Synthesis and characterization of a copolymer involving PVK and MEH-PPV for organic electronic devices

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ARTICLE INFO

Keywords:
A. Polymers
B. Chemical synthesis
C. Ab initio calculations
C. Optical properties

ABSTRACT

A statistic copolymer denoted (PVK)x-(MEH-PPV)y containing poly(N-vinylcarbazole) (PVK) as well as poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) building blocks was prepared by chemical oxidative way. Correlations structure-properties of the synthesized copolymer were investigated by using different experimental analyses (IR, XRD, ATG, optical absorption, PL and PLRT) combined with theoretical calculations (DFT). The new copolymer exhibits interesting properties compared to PVK and MEH-PPV homopolymers taken separately. The resulting copolymer has improved thermal stability and it exhibits original optical properties compared to the PVK and MEH-PPV ones as well as its revealed charge transfer process and the continuous donor acceptor existence. All these experimental and theoretical analysis argue the originality of this new material which could then be exploited in optoelectronics.

1. Introduction

The emergence of organic electronics is related, in particular, to the active layer which is generally a polymer or a composite including a polymer [1–6]. Among polymers, poly(p-phenylenevinylene) (PPV) [7], poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) [8] and Poly(N-vinylcarbazole) (PVK) have been a dominant active layer in organic displays. Thus, copolymers including PVK, PPV or MEH-PPV seems to be a perspective optoelectronic material for utilization in organic electronic. In this paper, we elaborate a new copolymer involving PVK and MEH-PPV by chemical oxidative way using the anhydrous FeCl₃ as oxidant. The purpose of synthesising this copolymer is to combine the properties of MEH-PPV and PVK and also to compare it with PVK-PPV copolymer previously prepared by M. Mbarek and all [9]. PVK-PPV have a very interesting properties adapted for organic electronic but its insolubly limit its deposition in thin films without risk of its decomposition. So this handicap limits its use as an active layer in organic devices. So we have substituted PPV (insoluble) with MEH-PPV which is soluble. Based on PVK-PPV properties and then of PVK as well as those of MEH-PPV, we try to synthesis the same material on subtitling PPV by MEH-PPV. In order to give a description of this new copolymer, various experimental measurements including infrared (IR) absorption, X-rays diffraction, thermogravimetric analysis, optical absorption, photoluminescence and time resolved photoluminescence are performed. The experimental part is completed by a theoretical studies based on Density Functional Theory (DFT) to better describe structure-properties relationship.

2. Experimental and computational details

2.1. Characterization techniques

The infrared spectrum was obtained with a Nicolet iS10 infrared spectrometer: note that the sample was put on a platinum substrate before measurement with OMNIC software adapted to this spectrometer. Thermal gravimetric analysis (TGA) of the copolymer were performed using TGAQ50 (TA instruments) controlled by a heat control program, the thermal degradation was carried out between 20 and 800 °C at a speed rate of 5 °C/min under a nitrogen atmosphere. Siemens 5000 diffractometer (Cu Kα radiation λ=1.5405 Å, generator voltage=40 kV and generator current=30 mA) was used to study the structural properties. All the optical spectrums were measured in solid state. The optical absorption measurements were realized using a Cary 5000 spectrometer at room temperature. The photoluminescence measurements (PL) were obtained using a Jobin-YvonFluorolog 3 spectrometer equipped with a Xenon lamp (500 W).

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http://dx.doi.org/10.1016/j.jpcs.2016.11.018
Received 26 June 2016; Received in revised form 11 November 2016; Accepted 15 November 2016
Available online 30 November 2016
0022-3697/ © 2016 Published by Elsevier Ltd.
Time-resolved photoluminescence (TR-PL) experiments were performed with a regenerative amplified femtosecond Ti: Sapphire laser system (Spectra Physics Hurricane X).

2.2. Synthesis

Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) (Mn = 40,000–70,000), poly(N-vinylcarbazole) (PVK) (Mn = 25,000–50,000), ferrichloride (FeCl3), chloroform, ethanol and hydrazine used for the synthesis of the copolymer were purchased from Sigma Aldrich.

The (PVK)x-(MEH-PPV)y statistic copolymer was synthesized by a chemical oxidative reaction using FeCl3 as the oxidizing agent. Firstly, 120 mg of PVK was dissolved and stirred in 25 ml of chloroform (CHCl3), before adding to this mixture another chloroform solution (25 ml again) containing 120 mg of MEH-PPV, 1 g of FeCl3 dispersed in 40 ml of CHCl3 and kept in a flask under argon was introduced to the stirred solution. The colour of the solution changed rapidly from orange to red dark then to black and the reaction was kept under stirring and heating at a temperature of 55 °C for 72 h. Then, to eliminate the residues of FeCl3, an excess of ethanol was added and the resulting solution was filtered several times. As expected with such experimental conditions and as evidenced by the colour changing, we should obtain the oxidized material [10]: this is why in order to obtain the polymer in the neutral state, we mixed then the crude solid into 40 ml of ethanol for 24 h, before adding 5–10 ml monohydrate hydrazine for 12 h. Once again we can follow the success of the depolymerisation by a colour modification, the solution tuning from dark black to beige. Finally, the precipitate was filtered under pressure then washed for several times with ethanol and dried under vacuum overnight. We obtained the (PVK)x-(MEH-PPV)y copolymer in neutral state with 57% polymerisation yield. It was insoluble in common solvents. To characterize the synthesized copolymer, two or three samples of copolymer are tested several times to ensure the stability and reproducibility of results.

2.3. Computational details

All calculations were performed with considering isolated molecules in the gas phase by the Gaussian 09 program [11] using the hybrid B3LYP (Becke three-parameter Lee-Yang-Parr) exchange correlation functional with the 6–31 G(d) basis set for the optimization and for the vibrational properties. Optical properties have been calculated using Dependent Density Functional Theory (TD-DFT) with the B3LYP functional [12]. The photoluminescence was obtained by a re-optimization using the configuration interaction singles (CIS) method [13] with 6–31 G (d) in the first time and then the photoluminescence was determined by ZINDO/6–31 G (d) method and after that it was compared with experimental data. The electronic transitions, their correspondent wave lengths and the oscillator strengths were obtained by using the same basis set via the SWIIZARD program [14]. Gaussian 2.2.5 program was used to carry out the density of states (DOs).

3. Results and discussion

3.1. Infrared analysis

As expected, the experimental FT-IR spectrum of our copolymer revealed the presence in majority of bands corresponding to PVK [9] homopolymer as well as those of MEH-PPV [15-16] homopolymer as observed in Fig. 1. Thus, the FT-IR spectrum shows the majority of PVK peaks at 721 cm\(^{-1}\) assigned to the ring deformation, at 742 assigned to the CH\(_2\) vibratation and at 929, 1022, 1126, 1155, 1220, 1325, 1600 and 1625 cm\(^{-1}\) corresponding to the C-C vibration, the C-C stretching, the C-H deformation in plane, the C-H deformation in plane of aromatic ring, C-N stretching, C-H deformation of vinlylidene groups, the CH\(_2\) stretching and the C-C stretching of benzene respectively. In another hand, we have identified the vibrations of MEH-PPV; these vibrations are the 869 cm\(^{-1}\) out-of-plane phenyl CH wag, the 1380 cm\(^{-1}\) symmetric alkyl CH\(_2\) deformation, the 1469 cm\(^{-1}\) anti-symmetric alkyl CH\(_2\) and the 1600 cm\(^{-1}\) asymmetric phenyl semicircular stretch. However, it must be noticed that some new bands appeared, indicating that during the oxidative reaction the two reactive polymers have been established a chemical bonding: in particular, a band located at 1076 cm\(^{-1}\) and also the band located at 792 cm\(^{-1}\), which can be related to the formation of bizarbazole units after the oxidative cross-linking [17]. But secondly and interestingly as well, we observed the disappearance of some MEH-PPV peaks located at 969, 1040 and 1506 cm\(^{-1}\) and of the PVK peaks situated at 840 and 1481 cm\(^{-1}\).

3.2. X-ray diffraction (XRD) and thermal analysis

To make easier the evaluation of crystalline structure of our copolymer, and to give more information of their thermal stability we have performed as well its X-Ray diffraction (XRD) patterns and the thermal degradation analysis in the same condition as for PVK and MEH-PPV homopolymers, even if these latter are largely described in literature. Results are shown in Fig. A and Fig. B (see Supplementary material).

3.3. Optical properties

Optical properties of the (PVK)x-(MEH-PPV)y copolymer (as well as of PVK and MEH-PPV homopolymers for comparison) have been investigated by UV–vis absorption, stationary photoluminescence and time-resolved photoluminescence (TRPL).

The UV–vis absorption spectrum of the copolymer (Fig. 2) shows several separated bands located at 225, 262, 311, 353, 423, 600 and 640 nm respectively, which is quite coherent with a copolymer incorporating both PVK homopolymer and MEH-PPV homopolymer entities. Indeed, to be more precise, we find in the copolymer spectrum (even if slightly blue shifted) a superposition of the common bands observed for PVK homopolymer (262 and 294 nm and perhaps 318 and 348 nm also) [9] as well as of the ones expected for MEH-PPV homopolymer (225, 275, and certainly 353 nm). Moreover, the appearance of the new bands located at 423, 600 and 640 nm for the copolymer evidence important interactions between PVK and MEH-PPV moieties into the statistic copolymer backbone and even suggest a charge transfer [18–20] between PVK and MEH-PPV blocks. This behaviour is similar to that of many conjugated polymers and it can be
explained by the changes in the effective conjugation length of the different polymer chains and that all channels participate in the formation of the absorption spectrum.

The stationary photoluminescence of (PVK)x-(MEH-PPV)y copolymer as well as of PVK and MEH-PPV homopolymers is depicted in Fig. 3. As for the optical absorption study, the copolymer spectrum shows an emission in a range of wavelengths (400–650 nm), which is placed between the emission of PVK homopolymer centred around 400 nm and the emission of MEH-PPV emission around 600 nm. More precisely, after deconvoluting the broad signal (dotted curves) obtained for our copolymer, we could explain this behaviour by the presence of five hands located at 417, 448, 495, 534 and 550 nm, which is quite different from MEH-PPV and PVK homopolymers spectra. We can also add that quantitatively, the area of the copolymer curve covers a larger zone of the PVK curve area (65% from the sum of common areas) compared to the MEH-PPV curve (35% from the sum of common areas). To enrich the discussion, we can compare as well the emission behaviour of our (PVK)x-(MEH-PPV)y copolymer with the precedent study we made on the corresponding PVK-PPV copolymer [9]. In fact, we observe that the PL spectrum of this copolymer is the precedent study we made on the corresponding PVK-PPV copolymer (red shifted by 30 nm (maxima at 465 nm and 495 nm respectively) in MEH-PPV). In fact, we observe that the PL spectrum of this copolymer is the precedent study we made on the corresponding PVK-PPV copolymer.

Table 1

<table>
<thead>
<tr>
<th></th>
<th>P1 (%)</th>
<th>P2 (%)</th>
<th>$\tau_1$ (ns)</th>
<th>$\tau_2$ (ns)</th>
<th>$\tau_{mean}$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVK</td>
<td>11.05</td>
<td>88.95</td>
<td>1.58</td>
<td>33.41</td>
<td>29.89</td>
</tr>
<tr>
<td>PVK-PPV</td>
<td>24.75</td>
<td>75.25</td>
<td>0.09</td>
<td>0.45</td>
<td>0.36</td>
</tr>
<tr>
<td>(PVK)x-(MEH-PPV)y</td>
<td>56.77</td>
<td>43.23</td>
<td>0.04</td>
<td>0.27</td>
<td>0.17</td>
</tr>
</tbody>
</table>

For the normalized PL intensity decays, we tested 3.1 eV (400 nm) as an excitation energy. Thus, Fig. D shows the normalized TRPL of PVK homopolymer, of our precedent PVK-PPV copolymer [9] and of the new one (on a logarithmic scale in the range of 0–1 ns and it was spectrally integrated between 350 and 750 nm) (see Supplementary material). This sample model, taken into account the contribution of apparatus function given by the Gaussian temporal dependence of the laser pulse, as previously reported [9,10].

From Table 1, our copolymer presents an average decay time $\tau_{mean}=0.17$ ns, with $\tau_1=0.04$ ns and $\tau_2=0.27$ ns which are shorter than the decay times observed for PVK homopolymer. Moreover, this (PVK)x-(MEH-PPV)y $\tau_{mean}$ value is comprised between i) on the one hand the exciton life time $\tau_{mean}=0.14$ ns of MEH-PPV homopolymer [21] and ii) on the other hand the $\tau_{mean}=0.36$ ns obtained for precedent PVK-PPV. These differences could reflect the steric hindrance effect caused by methoxy and ethyl-hexyloxy groups of MEH-PPV and vinyl groups of PVK which are responsible for the strong interchain interactions which enhances the trap process. In fact, the interchain interactions must favour a fast migration of excitons, providing consequently a fast decay as shown in the case of the (PVK)x-(MEH-PPV)y copolymer. Looking to the fractions of the photo-generated charge in the largest/shortest weighted segments which represent respectively 88.95% and 11.05% for the PVK. In the case of PVK-PPV these contributions are found to be 75.25% and 24.75% respectively. Quite differently, in our new (PVK)x-(MEH-PPV)y copolymer, these contributions become 43.23% and 56.77%: such behaviour could be explained by the fact that the decrease of photo-generated charge populations in the long segments induces a fastness in life time.

3.4. Prediction of the model structure of the copolymer

Based on experimental vibrational results (IR), we note the formation of dimer of N-vinylcarbazole after the oxidation of PVK with FeCl3 before the grafting of the MEH-PPV. As a consequence and in order to predict the chemical structure of the (PVK)x-(MEH-PPV)y, different models structures have been proposed and tested. For more clarity, the cross-linking of PVK moieties gives rise to a dimer of PVK then the grafting of the MEH-PPV blocks in the reactive sites on the dimer. After that we modulate the length of MEH-PPV blocks and the proprieties of the resulting model structure were tested. Our choice of the model structure is based on the model structure that encompasses several similarities with experimental results.

The structures (a), (b), (c), (d), and (e) presented in Fig. E (see Supplementary material), have been optimised in the ground state using DFT/B3LYP/6–31 G (d) and then they have been studied by the excited state TD-DFT /6–31 G (d) methods. Their theoretical absorbance spectra have been compared with the experimental spectrum of the synthesized copolymer in order to try to correlate experimental and computational measurements regarding our new statistic copolymer (Fig. F) (see Supplementary material).
whereas, it has been a small decreased in the carbazole units, it has been remain stable (from 140.964 to 141.121°), (Supplementary material). For the dihedral angle between the two groups in MEH-PPV has been replaced by a methoxy group, which could be said that in order to simplify the structure of the copolymer for the theoretical study by using the gauss view software, the ethyl-hexyloxy theoretical spectrum compared with experimental spectra, as well as the variation of these peaks intensity and also the low shift appearing in the experimental and theoretical peaks, we note that the majority of the vibration modes of experimental spectra are present in the theoretical spectrum of our (PVK)x-(MEH-PPV)y copolymer. By comparing these experimental and computational measurements, we can conclude that this new (PVK)x-(MEH-PPV)y material present better characteristics compared to PVK and MEH-PPV homopolymers taken separately, which could allow it to be more suitable for organic optoelectronic applications.

### 3.5. Vibrational properties

Fig. 4 shows the infrared absorption experimental and theoretical spectra of our (PVK)x-(MEH-PPV)y copolymer. By comparing the experimental and theoretical peaks, we note that the majority of the vibration modes of experimental spectra are present in the theoretical spectra with slight modifications in terms of intensity and position, shifts ranging from 0 to 20 cm\(^{-1}\). The presence of the other peaks, the variation of these peaks intensity and also the low shift appearing in the theoretical spectrum compared with experimental spectra, as well as other small differences can be explained by the fact that theoretically the molecule is considered in the gaseous state. Furthermore, it must be said that in order to simplify the structure of the copolymer for the theoretical study by using the gauss view software, the ethyl-hexyloxy group in MEH-PPV has been replaced by a methoxy group, which could as well modify a little the final modelling.

### 3.6. Geometrical study

By comparing the geometry of the model structure in the ground state and in the excited state, the (PVK)x-(MEH-PPV)y copolymer shows a slight increase in all dihedral angles (Fig. G) (see Supplementary material). We note that the segments of MEH-PPV are more planar in the excited state (increase of the dihedral angles from the interval of [165–177°] to at around 180° (Table A) (see Supplementary material). For the dihedral angle between the two carbazole units, it has been remain stable (from 140.964 to 141.121°), whereas, it has been a small decreased in the \(\Phi_2\) angle from 95.578° in the ground state to 113.254° in the excited state: this variation can be explained by a charge transfer between carbazole and MEH-PPV units. In addition, from Table A, it can be noted that, by going from the ground state to the excited state, the distances between the carbazole units and between carbazole and MEH-PPV blocks have been increased from 1.485 to 1.506 Å and from 1.493 to 1.508 Å respectively. This small increase is related to the relaxation of the molecule after the intramolecular interaction [22].

### 3.7. Molecular orbitals and density of states (DOS)

From the inspection of density of states (DOS) and the HOMO/LUMO molecular orbitals, computed by B3LYP/6–31 g (d) (Fig. 5), it can be noted that the LUMO energy level of the (PVK)x-(MEH-PPV) copolymer is localised at \(-1.79\) eV and the HOMO is localised at \(-4.41\) eV which would lead to a good capacity of holes injection. To sum up, the distribution of the electron density is localised on MEH-PPV units.

### 3.8. Emission spectra

Fig. 1 (see Supplementary material) shows the theoretical and experimental spectra PL that exhibit a strong emission centred at 495 nm, which have a good coincidence with the theoretical maximum emission (480 nm), usually attributed to the transition \(\pi-\pi^*\). In Table B (see Supplementary material) we present the oscillator strength and also the radiative lifetime which is determined by the following equation [23].

\[
\tau = \frac{C}{2fE}
\]

Where \(C\) is the light velocity, \(f\) is the oscillator strength and \(E\) is the energy of maximum emission.

### 4. Conclusion

New diblocks copolymer of PVK and MEH-PPV was prepared by an oxidative way using the anhydrous FeCl\(_3\). The successful synthesis of this new copolymer was reported and confirmed by various experimental analyses. The resulting copolymer showing a different structure with some new arrangement and an improvement in the thermal properties compared with the pristine homopolymers. The copolymer shows an original and unique optical properties and the continuous donor acceptor existence. The theoretical data obtained from the DFT method are in good agreement with the experimental data which allowed us to find a good correlation between the proposed chemical structure and the opto-electronic experimental properties recorded. Comparing these experimental and computational measurements, we can conclude that this new (PVK)x-(MEH-PPV)y material present better characteristics compared to PVK and MEH-PPV homopolymers taken separately, which could allow it to be more suitable for organic optoelectronic applications.

### Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jpcs.2016.11.018.

### References


