MESOSCOPIC MODELLING OF CHARGE EVOLUTION IN CONDUCTING POLYMERS

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ABSTRACT

We address here some of the issues relating to conducting polymer based devices. We examine the effects of polymer disorder on charge injection, transport, trapping and recombination in light-emitting diodes using a mesoscopic model which includes specific realizations of the electroluminescent polymer network. A key point of this model is to consider both the intermolecular and the interdomain charge carrier transport which are strongly influenced by structural polymer disorder. Simulations of bipolar charge evolution (electrons and holes) through a polydiacetylene film, which are injected in the polymer layer from the appropriated electrodes, have been used to give some insights to the issue concerns the fraction of polymer molecules contributing to the conduction process as well as to light emission. The effect of charge traps, such as cross-links, on space charge and recombination is also discussed.

Keywords: Mesoscopic modelling, conducting polymers, electroluminescence.

1. INTRODUCTION

Over the past decade, there has been major progress in the use of conjugated polymers as electroluminescent layers in light-emitting diodes (LEDs) [1,2]. However, the interpretation of the observed device characteristics remains controversial. A particular difficulty in interpretation arises from a diversity of the morphology and inhomogeneity of the polymer structure (even for samples prepared under the same polymerization conditions).

Therefore, further improvements in device performance requires a better understanding on the correlation between the polymer structure and device characteristics. As in other areas, theoretical modelling can play an important role in understanding the underlying science that controls the properties of these devices.

Although a vast amount of information about the electronic properties of conducting polymers has been accumulated, the mechanisms of bipolar carrier injection, transport and recombination are still far from being well understood. There is a complex link between the behaviour of individual polymer chains and descriptions of the polymer as a bulk semiconductor.

We address here some of the issues concerning the description of the ensemble of polymer strands as a bulk semiconductor. It is important to recognize that some polymer strands are shorter, others longer, some strands are straight, others curved, and some of them are influenced by the metallic electrode whether chemically or through polarization (the image charge). Thus, modelling of injection, transport and recombination processes regarding the polymer layer as a structureless continuum can be misleading [3]. A mesoscopic modelling, which works at an intermediate scale between atomic and macroscopic scale, is suggested as an adequate technique for the study of such multiscale phenomena.

The systematic dependence of optical properties on the number of units in polydiacetylenes (PDA's) chain makes them ideal model systems to discuss the processes involved in electroluminescence, which should also apply to other conducting polymers. The present work examines the charge evolution in polydiacetylene as a function of inhomogeneity of the polymer structure as a result of variable chain length and cross-linking in the polymer film.

2. DESCRIPTION OF THE MESOSCOPIC MODEL

2.1. Polymer network

In order to build realizations of a polydiacetylene network we have placed individual straight strands of finite and variable length perfectly oriented as in macroscopic single crystal [4]. The side groups of stable PDA oligomers were ignored and replaced with hydrogen atoms, so that sample molecules of PDA took the from $C_{4n+2}H_{2n+4}$. The number of units in each chain varies from 2 to 20 and it is chosen randomly, except in the chains bound to the electrodes where that number was set to 20. We have chosen to have long chains bound to the metallic electrodes in order to diminish the attraction between the electrodes and the injected charges (of either sign), through polarization, which could limit current flow. The highly oriented domains are separated by regions of about 10 Å width. Within each domain interchain distances of 7-14 Å have been used.

A diversity of polymer structures has also been obtained by assigning randomly a small rotation from the crystalline orientation to each strand. Only cross-linking between nearest neighbour chains has been allowed and no charge-induced distortion of the conjugated polymer backbone (figure 1), calculated by a self-consistent quantum chemical molecular dynamics method implemented in Harwell CHEMOS code [5], nor exciton distortion in PDA [5] have been considered.

Besides, we did not consider additional distortion of the oligomer chains, either parallel and perpendicular to molecular plane, as a result of chemical reaction at metal-on-polymer interface nor due to contaminants formed at electrode/polymer interfaces, depending on the cleanliness of polymer surfaces, chemical impurity of the polymer and/or vapour-deposition environment, as those reported by one of the authors for polyacetylene [6-8].

2.2. The rules for charge evolution

Electroluminescence from conjugated polymers has been modelled using a polydiacetylene film with the thickness of about 90 nm and a surface area of 100 nm^2 as the single semiconductor layer between metallic electrodes. Here periodic boundary conditions have been imposed. When this diode is sufficiently biased, the injection of positive and negative charge carriers occurs from opposite electrodes at good electrical contacts chosen randomly. All charge carriers are injected at same time. Here, we have not allowed for multiple charge to be injected in a sequence of events.

The charge injected from the appropriated electrode moves down at total electric field which includes the applied external field of 2×10^8 Vm^{-1} [9], the field of trapped charges within the region of the polymer layer and the field due to electrode polarization.

If the charge is injected at one end of the chain, it moves towards the centre to lower its energy. This charge moves then further along the chain under the influence of the applied field. Here we have not considered the distribution of charge along the polymer chains associated with the carriers (figure 2) nor charge rearrangement among the polydiacetylene atoms due to chemical interactions that occur at the metal-on-polymer interface. Our earlier work for polyacetylene gave substantial charge rearrangement among the polymer atoms not far from the reaction site [7-8].

A charge injected in the polyacetylene layer at good electrical contact percolates through the polymer film jumping only to the nearest neighbour chain which it has the greatest hopping probability $w/(\sum w)$. Here, the sum is over all the nearest neighbour strands and w is the jump rate. We assume that the jumping rate between two nearest neighbours strands is given by:

$$w = w_o \; f(E) \; g(R) \; h(Q) \qquad (1)$$

where w_o is a constant set to one, f(E), g(R) and h(Q) represents the effects of electric field, interchain distance and coulomb blockade on the jump rate, respectively. The mathematical expressions for f(E), g(R) and h(Q) are:

$$f(E) = A\,(\cos\theta + 1) \tag{2}$$

$$g(R) = \begin{cases} 0 & \text{for } R < R_{cl} \\ 1 & \text{for } R_{cl} \le R < R_o \\ B\exp\left(-\dfrac{R - R_o}{R_o}\right) & \text{for } R \ge R_o \end{cases} \tag{3}$$

and

$$h(Q) = \begin{cases} 1 & \text{for } Q_{ij} \le 0 \\ C\exp\left(-\dfrac{Q_{ij}/R}{kT}\right) & \text{for } Q_{ij} > 0 \end{cases} \tag{4}$$

where A, B and C are constants set to one, θ is the angle between electric the force field and the position vector of its neighour chain, R is the interchain distance, R_{cl} = 1.5Å is the maximum distance between cross-linked nearest neighbour chains, R_o=7Å is the interchain distance in macroscopic single crystals , Q_{ij} is the product of the charges on chains i and j, k is the Boltzmann constant and T is the ensemble temperature. If one considers the distributions of charge among the polymer atoms associated with the carriers, we have to adopt the following expression for h(Q)

$$h(Q) = \begin{cases} w_o & \text{for } E_f - E_i \le 0 \\ w_o \exp\left(-\dfrac{E_f - E_i}{kT}\right) & \text{for } E_f - E > 0 \end{cases} \tag{5}$$

where E_k is the internal energy of the strand k which is a function of the molecular charge, as it has been shown in our earlier work for polyacetylene [10,11].

The charge stops, but continues to contribute to the space charge, when the total electrical field on the charge is zero, when it meets a cross-link, or when $w<10^{-5}$. At a cross-link, the charge can continue to move within the region of the polymer layer if the hopping probability is greater than 95%.

When we simulate the bipolar charge evolution through a polydiacetylene layer, capture of oppositely charged carriers on the same chain gives rise to both radiative and non-radiative recombination depending on the chain length. Following Sixl [12], we have assumed that polydiacetylene chains with more than 8 units do not luminesce.

3. RESULTS AND DISCUSSION

In order to study the relationship between polymer structure and both electrical electroluminescence characteristics of light-emitting diodes, we have calculated charge carrier recombination and current flow efficiencies as a function of luminescent chain concentration, in five different polyacetylene structure realizations with no cross-linking between nearest neighbour chains. Figure 3 shows the radiative and the non-radiative recombination predicted within the polymer film, for a balance between the injection of the two charge carrier types (electrons and holes). In these calculations, we have considered that all polymer chains bound to the electrodes are good electrical contact, despite the fact that our earlier work [11] suggests that some of these contacts may never play part in the conduction process. Our results suggest that non-radiative recombination decreases as short chain concentration increases, whereas radiative recombination shows an opposite behaviour and its internal efficiency seems to saturate. The results shown in figure 3 also suggest that only a small fraction of the short chains might be responsible for light emission. External efficiencies can be deduced from our calculated internal efficiencies by division by a factor of $2n^2$ [13] where the refractive index, n, for the usual electroluminescent polymers is typically of the order of 1.5-2. Thus, the predicted external efficiencies are in good agreement with experimental external efficiencies [14] for the same film thickness.

The current efficiency (electrons (holes) that reach the anode (cathode) per electron (hole) injected) decreases as the number of luminescent chains increases (figure 4). Both recombination and current efficiencies decrease as short chain concentration increases as a result of the build-up of positively and negatively space charge within the polymer film (figure 5). In fact, a space-charge-limited current was observed experimentally in light-emitting diodes [15]. The dependence of recombination and current density on space charge was also predicted for trans-polyacetylene [16].

4. CONCLUSIONS

Mesoscopic modelling of charge injection, transport and recombination in conducting polymers, such as those reported here, can give some insights to the correlation between polymer structure and device properties at scales which can only be studied experimentally using a Scanning Tunnelling Microscope. A key point of this model is to consider contributions from different transport processes within the polymer, such as intermolecular and interdomain charge carrier transport which are strongly influenced by structural polymar disorder. Our results suggest a build-up of space charge within the polymer layer in relatively disordered structures due to a large concentration of short chains. We believe this is aplausible explanation for low electroluminescence efficiencies. Although the central results of this model are quite general and may also apply to other conducting polymers, extensions are probably needed for studying other electroluminescent polymers.

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FIGURE CAPTIONS

Figure 1: Dimerisation patterns in a positively charged polydiacetylene chain with 7 units. The dimerisation is defined [5] by the change in the bond lengths from their ground state values. The marks indicate the data points that were calculated explicitly. The curves are simply a guide to the eye.

Figure 2: Charge stored on carbon atoms of a positively charged polydiacetylene chain with 7 units. The marks indicate the data points that were calculated explicitly. The curves are simply a guide to the eye.

Figure 3: Recombination efficiency within the polydiacetylene film as a function of luminescence chain concentration for: (a) total recombination (diamonds), (b) radiative recombination (triangle) (c) non-radiative recombination (square). The marks indicate the average value of the data points that were calculated explicitly. The curves are simply a guide to the eye.

Figure 4: Current efficiency within the polydiacetylene film as a function of luminescence chain concentration for: (a) electrons (triangle) (b) holes (square). The marks indicate the average value of the data points that were calculated explicitly. The curves are simply a guide to the eye.

Figure 5: Charge stored within the polydiacetylene film as a function of luminescence chain concentration for: (a) negative space charge (triangle) (b) positive space charge (square). The marks indicate the average value of the data points that were calculated explicitly. The curves are simply a guide to the eye.

Figure 1

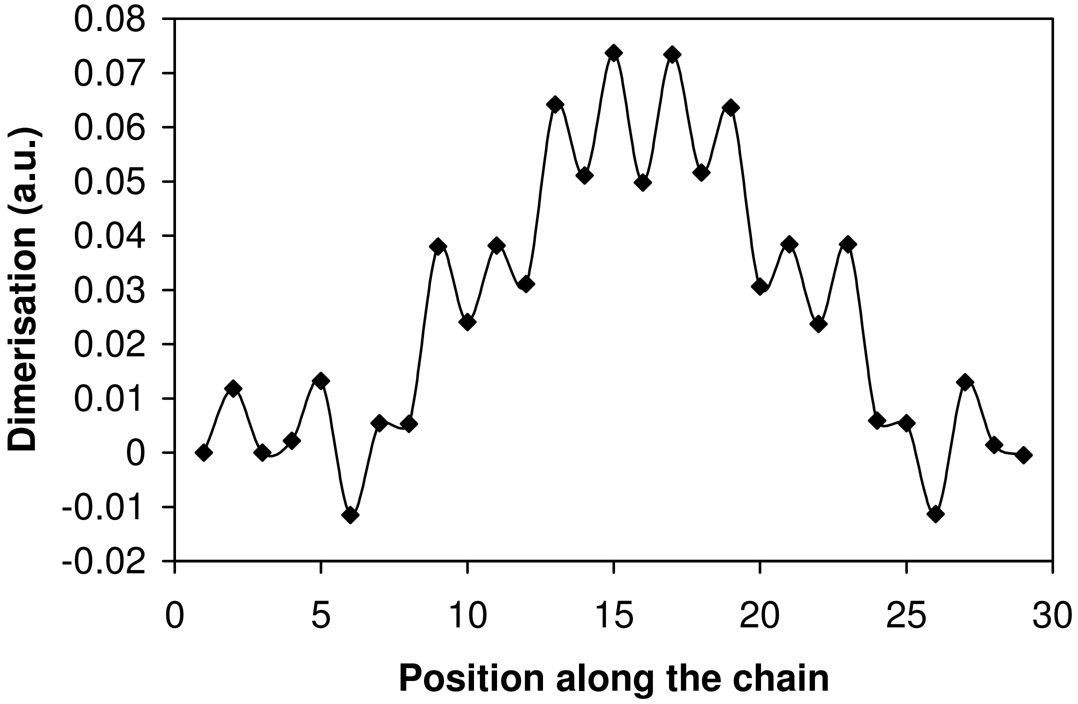

Dimerisation (a.u.)
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
-0.01
-0.02
0
5
10
15
20
25
30
Position along the chain

Figure 2

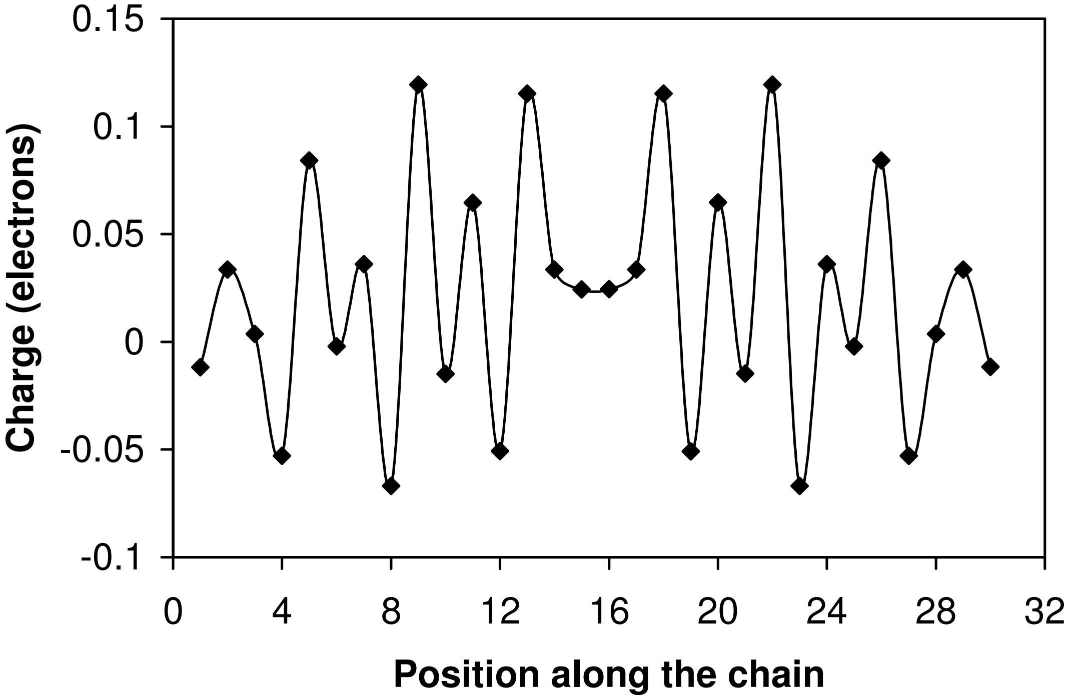

0.15
0.1
0.05
0
-0.05
-0.1
Charge (electrons)
0
4
8
12
16
20
24
28
32
Position along the chain

Figure 3

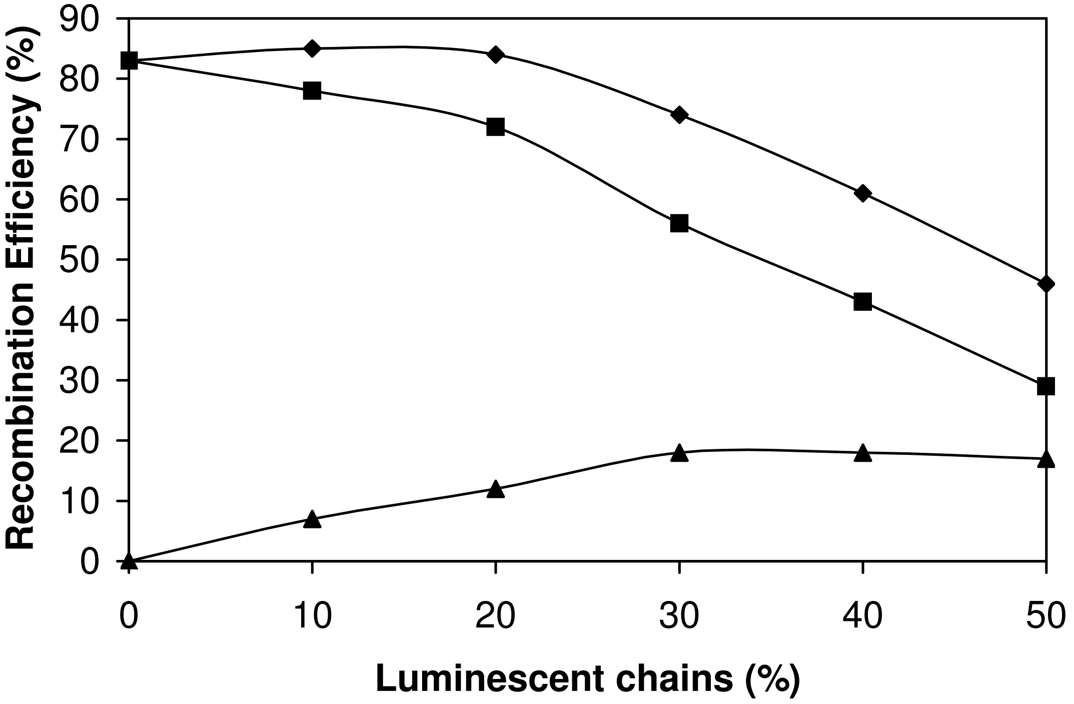

Recombination Efficiency (%)
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
Luminescent chains (%)

Figure 4

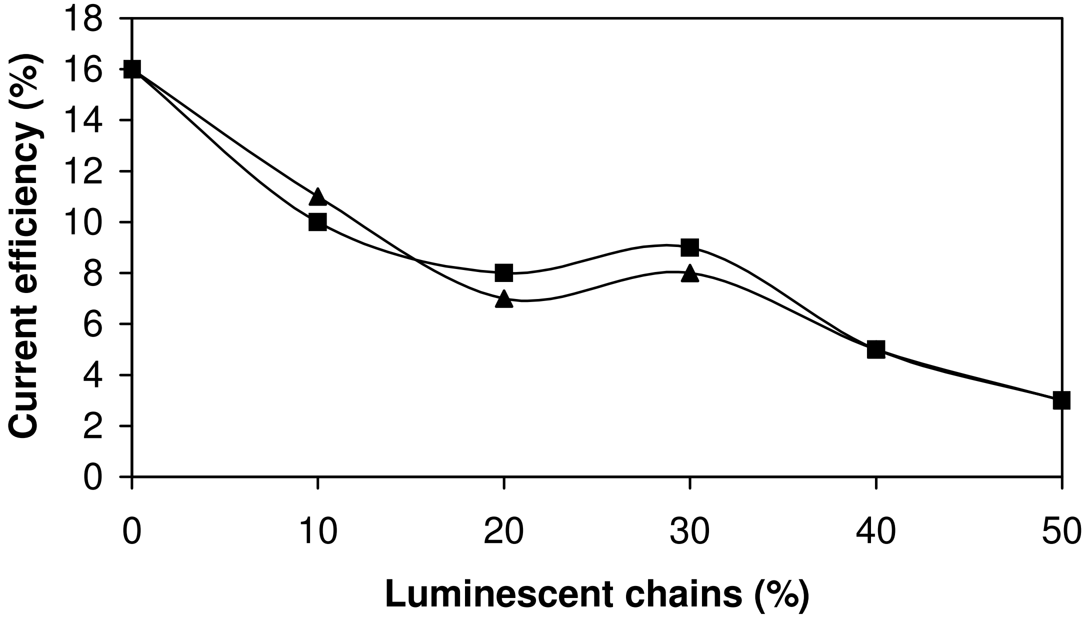
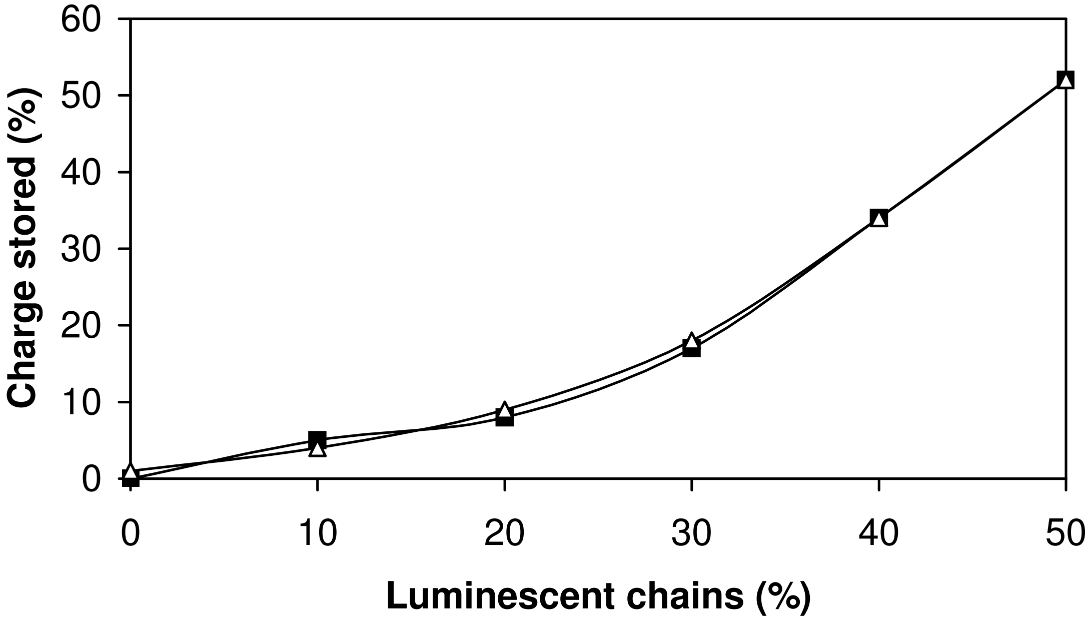

Current efficiency (%)
18
16
14
12
10
8
6
4
2
0
0
10
20
30
40
50
Luminescent chains (%)

Figure 5



Charge stored (%)
0
10
20
30
40
50
60
Luminescent chains (%)
0
10
20
30
40
50