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Effect of molecular properties on the performance of polymer light-emitting diodes

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Abstract

The performance of a single layer polymer light-emitting diode depends on several interdependent factors, although recombination between electrons and holes within the polymer layer is believed to play an important role. Our aim is to carry out computer experiments in which bipolar charge carriers are injected in polymer networks made of poly(*p*-phenylene vinylene) chains randomly oriented. In these simulations, we follow the charge evolution in time from some initial state to the steady state. The intra-molecular properties of the polymer molecules obtained from self-consistent quantum molecular dynamics calculations are used in the mesoscopic model. The purpose of the present work is to clarify the effects of intra-molecular charge mobility and energy disorder on recombination efficiency. In particular, we find that charge mobility along the polymer chains has a serious influence on recombination within the polymer layer. Our results also show that energy disorder due to differences in ionization potential and electron affinity of neighbouring molecules affects mainly recombinations that occur near the electrodes at polymer chains parallel to them.

Keywords: Modelling; Charge mobility; Recombination efficiency; Conducting polymer

1. Introduction

In 1990, Burroughes et al. [1] has demonstrated that light-emitting diodes (LEDs) can be fabricated from a single layer of conjugated polymers such as poly(*p*-phenylene vinylene) (PPV). One of the factors determining the performance of this polymer based LEDs is the fraction of injected electrons and holes that recombine in the polymer layer. However, the competition between bipolar charge transport, trapping and recombination depends both on the properties of individual polymer strands and on polymer chain arrangement.

Although recent experimental studies [2] have shown that polymer morphology has a remarkable influence on device properties, the effect of molecular properties on the device performance is still unknown. Since it is difficult in experimental measurements to isolate the effects of varying just one intra-molecular property, device modelling is required to understand how the properties of each polymer molecule, that have an influence on charge transfer within the polymer layer, affects recombination efficiency. Device

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model including intra- and inter-chain charge transport, discrete space charge and intra-molecular recombination is a useful tool for such studies, because it allows the effect of varying one property at molecular scale, such as intra-molecular mobility, to be examined whilst leaving the others unchanged.

In this paper we present result of a simple model for the evaluation of bipolar charge transport in PPV networks, where each PPV molecule in the network has a different ionization potential and electron affinity, depending on the chain length and molecular charge. The effect of the intra-molecular charge mobility on the network also depends on the strength of the local electric field. Using this model we aim to clarify the dependence of recombination on intra-molecular charge mobility and energetic disorder due to difference in ionization potential and electron affinity of the molecules in the polymer layer.

2. Model and method

In the order to build a polymer network to model the bipolar charge transport in a single layer PPV LED, one needs to know which is the minimum distance between two non-interacting PPV chains, so that the polymer chains in the network can be taken as rigid rods. Considering the large number of atoms involved in two PPV chains and the existing coupling between the atomic positions and the electronic structure of these conjugated polymers, we choose to use a self-consistent quantum molecular dynamics method, working at the CNDO (complete neglect of differential overlap) level, both to obtain the minimum inter-chain distance in the network and to calculate electronic and charge transport properties of single polymer chains with lengths ranging from 2 and 16 units. Results from these calculations can be found elsewhere [3–7] and they will be carried over to the model that simulates charge transport through the polymer network.

Polymer networks were obtained by placing individual straight strands of different lengths at random in the gap between two electrodes of 20 nm × 20 nm localized at the distance of 100 nm. The minimum inter-chain distance allowed was 0.65 nm and the number of the units in each strand varies from 2 to 14, chosen from a Gaussian distribution [8]. As a result, the density of polymer chains that could be deposited between the electrodes was 0.36 g/cm^3.

When an external electric field normal to the electrode surfaces is applied, one electron and one hole are injected, at each computer iteration, from the appropriated electrodes into the polymer strands in contact with the electrode. Since charge transport along one polymer chain is much faster than inter-chain transport [9], each iteration corresponds to one inter-chain jump.

In each iteration, the charge injected at each polymer chain moves towards its centre if the local electric field (it is the sum of the applied external field, the field of the other charges within the polymer network and the field due to electrode polarization) is lower than the field needed to move the charge along the chain [7], otherwise it moves towards the chain end favoured by the local field.

In this model the intra-molecular charge mobility of both electrons and holes is only considered when the local electric field is greater than 1.5×10^8 V/m. This electric field threshold value was obtained from self-consistent quantum molecular dynamics calculations [7].

In the following iteration, each charge hops to a strand for which the hopping probability is greater than 90%, chosen randomly, unless that the hopping rate is lower than 10^{-5}. The jump rate is assumed to be dependent on the direction of the local electric field, on the inter-chain distance, on the Coulomb blockade and on the difference between electron affinity (for hole transport) or ionization potential (for electron transport) of neighbouring PPV chains [8,10]. Since the difference between ionization potential of PPV chains is greater than the corresponding difference in electron affinity, the hopping from one molecule to another should be easier for holes than for electrons in accordance with the experiments. Recombination occurs during the simulation when two oppositely charge carriers meet on the same PPV chain. In our present work we do not allow inter-chain recombination.

3. Results and discussion

When multiple charges are injected in the polymer network continuously, some of the charge carriers simply carry current, others are trapped or in transit within the polymer layer whereas others recombine (radiatively or non-radiatively). Where within the device the recombination occurs may be important for the overall device efficiency.

Our results here concentrate on two factors: the effect of intra-molecular charge mobility and the effect of energetic disorder due to differences between ionization potential or electron affinities of the molecules involved in inter-molecular charge transport within the polymer network. Fig. 1 shows the effect of intra-molecular charge mobility on recombination efficiency as a function of time. These results suggest that when intra-molecular charge mobility is not allowed then recombination within the polymer network starts later and the recombination efficiency increases slowly with time, reaching greater recombination efficiency when a steady state is achieved. Similar results are obtained whether or not all the polymer chains having the same electron affinity or ionization potential.

When intra-molecular charge mobility is forbidden, the recombination behaviour presented in Fig. 1 arises from the following factors. For short times all the charges injected are trapped within the network close to the electrodes where they have been injected. As time increases, both electrons and holes move slowly in a random walk inside the polymer film and most of them undergo recombination in the centre of the film (Fig. 2). Therefore, only a few charge carriers reach the collecting electrodes. As a result recombination efficiency and charge trapping anti-correlate whereas current efficiency remains roughly constant. When intra-molecular charge mobility is allowed, the charge injected in the network move faster towards the opposite electrode leading to a competition between current flow and recombination, which gives rise to lower recombination efficiency. Another consequence is an increase of recombination close to both electrodes (see Fig. 2).

In contrast to the effect of intra-molecular charge mobility, the overall recombination efficiency depends weakly on the energetic disorder due to the difference between electron affinity (for hole transport) and ionization potential (for electron transport) of neighbouring PPV chains in the network. The main effects predicted were a decrease in the mean number of

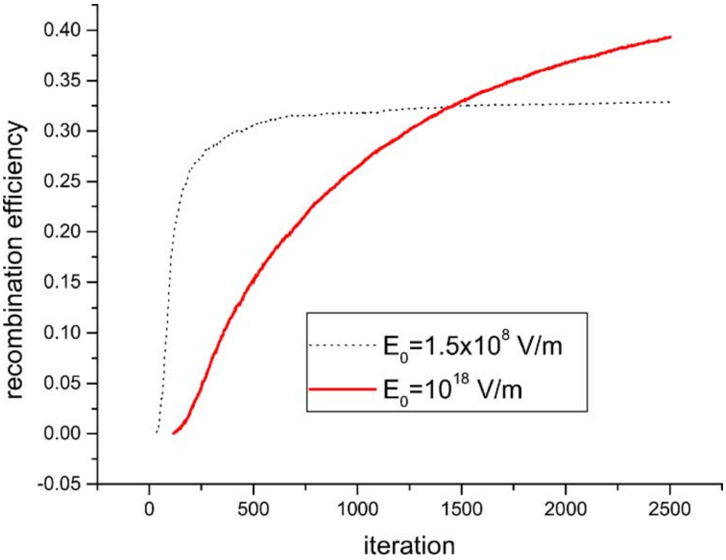

Fig. 1. Dependence of recombination efficiency (measured by the number of recombination events per electron–hole pair injected) on time for a single layer PPV LED with (i) intra-molecular charge transport allowed (broken line) and (ii) intra-molecular charge transport forbidden (solid line). The external applied electric field in the simulation is 2.5×10^8 V/m and intra-molecular charge transport is only considered when the local electric field is greater than the parameter E_0.

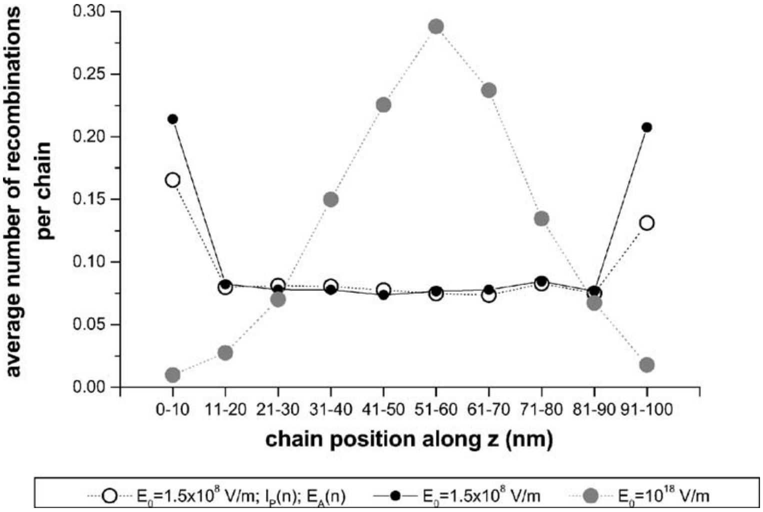

Fig. 2. The mean number of recombination events per polymer chain along the direction normal to the electrode surfaces in a single layer PPV LED when (i) both intra-molecular charge transport and energetic disorder are considered (open circles), (ii) both intra-molecular charge transport and energetic disorder are not considered (large closed circles) and (iii) intra-molecular charge transport is allowed and energetic disorder is not considered (small closed circles). The external applied electric field in the simulation is 2.5×10^8 V/m and intra-molecular charge transport is only considered when the local electric field is greater than the parameter E_0.

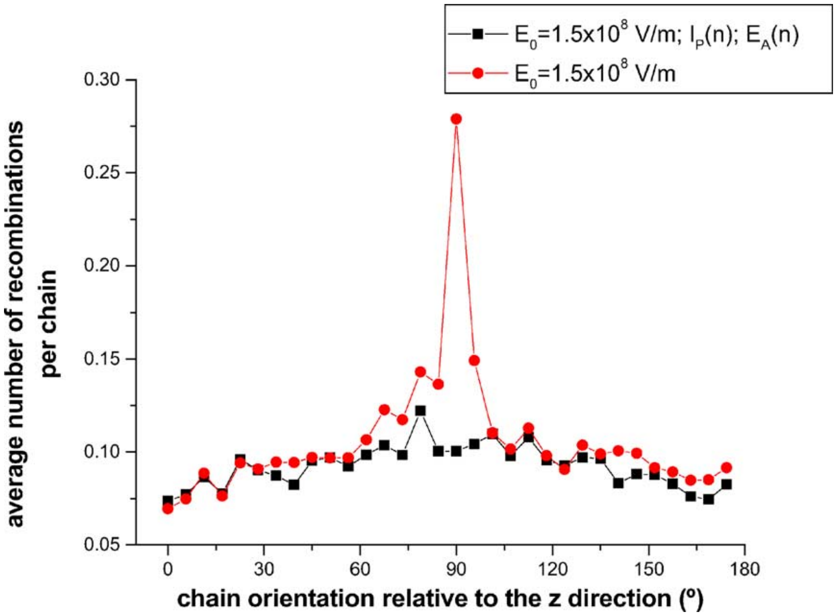

Fig. 3. The mean number of recombination events per polymer chain during the numerical simulation as a function of the angle between the chain's direction and the direction normal to the electrode surfaces when (a) intra-molecular charge transport is allowed and no energetic disorder is considered (circles) and (b) intra-molecular charge transport is allowed and energetic disorder is considered (squares). The external applied electric field in the simulation is 2.5×10^8 V/m and intra-molecular charge transport is only considered when the local electric field is greater than the parameter E_0.

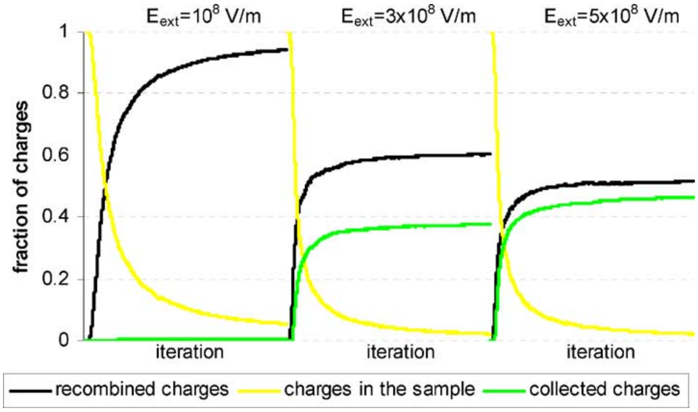

Fig. 4. Proportions of injected charge which are trapped, recombine or cross the polymer network to carry a current, as a function of time, for three different external applied electric fields. These results were obtained using an electric field threshold of 1.5×10^8 V/m and the data for ionization potential and electron affinity of PPV chains reported in reference [7].

recombinations per polymer strand near the electrodes (Fig. 2) as well as on the strands parallel to the electrodes (Fig. 3). Moreover, energetic disorder is relatively important when recombination takes place in the shortest chains. The number of recombinations that occurs in chains with two or three repeat units can be reduced by 10 times when energetic disorder is considered. The random walk described above gives rise to an increase in the number of recombination events on chains nearly parallel to the electrodes especially on those chains that for topological reasons act as trapping centres for the injected charges (Fig. 3). This effect is more pronounced when no energetic disorder is considered.

All the above results suggest that the integration of intra-molecular properties of the polymer molecules in the mesoscopic model is important for a more realistic description of bipolar charge transport in polymer based light-emitting diodes. The fact that there is competition between intra-molecular and inter-molecular charge transport processes leads to trends in current, trapping and recombination efficiencies for different applied electric fields which are by no means intuitive (see Fig. 4).

4. Conclusions

Our mesoscopic modelling of bipolar charge transport in single layer PPV LED, which includes the intra-molecular properties of the polymer molecules, has proven to be a successful method for obtaining insights on the implications of intra-molecular charge transport and energetic disorder on device performance. From our numerical modelling we have found that both intra-molecular charge mobility and energetic disorder reduce charge recombination which should affect device performance.

The proposed model can also be applied to a large variety of other polymeric materials and multilayer polymer LEDs.

Acknowledgements

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