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Charge transport in π-conjugated polymers from extraction current transients

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The transport properties, namely mobility, conductivity, and charge carrier concentration of three model polymers, regioregular poly(3-hexylthiophene) (RRPHT), poly(p-phenylene vinylene) (PPV), and a polyazomethine (PAM) are investigated by charge extraction in a linearly increasing voltage. We have numerically modeled the charge carrier transients including a Gaussian distribution of localized states and the typical Poole-Frenkel-type field-dependent mobility observed in these materials, and good agreement with measured values is obtained. From our calculation we can determine the reason for the field-dependent mobility, and we found that the field-dependent release time from the localized states, τ_R is very important in RRPHT and PPV, while PAM is governed by stochastic transport.

Time of flight (TOF) is a basic method to study the charge carrier drift mobility[1] in low mobility materials such as amorphous semiconductors, chalcogenide glasses and organic materials.[2] π-conjugated polymers are slightly different in the sense that poor sample quality and low mobilities often make the TOF measurements difficult.[3] However, by using materials with high order and good processing techniques, it is possible to get good transients, and an estimation of the mobility from the transient ''kink'' in the small charge drift current can be made.[4] Still, the estimation of the kink can be very difficult due to the dispersion of the sheet of charges drifting through the sample. Furthermore, the necessary conditions for the applicability of TOF techniques is that the dielectric relaxation time is larger than the charge carrier transit time, $\tau_\sigma > t_{\mathrm{tr}}$, otherwise the drifting charges will relax before they reach the opposite electrode. Moreover, the equilibrium charges will be sufficient to significantly redistribute the electric field inside the sample faster than t_{tr}. Finally, in TOF photogenerated charge carriers are studied, but it is also important to determine the transport of equilibrium charge carriers in order to understand the behavior in light-emitting diodes (LED's)[5,6] and field-effect transistors (FET's).

In this report we present a method to study the equilibrium charge transport in π-conjugated polymers, based on the charge extraction in a linearly increasing voltage (CELIV).[7] We have numerically modeled the charge transport involving the typical field dependence of the mobility found in these materials[3,5] and using a Gaussian distribution of localized states which has been suggested for π-conjugated polymers.[3] We have experimentally verified the results for three model polymers and found that we can determine the nature of the underlying mechanism for the field dependent mobility observed in these materials.

The idea of CELIV (Refs. 7 and 8) is based on the comparison of the extraction current transients of equilibrium charge carriers when two sequential voltage pulses of triangular shape $[U(t)=At]$ are applied to the sample (see Fig. 1). The sample is of sandwich type with at least one blocking contact. The very first initial current step $[j(0)=\varepsilon\varepsilon_0 A/d$, where d is the interelectrode distance$]$ is caused by the geometric capacitance of the sample and can be used for estimation of either the dielectric constant or the thickness of the active material. The rise speed of the current following $j(0)$ is caused by the bulk conductivity of the sample or, if we have a heterogeneous material, by the most conductive part in the device. The time to reach the extraction current maximum $t_{\max}$ is used for the estimation of the drift mobility of equilibrium charge carriers. For low conductivity materials, when $\tau_\sigma \geqslant t_{\mathrm{tr}}$ the condition $\Delta j = j_{\max} - j(0) \leqslant j(0)$ is fulfilled, and we can estimate the mobility μ from

$$t_{\max} = d\sqrt{\frac{2}{\mu A}}. \tag{1}$$

For high conductivity materials when $\tau_\sigma \ll t_{\mathrm{tr}}$ is valid, $\Delta j \gg j(0)$ and

$$t_{\max} = \sqrt[3]{3\frac{\tau_\sigma d^2}{\mu A}}. \tag{2}$$

The bulk conductivity σ can be estimated according to

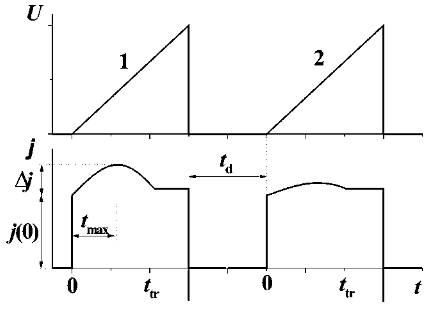

FIG. 1. Schematic illustration of the CELIV method. Here U is the applied voltage pulse $[U(t)=At]$, and j is the corresponding calculated current transient when $\tau_\sigma = t_{\mathrm{tr}}$ (first pulse) and partial equilibrium recovery (second pulse). $j(0)$ is the contribution from the capacitance, and Δj and $t_{\max}$ are indicated.

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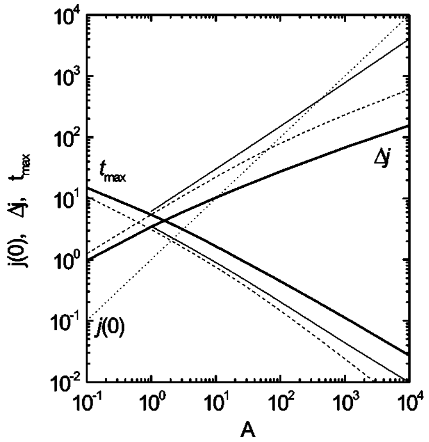

FIG. 2. Numerical modeling of Δj, $j(0)$ (dotted line) and $t_{\max}$ as a function of the speed of the voltage increase, *A*, using a Gaussian distribution of localized states with the dispersion parameter $\delta/kT=3$. As the electric field dependence on the drift mobility and release time we used $\mu\sim\exp(0.2\sqrt{F})$ (dashed line), $\tau_R\sim\exp(-0.2\sqrt{F})$ (thin solid line) and no electric field dependence (thick solid line).

$$\sigma=\varepsilon\varepsilon_0\left(\frac{d[j/j(0)]}{dt}\right)\Bigg|_{t=0} \tag{3}$$

and

$$\sigma=\frac{3\varepsilon\varepsilon_0\Delta j}{2t_{\max}j(0)}. \tag{4}$$

During the extraction of the charge carriers, the electric field is not constant. This affects the estimation of the electric field at which the value of drift mobility and conductivity were estimated when they are electric field dependent. However, the main extraction occurs at the moment $t=t_{\max}$ when the field is strongest. Therefore, the mobility calculated according to Eq. (5) and conductivity according to Eq. (4) roughly correspond to the values at an electric field $F(t_{\max})=At_{\max}/d$.

Experimentally it is most convenient to make measurements when $\Delta j\cong j(0)$. This may be achieved by choosing a proper *A* or samples of proper thickness. In this work μ is estimated taking into account the numerically estimated correction factor (arising from calculating the extraction depth, for details see Ref. 7)

$$\mu=\frac{2d^2}{3At_{\max}^2\left[1+0.36\dfrac{\Delta j}{j(0)}\right]}. \tag{5}$$

We can estimate the amount of charge carriers from the difference between the CELIV current pulses, and from its dependence on the delay time between the two pulses, we can estimate the recovery of the charge equilibrium.

We have numerically calculated the current transients by solving the continuity, current and Poisson equations.[7] We included a Gaussian distribution of localized states $N(E)\sim\exp(-E^2/2\delta^2)$, suggested for π-conjugated polymers.[3] In Fig. 2 the calculated $\Delta j(A)$ and $t_{\max}(A)$ curves are shown. However, using this distribution $\Delta j\sim A^{\beta}$ and $t_{\max}\sim A^{\gamma}$ are not exactly linear on a double logarithmic scale. Thus in both the theoretical and experimental analysis we have defined β and γ from the regions of intermediate $\Delta j\cong j(0)$ as

$$\beta=\frac{d(\ln j)}{d(\ln A)}\Bigg|_{\Delta j=j(0)} \tag{6}$$

and

$$\gamma=\frac{d(\ln t_{\max})}{d(\ln A)}\Bigg|_{\Delta j=j(0)}. \tag{7}$$

We found that $(\beta-\gamma)\cong 1$ for various parameters δ, while $(\beta+\gamma)$ is negative and it's absolute value increases with δ [see Fig. 3(a)].

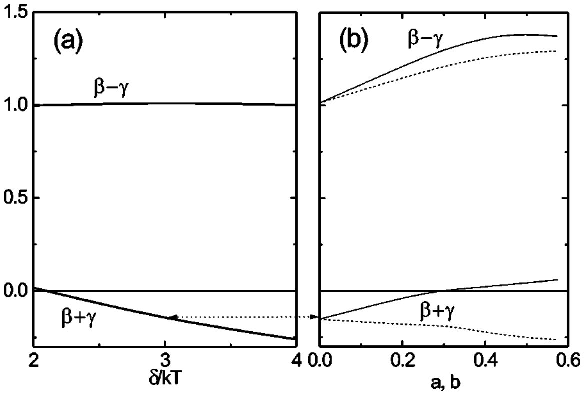

FIG. 3. Numerical modeling of $(\beta+\gamma)$ and $(\beta-\gamma)$ as a function of: (a) the dispersion parameter δ/kT of the Gaussian distribution of localized states; (b) the Poole-Frenkel parameters *a* in $\mu(F)$ (dashed line) and *b* in $\tau_R(F)$ (full line) using $\delta/kT=3$.

Organic materials typically show a Poole-Frenkel-type behavior where μ and σ are electric field dependent. In this case the current transient in the time interval $t<t_{\max}$ changes from sublinear to super-linear. We did the numerical modeling in two cases. First, when the drift mobility depends on the electric field as $\mu\sim\exp(a\sqrt{F})$. In this case $(\beta-\gamma)>1$, while $(\beta+\gamma)<0$ and independent of, or even decreases with *a* [See Fig. 3(b)]. Second, when the release time from localized states, τ_R depends on electric field as $\tau_R\sim\exp(-b\sqrt{F})$. Then $(\beta-\gamma)>0$ while $(\beta+\gamma)$ increases and even changes sign. Hence, from the β and γ parameters (and their temperature dependences) we can experimentally determine the nature of the charge carrier transport dependence on the electric field, whether it is due to μ or τ_R dependence on electric field or stochastic transport. We have measured β, γ, mobility, conductivity and carrier concentration for three different model polymers, namely regioregular poly(3-hexylthiophene) (RRPHT), unsubstituted poly(p-phenylene vinylene) (PPV), and the intermediate between RRPHT and PPV a polyazomethine poly (3,3″,4‴,3⁗-tetrahexyl-α-sexithienylene- azomethine-1,4′-biphenyleneazomethine) (PAM).[9]

RRPHT was purchased from Sigma Aldrich, dissolved into xylene or chloroform and spun from 1–5 mg/ml solutions for desired thickness on ITO covered glass (sheet resistance less than 10 $\Omega/\square$). PAM was synthesized according to Ref. 9 and spun from a chloroform solution. For the PPV samples we used the tetrahydrothiophene precursor route, and solution cast films from 1 mg/ml methanol solutions were converted in 220 °C in nitrogen atmosphere for a few

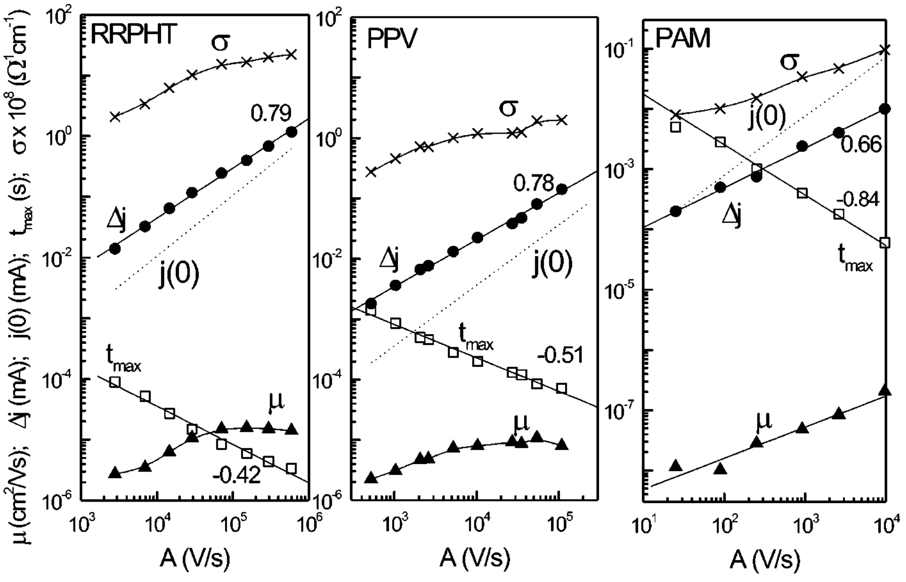

FIG. 4. Experimental results of Δj, $j(0)$, $t_{\max}$, and estimated mobility μ, and conductivity σ, as a function of the voltage rise speed A for RRPHT, PPV, and PAM, respectively. The numerical values of β and γ defined by $\Delta j \sim A^{\beta}$ and $t_{\max} \sim A^{\gamma}$ are given in the figure.

hours. To complete the device a 30–60 nm thick aluminum electrode was evaporated on top of the deposited polymer film. All samples were stored under vacuum but handled and measured in air.

The experimental equipment is very simple: two subsequent voltage pulses of reverse bias are applied to the sample, and the current transients of charge carrier extraction are recorded by an oscilloscope. The maximum magnitude of the triangular voltage pulse was 11 V and the duration of the pulse was changed between 100 ns and 1 s. The sample thickness was chosen, depending on the sample conductance and with a purpose to fulfill the criterion $\Delta j \cong j(0)$, as RRPHT $-$ $d=140$ nm, PAM $d=32$ nm, and PPV $d=1.1$ μm.

In Fig. 4 we show the $t_{\max}$, Δj, and $j(0)$ dependences on A. Additionally, the hole mobility calculated from Eq. (5) and the conductivity estimated from Eq. (4) are presented. The estimated hole mobility, concentration and conductivity dependences on $F(t_{\max})$ are presented in Fig. 5. From these results we may immediately draw the conclusion that $\mu(F)$ and $\sigma(F)$ have similar field dependences for all investigated materials and therefore the equilibrium charge carrier concentration is independent of the electric field. We would like to emphasize that under these conditions in these materials, and especially in RRPHT, TOF measurements at used electric fields would be impossible due to the relaxation of the drifting charges, i.e., $\Delta j > j(0)$ implying that $\tau_{\sigma} < t_{\rm tr}$. This electric field redistribution may cause an erratic decrease of the mobility as a function of field estimated from TOF measurements in Ref. 3.

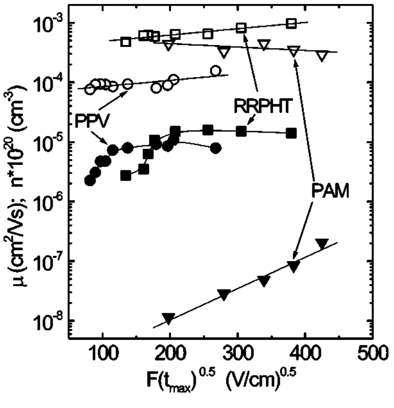

FIG. 5. Hole drift mobilities (solid symbols) and equilibrium carrier concentrations (open symbols) as a function of electric field in RRPHT (squares), PPV (circles), and PAM (triangles).

The validity of the inequality $(\beta-\gamma)>1$ for all the investigated materials points to the fact that μ or τ_R depends on the electric field. However, the inequality $(\beta+\gamma)>0$ obtained in RRPHT and PPV suggests that the field dependence of the release time from localized states is responsible for the observed transport [see Fig. 3(b)]. We have performed temperature measurements of β and γ in RRPHT and found that $(\beta+\gamma)$ increases when the temperature decreases. This is evidence for the important role of $\tau_R(F)$ under these conditions, since the a and b coefficients should have a temperature dependence of the type $b(T)=\tilde{b}(1/kT-1/kT_0)$.[5] In PAM, however, $(\beta+\gamma)<0$ and thus the charge transport in PAM is stochastic.

To conclude we have presented calculated and measured equilibrium charge extraction currents in π-conjugated polymer model systems. The advantages of the CELIV method are: (i) great simplicity and wide applicability to various materials and (ii) possibility to evaluate both mobility and bulk conductivity not influenced by contact barriers. We have presented numerical modeling, taking a Gaussian distribution of localized states and the typical Poole-Frenkel type of field-dependent mobility, which describe the model polymers RRPHT, PPV, and PAM very well. We found that we can experimentally determine the nature of the transport from the dependences of Δj and $t_{\max}$ on A. In RRPHT and PPV the field dependent release time from traps determines the transport, while for PAM the transport is stochastic.

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