Mesoscopic study of the electronic properties of thin polymer films

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ABSTRACT

Conjugated polymers are very interesting for light emitting diodes. Further improvement in device performance requires a better understanding on the correlation between the polymer structure and device characteristics. A mesoscopic study using a generalised Monte Carlo method of bipolar charge transport in thin poly(p-phenylene-vinylene) (PPV) films is presented in this paper. We show that energy and spatial molecular disorder have a serious influence on migration of charge carriers within the polymer layer. The transfer of carriers between two polymer chains is made dependent on the chemical potential difference as well as on other features such as the distance between both molecules involved and the direction of the electric field. The purpose of the present work is to clarify the effects of local energy and polymer structural disorder on current flow, trapping and recombination on polymer based devices.

INTRODUCTION

Luminescent polymers, such as poly(p-phenylene-vinylene) (PPV) are very promising as active light sources in Light Emitting Diodes (LEDs) [1,2]. Although the field has made great progress in the last decade, their performance is still rather poor. There is therefore considerable potential to improve the performance of semiconducting polymer LEDs. It is not trivial to do so, since the performance of such devices is limited by several interdependent factors [3]. However, higher efficiency requires improvements in charge transport within the polymer layer. The complexity of the charge transport process in the polymeric system arises from hopping between discrete levels localised on each polymer molecule aggravated with a high degree of disorder in many polymers. Our earlier work [4-9] suggests that a mesoscopic modelling, which works at an intermediate scale between atomic and macroscopic scale, is an adequate technique for the study of such phenomena if it includes information about intramolecular mobility of charge induced defects, molecular energy levels and nearest neighbour intermolecular distance.

Our emphasis in this paper is on the modelling at microscopic length scale: how can the ensemble of polymer molecules with the right electronic properties be organised to optimise device performance. Our aim is to produce several realisations of PPV networks and to carry out computer experiments in which bipolar charge carriers are injected in the polymer system from the appropriated electrodes. The properties of each PPV molecule are obtained from self-consistent quantum molecular dynamics calculations. In the calculations we report here, the trapping of charge, the percolation in charge transport, the recombination and the effects of other charges within the polymer layer as well the polarisation of the electrodes are included explicitly. The present work examines the effect of device parameters such as the applied bias voltage, the molecular properties (e.g. ionisation potential, electron affinity) as well as the distance between

the molecules involved in the polymer network and the direction of the local electric field on charge transport across the polymer and the competition between charge trapping and recombination in PPV diodes.

DESCRIPTION OF THE MODEL

In this model, energy and spatial molecular disorder have a serious influence on migration of charge carriers within the polymer layer. Therefore, before we deal with charge injection in the polymer network, we must consider the properties of each polymer molecule that have an influence on charge transfer within the polymer layer. For conjugated polymers such as PPV, where atomic positions and electronic structure are intimately coupled, methods combining molecular dynamics with self-consistent quantum mechanics techniques need to be used to study charge injection, transport and recombination at molecular level. Self-consistent molecular dynamics calculations with semi-empirical quantum chemistry at CNDO (Complete Neglect of Differential Overlap) level have been used to provide information on ionisation potential and electron affinities of individual polymer strands with different lengths [3]. We have adopted the same approach to determine the charge distribution associated with both the positive and the negative charge induced defects in various polymer strands and their mobility [8,10], when a bias voltage is applied, as well as to calculate the minimum distance between two neighbouring molecules.

In order to build a polymer network, a statistical distribution of strand length is chosen for a certain density of strands, and strands are distributed in a volume randomly, with random orientation, starting by the largest ones. The strands may have between 2 and 14 units. Each unit has a length of 0.625 nm, which is the size of the PPV monomer. Fig. 1 shows a partial view of a sample and a schematic of it. The minimum distance between two neighbouring straight molecules is 0.65 nm. A certain number of strands is chosen to be attached to the electrodes. Charges of either sign can enter and leave the sample only through the strands attached to the electrodes or by recombination.

A constant bias voltage is applied to the sample, in the direction perpendicular to the electrodes (labelled 'axis of the sample', or z axis). The charges always enter in pairs, one negative charge (an electron) from the anode ($z = 0$) and another positive charge (a hole) from the cathode, per computer iteration. Each charge may hop to another strand on the next iteration. There is a distribution of probability for every charge to jump to another strand.

In the work described in this paper, the charges may only jump to strands for which the jumping probability is at least 90% of the highest jump probability. The jumping rate between two strands is given by Eqn. (1) [4]:

$$w = w_0 \, f(E) \, g(R) \, h(Q) \, j(E_{ij}) \tag{1}$$

where w_0 is a constant set to one, $f(E)$, $g(R)$, $h(Q)$ and $j(E_{ij})$ represents the effects of electric field, inter-chain distance, coulomb blockade and molecular energy difference on the jump rate, respectively.
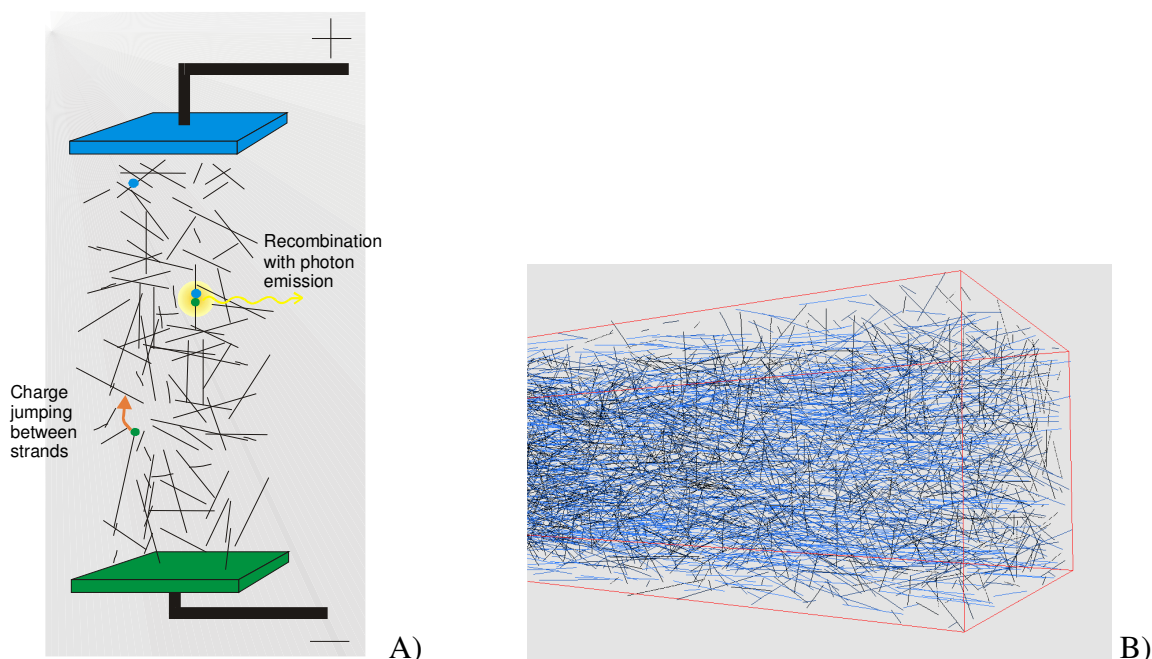
Figure 1. A) Schematic of the model, showing the electrodes and charges moving and recombining; B) Partial view of the polymer network with straight molecules represented by sticks. The stick length is proportional to the strand length.

Charges also contribute to the electric field, and periodic boundary conditions are set at the surfaces perpendicular to the electrodes. Charges can also be trapped and not move if the jumping rate becomes lower than 10^{-5}. If two charges of opposite sign get to the same chain they are assumed to recombine.

RESULTS AND DISCUSSION

Ten samples with an area of 20x20 nm^2 each at the electrodes and a thickness of 100 nm between the electrodes were generated (see Fig. 1). The results for the ten samples were averaged in order to improve the statistics of the calculations. The distribution of the strand sizes is shown in Fig. 2, and a density of 0.36 g/cm^3 was achieved. An external electric field was applied and charges were injected in the sample from the appropriated electrode.

Our molecular dynamics calculations have shown that the charge injected at one of the strands moves to the end if it is favoured by the local electric field greater than 1.5×10^8 V/m [10]. Otherwise, it moves towards the strand center. We have discussed the effect of this molecular property on charge evolution in PPV. The effect of other molecular properties such as ionisation potential and electron affinity have also been discussed [3].

Fig. 3 shows the percentage of charges that undergo recombination to the total number of injected charges in two representative situations: an applied electric field of 2.5×10^8 V/m and an applied electric field of 5×10^6 V/m.
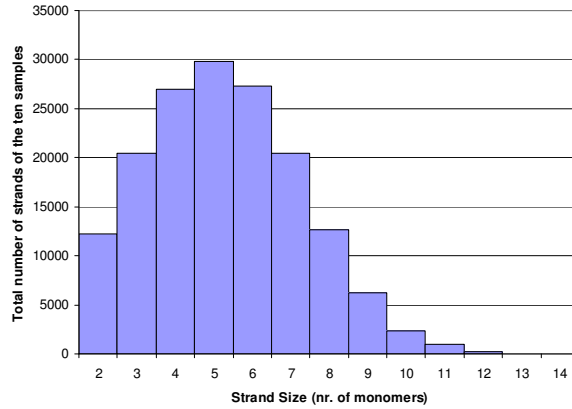
Figure 2. Strand length distribution in the polymer network.

There are two important factors that influence the results. One is that the electric field that a charge generates a few manometers away is of the order of 10^8 V/m, that is of the order of the highest applied field and 100 times higher than the lower one. This implies that for high bias voltage, the charges will be essentially driven by the applied field, while for low bias voltage the charges will be driven by the local field generated by the other charges in the sample. This second situation will lead to a random walk in the sample and it increases the time a charge takes to arrive to the opposite electrode. This leads to an increasing of both recombination efficiency (Figure 3) and charge density (Figure 4) in the sample, while the first situation will make the charges move as directly as possible to the opposite electrode. Therefore, recombination starts later for low bias voltage applied (Figure 3).
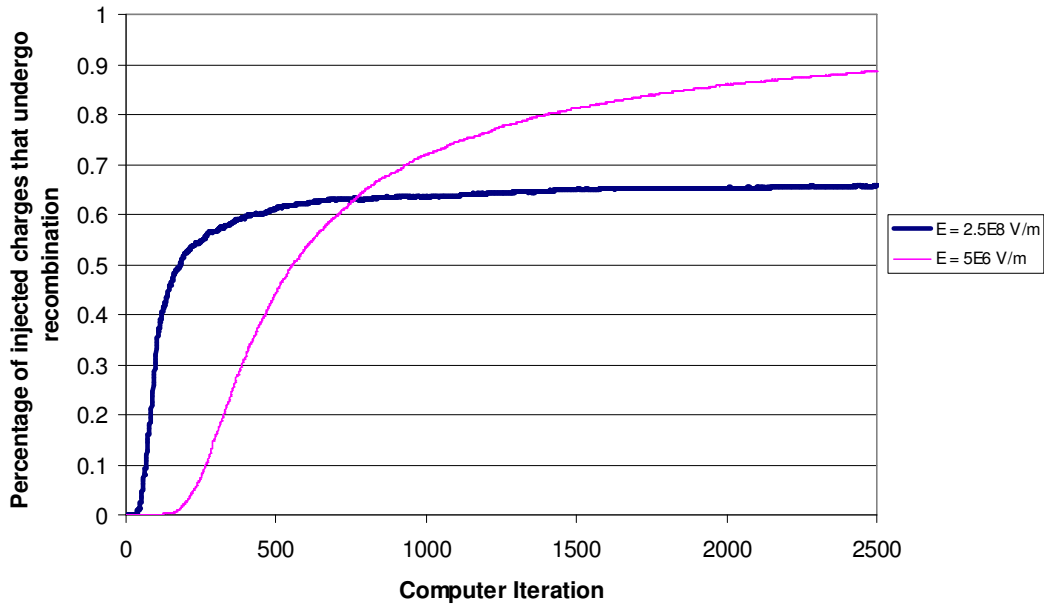
Figure 3. Percentage of injected charges that undergo recombination, for two values of the applied electric field.
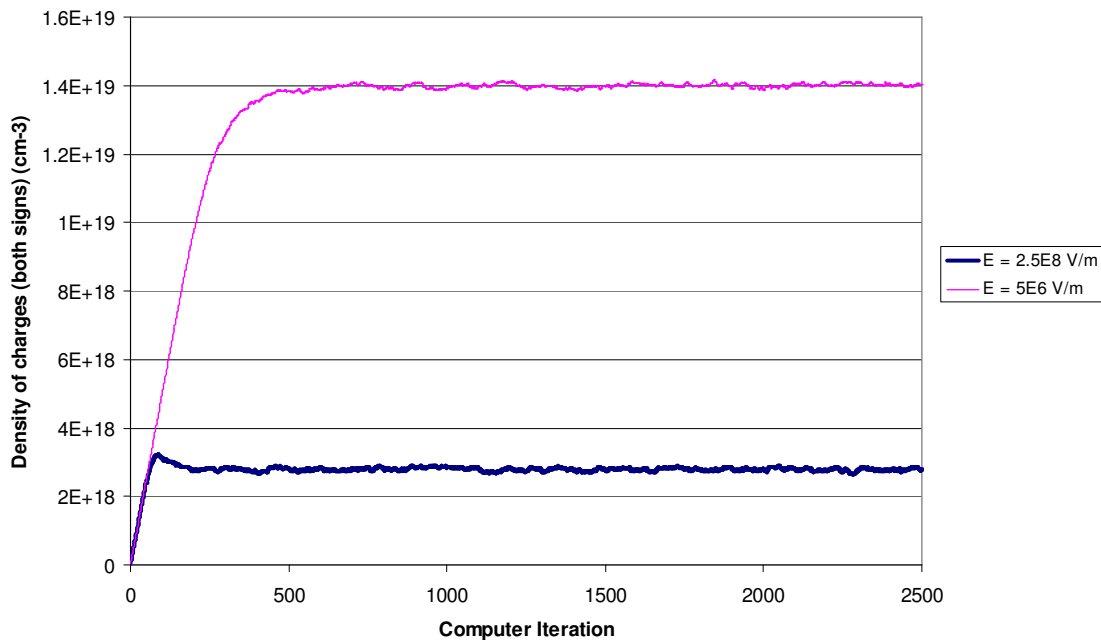
Figure 4. Density of charges of both signs stored in the sample, for two values of the applied electric field.

Another important factor is the mobility of the charges along the strand. If we don't let the charges move in the strand, so that they have to stay in the center of the chain, the charges will have a lot more difficulty in moving from strand to strand. Charges will tend to accumulate and saturate the sample. So it is important to include in the mesoscopic model the threshold for charge mobility along the strand.

The mean number of recombinations per chain as a function of its orientation relative to the sample axis depends on the bias voltage, as can be seen in Figure 5. For high bias voltage, the flux of charges is mainly parallel to the axis, and there is a trend to recombine in strands perpendicular to that axis, and so perpendicular to the flux of charges. When the bias is low, the local field generated by nearby charges dominates, and charges will much often be driven perpendicularly to the axis. In this latter case, the random-like walk of the charges makes the recombinations to occur most often in strands parallel to the axis.

Our results show that the mean number of recombinations per strand increases with the strand length, since it is more probable that two charges of opposite signs reach the strand by different paths if the strand is longer.

It was also observed that near both electrodes there are strands that act as dead ends for the charges. A charge arriving at a chain that ends near an electrode but which is not close enough stays there and contributes to the space charge.

When we assumed the dependence on chain length of ionisation potential and electron affinity, a difference in the distribution of recombinations was observed. Our results suggest a decrease in the number of recombinations in short strands and an increase in larger ones, which can be related to molecular energy differences. Therefore, it is important to include this molecular property in the mesoscopic model.
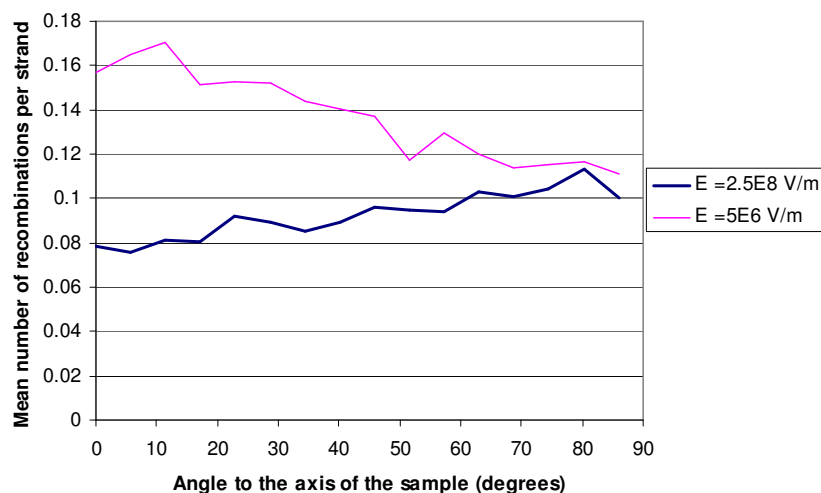
Figure 5. Mean number of recombinations per strand, for two values of the applied electric field.

CONCLUSION

The present work examines the bipolar charge transport in PPV layers as a result of a random orientation of polymer strands with variable length and the dependence of molecular properties on chain length. Our results concentrate on two factors: the effects of varying the applied electric field and the molecular properties.

We identified two regimes of charge transport at mesoscopic scale, one dominated by the applied electric field and the other dominated by the local electric field generated by the charges in the sample. These two regimes lead to different time evolution of recombination efficiency and charge density in the sample. Molecular properties show an unanticipated but important effect when the applied electric field is much lower than the threshold for charge mobility along the strand.

REFERENCES

1. J. H. Burroughes, D. D. C. Bredley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, A. B. Holmes, Nature **347**, 539 (1990)
2. R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, C. Taliani, D. D. C. Bredley, D. A. dos Santos, J. L. Brédas, M. Logdlund, W. R. Salaneck, Nature **397**, 121 (1999)
3. A. M. Stomeham, Marta M. D. Ramos, A. M. Almeida, Helena M. G. Correia, R. M. Ribeiro, H. Ness, A. J. Fisher, J. Phys.: Condens. Matter. **14**, 9877 (2002)
4. Marta M. D. Ramos, A. M. Stoneham, Comp. Mat. Sci. **17**, 260(2000)
5. A. M. Stoneham, Marta M. D. Ramos, J. Phys.: Condens. Matter. **13**, 2411 (2001)
6. Marta M. D. Ramos, A. M. Stoneham, Synthetic Metals **7718**, 149 (2001)
7. A. Mário Almeida, Marta M. D. Ramos, Synthetic Metals **7718,** 165 (2001)
8. Marta M. D. Ramos, A. M. Almeida, Vacuum **64**, 99 (2002)
9. António M. Almeida, Marta M. D. Ramos, Ricardo M. Ribeiro, Macromol. Symp. **181**, 479 (2002)
10. A. M. Almeida, M. M. D. Ramos, H. G. Correia, Comp. Mat. Sci. (in press)