Influence of Polymerization Irregularities on the Electronic Properties of Polythiophene

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Abstract. The influence of $\alpha - \beta'(2-4')$ linkages on the electronic structure of long polythiophene chains is investigated, with particular attention devoted to the spatial localization of the $\pi$ levels. The results demonstrate that the presence of $\alpha - \beta'$ linkages increases the energy gap and leads to a spatial localization of the uppermost occupied levels within segments without defect. Deeper-lying extended states are also found, characterizing a mobility edge for the system.

1 Introduction

Polythiophene is currently one of the most investigated conjugated polymers. In particular, its 3-alkyl derivatives have attracted much interest since they are soluble in a variety of common solvents and lead to processable, highly conducting films. Although it is experimentally established [1 - 3] that in polythiophene (2,5-polythienylene) the thiophene rings are preferentially connected in $\alpha$ positions ($\alpha - \alpha'$ linkages), the presence of small amounts of $\alpha - \beta'$ (Fig. 1) linkages cannot be discarded, especially in the electrochemically prepared samples. This kind of ring-connection defects is expected to limit the transport properties of the polymer upon doping by decreasing the conjugation length. In fact, Wegner and Rühé [4] have recently estimated that the electrical conductivity could reach about 10 000 S/cm upon doping of a perfectly regular poly (2,5-thienylene), i.e. a value 20-50 times larger than what is usually obtained for polythiophene. This clearly illustrates the negative influence of the $\alpha - \beta'$ linkages on the transport properties.

In this work, we present a theoretical investigation of the role of $\alpha - \beta'$ linkages on the electronic structure of polythiophene chains, in particular their influence on the conjugation length (delocalization) of the upper occupied valence states. To this effect, we use the Negative Factor Counting technique (appropriate for large systems lacking translational symmetry) [5] from a Valence Effective Hamiltonian (VEH) [6,7] description of the electronic interactions. Details of our approach can be found elsewhere [8].

The geometries used for the VEH calculations are obtained from full AM1 (Austin Model 1) molecular geometry optimizations on three thiophene tetramers in which; (i) all three linkages are taking place at $\alpha - \alpha'$ positions ($\alpha\alpha\alpha$-quaterthienyl); (ii) the central linkage involves a $\alpha - \beta'$ connection ($\alpha\beta\alpha$-...
Polythiophene chains with up to 100 rings and containing various percentages of randomly located $\alpha - \beta'$ connections have been constructed. The evolution of the bandgap value as a function of defect concentration has been evaluated. We have also considered the degree of localization of the upper occupied valence levels. The corresponding eigenfunctions are obtained using the Inverse Iteration Technique [9]. From the eigenfunctions, the degree of localization is calculated with the help of the Inverse Participation Number (IPN) approach [10]; a fully extended, delocalized electronic level corresponds to an IPN value tending to zero when the chain length is large and, on the contrary, the stronger the localization of an electronic level, the bigger the IPN value gets (IPN equal to 1 for a fully localized state).

2 Results and Discussion

We have carried out NFC calculations for 100-ring polythiophene chains in the following cases: (i) a regular (all $\alpha - \alpha'$ connected) chain; (ii) a chain containing 25 regularly located $\alpha - \beta'$ linkages; and irregular chains presenting; (iii) 6% and; (iv) 19% random $\alpha - \beta'$ connections. The main electronic parameters together with the HOMO IPN values are collected in Table 1. (We note that a fully delocalized level would here correspond to an IPN value of $(1/400 \approx) 0.25 \times 10^{-2}$ [7].

The analysis of the data displayed in Table 1 shows that the bandgap energies for the chains presenting $\alpha - \beta'$ linkages are higher than in the regular, $\alpha - \alpha'$ connected 100-ring chain. However, the increase in bandgap value is less pronounced when the $\alpha - \beta'$ linkages are randomly distributed than in the case where they appear regularly: 0.47 eV for the chain with 25 regularly distributed $\alpha - \beta'$ linkages, only 0.24 eV for the chain presenting 19 random $\alpha - \beta'$ connections. The spatial delocalization of the HOMO levels is characterized by the