Electric-field and temperature dependence of the hole mobility in poly(p-phenylene vinylene)

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The current-voltage characteristics of poly(dialkoxy p-phenylene vinylene)-based hole-only devices are measured as a function of temperature. The hole current is space-charge limited, which provides a direct measurement of the hole mobility μ_p as a function of electric field E and temperature. The hole mobility exhibits a field dependence $\ln\mu_p \propto \sqrt{E}$ as has also been observed from time-of-flight experiments in many molecularly doped polymers and amorphous glasses. For the zero-field hole mobility an activation energy of 0.48 eV is obtained. The combination of a field-dependent mobility and space-charge effects provides a consistent description of the hole conduction in conjugated polymer films as a function of voltage, temperature, and layer thickness. [S0163-1829(97)51602-X]

The combination of easy processing and electronic functionability makes conjugated polymers suitable candidates for large-area applications. After the discovery of electroluminescence in poly(paraphenylene vinylene) (PPV), investigations have especially been focused on this class of materials.[1,2] Temperature-dependent current density-voltage (J-V) measurements on PPV thin films revealed a thermally activated behavior at low voltages.[3] The absence of this behavior at higher voltages was attributed to field emission (Fowler-Nordheim tunneling) at the contacts.[3,4] However, the theoretical Fowler-Nordheim expression was not able to quantitatively account for the experimental J-V characteristics. The large deviations were tentatively attributed to thermionic emission,[5] space-charge effects,[6] and band-bending effects.[7] Recently, we have demonstrated that at low electric fields and at room temperature the conduction of holes in PPV devices is limited by space-charge effects in the bulk of the polymer and not by the charge injection from the contact.[8] At high electric fields, however, the strong field dependence of the current together with its decreased temperature dependence both seem to argue in favor of the tunneling model. Thus a consistent model describing both the low- and high-field regime of the J-V characteristics of holes in PPV as well as their temperature dependence has not been provided so far. Since the current in a polymer light-emitting diode (LED) is in many cases dominated by holes,[8] the availability of such a description is indispensable for a further development of polymer LEDs.

In the present study we investigate the J-V characteristics of holes in PPV at various temperatures. The observation of space-charge limited current enables us to obtain the charge-carrier mobility directly from the J-V characteristics in both the low- and high-field regime. We demonstrate that the hole mobility can be described by a field-dependent behavior as is also observed from time-of-flight (TOF) experiments on molecularly doped polymers.[9] Using this field-dependent carrier mobility in a space-charge limited conduction (SCLC) model we are now able to describe the J-V characteristics of holes in PPV, together with the corresponding electric field and carrier distributions as a function of position in polymer films.

The devices under investigation consist of a single polymer layer which is sandwiched between two electrodes on top of a glass substrate. The polymer is a soluble poly(dialkoxy p-phenylene vinylene)[10] (shown in the inset of Fig. 1) and is spin coated on top of a patterned indium-tin-oxide (ITO) bottom electrode which is used as a hole injector. As a top electrode an evaporated Au contact is used. In such a hole-only device the work functions of both the electrodes are close to the valence band of the conjugated polymer preventing electron injection from the negatively biased electrode. The J-V measurements are performed in a nitrogen atmosphere in a temperature range of 200–300 K. The detection limit of our setup is several pA, which corresponds to $\sim 10^{-6}$ A/m^2 for our electrode area of 10^{-5} m^2. In Fig. 1 the experimental J-V characteristics of hole-only devices at $T = 307$ K with thickness of the PPV film $L = 125$ nm and $L = 345$ nm are shown. The SCLC current[11]
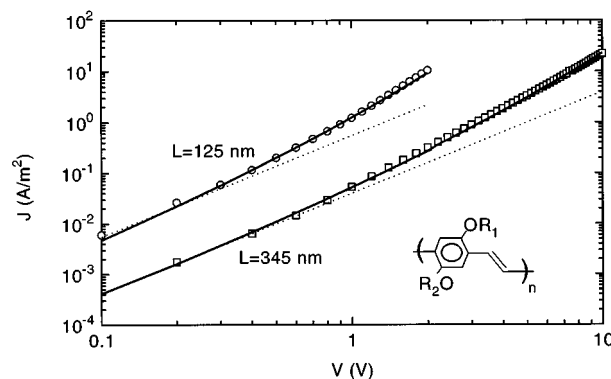

FIG. 1. Current density J versus voltage V of ITO/PPV/Au hole-only devices with thicknesses $L = 125$ nm (circles) and 345 nm (squares), measured at temperature $T = 307$ K. The calculated J-V characteristics according to the conventional SCLC model [Eq. (1)] are shown as dashed lines using a hole mobility $\mu_p = 5 \times 10^{-11}$ m^2/Vs and a dielectric constant $\epsilon_r = 3$. The solid lines represent the predictions from a SCLC model including the field-dependent mobility of Eq. (2). The inset shows the PPV used in this study with $R_1 = CH_3$ and $R_2 = C_{10}H_{21}$.

$$J = \frac{9}{8}\,\epsilon\mu_p\frac{V^2}{L^3}, \qquad (1)$$

with $\epsilon = \epsilon_0\epsilon_r$ the permittivity of the polymer and μ_p the hole mobility, provides a good description of the J-V characteristics at low voltage using $\mu_p = 5\times10^{-11}$ m^2/Vs and $\epsilon_r = 3$.

At higher voltages it is observed that the current density J is larger than expected from Eq. (1). First of all, it should be mentioned that this deviation cannot be due to the presence of traps or to charge injection at the contact, because then Eq. (1) would not apply for low voltage either.[11] A voltage dependence of the thickness L can also be excluded.[12] In fact, since SCLC depends only on the bulk-material parameters, a field dependence of the mobility is the most likely explanation. In this case, Eq. (1) is no longer applicable and deviations from the quadratic J-V characteristics are to be expected.

The canonical technique for measuring charge-carrier mobilities in disordered systems such as molecularly doped polymers, organic glasses, and conjugated polymers is the time-of-flight (TOF) experiment. However, due to the highly dispersive transient photocurrent traces, the determination of charge-carrier mobilities is often very complicated and at low fields practically impossible. In 1970 Pai[9] demonstrated that at high electric field E the mobility of photoinjected holes in poly(N-vinylcarbazole) (PVK) can be described by

$$\mu_p(E) = \mu_p(0)\exp(\gamma\sqrt{E}), \qquad (2)$$

where $\mu_p(0)$ denotes the mobility at zero field. The field dependence (2) through the coefficient γ is comparable to the Poole-Frenkel effect.[13] However, it was soon recognized that the physical origin of Eq. (2) — which appears to be applicable to a variety of molecularly doped polymers as well as molecular glasses — is not the presence of traps,[14,15] but is related to the intrinsic charge transport of disordered materials. Recently TOF measurements on a substituted derivative poly(1,4-phenylene-1,2,diphenoxyphenyl vinylene) (DPOP-PPV) of PPV[16] also provided mobilities in agreement with Eq. (2). This supports our assumption that the deviations from Eq. (1) are due to a field-dependent mobility.

In order to describe the hole conduction in PPV at both low and high fields, we combine the SCLC with the field-dependent mobility (2). The J-V characteristics of a hole-only device are now modeled by the following equations:[11]

$$J = p(x)e\mu_p[E(x)]E(x), \qquad (3)$$

$$\frac{\epsilon}{e}\frac{dE(x)}{dx} = p(x), \qquad (4)$$

with $p(x)$ the density of holes at position x. Assuming ohmic contacts, we have the boundary condition[8] $p(0) = N_v$, with the effective density of states in the valence band estimated as $N_v = 2.5\times10^{19}$ cm^{-3}. Equations (3) and (4) can be solved numerically for a given current J. The voltage is given by $V = \int_0^L E(x)dx$. As stated above, at low voltages the J-V characteristics of the holes are well described by the conventional SCLC of Eq. (1). This provides a direct measurement of the zero-field mobility $\mu_p(0) = 5\times10^{-11}$ m^2/Vs. In order to calculate the current at higher voltages we only need to determine the coefficient γ. In Fig. 1 the measured J-V char-
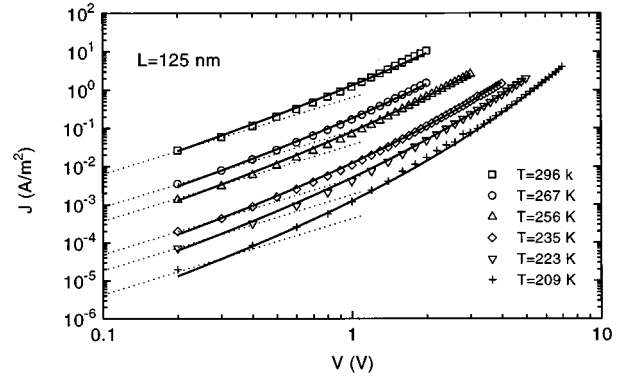

FIG. 2. Current density J versus voltage V of an ITO/PPV/Au hole-only device with thickness $L = 125$ nm for various temperatures. At low fields the predicted J-V characteristics according to the conventional SCLC model [Eq. (1)] are shown as dotted lines. The calculated J-V characteristics as predicted by a SCLC model using the field-dependent mobility given by Eqs. (2) and (6) are plotted as solid lines.

acteristics are compared with our calculations using $\gamma = 5.4\times10^{-4}$ (m/V)$^{1/2}$ for both $L = 125$ and $L = 345$ nm. The combination of the field-dependent mobility and space-charge effects provides a consistent description for the voltage and thickness dependence of the current in our hole-only devices at room temperature. This demonstrates that the mobility (2) is indeed applicable to hole conduction in our PPV.

In Fig. 2 the experimental J-V characteristics of a hole-only device with $L = 125$ nm are plotted for temperatures between $T = 209$ K and $T = 296$ K. The J-V behavior from Eq. (1) is also plotted at low fields. The zero-field hole mobility is shown in Fig. 3 in an Arrhenius plot. It decreases over more than 3 orders of magnitude while going from $T = 296$ K to 209 K. We observe a thermally activated behavior according to

$$\mu_p(0) = \mu_0\exp\left(-\frac{\Delta}{k_BT}\right), \qquad (5)$$
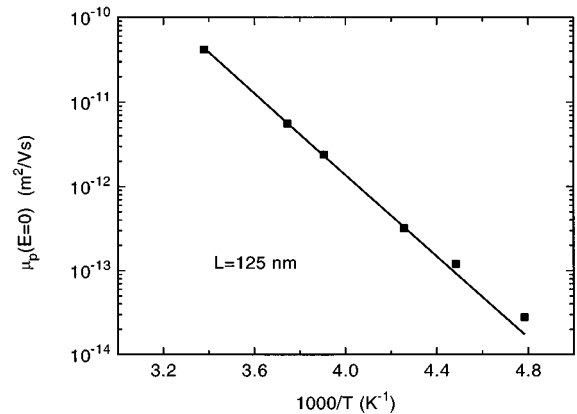

FIG. 3. Arrhenius plot of the zero-field mobility $\mu_p(0)$ versus temperature T. The mobility is obtained from the low-field part of the experimental J-V characteristics of Fig. 2 using Eq. (1). The solid line is according to Eq. (5), with activation energy $\Delta = 0.48$ eV and prefactor $\mu_0 = 3.5\times10^{-3}$ m^2/Vs.
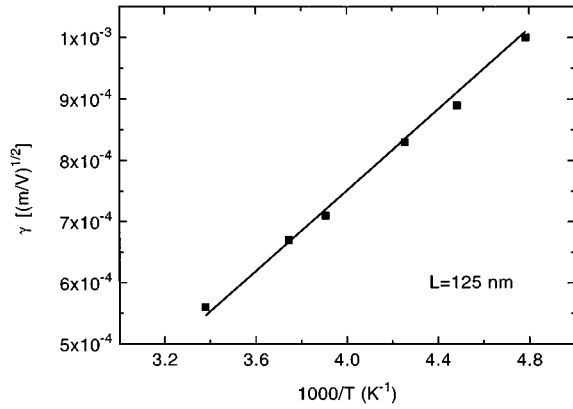
FIG. 4. The coefficient γ (which described the field dependence of the mobility) as a function of temperature T. The solid squares are obtained from the high-field J-V characteristics of Fig. 2. The solid line is according to Eq. (6), using $T_0 = 600$ K and $B = 2.9 \times 10^{-5}$ eV(m/V)$^{1/2}$. This empirical dependence of γ on T has originally been proposed by Gill for PVK.[8]

FIG. 5. Calculated distribution of the electric field E as a function of position x in a hole-only device biased at 2 V and at $T = 307$ K. The solid line gives the distribution for a field dependent mobility (2) with a coefficient $\gamma = 5.4 \times 10^{-4}$ (m/V)$^{1/2}$. For comparison the field distribution $E(x) = (2Jx/\epsilon\mu_p)^{1/2}$ for a constant mobility ($\gamma = 0$) is shown (dotted line). The injecting anode is located at $x = 0$ and the sample thickness $L = 125$ nm.

with activation energy $\Delta = 0.48$ eV and prefactor $\mu_0 = 3.5 10^{-3}$ m^2/Vs. Such a behavior has also been observed in molecularly doped polymers[9,14,15] and in DPOP-PPV.[16]

Let us now discuss the temperature dependence of the hole conduction at higher voltages. We again assume that the deviations from Eq. (1) are due to the mobility (2). From the experimental data in Fig. 2 and on the basis of Eqs. (2)–(4) we extract γ for our PPV at each temperature. In Fig. 4 γ is plotted against $1/T$. The experimental results show that there is a linear dependence, according to

$$\gamma = B\left(\frac{1}{k_B T} - \frac{1}{k_B T_0}\right),\qquad(6)$$

with $B = 2.9 \times 10^{-5}$ eV(m/V)$^{1/2}$ and $T_0 = 600$ K. The empirical temperature dependence of γ according to Eq. (6) was originally proposed by Gill[14] from TOF experiments on molecularly doped PVK. For this material, it was found that $B \approx 2.7 \times 10^{-5}$ eV(m/V)$^{1/2}$ and $T_0 \approx 520$–660 K. This remarkable agreement demonstrates that our method of determining the carrier mobility directly from the J-V measurements is able to yield equivalent information on the mobility as obtained by TOF experiments.

The set of experimental J-V characteristics as a function of temperature can now be described by Eqs. (2)–(6) using the following parameters: $\Delta = 0.48$ eV, $B = 2.9 \times 10^{-5}$ eV(m/V)$^{1/2}$, $T_0 = 600$ K, and $\mu_0 = 3.5 \times 10^{-3}$ m^2/Vs. In Fig. 2, it is demonstrated that this model provides an excellent description of the experimental J-V curves in both the low- and high-voltage regime. In particular, the high-voltage behavior, which has not been quantitatively described so far, is consistently modeled, using only two parameters B and T_0. The decrease of the total activation energy with increasing voltage is a direct result of the field enhanced carrier mobility and is not due to field emission at the contact as suggested before.[3,4] Furthermore, we have confirmed that our SCLC model with a field-dependent mobility correctly accounts for the thickness dependence of the experimental J-V characteristics as shown in Fig. 1.
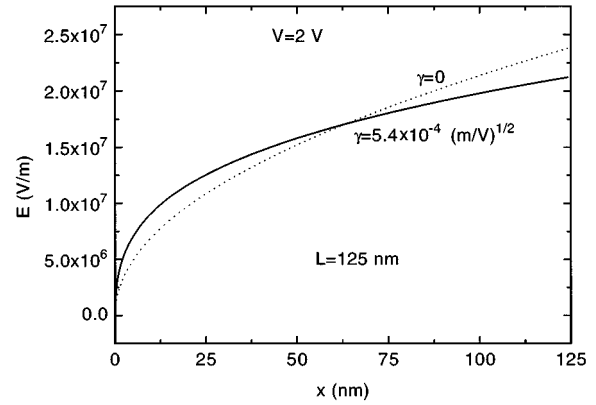
We now discuss the influence of the field-dependent mobility on the electric field and charge distributions in the PPV layer. For the conventional SCLC (Ref. 11) with a constant mobility, the electric field varies with position as $E(x) = \sqrt{2Jx/\epsilon\mu_p}$, and the hole concentration as $p(x) \propto x^{-1/2}$. Figure 5 compares the electric field for conventional SCLC with the case of the field-dependent mobility (2), for $V = 2$ V and $L = 125$ nm. The carrier distribution directly follows from the electric field through Eqs. (3) and (4). The injected carriers which are located close to the injecting contact will have a low mobility due to the small field in that region. The charge carriers in the high-field region close to the collecting contact on the other hand experience a field-enhanced mobility. However, the current through the layer is independent of position. Therefore, the mobility differences are compensated by increasing the electric field for the low-mobility carriers at the injecting contact and decreasing the field for the high-mobility carriers at the collecting contact. Note that the exact form of the field distribution is strongly dependent on the parameters used in Eq. (2) and, in contrast to the conventional trap-free SCLC, that it is also a function of temperature by means of the coefficient γ.

The field and temperature dependence of the hole mobility given by Eqs. (2), (5), and (6) appear to be generic for a large class of disordered materials. The variations in the parameters Δ, B, and T_0 describing this universal behavior is less than a factor of two.[15] This suggests that the conduction mechanisms in conjugated polymers are similar to molecularly doped systems, where highly localized charge carriers are transported by thermally assisted intermolecular hopping. Indeed, one may assume that due to disorder in conjugated polymer films in the form of kinks, cross-links, and impurities, the conduction depends critically on hopping between conjugated parts of the polymer chain. It will be of interest to test this assumption by studying conduction in more ordered films or in polymers with different side chains.

A microscopic theory for the observed mobility is still lacking. Monte Carlo simulations of hopping between sites that are subject to both positional and energetic disorder

only agree with Eqs. (2), (5), and (6) over a limited field range.[17] Recently, it has been demonstrated that taking into account spatial correlations in the energetic disorder improves agreement with experiment.[18] A theoretical explanation for the mobility (2), (5), and (6) — which appears to be valid for a large class of disordered materials — is highly wanted, since it would clarify the physical meaning of the invoked parameters.

In conclusion, we have demonstrated that the conduction of holes in a film of the conjugated polymer PPV is governed by a combination of a field-dependent mobility and space-charge effects. The mobility which is directly obtained from the J-V experiments is constant at low fields and exhibits a high-field dependence similar to the mobility of molecularly doped polymers and organic glasses as observed in TOF experiments. The occurrence of a field-dependent mobility leads to an enhancement of the electric field close to the injecting contact.

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