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Spin Dynamics in the Conducting Polymer, Polyaniline

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The frequency dependences of both proton NMR T_1 and ESR linewidth in polyaniline give evidence for quasi-1D spin diffusion. The on-chain diffusion rate, $D_\parallel$, is independent of the protonation level, while the transverse diffusion, $D_\perp$, exhibits a sudden drop at the percolation threshold. This behavior confirms the conducting-island picture, but it is concluded that a given conducting island consists of just a single conducting chain. The room-temperature data show a strong correlation between spin dynamics and transport properties, and suggest that conductivity is governed by interchain hoppings.

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The polyaniline family is known for its remarkable insulator-to-conductor transition as a function of protonation. Upon protonation of the emeraldine form of polyaniline the conductivity increases by 10 orders of magnitude while the number of electrons on the polymer chains remains constant.[1-3] Besides, a Pauli susceptibility appears, essentially proportional to the protonation level, which strongly suggests that, instead of being homogeneous, the protonation leads to phase segregation into fully protonated domains with high spin concentration (conducting islands) embedded in an unprotonated sea.[4] This picture of a "granular polymeric metal" is consistent with transport-property data,[5] but seems to be contradicted by the momentum dependence of the electron-energy-loss spectra.[6] The conducting state has been described with a polaron lattice model giving rise to a metal-like band structure.[4,7] However, evidence for disorder has been pointed out, and it has been suggested that a description in terms of a Fermi glass might be more appropriate.[8,9]

In this Letter we present the first study of spin dynamics in polyaniline. We confirm the existence of high-spin-concentration conducting domains and we are led to the remarkable and unexpected conclusion that these domains consist of only one single polymer chain. Furthermore, we give evidence that the conductivity is dominated by the transverse diffusion, as suggested by the parallel variation of conductivity with the protonation level.

Magnetic resonance techniques enable one to probe the spin motion and, since the spin carriers are also charge carriers (polarons),[10] the transport properties can be analyzed at the scale of the polymer chains. Of particular interest is the case of low-dimensional systems. Spin dynamics has been revealed to be a powerful tool for investigating the motion of the nonlinear excitations in conducting polymers, e.g., solitons in polyacetylène[11] and polarons in polypyrrole.[12] A unique advantage of the method is the possibility to determine the anisotropy of the motion, even for powder or amorphous samples.

We have achieved a comprehensive spin-dynamics study in polyaniline, which relies on both NMR and ESR data. Simultaneous use of these two independent methods enables unambiguous conclusions. The study has been performed as a function of the protonation level. The samples were obtained by chemical synthesis and protonated as described in literature.[13] The protonation level, y, was determined by elemental analysis of chlorine and nitrogen: $y = \mathrm{Cl/N}$. The spin motion spectrum has been determined from the frequency dependence of both proton and electronic spin-relaxation times. The proton spin-lattice relaxation time, T_{1N}, was measured using a π-$\pi/2$ pulse sequence, over the frequency range 6–340 MHz. The ESR linewidth has been measured at low field in the frequency range 30–500 MHz, as described elsewhere.[14] The spin concentration, c per ring, was determined by the Schumacher-Slichter (NMR-ESR) technique and with a SQUID susceptometer.

The room-temperature data of T_{1N}^{-1}, normalized to the spin concentration c, are given in Fig. 1.[15] All samples present a frequency dependence with gradual approach to $\omega^{-1/2}$ at high frequency. Such a law is characteristic of proton relaxation induced by electronic spins which are either diffusive along one dimension, or fixed and dilute. At very low protonation level ($y \leq 0.02$ and $c < 0.001$), the low-frequency T_1^{-1} data are above $\omega^{-1/2}$; they could be interpreted as nuclear-spin-diffusion-assisted relaxation due to fixed paramagnetic centers, such as the free radical present in insulating polyaniline. For $y \geq 0.04$ the data can be explained in terms of pseudo 1D diffusive spin motion. Furthermore, most of the spins correspond to polarons associated with

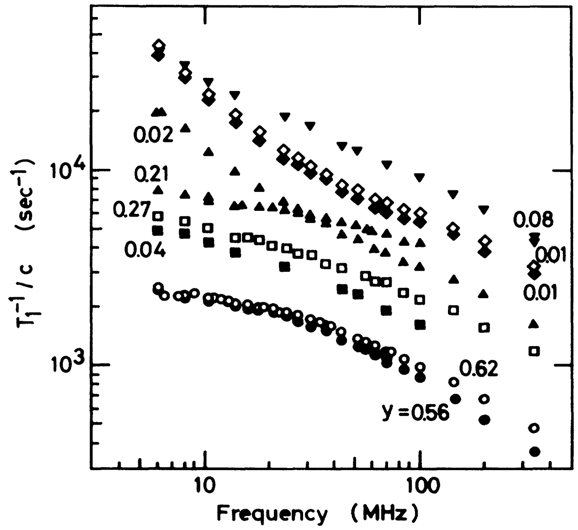


FIG. 1. Room-temperature proton spin-lattice relaxation rate in polyaniline (normalized to the spin concentration) as a function of frequency for different protonation levels y: ◇, ◆, $y=0.01$; △, 0.02; ■, 0.04; ▽, 0.08; ▲, 0.21; □, 0.27; ●, 0.56; ○, 0.60.

the protonation-induced conducting state.[10] Then, one has[16]

$$T_{1N}^{-1} = \tfrac{1}{4} c[\tfrac{3}{5} d^2 f(\omega_N) + (a^2 + \tfrac{7}{5} d^2) f(\omega_e)] , \quad (1)$$

where a and d are the scalar and dipolar hyperfine couplings, ω_e and ω_N are the electronic and nuclear Larmor frequencies, respectively, and $f(\omega)$ is the frequency spin-correlation function, i.e., the "motion spectrum." We have estimated the hyperfine couplings assuming homogeneous delocalization of the electron spin over a monomer unit.

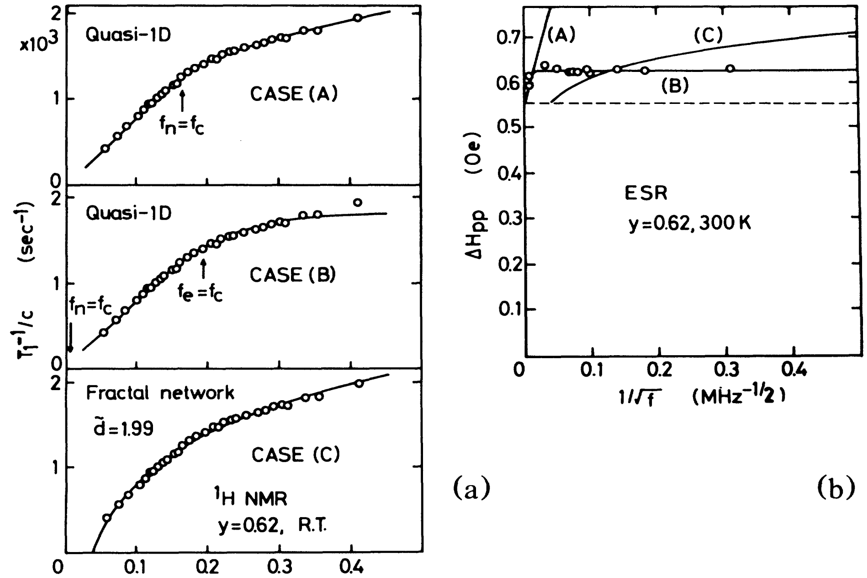
The electron spin-spin relaxation rate T_{2e}^{-1} has been obtained from the ESR linewidth. This procedure is valid since the ESR line is homogeneously broadened, even at low y, as evidenced by different features: (i) The width is unchanged upon deuteration, which rules out a hyperfine contribution to the linewidth, (ii) the line shape is essentially Lorentzian (in some samples, however, a superimposed non-Lorentzian line corresponding to less than 10% of the spins has been observed), and (iii) direct measurements of T_{2e} by an ESR pulsed experiment at the X band agrees with the linewidth data.[9] Then, one has

$$T_{2e}^{-1} = \tfrac{1}{10} cR^2[3f(0) + 5f(\omega_e) + 2f(2\omega_e)] , \quad (2)$$

where R^2 is the average sum of the spin-spin dipolar interactions.

For the motion spectrum two shapes have been tried: (a) The first was quasi-one-dimensional diffusion with $D_{\parallel} \gg D_{\perp}$, $D_{\parallel}$ and $D_{\perp}$ being the on-chain and interchain diffusion rates, respectively. This type of motion, which gives rise to a $\omega^{-1/2}$ divergence down to a cutoff frequency $\omega_c \sim D_{\perp}$, has been evidenced in numerous conducting, and magnetic, organic compounds. (b) Also tried was anomalous diffusion, i.e., a random walk on a fractal network, as recently proposed for the conducting polymer polypyrrole.[12]

In Fig. 2 we present data for the $y=0.6$ sample with



(a) (b)

FIG. 2. (a) Normalized proton spin-lattice relaxation rate and (b) ESR linewidth, as a function of inverse square root of frequency for a polyaniline sample equilibrated in a pH0 solution ($y=0.62$). The solid lines are theoretical curves for models A, B, and C (see text).

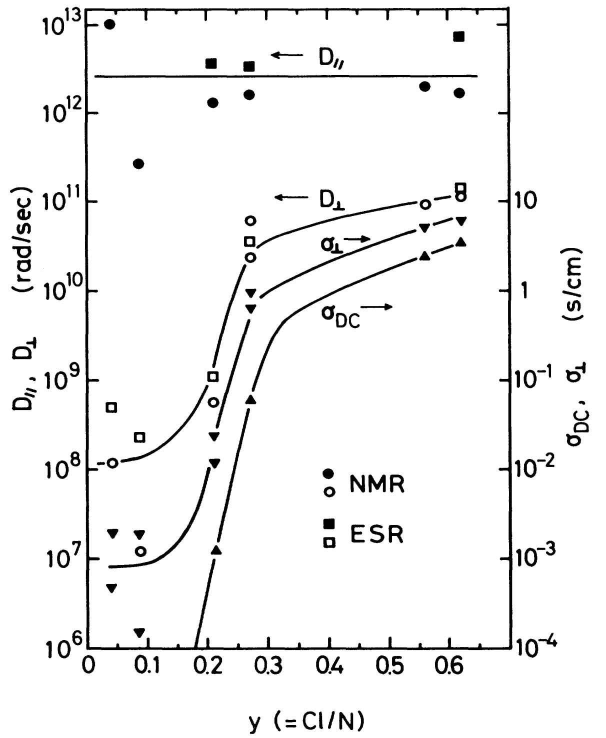


FIG. 3. Room-temperature spin-diffusion rates, as obtained from NMR (●,○) and from ESR (■,□), and conductivity in polyaniline as a function of the protonation level. $\sigma_{\rm dc}$ is the measured conductivity and $\sigma_{\perp}$ has been calculated from $D_{\perp}$, using $\sigma_{\perp} = ne^2 D_{\perp}/kT$, with n, the carrier concentration, proportional to y.

three possible fitting curves: model A, 1D diffusion with $\omega_c \sim \omega_N$; B, 1D diffusion with $\omega_c \sim \omega_e$; and C, fractal network diffusion. It turns out that all the models can fit the NMR data, but only case B can account for both the NMR and ESR data.

Thus, the data for $y \gtrsim 0.04$ have been interpreted in terms of pseudo 1D diffusion with a cutoff in the ω_e range, and with the two fitting parameters $D_{\parallel}$ and $D_{\perp}$. The values obtained for these parameters are given in Fig. 3 as a function of the protonation rate. It appears that $D_{\parallel} \sim 10^{12}$–$10^{13}$ rad sec^{-1} is almost independent of y. In other words, whatever the protonation level, and the total spin concentration, the spins have basically the same on-chain diffusion rate. This statement is in agreement with the conducting-island picture: The on-chain diffusion appears to be an intrinsic property of the conducting islands. However, the behavior of the transverse diffusion rate is quite different: $D_{\perp}$ exhibits a sudden drop of 2–3 orders of magnitude for $y \sim 0.2$–0.3, a value which appears as a percolation threshold y_p.

It is noteworthy that these results have been obtained from NMR and ESR data independently. Furthermore, we emphasize that our poor knowledge of the spin interaction parameters (a,d,R) in polyaniline only affects the absolute value of $D_{\parallel}$. The estimate of $D_{\perp}$ is quite reliable because it relies on the ω_c value, which comes directly from experiment. Thus, the two following points emerge: (a) In isolated clusters (islands) the spin motion is highly anisotropic ($D_{\perp}/D_{\parallel} < 10^{14}$), and (b) cluster interactions, which take place for $y > y_p$, result in a dramatic increase of interchain hopping. How can one explain that intercluster interactions can dramatically influence the interchain couplings, which should be essentially determined by interactions inside a given cluster? We propose that the protonated conducting clusters are composed of only one polymer chain. We note that this idea can also account for the nonobservance of any q dependence in electron-energy-loss spectroscopy.[17] Thus, the protonation process in polyaniline would give rise to fully protonated chains embedded in an unprotonated matrix. This picture agrees with the model of Choi and Mele,[18] which predicts first-order phase transitions and segregation into periodic structures of different filling factors, with the limiting cases consisting of empty (unprotonated) and saturated (full protonated) lattices. We also mention that the idea of first-order phase transition is consistent with the hysteresis observed for the protonation level as a function of pH.[9]

The spin-dynamics behavior can be related to the transport properties. Assuming that the diffusion coefficients for spin and charge-carriers have the same value, the conductivity can be estimated with the relation $\sigma_{\parallel,\perp} = ne^2 D_{\parallel,\perp}/kT$, where n is the charge carrier concentration. With $n = 0.4$ e^-/ring, one obtains $\sigma_{\parallel} \simeq 10^2$ sec/cm, which should be the value for the intrinsic on-chain conductivity. This is about 1 order of magnitude larger than the conductivity measured in $y = 0.6$ polyaniline ($\sigma = 3.5$ sec/cm), which is a compound which contains almost only protonated conducting chains. If we make the very reasonable assumption that the macroscopic conductivity is mainly governed by the interchain charge hopping, the transverse diffusion rate $D_{\perp}$ has to be used for the estimate. Then, one obtains $\sigma \simeq 6$ sec/cm, in remarkable agreement with the measured value. The tight relationship between transverse spin diffusion and macroscopic conductivity is also observed in their parallel variation as a function of y, as shown in Fig. 3. Both quantities drop suddenly at the percolation threshold. However, while σ is continuously decreasing for decreasing y, the decay of $D_{\perp}$ seems to saturate to a limiting value of $\sim 10^8$ rad sec^{-1}. In fact, if the interchain hopping can obtain vanishing values with increasing interchain distances, this is not the case for the cutoff frequency of the 1D spin diffusion. In particular the contribution of the intrachain spin-spin dipolar interactions can be estimated as in Ref. 19. One obtains $\omega_c \sim 10^7$–10^8 rad, which agrees with the apparent limiting value. We have also tested the relationship between conductivity and spin dynamics as a function of temperature. It turns out that the equality between spin and charge-carrier diffusions is essentially a high- (room-) temperature property. With decreasing temperature, $D_\perp$ decreases, but not so fast as σ, and seems not to go below $\sim 10^{10}$ rad sec^{-1}. As for $D_\parallel$, only a twofold or threefold decay is observed, which saturates around 100 K. We believe that spin exchange, which is almost temperature independent, becomes the dominant contribution to the spin-diffusion process at low temperature. One can estimate J and J', the intrachain and interchain exchange, respectively, by $J \sim D_\parallel$, and $\omega_c \sim J'(J'/J)^{1/3}$. With the low-$T$ spin-diffusion limiting values one obtains $J/k \sim 10$ K and $J'/k \sim 0.1$ K. Finally, using the room-temperature data one can estimate the charge-carrier mean free path l^* with the assumption of metallic behavior: $D_\parallel c_\parallel^2 = v_F l^*$, with $c_\parallel$ the unit-cell distance and v_F the Fermi velocity. One obtains $l^*/c_\parallel \simeq 6\times 10^{-3}$, a much too small value to be consistent with a metallic description, as has been proposed.[4]

In conclusion, from the spin dynamics data a novel picture emerges for the polyaniline features. Protonation gives rise to segregation into fully protonated, conducting, and paramagnetic chains embedded in an unprotonated, insulating matrix. At low protonation level these chains are isolated from each other resulting in a highly anisotropic behavior. Thus, polyaniline appears as a model material which presents a unique concrete example for the concept of a one-dimensional conducting system. When the protonated chains begin to percolate the interchain spin-diffusion rate increases dramatically and reaches the neighboring-chain limiting value. Finally, with the assumption that interchain spin diffusion reflects interchain hopping of the charge carriers a remarkable relation is found between spin dynamics and conductivity.

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[1] R. de Surville, M. Josefowicz, L. T. Yu, J. Perichon, and R. Buvet, Electrochim. Acta **13**, 1451 (1968).

[2] W. S. Huang, B. D. Humphrey, and A. G. MacDiarmid, J. Chem. Soc. Faraday Trans. **82**, 2385 (1986).

[3] J. P. Travers *et al.*, Mol. Cryst. Liq. Cryst. **121**, 195 (1985).

[4] J. M. Ginder, A. F. Richter, A. G. MacDiarmid, and A. J. Epstein, Solid State Commun. **63**, 97 (1987).

[5] F. Zuo, M. Angelopoulos, A. G. MacDiarmid, and A. J. Epstein, Phys. Rev. B **36**, 3475 (1987).

[6] A. Litzelmann, B. Scheerer, J. Fink, K. Meerholz, J. Heize, N. S. Sariciftci, and H. Kuzmany, Synth. Met. **29**, E313 (1989).

[7] S. Stafström, J. L. Brédas, A. J. Epstein, H. S. Woo, D. B. Tanner, W. S. Huang, and A. G. MacDiarmid, Phys. Rev. Lett. **59**, 1464 (1987).

[8] F. Wudl, R. O. Angus, F. L. Lu, P. M. Allemand, D. J. Vachon, M. Nowak, Z. X. Liu, and A. J. Heeger, J. Am. Chem. Soc. **109**, 3677 (1987).

[9] M. Nechtschein, F. Genoud, C. Menardo, K. Mizoguchi, J. P. Travers, and B. Villeret, Synth. Met. **29**, E211 (1989).

[10] F. Genoud, M. Guglielmi, M. Nechtschein, E. Geniès, and M. Salmon, Phys. Rev. Lett. **55**, 118 (1985); M. Nechtschein, F. Devreux, F. Genoud, E. Vieil, J. M. Pernaut, and E. Geniès, Synth. Met. **15**, 59 (1986).

[11] M. Nechschein, F. Devreux, R. L. Greene, T. C. Clarke, and G. B. Street, Phys. Rev. Lett. **44**, 356 (1980).

[12] F. Devreux and H. Lecavelier, Phys. Rev. Lett. **59**, 2585 (1987).

[13] J. C. Chiang and A. G. MacDiarmid, Synth. Met. **13**, 193 (1986).

[14] K. Mizoguchi, K. Kume, and H. Shirakawa, Synth. Met. **17**, 149 (1987).

[15] K. Mizoguchi, M. Nechtschein, J. P. Travers, and C. Menardo, Synth. Met. **29**, E417 (1989).

[16] F. Devreux, J. P. Boucher, and M. Nechtschein, J. Phys. **35**, 271 (1974).

[17] N. S. Sariciftci (private communication).

[18] H. Y. Choi and E. J. Mele, Phys. Rev. Lett. **59**, 2188 (1987).

[19] C. Jeandey, J. P. Boucher, F. Ferrieu, and M. Nechtschein, Solid State Commun. **23**, 673 (1977).