The Influence of Nanostructure on Polymer-based Optoelectronic Devices Functioning: a Computer Simulation Study

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Abstract

During the last years it has been clear that it is importance to understand and control the nanostructure of the active polymer layer used in optoelectronic devices, like polymer diodes, solar cells or field effect transistors. Several experimental studies have shown that the nanostructure of polymer thin films used in these optoelectronic devices depends on the conditions used to deposit the polymer layer between the electrodes. As a result, in solid state conjugated polymer chains tend to be stacked and aligned relative to the electrodes creating domains with different sizes that influence the performance of these devices. To understand how the spatial arrangement of polymer chains affects the

functioning of optoelectronic devices, we performed computer simulations using our mesoscopic model based on a generalized dynamic Monte Carlo method. We focus our study on the influence of the nanomorphology on the electric properties of polymer light emitting diodes. Our results show that for a pristine polymer layer and in the presence of ohmic contacts between the electrodes and the polymer layer, the electric properties of the device, namely current density, charge density, internal electric field and the number of charges that undergo recombination strongly depends on the polymer morphology at nanoscale.

Keywords: PPV, Dynamical Monte Carlo model, PLED, Nanomorphology

1. Introduction

Although electronic devices with an active layer made of an organic semiconductor have reached the commercial market, namely in the display industry, the application of these types of materials to other devices, like field effect transistors or solar cells is still in a premature stage. In the case of these devices the morphology of the organic semiconductor seems to play a major role in their performance, especially when the semiconductor is made of a conjugated polymer [1, 2].

There are several experimental results that suggest that the electronic and optoelectronic behaviours of polymer-based devices is influenced by the morphology of the polymer at nanoscale. Measurements of the electroluminescence across a PPV-derivative film by the scanning tunneling microscope showed a non-uniform emission which was attributed to changes on the spatial arrangements of polymer chains at nanoscale [3]. This assumption is supported by other studies that showed that in spin-

coated films, and depending on the experimental conditions used to deposit the film, most of the polymer chains tend to be aligned parallel to the electrode's surface in those films there are domains where polymer chains have perpendicular or random orientations[4, 5]. These different nanomorphologies of the polymer film affect not only the optical properties, namely the polarization and intensity of light emission from these films [5, 6], but also the electrical ones, like charge mobility in polymeric films [7-9], which strongly affects the overall functioning of polymer-based devices.

In solid state, the conjugation of long polymer chains is disrupted by the presence of kinks, twists or defects that lead to the chain packing [10]. At the end, each polymer film can be seen as an assembly of conjugated strands with different conjugation lengths [11] forming domains with a specific orientation of the strands relative to the electrode's surface.

Most of the theoretical studies performed to understand the functioning of polymer-based devices at nanoscale are based on the work of Bässler [10] who considers charge injection and transport as a result of charge hopping processes to or between localized states [12]. However, it was showed recently at experimental [13] and theoretical [14] level that charge mobility along conjugated segments can contribute to charge transport throughout the polymer network. Since in a real polymer film there are a large number of domains with conjugated segments with different orientations, it is difficult to obtain from the experiments the influence of each domain on the functioning of polymer-based devices. It is in this context that computational experiments can have an added value, since they allow us to study the influence of each individual domain on the device functioning. For that purpose we use our mesoscopic model, based on a

generalized dynamic Monte Carlo method, to study the influence the nanomorphology on the functioning of polymer light emitting diodes (PLEDs) with poly(p-phenylenevenylene) (PPV) as the active component. Our model includes explicitly the arrangement of PPV strands at nanoscale as well as the intramolecular charge transport and the molecular properties of the polymer obtained by atomistic calculations.

2. Computational model and simulation conditions

In order to understand how the different conjugated segments arrangements relative to the electrode's surface influence the functioning of a PLED, we started to mimic these polymer morphologies by creating 3D-networks with PPV conjugated segments parallel, perpendicular and randomly oriented relative to the electrodes surface. Each polymer network is built by placing randomly in the gap between two planar electrodes, separated 100 nm from each other (model axis), straight conjugated segments whose length is taken from a gaussian distribution of segment lengths considering a mean value of 7 monomers [11, 15]. In our model we assume that each conjugated segment can be seen as a rigid rod, where the minimum distance allowed between two polymer segments and between those and the electrodes is 0.650 nm, as obtained from atomistic calculations [15]. Fig. 1 shows the three polymer morphologies considered in our simulations, where each line represents the molecular axis of the polymer segments with the parallel, perpendicular and random orientations relative to the electrode's surface.

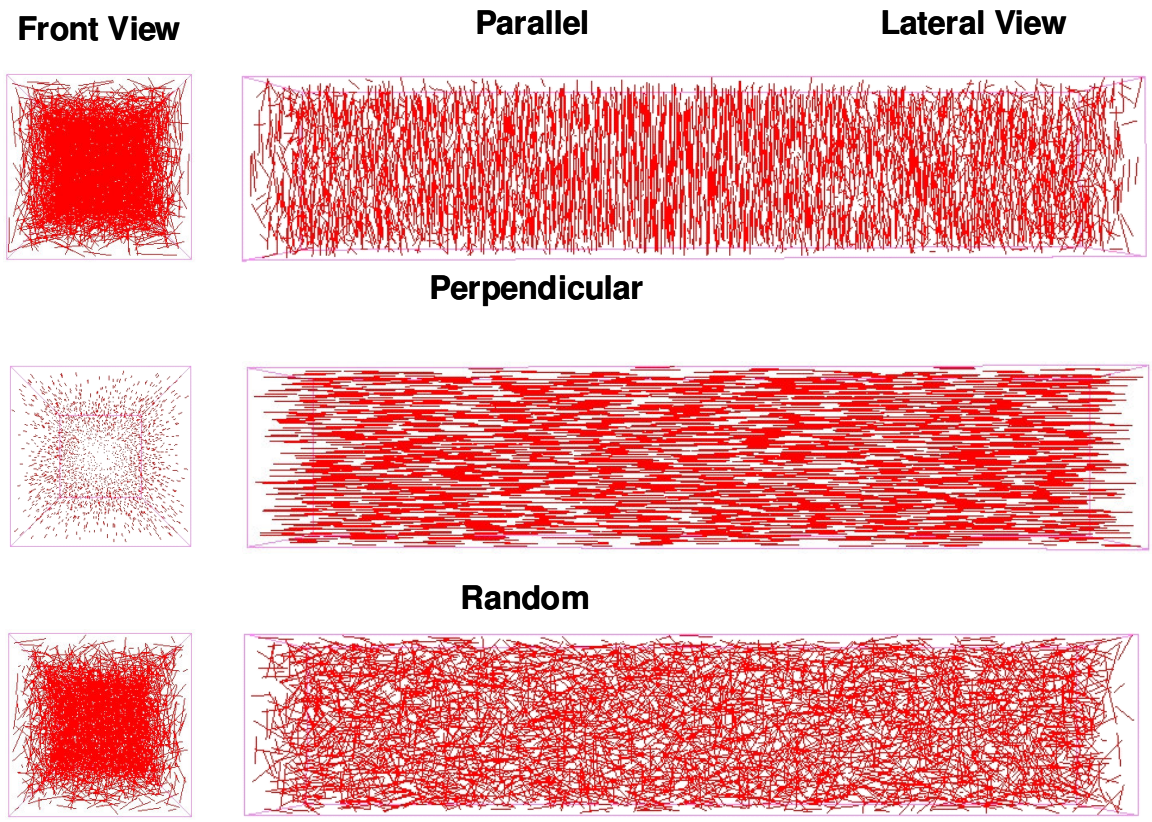

Fig. 1 – Representation of the polymer networks with parallel, perpendicular and random morphologies viewed in the direction perpendicular (front view) and parallel to the electrodes surface. The lines represent the molecular axis of the conjugated segments.

Our mesoscopic model includes the processes of charge injection, transport, recombination and collection by the electrode opposite to the injection one, that are on the base of a PLED functioning and takes into account the atomistic results obtained by Ramos and co-workers [15]. These results showed the formation of a polaron-type defect after a charge be injected in a conjugated segment due to electron-lattice coupling. When the strength of the local electric field (i.e. the sum of the applied electric field, the electric field created due to space charge distribution and the electrodes polarization) along the segment axis is smaller than the threshold for intramolecular polaron mobility, the

injected charge moves towards the segment central region otherwise the it moves to the segment end favoured by that electric field (i.e. intramolecular charge transport). From that position, the created negative/positive polaron can then hop to another segment (i.e. intermolecular charge transport), depending on the difference between the electron affinity (EA)/ionization potential (IP) of the conjugated polymer segments involved obtained from atomistic calculations [15], as well as the strength of the electric field.

In our mesoscopic model 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:

$$w_{ij,hop} = w_{0,hop} \times f(r_{i,j}) \times g(\Delta E_{i,j}) \times h(\theta) \quad (1)$$

where the term $w_{0,hop}$ represents the *attempt-to-escape* frequency while the following terms represent the influences of the hopping distance ($f(r_{i,j})$), the energy barrier height that a charge has to overcome between hopping sites ($g(\Delta E_{i,j})$) and the angle between the local electric field direction and the hopping direction ($h(\theta)$).

In our simulations we consider that the electrode/polymer interfaces are perfectly ohmic so that main factor affecting bipolar charge injection and transport is the arrangement of the polymer segments within the network. When two charges of opposite sign meet in the same polymer segment they can recombine if the local electric field along the segment axis is not strong enough to maintain the two charges apart.

The time evolution of all electronic processes is obtained using the first reaction method. For each electronic process associated with a charge (e.g. injection/collection from/by the electrode, hopping between neighbouring segments, recombination) a time of occurrence is attributed, and the electronic process that takes place at each Monte Carlo

step is the one that presents the smallest time of occurrence. During the simulation we follow charge percolation throughout the polymer network as a function of time until the steady state is reached.

A detailed description of the injection/collection and transport processes involved in our mesoscopic model for simulating a polymer diode functioning with ohmic contacts can be found elsewhere [16, 17].

3. Simulation results and discussion

By using the mesoscopic model described above we study bipolar charge injection, transport and recombination in pristine 3D-PPV networks with parallel, perpendicular and random morphologies, for an applied electric field ranging from 0.35MV/cm to 0.75MV/cm.

Fig. 2 shows the current density (J) and the recombination rate (i.e. the number of injected charges that undergo recombination per unit time) for the three polymer morphologies considering in this work as function of the applied electric field (E). Our results show clearly an increase of current density and recombination rate with the increase of the applied electric field for parallel and random strand orientation relative to the electrode's surface, being this effect more pronounced for parallel morphology.

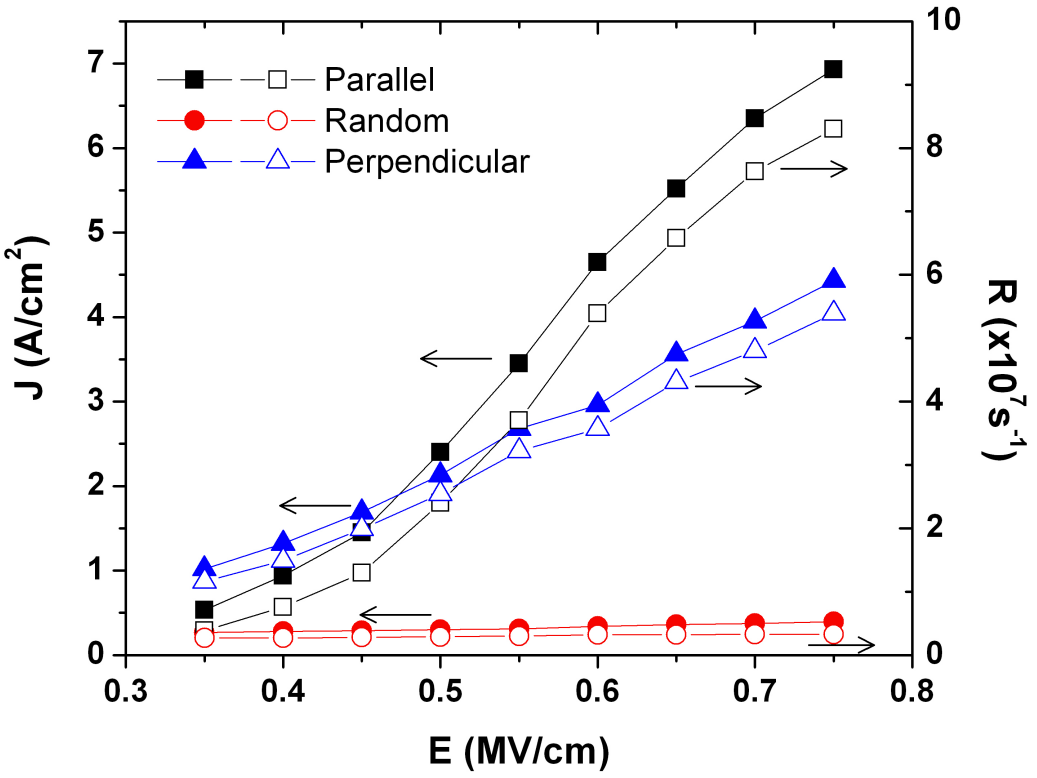

Fig. 2 – Current density (J) (closed marks) and charge recombination rate (R) (open marks) as a function of the applied electric field (E) for polymer networks of PPV with parallel (squares), random (circles) and perpendicular (triangles) morphologies. The lines are just a guide to the eyes.

The different dependences of the current density with the applied electric field for the different polymer morphologies are explained considering the different contributions that both intramolecular and intermolecular charge mobilities have the overall charge transport throughout the polymer networks. For the case of polymer layers with parallel morphology, the applied electric field is normal to the molecular axis of the polymer strands and charge transport within the polymer network is mainly due to the charge hopping between strands, which is mainly governed by the energetic disorder (i.e. the

energy barriers that a charge has to overcome to hop between strands). An increase of the applied electric field reduces the energy barrier height between strands, which leads to an increase on intermolecular charge transport perpendicular to the electrode's surface and, thus, an increase in current density.

For polymer layers with strands perpendicular to the electrodes surface, the applied electric field is parallel to the molecular axis of the conjugated segments. Since the applied electric field is much smaller than the electric field threshold needed for intramolecular charge transport (1.55 MV/cm for electrons and 1.95 MV/cm for holes [18]), the injected charges tend to move towards the middle of the strands for perpendicular morphology and intermolecular charge transport is very difficult, because the average hopping distance between neighbouring strands along the direction perpendicular to the electrodes is the largest one. Therefore, for the perpendicular morphology charge percolation is mainly governed by the spatial disorder (i.e. arrangement of the polymer strands). As a consequence, the current density does not change significantly with the strength of the applied electric field for polymer networks with perpendicular morphology.

For the case of the random morphology, the orientation of the polymer strands relative to the electrode's surface leads to a contribution of both intermolecular and intramolecular processes to the overall charge transport, being the influence of the last one less pronounced than for the perpendicular morphology. For higher applied electric field, the dependence of the current density with the field strength presents an intermediate behaviour between the ones obtained for parallel and perpendicular morphologies. However, the current density for random morphology is higher than for

parallel morphology for applied electric filds, which suggest that the domains with this morphology have an important role in a PLED functioning at low bias.

The dependence of current density with the applied electric field in PLEDs is similar to the one obtained for single-carrier diodes for the same polymer morphology [19]. Nevertheless, it is interesting to notice that for all polymer morphologies, the charge recombination rate presents the same dependence with the applied electric field as the current density, being this result for parallel in agreement with the ones obtained at experimental level for polymer light emitting diodes [20] whereas the current density increases almost exponentially with the increase of the applied electric field [21].

In order to increase PLED efficiency at experimental level one must use ohmic contacts at electrode/polymer interfaces since they will allow an increase of charge injection, and thus current density, increasing in this way the number of charges that undergo recombination [22]. This assumption is based on the fact that the probability of two charges of opposite sign undergo recombination is proportional to charge density inside the polymer network.

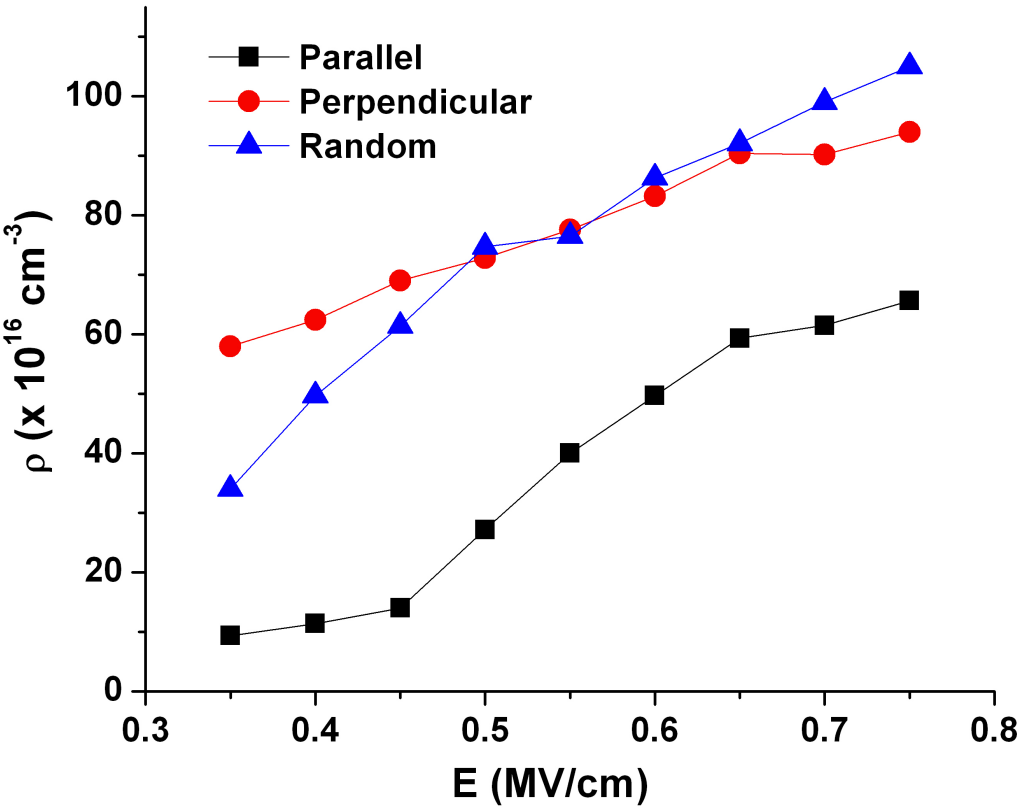

Fig. 3 – Charge density (ρ) for PPV layers with parallel, random and perpendicular morphologies as a function of the applied electric field (E). The lines are just a guide to the eyes.

Fig. 3 shows the dependence of charge density (ρ) with the applied electric field for parallel, perpendicular and random morphologies. The charge density storage within the polymer network with parallel morphology is smaller compared to perpendicular and random morphologies. This behaviour is opposite to the one obtained for the current density. The differences obtained in the charge density accumulation for the different polymer morphologies are a result of the fact that charge percolation tends to be more easy in the polymer networks with parallel morphology than for the other two

morphologies. This result suggest that the efficiency of two charges undergo recombination is more dependent on the easiness of charge percolation inside the network than on the amount of charge inside the polymer network.

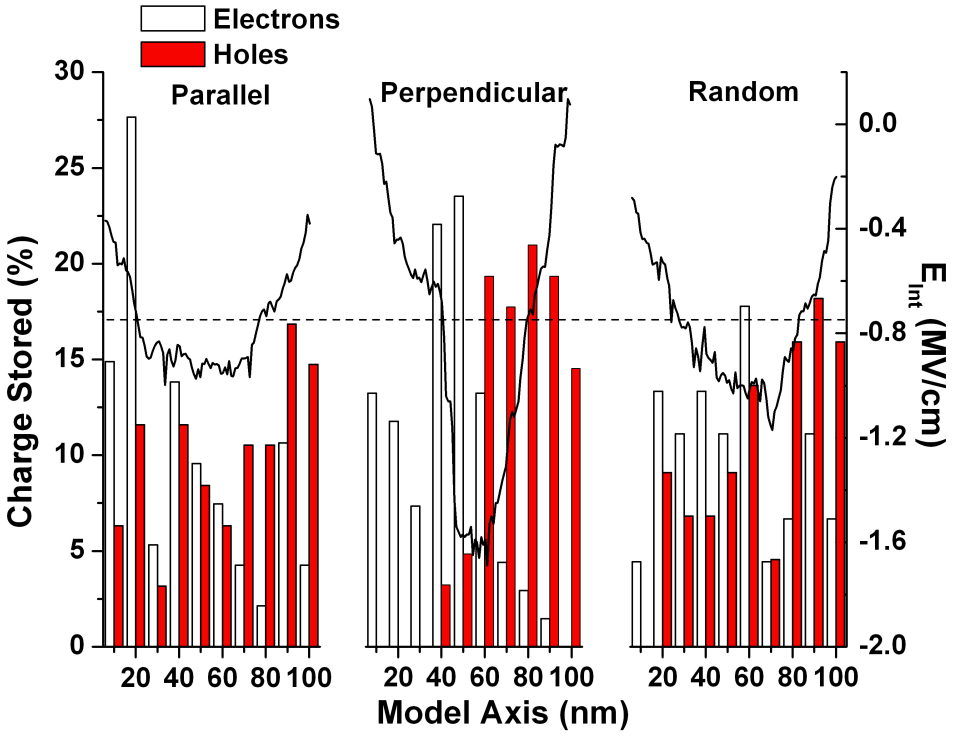

Fig. 4 – Fraction of hole (full rectangles) and electron (empty rectangles) distribution along the axis perpendicular to the electrode's surface (model axis) as well as the internal electric field ($E_{Int.}$) for polymer diodes with parallel, random and perpendicular morphologies and for an applied electric field with the strength of 0.75 MV/cm (dashed line).

In Fig. 4 we compare the charge and the internal electric field distributions inside the polymer layer at the steady state for different morphologies and an applied electric field of 0.75 MV/cm. The difficulty on charge percolation inside the polymer networks

with perpendicular morphology leads to an asymmetric charge distribution along the model axis, being this effect less pronounced for parallel and random morphologies. As a result of the asymmetric space charge distribution, the internal electric field strength in the polymer network with perpendicular morphology near the anode (100 nm)/cathode (0 nm) is significantly different as compared with the applied electric field (dashed line in Fig. 4). This effect is less pronounced for random and parallel morphologies.

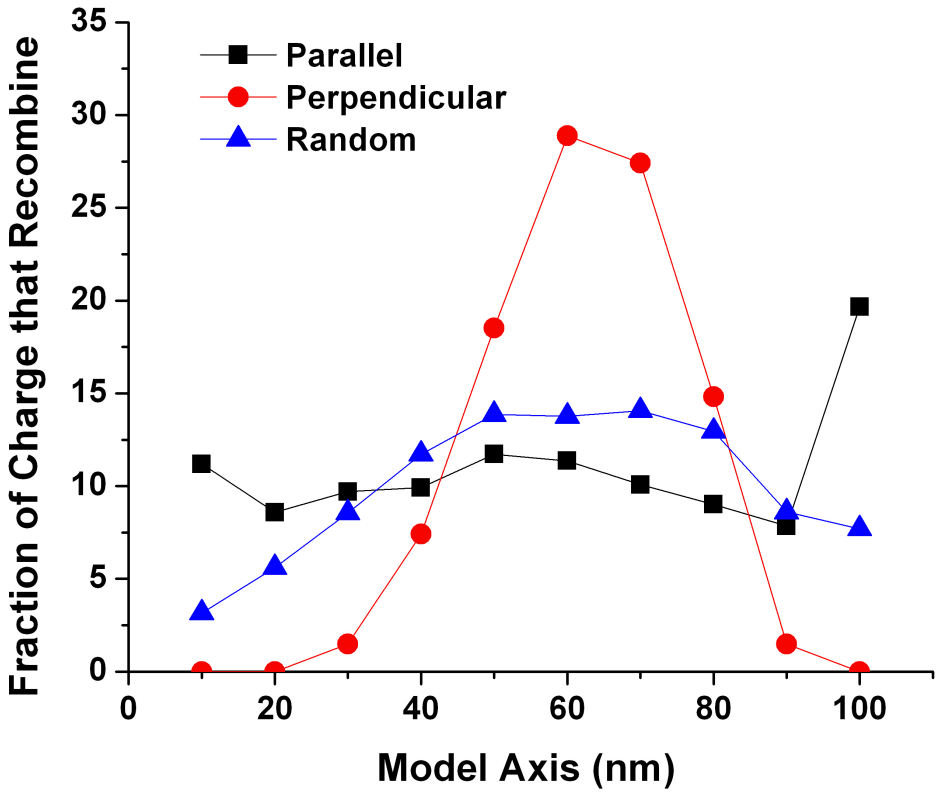

Fig. 5 – Fraction of injected charge that undergoes recombination along the axis perpendicular to the electrode's surface (model axis) in a PLED based on PPV with parallel (rectangles), perpendicular (circles) and random (triangles) and for an applied electric field of 0.75MV/cm (dashed line).

The charge distribution profile obtained in our simulations can be well understood when we look at Fig. 5 that shows the fraction of charges that undergo recombination along the model axis, for all polymer morphologies considered in this work and for an applied electric field of 0.75 MV/cm. Our results show clearly that for the perpendicular morphology there is a significant increase of charge recombination at the middle of the polymer layer than near the electrode/polymer interfaces. This result is a consequence of low charge transport in polymer networks with this type of morphology, leading to an increase in the recombination probability at the middle of the polymer layer, which reduces charge density in this region as it was shown in Fig. 4. However, the increase of charge transport as we go from polymer networks with random to parallel morphologies reduces the probability of two charges of opposite signs recombine at the middle of the polymer layer and increases near the electrode/polymer interfaces, being this effect more pronounced for the polymer layer with the parallel morphology. Considering that the number of singlet excitons formed is proportional to the probability of two charges of opposite sign recombine, these last results suggest that the effect of the electrodes on exciton quenching is higher for polymer layers with parallel morphology than for random and perpendicular morphologies.

4. Conclusions

In order to improve polymer-based device's efficiency, a deep understanding of the influence of the polymer morphology at nanoscale is required. Although our mesoscopic model just takes into account the main electronic process that are underlying PLED's functioning, the results obtained by us are in agreement with the ones published

elsewhere. Besides that, the use of our computational model allows us to shed some light on the influence of polymer morphology at nanoscale on PLED functioning, namely the different arrangements of the conjugated polymer segments, which is difficult to achieve at experimental level.

Our results show that different arrangements of polymer segments relative to the electrode's surface influence the electric behaviour of bipolar PPV-diodes. In the presence of a pristine polymer layer and perfect ohmic contacts at electrode/polymer interfaces, our results show that the electric behaviour for a polymer layer with strands parallel to the electrodes surface is mainly dominated by the energetic disorder which leads to a higher current density and lower charge density than polymer layers with perpendicular and random orientations. Although the probability of two charges undergo recombination far from the electrodes is higher for polymer layers with perpendicular morphology, these layers present small recombination rates and high variations of the internal electric field that can cause exciton dissociation.

The results obtained by us lead us to conclude that in a real PLED prepared by the spin-coating technique, its electric behaviour is dominated by the domains where the polymer strands are parallel to the electrodes surface, since it is for these domains that our results most resemble to the ones published in the literature. Besides, our results suggest that the presence of domains with the random morphology can significantly contribute to PLED functioning at low bias being its functioning limited by the presence of domains with perpendicular morphology.

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References

[1] M. Jaiswal, R. Menon, Polym. Int. 55 (2006) 1371-1384.
[2] E. Moons, J. Phys.-Condes. Matter 14 (2002) 12235-12260.
[3] D. G. Lidzey, S. F. Alvarado, P. F. Seidler, A. Bleyer, D. D. C. Bradley, Appl. Phys. Lett. 71 (1997) 2008-2010.
[4] J. S. Kim, R. H. Friend, I. Grizzi, J. H. Burroughes, Appl. Phys. Lett. 87 (2005) 3.
[5] K. Koynov, A. Bahtiar, T. Ahn, R. M. Cordeiro, H. H. Horhold, C. Bubeck, Macromolecules 39 (2006) 8692-8698.
[6] T. G. Backlund, H. G. O. Sandberg, R. Osterbacka, H. Stubb, M. Torkkeli, R. Serimaa, Adv. Funct. Mater. 15 (2005) 1095-1099.
[7] J. F. Chang, B. Q. Sun, D. W. Breiby, M. M. Nielsen, T. I. Solling, M. Giles, I. McCulloch, H. Sirringhaus, 16 (2004) 4772-4776.
[8] W. Geens, S. E. Shaheen, B. Wessling, C. J. Brabec, J. Poortmans, N. S. Sariciftci, Org. Electron. 3 (2002) 105-110.
[9] R. J. Kline, M. D. McGehee, Polym. Rev. 46 (2006) 27-45.
[10] H. Bassler, Phys. Status Solidi B-Basic Res. 175 (1993) 15-56.
[11] B. G. Sumpter, P. Kumar, A. Mehta, M. D. Barnes, W. A. Shelton, R. J. Harrison, J. Phys. Chem. B 109 (2005) 7671-7685.
[12] G. Meller, L. Li, S. Holzer, H. Kosina, Opt. Quantum Electron. 38 (2006) 993-1004.
[13] P. Prins, F. C. Grozema, J. M. Schins, S. Patil, U. Scherf, L. D. A. Siebbeles, 96 (2006).
[14] H. M. G. Correia, M. M. D. Ramos, J. Mater. Sci.: Mater. Electron. (2006) S339-S342.
[15] A. M. Stoneham, M. M. D. Ramos, A. M. Almeida, H. M. G. Correia, R. M. Ribeiro, H. Ness, A. J. Fisher, J. Phys.-Condes. Matter 14 (2002) 9877-9898.
[16] H. M. C. Barbosa, M. M. D. Ramos, Plasma Process. Polym. 4 (2007) S104-S107.
[17] M. M. D. Ramos, H. M. G. Correia, J. Phys.: Condens. Matter 18 (2006) S429-S438.
[18] A. M. Almeida, M. M. D. Ramos, H. G. Correia, Comput. Mater. Sci. 27 (2003) 128-132.
[19] H. M. C. Barbosa, M. M. D. Ramos, Mat Sci Eng B (2008).

[20] F. J. J. Janssen, J. M. Sturm, A. W. D. van der Gon, L. J. van Ijzendoorn, M. Kemerink, H. F. M. Schoo, M. J. A. de Voigt, H. H. Brongersma, 4 (2003) 209-218.
[21] T. M. Brown, R. H. Friend, I. S. Millard, D. J. Lacey, T. Butler, J. H. Burroughes, F. Cacialli, J. Appl. Phys. 93 (2003) 6159-6172.
[22] P. W. M. Blom, M. J. M. De Jong, Philips J. Res. 51 (1998) 479-494.