

Electronic Properties of Conjugated Polymers Studies by Quantum Molecular Dynamics Simulations

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Summary: The growing interest in using organic materials, specifically polymers, as active media for optoelectronic devices demands a deep knowledge of the properties and behaviour at the molecular level. The lack of experimental studies at the molecular scale drives the attention to theoretical methods used to solve the Schrödinger equation of large clusters with suitable approximations. Here we present the structural and dynamic results obtained for individual molecules of poly(*p*-phenylene vinylene) (PPV) and polydiacetylene (PDA), through self-consistent molecular dynamics calculations with semi-empirical quantum chemistry at the complete neglect of differential overlap (CNDO).

Introduction

Since the early 90s there has been a tendency for using polymer based semiconductor materials for electroluminescent and photovoltaic devices with encouraging results concerning the performance, efficiency, applications, durability, relative ease of fabrication and low cost.^[1-3] For these reasons their field of applications is wider than that of the commonly used silicon technology.

The advances in this new technology have been achieved almost entirely by empirical progress since the theoretical methods either deal with large-scale materials under a statistical point of view, or do not go beyond the molecular level. Therefore, there is a lack of knowledge of what happens at the mesoscopic scale. To perform realistic mesoscopic simulations of a polymer's electronic activity one needs to know the properties and behaviour of individual molecules under different conditions. That need is the motivation to study the electronic properties of individual molecules and to use these results to the build up of a model at a higher scale, in order to provide information that is relevant for further development of electronic devices based on conducting polymers.

The Method

The theoretical method has already been described elsewhere^[4] and it is based on the

combination of a molecular dynamics calculation with the widely used complete neglect of differential overlap (CNDO) method using a linear combination of atomic orbitals (LCAO) and a cluster framework. This method is implemented in the CHEMOS code.^[5] We have performed simulations of the following systems: non stretched PPV and PDA molecules with different number of units, either neutral or charged, and stretched molecules of PPV with a length 10% longer than the non stretched molecule (hereafter referred as stretched PPV or PPVst), both charged and uncharged. The stretching was obtained by the elongation of the bonds along the polymer axis with a consequent reduction on the perpendicular direction.

Molecular Structure

Isolated PPV ($C_{8n}H_{6n+2}$) and PDA ($C_{4n+2}H_{2n+4}$) molecules show a planar geometry. In Figure 1 are depicted the configurations of each molecular building unit. When charge (electrons or holes) is injected, structural defects arise and their localisation depend on the number of positive or negative charges injected,^[4,6,7] but the clusters keep their planar configuration.

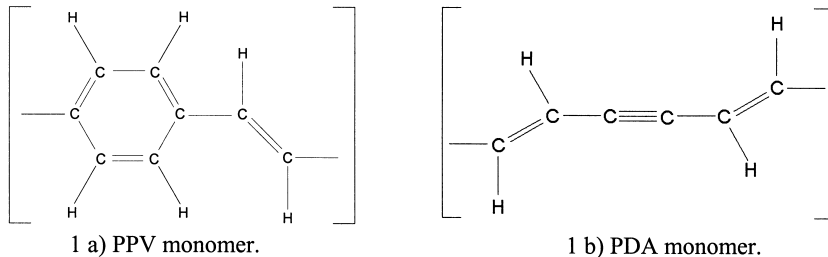


Figure 1. Sketch of molecular configurations.

Charge Distribution

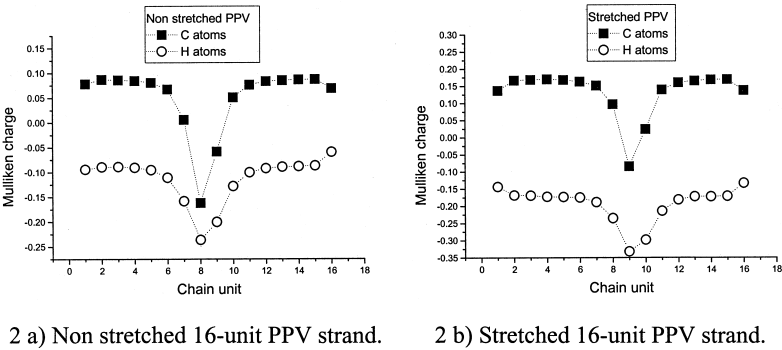
There has been experimental evidence that electronic density in a negatively charged polyacetylene molecule exhibits an odd pattern^[8] which consists on charge alternation at the carbon atoms. Results from the method here described reinforce those observations^[9] and from our simulations similar patterns for charged PPV and PDA molecules were obtained.^[4,7] The same method has been used to evaluate the amount of charge stored in each type of atom of the molecule (see Table 1).

Table 1. Charge distribution per atom type of 16-unit polymer chains.

	Polymer net charge=-1		Polymer net charge=+1	
	Stored charge (%)		Stored charge (%)	
	C atoms	H atoms	C atoms	H atoms
PDA	72 ^[10]	28 ^[10]	73	27
PPV	55 ^[10]	45 ^[10]	54	46
PPVst	55	45	57	43

The atomic Mulliken charge is defined as the variation of the electron density of an atom in the molecule from its isolated state value. For a neutral PPV chain with 16 repeated units, the sum of the Mulliken charge for all carbon atoms is +1.36. Symmetrically, the Mulliken charge stored in all hydrogen atoms is -1.36. These figures change when the molecule is stretched, and for a PPVst strand, the Mulliken charge for both type of atoms is ± 2.65 .

Noticeable is also the geometric distribution of the charge in a molecule, depending on the number of charges injected but almost independent of its sign.^[4] In Figure 2a it is shown how the net charge of one electron is distributed by the 16 units of an isolated PPV chain as well as the charge distribution associated with both carbon and hydrogen atoms. In Figure 2b the same situation is illustrated for the stretched PPV molecule.



2 a) Non stretched 16-unit PPV strand. 2 b) Stretched 16-unit PPV strand.

Figure 2. Mulliken charge distribution among the strand units per atom type for a total net charge of -1.

Charge Mobility

Intramolecular charge mobility is the measure of how easy it is for the injected charge

to move along the chain under the effect of an electric field. It is thus defined as:

$$v = \mu E \quad (1)$$

where v is the charge velocity, E is the applied electric field and μ is the charge mobility.

With the information gathered before we can then simulate the application of a uniform electric field and see what happens to the charge injected in those molecules. Therefore, if we can see the movement of the charge during the simulation experiment it is possible to estimate the charge mobility.

The results of the application of an electric field to a single charged molecule show four main features. First, the injected charge does not move along the polymer chain if the field is too weak. Second, if the field is too strong, that causes a complete rupture of the chain letting the atoms to split apart. In Table 2, we present the electric field lower and upper limits for intramolecular charge mobility in PPV and PDA molecules.

Table 2. Electric field limits for intramolecular charge mobility of 16-unit polymer chains.

	Electric field ($\times 10^6 \text{ Vcm}^{-1}$)			
	Polymer net charge=-1		Polymer net charge=+1	
	Lower limit	Upper limit	Lower limit	Upper limit
PDA	2.35 ^[10]	14.7	1.60	14.9
PPV	1.55 ^[10]	11.0	2.00	11.0
PPVst	2.121	10.0	1.90	11.0

Third, it is possible to estimate the charge mobility for intermediate values of the electric field by evaluating the Mulliken charge at each atom as a function of time. Thus, the charge pattern can be seen moving from its initial localisation and its velocity can be measured.

The fourth feature emerges from stronger electric fields, but below the upper limit. In these cases, the field is so strong that it displaces the charge to the chain end after the first time-step of the simulation. Then, one can only make a rough estimate for the minimum value of the charge mobility.

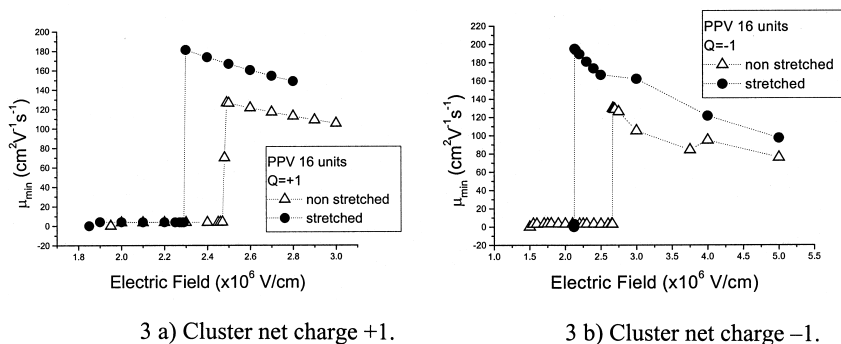


Figure 3. Estimate of minimum intrachain charge mobility in PPV.

These results can be best seen in the Figure 3. The straight lines almost parallel to the electric field axis correspond to charge mobility due to the application of a moderate electric field (its actual value is greater than $3 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ in all cases). Strong electric fields yield much higher estimates for the charge mobility.

Conclusions

The charge mobility and the electric field thresholds for PDA, PPV and PPVst depend on the injected charge sign.

The stretching of the PPV molecule induces notorious changes in the Mulliken charge distribution along the chain. As a consequence of the stretching, the intramolecular charge mobility seems to be higher under the effect of strong electric fields.

The interval between moderate and high charge mobility corresponds to a change in the electric field of less than $2 \times 10^4 \text{ V/cm}$.

- [1] J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackay, R.H. Friend, P.L. Burns, A.B. Holmes, *Nature* **1990**, 347, 539.
- [2] R.H. Friend, R.W. Gymer, A.B. Holmes, J.H. Burroughes, R.N. Marks, C. Taliani, D.D.C. Bradley, D.A. dos Santos, J.L. Brédas, M. Logdlund, W.R. Salaneck, *Nature* **1999**, 397, 121.
- [3] R. Friend, J. Burroughes, T. Shimoda, *Phys. World* **June 1999**, 35.
- [4] M.M.D. Ramos, A.M. Almeida, *Vacuum* **2001**, 64, 99.
- [5] D.S. Wallace, M. Stoneham, W. Hayes, J. Fisher, H. Harker, *J. Phys. Condens. Matter* **1991**, 3, 3879.
- [6] A.M. Almeida, M.M.D. Ramos, *Syn. Metals* **2001**, 122, 165.
- [7] M.M.D. Ramos, A.M. Almeida, J.P.M. Carneiro, A.M. Stoneham, *Le Vide: science, techniques et applications*, in print.
- [8] M. Sasaki, H. Fukutome, *Solid State Commun.* **1986**, 58, 735.
- [9] M.M.D. Ramos, J.P.P. Almeida, *Comput. Mater. Sci.* **1998**, 10, 184.
- [10] A.M. Almeida, M.M.D. Ramos, A.M. Cadilhe, *Comput. Mater. Sci.*, in print.

