CHARGE INDUCED-DEFECTS IN POLY(P-PHENYLENE VINYLENE) (PPV)

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Abstract

We use a molecular dynamics method with semi-empirical quantum chemistry at the CNDO (Complete Neglect of Differential Overlap) level to study the charge-induced structural relaxation of poly(p-phenylene vinylene) (PPV) backbone, as a result of charge injection in light emitting diodes. Our results suggest that structural relaxation of PPV is accompanied by a local change in the electronic structure of the polymer leading to commonly called defects. The mobility of these defects along the polymer chains of different finite length were estimate from computer experiments. The charge rearrangement among the PPV atoms is also discussed.

1. Introduction

Organic semiconductors, like conjugated polymers, have been extensively used for constructing optoelectronic devices. Their semiconducting behaviour derives from the π molecular orbitals delocalized along the polymer chain.

Poly (p-phenylene-vinylene) (PPV) is a promising polymer to be used as an active medium for both electroluminescent and photovoltaic devices since high quality films can be easily made and it has a yellow-green photoluminescent band centred at 2.2 eV [1], just below the gap between π and π^* states which is about 2.5 eV [2]. Suitable choices of electrodes, dopants and molecular derivatives may

enhance the performance of these organic-based devices allowing them to be competitive with their inorganic counterparts such as silicon-based devices [2].

Most of the experimental research on conducting polymers has been focused on solution processable polymers and current theoretical approaches assume that conducting polymers are simple semiconductors, and they can be treated using classical theories of inorganic crystalline semiconductors like silicon. Therefore, no account has been taken of varied chain lengths, molecular charge, cross-linkings, or side groups within a realistic description of conducting polymers. Yet, these effects are important in the interpretation and understanding of the observed device characteristics and they can be handled using self-consistent molecular dynamics.

Thus, the electrical and optical properties of luminescent polymers, such as PPV, depend both on properties of individual polymer strands and on molecular arrangement. At molecular level there are a few simple descriptions of individual molecules and their intrinsic properties [3]. The aim of this work is to perform atomistic modelling of chain growth in the polymerisation of PPV to shed some light on its structure and electrical properties. The effect of an applied electric field on the injected charge is also discussed.

2.   Theory and method

We have performed a self-consistent calculation of both electronic structure and molecular geometry using the CHEMOS code [4], which combines molecular dynamics with the widely used CNDO (Complete Neglect of Differential Overlap) molecular orbital method. These calculations were performed within LCAO (linear combination of atomic orbitals) and a cluster framework.

Starting off with one isolated PPV monomer, for which we have chosen a geometry based on typical bond lengths and bond angles between carbon and hydrogen atoms (see fig. 1), the computer program uses a variational calculation to find the best charge distribution that minimises the electronic energy of the molecule. Once the electronic problem has been solved, it is possible to consider atomic motion for a short time (typically 1.05 fs), under the forces obtained directly from the electronic structure calculation, using a molecular dynamics method. Both electronic structure and atomic relaxation are repeated until an energy minimum is achieved.

After the monomer optimised geometry was obtained a chain with two monomers was built by adding another monomer and let the chain relax. This procedure was repeated until a 16 monomer chain was built, which corresponds to a polymer with 106 Å in length.

The computer program output contains not only the cluster geometry and internal energy but also the electronic structure, wave functions, Mulliken atomic charges (the net charge at each atom) and the molecular dipole moment.

The CHEMOS code has also been used to simulate the behaviour of charged clusters (in this article we present results for PPV chains from 2 to 16 monomer units with molecular charges ranging from –2 to +3 electrons) and with and without an uniform electric field being applied. The application of an electric field allows us to evaluate charge mobility.

3. Results

3.1. Molecular electronic states

From the chemical formula for PPV, $C_{8n}H_{6n+2}$, it is immediate to notice, no matter the number of monomers n, there is always an even number of electrons for

neutral chains, so, the lowest molecular energy state has to be a singlet. For chains single charged there will be an odd number of electrons and then the lowest energy electronic configuration imposes an unpaired electron: these states are doublets. Doublets are also observed to be the lowest energy states for clusters where 3 electrons were injected.

Things are different in case of the injection of two charges, either positive or negative, in PPV polymer chains. In fact, as it can be seen in Table 1, a few smaller clusters have shown to prefer to be in a singlet state, whereas most of the longer clusters are clearly in triplet states. These results were carefully checked since neither of the singlet clusters were ever relaxed as triplet or vice-versa: they disaggregate when such simulations were carried out.

3.2. Coplanarity

All the clusters exhibit planar geometry for the minimum energy configuration when the simulation is to be performed from the geometry closed to the final relaxed structure, which can be anticipated by suitable choice of both the bond lengths and bond angles of the first monomer, this being the main difficulty. In fact, to obtain a reliable configuration for the PPV monomer several constraints have to be imposed to prevent disaggregation of H atoms from C atoms. Then, the first acceptable geometry was let to relax without constraints and the relaxed geometry obtained was somehow unexpected since the phenyl ring was perpendicular to the plane containing atoms e and f (see fig. 1). Theoretical and experimental results for trans-stilbene "in vacuo" support our predictions [5].

To overcome this situation, which is most inconvenient since it inhibits the possibility of obtaining large conjugated systems, the molecule was forced to relax in

a planar configuration. This has shown to be a good procedure since the cluster binding energy is exactly the same for both cases.

When charge is injected in chains with 3 and 4 monomers a drastic deviation from a planar conformation is predicted if, for instance, we slightly squeeze a phenyl ring. This is a most interesting feature since in PPV films the planar geometry is not characteristic due to multiple and chaotic aggregation of polymer strands.

3.3. Charge induced defects in PPV

Charge injection leads to a distortion of the PPV chains parallel to the molecular plane, which, in turn, leads to a change in the electronic structure of the polymer. To observe the effect of charge injection we may focus on what happens to the bond lengths between carbon atoms.

Thus, we define the dimerisation parameter as the absolute difference in bond lengths of a carbon atom relative to its two carbon neighbours:

$$d_n = |b_{n-1} - b_{n+1}| \qquad (1)$$

where d_n is the dimerisation parameter for carbon atom n and $b_{n\pm1}$ is the bond length between carbon atoms n and $n\pm1$.

The evaluation of the dimerisation parameter is performed for the carbon atoms found in a direct ride from one end to other of a polymer chain. We observe three typical values for this parameter corresponding to three types of carbon-carbon bond length differences in a chain, namely those at atoms b or c, a or d and e or f (fig. 1). The figure 2 shows the dimerisation parameter for a neutral 16 monomer chain.

When a charge is injected in the molecule the previous pattern is distorted. Then, we rather look into the variation of the dimerisation parameter relative to the uncharged cluster. As it can be seen in fig. 3, the number of structural distortions is

the same as the number of charges injected. The location and shape of the distortion is independent of the charge sign for chains with more than 5 monomers. For shorter chains the distortion effects caused by the charge injection depend dramatically on its sign.

3.4. Charge distribution among the PPV atoms

Charge injection in PPV strands causes charge rearrangement among the polymer atoms. When one, two or three charges are injected, the patterns for change in the atomic charges of the same carbon atoms used in the dimerisation parameter calculations, look very much the same as the corresponding dimerisation patterns. The dependence on charge sign is noticed in the pattern orientation (fig. 4).

Remarkable is also the fact that charge injection, independently of its sign, imposes a charge alternation on the carbon atoms. The same behaviour was predicted for polyacetylene [6], which is consistent with the interpretation of XPS experiments [7].

3.5. Effect of an electric field on a charged cluster; charge mobility

Simulations were performed on a large charged cluster (16 monomer chain positive or negative charged) under the influence of a strong electric field.

There are two types of results obtained from these computational experiments: charge mobility along the chain and behaviour of the charge induced defect.

For an uniform electric field of 5×10^6 V/cm applied along the polymer length, the charge was displaced to the chain right after the first molecular dynamics step.

As to the structural defect, induced by the charge, it does not move along the polymer chain. Indeed, what can be seen is the defect disappearing from its original localisation and growing in the new charge site. Moreover, the old and the new defects do not vanish and grow in only one direction. In fact, both oscillate until one completely disappears and the other is definitely formed. This behaviour can be seen in fig. 5.

For lower field intensity (2.5×10^6 V/cm) the charge mobility can be best evaluated. A value of 4.04 cm^{2}V^{-1} s^{-1} was obtained.

4. Conclusions

It is an experimental evidence that no more than 25% of the conjugated polymers in a device are electroluminescent and recent theoretical work at mesoscopic scale reenforces that [8]. Our results, obtained at atomic scale, suggest that short polymer strands, which are electroluminescent, are at singlet states when doubly charged. These results are consistent with spin allowed radiative emission from only singlet states.

The charge injection induces charge rearrangements among the PPV atoms. Despite the presence of a conjugated system, charge rearrangement is well localised within the distortion region.

When no electric field is applied, the distortion, due to the injected charge, moves towards the centre of the chain where it is located in order to minimize the ground-state energy of the relaxed chain. Under high intensity electric field an already formed charge-induced defect is predicted to dissociate moving the charge towards the chain end faster than the structural distortion of the polymer backbone. This has major implications for the electrical characteristics of LEDs at high electric fields.

References

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Caption of the figures

Figure 1: Schematic diagram of PPV. The carbon atoms are represented by letters.

Figure 2: Dimerisation parameters for a 16 monomer PPV neutral chain.

Figure 3: Variation of the dimerisation parameters for charged 16 monomer PPV chains: a) $Q = \pm e$; b) $Q = \pm 2e$; c) $Q = 3e$.

Figure 4: Variation of the charge in each carbon atom in charged 16 monomer PPV chains: a) $Q = \pm e$; b) $Q = 2e$; c) $Q = 3e$.

Figure 5: Time evolution of a charge induced structural defect under the action of an electric field: $E=5\times10^{6}$ V/cm. The dimerisation parameter variation is calculated relative to the uncharged 16 monomer cluster.

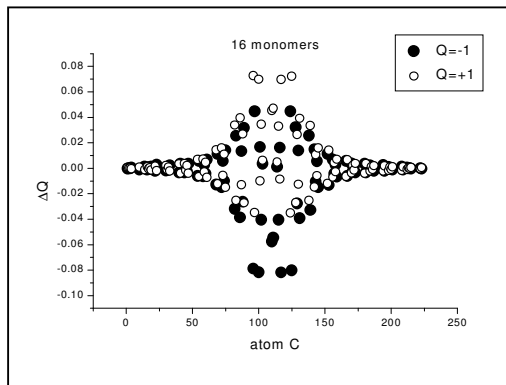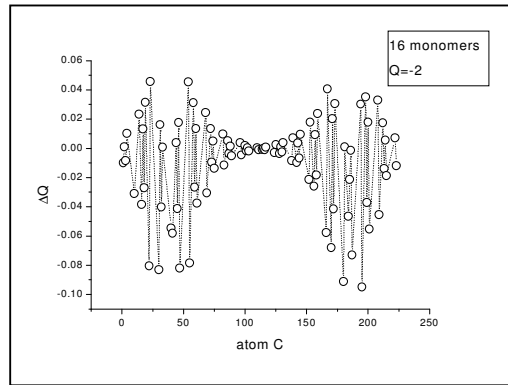Each step corresponds to $\Delta t=1.05$ fs.
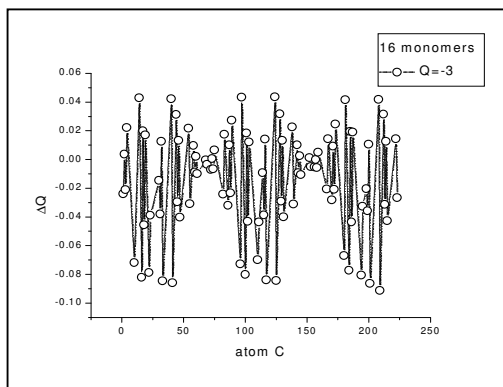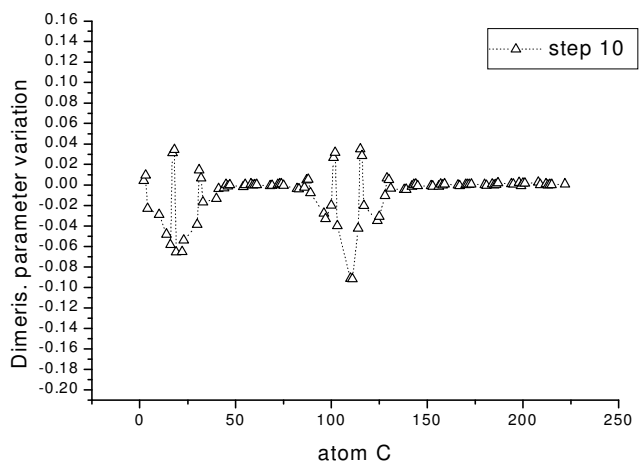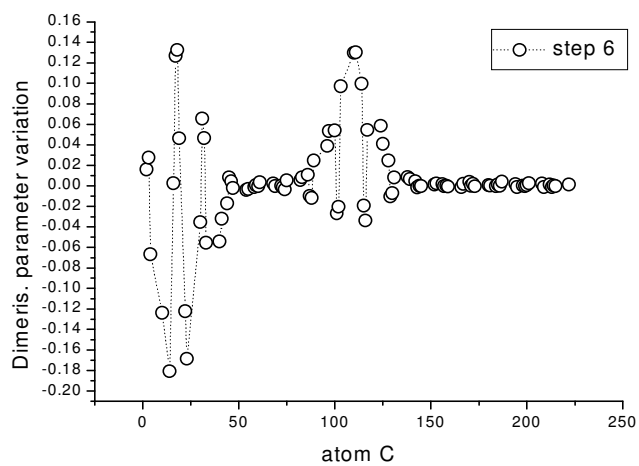
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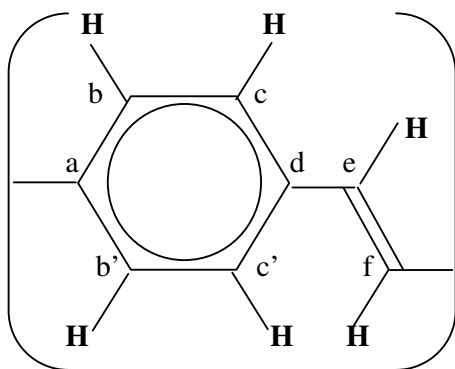
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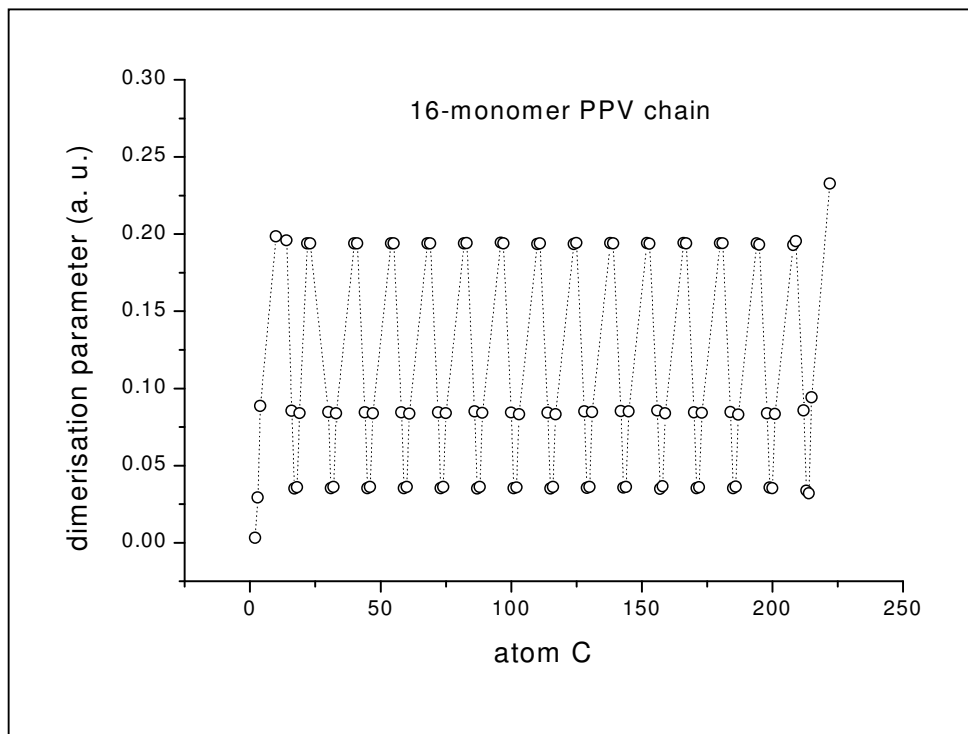
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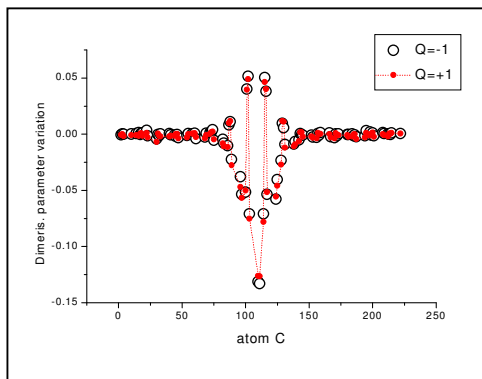
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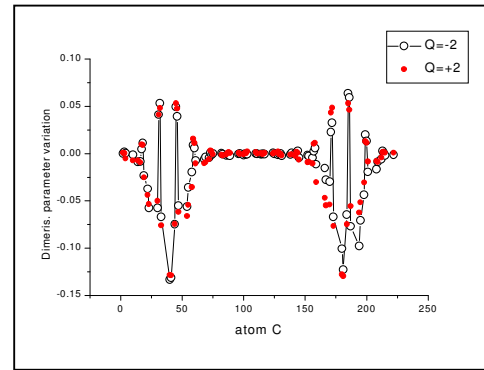
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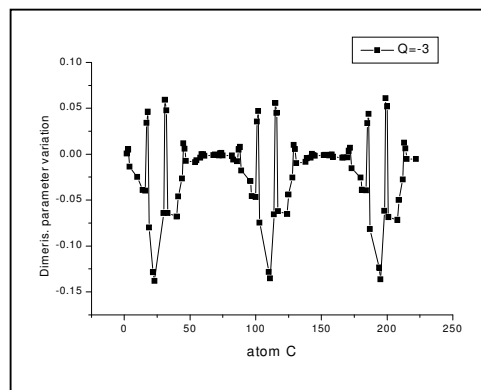
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Figure 4

a)

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Figure 5
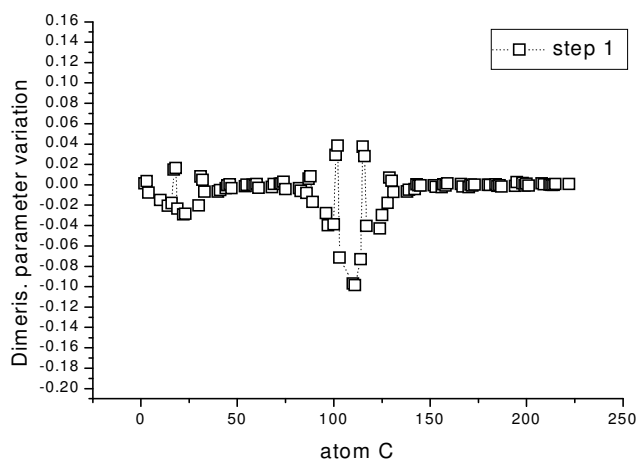
Table 1

PPV molecular orbital states.

# of monomers	Cluster net charge (×e)					
	3	2	1	0	-1	-2
1			D	S	D	
2	D	S	D	S	D	S
3	D	S	D	S	D	T
4	D	S	D	S	D	S
5	D	T	D	S	D	S
6 - 16	D	T	D	S	D	T

e – electron charge

S – Singlet state

D – Doublet state

T – Triplet state