Electric-Field-Dependent Charge-Carrier Trapping in a One-Dimensional Organic Solid

U. Seiferheld and H. Bässler
Fachbereich Physikalische Chemie, Philipps-Universität, D-3550 Marburg, West Germany

and

B. Movaghar
GEC Research Laboratories, Hirst Research Centre, Wembley, United Kingdom

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The relaxation of photoconduction in a polydiacetylene crystal containing a high density of defects is shown to follow the predictions of the theory for field-dependent diffusion in one dimension. At intermediate times and fields an $\exp[-3(t/\tau_1)^{1/3}]$ law is observed merging into an $\exp(-t/\tau_2)$ behavior as $t\to\infty$. The predicted functional change of $\tau_2(E)$ at a critical field is recovered.

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Recent theoretical work[1-3] has led to the recognition that trapping of an elementary excitation in a condensed system, often considered to be a first-order process with a time-independent rate constant, does not in general follow an exponential decay law. The exact time dependence of the survival probability of a particle walking randomly on a discrete lattice containing static traps depends on the system parameters, notably its dimensionality. Whereas in a three-dimensional (3D) system the deviations from a pure exponential law are small[2] and probably outside experimental detectability,[4] they are significant in one dimension. The qualitative reason is that the probability of a particle encountering a trap is related to the number of new sites visited ($n_{\rm NSV}$) in course of its motion. This quantity is a linear function of the total number of jumps (N) executed only in 3D. In 2D or 1D, $n_{\rm NSV}$ increases sublinearly with N implying that the trapping rate becomes time dependent. An analytic treatment by Movaghar *et al.*[3] showed that in 1D the long-time behavior of the decay of an excitation is governed by an $\exp[-(t/\tau_0)^{1/3}]$ law. This law, which is characteristic for one-dimensional trapping kinetics, has recently been observed by Hunt, Bloor, and Movaghar[5] in the disordered polymer polydiacetylene 10*H*.

The situation becomes more complex if the particle is a charge carrier moving under the influence of an external electric field E. Again, at fields of practical interest the field effect on the trapping rate is negligible in 3D, yet strong in 1D. The reason is that, because of its restricted motion in 1D, a carrier will find a trap faster in the presence of a drain field. Haarer and Möhwald[6] first reported a field-dependent trapping time in the organic charge-transfer salt phenanthrene–pyromellitic acid dianhydride (PMDA). From the value of the crossover field the authors were forced to conclude that interchain motion was playing an important role in the trapping kinetics. A quantitative analysis of the influence of interchain motion was given by Scher, Alexander, and Montroll[7] using the first passage time approximation. Very recently Movaghar, Pohlmann, and Würtz (MPW)[8] derived an exact solution for the time dependence of the trapping probability. They showed that in the limit $t\to\infty$ a simple exponential law should be approached, the decay time being $\sim E^{-2}$ below a critical field E_c and $\sim E^{-1}$ above E_c.

In this Letter we wish to report for the first time on experiments revealing the trapping kinetics of charge carriers in a 1D system over a large range of electric fields and time. As a test object we chose a polydiacetylene single crystal [polydiacetylene-bis(toluenesulfonate), abbreviated as PTS]. This class of materials is unique in the sense that it combines the anisotropy of classic polymers, arising from the large degree of anisotropy of binding forces along and perpendicular to the polymer chain, with crystalline order. Since the lowest electronic levels are those of the conjugated polymer backbone, it is the extended chain which determines the charge-carrier transport properties of the system. The macroscopic anisotropy of current transport in PTS has been found to be $\sim 10^3$,[9] although the microscopic anisotropy must be $\gg 10^4$,[10] similar to what has been reported for polyacetylene.[11] Measuring the relaxation behavior of a photocurrent in PTS should therefore provide a simple probe for trapping in a quasi 1D system.

Since as grown PTS crystals contain no recombination centers for carriers,[12] their decay after terminating the carrier generation process is usually governed by thermal release from moderately deep traps followed by discharge at the contacts. In order to render the carrier trapping process rate determining we deliberately introduced additional traps and, concomitantly, recombination centers by bombarding the [100] face of a high-quality PTS crystal with 1 μC/cm^2 of 100-keV helium ions. Considering that about 2% of the repeat units of the polymer chain are hit by a He$^+$ ion and that about 100 eV is dissipated in the course of its passage through one lattice plane (under the assumption of a penetration depth of 1 μm), a fractional concentration $x \lesssim 0.02$ of broken bonds appears to be a realistic estimate. The crystals were contacted with surface contacts in gap arrangement (see inset in Fig. 1), the field direction being parallel to the polymer chain. A Hg high-pressure lamp was used to excite steady-state photocurrents whose decay was followed, after switching off the light source, with conventional detection techniques. The penetration depth of the exciting light in the spectral range where the photosensitivity of PTS is large[13] is of order 10^{-5} cm, i.e., much less than the depth of the doping profile. All measurements were done in a vacuum chamber (10^{-6} mbar) at ambient temperature.

Figure 1 presents a family of photocurrent relaxation curves in $\log i$ vs $t^{1/3}$ representation after subtracting the steady-state dark current. After a fast initial decay with instrument-limited time constant (~ 2 s) a linear decay law is observed. In the extreme case ($E = 1.7 \times 10^3$ V cm^{-1}) it extends over two decades in current and three decades in time. As the field increases the asymptotic current decay in the long-time limit becomes progressively steeper. Plotting the relevant data on a $\log i$ vs t scale reveals that a simple exponential law is approached (Fig. 2). The decay time (τ_2) is found to be $\sim E^{-2}$ below critical field $E_c \approx 10^4$ V cm^{-1} and $\sim E^{-1}$ above E_c (Fig. 3).

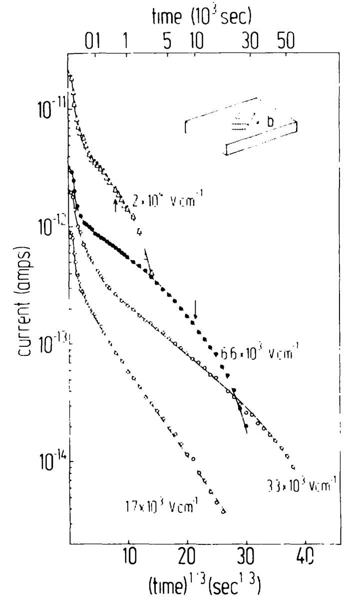

FIG. 1. $\log i$ vs $t^{1/3}$ plot of the time dependence of the current measured with a defect-doped PTS crystal after switching off steady-state illumination (data points are taken from continuous recorder traces). Values of the applied electric field are as shown. Arrows here and in Fig. 2 indicate identical times in the corresponding figures. The inset shows the electrode arrangement (gap: 0.03 cm, length: 0.2 cm). $\vec{b}$ indicates the direction of the polymer chains in PTS.

These observations confirm the predictions of the MPW theory which expresses the decay of the carrier concentration as a function of fractional trap concentration x and reduced electric field $\eta = eEa/2kT$, a being the lattice constant. The theory, which is exact for one-dimensional diffusion, predicts that the survival fraction $n(t,\eta)$ should behave as

$$n(t,\eta) = P(t,\eta),$$

where

$$P(t,\eta) = \frac{4}{\pi^2}\exp(-\eta^2 Wt)\int_0^\infty \frac{S\,dS}{[1+(\eta S/\pi x)^2]^2} \times \exp\left(\frac{-\pi^2 x^2 Wt}{S^2}\right)\left[\frac{e^{-S}}{1-e^{-S}} + \frac{\exp[-S(1-\eta/x)]}{2\{1+\exp[-S(1-\eta/x)]\}} + \frac{\exp[-S(1+\eta/x)]}{2\{1+\exp[-S(1+\eta/x)]\}}\right] \tag{1}$$

in the range $0 \leq \eta \leq x$. For $\eta > x$, the corresponding expression is

$$n(t,\eta) = P(t,\eta) + 8x^2(\eta - x)^2 \exp(-\eta^2 Wt)\sum_{n=0}^{\infty} \frac{(n+\frac{1}{2})\exp\{Wt[(\eta - x)/(2n+1)]^2\}}{[2n\eta + x]^2[2(n+1)\eta - x]^2}. \tag{2}$$

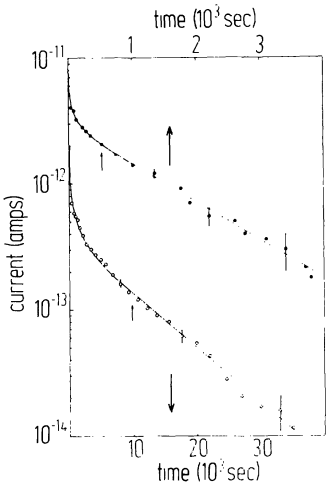

FIG. 2. Long-time behavior of $i(t)$ for two different fields (lower curve $E = 6.6\times 10^3$ V/cm, upper curve $E = 2\times10^4$ V/cm) in $\log i$ vs t representation (data are from Fig. 1). Note that there is a different time scale for each curve. Arrows: See caption to Fig. 1.

In the long-time limit we can identify the current decay with $n(t)$ for which the long-time behavior is easily obtained from Eqs. (1) and (2).

In the range $0<\eta<x$, $i(t)$ is dominated by the term

$$i(t)\propto \exp[-3(t/\tau_1)^{1/3}]\exp[-t/\tau_2]$$

where $\tau_1 = 4[\pi^2(x-\eta)^2 W]^{-1}$ and $\tau_2 = (eEa_h/2kT)^{-2}W^{-1}$; W is the zero-field jump rate between adjacent hopping sites at a distance a_h along the chain.

For intermediate times we should obtain an $\exp[-3(t/\tau_1)^{1/3}]$ law and for long times an exponential law with $\tau_2 \propto 1/E^2$. In the high-field case, $\eta > x$, the situation changes drastically; from the second term of Eq. (2) which is dominant in the intermediate and long-time domain we now have $i(t)\propto \exp[-(2\eta x - x^2)Wt]$ and a time constant $\tau \propto 1/E$ $(\eta \gg x)$. Figure 3 not only verifies the predicted functional change of $\tau_2(E)$, but allows calculation of the concentration of trapping sites. From the critical field $E_c = 2kTx/ea_h$ at which $\tau_2(E)$ changes from a quadratic to a linear behavior, $x = 0.012$ follows if a is identified with the length of the polymer repeat unit in PTS (4.9 Å).[14] This value is close to the defect concentration estimated on the basis of the irradiation dose.

The predicted field-sensitive transition from the cube-root decay law to the linear decay law in time is clearly borne out by Figs. 1 and 2. The ratio of the decay times τ_1 and τ_2, measured at a given field E, allows an independent estimate for the concentration x of deep traps. Inserting experimental numbers into the expression $\tau_1/\tau_2 \simeq (ea_h E/\pi x kT)^2$ gives $x/a_h = 5\times 10^4$ cm^{-1}. For $a = a_h = 5$ Å, $x = 2.5\times 10^{-3}$ would follow, a factor of 5 less than the value given above. Although some difference might be expected to arise from the approximations inherent to the analytical treatment, we believe that in essence it arises from the fact that carrier transport in a PTS crystal damaged by He$^+$ bombardment is limited by shallower trapping centers. This conclusion is independently arrived at by considering the large relaxation times of the photocurrent.

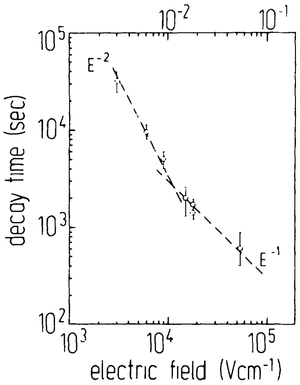

FIG. 3. Field dependence of the decay time τ_2 derived from $\log i$ vs t curves. η is the reduced electric field $(= eEa/2kT)$.

Evaluating the effective carrier jump rate W from the expression for τ_1 gives $W \approx 1$ s^{-1}, whereas a carrier mobility of order 10 cm^2 (V s)$^{-1}$ (Ref. 15) would imply $W \sim 10^{14}$ s^{-1} if analyzed in terms of carrier hopping across a distance of 5 Å. We are therefore forced to conclude that the motion of a carrier along a PTS chain before becoming ultimately removed from the conduction process is modulated by moderately deep trapping centers characterized by a maximum trap depth which is ~0.8 eV. It is interesting to note that this trap determines both the onset of photoconduction[16] and the activation energy of the dark current[17] in the unbombarded material. Since bombardment must be expected to produce a concentration of traps (or barriers) with a distribution of energies, carrier motion along the polymer chains will be dispersive up to times of the order of the inverse release rate of the deepest traps ($t \sim 1$ s). For $t \lesssim 1$ s the carriers will have an electric field and time dependent mobility. Taking an exponential distribution of barrier heights will, for example, give a corresponding jump rate distribution of the form $\rho(W) \sim W^{-\alpha}$ and the drift velocity V_d will scale as $V_d \sim E^{1-\alpha}/t^{\alpha}$ in the time-dependent domain. In the dc limit ($t \gg 1$ s) carrier drift becomes "normal" with $V_d = 2D\eta/a$ where $D = a^2 W$ and denotes the (long-time) diffusivity on the polymer chain. In the time domain studied here ($t \gg 1$ s), the motion is therefore no longer dispersive, the inhomogeneity of the initial carrier distribution is negligible, and the effective jump rate W is given by the long-time diffusivity on the polymer chain. We also note that the difference in the values for x given above vanishes if $a_h \sim 5a$, i.e., every fifth chain unit acts as a localization center for a carrier. We thus conclude that He$^+$ bombardment of a PTS crystal generates both traps deep enough to capture a carrier until it ultimately recombines with a counter charge and "shallower" traps which considerably reduce the (long-time) mobility by localization along the chain without destroying the 1D character of carrier motion. Whereas the former control the decay of photogenerated charge carriers in the time domain studied here, the latter appear to be already present in the unbombarded material with smaller concentration.[17]

In summary we have studied the relaxation behavior of steady-state photoconductivity in a polydiacetylene crystal containing a large defect concentration. It exhibits trapping kinetics in accord with the MPW theory for a 1D system in presence of a bias field. In particular, both the existence of the field-independent $\exp[-(t/\tau_0)^{1/3}]$ decay law governing the low-field intermediate time regime, the field-dependent decay in the limit $t \to \infty$, and the predicted change in the decay characteristics at $\eta = x$ are observed.

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