diffusion-fundamentals.org

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Dispersive Gaussian Hole Transport in a Molecularly Doped Polymer

N. Schupper, R. Kahatabi, R. Diamant and D. Avramov

Hewlett–Packard Indigo Ltd, Kiryat Weizmann P.O. Box 150, Rehovot, Israel
Rehovot, Israel, E-mail:Nurith.Schupper@hp.com

1. Introduction

Organic photoconductors (OPC), such as conjugated and molecularly doped polymers (MDP) are widely studied due to their applications in various electronic devices, e.g. electrophotography. Understanding charge carrier motion and parameters influencing it are of crucial importance.

A common experimental technique used to measure charge transport in OPC's is Time of Flight (TOF) [1]. The OPC is initially negatively charged so a capacitor with an applied uniform electric field is formed. A monochromatic short pulse of light is flashed upon the sample and creates electron-hole pairs which are pulled apart by the external field. Holes travel along the sample until they discharge the front electrode and thus produce a displacement current. By the signal shape and magnitude hole transport can be studied. A transient of rectangular shape is produced by a well-defined sheet of charge carriers moving at a constant velocity. The decay of an actual current, however, shows rounded fall-off near t_τ, the carrier transit time, due to *normal (Gaussian) diffusion* superimposed on the field-induced drift. For some amorphous semiconductors [2] the current decreases continuously, and its flow extends to very long times so that in a double logarithmic scale it will show two slopes demarcated at an effective transit time. This implies that drifting carriers slow down even before they exit the sample and the spread of arrival times in this *anomalous (dispersive) transport* is much greater than expected from normal diffusion. Hole transport mechanism is visioned as a field-driven chain of electron transfer events from neutral molecules to radical cations by a *hopping mechanism* in a manifold of localized states. In MDP's charge transport can be either normal, anomalous or exhibit a transition between the two. In the present work we study charge transport in an MDP and show that although carrier motion occurs through normal diffusion, its properties differ from normal diffusion, because the spread of velocities is anomalously large increasing with the electric field.

2. Experiment

The OPC consists of two-layers: a thin (~0.3 μm) Charge Generating Layer (CGL) of organic pigment and a thicker (L~18 μm) Charge Transport Layer (CTL) fabricated from hydrazone based organic molecules dispersed in polycarbonate. A thick layer of Mylar serves as a substrate and a thin film of Al is deposited on it. A top conductive semi transparent gold electrode is spattered on the CTL. An applied voltage of 300-900 V charges the sample which is used as a capacitor in an RC circuit and then a highly absorbed laser-flash of 1μsec and 650 nm photogenerates charges; electrons go immediately to the Al electrode while holes drift through the CTL to the gold electrode. The energy per pulse was adjusted so that the charge generation was less than 0.03 CV in order to prevent space charge carrier effects.

3. Results and Discussion

Typical TOF transients at 30^0C are shown in Figure 1(a). All transients consist of a discernible transit time implicating Gaussian transport. In order to assure this and to extract mobilities and diffusion coefficients we analyze the data as follows [3]; The current $I(t)$ is treated as a combination of a function describing the current which would flow if the sample were unbounded, reduced by a factor that accounts for exiting carriers, $I(t) = I_0\left[1-\int_0^t p(t')dt'\right]$, $p_t(t)$ is a first passage time distribution. Trial functions were chosen so that they allow for both regular and anomalous transport; $I_0(t) = A \cdot t^{1-\alpha}$ is a fractional power-law form of [2] where A provides an overall scale for the signal and α gives the dispersion so that $\alpha \to 1$ for a non-dispersive signal. Fitting this form gives values of α in the range of 0.92-0.99 as is expected by the plateaus observed in Figure 1(a). Transit time distributions are shown in Figure 1(b) and fit the *inverse Gaussian,* $p_t(t) = \left(L/\sqrt{2\pi\sigma^2 t^3}\right)\exp\left[(L-\bar{v}t)^2/2\sigma^2 t\right]$ which stems from a distribution in positions of $x(t)\sim N(\bar{v}t, \sigma^2 t)$. The entire time dependence was subsequently fit to: $I(t) = A\, t^{-(1-\alpha)}\left[1+\mathrm{erf}\left(\frac{L/t - v}{\sigma\sqrt{2}}\right)\right]/2$, with high quality for temperatures in the range 15^0C-41^0C (Figure 1a). TOF photocurrents were also produced by a 1D Brownian motion simulation with probabilities and delay times extracted from the velocities and standard deviations obtained by the fit.

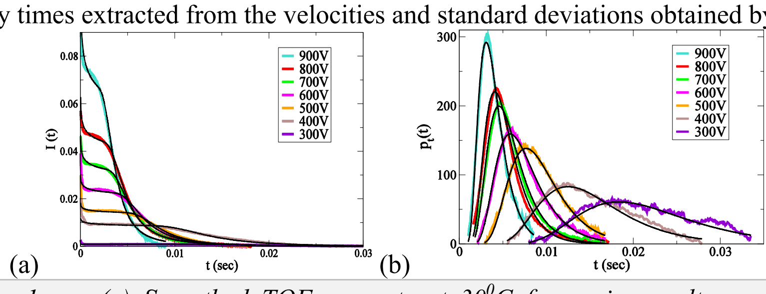

Figure 1 (a) Smoothed TOF currents at 30^0C for various voltages and a theoretical fit. (b) First passage waiting time distribution.

Average velocities $\overline{v}$ and diffusion coefficients $D = \sigma^2/2$ are obtained separately from which we extract transit times $t_\tau = \frac{L}{\overline{v}}$ and hole mobilities $\mu = \overline{v}/E$. The dependence of the mobility on the electric field at different temperatures is plotted in Figure 2(a), showing a Poole-Frenkel (PF) behavior $\mu(E,T) = \mu_0(T)\exp\left(\beta\sqrt{E}\right)$ [1]. Einstein relation states that mobility and diffusion coefficient are related by $D = \mu kT/e$. Figure 2(b) shows that *eD/μkT* is not constant and increases monotonously with electric field. We propose a functional form of $D/\mu kT = 1 + \left(E/E_0\right)^\gamma$, with γ~1.32. Thus although transients stem from Gaussian transport, the spread of velocities is anomalously large and this can be associated with energetic and positional disorder so that in the presence of a field some carriers are anomalously delayed. This behavior is situated between the two extremes of normal and anomalous transport and is therefore termed *Dispersive Gaussian Transport* [4]. From the dependencies of mobility and diffusivity on the electric field and using the 1D simulation electrophotographic discharge curves can be produced in the high voltage limit where space charge effects are negligible.

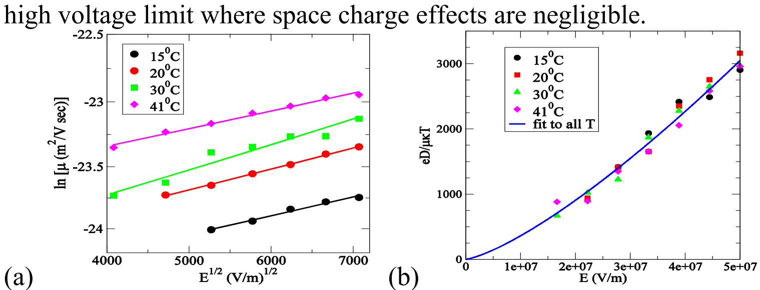

Figure 2. (a) PF behavior of the mobility, (b) Dependence of eD/μkT on the electric field showing violation from Einstein relation.

4. Conclusions

Hole transport in an MDP was studied using the TOF technique. Although transport mechanism was found to be normal, diffusion coefficients grow with the electric field much faster than mobilities and the charge carrier mechanism deviates from regular diffusion theory.

[1] D. Hertel, H. Bassler, ChemPhysChem 9, (2008). 666-688; Borsenberger P.M., Weiss D.S. Organic Photoreceptors for Imaging Systems, Rochester, New York (1993) Ch. 7,8.
[2] Scher H. and Montroll E. W. Phys. Rev. B 12, (1975) 2455-2477.
[3] J. C. Scott, L. Th. Pautmeier, L. B. Schein, Phys. Rev. B, 46, (1992) 8603-8606.
[4] Yuh H. J., Stolka M., Phil. Mag. B, 58 (1988), 539-549;Richert R., Pautmeier L. and Bassler H. Phys. Rev. Lett.31 (1989), 547-550.