Transport properties of highly aligned polymer light-emitting diodes

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We investigate hole transport in polymer light-emitting diodes in which the emissive layer is made of liquid-crystalline polymer chains aligned perpendicular to the direction of transport. Calculations of the current as a function of time via a random-walk model show excellent qualitative agreement with experiments conducted on electroluminescent polyfluorene demonstrating nondispersive hole transport. The current exhibits a constant plateau as the charge carriers move with a time-independent drift velocity, followed by a long tail when they reach the collecting electrode. Variation of the parameters within the model allows the investigation of the transition from nondispersive to dispersive transport in highly aligned polymers. It turns out that large interchain hopping is required for nondispersive hole transport and that structural disorder obstructs the propagation of holes through the polymer film.

During the last few years there has been great development both in the understanding of the underlying physics and the use of conjugated polymers as the emissive layer in light-emitting diodes.[1] Recently, there has been much interest in organic electroluminescent devices which are based on aligned conjugated polymers that emit polarized light[2] since the latter could be used directly in conventional liquid crystal displays.[3] Time-of-flight experiments in films of electroluminescent polyfluorene[4] have shown nondispersive hole transport with high mobility and weak field dependence, which indicates low energetic and positional disorder. Moreover, it has been demonstrated[5] that mesophase alignment can enhance carrier mobilities for conjugated main-chain liquid-crystalline polymers resulting in a more than one order of magnitude increase in time-of-flight hole mobility normal to the alignment direction.

Previous theoretical studies have concentrated on the identification of the field and temperature dependence of the carrier mobility in disordered molecular materials, such as molecularly doped polymers, small molecule glasses, and conjugated polymers, in terms of the disorder model.[6] The latter assumes that the charge transporting states, e.g., dopant molecules, are energetically localized, and the energy of these states is subject to a random distribution introduced by disorder. Nevertheless, recent experimental activity concerns the performance of devices made of a layer of liquid-crystalline polymers, which are systems of high order and orientation. In this paper, we present a simple model, based on random walks, which studies charge transport through a film of highly aligned polymers, and explains the mechanisms that enhance or hinder current in the simplest possible way. The model simulates charge carrier transport through an organic layer of liquid-crystalline polymers oriented perpendicular to the direction of transport and sandwiched between two electrodes, under the influence of an externally applied electric field E. Charge carriers of one type are injected in one of the electrodes, and by moving within the polymer film due to the presence of the field E they reach the other electrode where they are discharged. We assume injection of holes in accordance with the experiments in which it was not possible to measure any current from electrons as the latter current is highly dispersive. The term ''dispersive'' has been used in various contexts and with different meanings.[7] In this context dispersive transport describes the situation where the mean velocity of the carriers decreases with time. Our calculation of the current as a function of time shows a constant current plateau followed by a long tail, a behavior which was observed in experiments on electroluminescent polyfluorene and was linked to excellent purity and chemical regularity of the material,[4,5] and is typical of Gaussian propagating packets. Investigation of the hopping probabilities across the film of highly aligned polymers clearly demonstrates that the nondispersive character of hole transport is retained only in the case of adequate interchain hopping along the direction of transport, becoming dispersive otherwise. An additional feature implemented in our model is structural order which is also important for transport, since positional defects (voids) act as traps, immobilizing the charge carriers within the polymer film and resulting in dispersive hole current.

The polymer film is described by a two-dimensional discrete lattice, with x being the direction of transport and with periodic boundary conditions along the y direction. The polymer film is of thickness $d = D a_x$ sites, where $D = 100$ and the ''lattice constant'' is $a_x = 10$ Å. The choice of a_x was based on the fact that in real devices liquid-crystalline polymer chains have a typical interchain distance of about 12 Å.[8] We have considered that the polymer chains are rigid rods, basing this approximation on the extended ''backbone'' conjugation of most polymers that makes them stiff and on bond vibrations being of high frequency and very low amplitude. The chains are of length $L = 10 a_y$, where $a_y = 1$ Å, and are all oriented along the y direction. The construction of the polymer film is based on a random process. After choosing randomly any of the equivalent sites of the lattice, we extend the chain across the transverse direction only if a line of

length L along y is unoccupied. This prohibits both the occupation of the same space by more than one chain and any cross-linking between different chains. As a result, there is an upper limit ($\sim 77\%$) on the density of polymer chains that can be deposited between the electrodes which depends on the initial site chosen. The change in this upper limit between different configurations is of the order of 0.5% or less, so that its effect on the resulting current is negligible. The holes are injected into the polymer film at the anode and they move towards the collecting electrode under the effect of an external (positive) electric field E. The motion of the charge carriers is due to hopping, which is simulated via a random-walk process. Each carrier at a particular site hops to one of its nearest-neighboring sites on a polymer chain, with p_{+x}, p_{-x}, being the probabilities for hopping along the positive (right), negative (left) x direction, respectively, describing interchain hopping, and with p_{+y}, p_{-y} being the probabilities for hopping along the positive (up), negative (down) y direction, respectively, which account for intrachain hopping. Because of the presence of the positive field in the direction of transport p_{+x} is larger than p_{-x}, p_{+y}, and p_{-y}, and the strength of the electric field is $|E| \propto p_{+x} - p_{-x}$. Since the polymer chains are aligned normal to the direction of transport the biased hopping probability indicates that interchain hopping should be an important parameter. The drift of the carriers under the external electric field results in a time-dependent current $I(t)$. Each step of the random walk corresponds to one unit of time, $\delta t = 1$, in arbitrary units. The total current at each time t is then given by[9]

$$I(t) = -\frac{\delta}{\delta t} \sum_{x=1}^{d} \rho(x) + \frac{1}{d}\frac{\delta}{\delta t} \sum_{x=1}^{d} x\rho(x) \qquad (1)$$

where $\rho(x)$ is the charge density, integrated over y. The first term of Eq. (1) gives the conduction current, whereas the second term corresponds to the displacement current, for which detailed investigation has shown that it is a small correction to the conduction term.

Figure 1(a) shows the current transient from such simulations obtained for hopping probabilities $p_{+x} = 0.4$, $p_{-x} = 0.1$, $p_{+y} = 0.25$, and $p_{-y} = 0.25$. For small times the current shows a spike, which becomes a constant plateau as time increases, indicating that the injected carriers have the same mobility μ, as observed in the experiments.[4,5] This plateau is followed by a long tail when most of the charge carriers are discharged at the second electrode. This shape of the current transient is typical of Gaussian packets which propagate with time.[10] The latter has been verified in our simulations, as shown in the inset of Fig. 1(a) where the charge density $\rho(x)$ is plotted for three different times. When the charge carriers are injected at one of the electrodes, $\rho(x)$ is a δ function centered at the electrode. When an electric field E is applied, the carriers move inside the film, and $\rho(x)$ is described by an extended Gaussian distribution which propagates with time. The upper graph of Fig. 1(b) shows the same current transient as in Fig. 1(a) in a double logarithmic scale. The intersection point of the asymptotes (indicated by the arrow) defines the transit time for the arrival of the carriers at the collecting electrode. The transit time is related to the carrier
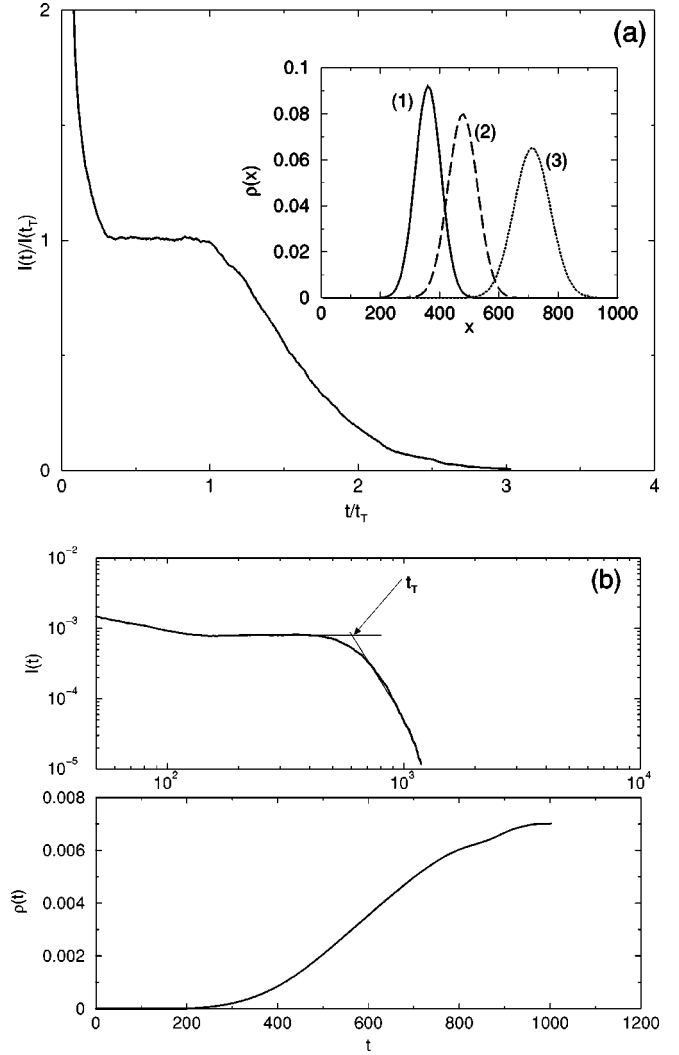

FIG. 1. (a) Current versus time for hopping probabilities $p_{+x} = 0.4$, $p_{-x} = 0.1$, $p_{+y} = 0.25$, $p_{-y} = 0.25$. In the inset the charge density is calculated for three different times: (1) $t/t_T = 0.3$, (2) $t/t_T = 0.4$, (3) $t/t_T = 0.6$. (b) The upper plot shows the double logarithmic representation of the current with respect to time. The arrow indicates the transit time t_T. The lower graph shows the charge accumulated at a capacitor connected at the collecting electrode at each time step. At both graphs the axes are in arbitrary units.

mobility μ and the external electric field E via the relation $\mu = d/(t_T E)$, and it is the experimentally measured quantity from which the carrier mobility is derived.

An alternative way to measure t_T experimentally is by connecting the discharging electrode to a capacitor and measuring the charge that accumulates there. The time at which the charge in the capacitor has half of its maximum value must be equal to t_T. The lower graph of Fig. 1(b) shows the results of such a numerical calculation. Both techniques yield the same value of t_T, which is around $t_T = 600\delta t$. In all the results presented in this paper we have normalized the current transients to their value at the transit time. Figure 2 shows the transit time t_T as a function of the electric field E. Since t_T decreases linearly as the electric field becomes larger, we conclude that the mobility will have a weak dependence on the electric field, as was seen in experiments.[4,5]
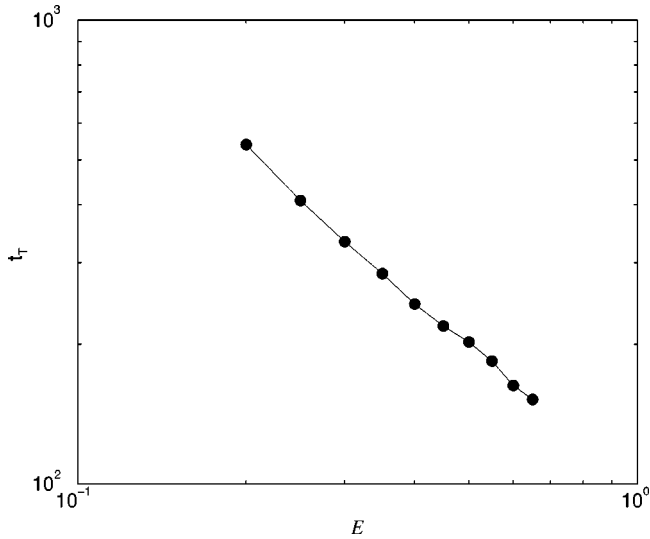
FIG. 2. Double logarithmic representation of the transit time t_T versus the externally applied electric field $|E| \propto p_{+x} - p_{-x}$, in arbitrary units.

So far we have demonstrated that a hopping model based on random walks describes adequately hole transport within a polymer film of highly aligned polymers, being in agreement with the experiments which show nondispersive hole currents. Our next aim is to point out which are the parameters that affect transport, and when the current changes from nondispersive to dispersive. Figure 3 shows the current transients for different applied fields, thus for different hopping probabilities in the direction of transport. Curve (1) corresponds to $|E| \propto p_{+x} - p_{-x} = 0.2$, which is smaller than that of Fig. 1(a). The current plateau is retained and the transport remains nondispersive. However, if we reduce further the electric field, as in curve (2), the plateau disappears and the
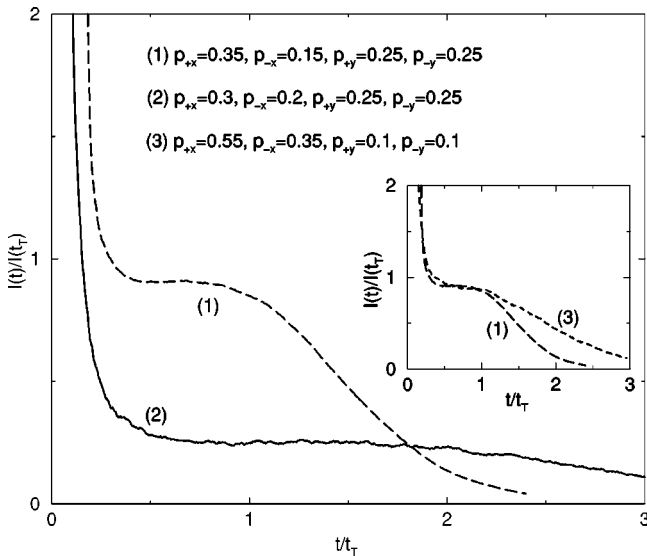

FIG. 3. Current versus time for two different strengths of the externally applied electric field E (different hopping probabilities across x). In the inset we have plotted the current versus time for two different hopping probabilities across the y direction.
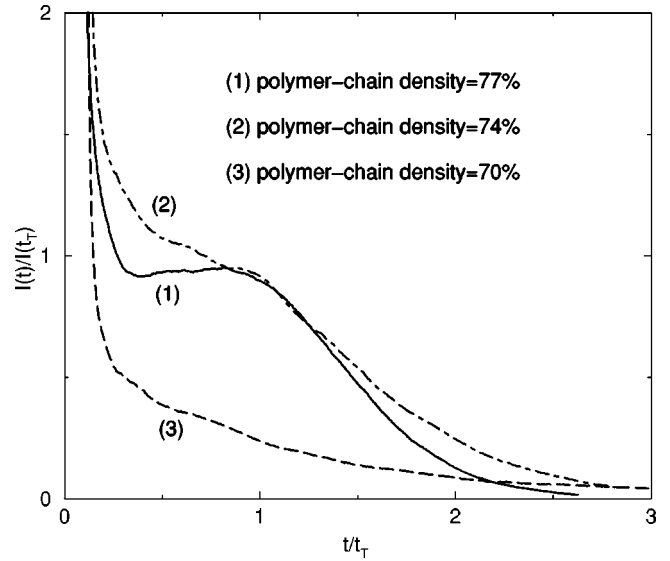

FIG. 4. Current versus time for different densities of polymer chains between the two electrodes ($p_{+x} = 0.4$, $p_{-x} = 0.1$, $p_{+y} = 0.25$, $p_{-y} = 0.25$).

current decreases rapidly. Note that even though the plateau does not exist anymore so that we cannot identify any transient time in this case, we have divided the current of curve (2) with I_T of curve (1) to make a direct comparison between the two curves. The decrease of the current means that most of the charge remains trapped within the polymer film and much fewer carriers make it to the collecting electrode. If we keep the same strength of the electric field, $E \propto 0.2$, but decrease p_{+y} and p_{-y}, as is shown in the inset of Fig. 3 [curve (3)], the current remains nondispersive with a larger tail, thus, more holes will reach the collecting electrode. We conclude from these results that in systems of liquid-crystalline polymers interchain hopping (hopping along the x direction)
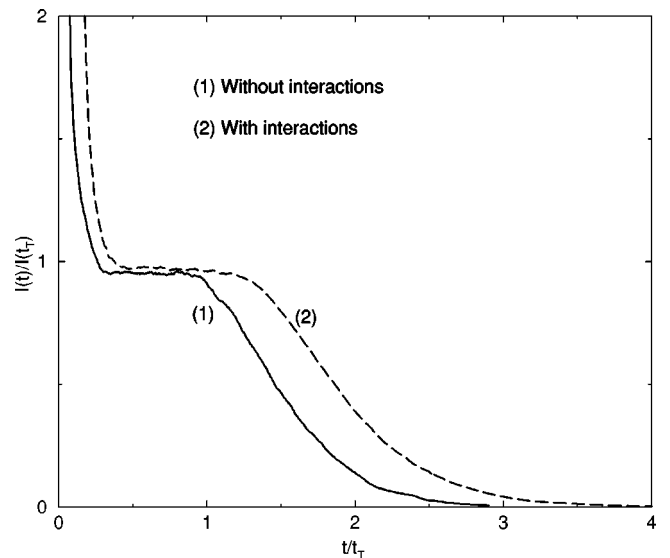

FIG. 5. Current versus time with respect to the presence or absence of on-site repulsive interactions between the charge carriers ($p_{+x} = 0.4$, $p_{-x} = 0.1$, $p_{+y} = 0.25$, $p_{-y} = 0.25$).

is the essential mechanism for the transport of holes (interchain hopping along y is not permitted in our model).

Figure 4 shows the current transient for different densities of polymer chains deposited in the emissive layer. If we allow fewer polymer chains than the maximum allowed occupation density of the space between the electrodes, the plateau is destroyed [curve (2)], while upon further decrease the current becomes dispersive once again [curve (3)]. This is due to the presence of large gaps in the space between the electrodes (voids), which act as traps for the carriers. A threshold density of chains, dependent upon the chain configuration, is found (68% in this case) below which transport of the carriers from one electrode to the other is totally prohibited. In other words, positional disorder strongly affects transport and a highly ordered polymer film is required for best device performances.

All the above results have been obtained without taking into account the effect of repulsive interactions between the charge carriers. Inclusion of the latter interaction can be incorporated within our model by not allowing any two carriers to occupy the same site at each time step. If all the neighboring sites of a carrier are occupied, it remains in the same position until one of these sites becomes free, otherwise it gets trapped in this site. Figure 5 shows the current with respect to time in the absence [curve (1)] and the presence [curve (2)] of on-site repulsive interactions. In the latter case the qualitative behavior of the current does not change, even though the plateau is larger and clearer and it takes more time for the charge carriers to reach the second electrode and get discharged.

In summary, our random-walk model for the description of hole transport in light-emitting diodes whose active element is a polymer film of highly aligned conjugated polymers, has added to the understanding of the phenomenology of such devices. The experimentally measured nondispersive current transient has been verified by the numerical simulations, which also show the constant current plateau and the long tail, typical of Gaussian propagating packets. Moreover, the model specifies the conditions under which transport becomes dispersive, by stressing out the importance of interchain hopping for transport in these liquid-crystalline polymers. The effect of structural disorder is also discussed in connection with better device performance, underlining the need of very clean and ordered polymer films in order to avoid the presence of traps, which will hinder transport and result in poor device performances.

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