

SPIN DYNAMICS STUDY IN POLYANILINE

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ABSTRACT

Proton spin lattice relaxation time T_1 has been measured in the frequency range 6-340MHz in a set of nine polyaniline samples equilibrated at different pH. With additional ESR data, T_{1e} and T_{2e} measured as a function of the frequency, it is concluded that electronic spin motion is dominated by a quasi 1-D diffusion. The diffusion rate along the chain, D_{\parallel} is almost independent of the protonation rate γ , but the cutoff frequency f_c increases suddenly by 3 orders of magnitude accross the insulator-to-conductor transition. This is interpreted in terms of percolation between protonated cluster just consisting in one conducting chain. Conductivity estimated from D_{\parallel} agrees with the measured dc conductivity, but the carrier mean free path is too small to be consistent with metallic conductivity.

INTRODUCTION

Polyaniline (PANI) is known for its remarkable Insulator-to-Conductor transition as a function of the protonation. The conductivity can change by ten orders of magnitude while the number of electrons of the polymer chains remains the same [1]. The transition to a conducting state is accompanied by an increase of spin susceptibility [2], which has been shown to be of Pauli type [3]. It has been proposed that the conducting state was of metallic type, and evidence as been provided for phase segregation into small metallic particles. Besides the role of disorder has been pointed out and a description in terms of a Fermi glass has been suggested [4].

In this work we report spin dynamics data, which supply new results for the understanding of the conducting state in PANI. Spin dynamics enables one to probe the spin motion, and since the spin carriers (polarons) are also charge

carriers the transport property can be analyzed at the very molecular scale. Spin dynamics has revealed to be a powerful method for investigating the motion of the non linear excitations in conducting polymers e.g. solitons in polyacetylene [5-6] and polarons in polypyrrole [7]. We here present the first spin dynamics study devoted to polyaniline. Comparatively to other conducting polymers the study is more laborious in PANI because one does not deal with a single compound, but with a whole compound family, according to the protonation level. We have made a comprehensive spin dynamic study as a function of the protonation level. Measurements have been performed on 9 samples equilibrated in different pH. In the following, the samples will be named by their equilibrating pH. Systematic investigation as a function of the protonation level enables us to bring out the role of this parameter.

EXPERIMENTAL

PANI was chemically synthesized by oxidative polymerization of aniline in 1M aqueous HCl solution with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as an oxidant [9]. The obtained powder was equilibrated in 0.1M NH_4OH . Then it was equilibrated for at least 40 hours in aqueous HCl solution of given pH. Nine different compounds have been prepared : at pH = 0, 1.1, 2.2, 2.5, 3.2, 3.5, 4.1, 4.8, and 10. After sufficient dynamic pumping to remove water and unreacted HCl, samples for NMR measurements were sealed in 5mm \varnothing glass tubes with Helium gas for thermal contact. Protonation level, y , was determined by quantitative chemical analysis of Chlorine and Nitrogen : $y = \text{Cl}/\text{N}$. Spin concentration, c per aniline unit, was determined by Schumacher-Slichter (NMR-ESR) technique at room temperature and by SQUID susceptometer at low temperatures.

Proton spin lattice relaxation times T_1 were measured using π - $\pi/2$ pulse sequence with a Bruker SXP spectrometer, over the frequency range 6-340MHz and between room temperature and 20K for samples pH0 and pH2.2. Single exponential for magnetization recovery was observed for the six samples pH = 0, 1.1, 2.2, 4.1, 4.8 and 10. For the other three (pH = 2.5, 3.2, and 3.5), which are within the Insulator-to-Conductor crossover, mainly two exponentials can be distinguished for the recovery. For these samples T_1 has been taken as the time for the magnetization to recover 1/e of its equilibrium value after a π pulse.

ESR linewidth (T_{2e}^{-1}) was studied at room temperature, in the frequency range 30 to 500MHz for samples pH = 0 and 2.2. Electronic spin lattice relaxation time, T_{1e} , was determined at 100MHz by CW saturation, and at X-band by π - $\pi/2$ pulse technique.

RESULTS AND DISCUSSION

Fig.1 shows the log-log plot of all the room temperature data for T_1^{-1} normalized by the electron spin concentration c . It is noteworthy that all samples present a frequency dependence, which is a typical behavior for low

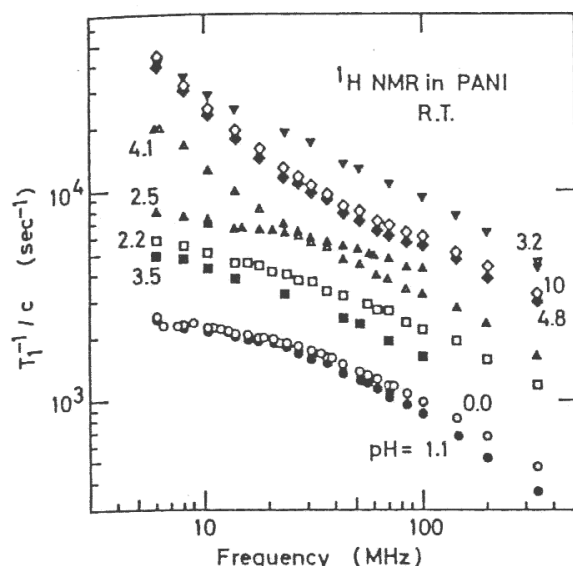


Fig. 1. Proton spin lattice relaxation rates (normalized to the spin concentration) as a function of frequency for PANI samples from different equilibrating solutions.

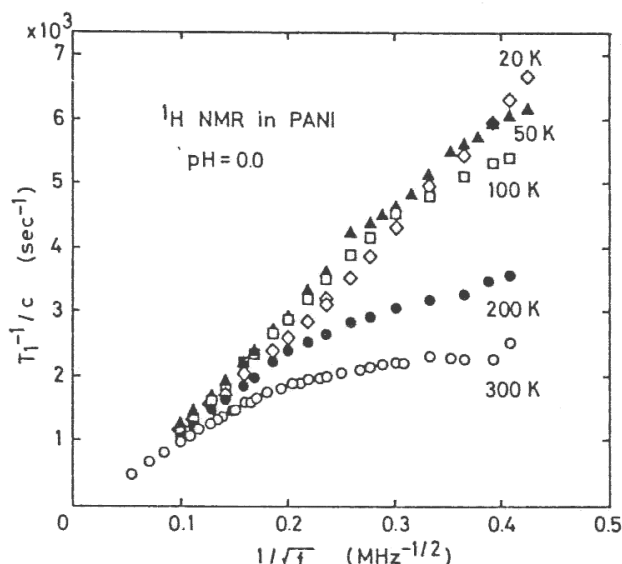


Fig. 2. Proton spin lattice relaxation rate for pH 0 PANI sample as a function of $f^{-1/2}$ at different temperatures.

dimensional motion. At high frequency all samples show gradual approach to $\omega^{-1/2}$. Such a law can be either characteristic of a 1D diffusion, or of relaxation by fixed dilute paramagnetic centers. At low frequency we notice that the samples with $\text{pH} > 4$ exhibit a steeper frequency dependence than $\omega^{-1/2}$, while for the sample with $\text{pH} < 4$ the frequency dependence is slower than $\omega^{-1/2}$. Taking into account that a) a frequency dependence steeper than $\omega^{-1/2}$ reflects a narrow motion spectrum and b) the spin concentration for the samples with $\text{pH} > 4$ drops by two orders of magnitude as compare to the samples with $\text{pH} < 3$, we can reasonably explain the data by two different relaxation mechanisms :

- for $\text{pH} < 4$ samples most of the spin correspond to polarons associated with the protonation induced conducting state [8]. The high spin concentration of these compounds ($c \sim 0.1$ to 0.01 spin/ring) gives evidence that the proton relaxation is directly due to spin motion. This spin motion exhibits low dimensional behavior with gradual cutoff frequency increase as pH is lowered.
- for $\text{pH} > 4$ samples c is smaller ($c < 0.001$) and may correspond, for a non negligible part, to free radicals present in the insulating PANI as structural defects. Then a nuclear spin diffusion assisted relaxation is expected.

Shape of the spectrum motion

In Fig. 2, the normalized relaxation rates, measured at different temperatures, have been plotted as a function of $f^{-1/2}$ for sample pH 0. At 20K an almost

ideal 1D diffusion behavior is observed. When temperature increases departure from 1D diffusion takes place gradually. There are two ways for interpreting deviations from 1D diffusion : a) quasi-one-dimensional diffusion with inter-chain hoppings introducing a cutoff frequency ω_c , and b) spectral dimension [7].

Firstly, if the spin diffuses rapidly along the chain with the on-chain diffusion rate D_{\parallel} and D_{\perp} between neighbouring chains at the rate $D_{\perp} = \tau_{\perp}^{-1} = \omega_c$ the spectrum is given by [6b] :

$$f(\omega) = \left(\frac{\tau_{\perp}}{2D_{\parallel}} \right)^{1/2} \left[\frac{1 + (1 + \omega^2 \tau_{\perp}^2)^{1/2}}{1 + \omega^2 \tau_{\perp}^2} \right]^{1/2} \quad (1)$$

which reduces to

$$f(\omega) \cong \frac{1}{\sqrt{2D_{\parallel}\omega}} \quad \text{for } D_{\perp} \ll \omega \ll D_{\parallel} \quad (1\text{-D limit}) \quad (1a)$$

$$f(\omega) \cong \frac{1}{\sqrt{D_{\parallel}D_{\perp}}} \quad \text{for } \omega \ll D_{\perp} \quad (3\text{-D limit}) \quad (1b)$$

Secondly, if the spin diffuses on a fractal network, one expects [7] :

$$f(\omega) = A \omega^{\frac{\tilde{d}-1}{2}} + B \quad \tilde{d} < 2 \quad (2)$$

where \tilde{d} is the spectral dimension. Evidence for such a behavior has been given in the conducting polymer polypyrrole [7], with \tilde{d} being temperature dependent, as for a random walk on an energetically disordered lattice [9]. In the case of PANI such a behavior might be also expected if one assumes a percolative process for the protonation induced Insulator-to-Conductor transition. For a random walk on a percolation cluster the spectral dimension is expected to be $\tilde{d} \cong 4/3 = 1.33$ [10].

Departure from $f(\omega) \propto \omega^{-1/2}$ should also be observed at high frequency. The spectrum drops for $\omega > D_{\parallel}$ since one goes out from the diffusion regime. It might vanish for lower frequency if the spin is delocalized over L units ($L > 1$) [11]. In that case there is a high frequency cutoff and the spectrum is given by :

$$f(\omega) = \frac{1}{\sqrt{2D_{\parallel}\omega}} - \gamma \frac{L}{D_{\parallel}} \quad \omega \ll D_{\parallel} \quad (3)$$

where $\gamma \approx 0.33$ (for $L \gg 1$) is a geometrical factor.

Relaxation rates

The motion spectrum is included in the expressions of the relaxation rates as follows. For the nuclear spin lattice relaxation one has [5] :

$$T_1^{-1} = kT \chi \left[\frac{3}{5} d^2 f(\omega_N) + (a^2 + \frac{7}{5} d^2) f(\omega_e) \right] \quad (4)$$

where χ is the spin susceptibility ; ω_e and ω_N are the electronic, and nuclear Larmor frequencies, respectively ; a and d are the scalar and dipolar hyperfine couplings. For the hyperfine couplings, assuming homogeneous delocalization for the electron spin over the 6 Carbon and the Nitrogen atoms of a monomer unit, we have taken $a/\gamma_e = 23.4/7 \approx 3.3$ Gauss, and we have used $d \approx a/2$, as usual for aromatic Carbons. It can be shown that reduction of the spin density by delocalization over several monomer units is compensated by an increase of the spin motion correlation [11].

For the electronic spins the electron-electron dipolar coupling is the main source of relaxation for both T_{1e} and T_{2e} . This is evidenced for instance by the fact that there is no change in the ESR linewidth if one replaces the protons by deuterium. One thus can use the following expressions :

$$T_{1e}^{-1} = cR^2 [0.2 f(\omega_e) + 0.8 f(2\omega_e)] \quad (5)$$

$$T_{2e}^{-1} = cR^2 [0.3 f(0) + 0.5 f(\omega_e) + 0.2 f(2\omega_e)] \quad (6)$$

where R^2 is a geometrical coefficient which represents the average sum of the spin spin dipolar interactions.

Fittings

The data of Fig.2 have been fitted in the two cases : quasi 1-D diffusion and spectral dimension.

1-D diffusion (cases A and B). There are two fitting parameters : D_{\parallel} and D_{\perp} . One can fit Eqs. (1) and (4) with two different sets of values : $D_{\parallel} = 2.5 \times 10^{13}$ and $D_{\perp} = 2.3 \times 10^8$ rad/sec (case A) ; $D_{\parallel} = 1.8 \times 10^{12}$ and $D_{\perp} = 1.1 \times 10^{11}$ rad/sec (case B). The knee-shape of the data corresponds to the cross-over from 1D to 3D behavior at the cutoff frequency. For the pH0 sample at room temperature, in

case A the 1D-3D cross-over lies in the ω_N range : $f_c = D_{\perp}/2\pi = 36\text{MHz}$. In case B $f_c = 18\text{ GHz}$ is in the ω_e range.

Spectral dimension (case C). The fitting parameters are the spectral dimension \tilde{d} , the amplitude A, and the constant B. We have taken $\tilde{d} \approx 2$. With the use of 3 parameters the fitting of the data with Eqs.(2) and (4) is rather flexible.

In Fig.3 typical fitting curves for pH0 sample at room temperature are presented for the above three cases. We see that good fits are obtained in the three cases. Thus, one cannot discriminate between the three cases only by NMR data. Use of ESR will enable us to find which case is the right one. The basic

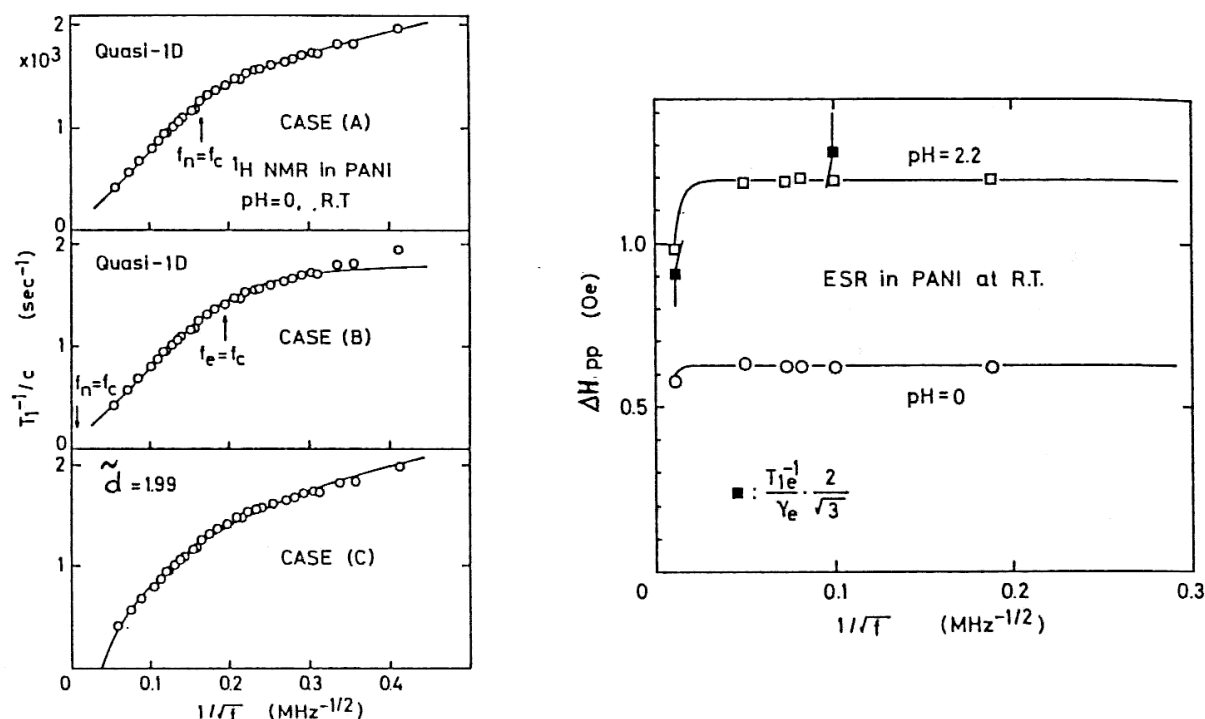


Fig. 3. Typical fitting curves for the R.T. data of Fig. 2 in the three cases A, B, and C (see text).

Fig. 4. ESR T_{1e}^{-1} and T_{2e}^{-1} versus $f^{-1/2}$ for pH0 and pH2 samples. The solid lines have been obtained with Eqs. 5, 6.

difference with ESR is that the motion spectrum is no more probed at ω_N , but essentially at ω_e . Figure 4 shows the frequency dependence of T_{1e}^{-1} and T_{2e}^{-1} in about the same frequency range as the NMR data. If we were dealing with cases A or C we would expect the same rise for the electronic relaxation rates at low frequency as that one which is observed for T_1^{-1} in Fig.2 because of the similar functional dependence on ω (see Eqs. 4-6). Instead, a plateau is observed giving evidence for cutoff frequency $f_c \gtrsim 10\text{ GHz}$, in agreement with case B. The solid curves in Fig.4 have been obtained with Eqs.5 and 6, using the case B NMR diffusion rates and taking R^2 as a fitting parameter.

Protonation dependence of the diffusion rates

The room temperature protonation dependence of D_{\parallel} and D_{\perp} is given in Fig.5. The striking point of these data is the sudden drop in D_{\perp} at $y \sim 0.2 - 0.3$,

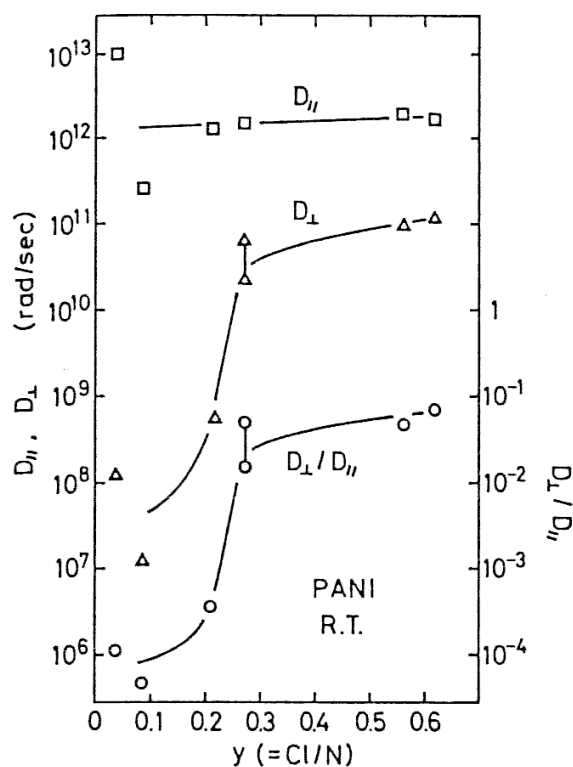


Fig. 5. Room temperature diffusion rates D_{\parallel} and D_{\perp} , and anisotropy D_{\perp}/D_{\parallel} for pH0 sample as a function of the protonation rate.

while D_{\parallel} remains roughly constant. Thus, the spin motion is much more anisotropic at low than at high protonation level, that is for isolated protonated clusters than for interacting clusters. The idea which then comes in mind is that these protonated-conducting clusters could be composed of only one (or very few) polymer chain(s). This could explain the high anisotropy at low y (conducting chains isolated from each other) and the drastic decay of this anisotropy when the conducting chains begin to percolate.

Spin diffusion and conductivity

One can estimate the mean free path l^* with the assumption of metallic behavior: $D_{\parallel} C_{\parallel}^2 = v_F l^*$, with v_F the Fermi velocity. One obtains $l^*/C_{\parallel} \approx 6 \times 10^{-3}$, a much too small value to be consistent with a metallic description. The dc conductivity can be estimated from D_{\parallel} with the relation $\sigma = n e^2 D/kT$ where n is the charge carrier concentration. With $n = 0.4 e^-/\text{ring}$ one obtains $\sigma_{\parallel} = 80 \text{ S/cm}$, and $\sigma_{\perp} \approx 6 \text{ S/cm}$. These values agree satisfactorily with the measured dc conductivity 3.5 S/cm for pH0 sample.

CONCLUSIONS

Spin dynamics has revealed as a fruitful method for thorough study of polyaniline properties. We have demonstrated the quasi one-dimensional features of the spin motion. We have found that the anisotropy of the spin motion undergoes a sudden drop when the conducting clusters begin to percolate, a striking and unexpected result which suggests strongly that the clusters contain just a single conducting chain. The transport properties deduced from the NMR data agrees with the measured dc conductivity but contradict a true metallic behavior.

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