Charge transport at low electric fields in π-conjugated polymers

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In low-mobility materials the charge carrier mobility is usually measured using time-of-flight (TOF) methods. However, the use of TOF methods calls for a necessary condition to be fulfilled: viz., that the dielectric relaxation time must be bigger than the charge carrier transit time, $\tau_\sigma \gg t_{tr}$, through the interelectrode distance d. If this condition is not fulfilled, then the equilibrium charge carrier concentration p_0 is sufficient to redistribute the electric field inside the sample during a time interval shorter than the small-charge drift time. Consequently, in the low-field region, the apparent charge carrier mobility estimated by the TOF method increases when the electric field decreases, while in reality the mobility does not increase. We show how to estimate the real mobility values, using extraction current transients [G. Juška *et al.*, Phys. Rev. Lett. **84**, 4946 (2000)] for which the fulfillment of the $\tau_\sigma > t_{tr}$ condition is unnecessary. We demonstrate this effect in regioregular poly(3-octyl thiophene) using both the TOF and carrier extraction by a linearly increasing voltage methods and show that the true mobility does not increase as a function of decreasing field.

I. INTRODUCTION

Organic materials, such as π-conjugated polymers and oligomers, are used extensively in light-emitting[1] and field-effect[2] devices. In these devices the injection and subsequent transport of charge carriers are of fundamental importance for the device operation, and knowledge of the transport will help understanding and developing the devices and materials. In the region of low electric fields, F, an increase of the charge carrier mobility μ with decreasing electric field has been reported in various organic materials.[3–8] On the basis of Monte Carlo simulations the decrease of the charge carrier mobility has been interpreted as hopping in the simultaneous presence of diagonal (energetic) and off-diagonal (positional) disorder.[9] In the high-field region the charge carrier mobility dependence on electric field, $\ln \mu \propto \sqrt{F}$, has been explained by the increased probability of electric-field-stimulated release from localized states, according to the Poole-Frenkel model.

In low-mobility materials the charge carrier mobility is usually measured using time-of-flight (TOF) methods. However, the use of TOF methods, calls for a necessary condition to be fulfilled: viz., that the dielectric relaxation time must be bigger than the charge carrier transit time ($\tau_\sigma \gg t_{tr}$) through the interelectrode distance, d. This condition has not been met in the low-field regime (up to 10^5 V/cm) in the results presented in Refs. 5–8. Kaneto *et al.* presented a model where the bias is concentrated in the depletion layer and the transit time is determined by carrier drift through the low-field region, causing a reduced mobility value.[10] In this paper we demonstrate that in π-conjugated polymers at low electric fields, the equilibrium charge carrier concentration p_0 can be sufficient to redistribute the electric field inside the sample during a time interval shorter than the small-charge drift time. As a consequence, the apparent charge carrier mobility estimated by the TOF method increases when the electric field decreases, while in reality the mobility does not increase. We show how to estimate the real mobility values,

using a novel carrier extraction by a linearly increasing voltage (CELIV) method,[11–13] for which the fulfillment of the $\tau_\sigma > t_{tr}$ condition is unnecessary.

II. THEORY

In TOF measurements, blocking contacts are necessary to avoid charge carrier injection. The necessary condition for TOF, $\tau_\sigma = \varepsilon \varepsilon_0 / e p_0 \mu > t_{tr} = d / \mu F$ (where ε is the dielectric permittivity), means that the amount of equilibrium charge carriers ($e p_0 d$) must be smaller than the amount of charge carriers on the electrodes ($\varepsilon \varepsilon_0 U / d$). In the opposite case (i.e., $\tau_\sigma < t_{tr}$) the amount of bulk charge carriers is sufficient to redistribute the electric field during the time interval $\sqrt{\tau_\sigma t_{tr}}$. Thus, the photoexcited charge carriers, generated by light at the semitransparent electrode, will drift in a redistributed electric field.

For clarity, let us examine a simplified case, where both charge carrier diffusion and trapping are neglected. When the voltage is applied to the sample electrodes, the equilibrium charge carriers will be extracted and the electric field in the sample will be redistributed according to Poisson's equation as [see Fig. 1(a)] $F(x) = (e p_0 / \varepsilon \varepsilon_0)(l - x)$, where $l = \sqrt{2 U \varepsilon \varepsilon_0 / e p_0}$ is the extraction depth. It should be noted that the extraction depth equals the interelectrode distance ($l = d$) when $t_{tr} = 2 \tau_\sigma$: i.e., at the critical voltage

$$U_C = \frac{e p_0 d^2}{2 \varepsilon \varepsilon_0}. \tag{1}$$

The photogenerated small charge (Q_0) drift current through the depletion region may be obtained from the system of equations

$$j(t) = \frac{Q_0}{d} \mu F(x),$$
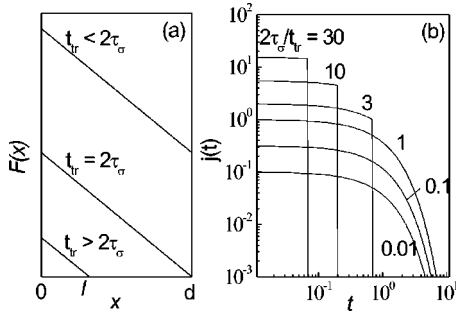
$$\frac{dx}{dt} = \mu F(x), \tag{2}$$

FIG. 1. In (a) schematic view of the electric field distribution after extraction of equilibrium charge carriers as a function of distance (d is the interelectrode distance) for different voltages. The extraction depth l is shown in the figure. In (b) the corresponding transients of the charge carrier drift currents using $2\tau_\sigma/t_{tr}$ as a parameter calculated using Eq. (3) are shown.

which give

$$j(t) = Q_0 \sqrt{\frac{2}{\tau_\sigma t_{tr}}} \exp\left(-\frac{t}{\tau_\sigma}\right) \quad \text{when} \quad U < U_C (2\tau_\sigma < t_{tr}),$$

$$j(t) = Q_0 \left(\frac{1}{t_{tr}} + \frac{1}{2\tau_\sigma}\right) \exp\left(-\frac{t}{\tau_\sigma}\right)$$

$$\text{when} \quad U > U_C \quad \text{and} \quad t < t_{tr}^*,$$

$$j(t) = 0 \quad \text{when} \quad U > U_C \quad \text{and} \quad t > t_{tr}^*, \quad (3)$$

where the transit time in the redistributed electric field $t_{tr}^* = \tau_\sigma \ln[(2\tau_\sigma + t_{tr})/(2\tau_\sigma - t_{tr})]$. In Fig. 1(b) we show the calculated kinetics of the drift current using Eqs. (3) with no dispersion, showing the apparent $\mu(U/d)$ dependence. In case of dispersive transport the drift time of the moving charge carriers is estimated from the kink in the log j-log t plot.[3–8,14] In this work, we have calculated the mobility through the usual relation $\mu = d^2/U t_{tr}$, using the more accurate estimate of the transit time from the moment when the photocurrent has decreased by half from the plateau $[j = j(0)/2]$.

Thus, assuming that the transit time corresponds to charge carrier drift through the whole sample thickness, while in reality it only drifts through the carrier extracted region (depleted region), the apparent mobility value μ_{app} is estimated as

$$\mu_{app} = \mu \frac{t_{tr}}{\tau_\sigma \ln 2} = \frac{2U_C}{\ln 2} \frac{1}{U} \quad \text{when} \quad U < 3U_C,$$

$$\mu_{app} = \mu \frac{t_{tr}}{t_{tr}^*} = \mu \frac{t_{tr}}{\tau_\sigma \ln \dfrac{2\tau_\sigma + t_{tr}}{2\tau_\sigma - t_{tr}}} \quad \text{when} \quad U > 3U_C. \quad (4)$$

Note that when $U \gg U_C$, μ_{app} approaches the true mobility value. In Fig. 2 the calculated mobility, using a Poole-Frenkel type of field-dependent mobility for both CELIV and TOF [according to Eq. (4)], is shown.
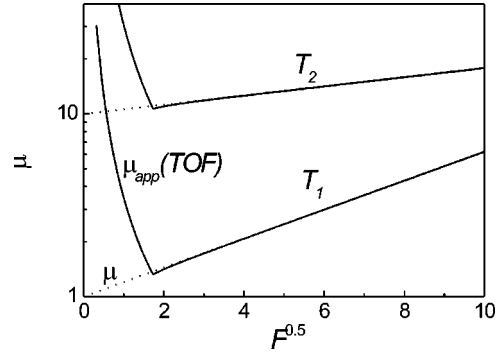

FIG. 2. Comparison of the calculated electric field dependences of the apparent mobility (solid line) and true mobility (dotted line) for two different temperatures ($T_2 > T_1$). The calculations are done according to Eq. (4) including the Poole-Frenkel-type field-dependent mobility but no diffusion or trapping.

III. EXPERIMENT

The regioregular poly(3-octylthiophene) was purchased from Sigma Aldrich and used as received. We dissolved the polymer in chloroform in a concentration of 10 mg/ml. The solutions were filtered through a 0.20 μm filter before the solution was cast onto prepatterned ITO-covered glass substrates (Planar International). Finally a 30 nm (semitransparent) aluminum top electrode with typical dimensions 5–12 mm^2 was evaporated under a vacuum of 10^{-5} mbar. The films were solution or spin casted in air, but stored and measured in a closed-cycle cryostat (Oxford CCC1104) under vacuum to make temperature measurements possible. We note that regioregular PAT films are sensitive for oxygen and water,[15,16] with increasing conductivity as a result. We have taken appropriate measures to make sure that the extrinsic (unintentional) dopants are minimized in our measuring system, confirmed by the fact vacuum annealing at elevated temperatures before evaporating the top electrode does not change our results.

The theory behind CELIV has been presented elsewhere,[11–13] and it is based on the charge carrier extraction current, which causes the electric field redistribution, and the true mobility value is therefore obtained. CELIV has the advantage of being experimentally very simple; a variable pulse generator (Stanford DS345) and a memory oscilloscope (Tektronix TDS680B) were used to record the extraction currents. The only restriction imposed by the experimental setup is that at least one contact of the sample should be (partially) blocking. The voltage rise speed A, used in these experiments, ranged between 10 and 10^6 V/s. The very initial current step (see Fig 3, inset) $j(0)$ is caused by the geometrical capacity of the sample and can be used for estimation of d or ε of the sample. The extraction current $\Delta j = j(t) - j(0)$ is caused by the conductivity of the sample and we can estimate the bulk conductivity, without interference from the contact barriers, as[11,12]

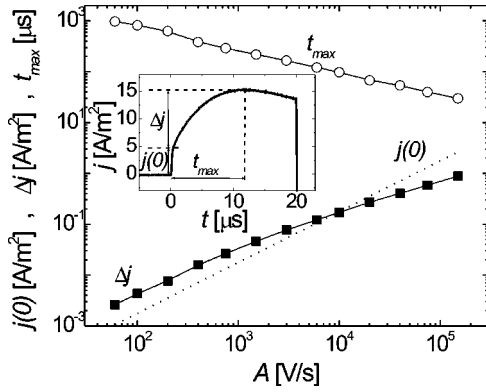$$\sigma = \frac{3\varepsilon\varepsilon_0 \Delta j}{2t_{max}j(0)}, \quad (5)$$

FIG. 3. Extraction current Δj, capacitance part $j(0)$, and the time to reach extraction current maximum t_{max} dependences on the voltage increase rate A obtained in CELIV for a 923-nm-thick RRPOT film. Insert: an experimental extraction current transient at $A=3$ V/20 μs in a 923-nm-thick RRPOT film with Δj, $j(0)$, and t_{max} defined.

where t_{max} is the time to reach the extraction current maximum. For experimental reasons, the most suitable measurement regime is when Δj is comparable to $j(0)$ (see Fig. 3, inset). In this region we estimate the mobility of the equilibrium charge carrier as[11,12]

$$\mu = \frac{2d^2}{3At_{max}^2 \left[1 + 0.36 \dfrac{\Delta j}{j(0)} \right]}. \quad (6)$$

For the TOF measurements, a nitrogen laser (Oriel), with a pulse width of 7 ns, energy 3.55 eV, and energy per pulse of 500 μJ, was used together with the pulse generator and a delay function generator (Stanford DG 535) to ensure proper delay time between voltage and light pulses. TOF was measured with 50 Ω input impedance on the oscilloscope.

IV. RESULTS AND DISCUSSION

We pursued comparing the mobility values obtained experimentally by TOF and CELIV methods in the same sample. As follows from Ref. 11, the condition $2\tau_\sigma \cong t_{tr}$ cor-
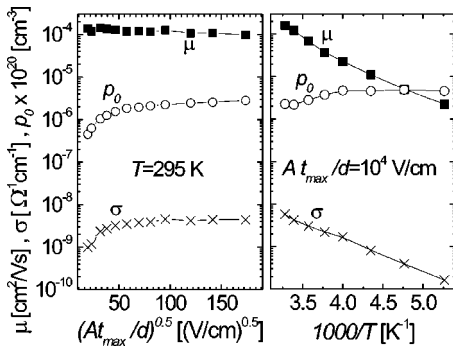

FIG. 4. Electric field (at $T=295$ K) and temperature dependences (at a field of $At_{max}=10^4$ V/cm) of conductivity σ, equilibrium hole concentration p_0, and drift mobility μ in RRPOT as measured using CELIV. Note the (almost) temperature-independent hole concentration.
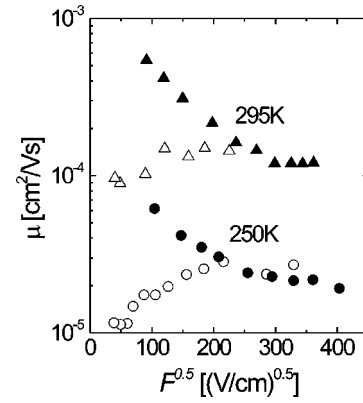

FIG. 5. Electric field dependence of drift mobility in RRPOT measured using TOF (solid dots) and CELIV (open dots) at 295 K and 250 K.

responds to a voltage increase rate A in the region, for which Δj equals the contribution from the geometrical capacitance of the sample, $j(0)$ (see inset in Fig. 3). For demonstration, we chose a 923-nm-thick regioregular poly(3-octyl thiophene) (RRPOT) film and in Fig. 3 the Δj, $j(0)$, and t_{max} dependences on A are shown, from where we can see that $\Delta j = j(0)$ at $U/d = At_{max}/d \sim 10^4$ V/cm.

In Fig. 4, we show the conductivity, equilibrium charge carrier concentration, and mobility dependences on electric field (when $t = t_{max}$) and temperature in RRPOT as obtained from the CELIV measurements. From these measurements we can immediately see the temperature-independent charge carrier concentration p_0. The calculated electric field, at which the decreasing μ_{app} as a function of electric field changes to increasing, is $3U_C/d = 2.9 \times 10^4$ V/cm and should be independent of temperature. This is observed in Fig. 5 where mobility measurements using both TOF and CELIV at 295 K and 250 K are shown. These results clearly demonstrate that using TOF the decreasing apparent mobility as a function in increasing electric field is caused by redistribution of the electric field, when $\tau_\sigma \simeq t_{tr}$. This is not only true for RRPOT, but in the whole family of regioregular poly(alkylthiophenes),[5–8] as well as in poly(p-phenylene vinylene),[3,14] a redistribution of the electric field has been shown to be an important factor.

V. CONCLUSION

To conclude, we have in these materials demonstrated that the decrease of the mobility as a function of electric field, estimated using TOF in the low-electric-field regime where $\tau_\sigma < t_{tr}$, is caused by redistribution of the electric field due to equilibrium charge carrier extraction. We have also shown that the CELIV method can be used to correctly estimate the mobility also when the necessary TOF conditions cannot be fulfilled.

ACKNOWLEDGMENTS

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