Slow Relaxation in Conducting Polymers

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The potential at which conducting polymers can be electrochemically doped to the conducting state shifts slowly when the material is maintained in the insulating state. A logarithmic law for the shift as a function of the wait time in the insulating state has been observed over the range 10^{-4}–10^{5} s. The influence of temperature, pressure, and nature of the electrolyte has been studied. A logarithmic shift is also observed as a function of the scan rate, which indicates that the relaxation process concerns kinetic parameters of the reaction rather than the thermodynamical redox potential. The kinetics of the doping process is shown to obey a universal law, which resembles the aging process of glassy materials.

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It has been recognized for several years that relaxation in complex and disordered systems does not usually obey the "conventional" exponential decay, but follows much slower processes. Many examples of "stretched exponential," or Kohlraush, behavior have been reported, and the relevance of their description in terms of parallel or serial relaxation processes has been discussed [1]. Some cases of logarithmic time dependence were also found, for instance, for the recovery dynamics of photochemically hole-burnt systems [2], or for the relaxation of photoconductance near semiconductor interfaces [3]. Indeed, unambiguous determination of the time-dependence law requires many decades of observational time. In this Letter, we present data which evidence a logarithmic relaxation over at least nine decades. These data concern the potential at which conducting polymers exhibit an insulating-to-conducting transition upon electrochemical doping. Namely, this potential is shifted as $\log_{10}t_w$ if t_w denotes the wait time, that is, the time spent in the insulating state.

Doping, i.e., addition or removal of electrons from the polymer chains, is the central key which governs the main properties of conducting polymers (CP). In particular, CP immersed in an electrolyte can be electrochemically switched between an insulating (neutral) and a conducting (charged) state by controlling the applied potential V. Monitoring the current gives $I(V)$ or $I(t)$ profiles, which are characteristic of the doping process. Complex nonequilibrium behavior is observed, such as hysteresis [4]. Moreover, it has been shown that the response to an applied potential depends on the electrochemical history of the sample. For instance, it was observed in polyaniline that the kinetics of polaron creation upon application of a potential step, as monitored by ESR, becomes slower when the time spent in the neutral insulating state increases [5]. In cyclic voltamperommetry (CV) experiments, the oxidation peak of the first cycle, i.e., the first run after the sample has been left for time t_w in the neutral state, is narrower and is shifted towards more positive potential than the peak observed in steady-state conditions. The wait time was shown to be the relevant parameter to define the electrochemical history of the sample, which is erased by passing through the conducting state [6–9]. These results demonstrate clearly that a slow relaxation process is taking place when the film is maintained in its neutral insulating state. In fact, the same feature is commonly observed in the electrochemical behavior of modified redox electrodes, i.e., electrodes covered by an electroactive polymeric film [10].

The origin of the relaxation effect is not understood yet, although several explanations have been proposed. They can be summarized as follows: (1) The long time scale of the process may suggest a structural relaxation, involving the rearrangement of the chain configuration that follows the incorporation and extraction of counterions upon oxidation and reduction. For instance, the expulsion of counterions during the discharge leaves opened channels, which may close slowly. Consequently, reoxidation would require more and more energy. (2) Another idea relies on the chain twist which accompanies the quinoid-to-benzoid transformation upon reduction. A long persistence of nonequilibrium forms of quinoid could favor reoxidation [11]. (3) Alternately, one may think of the possible role of ions. It has been proposed that on reduction, in preference to the ejection of anions from the polymer matrix, cations can enter to ensure electroneutrality. Then, slow departure of these ions from the polymer matrix could explain a slow variation of its redox characteristics [12]. (4) Considering the doping as a two-step process (neutral state → polaron → bipolaron), the change of the polaron-bipolaron gap may be also envisaged as a mechanism [7].

In this Letter, the main features of the relaxation effect are reviewed. None of the different explanations proposed so far are consistent with experiment. An important finding is that the shift increases with the scan rate of the applied potential. This is evidence that the relaxation concerns the kinetics of the redox process, rather than a thermodynamical equilibrium parameter.

In previous papers, we have reported a quantitative characterization of the relaxation effect observed in CP [6–9]. Use has been made of the potential pulse sequence shown in Fig. 1(a). First, a preparation pulse brings the polymer into the oxidized state. Then, the potential is stepped and maintained for a given wait time t_w at a value where the film relaxes. Last, the redox current generated by a triangular potential scan is recorded. The resulting $I(V)$ profiles, for a polyaniline film of ~ 0.1 μm thickness, are displayed in Fig. 1(b) for different t_w. Relaxation is characterized by the following features: Both the peak potential V_r and the peak height I_r of the relaxed wave oxidation current obey a logarithmic law as a function of t_w. Data of peak potential versus t_w in the range 10^{-4}–10^5 s are given in Fig. 2(a). The range has been covered with the use of two different techniques: millimetric electrodes at long wait time and slow scan rate ($t_w \sim 10$–10^5 s, $u < 1$ V/s), and microelectrodes (5 μm in diameter) for short wait time and fast scan rate [$t_w \sim 10^{-4}$–10 s, $u \sim 10^2$–(2×10^5) V/s] [13]. As shown by Fig. 2(a) V_r is scan-rate dependent. We have established that V_r vs u also follows a logarithmic law. The data of Fig. 2(b) are well fitted by

$$V_r = V_0 + a\log_{10}(t_w + t^*) + b\log_{10}(u)\,, \qquad (1)$$

where $t^* = \Delta V/u$ is the additional wait time which takes into account the relaxation during an effective potential range ΔV. V_0 is a constant, and a will be called the slope of relaxation. Typical values determined on polyaniline films are $a \sim 10$ mV/decade, $b \sim 15$ mV/decade for $u < 1$ V/s, and $a \sim 35$–60 mV/decade for $u > 10$ kV/s.

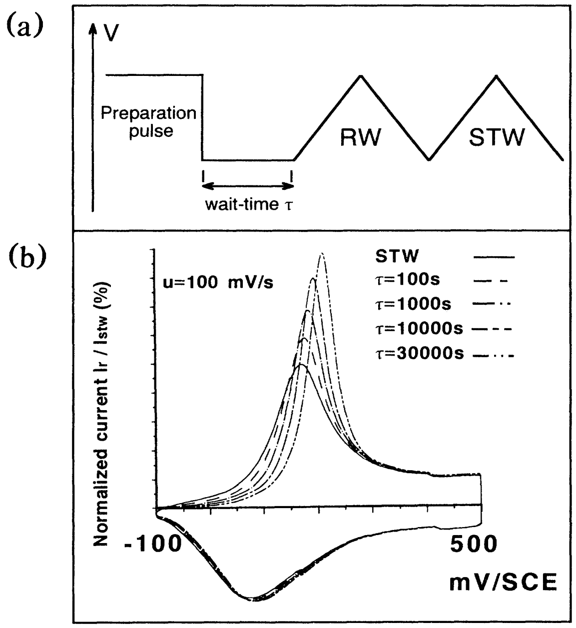

FIG. 1. (a) Potential sequence applied to the polymer film. The redox current is recorded during the triangular scans for different wait times. Wait-time-dependent responses, i.e., "relaxed waves" (RW), are obtained during the first scan. In contrast, during the following scans steady-state waves (STW) are observed. (b) Typical cyclovoltammograms of a ~ 0.1-μm film of polyaniline in $1M$ HCl aqueous solution, after different wait times t_w in the neutral state.

Systematic studies of the parameters which can influence a have been performed and will be published in a subsequent paper. We here summarize the main results. Effects of temperature T and pressure have been tested in the case of thin polyaniline films in HCl aqueous solution. Temperature has been varied between 260 and 350 K, which is the maximum range allowed by our aqueous electrolyte and the film stability. Within the error bars one has $a \propto T$. Such a weak temperature dependence suggests either a relaxation of a strongly disordered system where temperature has little influence (logarithmic relaxation with a slope of k_BT instead of exponential decay), or a nonactivated process. A hydrostatic pressure of 1.5×10^3 kg/cm^2 or a uniaxial pressure of 2×10^2 kg/cm^2 has been applied to the sample during relaxation. In both cases, no change in the shape of $I(V)$ resembling a relaxation behavior has been observed. The absence of significant temperature and pressure dependence gives evidence that a structural origin of relaxation is unlikely. In order to test the ionic hypothesis, experiments have been performed on poly(3-methylthiophene) in electrolytes with different salts, in particular, $\mathrm{Li^+ClO_4^-}$ and $\mathrm{Bu_4N^+PF_6^-}$, which are known to have quite different

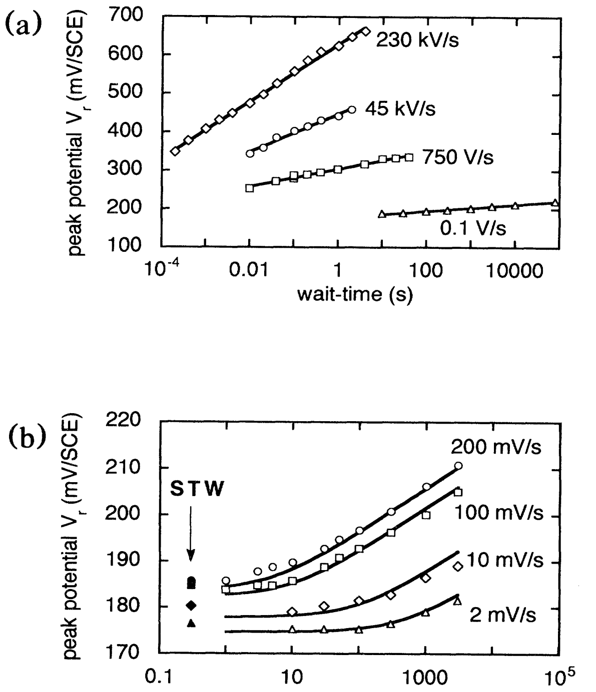

FIG. 2. Potential of the relaxed oxidation peak vs saturated calomel electrode (SCE) as a function of wait times for different scan rates. The data at high scan rates ($u > 750$ V/s) have been obtained on microelectrodes; those at low scan rates ($u < 1$ V/s) on millielectrodes. (a) Data obtained from different samples. (b) Data obtained from the same sample. Solid lines correspond to Eq. (1) with $a = 10$ mV/decade, $b = 15$ mV/decade, $\Delta V = 1$ V.

characteristics. The slope of relaxation a remains the same irrespective of the salt. Therefore, this is in disagreement with the ionic origin [8]. This conclusion is consistent with the result of Baudouin, Chao, and Costa, who noted that even after complete elimination of the ions by rinsing, relaxation still occurs [12]. Finally, a change of the polaron-bipolaron gap during relaxation has already been eliminated by the observation that the polaron concentration is independent of the wait time [7]. Besides the study of the factors which could influence the relaxation, we have searched for possible changes of spectroscopic characteristics of the sample *during* relaxation: UV-visible spectrometry, ellipsometry, and ESR data have been investigated. No change has been detected. Of course, negative results cannot be conclusive. However, it turns out that relaxation does not correspond to a sizable variation of the bulk characteristics of the polymer film.

The influence of the potential during the wait time, V_w, has also been investigated. We have found that relaxation can be observed in polyaniline if V_w is maintained at a value corresponding to the superoxidized state (pernigraniline), which, as the neutral state, is also an insulating state [9]. This is evidence that the relaxation is more likely connected to the transition from the insulating to the conducting state than to the neutral-to-oxidized crossover. We believe this result to be an important piece of information for the origin of the relaxation. Another basic point is the dependence of V_r upon scan rate. Thus, the peak potential, $V_r = V_r(t_w, u)$, instead of being an intrinsic property of the film, is controlled by a kinetically limited redox reaction $P^0 \rightarrow P^+ + e^-$, where P^0 and P^+ denote neutral and charged polymer sites, respectively. Let k_f be the reaction constant: $k_f = k_0 \exp\{-\alpha[V(t) - V_{\rm ox}]/\theta\}$, with $\theta = k_B T/e$, k_0 being the intrinsic rate constant, and $V_{\rm ox}$ the normal redox potential. It can be shown [14] that the oxidation current, $|i/e| = -d[P_0]/dt$, presents a peak at potential $V_{\rm pk}$:

$$V_{\rm pk} = V_{\rm ox} + (\theta/\alpha)[\log_{10} u - \log_{10}(\theta k_0)] , \qquad (2)$$

where α is a potential barrier shape factor [14] (typically $\alpha \sim 0.5$ and $\theta = 60$ mV/decade at room temperature). This scan-rate dependence is in agreement with experimental data, as represented by Eq. (1). Furthermore, the wait-time dependence could also be accounted for by assuming a power law for k_0: $k_0 \propto t_w^{-\lambda}$, with $\lambda = a\alpha/\theta$. As t_w increases the rate of the reaction decreases. One obtains $\lambda = 0.1$ and 0.4 for millielectrode and microelectrode experiments, respectively.

Another way to follow the redox reaction consists of recording the time response of the current $I(t)$ during a potential step V applied after t_w [Fig. 3(a)]. Data for different t_w are given in Fig. 3(b). In Fig. 3(c) the data are represented in reduced units: $I/I_{\rm max}$ vs $t/t_{\rm max}$, where $t_{\rm max}$ is the time at maximum current $I_{\rm max}$. It appears that, as t_w increases, the doping process gets slower and slower, but obeys a universal law for $t > t_{\rm max}$. Furthermore, as shown by Fig. 3(d), $t_{\rm max}$ varies with t_w according to a power law: $t_{\rm max} \propto t_w^{\mu}$. We have obtained $\mu \sim 0.2$ and 0.6 for millielectrode and microelectrode experiments, respectively. Since $t_{\rm max}$ is a characteristic time of the doping process, one expects $t_{\rm max} \propto k_0^{-1}$, and thus, $\lambda = \mu$. Indeed, this is in semiquantitative agreement with the data. It is noteworthy that such a behavior resembles the aging processes observed in spin glasses [15] and glass polymers [16].

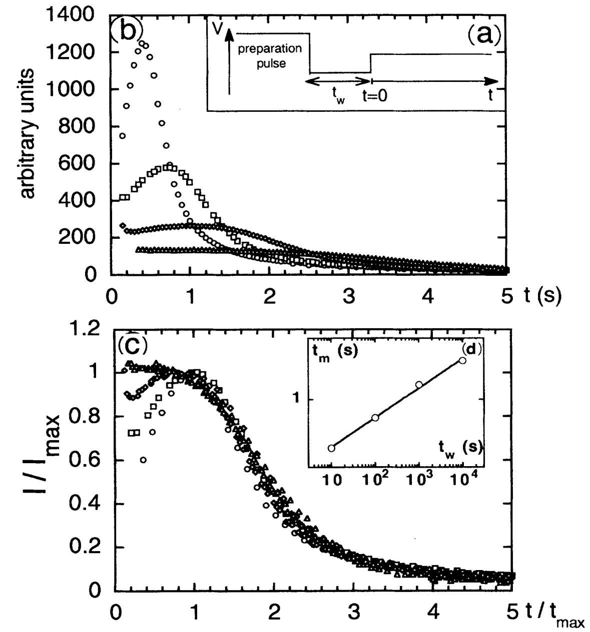

FIG. 3. (a) Pulse potential sequence. The current is recorded during the potential step applied after a wait time t_w. (b) Current vs time of a $\sim$0.1-μm film of polyaniline in 1M HCl for different wait times t_w: ○, 10 s; □, 100 s; ◇, 1000 s; △, 10 000 s. (c) Normalized current $I/I_{\rm max}$ from data of (b) vs the reduced time $t/t_{\rm max}$. $t_{\rm max}$ denotes the time at maximum current $I_{\rm max}$. (d) Time $t_{\rm max}$ vs t_w.

Concerning the microscopic origin of the relaxation effect, no definite description can be given yet. We think that it should be considered that the effect is taking place in a medium (a) which is electronically insulating and (b) which has a high effective dielectric constant (due to impregnation by the electrolyte). These points suggest a mechanism based on a slow rearrangement of space charges. Different possible pictures can be envisaged. For instance, one can imagine that a potential barrier —like a Schottky barrier—is growing up at the polymer-metal interface to maintain the continuity of the Fermi levels when the polymer has been switched into the insulating state, and which would have to be surmounted for reoxidation. The reaction constant rate can be understood as the probability to jump over a barrier E_b: $k_0 = \nu_0 \exp(-E_b/k_B T)$, with $\nu_0 \sim k_B T/h$. The time dependence of k_0 is then reflected by a time variation of the barrier height E_b, which should follow, as suggested by the data, $E_b \sim \lambda k_B T \log_{10} t_w$. Such a logarithmic dependence is observed for the relaxation of excess charges created by photoillumination at a semiconductor interface [3]. It is also expected in a disordered material, where the barriers are distributed. We can imagine that, just after the film has been switched to the insulating state, residual electronic charges remain in the polymer bulk. These charges are gradually evacuated towards the metal electrode, and a chargeless highly insulating area grows in the polymer at the interface. As this area gets wider it becomes more and more difficult for the remaining charges to be evacuated (logarithmic law). Reciprocally, the reoxidation of the film requires jumps over the same highly insulating area, and thus it slows down.

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