Trap-limited electron transport in disordered semiconducting polymers

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(Received 2 March 2007; published 24 May 2007)

The electron transport in diodes of poly(dialkoxy-*p*-phenylene vinylene) (PPV) derivatives is strongly reduced as compared to the hole transport. A recent reexamination [M. M. Mandoc *et al.*, Phys. Rev. B **73**, 155205 (2006)] revealed that the room-temperature electron current shows the fingerprints of trap-limited transport with a distribution of traps in energy. Here, we report on the measured temperature dependence of the electron current in these PPV derivatives. This dependence is weak and seems to be in contradiction with existing trap-limited models. We demonstrate that the presence of a Gaussian density of states (DOS) for the mobile carriers, being characteristic for disordered semiconductors, reduces the temperature dependence of the trap-limited charge transport. The reduction is governed by the width of the Gaussian DOS and originates from the equilibrium concentrations of the mobile and trapped carriers.

DOI: 10.1103/PhysRevB.75.193202 PACS number(s): 72.20.Jv, 72.80.Le

Poly(dialkoxy-*p*-phenylene vinylene) (PPV) derivatives have been widely studied for their potential use in organic semiconducting devices such as light-emitting diodes (LEDs), field-effect transistors, or solar cells. The hole transport in PPV-based diodes was explained by a space-charge-limited current[1] (SCLC) in combination with a temperature- and field-dependent mobility.[2] The mobility originates from a hopping process between localized sites in a Gaussian density of states (DOS),[3] which is broadened due to disorder. Recently, it has been demonstrated that at room temperature, the dependence of the mobility on carrier density governs the hole conduction, whereas at low temperatures, the field dependence prevails.[4,5] Based on this observation, a charge transport model that reproduces the dependence of the hole mobility on temperature, carrier density, and electric field has been developed.[6]

For the conduction of electrons in PPVs, such an extensive description of the charge transport has not been given so far. The major reason for the existing lack of experimental data is that for the investigation of the electron transport, devices have to be fabricated on hole-blocking bottom electrodes, requiring sufficiently low work functions. However, low-work-function bottom electrodes such as Ca or Ba are highly reactive and, consequently, are incompatible with processing from solution. The strongly reduced electron currents observed in an early study on poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-*p*-phenylene vinylene (OC_1C_{10}-PPV) were attributed to trap-limited conduction.[1] The strong dependence of the electron current on applied voltage and sample thickness at room temperature was approximated with an exponential distribution of trapping sites in energy. Such an exponential trapping model had also been proposed by Burrows and Forrest[7] and Shen *et al.*[8] for the electron transport. Later, an alternative explanation for the reduced electron current in PPV-based electron-only devices, based on a trap-free SCLC with an intrinsically low electron mobility,[9] has been reported. However, we reexamined[10] electron currents in OC_1C_{10}-PPV by using a variety of hole-blocking bottom electrodes. The current-voltage characteristics were numerically calculated using the exponential trap model and by taking into account the density (n) and field dependence (E) of the mobility of the mobile carriers. It was assumed that the mobility of the free electrons is equal to the mobility of the free holes, for which these dependences $\mu_p(E,p,T)$ are known.[5,10] This assumption is supported by recent observations of Chua *et al.*, who demonstrated that in field-effect transistors, the free electrons are as mobile as holes for OC_1C_{10}-PPV.[11] Using $\mu_e=\mu_p$, the numerical calculations consistently describe the voltage and thickness dependences of the electron current in OC_1C_{10}-PPV at room temperature.[10] The strong thickness dependence observed experimentally on aluminum bottom electrodes confirms that the bulk properties are measured.

In order to further verify the applicability of trap-limited transport models to the electron transport in conjugated polymers such as PPV, the temperature dependence also needs to be addressed. So far, a systematic study on the temperature dependence of the electron transport in conjugated polymers has not been performed. As a result, a transport model that consistently describes the field, temperature, and thickness dependences of the reduced electron transport in conjugated polymers is presently lacking. In this Brief Report, we investigate the temperature dependence of the electron current in a number of PPV derivatives. A model for trap-limited transport that explains the apparent discrepancy of a strongly trap-limited electron transport in combination with a reduced temperature dependence is presented.

For a long time, it has been almost standard to analyze current characteristics in organic LED using the well-known expression for trap-limited SCLC [given below, Eq. (4)]. However, for the disordered organics, it is worth recalling the basic assumptions underlying this model. Actually, Mark and Helfrich[12] (MH) have first discussed the effect of an exponential distribution of traps on space-charge-limited cur-

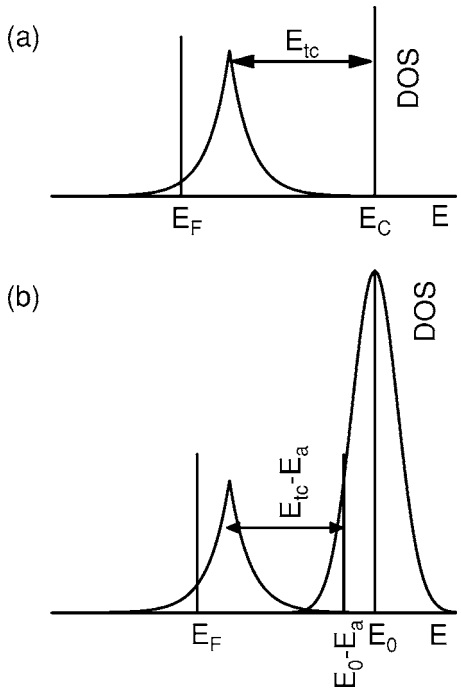

FIG. 1. The exponential trap distribution with respect to (a) a conduction-band edge, and (b) in the case of a disordered system with a Gaussian DOS. In both cases, the Fermi energy E_F is supposed to lie below the center of the trap DOS.

rents. The derivation is easily extended for the case of an exponential trap DOS,

$$D_t(E) = \frac{N_t}{kT_t} e^{|E-(E_C-E_{tc})|/kT_t}, \tag{1a}$$

centered at a distance E_{tc} below the conduction-band edge E_C [see Fig. 1(a)]. N_t is the total concentration of traps below its center. The width of the exponential energy distribution of the traps is characterized by the trap temperature T_t. For $T_t \gg T$ and a Fermi level E_F below the center of the DOS, the density of trapped carriers can be approximated as

$$n_t(E_F) = N_t e^{E_{tc}/kT_t} e^{(E_F-E_C)/kT_t}, \quad E_F < (E_C-E_{tc})-2kT, \tag{1b}$$

with N_t the total concentration of traps. Using Boltzmann statistics, the density of mobile carriers in the conduction band is given by

$$n(E_F) = N_C e^{(E_F-E_C)/kT}, \tag{2}$$

where N_c is the effective density of states and T the temperature. Combining Eqs. (1b) and (2) yields the relation between free and trapped carriers,

$$\frac{n}{N_c} = \left(\frac{n_t}{N_t e^{E_{tc}/kT_t}}\right)^r, \quad r = \frac{T_t}{T}, \tag{3}$$

where $N_t e^{E_{tc}/kT_t}$ can be defined as the effective trap concentration. Combining Eq. (3) with the Poisson equation and neglecting diffusion currents lead to[12]

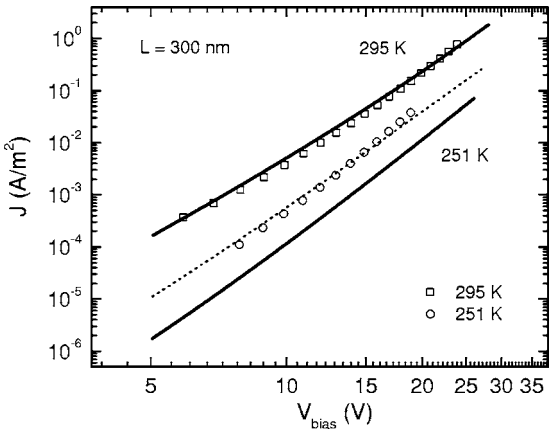

FIG. 2. Electron J-V characteristics of OC_1C_{10}-PPV at 295 K (squares) and at 251 K (circles), for a sample with thickness L = 300 nm. The solid lines are calculated using the classical trapping model [Eq. (4)], with free-electron mobility values derived from the hole transport, and the trapping parameters $N_t e^{E_{tc}/kT_t} = 6.0 \times 10^{23}$ m^{-3} and $T_t = 1500$ K, for the two temperatures. The dotted line shows the calculation for 251 K, with the room-temperature mobility value.

$$J = N_c q \mu_e \left(\frac{\varepsilon_0 \varepsilon_r}{q N_t e^{E_{tc}/kT_t}}\right)^r \left[\left(\frac{2r+1}{r+1}\right)^{r+1}\left(\frac{r}{r+1}\right)^r\right] \frac{V^{r+1}}{L^{2r+1}}, \tag{4}$$

with q the elementary charge, $\varepsilon_0\varepsilon_r$ the dielectric constant, V the applied voltage, L the sample thickness, and μ_e the free-electron mobility. This trap-limited space-charge-limited current is temperature dependent by the mobility $\mu_e(T)$ and by the trapping terms depending on $r = T_t/T$ (essentially by the dimensionless quantity $[\varepsilon\varepsilon_0 V/(qN_t e^{E_{tc}/kT_t} L^2)]^r$). For highly disordered materials such as OC_1C_{10}-PPV, the activation energy of the mobility typically amounts to ~0.5 eV.[2] In Fig. 2, the current density-voltage (J-V) characteristics for a OC_1C_{10}-PPV bulk-limited electron-only device on Al bottom electrodes are shown for two temperatures, T=295 K and T=251 K. As a top contact, a 5 nm barium layer is evaporated and capped with 100 nm aluminum. Also included are the numerically calculated J-V characteristics using Eq. (4) with $\mu_e(E,n,T) = \mu_p(E,p,T)$.[10] It is observed (solid lines) that at low temperatures, the exponential trap model predicts a much stronger temperature dependence than measured. A possible explanation for this disagreement could be that the assumption $\mu_e = \mu_p$ is not valid and μ_e is less temperature dependent than μ_p. In order to disentangle trapping and mobility effects, we also calculated the J-V by only incorporating the temperature dependence of the trapping term and keeping the mobility constant (dotted line). Although it agrees rather well with the measurement, a temperature-independent carrier mobility in such a strongly disordered semiconductor is not realistic.

In the case of disordered organic semiconductors such as conjugated polymers, the transport of free charges has been described by hopping in a Gaussian DOS.[3] Instead of a sharply defined conduction-band edge, there is a broad distribution of states of the lowest unoccupied molecular orbital

through which the transport occurs, as schematically shown in Fig. 1(b). The influence of this distribution has been taken into account in the mobility. However, one has in addition also to reevaluate the MH derivation[12] for a system with a Gaussian DOS centered around E_0. In this case, E_{tc} represents the energy distance between the center of the trap distribution and the middle of the Gaussian E_0 [Fig. 1(b)]. We mention that in a disordered system of localized states, there are no real free carriers since all carriers are localized. The distinction made in this Brief Report is between mobile carriers that hop between localized states and are referred to as "free," and immobile ones, which are trapped. For the trapped carriers with E_F located below the center of the trap distribution, the density $n_t(E_F)$ is again given by Eq. (1). However, the free-carrier density $n(E_F)$ determined by the Gaussian DOS is now given by[13]

$$n(E_F) = \int_{-\infty}^{\infty} \frac{N_0}{\sqrt{2\pi\sigma}} \exp\left[-\frac{1}{2}\left(\frac{E-E_0}{\sigma}\right)^2\right] \frac{1}{e^{(E-E_F)/kT}+1} dE$$

$$\rightarrow N_0 e^{[E_F-(E_0-E_a)]/kT} \quad \text{for } E_0 - E_F \geqslant 2E_a, \quad E_a = \frac{\sigma^2}{2kT}, \tag{5}$$

where N_0 is the density of hopping sites and σ the variance of the Gaussian DOS. The second line is the nondegenerate (Boltzmann) limit which is valid for a sufficiently low-lying Fermi energy. E_a is a characteristic energy determined by the variance and T. Comparison of this limit with Eq. (2) shows that $E_0 - E_a$ is formally equivalent to the conduction-band edge. However, Eq. (5) describes the equilibrium, whereas all the transport properties enter separately the mobility. Combining Eq. (1b) and the nondegenerate approximation [Eq. (5)] now yields

$$\frac{n}{N_0} = \left(\frac{n_t}{N_t e^{(E_{tc}-E_a)/kT_t}}\right)^r. \tag{6}$$

Finally, following the MH formalism, a current-voltage characteristic is obtained, which is of the form

$$J = N_c q \mu_e \left(\frac{\varepsilon_0 \varepsilon_r}{q N_t e^{(E_{tc}-E_a)/kT_t}}\right)^r \left[\left(\frac{2r+1}{r+1}\right)^{r+1}\left(\frac{r}{r+1}\right)^r\right] \frac{V^{r+1}}{L^{2r+1}}. \tag{7}$$

Compared to Eq. (4), the energy shift E_a now mimics the role of the conduction-band edge relative to E_0, which for this case is, however, temperature dependent. This temperature dependence can be taken into account by incorporating E_a in the effective concentration of traps

$$N_{t(eff)} = N_t \exp[(E_{tc} - E_a)/kT_t], \tag{8}$$

varying with temperature as $\exp\{-[1/2(\sigma^2/\mathrm{kT})]/kT_t\}$. The total concentration of traps N_t is a constant value and can only be determined if the energy position of the distribution E_{tc} is known. It should be noted that the inclusion of E_a in the trap model does not add a new parameter: the values of σ for all PPV derivatives studied here have been independently determined from the temperature dependence of the hole mobility.

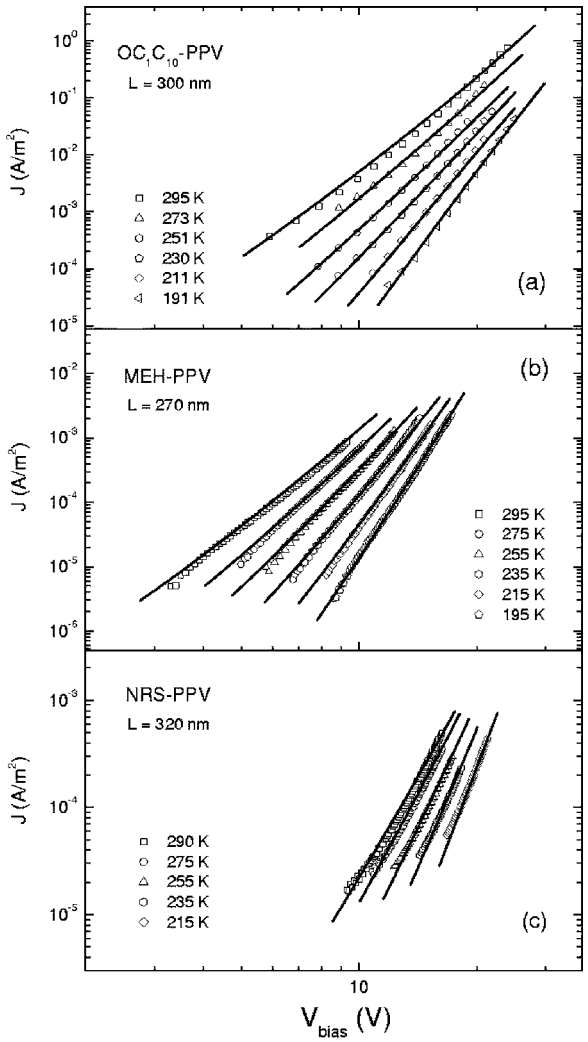

FIG. 3. (a) Temperature-dependent J-V characteristics of the electron current in OC_1C_{10}-PPV (symbols) for a sample with thickness L=300 nm. The calculated lines make use of the temperature-dependent level $E_a=\sigma^2/2kT$, with σ=0.11 eV, and an exponential trap distribution with T_t=1500 K [Eq. (7)]. (b) Temperature-dependent electron J-V characteristics of MEH-PPV for an active layer of 270 nm (symbols) and the calculated lines for an exponential trap distribution with T_t=1500 K and a temperature-dependent DOS level, $E_a=\sigma^2/2kT$, with σ=0.105 eV. (c) Temperature-dependent electron J-V characteristics of NRS-PPV, for an active layer thickness of 320 nm (symbols) and the calculated lines for an exponential trap distribution with T_t=1850 K, and a temperature-dependent energy level $E_a=\sigma^2/2kT$, with σ=0.125 eV.

In Fig. 3(a), the temperature-dependent J-V characteristics of the OC_1C_{10}-PPV electron current are shown. As a first step, we numerically model the experimental data of Fig. 3(a) and fit $N_{t(eff)}$ at each temperature, and the result is shown in Fig. 4 (triangles). The obtained temperature dependence is excellently described by Eq. (8) using σ=0.11 eV, which is equal to the value determined from OC_1C_{10}-PPV hole-only devices.[14] Furthermore, from electrochemically doping of OC_1C_{10}-PPV, it has been observed that at low energies, density of states resembles a Gaussian DOS with a width of 0.11 eV.[15] Thus, incorporation of a temperature-

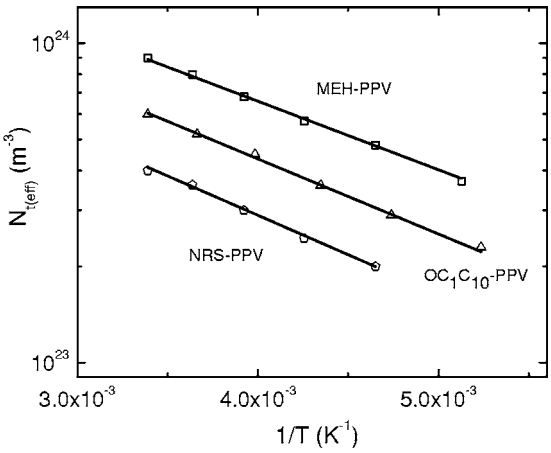

FIG. 4. Temperature dependence of the effective density of traps $N_{t(\mathrm{eff})}$ of electron current for MEH-PPV (squares), OC_1C_{10}-PPV (triangles), and NRS-PPV (pentagon) following Eq. (8) with the corresponding disorder parameters and trap temperatures.

dependent E_a provides a consistent description of the electron current in OC_1C_{10}-PPV for the entire range of temperatures measured, as shown in Fig. 3(a) (solid lines). Since the variance of $N_{t(eff)}$ with temperature is governed, through E_a, by the width of the Gaussian density of states σ, we further test the validity of the model by investigating the electron transport in two other PPV derivatives with different σ. In Figs. 3(b) and 3(c), the electron currents of MEH-PPV, with σ=0.105 eV (Ref. 16) and NRS-PPV, a more disordered material with a larger σ of 0.125 eV,[16] are shown. As shown in Fig. 4, for both polymers, the variation of $N_{t(eff)}$ with temperature is again in perfect agreement with the expected variation given by Eq. (8). Thus, the modified MH formalism consistently explains the field, temperature and thickness[10] dependences of the electron transport in these PPV derivatives. A reduced temperature dependence had also been found in model calculations on charge transport in a disordered system with Gaussian distributions for both transport and trapping states.[17,18] The calculated reduction of the activation energy of the calculated effective mobility originated from the fact that at low temperatures, traps no longer control the transport but actually participate in it. It should be noted that in the model presented here, the reduced temperature dependence of the electron current for all three PPV derivatives stems solely from the equilibrium conditions and the use of the Boltzmann approximation for the electrons in the Gaussian DOS. This analysis clearly demonstrates the influence of disorder on trap-limited transport characteristics in conjugated polymers. For free charge carriers, an increase of the degree of energetic disorder, characterized by σ, enhances the temperature dependence of the charge transport.[3] For trap-limited systems, however, it decreases the temperature dependence of the transport.

In conclusion, the reduced temperature dependence observed for the electron currents in light-emitting conjugated polymers such as derivatives of PPV cannot be explained by the MH exponential trap model derived within the band transport formalism. Incorporating the effect of energetic disorder for the mobile carriers into the model leads to a characteristic energy $E_a=\sigma^2/2kT$. The total density N_0 is apparently concentrated at a distance E_a below the center of the Gaussian DOS. With decreasing temperature, E_0-E_a becomes closer to the trap distribution, which can be expressed as a reduction of the effective amount of traps. For the three PPV derivatives investigated, this modified trap model consistently describes the reduced temperature dependence as observed in the experiments.

This work is part of the Dutch Polymer Institute Research Program (Project No. 324). The authors acknowledge L. J. A. Koster and A. J. Hof for their assistance, M. Mulder for technical support, and J. Wildeman for the synthesis of MEH-PPV.

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