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PREDICTION OF COPOLYMERIZATION MECHANISM OF POLY(VINYL)CARBAZOLE AND 3-METHYLTHIOPHENE

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Abstract

In order to explore polymers with precisely defined molecular architecture and to better explore structure-propertie relationships, spectroscopic results are combined with theoretical ones in order to describe the copolymerization mechanism of poly(vinyl)carbazole and 3-methylthiophene. The umpaired electron spin densities of radical cations are determined at the differents 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 witch the emitting layer is formed by PVK blended with oligothiophene have shown remarquable increase in luminescence efficiency [6]. There still existing demand for searching more efficient material with the simplified architecture. In this context, copolymers with altenating patterns of a low gap poly(3-octylthiophene) or poly(3-methylthiophene) and PVK were sythesized 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-propertie 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 $FeCl_3$ oxidative coupling reaction and characterized.

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

Then, we explore these quantum chemical calculations to provide a complete characterization of the molecular geometry, electronic structure and spectroscopic charcterisctics of this oligomer, which may be envisaged as a 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 case 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.
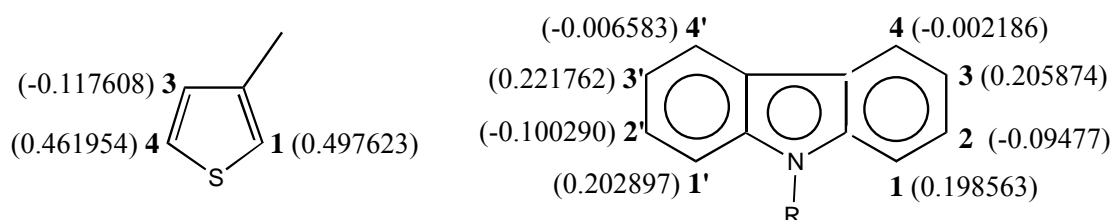

Fig. 1: Calculated total atomic spin densities of radical cations for 3-methylthiophene (T) and N-propylcarbazole (Cbz)

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 occured 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-methulthiophene (T) are chemically coupled with N-propylcarbazole (Cbz), we can generate the oligomer named TCbzT as shown in Fig. 2.
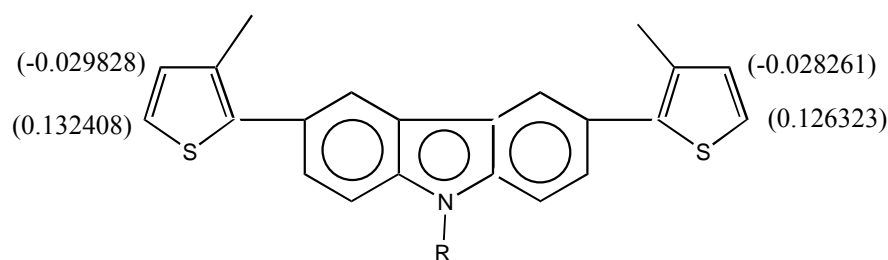

Fig. 2 : TCbzT

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.
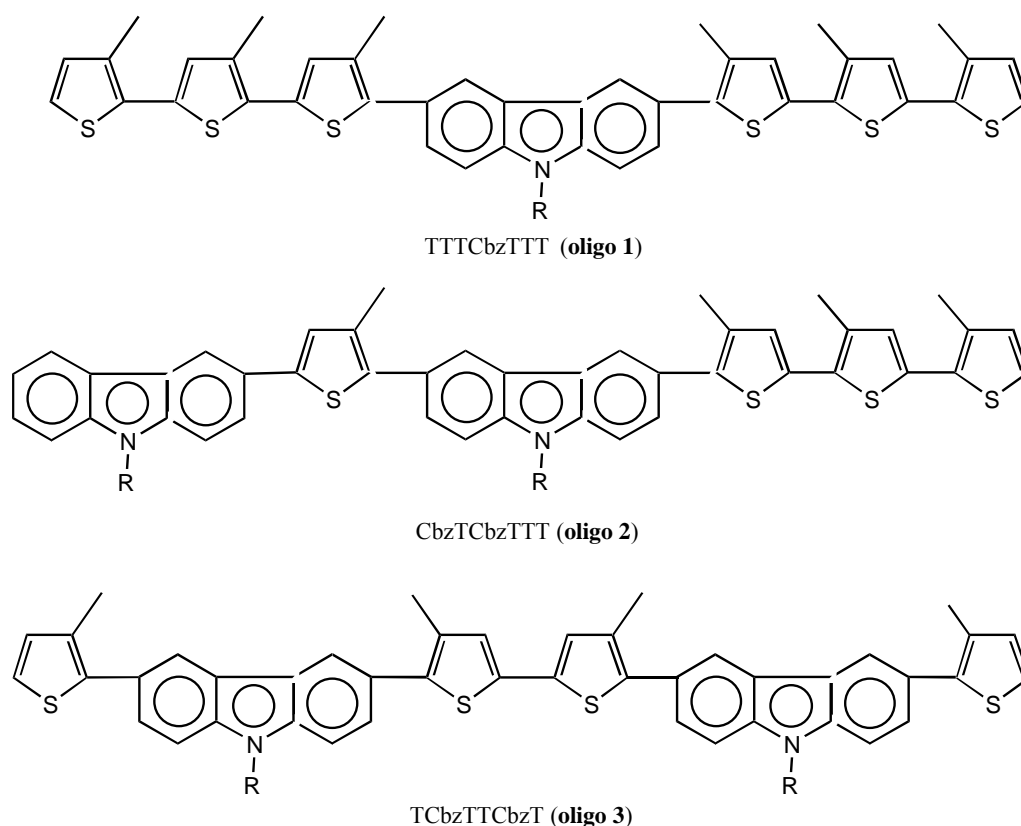

TTTCbzTTT (**oligo 1**)

CbzTCbzTTT (**oligo 2**)

TCbzTTCbzT (**oligo 3**)

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).
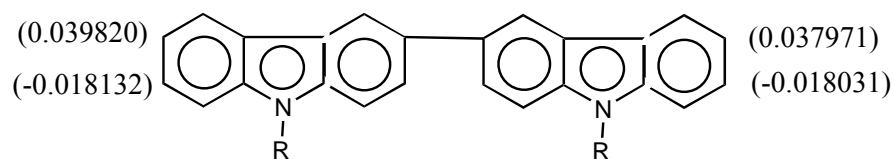
(0.039820)   (0.037971)
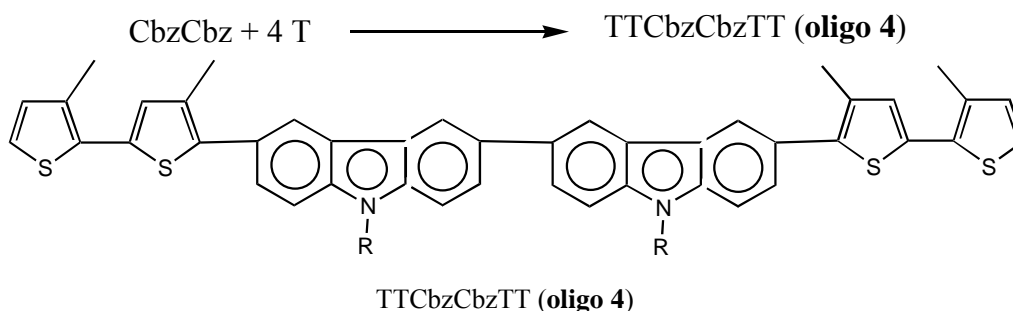(-0.018132)   (-0.018031)

Fig. 4: CbzCbz

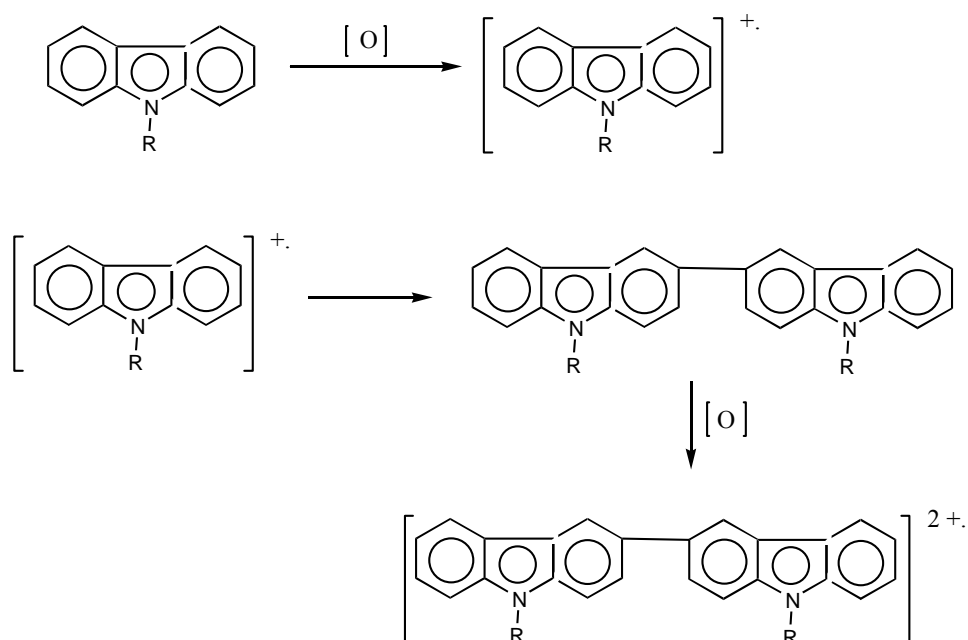CbzCbz + 4 T ⟶ TTCbzCbzTT (**oligo 4**)

TTCbzCbzTT (**oligo 4**)

Fig. 5: TTCbzCbzTT (**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 oxydant)
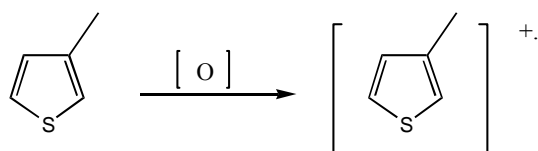
Scheme 2: Formation of radical cation of 3-methylthiophene
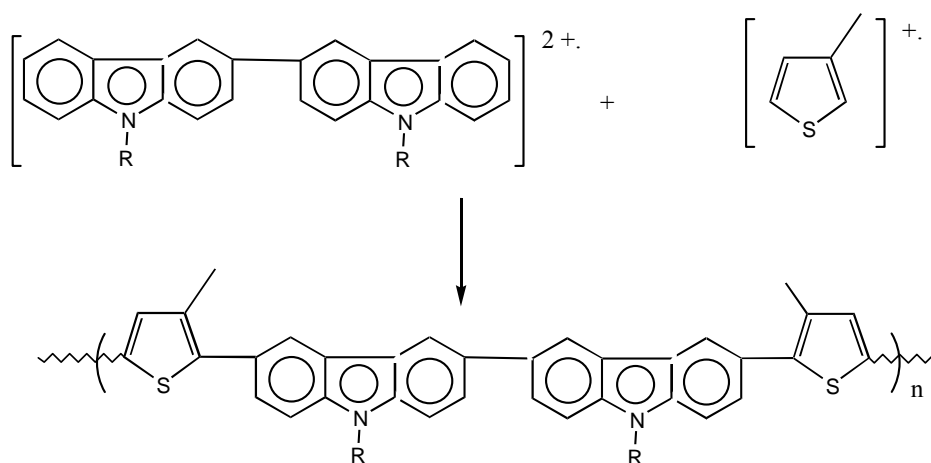
Scheme 3: Grafing of 3-methylthiophene onto dimer of PVK

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 sowhn 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), diplayed in Fig 6, seems to be the better reflecting the experimental properties.
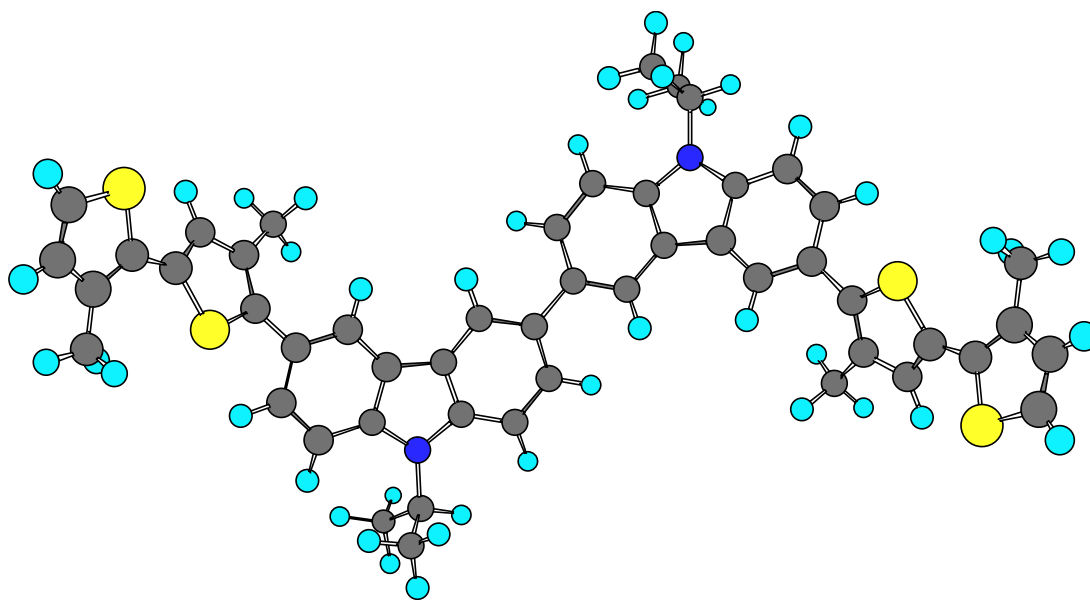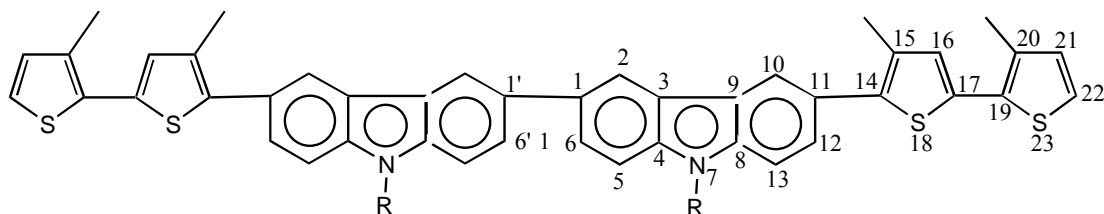

Fig. 6: Optimized structure of TTCbzCbzTT

The inter atomic distance (Å), the angles and dihedralangles (°) of the optimized geometry of this oligomer are listed in Table 1.

Table 1: Calculated atomic distance, the angles and dihedralangles of oligo 4

Bond		Angles and dihedral angles	
C_1-C_1'	1.485	$C_6'-C_1'-C_1$	120
C_1-C_2	1.400	$C_1-C_1'-C_2$	121.128
C_2-C_3	1.397	$C_2-C_3-C_9$	132.955
C_3-C_4	1.420	$C_{12}-C_{11}-C_{14}$	120.92
C_4-N_7	1.396	$C_{11}-C_{14}-C_{15}$	129.94
C_8-C_9	1.419	$C_{18}-C_{17}-C_{19}$	122.755
C_9-C_{10}	1.396	$C_6'-C_1'-C_1-C_6$	38.931
$C_{10}-C_{11}$	1.402	$C_{12}-C_{11}-C_{14}-S_{18}$	41.837
$C_{11}-C_{14}$	1.471	$S_{18}-C_{17}-C_{19}-S_{23}$	148.067
$C_{14}-C_{15}$	1.383		
$C_{15}-C_{16}$	1.425		
$C_{16}-C_{17}$	1.378		
$C_{17}-C_{19}$	1.453		
$C_{14}-S_{18}$	1.755		
$C_{19}-C_{20}$	1.358		
$C_{20}-C_{21}$	1.431		
$C_{21}-C_{22}$	1.365		
$C_{22}-S_{23}$	1.731		

Considering these goemetries, we have presented in Fig. 7 as an exemple of the energy diagram of oligo 4.

HOMO   LUMO

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 ΔE (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 ΔE (gap) (eV) of obtained oligomers as wel as experiemental gap of copolymers.

	Oligo1	Oligo2	Oligo3	Oligo4	Copolymer**
E(LUMO) (ev)	-1.554	-1.465	-1.574	-1.061	
E(HOMO) (ev)	-4.860	-4.751	-4.827	-4.820	
ΔE (gap)	3.305	3.28	3.252	3.76	4.033

** 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 calculatd Wavenumbers of IR bands

Exp Freq of copolymer (cm^{-1})	Calculated freq of oligo 4 (cm^{-1})	Assignments
695 785	816	C-H out of plane vibration of thiophene
1157	1311	C-H panel de f of aromatic ring
1319	1419	C-H deformation of vinylidene group
1624	1547	Ring vibration of carbazole
3060	3192	Stretching of aromatic structure

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 term 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) sems to be the better reflecting the experimental properties.

Acknowledgements

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