MODELLING THE EFFECT OF NONPLANARITY ON CHARGE TRANSPORT ALONG CONJUGATED POLYMER CHAINS

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Abstract

Conjugated polymers show interesting properties that make them appropriated for nanoelectronics. Several studies of poly(p-phenylene vinylene) (PPV) have suggested that each polymer chain consists of several planar segments, with conjugation length of nanoscale dimension, linked by twists or kinks. A pronounced twist between two planar segments in a PPV chain not only causes loss of main-chain conjugation but it may also alter electron and hole mobility along the chain, which has further implications for the percolation of charge through the polymer film.

We used self-consistent quantum molecular dynamics calculations to provide information on the electric field needed to move the injected charges (either electrons or holes) along the planar segments of PPV and to cross the twist between two planar segments perpendicular to each other. Field-dependent charge mobility was also estimated for conjugated segments of various lengths. Our results suggest that electrons can cross the twist between adjacent planar segments for lower applied electric fields than holes if there is no more than one electronic charge (electron or hole) on the PPV chain, otherwise similar fields are needed.

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1. Introduction

Despite the technological importance of materials such as conjugated polymers in nanoelectronics, most charge transport studies reported so far have assumed the polymer layer of nanometric thickness as a continuous medium. Walker *et al*. [1] review the main results obtained using continuum macroscopic models. Recently, we made the first attempts to simulate the charge transport along fully conjugated polymer chains of poly(p-phenylene vinylene) (PPV) and some of its derivatives, using a quantum molecular dynamics method [2-4]. The comparison between results obtained by this method and the experimental ones permits one to conclude that generally the self-consistent quantum molecular dynamics approach yields reliable predictions of intra-molecular charge mobility.

Theoretical studies performed by Sumpter *et al.* [5] suggest that PPV chains have a large number of conjugated segments with an average conjugation length between 6 and 12 monomer units. However, the number of units in each segment is not controlled exactly and the segments may be twisted. This chain structure has important consequences for intra-molecular charge transport which has further implications for the transport of electrons and holes through the polymer film in polymer-based devices.

In the present paper, we shall discuss the modelling of charge transport along individual PPV chains with 16 repeat monomer units, emphasizing the effects of electron-phonon coupling and the twisting of two conjugated segments with variable length.

2. Theoretical method

Because the charge transport along the conjugated polymer chains involve both atomic and electronic motion, the approach we adopt, based on the CHEMOS Code [6, 7], combines molecular dynamics (MD) with self-consistent electronic structure calculations performed at CNDO (Complete Neglect of Differential Overlap) level, using the parameters proposed by Pople and Beveridge [8], a LCAO (Linear Combination of Atomic Orbitals) and a cluster

model framework. The interatomic forces are evaluated from CNDO calculations as the simulation proceeds.

When an external electric field is applied, the CNDO core Hamiltonian of the polymeric system is modified to account for the added potential. As a result, this quantum molecular dynamics approach treats the electronic states of the polymer chain explicitly and follows their evolution as the nuclei move in the presence of the applied electric field.

3. Results

3.1 Starting geometry

Before any dynamic simulation of internal rotation of two conjugated segments, the PPV chain with 16 repeat units is fully relaxed to equilibrium, starting off with the planar conformation.

In dealing with rotation of a conjugated segment around a carbon-carbon single bond, the atoms located at one side of that bond are rotated clockwise whilst the other atoms of the PPV chain are prevented to move out of their initial conjugation plane. This procedure allows one to perform dynamic twisting of two conjugated segments with simultaneous geometry optimisation. Typical angular velocities of the order of 0.05 degrees per time-step are used.

In modelling the effect of non-planarity on intramolecular charge transport, we have considered only the fully relaxed PPV chains with two planar conjugated segments perpendicular to each other depicted in figure 1. The orthogonal conformation corresponds to the saddle point with the highest maximum energy in the potential energy surface for internal rotation about C – C bond in PPV [9]. This conformation is in agreement with other calculated results reported in the literature for the relaxed conformation of the same conjugated polymer in dichloromethane [5].

3.2 Charge-induced defect

On adding a single electron or hole to a PPV chain with two conjugated segments perpendicular to each other, the structural relaxation of the polymer chain around the injected charge creates a polaron-type defect at the centre of the longer segment to attain the lowest energy (see figure 2). Our calculations predict no significant difference between the geometric distortion in the carbon-carbon bond length distribution of polarons of both charges and the distortion in a defect-free PPV chain with the same number of monomer units. If the two perpendicular planar segments have the same length, a polaron-type defect is still formed but the centre of the conjugated segment where it is formed is different for electron injection and hole injection as a result of different terminations of both segments. For both positive and negative charged polarons formed, a charge alternation on the carbon atoms is predicted.

The injection of two charges of the same sign (electrons or holes) to PPV chains with two perpendicular conjugated segments leads to a charge-induced structural change of the polymer backbone localized on both chain ends (see figure 3). These charge-induced defects resemble those obtained for a planar PPV chain [10] and their location does not depend on the relative length of both conjugated segments.

3.3   The effect of conjugation length on field-dependent charge mobility

In order to study the effect of the conjugation length on intramolecular charge mobility, we calculate the velocity of a single injected charge (electron or hole) and the corresponding structural defect moving towards the chain-end closer to it, without crossing the twist between both segments, as a function of the strength of the applied electric field along the conjugated segment. The field-dependent charge (either electron or hole) mobility along the conjugated segment was obtained by calculating the injected charge velocity per unit applied electric field. The results obtained are shown in figure 4. From these results it is clear that the conjugation length affects mainly the electric field needed to move the injected charge along the segment, the electric field range for low mobility of the polaron-like carriers and the field needed to break the polaron-like carrier leading to a high-mobility regime. Low and high

mobility regimes are observed for electrons and holes regardless of the conjugation length. The low mobility regime corresponds to both charge and distortion patterns move together along the conjugated segment, whereas for the high mobility regime the charge is already found at the chain end on the first molecular dynamics time step leaving the lattice distortion on its initial position in the absence of the applied electric field.

The most important features that we find is that the electric field threshold for the high-mobility regime of both positive and negative injected charges decreases as the length of the conjugated segment increases, but the extension of the plateau corresponding to the low mobility of polaron-like carriers shows an opposite behaviour. Although the electric field range for polaron-like carriers to move along the PPV chain is dependent of the conjugation length, no significant difference was predicted for their mobility for the same applied electric field.

3.4 The effect of twisting conjugated segments on intramolecular charge mobility

To study the effect of twisting conjugated segments on charge transport along the entire PPV chain, we reverse the direction of the applied electric field. The results obtained are summarised in Table 1.

Our results suggest that the electric field threshold to move one electron or hole along the conjugated segment towards the twist between two planar segments perpendicular to each other and to cross it depends on the sign and number of the injected charge, as well as on the relative length of the conjugated segments.

If a single electron (or hole) is injected into the PPV chain and the length of the two conjugated segments is similar, no polaron movement occurs towards the twist between segments and the injected charge can only cross the twist if the applied electric field is large enough to break the polaron-like carrier. When the two segments have different length and the applied electric field is just above the threshold for charge mobility, positive and negative polaron-like carriers move along the PPV chain towards the twist and stop there if they do not

have enough kinetic energy to overcome the potential barrier. Nevertheless, injected charge of both signs can cross the twist with high-mobility when the applied electric field is greater than the one needed to break the polaron-like carrier.

If there are two polaron-like carriers of the same sign localized at both chain ends and the applied electric field is large enough to move one of them towards the other one, that charge carrier moves along the PPV chain with very low mobility and crosses the twist regardless of the sign of the injected charge and the length of the conjugated segment where is it initially located in the absence of the applied field.

Positive and negative injected charges can cross the twist between adjacent planar segments at lower applied electric fields if there is only a single electron or hole in the PPV chain. In this case, the electron needs a lower field to cross the twist than the hole. The opposite behaviour is predicted when there are two charges of the same sign on a chain with conjugated segments of similar length. Similar fields are needed to move either negative or positive polaron-like carriers along the chain towards each other and to cross the twist between segments of different length.

4. Conclusions

We have studied the structural changes induced by the injection of one or two electrons (or holes) into a PPV chain with 16 repeat monomer units and two planar conjugated segments perpendicular to each other. We have shown that each one of the injected charges gives rise to charge-induced defects of polaronic type.

The electric field range for charge mobility along the PPV chain depends on the length of the conjugated segment as well as on the sign of the injected charge.

Our results also suggest that the electric field needed for electrons to cross the twist between adjacent conjugated segments is lower than the corresponding field for holes if there is no more than one injected charge (electron or hole) on the PPV chain, the effect being more pronounced for chains with segments of similar length. Larger applied electric fields are

needed to allow electrons or holes to cross the twist if two charges of the same sign are present on the same chain. In this case, holes can cross the twist between segments for lower applied electric fields than electrons when their lengths are similar, otherwise similar fields are needed.

The results described above should affect the percolation of electrons and holes in polymer-based devices with PPV films as active components and they should be included in the mesoscopic modelling of bipolar charge transport in those devices.

Acknowledgement

References

[1]   A.B. Walker, A. Kambili, S.J. Martin, J. Phys., Condens. Matter 14 (2002) 9825.

[2]   A.M. Stoneham, M.M.D. Ramos, A.M. Almeida, H.M.G. Correia, R.M. Ribeiro, H. Ness, A.J. Fisher, J. Phys., Condens. Matter 14 (2002) 9877.

[3]   H.M.G. Correia, M.M.D. Ramos, Mater. Sci. Eng. C-Biomimetic Supramol. Syst. 23 (2003) 773.

[4]   H.M.G. Correia, M.M.D. Ramos, Comput. Mater. Sci. 33 (2005) 218.

[5]   B.G. Sumpter, P. Kumar, A. Mehta, M.D. Barnes, W.A. Shelton, R.J. Harrison, J. Phys. Chem. B 109 (2005) 7671.

[6]   D.S. Wallace, D. Phil. Thesis, University of Oxford, 1989.

[7]   D.S. Wallace, A.M. Stoneham, W. Hayes, A.J. Fisher, A.H. Harker, J. Phys., Condens. Matter 3 (1991) 3879.

[8]   J.A. Pople, D.L. Beveridge, Approximate Molecular Orbital Theory, McGraw-Hill, New York, 1970.

[9]   H.M.G. Correia, H.M.C. Barbosa, M.M.D. Ramos, Journal of Non-Crystalline Solids (2006) in print.

[10] M.M.D. Ramos, A.M. Almeida, Vacuum 64 (2001) 99.

Table 1: The electric field needed to move the injected electrons (Q = -1 for one electron and Q= -2 for two electrons) or holes (Q = +1 for one hole and Q= +2 for two holes) along the planar conjugated segments of a PPV chain with two twisted segments of variable length. The field values needed to move one of the injected charges towards the twist and to cross it are reported. When the applied electric field is positive the injected hole (electron) moves toward the right-hand (left-hand) chain end shown in figure 1 and when it is negative the charge moves towards the opposite chain end. The type of mobility for the charge crossing the twist between segments is identified: the low mobility regime corresponds to crossing of polaron-like carriers whereas for high mobility regime the injected charge cross the twist leaving the lattice distortion behind.

PPV chain with two twisted segments	Chain Net charge	Electric field (MVcm^{-1})		Mobility regime for charge crossing the twist
		Field needed to move the charge towards the twist	Field needed for charge crossing the twist	
8 units perpendicular to 8	-1	+1.241	+1.241	High mobility
	+1	+2.522	+2.522	High mobility
	-2	+3.155	+3.155	Low mobility
	-2	-3.086	-3.086	Low mobility
	+2	+2.449	+2.449	Low mobility
	+2	-2.108	-2.108	Low mobility
11 units perpendicular to 5	-1	-0.202	-1.739	High mobility
	+1	+0.760	+1.930	High mobility
	-2	+3.533	+3.533	Low mobility
	-2	-3.656	-3.656	Low mobility
	+2	+3.630	+3.630	Low mobility
	+2	-3.615	-3.615	Low mobility

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Figure 1 – Optimized geometry of PPV chain with 16 repeated monomer units and two planar segments perpendicular to each other and with the following lengths: (a) 8 monomer units each $(8 \perp 8)$; (b) one with 11 monomer units and the other with 5 monomer units $(11 \perp 5)$.

Figure 2 – Changes in the charges of carbons atoms (left-hand side) and dimerization pattern (right-hand side) of PPV caused by the injection of one electron (Q = -1) and one hole (Q = +1) in the PPV chain with 16 monomer units and two conjugated segments perpendicular to each other and with the following lengths: (a) 8 monomer units each $(8 \perp 8)$; (b) one with 11 monomer units and the other with 5 monomer units $(11 \perp 5)$. The marks indicate the data points that were calculated explicitly, whilst the curves are simply a guide to the eye. The vertical broken lines indicate the position of the twists.

Figure 3 – Changes in the charges of carbons atoms (left-hand side) and dimerization pattern (right-hand side) of PPV caused by the injection of two electrons (Q = -2) and two holes (Q = +2) in the PPV chain with 16 monomer units and two conjugated segments perpendicular to each other with 8 monomer units each $(8 \perp 8)$. The marks indicate the data points that were calculated explicitly, whilst the curves are simply a guide to the eye. The vertical broken lines indicate the position of the twists.

Figure 4 – Calculated mobility of a single injected electron (Q = -1) and hole (Q = +1) along the planar conjugated segments of a PPV chain with 8 (circles), 11 (triangles) and 16 (stars) monomer units. The marks indicate the data points that were calculated explicitly, whilst the curves are simply a guide to the eye.
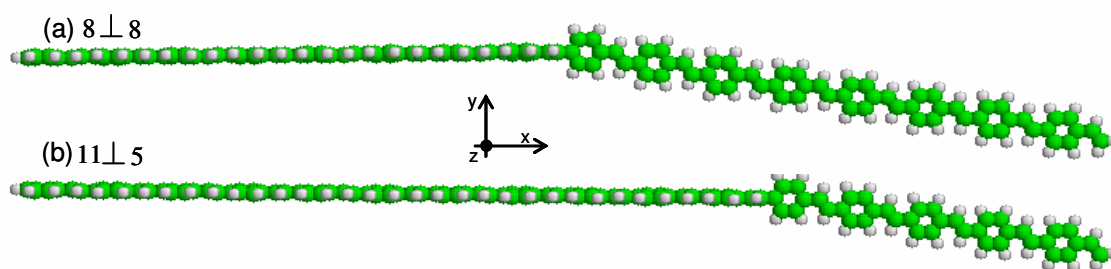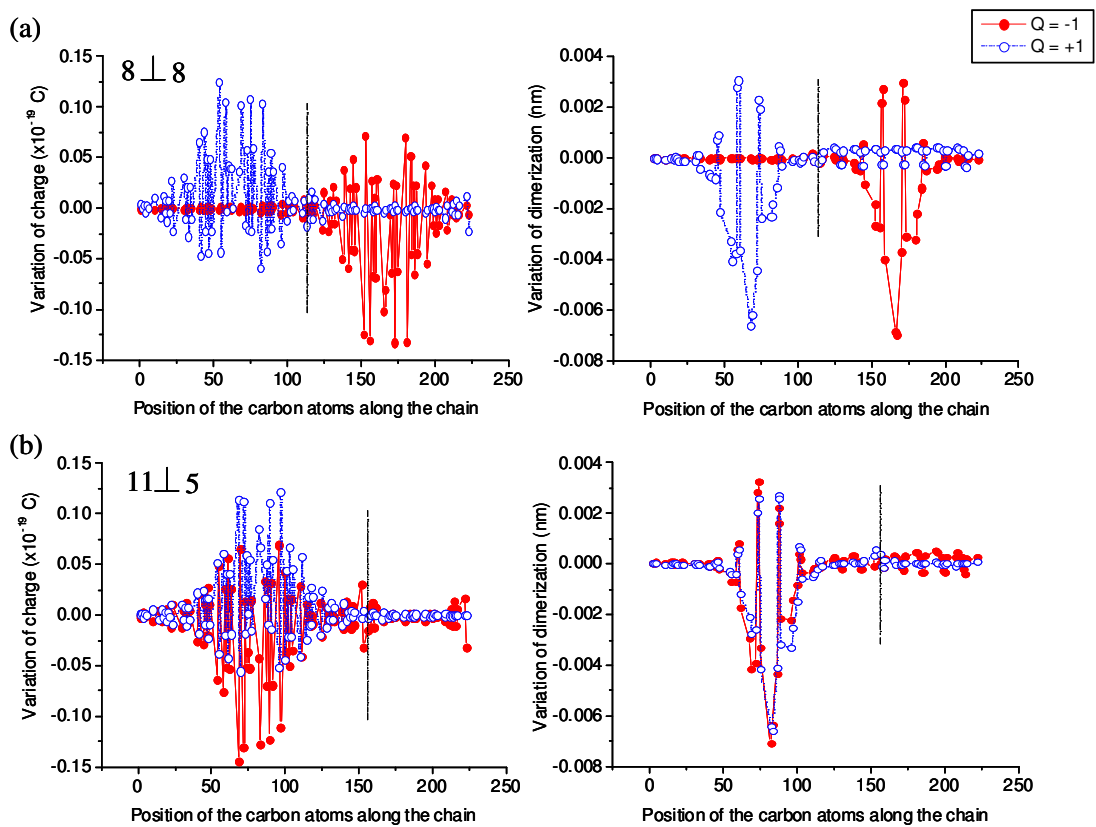
Figure 1

(a) 8⊥8

(b) 11⊥5
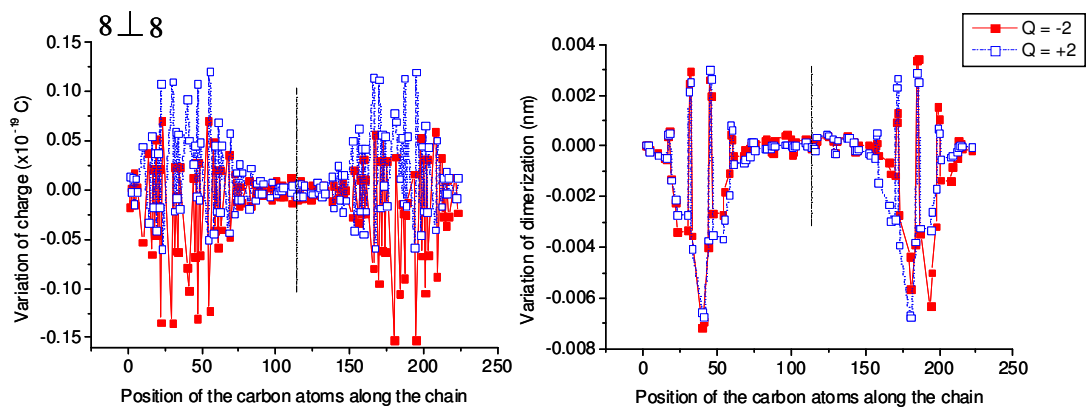
Figure 2

(a)

8⊥8

(b)

11⊥5

Figure 3

Figure 4