# Dispersive Hole Transport in Poly($p$-Phenylene Vinylene)

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The transient hole transport in poly($p$-phenylene vinylene) (PPV) is investigated by measuring the response times of PPV-based light-emitting diodes. It is demonstrated that the observed response times are governed by the dispersive transport of holes in PPV. In terms of the stochastic transport model of Scher and Montroll, the results correspond to a dispersion parameter $\alpha = 0.45$, independent of temperature. This indicates that the dispersion in hole transport in PPV is due mainly to structural disorder, rather than to energetic disorder. [S0031-9007(98)05908-0]

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The advantage of easy processing and mechanical flexibility makes polymer light-emitting diodes (PLEDs) suitable candidates for large area display technologies. Electrical characterization of poly(phenylene vinylene) (PPV) based LEDs has been focused mainly on the direct current (dc) device characteristics [1–4]. Recently, current density-voltage ($J$-$V$) measurements on PPV-based hole-only and electron-only devices have revealed that the hole current is dominated by space-charge effects, whereas the electron current is reduced strongly by traps [5]. At low electric fields, a hole mobility of $5 \times 10^{-11}$ m$^2$/V s is obtained at room temperature, independent of electric field. The fact that electrons are relatively immobile has also been observed in photoconductivity experiments [6]. Investigation of the $J$-$V$ characteristics as a function of temperature $T$ and layer thickness $L$ has shown that, at high fields, the dc hole mobility $\mu_p$ in PPV can be described accurately as a function of electric field $E$ according to [7]

$$\mu_p(E) = \mu_0 \exp\left[-\frac{\Delta}{k_B T} + B\left(\frac{1}{k_B T} - \frac{1}{k_B T_0}\right)\sqrt{E}\,\right], \tag{1}$$

with typically $\Delta = 0.48$ eV, $B = 2.9 \times 10^{-5}$ eV (V/m)$^{-1/2}$, $T_0 = 600$ K, and $\mu_0 = 3.5 \times 10^{-3}$ m$^2$/V s. The dc mobility (1) appears to be generic for a large class of disordered materials [8–10] such as molecularly doped polymers and amorphous glasses, with relatively small variations in the parameters $\Delta$, $B$, and $T_0$. At present, the physical origin of this universal field and temperature dependence of the dc hole mobility [Eq. (1)] is not quite clear. Monte Carlo simulations of hopping between sites that are subject to both positional and energetic disorder agree with Eq. (1) over a limited field range [11]. This range may be increased by taking into account spatial correlations in the energetic disorder [12].

Transient experiments provide additional information on the microscopic origin of charge transport in disordered materials. Studies of the transient hole transport in a number of disordered solids [13] have revealed dispersive current traces which were attributed to a broad distribution in transit times of the individual carriers. The dispersion of transit times has been described in a stochastic transport model by Scher and Montroll (SM) [14], in which the transport is represented as a chain of hopping events. If one describes the waiting time between two hops by a distribution $\psi(t)$ with an algebraic time dependence $\psi(t) \sim t^{-(1+\alpha)}$, all of the essential features of dispersive transport are reproduced. The dispersion is characterized by a parameter $\alpha$ $(0 < \alpha < 1)$ which depends on the microscopic transport mechanism. In the case of hopping, small variations of the hopping distance introduce a broad distribution in hopping times. The corresponding dispersion parameter $\alpha$ is then temperature independent, as has been observed in amorphous arsenic triselenide ($a$-As$_2$Se$_3$) [15] and polyvinylcarbazole [16]. Similarly, in the case of multiple trapping transport, broad release time distributions can be obtained for small variations in the trap depth. This gives rise to a temperature-dependent $\alpha$, as found in triphenylamine doped polycarbonate [13]. Furthermore, Monte Carlo simulations have demonstrated that hopping between sites which are exponentially distributed in energy also gives rise to a similar temperature-dependent dispersion [17]. Thus the observation of dispersive transport is common to many disordered conductors, and it provides information on the microscopic transport mechanisms.

In various conjugated polymers, e.g., polyacetylene [18], poly(dodecylthiophene) [19], and poly($p$-phenylene vinylene) [20], transient photocurrents decaying as a power law have been observed, which suggests that the transport in this class of materials is dispersive as well. However, it should be noted that disordered conductors often exhibit some spread in the transit times leading to approximate power-law decay, whereas the transport is not dispersive in the sense of the SM theory [11,21]. An unambiguous sign of SM dispersive transport is a universal scaling of the transit time with sample thickness and electric field, arising from the algebraic waiting-time distribution. To our knowledge, this universal scaling has not been observed in conjugated polymer systems.

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Usually, transient transport is studied using the time-of-flight (TOF) technique, where charge carriers are created optically close to one of the electrodes. As a result, film thicknesses of at least several $\mu$m are required in order to prevent a homogeneous illumination throughout the film. Experimentally, TOF experiments on thick films of conjugated polymers are difficult due to the extremely low mobilities of these materials. From TOF measurements, Meyer *et al.* [22] have determined the hole mobility of poly(1,4-phenylene-1,2-diphenoxyphenyl vinylene), which is a high-mobility derivative of PPV ($\mu_p \sim 10^{-8}$ m$^2$/V s at room temperature). The mobility of this material exhibits the same temperature and field dependence as given in Eq. (1), which has been interpreted in terms of a multiple trapping model. However, for standard PPV with a mobility which is typically a few orders of magnitude lower [5], their photocurrent showed a featureless decay without a discernible transit time and a mobility could not be determined.

Recently, studies by Vestweber [23] and Karg [24] have revealed that there is a time lag between the application of a voltage pulse and the onset of the electroluminescence (EL) in a PLED. As a result of the unbalanced charge transport [5] in a PLED, the EL is confined to a region close to the cathode [25]. After application of a voltage, the injected holes will first have to flow to the cathode before light generation occurs. Thus the observed time lag is related directly to the transit time of holes towards the cathode. The equivalence of transit times obtained from delayed electroluminescence and from TOF measurements has been confirmed experimentally by Ranke *et al.* [26]. An advantage of this method compared to the TOF technique is that it can be applied to PPV films with a thickness less than the penetration depth of light.

In the present study, we investigate the response time of PPV-based PLEDs after application of a voltage pulse as a function of electric field and temperature. Our study reveals that the observed response times are faster than the hole transit times as expected from the dc hole mobility (1). This discrepancy originates from the fact that the hole transport is dispersive as is demonstrated from the universal scaling of the response times with sample thickness and electric field. The observed response times are dominated only by the fastest part of the injected holes, whereas the dc mobility represents the transport of holes on a time scale much longer than the observed response times.

The devices used in this study consist of a single polymer layer sandwiched between two electrodes on top of a glass substrate. The polymer is soluble poly(dialkoxy-*p*-phenylene vinylene) [5], which is spin coated on a patterned indium-tin-oxide (ITO) bottom electrode. As a top electrode, an evaporated Ca contact is used. The measurements are performed in a nitrogen atmosphere. Pulses of known voltage $V$ and duration $\tau_{\text{pulse}}$ are applied to our devices at a repetition rate of 4 kHz using a HP214B pulse generator. As a result, light pulses will be generated, typically delayed with regard to the voltage pulse with a delay time $\tau_d$, as schematically indicated in the inset of Fig. 1. The integrated light output $I_{\text{int}}$, represented by the shaded area, is measured by a Keithley 617 electrometer in current mode. In Fig. 1, $I_{\text{int}}$ vs $\tau_{\text{pulse}}$ is shown for various applied voltages for a device with thickness $L =$ 100 nm. For long $\tau_{\text{pulse}}$ ($\gg \tau_d$), the integrated light output $I_{\text{int}}$ increases linearly with $\tau_{\text{pulse}}$, as expected since the missing light output as a result of $\tau_d$ can be neglected. The intercept of the linear part with the $\tau_{\text{pulse}}$ axis is then a measure for $\tau_d$. The observed delay time $\tau_d$ decreases from 38 $\mu$s at 2 V to 2.8 $\mu$s at 2.8 V and is used as a measure for the responsivity of the PLED throughout this paper. An advantage of this method is that it is very sensitive: At low voltages, where the light emission is small, delay times can still be obtained. The *RC* time constant of the PLED circuit, which limits the time resolution of our setup, was determined from the response of the device current using a digital oscilloscope and amounts to 0.1–0.3 $\mu$s for the various devices.

As stated above, the response time is expected to be dominated by the transit time of holes towards the cathode, where light generation occurs. In the case of nondispersive transport, the hole transit time then directly provides information about the dc hole mobility $\mu_p$ according to

$$\mu_p = \frac{L^2}{\tau_d(V - V_{\text{bi}})}, \tag{2}$$

where $\tau_d$ is the observed response time and $V$ is the applied voltage. It should be noted that we have corrected the applied voltage with a built-in voltage $V_{\text{bi}}$ of 1.5 V, which is present due to the work function difference between ITO and Ca. The electric field pulling the front of the charge

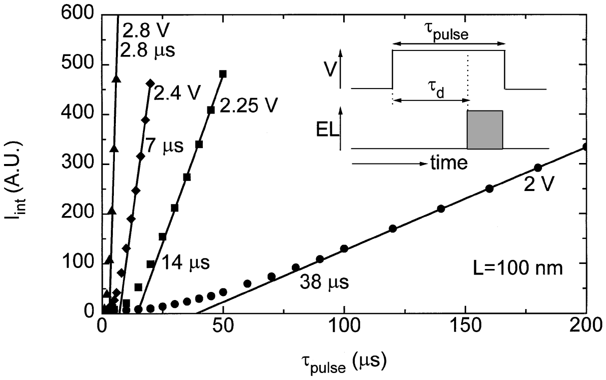

FIG. 1. Time-integrated light output $I_{\text{int}}$ vs pulse length $\tau_{\text{pulse}}$ for a PLED with a thickness of 100 nm at $T = 295$ K. The inset shows a schematic representation of a PLED exhibiting a delay time $\tau_d$ between the application of a voltage pulse and the first observation of EL. For voltage pulses with $\tau_{\text{pulse}}$ comparable to $\tau_d$, the integrated light output $I_{\text{int}}$, represented by the shaded area, is relatively small. With increasing pulse length, $I_{\text{int}}$ will increase strongly until $\tau_{\text{pulse}}$ is much longer than $\tau_d$. Then the missing light output during $\tau_d$ can be neglected and $I_{\text{int}}$ vs $\tau_{\text{pulse}}$ will approach a linear behavior. By extrapolating the linear regime to $I_{\text{int}} = 0$, the delay time $\tau_d$ is obtained. The extrapolated $\tau_d$ decreases from 38 $\mu$s at $V = 2$ V, which is just above the threshold for light emission, to 2.8 $\mu$s at $V = 2.8$ V.

carriers is unaffected by space charge, as has been shown both experimentally [27] and theoretically [28]. As a result, an eventual inhomogeneous distribution of the electric field due to space charge in the device can be neglected in Eq. (2). From the observed response times, as shown in Fig. 1, $\mu_p$ can now be calculated using Eq. (2) as a function of $E_{\mathrm{av}} \equiv (V - V_{\mathrm{bi}})/L$. In Fig. 2, $\mu_p$ following from the response times as observed for $L = 100$, 200, and 300 nm are shown together with $\mu_p$ as obtained from the dc $J$-$V$ measurements [Eq. (1)]. The most striking feature is that the "mobility" as obtained from the response times depends on the device thickness. Futhermore, these "mobilities" are larger than the dc mobility [Eq. (1)], and they exhibit a stronger field dependence.

The difference between dc and transient mobilities [29] as well as a thickness dependent transient mobility [15,30] are strong indications of dispersive transport. According to the SM theory [14], the transit time $\tau_d$ of the fastest charge carriers is given by the universal scaling law

$$\tau_d \sim \left(\frac{L}{l(E)}\right)^{1/\alpha} \exp\left(\frac{\Delta_0}{k_B T}\right), \tag{3}$$

where $\Delta_0$ is the average zero-field activation energy, $l(E)$ is the mean displacement of the carrier between two pausing events (hopping, trapping), and $\alpha$ is the dispersion parameter. At low fields, one may assume [14] $l(E) \sim E$, such that $\tau_d$ is given by

$$\tau_d \sim \left(\frac{L}{E}\right)^{1/\alpha} \exp\left(\frac{\Delta_0}{k_B T}\right). \tag{4}$$

Clearly, in a system with dispersive transport, an analysis in terms of a mobility using Eq. (1), which leads to a thickness dependent mobility $\mu \sim (E/L)^{(1-\alpha)/\alpha}$, is not meaningful. According to Eq. (4), the observed response times at a given temperature are expected to scale as $(E/L)$. In Fig. 3, the observed response times $\tau_d$ are plotted against $E_{\mathrm{av}}/L$ for various temperatures. We find that, for $T = 296$ K, the observed $\tau_d$ for $L = 100$, 200, and 300 nm coincide on a single curve when plotted against $E_{\mathrm{av}}/L$, in contrast to the mobility plot of Fig. 2. This demonstrates that at room temperature the hole transport follows the SM scaling law.

At lower temperatures, however, the response times start to deviate from the scaling law (4), as becomes evident in Fig. 3. This deviation is due to the fact that the linear approximation $l(E) \sim E$ no longer holds at low temperatures or high fields. In order to describe the high field dispersive transport in $a$-As$_2$Se$_3$, Pfister has introduced the phenomenological expression $l(E) \sim \sinh(eRE_{\mathrm{av}}/2k_B T)$ [31]. This expression describes the asymmetry between hops in the direction of and against the applied field between two sites at a distance $R$, when the applied field lowers the activation energy for jumps in the field direction [32]. Note that, at low fields or high temperatures, $l(E)$ still approaches linear behavior. Using this expression for the field enhancement of the mean step displacement $l(E)$, we find that the response times obey the scaling law [Eq. (3)] for all temperatures and fields. Using an average activation energy $\Delta_0 = 0.34$ eV and an average site distance $R = 30$ Å, all data coincide on one curve characterized by a single dispersion parameter $\alpha = 0.45$ (see Fig. 4). From the average hopping distance $R = 30$ Å, a site density $N_h = (4\pi R^3/3)^{-1}$ of $10^{25}$ m$^{-3}$ can be estimated. A temperature-independent $\alpha$, as also observed in $a$-As$_2$Se$_3$ [15], indicates that the dispersion in the transit times in PPV is due mainly to structural disorder, i.e., disorder in the positions and local orientations of the polymer chains, rather than due to energetic disorder. This observation strongly favors hopping as the dominant transport mechanism in PPV rather than extended state transport with trapping in a distribution of trapping levels, which would give rise to a temperature-dependent dispersion.

The response time $\tau_d$ of a PLED at high electric fields is relevant for its use in pixilated displays where multiplexing is required. Because of the dispersive character of the charge transport, the response time of a PLED is determined only by the fastest part of the injected charge

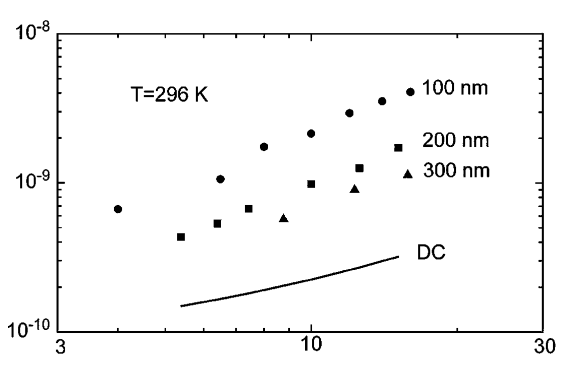

FIG. 2. Hole mobility $\mu_p$ calculated from the observed response times using Eq. (2) as a function of applied electric field $E_{\mathrm{av}}$ (symbols) for PLEDs with $L = 100$, 200, and 300 nm together with the hole mobility of Eq. (1) as obtained from dc $J$-$V$ measurements [7] (solid line).

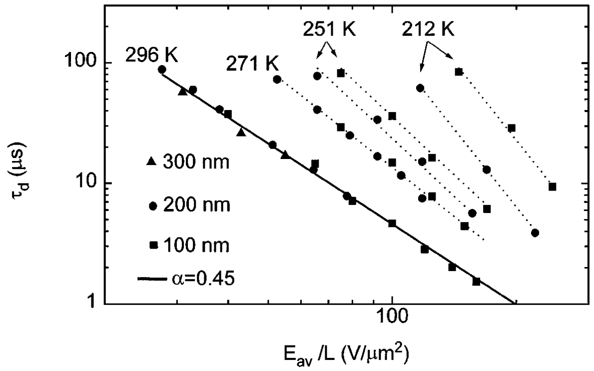

FIG. 3. Response time $\tau_d$ of PLEDs with thicknesses $L = 100$, 200, and 300 nm as a function of $E_{\mathrm{av}}/L$ for various temperatures. At $T = 296$ K, the response times follow the scaling law [Eq. (4), $\alpha = 0.45$] as predicted by Scher and Montroll for stochastic transport at low electric fields.

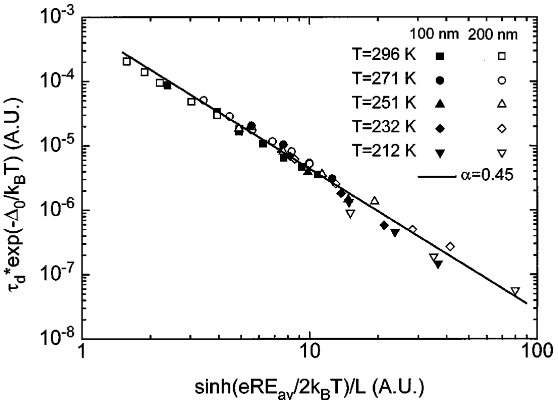

FIG. 4. Response time $\tau_d$ of Fig. 3 multiplied by $\exp(-\Delta_0/kT)$ as a function of $\sinh(eRE_{\mathrm{av}}/2kT)/L$. Using the approximate $l(E) \sim \sinh(eRE_{\mathrm{av}}/2kT)$ the observed $\tau_d$ (symbols) follow Eq. (3) with $\Delta_0 = 0.34$ eV, $R = 30$ Å, and $\alpha = 0.45$ (solid line) for various electric fields, temperatures, and sample thicknesses ($L = 100$ and 200 nm).

carriers. As a result, the field dependence of the observed response times cannot be compared directly to the field dependence of the dc mobility [Eq. (1)], which reflects the time-averaged behavior of the charge transport. Extrapolating Eq. (4) towards high fields [without including the nonlinear field dependence of $l(E)$], we deduce, as an upper limit for a 100 nm PLED operated at 10 V, a response time of only 20 ns at $T = 295$ K. Thus at high fields PLEDs are extremely fast devices, in agreement with the observation of Braun *et al.* [33].

In conclusion, we have demonstrated that the response of PPV-based PLEDs under pulsed operation is dominated by the dispersive transport of holes towards the cathode. The transit times of the holes follow the universal SM scaling law as a function of layer thickness, electric field, and temperature. As a result, an interpretation in terms of a charge carrier mobility is not meaningful. The dispersion in transit times appears to be independent of temperature, indicating that it originates from structural disorder, rather than energetic disorder.

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