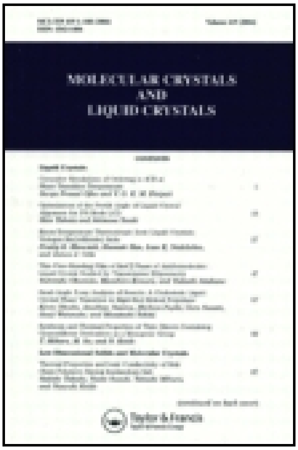

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TRANSPORT AND MAGNETIC RESONANCE STUDIES OF POLYANILINE

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Abstract Conductivity, thermoelectric power, spin concentration and spin dynamics has been measured in polyaniline samples equilibrated at different pH. Data provide evidence for Metal-Insulator transition upon pH variation.

INTRODUCTION

Polyaniline (PANI) obtained by polymerisation of aniline either by chemical or electrochemical methods has been known for many years as an organic conducting compound[1-2]. Very high redox activity of PANI in acidic medium has been reported[3]. Although a definite mechanism of the redox reaction has not yet been established, the importance of proton-exchange processes for redox activity has long been recognized[1]. We report here results showing correlation between the proton exchange processes on one hand, and the transport and magnetic properties of PANI on the other.

SAMPLE PREPARATION

The PANI samples have been obtained by oxidation of aniline by $S_2O_8Na_2$ or $K_2Cr_2O_7$ in sulfuric acid medium and subsequently equilibrated for 18 hours in solutions of a given pH. The final pH value reached by the sample-solution system has been assumed to be the equilibrium pH for the polymer. The samples were washed in acetonitril in a Soxhlet for 12 hours and dried under vacuum. Compressedpowder pellets were prepared for the thermoelectric power (TEP) and the conductivity (σ) measurements.

CONDUCTIVITY

Four-probe conductivity measurements were performed at temperatures varied from 5 to 300 K on PANI samples equilibrated at $0 < pH < 6$. As already reported[1-2] variation of pH has a dramatic effect on σ. For instance, at room temperature, changing pH from 0 to 6 decreases σ by 6 orders of magnitude.

The temperature dependence of σ is well accounted for by the expression for a variable range hopping (VRH) process,

$$\sigma(T) = K_0 \, T^{-1/2} \exp[-(T_0/T)^{1/4}]$$

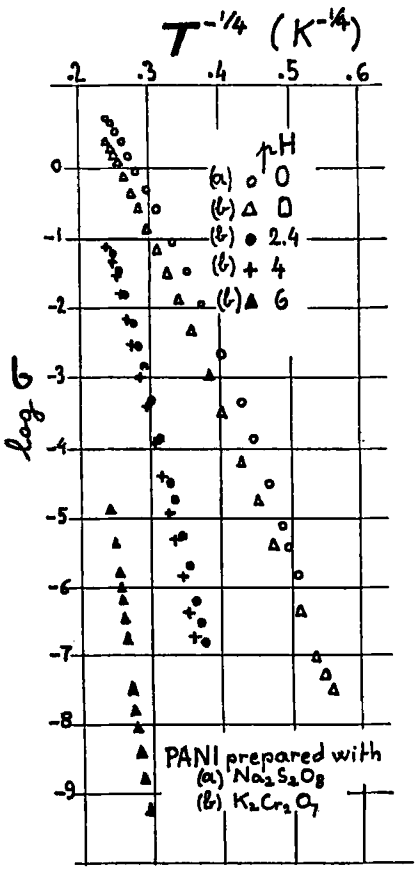

FIGURE 1 Log σ as a function of $T^{-1/4}$ for PANI samples equilibrated at different pH.

pH	0(a)	0(b)	2.4(b)	4(b)	6(b)
T_0/K	1.5×10^7	1.3×10^7	12×10^7	17×10^7	180×10^7
K_0	1.7×10^8	3.1×10^8	2×10^{11}	1.4×10^{12}	1.9×10^{18}

prepared with : (a) $S_2O_8Na_2$; (b) $K_2Cr_2O_7$

The mean square least values for T_0 and K_0 are given in table above for samples prepared at different pH.

In principle the density of states at the Fermi level $\eta(E_F)$, and the electron localization length α^{-1} can be derived from T_0 or $K_0{}^4$. It is expected that changing pH would mainly affect $\eta(E_F)$. However, using the Mott's expression for σ in VRH and assuming that only $\eta(E_F)$ is pH dependent, opposite variation of $\eta(E_F)$ as a function of pH is obtained depending whether the latter is derived from T_0 or from K_0. Thus, inspite of the fact that the equation accounts well for the data, providing evidence that the VRH is a basic conduction process in PANI, a satisfactory quantitative description of conductivity has not yet been achieved.

THERMOELECTRIC POWER (TEP)

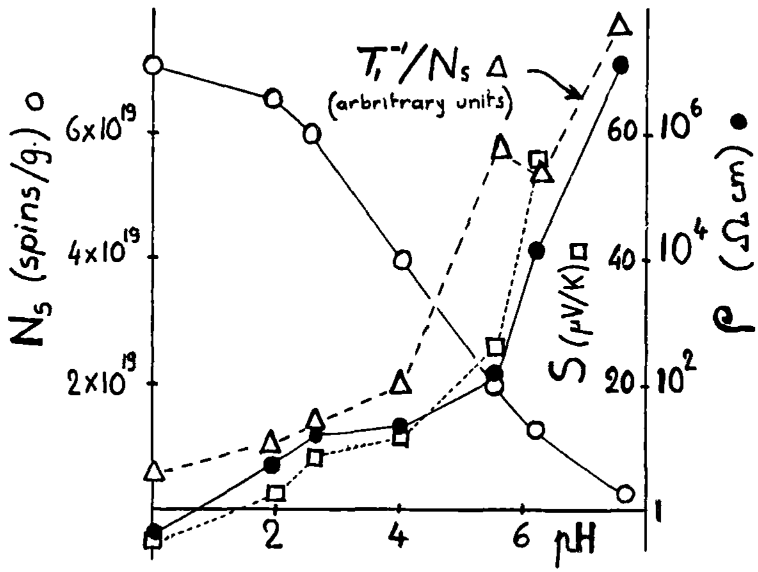

FIGURE 2 Room temperature resistivity (ρ), thermopower S, spin concentration (N_s) and reduced proton spin-lattice relaxation rate $T_1{}^{-1}/N_s$ as a function of pH for PANI samples prepared in $S_2O_8Na_2$

Fig. 2 shows a striking ressemblence of the dependence of TEP and of log σ upon pH. Such a parallel variation of these two quantities has already been reported in other systems[5]. At low pH, the small value of the TEP and its linear dependence upon T are typical for metallic behavior. At pH $\approx$ 1 TEP changes sign, indicating a transition from the hole-dominated to the electron-dominated transport, when decreasing pH. Thus, it turns out, somewhat paradoxically, that the lowering of pH - i.e. the increasing of the H^+ concentration in the polymer-results in a predominantly electron conduction.

SPIN SUSCEPTIBILITY AND SPIN DYNAMICS

While a tight correlation between the concentration of electron spins, N_s, and polaron formation upon oxidation exists in electrochemically prepared PANI[6], in compounds obtained by chemical method the origin of the spins is yet unclear. ESR measurements show that N_s is about 1 spin per 10^2 rings in the most conducting material (pH ~ 0). We note that when pH is increased both N_s and σ decrease. A similar concomitant variation of N_s and σ is observed for electrochemical reduction, although it is not possible to assert that these parallel behaviors are not fortuitous.

Both N_s and the ESR linewidth ΔH are affected by exposure to oxygen. Upon pumping under vacuum N_s increases by ~ 50 % and ΔH decreases by a factor of about two. Both effects are reversible.

The proton spin-lattice relaxation time T_1 lies in the range 10 to 100 ms, depending on the frequency and on the material characteristics. The frequency dependence can be fitted with the law $T_1^{-1} = A\omega^{-\frac{1}{2}} + B$ for frequency varied from 10 to 100 MHz. For high N_s (~ 10^{19} spin/g) the proton relaxation reflects the electron spin fluctuations. In Fig. 2 we have plotted T_1^{-1}/N_s (in arbitrary units) i.e. the proton relaxation rate per electron spin. This quantity is proportional to the low frequency amplitude of the electron spin motion spectrum. It turns out that T_1^{-1}/N_s versus pH varies like the logarithm of the resistivity and the TEP. We believe this to be another manifestation of the metal-insulator (M-I) transition. In the metallic regime small relaxation rates are observed, which is consistent with short electron correlation times. We should note that the magnetic properties we report concern PANI prepared with $S_2O_8Na_2$. In the samples prepared with $K_2Cr_2O_7$ the transport properties are similar but the magnetic properties are quite different : T_1 is very short (2ms) and is neither frequency nor temperature dependent. This is probably not an intrinsic behavior, likely due to residual chromium impurities.

CONCLUSION

Behavior of σ, TEP, and spin dynamics with varying pH strongly suggests the occurence of a proton-induced M-I transition in PANI. We cannot propose, at this stage, a precise model for the M-I transition. We suggest that the binding of protons to N atoms in the PANI chain results in the removal of electrons from the π band. The displacement of the Fermi level in the π band that this process entails provides a qualitative explanation of our data.

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