

# Theoretical study of charge-induced defects at metal/polymer interface

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## Abstract

Conducting polymers have attracted much attention concerning the possibility of their use as active components of electronic and optoelectronic devices. We use a molecular dynamics method with semi-empirical quantum chemistry at CNDO (complete Neglect of differential overlap) level to study the chemical interactions between aluminium atoms and *trans*-polyacetylene during the interface formation. Our results suggest that aluminium dimer ( $\text{Al}_2$ ) bound to a polymer chain is energetically more favourable than the adsorption of isolated aluminium atoms. In both cases, the compound formation is accompanied by charge transfer between metal and polymer. As a result charge rearrangement among the polyacetylene atoms is induced. We shall describe the charge-induced structural relaxation of the *trans*-polyacetylene backbone which is accompanied by a local change in the electronic structure of the polymer, commonly called defects. Copyright © 1998 Elsevier Science B.V.

*Keywords:* Atomistic modelling; Defects; Polyacetylene; Interfaces

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## 1. Introduction

Conjugated polymers exhibit metal-type conductivities while retaining the physical and mechanical properties characteristic of polymer materials. Because of their low cost and easy processing, these conducting polymers constitute a field of increasing scientific and technological interest, offering the potential to be used as electro-active materials [1–3]. Several difficulties exist in the interpretation of the observed device characteristics, namely those which arise from the formation of interfaces through reaction of metal electrodes with the polymer. Since the interfacial properties are directly influenced by the way in which the interface is formed, atomistic modelling can play an impor-

tant role in understanding the nature of metal–polymer interface, as well as it may suggest new methods for controlling or optimising interfaces.

The softness of conjugated polymers leads to strong coupling between the polymer's electrons and lattice vibrations (phonons) [4,5]. Therefore, it is necessary to perform self-consistent calculations of electronic wave functions and atomic positions in order to study the charge-induced defects in conjugated polymers as a result of chemical bonding at metal–polymer interface. We report here a self-consistent quantum chemistry molecular dynamics calculation of the interaction of aluminium atoms with an individual *trans*-polyacetylene strand. The chemical interaction of aluminium atoms with doped *trans*-polyacetylene is also discussed. It seems likely that the principles discussed will be applicable to other conducting polymers, with appropriate modifications dictated

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by differences in chemical composition, molecular structure and morphology. This study is also the stepping stone for further investigation of charge injection mechanisms in conjugated polymers.

## 2. Theoretical methods

Because of the very nature of the atomic processes, studies of both the chemical and the electronic structure of interfaces are essential. The approach we adopt, based on the Harwell CHEMOS code, consists in the self-consistent calculation of both electronic structure and molecular geometry of metal/polymer system, using a semi-empirical molecular orbital method [5–7]. The molecular orbital calculations were performed at CNDO (complete neglect of differential overlap) level using a linear combination of atomic orbitals (LCAO) and a cluster model framework. A molecular dynamical method was used in parallel to perform geometry optimisation. Forces on atoms are evaluated from electronic quantum-mechanical calculations. Our earlier work [8,9] gave results for static and dynamic behaviour of *trans*-polyacetylene in contact with metal electrodes modelled as a half-space with a well-defined Fermi level. We have extended our previous work by including chemical interactions between metal atoms and between those and the polymer.

## 3. Results and discussion

### 3.1. The isolated *t*-PA chain

In the course of modelling aluminium–polyacetylene interfaces, we will concentrate on the properties of an individual *trans*-polyacetylene (*t*-PA) strand. Before any chemical interaction is considered we have relaxed the geometry of a finite *t*-PA chain to equilibrium, starting off the planar configuration.

The charge transfer between different species is induced by their chemical potential difference. Since the calculated chemical potential of *t*-PA decreases as a function of chain length to a nearly constant value for

a chain of 20 carbon atoms [8], the ground state geometry of a free-defect *t*-PA chain was found examining a  $t\text{-C}_{20}\text{H}_{22}$  molecule. Our results are in good agreement with experimental observations of the dimerisation amplitude [10].

We have addressed the interaction of aluminium atoms with doped *t*-PA by examining the behaviour of the  $t\text{-C}_{19}\text{H}_{21}$  molecule as a model for a soliton in *t*-PA. The (positively and negatively) charged and uncharged solitons have been considered. These are the defects generated in individual polyacetylene molecules by n-type and p-type dopants [11].

### 3.2. Aluminium atoms on *t*-PA

In order to study the interactions of evaporated aluminium atoms with *t*-PA, we have simulated the bonding of two Al atoms to an individual *t*-PA molecule, in accordance with low coverage UPS experiments. The aluminisation of *t*-PA was modelled in the following way. Two aluminium atoms were brought close to the polymer, while the *t*-PA atoms were kept frozen. When the equilibrium was reached for metal atoms, the entire system was allowed to relax.

#### 3.2.1. Preferential reaction sites

Aluminium atoms are found to interact strongly with *t*-PA chain either isolated or as dimers ( $\text{Al}_2$ ), both bonding positions being stable. A binding energy difference of approximately 3 eV was obtained for the adsorption positions indicated above. The fundamental interaction unit predicted corresponds to the formation of  $\text{Al}_2$ –polyacetylene complex. Our results also suggest that the most stable position for the aluminium dimer is out of the polymer plane with both aluminium atoms adsorbed onto twofold site. These results hold for *t*-PA with and without a soliton-type defect.

Preliminary calculations suggest serious overestimates of the magnitudes of binding energies [12]. Whilst we should not regard binding energies as accurate, we expect the predicted trends for preferred reaction sites to be reliable.

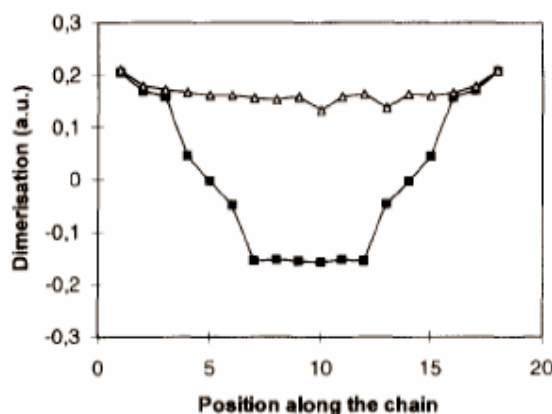


Fig. 1. Dimerisation patterns in a *t*-PA chain with 20 carbon atoms when: (a) two isolated aluminium atoms are bound to *t*-PA (square); (b) an aluminium dimer ( $\text{Al}_2$ ) is bound to the polymer chain (triangle). The dimerisation is defined [5,6] by the difference in C–C bond lengths at each carbon (e.g. left-hand bond length minus right-hand bond length, so the dimerisation changes sign across a soliton). The marks indicate the data points that were calculated explicitly. The curves are simply a guide to the eye.

### 3.2.2. Defect states in *t*-PA

The chemical interaction between aluminium and *t*-PA leads to a distortion of the *t*-PA fragment both parallel and perpendicular to the molecular plane, which, in turn, leads to a local change in the electronic structure of the polymer. The new localised electronic states, commonly called defects, arise within the *t*-PA energy gap due to electron–lattice coupling.

The geometrical distortion in the bond length distribution of a free-defect *t*-PA chain corresponding to the aluminium adsorption indicated above is shown in Fig. 1. The resulting distortion patterns show three main features. First, the degree of dimerisation increases slightly towards the ends of the polymer chain. Second, the distortion due to an aluminium dimer bound to a single *t*-PA chain loosely resembles that of a polaron-type defect [4,5], with a more marked distortion on a few atoms at the centre of the defect. Third, the adsorption of two isolated Al atoms to *t*-PA gives two well-separated solitons. Both chemical interactions lead to a molecular distortion perpendicular to the polymer plane as well as in-plane distortion, the latter being the dominant term.

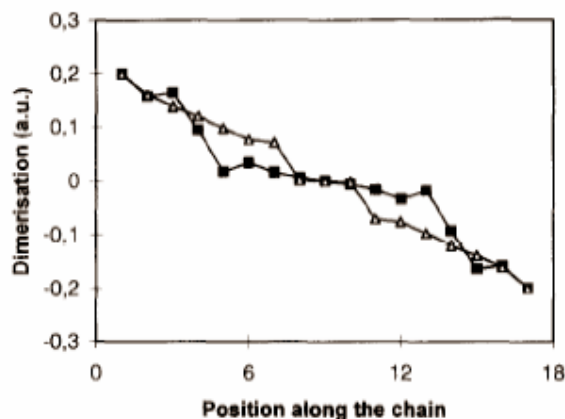


Fig. 2. Dimerisation patterns for a positive soliton in *t*-PA when: (a) two isolated aluminium atoms are bound to *t*-PA (square); (b) an aluminium dimer ( $\text{Al}_2$ ) is bound to the polymer chain (triangle). The dimerisation is defined [5,6] by the difference in C–C bond lengths at each carbon (e.g. left-hand bond length minus right-hand bond length, so the dimerisation changes sign across a soliton). The marks indicate the data points that were calculated explicitly. The curves are simply a guide to the eye.

The effects of aluminium bonding on dimerisation pattern of positive soliton in *t*-PA are shown in Fig. 2. The calculated dimerisations loosely resemble that of a soliton in *t*-PA [4,5]. Moreover, the dimerisation is reduced in the centre of the positively charged  $t\text{-C}_{19}\text{H}_{21}$  molecule when two isolated Al atoms are bound.

### 3.2.3. Aluminium-induced charge transfer

When a free-defect *t*-PA molecule is put in contact with aluminium atoms charge will flow until the chemical potentials of both materials are equal [13]. The electron affinity  $A(N)$  and ionisation energy  $I(N)$  can be combined to yield the chemical potential, and the arithmetic average of  $I(N)$  and  $A(N)$  [8]. Electron transfer from aluminium to *t*-PA is predicted for the adsorption of two isolated aluminium atoms while electron transfer in opposite direction is predicted for an aluminium dimer bound to a *t*-PA chain (containing or not a defect).

The charge transfer from or to a free-defect *t*-PA chain is found to be about 0.4 electrons. Our results also suggest that approximately 30% of the charge is stored on the hydrogen atoms, rather than the entire charge resting on the carbon atoms of chain. The



Table 1

Atomic (Mulliken) charges of aluminium, carbon and hydrogen atoms when an aluminium dimer ( $\text{Al}_2$ ) is bound to a (positively and negatively) charged and uncharged *t*-PA molecule with a soliton-type defect (chain of 19 carbons)

Molecular charge	Atomic charge (electrons)		
	Aluminium atoms	Carbon atoms	Hydrogen atoms
Positive	-0.1392	0.7659	0.3729
Negative	-0.4466	-0.1384	-0.4150
Neutral	-0.3497	0.3414	0.0081

amount of charge transferred to a soliton in *t*-PA due to the adsorption of an aluminium dimer is shown in Table 1. For a positive or a negative soliton in *t*-PA we find a charge alternation on carbon atoms, which is consistent with the interpretation of XPS experiments [14]. The charge stored on hydrogen atoms do not display this alternation.

#### 4. Conclusions

We have studied localised electronic states in individual *t*-PA molecules as a result of chemical bonding at aluminium–polyacetylene interface. The reaction of aluminium atoms with a free-defect *t*-PA chain could lead to the formation of either a polaron-type defect or two well-separated solitons. In the case of doped *t*-PA, changes in soliton deformation pattern apparently occur. Moreover, the metal induces electron transfer from or to *t*-PA depending on the relative position of the Fermi levels of both materials.

Self-consistent quantum chemistry molecular dynamics calculations, such as those reported here, are a useful tool for atomistic modelling of interfacial

bonding at metal–polymer interface as well as for providing data which is currently impossible to obtain experimentally.

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