The mesoscopic modelling of multilayered polymer diodes

by

Ricardo Mendes Ribeiro

Universidade do Minho
Departamento de Física
Universidade do Minho
Campus de Gualtar, Braga, Portugal

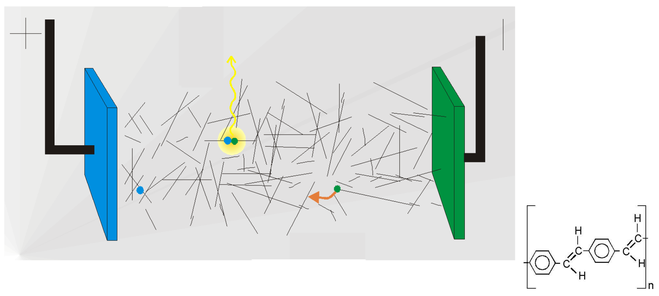
Universidade do Minho
Departamento de Física
Universidade do Minho
Campus de Gualtar, Braga, Portugal

Abstract

The performance of transparent devices based on semiconducting polymers depends on the component polymer molecules, on the device design, and on the polymer texture.
The role of this texture and multilayers of different textures is the focus of this work. In modelling the texture, there has to be a description of the relative arrangements of polymer molecular strands of various lengths in an amorphous structure with various patterns of orientations, bends and cross-links.
The appropriate scale for modelling texture is either at the polymer molecular scale, or at a scale corresponding to subunits of these molecules. Clearly, connection must be made both with the electronic structure at the atomic scale, and with the device design and macroscopic electromagnetic properties on a larger scale.
In this work, we build on the approaches described elsewhere to build up a more systematic description of the way texture affects recombination and other processes in simple devices. Our methods do not need major computing power, and could be applied in the optimisation of devices.
The results show a clear dependence of the electron-hole recombination rate on the texture of the polymer, which can be used to increase the performance of devices.

Description of the model

Mesoscopic structures

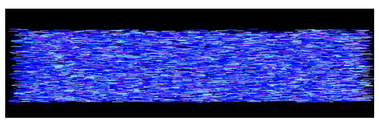


It is adequate to study combinations of configurations parallel and perpendicular to the electrodes.

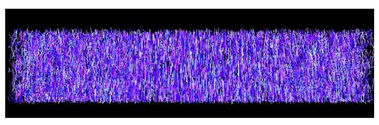
These structures can be produced by the Langmuir-Blodgett technique, for instance.

Specific realisations studied We have studied in detail several basic configurations. Constructed 20 realisations of each in order to get a better statistics. Area 20x20 nm^2 at the electrodes, distance of 100 nm between electrodes.

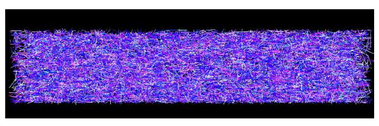
- All strands approximately perpendicular to the electrodes (structure A)



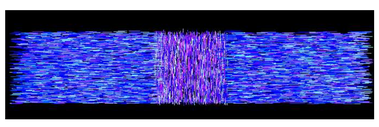
- All strands approximately parallel to the electrodes (structure B)



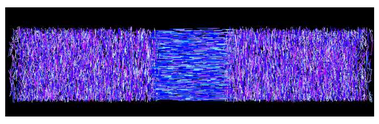
- All strands with random orientations (structure C)



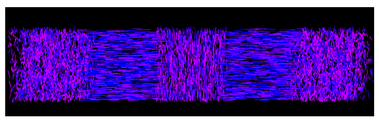
- All strands parallel to the electrodes and to each other (structure D)
- ABA structures



- BAB structure



- BABAB structure



- A, B, C and D structures with a dielectric nanoparticle

Electronic structure issues

- We shall simulate PPV polymer
- We use atomistic simulations for the trends and energies we need
- We use the intrachain carrier mobilities, account for the minimum distance between strands
- There is an energy cost to bending an isolated PPV molecule
- When a charge is injected (electron or hole), it moves to the centre of the strand
- If a sufficiently high electric field is applied (1.5 x 10^8 V/m), the potential barrier stabilising the charge in the centre is overtaken, and the charge moves to one side
- we can estimate electron affinities and ionisation potentials as a function of strands length

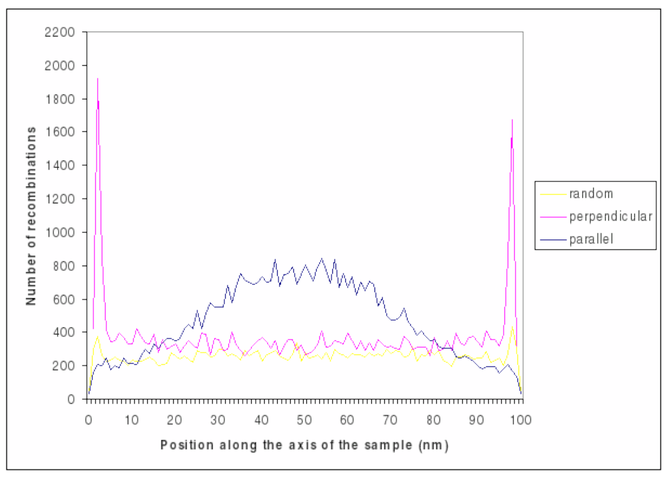
This information was used in the mesoscopic model that we now discuss.

Carrier dynamics

- Inject charges in the samples
- Assume that carriers can only tunnel directly over short distances between the electrodes and strands
- Carriers will move under any applied electric field and under the discrete space charge
- Electrodes also show image charges
- Sample is reproduced eight times around it in order to account for boundary conditions
- Local electric field drives the movement of carriers within individual molecules
- If the field exceeds 1.5x10^8 V/m the charge will move to an end strand; if not, the carrier will stay near the centre
- Inter-molecular jump rates underlie the Monte Carlo calculations
- In each iteration, an electron was injected from the cathode and a hole from the anode
- Program ran for 2500 iterations
- Simulations were performed for applied electric fields, from 10^8 V/m to 5x10^8 V/m

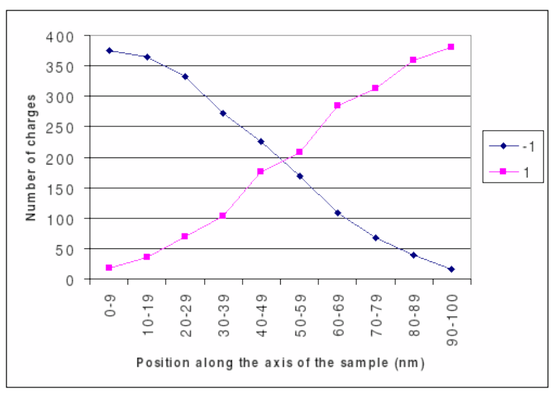
Results and Discussion

Homogeneous structures

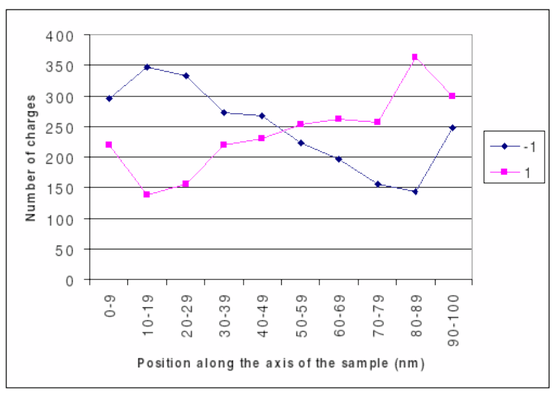


Number of recombinations as a function of the position in the sample, for three different types of samples, for an applied electric field of 5x10^8 V/m.

- When the strands are perpendicular to the electrodes, the number of inter-chain jumps needed to reach a certain distance is much smaller than when the strands are parallel to the electrodes
- The charges move much faster across the sample for structure A than for structure B



Number of charges (both positive and negative) as a function of the position in the sample, for samples of type B, after 2500 iterations.

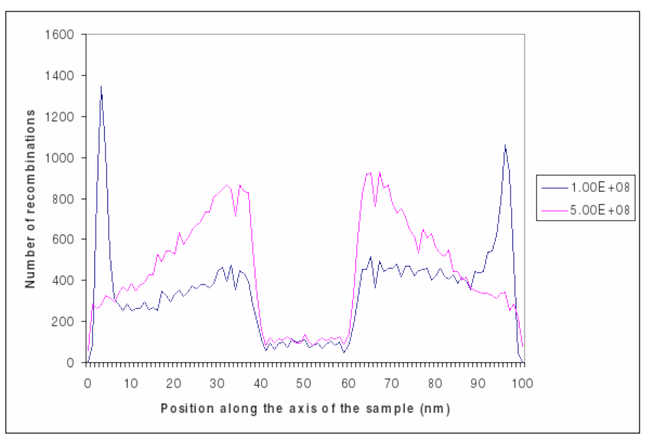


Number of charges (both positive and negative) as a function of the position in the sample, for samples of type A, after 2500 iterations.

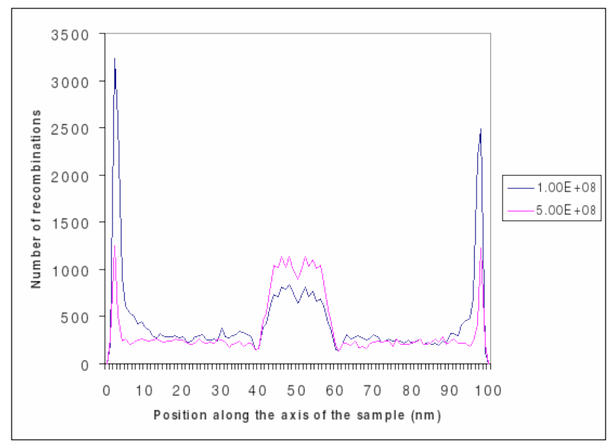
Strands perpendicular to the electrodes are the ones that determine how rapidly carriers move into the sample.

Inhomogeneous structures

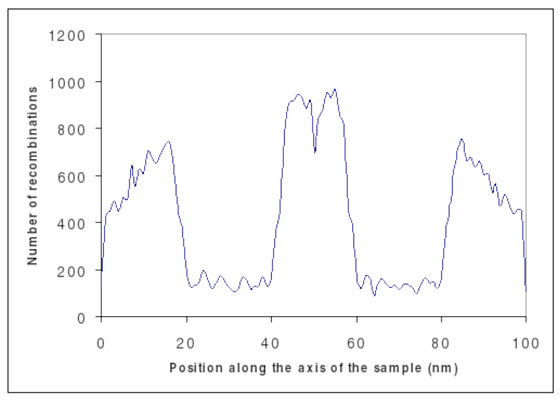
The differences in behaviour between simple A and B structures continue to be evident in the sandwich structures (ABA, BAB, BABAB).



Number of recombinations as a function of the position in the sample, for sample BAB, for applied electric fields of 10^8 V/m and 5x10^8 V/m.



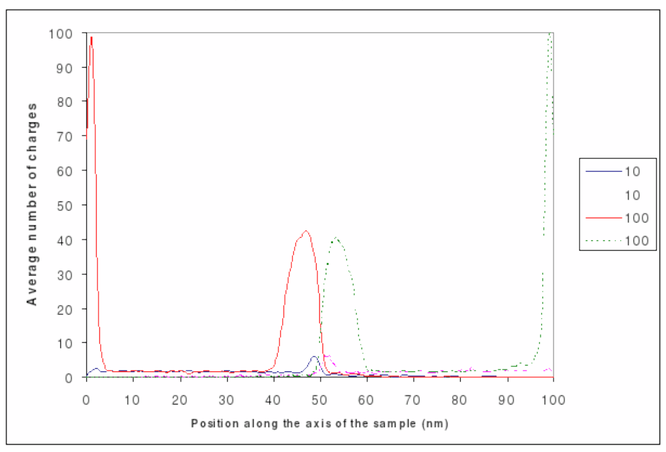
Number of recombinations as a function of the position in the sample, for sample ABA, for applied electric fields of 10^8 V/m and 5x10^8 V/m.



Number of recombinations as a function of the position in the sample, for sample BABAB, for an applied electric field of 5x10^8 V/m.

Structures with a nanoparticle

- Nanoparticles with dielectric constant equal to 10 and to 100
- Nanoparticle was assumed to be like a dipole positioned in the centre of the nanoparticle
- Nanoparticles were embedded in samples of type A, B, C and D
- Two different electric fields were applied, one bellow the threshold (1x10^8 V/m) and the other above (5x10^8 V/m)



Average number of charges along the axis of the sample, for two dielectric constants of the nanoparticle (10 and 100), embedded in a sample of type D. Solid lines represent electrons and dashed lines represent holes.

- The recombination rate is very high and localized near the nanoparticle
- When the dielectric constant increases from 10 to 100, the number of charges near the nanoparticle significantly increases
- An increase in the applied electric field leads to an increase in the number of charges around the nanoparticle for structures B and D, while is about the same for A and lower for C
- Texture around the nanoparticle influences the distribution of the charges and so the number of recombinations

Conclusion

At low applied electric fields, there will be a more random walk of the carriers in the sample, and so less sensitivity to the orientation of the strands relative to the electrodes.

It is important to encourage recombinations to occur in the middle of the sample.

Exploiting different textures of polymers, even for the same molecular species, can help to control where the recombinations occur and so improve performance of the device. Texture control in device construction can therefore make significant difference in the efficiency of the device.

Blending structures can be also beneficial to the control of the place where recombinations occur.

The distribution of charges around the nanoparticle and the number of recombinations depends on the texture surrounding the nanoparticle, as well as the applied electric field and the dielectric constant of the nanoparticle.

Ackowledgement

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