

The Effect of the Intramolecular Properties in Single-Carrier Polymer Diodes

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Abstract

The electric behaviour of polymer diodes has the influence of several factors such as the electrodes work function, the experimental conditions used to deposit the active component or the chemistry of the polymer. Although experimentally it is possible to study the effect of some of these factors on the device performance, for instance by changing the chemical structure of the polymer used or the type of electrodes, it is impossible to study individually each one of these effects because changing one of them can influence the others. Quantum mechanical calculations have shown that depending on the chemical structure of the polymer, its intramolecular properties (e.g. ionization potential, electron affinity or intramolecular charge mobility) can be changed. To understand the effect of the intramolecular properties in the performance of polymer diodes we use a generalized dynamical Monte Carlo method that considers the nanostructure of the polymer layer and the main electronic processes involved in diode

functioning. Our results show that the influence of the intramolecular properties on the electric behaviour of pristine polymer-diodes with ohmic contacts depends on the morphology of the polymer layer at nanoscale that can alter not only hole and electron current density for the same applied electric field but also charge density and charge distribution inside the polymer layer.

Keywords: PPV, Monte Carlo model, polymer diode

1. Introduction

Although the number of organic-based electronic devices that have been appearing recently in the commercial market is increasing, some limitations like the device life-time (e.g. the decrease of efficiency and failure along time) or the low efficiency limits their applications in large scale.

In organic diodes one of the key factors that influence the device performance is the electrode/organic interfaces. Several studies have demonstrated a strong asymmetry between the top and bottom organic/electrodes interfaces [1] due to the different deposition techniques used to form both interfaces, as well as different charge trapping, doping, chemical bonding, etc [2, 3] at both interfaces that influences charge injection. But even in the presence of electrodes that exhibit small chemical interaction with the organic layer, there is charge transfer between the electrodes and organic component [4] that can influence the charge injection process. Nevertheless, no attention has been paid to the influence of the polymer chains orientation on the injection process and thus on the polymer diodes functioning.

In the last years Ramos and co-workers [5-7] have studied the processes of charge injection and transport along conjugated polymer segments of different lengths and have showed that both processes depend on the polymer chemistry and charge sign. In the absence of an external electric field, when a charge is injected in a polymer strand, there is a coupling between the charge and the polymer chain creating polaron-type defect in the middle of the strand. Depending on the strength of the local electric field along the strand, the charged defect can move to the strand end favoured by the field and even hop to another strand. Both intramolecular and intermolecular charge transport processes depend on the intramolecular properties of the polymer strands (i.e. ionization potential, electron affinity and the electric field threshold for charge transport along the polymer strand) and they are strongly dependent on the strength and direction of the local electric field. Therefore, it seems clear that the orientation of the strands relative to the electrode surface will influence charge injection and charge transport throughout the device.

To understand the influence of the intramolecular properties in the electric behaviour of polymer diodes we performed computational experiments using 3D-polymer networks of poly(p-phenylenevinylene) (PPV) with different orientations of the polymer strands relative to the electrodes, using a generalized dynamic Monte Carlo method which includes the intramolecular properties of the polymer strands obtained from atomistic calculations as input parameters.

2. Computational Model and Simulation Conditions

The deposition of the polymer layer on the anode usually is made by solution-based techniques. After the solvent evaporation, the conjugated polymer chains in the

bulk tend to be bent and twisted, forming a structure similar to “cooked spaghetti”. The bent of the polymer chains disrupt the conjugation and thus the possibility of charge transport along the long polymer chains. As a result the long polymer chains can be seen as an assemble of stiff conjugated segments with different lengths and orientations connected by kinks and twists (see Fig. 1). The self-organization in solution-processed conjugated polymer thin films results in a complex microstructure, which exhibits domains of different size with highly aligned conjugated segments but different orientations relative to the electrodes surface (e.g. polymer strands with their molecular axis parallel or perpendicular to the electrodes surface) or having a random orientation. In all the domains a spatial disorder is always present since the distance between two strands is not always the same. In order to understand how these molecular alignments relative to the electrodes influence the functioning of polymer diodes, we placed straight conjugated segments (considered as rigid rods) randomly in the gap between two planar electrodes, separated 100 nm from each other (model axis), with their molecular axis parallel, perpendicular or random oriented relative to the electrodes surface. In all the polymer networks built, minimum distances of 0.650 nm were allowed between the polymer strands and between those and the electrodes and the length of each polymer strand was taken from a Gaussian distribution of strand lengths with mean value of 7 monomers, as suggested by previous theoretical and experimental results reported elsewhere [7, 8].

The percolation of charges inside the polymer networks results from the fact that they can be transport along these strands or hop between different stiff conjugated segments from the same chain or from different chains. The percolation process depends

on the intramolecular properties of the polymer strands as well as the orientation and strength of the local electric field.

Although most of the models published in the literature [9, 10] only consider intermolecular charge hopping between lattice points with energies taken from Gaussian distribution, very little work has been carried out using modified Gaussian Disorder models that consider the possibility of both intramolecular and intermolecular charge transport and some specificities of the polymer morphology [11-13]. To the best of our knowledge, the only model that takes into account explicitly the arrangement of the conjugated strands within the network and the effect of the intramolecular properties, obtained by quantum molecular dynamics calculations, on both intra and intermolecular charge transport is the one proposed by Ramos and co-workers for polymer light-emitting diodes [14]. In this work we have modified that model in order to consider the main electronic processes involved in a single-carrier polymer diode such as charge injection/collection by the electrodes with the possibility of a backflow current, charge (electrons and holes) percolation throughout the polymer network by intramolecular transport along the polymer strands and intermolecular transport (e.g. charge hopping between neighbouring strands), and the possibility of charge trapping in a strand. All these processes are dependent on the local electric field (which is the sum of the applied electric field, the field due to charge distribution within the polymer network and the field due to electrode polarization).

Our computational model of charge injection and transport is based on a generalized dynamic Monte Carlo method, where a queue of increasing time steps associated to the occurrence of the all electronic processes described above is used to

follow the time evolution of the charges in the device, which is based on the first reaction method (FRM) [15]. For each electronic process associated to a charge there is a waiting time given by:

$$\tau = -\frac{\ln(X)}{w_{ij}} \quad (2)$$

where w_{ij} is the hopping frequency associated to an electronic process, and X is a random number uniformly distributed between 0 and 1. At each computer iteration the first electronic process on the queue takes place and is removed from it. The lapse of time associated with that process is subtracted to all waiting times, and new electronic processes are inserted in the queue due to the injection of a new charge, or displacement of a charge within the network or charge collection by the electrode.

The hopping rates associated to the electronic processes of charge injection/collection from/by the electrodes and intermolecular charge hopping within the 3D-polymer network are given by [14]:

$$w_{ij} = w_0 \times \cos \theta \times \exp\left(-\frac{r_{ij} - r_0}{r_0}\right) \times \begin{cases} \exp\left(-\frac{\Delta \varepsilon_{ij}}{k_B T}\right), \text{ for } \Delta \varepsilon_{ij} > 0 \\ 1, \text{ for } \Delta \varepsilon_{ij} < 0 \end{cases} \quad (1)$$

where the first term represents the *attempt-to-escape* frequency and the following terms represent the influences of the local electric field direction, the hopping distance and the energy barrier height (which depends on the ionization potential and electron affinity of the involved polymer strands and the bias between them due to the local electric field) on the hopping process. Only the electronic process with the highest hopping probability takes place. Intramolecular charge transport occurs only if the local electric field along the strand axis is higher than the field needed to move the injected charge along that

polymer strand. A detailed description of the injection/collection and transport processes for ohmic contacts can be found in ref. [14, 16] and the molecular properties used in this work as input parameters were taken from ref. [7].

In this work, we use pristine 3D-polymer networks with the three morphologies described above and simulate single-carrier (holes or electrons) charge injection and transport in polymer diodes for applied electric fields ranging from 0.35 MV/cm to 0.75 MV/cm. All the simulations finish after the steady state is reached (i.e. the charge density (ρ) inside the polymer layer remains roughly constant) and the simulation time allowed is over.

3. Simulation Results and Discussion

Fig. 2 shows the current density for holes (J_h) and electrons (J_e) as a function of the applied electric field (E), for the three polymer morphologies consider in this work. Our results show an increase of current density with the increase of the applied electric field for all strand orientation relative to the electrodes surface, the effect being more pronounced for polymer layers with parallel morphology. In polymer layers with parallel morphology, charge transport is mainly due to charge hopping between strands since the applied electric field is normal to the strands axis, whereas for the polymer layers with random and perpendicular morphology intramolecular charge transport can also occur whenever the local electric field is greater than the field needed for intramolecular charge transport (1.55 MV/cm for electrons and 1.95 MV/cm for holes [5]). Since the average hopping distance between the neighbouring strands along the direction perpendicular to the electrodes is the largest one for the perpendicular morphology and the smallest one

for the parallel morphology, charge percolation in polymer layers with parallel morphology is mainly governed by the energetic disorder (i.e. the energy barriers that a charge have to overcome to hop) while in the case of perpendicular and random morphologies is mainly dominated by the charge transport along the polymer strands and the hopping distance.

These effects also influence the differences between J_h and J_e predicted for the different morphologies. On the parallel morphology, the energetic disorder for hole injection at the electrode/polymer interfaces due to the difference in strand lengths is higher than for electrons. This means that near the electrodes the distribution of energy barriers for hole injection is larger than for electron injection and, consequently, that are more strands available for hole injection which reduce hole backflow to the injection electrode as compared to electrons. This effect will allow that holes be more easily injected contributing to hole current density.

For the perpendicular morphology, spatial disorder minimizes the effect of the energetic disorder since it allows intramolecular charge transport. The fact that electrons exhibit a smaller electric field threshold for intramolecular charge mobility than for holes, will allow that electrons be easily transport far from the electrodes reducing the effect of current backflow to the injection electrode. This effect is also present in polymer layers with random morphology, but in this case the spatial disorder allows that charge hopping between strands along the direction perpendicular to the electrodes surface be more easier than for the perpendicular morphology.

The dependence of current density, and thus charge transport, on strand orientation relative to the electrodes is also reflected on hole and electron charge density

(ρ_h and ρ_e) within the polymer layer. Figure 3 shows how charge density varies with the increase of applied electric field. For all polymer morphologies, charge density increases with the increase of the applied electric field. However, since charge percolation tends to be more difficult as the angle between the strands axis and the electrodes increases, the perpendicular morphologies tends to store more charge when compared to the parallel and random morphologies. It is interesting to note that for the layers with polymer strands parallel to the electrodes, current and charge densities tend to increase almost exponentially with the increase of the applied electric field whereas for random and perpendicular morphologies the increase is almost linear.

When we compare the charge and the internal electric field distributions inside the polymer layer for different morphologies (see Fig. 4), we can see that for the random and perpendicular morphologies there is a smooth charge distribution within the polymer layer along the direction perpendicular to the electrodes surface. This is due to the fact that the both morphologies tend to store more charge leading to a more uniform space charge distribution. Although the charge distribution for parallel morphology is less uniform, the internal electric field profiles for electrons and holes have the same linear shape as for random and perpendicular morphologies. Independently of the injected charge sign, the slope of the internal electric field inside the polymer layer along the model axis for the perpendicular morphology is more pronounced than for random and parallel morphologies. The significant increase of the internal electric field strength near the anode (100 nm)/cathode (0 nm) as compared to the applied electric field (dashed line in Fig. 4), strongly limits charge injection for the perpendicular morphology. This effect is less pronounced for random and parallel morphologies.

4. Conclusions

The improvement of polymer light emitting diodes efficiency requires a deep understanding of how the molecular properties and the morphology at nanoscale can affect charge transport and current density in order to increase the number of charge recombinations. At experimental level the effect of the polymer chemistry or the morphology on charge transport is study performing experiments in single-carrier devices. Nevertheless is difficult to reveal which factors (i.e. polymer chemistry, morphology, traps or interfaces) determine the device performance since changing one of them can affect the others.

In this work we shed some light on how the intramolecular properties of polymer strands can influence the electric behaviour of single-carrier PPV-diode with different orientations of the strands relative to the electrodes surface. For a pristine polymer layer and perfect ohmic electrode/polymer interfaces, our results show clearly that the electric behaviour of the polymer layer with strands parallel to the electrodes surface is mainly ruled by the energetic disorder present in the polymer network due to the effect of strand length on ionization potential and electron affinity, leading to a high current density and low charge density compared to other orientations of the strands. The same energetic disorder is responsible for higher current density for holes than for electrons, regardless of the applied electric field. In the polymer layers with perpendicular and random oriented strands relative to the electrodes surface, the spatial orientation of those strands allows that charges can be transport along the polymer strands. However in these cases the intermolecular charge transport along the direction perpendicular to the electrodes surfaces is limited by the hopping distance of the polymer strands along that direction,

being this effect more pronounced for layers with perpendicular morphology. As a result, for the perpendicular morphology there is low current density and a high charge density since the internal electric field strongly limits charge injection.

These results lead us to conclude that in real polymer layers, the domains with polymer strands parallel to the electrodes are the main pathways for charge transport being the current density limited by the presence of domains with polymer strands with other orientation relative to the electrodes surface, being desirable at experimental level increase the alignment of polymer strands parallel to the electrodes surface to improve the electric behaviour of polymer-based diodes as well as field effect transistors.

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Figure 1 – Scheme of a polymer light emitting diode with a representation of the morphology of the polymer chains at nanoscale.

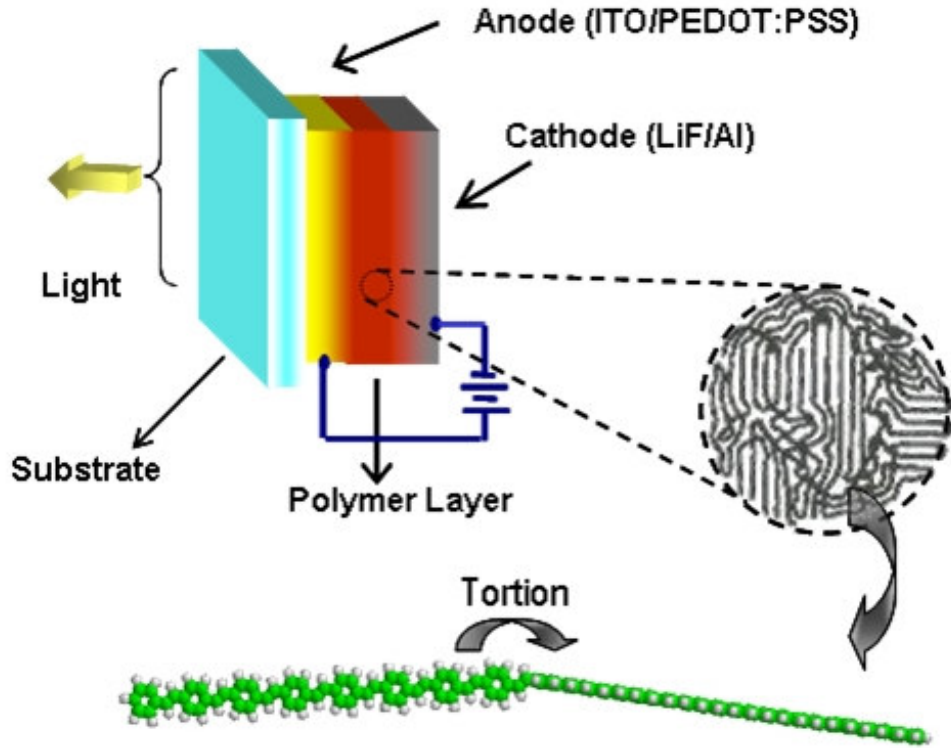


Figure 2 – Hole (circle) and electron (square) current density (J) for polymer layers with parallel, random and perpendicular morphologies as a function of the applied electric field (E). The lines are just a guide to the eyes.

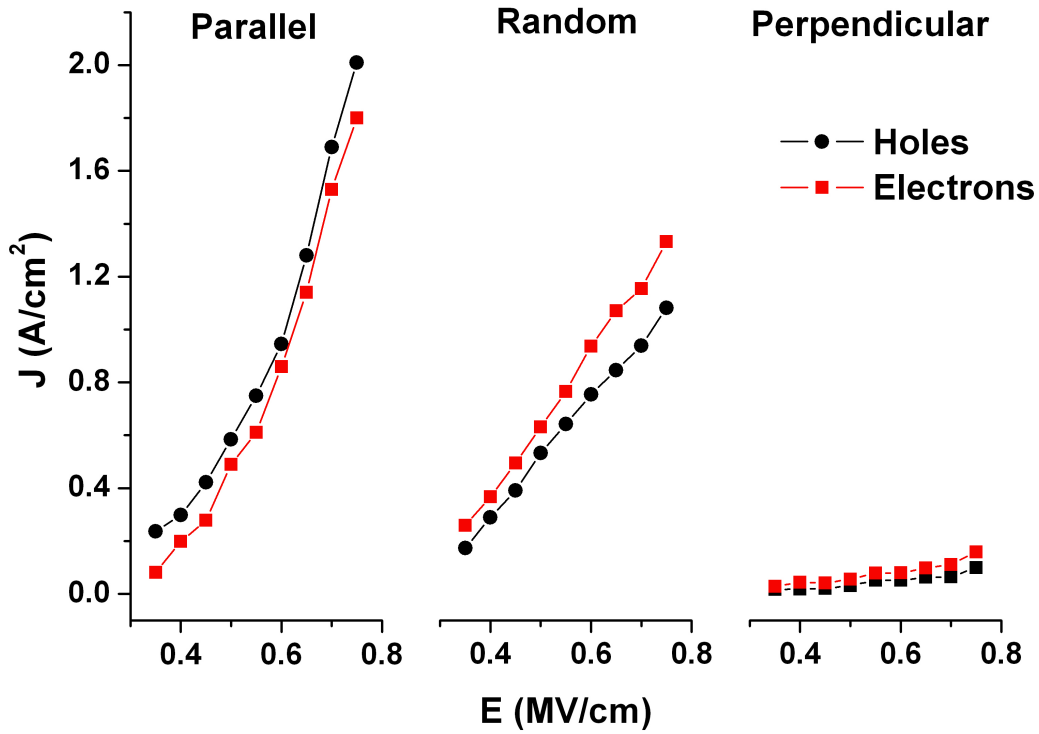


Figure 3 – Hole (circle) and electron (square) charge density (ρ) for polymer layers with parallel, random and perpendicular morphologies as a function of the applied electric field (E). The lines are just a guide to the eyes.

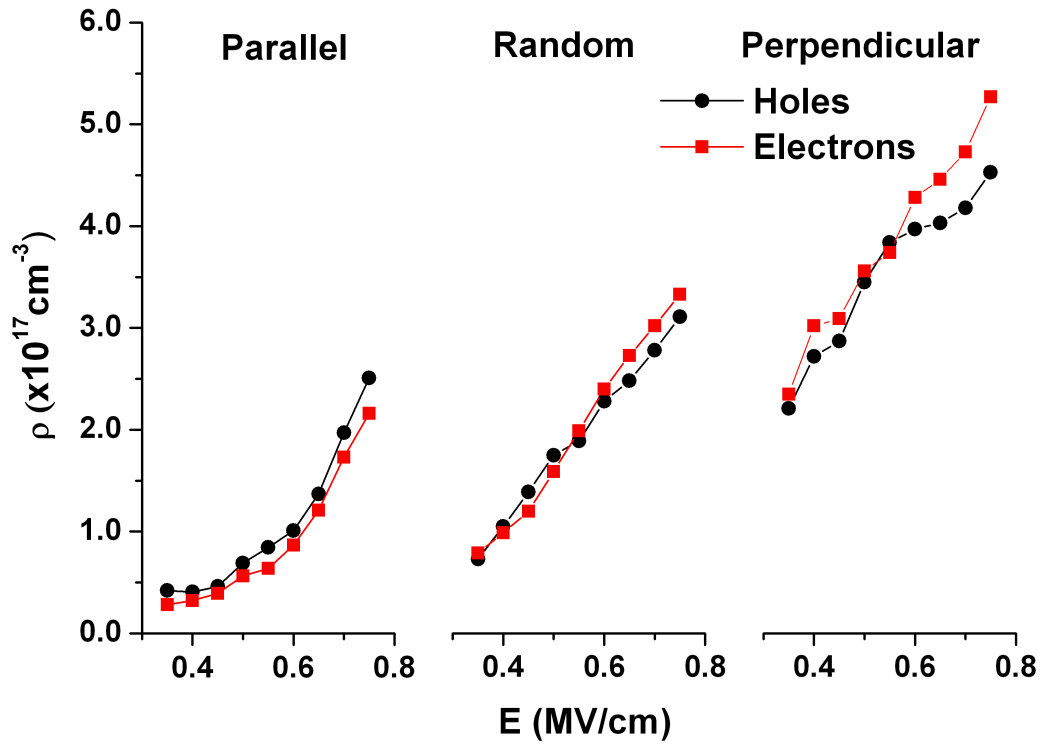


Figure 4 – Fraction of hole (sparse rectangles) and electron (empty rectangles) distribution along the model axis perpendicular to the electrodes surface as well as the internal electric field for hole (solid line) and electron (dot line) polymer diode and for an applied electric field of 0.75 MV/cm (dashed line).

