Abstract
In order to explore polymers with precisely defined molecular architecture and to better explore structure-property relationships, spectroscopic results are combined with theoretical ones in order to describe the copolymerization mechanism of poly(vinyl)carbazole and 3-methylthiophene. The unpaired electron spin densities of radical cations are determined at the different steps during the oligomerization using DFT calculations. The purpose is to propose an oligomer model that reflect properties of the copolymer (PVKMeT).

Keywords: conjugated polymers, PVK, DFT calculations, copolymerization mechanism.
Introduction

Polymers with carbazole groups such as polyvinylcarbazole (PVK) [1] were largely investigated because of their photoconductivity, photoluminescence and hole transport properties [2]. PVK has attracted attention in applications related to organic light emitting diodes (OLED) [3]. Trends of organic EL devices based on PVK have been focused both on optimizations of EL structure and developing new materials [4]. Different types of EL structures have been proposed [5]. Devices in which the emitting layer is formed by PVK blended with oligothiophene have shown remarkable increase in luminescence efficiency [6]. There is still existing demand for searching more efficient material with the simplified architecture. In this context, copolymers with alternating patterns of a low gap poly(3-octylthiophene) or poly(3-methylthiophene) and PVK were synthesized and characterized [7]. An increase of the external quantum efficiency in diodes based on these materials was observed.

In order to explore polymers with precisely defined molecular architecture and to better explore structure-property relationships, we propose in this work a combined experimental and theoretical results of a copolymer based on poly(vinyl)carbazole and 3-methylthiophene (PVKMeT). This copolymer has been synthesized by FeCl₃ oxidative coupling reaction and characterized.

Firstly, spectroscopic results are combined with theoretical ones in order to describe the copolymerization mechanism. The unpaired electron spin densities of radical cations, which allow the knowledge of the reactivity for coupling reactions are calculated at the different steps during the oligomerization using DFT calculations. The purpose is to propose an oligomer model that reflects properties of the copolymer.

Then, we explore these quantum chemical calculations to provide a complete characterization of the molecular geometry, electronic structure and spectroscopic characteristics of this oligomer, which may be envisaged as the simplest model of the PVKMeT copolymer. These properties have been predicted using DFT calculation (B3LYP/6-31G*). Thus, DFT calculations have been used intensively by our group in various cases to predict torsional potentials and electronic properties existing in the real polymers based on thiophene and phenylene [8]. We hope that the present results could help to clarify whether the structure of the neutral copolymer as suggested by experimental results [7].

Computational methods

The unpaired electron spin densities of radical cations are calculated using density functional theory (DFT) of three-parameter compound functional of Becke (B3LYP) [9]. The 6-31G(d) basis set was used for all calculations [10]. The geometric structures of neutral molecules were optimized under no constraints. Furthermore, geometry structures of radical cations were optimized independently from the neutral molecules prior to the calculations of spin densities. Radical cations were treated as open shell systems (UB3LYP). The HOMO, LUMO and gap’s energies were also
deduced for the stable structure of the neutral and oxidized forms. Electronic transition energies and oscillator strengths of oligomers were obtained by the semi empirical ZINDO method [11]. All calculations were performed using the Gaussian 98 program [12].

Results and discussion

A generally accepted mechanism for the coupling reaction of conjugated monomers, which consists of two step reactions. The first step is one-electron oxidation of the monomer to form its radical cation. The second step is a coupling reaction of two radical cations to form a dihydro-dimer cation which is followed by the elimination of two protons two form a neutral dimer [13].

To simplify calculations, we have used the N-propylcarbazole as a model of the PVK. Fig 1 lists the calculated total atomic spin densities of radical cations for 3-methylthiophene and N-propylcarbazole.

Fig. 1: Calculated total atomic spin densities of radical cations for 3-methylthiophene (T) and N-propylcarbazole (Cbz)

The highest spin densities are observed respectively at C1 of 3-methylthiophene and C3, C3’ of the carbazole. In contrast, low spin densities are obtained at C3 of the thiophene ring and C4, C4’ of the carbazole (Fig. 1). For examining the initiating and propagating reactions, it is reasonable to assume that coupling reactions preferentially occurred between carbones having higher spin densities [14]. These facts indicates that the reactivity for the propgation reaction of the radical cation can be realized from C1 of 3-methylthiophene and C3, C3’ of the carbazole. When two molecules of 3-methylthiophene (T) are chemically coupled with N-propylcarbazole (Cbz), we can generate the oligomer named TCbzT as shown in Fig. 2.

Fig. 2: TCbzT
The calculated spin densities of this oligomer are shown in brackets. Fig 3 summarises the reaction paths of succeeding coupling reaction of TCbzT based on calculated spin densities. Three oligomers can be generated as shown in Fig.3.

![TTTCbzTTT (oligo 1)](image1)

![CbzTCbzTTT (oligo 2)](image2)

![TCbzTTcTZ (oligo 3)](image3)

**Fig. 3: Reactions paths of the oligomerization**

On the other hand, when two molecules of Cbz are chemically coupled with each other, another dimer can be generated named CbzCbz as shown in Fig.4. The coupling with two molecules of T gives another oligomer named oligo 4 (Fig.5).

![CbzCbz](image4)

**(0.039820)
(-0.018132)**

**Fig. 4: CbzCbz**

![CbzCbz + 4 T → TTTCbzCbzTT (oligo 4)](image5)

**Fig. 5: TTTCbzCbzTT (oligo 4)**
According to the experimental preparation of the copolymer PVKPMeT, we believed that firstly we formed a cross linked PVK as shown in scheme 1. Then, when we added the 3-methylthiophene (T), it oxidizes to form a radical cation (Scheme 1).

Scheme 1: (Cross linking reaction involving PVK and FeCl₃ as oxidant)

Scheme 2: Formation of radical cation of 3-methylthiophene

Scheme 3: Grafting of 3-methylthiophene onto dimer of PVK
These features are somewhat similar to those reported by Block et al. [15]. Since the oxidation of dimer is easier than that of the monomer, the reactivity of the second step should be between a radical cation of this dimer (PVKPVK) and the radical cation of the dimer of 3-methylthiophene as shown in Scheme 3.

For our theoretical study basis on calculated spin densities using DFT. We have proposed four oligomer structures. The structure of the last oligomer (oligo 4), displayed in Fig 6, seems to be the better reflecting the experimental properties.

![Optimized structure of TTCbzCbzTT](image)

**Fig. 6: Optimized structure of TTCbzCbzTT**

The inter atomic distance (Å), the angles and dihedral angles (°) of the optimized geometry of this oligomer are listed in Table 1.
Table 1: Calculated atomic distance, the angles and dihedral angles of oligo 4

<table>
<thead>
<tr>
<th>Bond</th>
<th>Atomic Distance</th>
<th>Angles and dihedral angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1-C1'</td>
<td>1.485</td>
<td>C6'-C1-C1</td>
</tr>
<tr>
<td>C1-C2</td>
<td>1.400</td>
<td>C1-C1-C2</td>
</tr>
<tr>
<td>C2-C3</td>
<td>1.397</td>
<td>C2-C3-C9</td>
</tr>
<tr>
<td>C3-C4</td>
<td>1.420</td>
<td>C12-C11-C14</td>
</tr>
<tr>
<td>C4-N7</td>
<td>1.396</td>
<td>C11-C14-C15</td>
</tr>
<tr>
<td>C6-C9</td>
<td>1.419</td>
<td>C18-C17-C19</td>
</tr>
<tr>
<td>C9-C10</td>
<td>1.396</td>
<td>C6'-C1-C1-C6</td>
</tr>
<tr>
<td>C10-C11</td>
<td>1.402</td>
<td>C12-C11-C14-S18</td>
</tr>
<tr>
<td>C11-C14</td>
<td>1.471</td>
<td>S18-C17-C19-S23</td>
</tr>
<tr>
<td>C14-C15</td>
<td>1.383</td>
<td></td>
</tr>
<tr>
<td>C15-C16</td>
<td>1.425</td>
<td></td>
</tr>
<tr>
<td>C16-C17</td>
<td>1.378</td>
<td></td>
</tr>
<tr>
<td>C17-C19</td>
<td>1.453</td>
<td></td>
</tr>
<tr>
<td>C14-S18</td>
<td>1.755</td>
<td></td>
</tr>
<tr>
<td>C19-C20</td>
<td>1.358</td>
<td></td>
</tr>
<tr>
<td>C20-C21</td>
<td>1.431</td>
<td></td>
</tr>
<tr>
<td>C21-C22</td>
<td>1.365</td>
<td></td>
</tr>
<tr>
<td>C22-S23</td>
<td>1.731</td>
<td></td>
</tr>
</tbody>
</table>
Considering these geometries, we have presented in Fig. 7 as an example of the energy diagram of oligo 4.

![HOMO and LUMO orbitals of oligo 4](image)

**Fig. 7**: The energy diagram of HOMO and LUMO orbitals of oligo 4

In Table 2, we present the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy and $\Delta E$ (the calculated energy differences between LUMO and HOMO). The theoretical calculated band gap of oligo 4 agree to within 0.5 with experiment. We believe that this difference results from the intermolecular effects that they must be taken into account when we consider the copolymers with long chain.

**Table 2**: Calculated HOMO (eV), LUMO (eV) and $\Delta E$ (gap) (eV) of obtained oligomers as well as experimental gap of copolymers.

<table>
<thead>
<tr>
<th></th>
<th>Oligo1</th>
<th>Oligo2</th>
<th>Oligo3</th>
<th>Oligo4</th>
<th>Copolymer**</th>
</tr>
</thead>
<tbody>
<tr>
<td>E(LUMO) (ev)</td>
<td>-1.554</td>
<td>-1.465</td>
<td>-1.574</td>
<td>-1.061</td>
<td></td>
</tr>
<tr>
<td>E(HOMO) (ev)</td>
<td>-4.860</td>
<td>-4.751</td>
<td>-4.827</td>
<td>-4.820</td>
<td></td>
</tr>
<tr>
<td>$\Delta E$ (gap)</td>
<td>3.305</td>
<td>3.28</td>
<td>3.252</td>
<td>3.76</td>
<td>4.033</td>
</tr>
</tbody>
</table>

**Experimental value

The vibrational assignments of the FTIR spectra of the neutral copolymer have been previously reported [16]. In addition, to confirm the proposed assignment, theoretical vibrational calculations were performed using DFT. The experimental and calculated wavenumbers and the assignments are presented in Table 3. Although, a little difference (about 100 cm$^{-1}$), which was already explained, a good agreement with experimental values was observed.
Table 3 : Experimental and calculated Wavenumbers of IR bands

<table>
<thead>
<tr>
<th>Exp Freq of copolymer (cm⁻¹)</th>
<th>Calculated freq of oligo 4 (cm⁻¹)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>695</td>
<td>816</td>
<td>C-H out of plane vibration of thiophene</td>
</tr>
<tr>
<td>785</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1157</td>
<td>1311</td>
<td>C-H panel deformation of aromatic ring</td>
</tr>
<tr>
<td>1319</td>
<td>1419</td>
<td>C-H deformation of vinylidene group</td>
</tr>
<tr>
<td>1624</td>
<td>1547</td>
<td>Ring vibration of carbazole</td>
</tr>
<tr>
<td>3060</td>
<td>3192</td>
<td>Stretching of aromatic structure</td>
</tr>
</tbody>
</table>

**Conclusion**

The reactivity for coupling reaction between 3-methylthiophene and polyvinylcarbazole are inferred from the calculated unpaired electron spin densities of the respective radical cations. The major regioselective products of the polymerization reactions were well understood in terms of the magnitude of calculated spin densities of several oligomers. Based on the reactivity of C1 of 3-methylthiophene and C3’ of N-propylcarbazole, we predict the most oligomerization mechanism via the proposed reaction paths of the succeeding coupling reactions of these two monomers. Four oligomers can be generated and according to the experimental results, it appears that the structure of the oligo 4 (TCbzCbzT) seems to be the better reflecting the experimental properties.

**Acknowledgements**

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References