Cross linking-dependent properties of PVK-MEH-PPV bi-block copolymer: Vibrational, thermal and optical properties

Faten Abbassi¹, Mohamed Mbarek¹, David Kreher², Kamel Alimi³,∗

¹ Laboratoire Synthèse asymétrique et Ingénierie moléculaire des Matériaux Organiques pour l’Électronique Organique (LR 18ES19), Faculté des Sciences, Université de Monastir, 5000, Tunisie
² Institut Parisien de Chimie Moléculaire (IPCM), Chimie des Polymères, Sorbonne Université, UPMC Université Paris 06, UMR 8232, F-75005, Paris, France

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ABSTRACT

Despite its interesting optoelectronic properties, the insolubility of poly (N-vinylcarbazole-poly [2-methoxy-5-2 (ethylhexyloxy)-1,4-phenylenevinylene] (PVK-MEH-PPV) bi-block copolymer has caused some difficulties especially for the elaboration of new composites based on this copolymer and [6,6]-phenyl-C61-butanoate of methyl (PCBM). To solve the problem of insolubility, we first modify quantitatively a main parameter in the chemical synthesis, namely the oxidant agent and then replaced with a new one. Dramatic changes in the vibrational and optical properties are founded by varying the FeCl3 amount in the synthesis way due to the cross-linking of PVK units. This is induces the modulation of copolymers properties particularly theirs emissive properties due to the modulation of PVK and MEH-PPV contribution. A red shifting of the maximum of photoluminescence and a quenching was observed with increasing of the oxidation yields. Composite based PCBM and copolymer was elaborated due the solubility of one copolymer by changing the oxidant agent.

1. Introduction

Intensive efforts were deployed to synthesis new organic polymers involving different conjugated monomers [1–4]. The first aim is to obtain a copolymer with the optimum properties of each monomer. The second aim is to ameliorate their solubility [5–7] in order to make easy their elaboration in thin films with a controlled thickness [8–10].

Thus, it is interesting to synthesis new soluble copolymer with a well understand of its intimate relationship between its structure and its optoelectronic properties. For this reason, the synthesis methods have been diversified [11,12]; also, several parameters have been changed within the chemical reaction in order to obtain organic products possessing advantageous and important optical properties. In this context, in our previous work [13], a new copolymer has been synthesised based on i) poly (N-vinylcarbazole) (PVK) [14–17] and ii) poly [2-methoxy-5-2 (ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) [18–20]. The first homopolymer is a semiconducting polymer widely used as an electronic and a luminescent material emitting in blue and the second is electroluminescent and has been widely studied for its optoelectronic properties. This copolymer was synthesized by oxidative route using anhydrous ferrochloride (FeCl3) as the oxidant agent. Based on different experimental analyses combined with calculations based on DFT the new copolymer present an interesting optical properties which make it suitable for organic electronic. However its insolubility makes its use in multilayer structures very difficult. In order to overcome this handicap, the new PVK-MEH-PPV copolymer has been re-synthesised by using different amounts of FeCl3. Furthermore, we have substituted the FeCl3 oxidant by tetrachloride (TiCl4). The effect of nature and quantity of oxidant agent on the properties of PVK-MEH-PPV is investigated using different experimental measurements as well as those of composite PVK-MEH-PPV:PCBM. Varying oxidant agent amount can modulate the vibrational and photo-emissive properties of copolymers. It was found that changing FeCl3 by TiCl4 gives a soluble copolymer, this is raise the handicap of insolubility and make possible the functionalization with PCBM particles in order to elaborate a nanocomposites based PVK-MEHPPV.

2. Experimental part

2.1. Materials

Poly [2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) > 99% (Mn 25,000–50,000), poly (N-vinylcarbazole) (PVK) (Mn, 25,000–50,000) with average molecular weight Mw = 1,100,000 [6,6]-phenyl-C61-butanoate of methyle (PCBM), ferrochloride (FeCl3), titanium tetrachloride (TiCl4), chloroform anhydrous ≥ 99%, methanol,

* Corresponding author.
E-mail addresses: kamel.alimi@fsm.rnu.tn, kamealimi@yahoo.fr (K. Alimi).

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ethanol and hydrazine were purchased from Sigma Aldrich.

2.2. Synthesis of PVK-MEH-PPV copolymers

As previously recorded [13], the PVK-MEH-PPV diblock copolymer (Copolymer (A)) was synthesized by a chemical oxidative reaction using FeCl3 as oxidant. We have resynthesized copolymers by the same method [13] by changing the FeCl3 amounts: 250 mg (Copolymer 1), 500 mg (Copolymer 2) and 750 mg (Copolymer 3). It should be noted that for these three copolymers we have used 40 mg of PVK and 40 mg of MEH-PPV also. For the synthesis using TiCl4, the reaction was started with the amount of 120 mg of PVK dissolved in 50 ml of CHCl3, 120 mg of MEH-PPV dissolved in 50 ml of CHCl3 and 1 g of TiCl4. The obtained mixture was further stirred for about three days. The reactant solution was precipitated into methanol. Then 5–8 ml of hydrazine was added in order to obtain the product in the neutral state. The resulting precipitate was collected by filtration. (We obtain a soluble compound in chloroform (Copolymer (B))).

2.3. Characterisation techniques

The infrared spectra were obtained with a Nicolet IS10 infrared spectrometer related to OMNIC® software. Samples were prepared in pellets of KBr mixed with the organic compound. Thermal characterisations of all compounds were performed using TGA50Q (TA instruments) controlled by a heat control program. For soluble compounds, the optical absorption measurements were realized using a Cary 300 Scan UV-visible spectrometer at room temperature and the photoluminescence measurements (PL) were obtained using a Cary Eclipse Fluorescence spectrometer. For insoluble compounds, a Cary 5000 spectrometer and a Jobin-Yvon Fluorolog 3 spectrometer were used to determine the optical absorption and photoluminescence (PL), respectively. The copolymers were prepared by inserting the powder into a hole on the small metal support. This hole is filled with the powder and then a quartz substrate is put on top. For all PL and optical absorption of soluble copolymer and the obtained composite the measurement are taken in chloroform solution phases (≈3 ml) using quartz cuvette using with a thickness of 1 cm. View the absence of chromatography equipment as well as mass spectroscopy in our physics laboratory both within our University; we are sorry not to give more chemical details of synthesized copolymers like (molar mass, chromatography equipment as well as mass spectroscopy).

3. Results and discussion

3.1. Copolymers synthesised by FeCl3

3.1.1. Infrared analysis (IR)

By comparing the different normalized IR spectra of the PVK-MEH-PPV copolymers synthesised with different amounts of FeCl3 (Fig. 1), we can say that all curves shows almost the same vibrational bands, even if some modifications appear notably in the intensity of few of them. We can suggest so the reproducibility of copolymers. To try to elucidate this change, we compared the intensities of some common characteristic bands of PVK and MEH-PPV vibrations both. First, the band located at about 790 cm−1 attributed to the benzene ring vibration of dimer of PVK (bicarbazole) [21,22] was increased when the amount of FeCl3 increases, which indicates that the phenomena of cross linking of PVK chains increase proportionally with the amount of FeCl3 [23] (Fig. 2 in Supplementary Materials). To estimate the degree of cross-linkage, we have computed the intensity ratio of two peaks C-C ring vibration of (PVK) at 1450 cm−1 and C-C (MEH-PPV) at 1506 cm−1. \(\frac{I_{790}}{I_{720}}\) was founded to be 1 for copolymer (3), 0.72 for the copolymer (2) and 0.56 in the case of copolymer (1). We examined the intensity ratio band located at 790 cm−1 attributed to the crosslinking PVK and band located at 720 and 745 cm−1 the ratio value \(\frac{I_{790}}{I_{720}}\) was found to be 1.3 for copolymer (3), 0.78 for the copolymer (2) and 0.43 in the case of copolymer (1). The same values are almost found for \(\frac{I_{790}}{I_{745}}\) the ratio value \(\frac{I_{790}}{I_{745}}\) was 1.2 for copolymer (3), 0.8 for the copolymer (2) and 0.35 in the case of copolymer (1). We can note that the crosslinked yield is maxima when FeCl3 increase. The degree of crosslinking was estimated to be 100% for 750 mg of FeCl3, 76% for 500 mg and 44% for 250 mg. Thus, the contribution of MEH-PPV units is inversely proportional to the PVK cross-linking yield. Consequently the contents of PVK segments cross-linked probably prevent the grafting MEH-PPV segments on the PVK skeleton. This is also clear for the two PVK bands situated at about 720 and 745 cm−1 [21] which have experienced an increase in their intensity. Furthermore, some other PVK characteristic bands [21] have been extended by the increase of FeCl3 amount, like the band located at 1483 cm−1 assigned to the antisymmetric C=C stretching, the band located at 1450 cm−1 assigned to the ring vibration and also the 1151 cm−1 band attributed to C-H in plane deformation of aromatic ring of PVK. In another band, a reverse aspect has been noticed for the characteristic bands of MEH-PPV [24,25] especially the band localised at 1406 cm−1 assigned to CH2 deformation of vinylene group, we note also the decrease of the intensity of the MEH-PPV characteristic band located at 1506 cm−1 assigned to semi-circular phenyl stretch and as well its disappearance in the copolymer 3. Going from copolymer 3 to copolymer 1 (decreasing of FeCl3 amount), we notice a progressive smothering of the PVK vibration bands observed towards 921 cm−1, 1080 cm−1 and 1220 cm−1 corresponding respectively to C-C vibration, C-H deformation in plane of aromatic ring, and C-N stretching. This can be related to the increase of MEH-PPV grafting to the PVK which limit the rotation and the vibration of PVK blocs. In the otherwise a increasing was noted in intensity of the band located at 1037 cm−1 assigned to stretching of alkyloxyl groups of MEH-PPV. From all these modifications it can be noted that the change of FeCl3 amount involves the proportion of PVK and MEH-PPV in the copolymer skeleton. Indeed, counter to PVK, the increase of FeCl3 amount produces the decrease of MEH-PPV units; which was more illustrated by calculating the intensity ratio between the PVK band situated at 1483 cm−1 and the band at 1204 cm−1 attributed to phenyl-oxygen vibration of MEH-PPV. This ratio was increasing from 0.66 to 1.24 by going from copolymer 1 to copolymer 3.

The thermal degradation analysis of the synthetic copolymers (Fig. 1) was discussed (see Supplementary Materials).

3.1.2. Optical properties

Fig. 2 shows the optical absorption spectra of copolymers 1, 2 and 3. Despite the presence of some common bands in the three spectra, the first impression that can be noted is the difference in their shape. Whereas this shape has been transformed by going from copolymer 1 to copolymer 3 to be similar to the PVK absorption spectrum. From this interpretation we can conclude that the increase of the FeCl3 amount involves the proportion of PVK and MEH-PPV in the copolymer skeleton. Indeed, counter to PVK, the increase of FeCl3 amount produces the decrease of MEH-PPV units; which was more illustrated by calculating the intensity ratio between the PVK band situated at 357 nm has been decreased almost disappeared in copolymer 3 and also the band attributed to the charge transfer [13] was less and less accentuated because of a decrease in the charge transfer between PVK and MEH-PPV segments. The charge transfer band has also undergone a bleu shift, where it was moved from the [600–700 nm] area for copolymer 1, to the [500–650 nm] area for copolymer 2, to [450–600 nm] area for copolymer 3, the cause that allows finding that the FeCl3 reduce the effective conjugation length.
PL spectra of the copolymer 1, 2 and 3 presented in Fig. 3 range from 400 to 650 nm and were recorded in the same experimental conditions at room temperature. Firstly, we note the increase of PL intensity with the increase of FeCl₃ amounts caused by the PVK cross-linking [23]. This phenomenon is more confirmed by PVK band situated at about 400 nm which is more accentuated by going from copolymer 1 to copolymer 3 which confirms the increase of PVK blocks contribution due to the PVK cross-linking. We can also note that the common maximum band is red shifted by 10 nm from copolymer 3 (482 nm) to copolymer 1 (492 nm). This shift is caused by the presence of MEH-PPV ramifications (metoxy and ethyl-hexyloxy) [13] which confirms the decrease of the contribution of MEH-PPV units with the increase of FeCl₃ amounts which is in good agreement with infrared and optical absorption analyses.

3.2. Copolymer synthesised by TiCl₄ (Copolymer (B))

The substitution of FeCl₃ by TiCl₄ has allowed improving the solubility of the PVK-MEH-PPV copolymer.

3.2.1. Infrared (IR)

The normalized infrared IR spectra of the copolymer (A) and (B) are shown in Fig. 4. Practically, all vibrational bands of the previous copolymer (A) [13] are present in the new one (B). But some differences are clearly remarkable. Indeed, an increase of some MEH-PPV band intensity in copolymer (B) is observed especially the bands located at 1040 and 1505 cm⁻¹. At the same time, a decrease of PVK intensity bands [21,22] especially those located at 1600 and 1625 cm⁻¹ as well as the benzene ring vibration of bicarbazole band situated at about 790 cm⁻¹. This can evince the decrease of cross-linking of PVK chains by substituting FeCl₃ by TiCl₄. In fact, the decrease of the cross-linking,
which means the decrease of the bcarbazole bridges, promotes the li-
theness of the grid of atoms of the polymer and therefore the en-
hancement of its solubility. In the whole, it can be noted that the two IR
spectrums possess almost the same shape with same little changes in
term of band intensity, but we can conclude that the two PVK-MEH-PPV
copolymers synthesised with FeCl₃ [13] and TiCl₄ seem to present the
same molecular composition despite some difference in term of poly-
merisation degree of MEH-PPV and PVK.

The thermal degradation analysis of the new synthetic copolymer
(B) compared to copolymer (A) was elucidated in Fig. 2 (Supplementary
Materials).

3.2.2. Optical properties

Fig. 5, shows the UV-Vis and PL spectrum of PVK, MEH-PPV and
copolymer (B) (solution). From Fig. 5-a, the absorption region of co-
polymer (B) seems to be the superposition of PVK and MEH-PPV ab-
sorption spectrum. Indeed, we note the presence of the five PVK char-
acteristic bands located at 243, 262, 295, 330 and 344 nm. The UV-Vis
spectra of the copolymer present also the MEH-PPV characteristic peak
situated at about 500 nm (in native MEH-PPV) with a decrease in term
of intensity and also it has been performed a blue shift (440 nm for the
copolymer) which marks the decrease in the number of MEH-PPV units
in the copolymer by comparing it with the homopolymer. In another
hand, a large band appears, located in the range of [570–750 nm] at-
tributed to the charge transfer between homopolymers (PVK and MEH-
PPV). This band correspond to an optical gap of 1.56 eV (1.7 eV for the
previous copolymer (A)) [13]). In other hand, the photoluminescence

Fig. 4. Infrared spectrum of copolymer (A) [13] and copolymer (B).

Fig. 5. (a) Optical absorption spectra of PVK, MEH-PPV and copolymer (B) in Chloroform, (b) PL spectra of PVK, MEH-PPV and copolymer (B).

Fig. 6. Optical absorption spectra of composites with different PCBM percentages in Chloroform.

Fig. 7. PL spectra of composites with different PCBM percentages in Chloroform.
proposition suggested in the optical absorption study that the polymerization degree of the MEH-PPV segments has been increased. Moreover, the PL spectrum of copolymer (B) is extended in a range from 350 to 750 nm. It's also clear that the spectrum of the copolymer is red shifted compared to PVK spectrum, which demonstrates that the effective conjugation length is higher in the case of copolymer. This can be related to conformational changes which increase the extent of conjugation in the copolymer backbone. A slight red-shift of absorption and PL spectrum is observed going from the solid state to copolymer (C) in chloroform solvent. This can be related to a dipole interaction between solvent molecules and the solute. The corresponding excitation energies show a red shift compared to the same insoluble copolymers previously synthesis. This is due to the charge transfer states caused by the solvent. This shift is more pronounced for the transition S1 → S0 which is mainly due to the transition HOMO–LUMO PLmax from 495 nm to 538 nm in the solvent. Therefore, solvent clearly enhances the probability of this transition and then eases the charge transfer process.

3.2.3. Optical study of the (Copolymer (B):PCBM) composites

For the optical absorption spectra of the three PVK-MEH-PPV:PCBM composites prepared with different ratios: [1:0.5], [1:0.75] and [1:1] (Fig. 6), we noticed that more the proportion of PCBM increase, more the intensity of PCBM characteristic bands located at 263 and 329 nm increase without any observed shift for the PVK characteristic bands. Whereas, for the characteristic bands of MEH-PPV and apart from the quenching phenomena, it has been undergone a red shift which indicates a change in the organization of the copolymer chains especially for the segments of MEH-PPV where its organization was disturbed by the addition of PCBM.

The emission spectra of copolymer and composites with different proportions of PCBM are shown in Fig. 7. The first observation is the quenching in PL intensity of the most intense peak of the copolymer situated at 539 nm by increasing the PCBM percentage. Furthermore, a modification is observed in the shape of the emission spectra especially for the 50 and 75 wt or percentage (Wt%) PCBM composites in the [400–500 nm] range. More precisely, the emission bands in this ranges for these composites was increasing compared to the copolymer (B) only. In another hand, two essential aspects are observed: i) a red shift is made in the emission spectra of composites with 50 and 75% of PCBM and ii) a blue shift is made in the [1:1] composite. All these observations confirm the charge transfer between copolymer (B) and PCBM. The value of charge transfer efficiency of each composite (Table 1) was calculated using the following relation:

\[
\eta_T = \frac{I_{PL}}{I_d}
\]

Where \(I_{PL/d}\) are the integrated PL intensity of the donor (copolymer) in the presence and absence of the acceptor (PCBM), respectively.

4. Conclusion

New copolymers based on PVK and MEH-PPV homopolymers were synthesized by oxidative way using FeCl₃ and TiCl₄ as oxidative agents. Acting on cross-linking of PVK in the synthesis pathway of PVK-MEHPPV copolymer, we have shown a dramatic change in vibrational and optical properties. Thus, a modification of the respective contribution of PVK and MEH-PPV segments in the photo-physical properties was proved by changing the oxidant agent amount. PVK cross-linking significantly affects the vibrational, the optical properties and the charge transfer. The contribution of PVK segments is accentuated when FeCl₃ increased causing a PL red-shifting. Changing FeCl₃ by TiCl₄ modulates the solubility of synthetic copolymer and giving the ability to elaborate new composite based PVK-MEHPPV/PCBM. Thus, changing oxidant agent in the prepared copolymers can modulate the electronic and molecular structures of copolymers; this is also can vary their organic optoelectronic application.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jpcs.2018.08.004.

References


