Memory Effects in Conducting Polymers

B. Villeret and M. Nechtschein

Dynamique de Spin et Propriétés Electroniques, Service de Physique Département de Recherche Fondamentale,
Centre d'Etudes Nucléaires de Grenoble, 85X, 38041 Grenoble CEDEX, France
(Received 8 March 1989)

The kinetics of electrochemical doping of polyaniline films has been studied using *in situ* ESR experiments. It has been found that the kinetics and the doping level achieved during a potential-reading step depend on the previous electrochemical events undergone by the sample. It is shown that a slow relaxation process takes place in the polymer film while it is maintained in the neutral state. Possible relations to hysteresis effects are discussed.

Conducting polymers have been the subject of a considerable amount of work in the last ten years. Conjugated polymers were known as semiconducting materials since the 1950s when Chiang *et al.*[1] reported the tremendous increase in conductivity in polyacetylene upon doping. Doping, i.e., addition or removal of electrons on the polymeric chains, appears to be the central key which governs the main properties of conducting polymers. At first, doping was achieved by chemical methods. Then electrochemistry turned out to be the most convenient and flexible method. In particular, the doping level can be electrically monitored by an applied potential. Numerous *in situ* experiments have been described, which correlate different properties, such as optics,[2] magnetic susceptibility,[3] conductivity,[4] etc., with the doping level. A large amount of work has been devoted to the doping process, and a rather satisfactory level of understanding has been reached. However, it is generally assumed that the observed phenomena concern thermodynamical equilibrium processes. But there exists evidence that a thermodynamical equilibrium description is oversimplified.[5] Furthermore, effects of hysteresis on potential scanning have been noticed.[6-8]

In this Letter we establish that the doping process as achieved by electrochemical methods exhibits memory effects. Namely, the doping response of the material to an applied potential depends on the history of previous electrochemical events. The "memory" of the system extends over several decades of time: from 1 to 10^5 sec. Such effects have been observed in different compounds, e.g., polypyrrole, polythiophene, polyaniline (PANI), etc. We believe them to be a rather general property of conducting polymers. However, most of our experiments have been carried out on PANI, because very stable films of this compound can be prepared.

The polymer samples consist of thin films, about 0.1–0.5 μm thick, obtained by electropolymerization on a platinum electrode, a 0.2-mm-diam thread. The sample mass and thickness are defined by the electrical charge used for the synthesis. In the following we are concerned with the response of the redox state of the sample upon application of a potential to its support

electrode, used as a working electrode in an electrochemical cell.

Different quantities can be measured, as representative of the redox state. Integration of the current crossing the film should give directly the doping level. However, such a measurement is not easily made reliable, due to inevitable leakage currents. For this reason we have preferred to follow the charge carriers by their spin, using *in situ* ESR experiments as described elsewhere.[3] This method takes advantage of the insensitivity of the spin signal to leakage currents and to any spurious redox process which could proceed outside of the film. However, the identity between spin and charge carriers (polarons) is only valid at low doping level. At higher doping levels, spin concentration is reduced by pairing of polarons into bipolarons, a doubly charged and spinless species.[3] Furthermore, in some cases, crossover from Curie to Pauli susceptibility can also reduce the spin susceptibility.[9] The difference of behavior between spin and charge carriers is illustrated in Figs. 1(a) and 1(b) where the spin and charge concentrations, respectively, are given as a function of the applied potential. The data obtained by slow-potential scanning (0.2 mV/s) are not far from those of quasiequilibrium conditions. Hysteresis effects
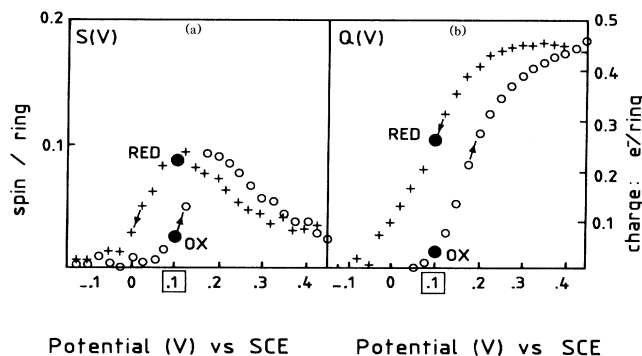

Potential (V) vs SCE   Potential (V) vs SCE

FIG. 1. (a) Spin concentration and (b) injected charge in a polyaniline film vs potential. The film was 0.5 μm thick and immersed in a 1M HCl aqueous solution. The average rate of the potential scanning was 0.2 mV/s.
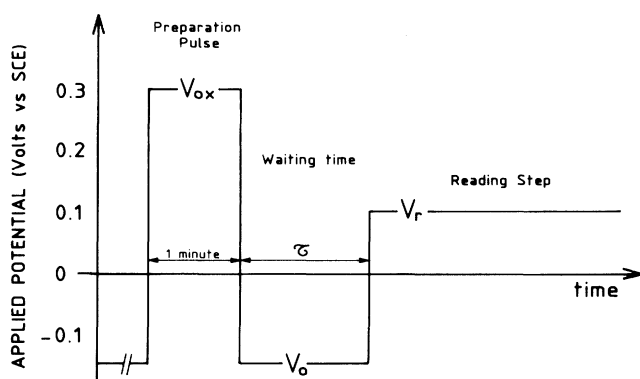
FIG. 2. Pulse sequence applied to the polymer film. During the preparation pulse the film is oxidized. Then, it is maintained for a variable waiting time τ in the neutral state, and the kinetics of doping is followed during a reading potential step.

are clearly apparent. We notice, in particular, that for $V_{appl} \simeq 0.1$ V two states of quite different doping levels exist, depending on whether this value has been reached from rising potentials (oxidation) or decreasing potentials (reduction).

In the transient experiments V_{appl} is switched between three characteristic values: (1) $V_0 = -0.15$ V (neutral form), (2) $V_{ox} = 0.3$ V (oxidized form), and (3) $V_r = 0.1$ V. The double-pulse (DP) sequence of Fig. 2 has been used. First, a preparation pulse (PP) leads the film to the oxidized state $(V = V_{ox})$ and brings it back to the neutral state $(V = V_0)$. Then, after a waiting time τ, a reading step (RS) of $V = V_{obs}$ is applied. During RS the

spin concentration, as representative of the redox state, is recorded. We have used overmodulation of the ESR line, the magnetic field being set just off resonance, a procedure which gives a spin signal almost insensitive to possible linewidth variations. In Fig. 3 the time evolution of the spin concentration during RS is given for different waiting times τ. The striking point is that the spin response is highly dependent on the waiting time. This result concerns both the steady-state value and the kinetics. For short τ, namely a few seconds, high spin concentration is obtained with short time constant. The spin response shows an overshoot [see Fig. 3(b)] which is simply evidence that polarons are created in excess with respect to the thermal polaron-bipolaron equilibrium populations. With increasing τ the kinetics slow down and the steady-state value decreases. Thus, the system seems to "remember" that it was led to the oxidized state and, then, maintained for a time τ in the neutral state. In other words, while maintained in the neutral state, the system is not in thermodynamical equilibrium. A slow relaxation process is taking place. We have obtained data showing that the system is still evolving after $\tau \sim 10^5$ sec.[10]

We have obtained data which show that, in our experiments, the spin response was not dependent on the film thickness. As a characteristic parameter for the spin response kinetics we have considered the starting slope, s, of spin concentration versus time. Plotted as a function of the waiting time, s can be fitted with a power law over more than 2 orders of magnitude: $s \propto \tau^\beta$, with $\beta = 0.6 \pm 0.1$. No significant change of β has been noticed for films of different thicknesses (synthesized with 14, 36, and 116 mC). Thus, we conclude that the memory effect
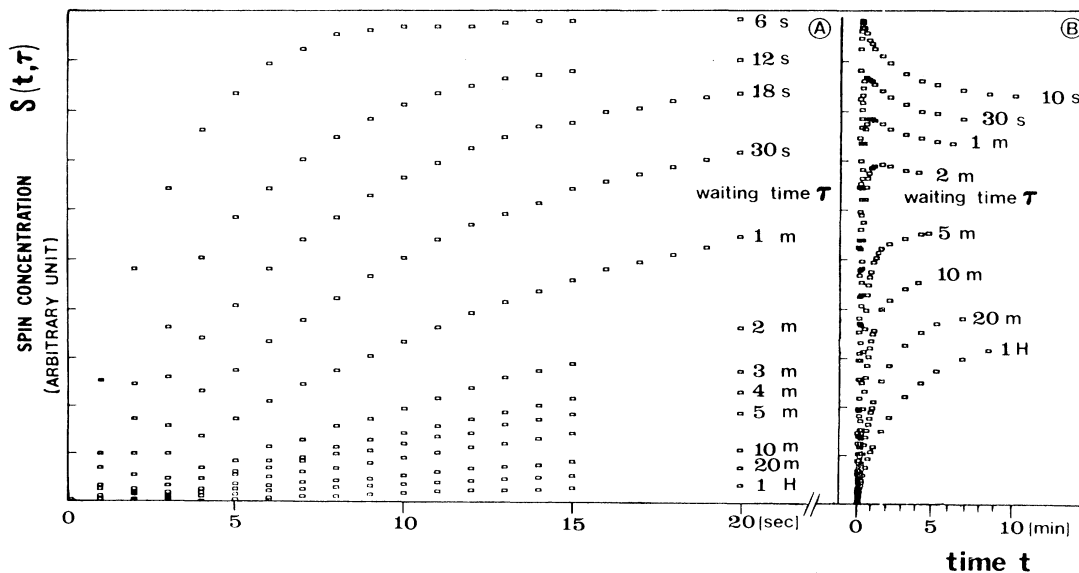

FIG. 3. Spin concentration of a polyaniline film recorded during the reading potential step for different waiting times τ (see Fig. 2). (a) Short and (b) long time behavior of the spin response have been represented.

is not controlled by ion diffusion.

We note in Fig. 3 that not only the kinetics but also the asymptotic value of the spin concentration depends on the waiting time. If RS is applied a short time after PP (small τ), a high spin concentration is obtained. With increasing τ the limiting spin concentration decreases. This result can be considered together with the data of Fig. 1 obtained in quasi-steady-state (QSS) conditions. In particular, for $V_{obs} = 0.1$ V two spin concentration values are obtained: S_{red} and S_{ox}, for the reduction and the oxidation half cycle, respectively. We suggest that the hysteresis effect observed in QSS conditions and the memory effect observed in the transient DP experiments could be connected. Namely, S_{red} should correspond to the spin concentration observed in DP experiments with $\tau \rightarrow 0$ (since for $\tau = 0$ the spin concentration is measured on a system prepared in the oxidized state, and then set at $V_{obs} = 0.1$ V). On the other hand, S_{ox} is measured on a system which has been left for a long time in the neutral state and then brought to $V_{obs} = 0.1$ V. Consequently, it should correspond to the spin concentration measured in a DP experiment with a long τ, of the order of the time used for scanning the potential from -0.2 to 0.1 V in the QSS experiment.

The important question which now arises is what might be the origin of the relaxation process. At this stage of the study no definite answer can be given. Let us summarize the main points of the process. The polymer chains, being initially charged (oxidized), are suddenly discharged (put in the neutral state). If one tries to recharge the polymer just after the discharge, it has a high ability to be recharged, but this ability decreases with time. In other words, just after discharging the system has a strong "reminiscence" of the charged state. This reminiscence enables fast recharge, and corresponds to nonequilibrium states which relax gradually.

Taking into account the long time scale of the process, it is reasonable to think that a structural relaxation is involved. A possible mechanism could be connected to the rearrangement of the chain configuration which follows the incorporation and extraction of the counter ions upon oxidation and reduction. Just after discharging opened channels are left by the counter ions, and reoxidation requires just the normal redox potential of the polymer. However, with increasing τ the channels get closed gradually, and reoxidation will require increasing extra ener-

gy to reopen the channels. Another possible geometrical relaxation process has been proposed by Heinze, Störzbach, and Mortensen[7] to account for the hysteresis effect. This process relies on the relaxation from the planar to the twisted form which should accompany the quinoid-to-benzoid molecular transition upon discharging. It is closely related to the mechanism previously introduced by Chung et al.[8]

In conclusion, we have shown the existence of memory and slow relaxation effects in conducting polymers. More work has to be done to establish the veritable nature of the phenomena but we think that the study of such nonequilibrium processes is a promising field for the physics of conducting polymers.

[1]C. K. Chiang, C. R. Fincher, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gan, and A. G. MacDiarmid, Phys. Rev. Lett. **39**, 1098 (1977).

[2]J. H. Kaufman, N. Colaneri, J. C. Scott, and G. B. Street, Phys. Rev. Lett. **51**, 1005 (1984).

[3]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).

[4]E. W. Paul, A. J. Ricco, and M. S. Wrighton, J. Phys. Chem. **89**, 1441 (1985).

[5]F. Devreux, F. Genoud, M. Nechtschein, and B. Villeret, in *Electronic Properties of Conjugated Polymers,* edited by H. Kuzmany, M. Mehring, and S. Roth, Springer Series of Solid State Sciences Vol. 76 (Springer-Verlag, New York, 1987), p. 270.

[6]S. W. Felberg and I. Rubinstein, J. Electroanalytical Chem. **240**, 1 (1988).

[7]J. Heinze, M. Störzbach, and J. Mortensen, Ber. Bunsen-Ges. Phys. Chem. **91**, 960 (1987).

[8]T. C. Chung, J. H. Kaufman, A. J. Heeger, and F. Wudl, Phys. Rev. B **30**, 702 (1984).

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

[10]C. Odin et al. (to be published).