

The effect of variable chain length on the electronic properties of electroluminescent polymers

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Abstract

We have used self-consistent molecular dynamics calculations with semi-empirical quantum chemistry at the complete neglect of differential overlap (CNDO) level to discuss some of the issues relating to the electronic processes involved in electroluminescence of a particular conjugated polymer: poly(*p*-phenylene-vinylene) (PPV). Specifically addressed are the effects of chain length and molecular charge on the electronic properties of individual PPV strands, such as chemical potential, charge induced defects and charge rearrangement among the polymer atoms. The effect of high electric fields on charge-induced defects already formed is also discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Molecular dynamics; PPV; Charge-induced defects; Chemical potential

1. Introduction

Poly(*p*-phenylene-vinylene) (PPV) is a promising polymer to be used as an active medium for both electroluminescent and photovoltaic devices. 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.

Most of the experimental research on conducting polymers has been focused on solution processable polymers. PPV, which has been used to fabricate light emitting diodes (LEDs), exemplifies this. Therefore, current theoretical approaches assume that conducting polymers are simple semiconductor, and they can be treated using classical theories of inorganic crystalline semiconductors like silicon. No account is 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 single molecules and their intrinsic properties [1]. 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. Theoretical method

We have performed a self-consistent calculation of both electronic structure and molecular geometry using the CHEMOS code [2], which combines molecular dynamics with the widely used CNDO molecular orbital method. These calculations were performed within linear combination of atomic orbitals (LCAO) and a cluster framework.

3. Results and discussion

3.1. Free PPV molecules

Before any charge injection, we have relaxed the geometry of several clusters to equilibrium starting off a monomer and a planar configuration. The number of units in each PPV chain varies from 1 to 16. The value of 106 Å was obtained for the length of a chain with 16 monomers.

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3.2. Charge-induced defects in PPV

In order to study the effects of positive or negative charge injection on individual straight strands we have calculated the electronic structure and the relaxed geometry of finite and variable chain length with various extra charges, ranging from -2 to $+3$ electrons.

The charge injection leads to a distortion of the PPV parallel to the molecular plane, which, in turn, leads to a change in the electronic structure of the polymer. The geometric distortion in the bond length distribution of a free-defect PPV chain with 16 monomers corresponding to the injection of two electrons is shown in Fig. 1(b). The resulting dimerisation pattern shows well-separated distortion regions, each one associated with a single injected charge.

The dimerisation parameter plotted in Fig. 1(b) was calculated by the difference in C-C bond lengths at each carbon atom in the charged chain minus the corresponding bond length difference in the neutral free-defect chain.

3.3. Charge distribution among the PPV atoms

The changes in Mulliken atomic charges of PPV due to the injection of two electrons in a free-defect chain is shown

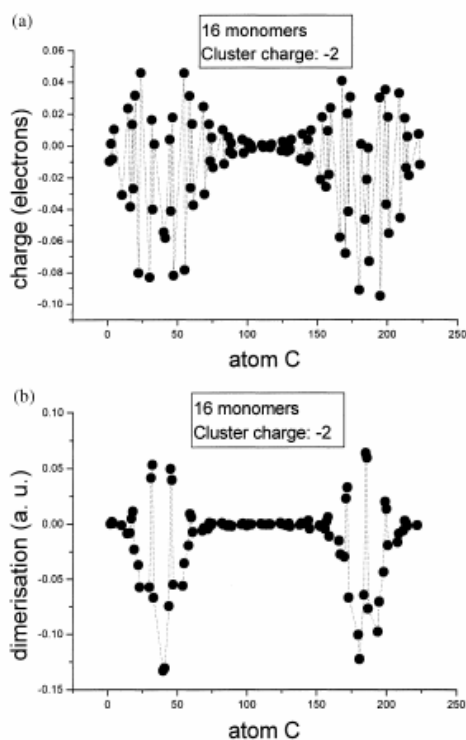


Fig. 1. (a) Changes in Mulliken atomic charge for carbon atoms of a single PPV chain with 16 monomers caused by the injection of two electrons to the neutral free-defect chain. (b) Dimerisation patterns in the same PPV chain as (a). The marks indicate data points explicitly calculated. The curves are simply a guide to the eye.

in Fig. 1(a). The charge injection induces charge rearrangements among the PPV atoms. Despite the presence of a conjugated system, charge rearrangement is well localized within the distortion region. The charge is mainly stored in the carbon atoms. For a positive or a negative charge injection, we find a charge alternation on the carbon atoms. The same behaviour was predicted for polyacetylene [3], which is consistent with the interpretation of XPS experiments [4].

3.4. Chemical potential

The interchain charge transfer is driven by the chemical potential difference. The chemical potential of each finite chain can be obtained both by the self-consistent arithmetic average of ionization potential and electron affinity calculated explicitly from total energies for different charge states, or by the more approximated form using Koopmans theorem, in which the chemical potential is the arithmetic mean of the energies of the highest occupied and lowest unoccupied levels. The results obtained by both approaches fairly agree for the longer chains yielding 4.7 and 4.5 eV, respectively.

3.5. The effect of an applied electric field on the carriers

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 minimise the ground-state energy of the relaxed chain. In fields equal to 5×10^6 V/cm, 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. The charge mobility predicted is greater than 10^{-2} cm V/s Fig. 2.

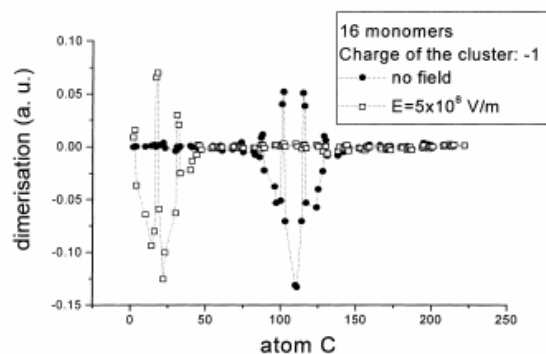


Fig. 2. Dimerisation pattern in a PPV 16-monomer chain with a net charge of one electron when: (a) no electric field is applied (circles); (b) an electric field of 5×10^6 V/cm is applied along the chain during 860 fs (squares).

4. Conclusion

We have studied the electronic properties of individual PPV chains of finite and variable lengths such as chemical potential and charge-induced defects, which concern the description of charge transport and recombination in LEDs.

Our results suggest that electron or hole injection to an individual PPV chain leads to chain distortion and charge rearrangement among the polymer atoms. Moreover, the charge-induced defect seems to dissociate under high electric fields.

Self-consistent quantum chemistry molecular dynamics calculations, such as those reported here, are a useful tool

for studying the behaviour of isolated polymer strands impossible to obtain experimentally by scanning tunnelling microscopy.

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