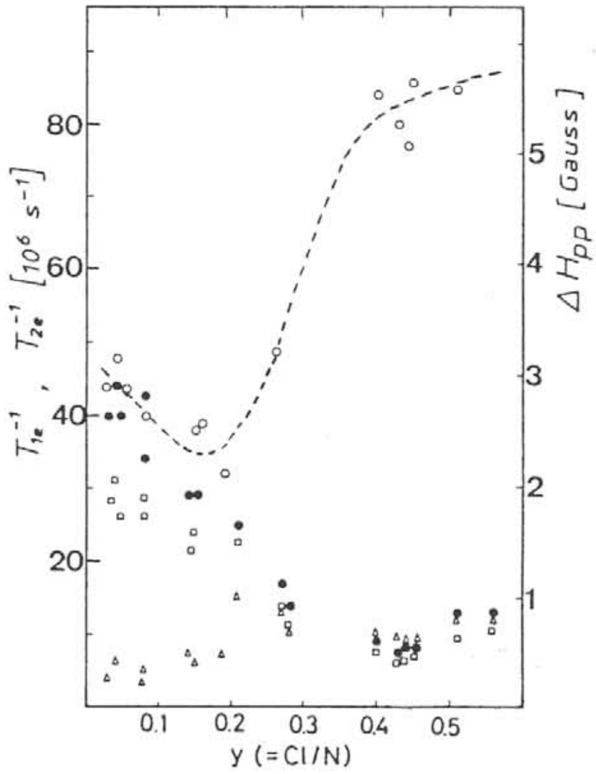
Fig. 3. Susceptibility as measured by SQUID : Pauli (•), and Curie (○), as a function of the protonation rate. The conductivity vs protonation rate is represented by a hachured area to take into account the large spread in the data.

Taking into account the large spread of the data, the σ variation is represented by a hachured area. The advantage of the linear plot is to make apparent a percolation like behavior of conductivity, with a percolation threshold around $\mathbf{y} = 0.3$, which corresponds to $p_c \simeq 0.6$ for the conducting volume ratio. The data for χ_p are consistent with a linear variation, as already reported by Epstein et al. [5]. The striking point is the absence of any sudden change of χ_p and χ_c, when crossing the Insulator-to-Conductor transition. This can be explained by non homogeneous protonation, giving rise to conducting islands (clusters) embedded in an insulating sea. Further evidences for this picture are supplied by the spin dynamics data.

Spin dynamics versus protonation

An analysis of the spin dynamics in the conducting state is presented in another contribution to this conference [17]. Here, we concentrate our attention on the evolution of the spin dynamics as a function of the protonation level.

Firstly, we analyze the vacuum sealed sample data of Fig.4. The spin spin (T_{2e}^{-1}), and spin lattice (T_{1e}^{-1}) relaxation rates, are given versus $\mathbf{y}$. They have been measured by pulse ESR. These two relaxation rates probe the electronic spin motion spectrum, $f(\omega)$. With T_{1e}^{-1} the motion is probed at the Larmor frequency, ω_e, while T_{2e}^{-1} also includes contribution at zero frequency. At high $\mathbf{y}$ a narrow line is observed, and one has $T_{1e}^{-1} = T_{2e}^{-1}$. This is evidence for strong



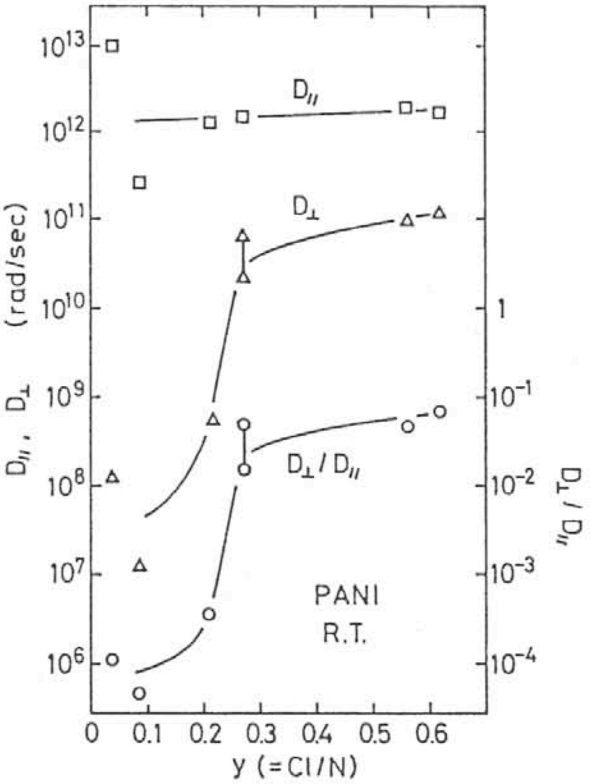


Fig. 4. X band ESR linewidth for sealed under vacuum (●) and opened to air (○) PANI samples ; inverse spin-spin relaxation time : T_{2e}^{-1} *(□) and inverse spin-lattice relaxation :* T_{1e}^{-1} *(△) for sealed under vacuum samples, as a function of the protonation rate. The relaxation times* T_{1e} *and* T_{2e} *have been measured by pulse ESR.*

Fig. 5. Parallel (□), transverse (△) spin diffusion rates, and motion anisotropy : $D_{\perp}/D_{/\!/}$ *(○) as a function of the protonation rate. The diffusion rates* $D_{/\!/}$ *and* $D_{\perp}$ *have been determined from measurements of the proton relaxation time* T_1 *as a function of the frequency.*

motional narrowing and for $f(\omega_e) = f(0)$. For **y** < 0.3 the linewidth (T_{2e}^{-1}) increases with decreasing **y**, while T_{1e} remains roughly the same, so that one has $T_{2e}^{-1} \gg T_{1e}^{-1}$ at low **y**. The linewidth is not originated in hyperfine interactions (no change of ΔH on deuteriation), nor in *g* anisotropy (no decrease of ΔH at low fields). Thus we can state that at low **y** the spin spin interactions are still responsible for the linewidth, which is evidence for high spin concentration clusters. Furthermore one has $f(0) \gg f(\omega_e)$, which is typical of low dimensional behavior, with a very low cutoff frequency : $\omega_c \ll \omega_e$. Thus, for isolated clusters we deduce low dimensional motion with very weak inter-chain coupling. These results are in complete agreement with those obtained from the T_1 NMR data, which evidence one dimensional motions both in high and low **y** regions [17]. The motion is highly anisotropic in the low y region ($D_{/\!/}/D_{\perp} \simeq 10^4$), and the anisotropy drops by more than 2 orders of magnitude for y near the percolation crossover, as shown in Fig.5. Then, we have to face the following puzzling question. How can the inter-cluster interactions be more efficient in lowering the anisotropy than the inter-chain interactions ? This problem can be explained easily if we admit that *a given spin cluster is just composed of a single magnetic chain.* We note that this statement is consistent with the thermodynamic arguments for the existence of fully protonated areas.

We now comment on the data of the opened to air samples. At low y the linewidths are about the same as for the vacuum sealed samples, but a dramatic increase occurs around $y = 0.3$. This can be explained as follows. Line broadning upon air contamination is due to a drastic shortening of T_{1e} by paramagnetic oxygen collisions. At low y only the surface clusters are affected. For y above percolation the short T_{1e} of the surface spins is rapidly transmitted to the bulk. Then, the effect on the linewidth is observed.

Finally, we discuss the nature of the conducting state to the light of the spin dynamics features. From the value found for the diffusion rate ($D_{/\!/} \simeq 2.10^{12}$ rad/s) we estimate the conductivity $\sigma = n_c e^2 D_{/\!/} c^2/kT$, where n_c is the charge carrier number. We assume that for the bipolarons, which are not concerned with spin dynamics, $D_{/\!/}$ is the same, and we take $n_c = 0.4$/ring. One obtains $\sigma = 80$ S/cm. This is just an order of magnitude larger than the measured value. Taking into account that real conduction implies inter-chain hoppings, $D_{/\!/}$ should be replaced by $D_{\perp}$, and good agreement with experiment is obtained. We are, thus, confident that the determined spin dynamics does reflect also the charge motion [18]. Assuming a metallic state, from the density of states at the Fermi level : 1.5 state/eV/ring, and from $D_{/\!/}$ we calculate the carrier mean free path along the chains, l^*. The obtained value : $l^* = 6.10^{-3}$ unit cell distances, is inconsistent with any coherent motion, characteristic of a metallic state. Spin dynamics reflects a motion which is intrinsically incoherent.

CONCLUSIONS

Our data are consistent with the model of fully protonated conducting islands. However, we were led to the conclusion that these conducting islands have very special shape : they are nothing but single conducting polymer chains. Polyaniline presents this unique property to content almost ideally isolated conducting chains. In a given all protonated chain, polarons are formed upon charge injection. At high doping level they tend to combine into bipolarons, but the bipolaron formation is hindered by disorder and/or chain end effects. As shown also by the incoherent nature of the spin dynamics, disorder should be taken into account in the description of the conducting chains.

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