

Photoluminescence Properties of New Poly(*N*-vinylcarbazole)-3-methylthiophene (PVK-3MeT) Graft Copolymer

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ABSTRACT: Steady-state and time-resolved photoluminescence (TRPL) measurements are used in order to investigate the emission properties of new graft copolymer involving poly(*N*-vinylcarbazole) (PVK) and poly(3-methylthiophene) (PMeT) named PVK-3MeT. The photo-generated species in PVK-3MeT are identified as singlet intrachain excitons. Furthermore, radiative and nonradiative lifetimes have been calculated. The observed changes in the photo-physical properties of the different condensed phases could be directly related to the nanostructure of the material. The

use of PVK in the chemical synthesis allows the obtaining of a new organic material with better emission and slowly radiative recombination compared to those of polythiophenes indicating that the radiative channel is more enhanced. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 126–132, 2012

Key words: PVK-3MeT graft copolymer; UV-vis spectroscopy; time resolved photoluminescence (TRPL)

INTRODUCTION

Nowadays, the synthesis of conjugated polymers with specific and reproducible properties that could be used as an active layer in optoelectronics devices organic light emitting diodes (OLED),^{1,2} organic photovoltaic cells (OPC),^{3,4} and organic field-effect transistor (OFET)⁵ is attracting great attention. In fact since the first report of the elaboration of OLED based on poly (Para-Phenylene-Vinylene) (PPV),⁶ the synthesis of a variety of π -conjugated polymers exhibiting electroluminescence properties^{1,7} has been reported. Polythiophene and its derivatives are a special class of π -conjugated polymeric materials for OLEDs thanks to their excellent environmental stability, good red color purity, and their easiness of processing.^{8–10} However, their exploitation in manufacturing organic light emitting diodes has been limited due in particular to their low photoluminescence and electroluminescence quantum yield efficiencies.^{11,12}

On the other hand, poly(*N*-vinylcarbazole) (PVK) is considered as a good hole transporting material,

and was used in multilayer structure for manufacturing new promising OLEDs.^{13–15} Added to that, when PVK is mixed with conjugated polymers, it can strongly improve their optical properties.^{16–18}

In this context, we have chemically synthesized in our previous paper¹⁹ a new graft copolymer based on poly(*N*-vinylcarbazole) PVK and poly(3-methylthiophene) (PMeT) named PVK-3MeT (Scheme 1). Added to the experimental results, a theoretical study was performed²⁰ confirming the grafting of PMeT main chain in the formed bicarbazole units.

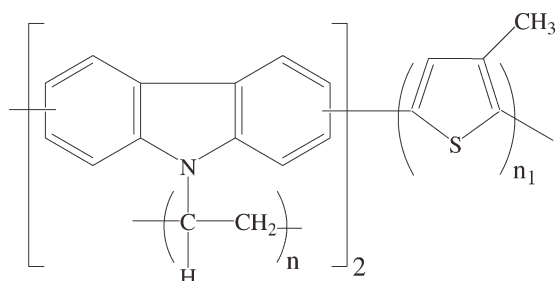
In this article, our aim is focused on photoluminescence properties of PVK-3MeT. Thus state and transient PL (TRPL) are undertaken in order to give a more description of the photo-physical properties and to describe the photo-generated charges of the PVK-3MeT for different morphological states (powder, film, and dilute solution), as well as the nature of the excited states, their life time, and decay process. To make easy the reading of this article the optical properties of the pristine copolymer are compared with those of poly(3-methylthiophene) (PMeT) and poly(3-hexylthiophene) (PHeT).

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EXPERIMENTAL DETAILS

The investigated copolymer in this work named PVK-3MeT (Scheme 1) was synthesized by a chemical oxidative way using FeCl₃ as an oxidant. More



Scheme 1 Chemical structure of the PVK-3MeT graft copolymer.

details of the synthesis procedure, spectroscopic characterization, and theoretical investigation have been described elsewhere.^{19,20} As said before and in order to compare the optical properties of PVK-3MeT to those of poly (alkylthiophenes) family, we have synthesized poly (3-methylthiophene) homopolymer (PMeT) by chemical polymerization of 3-methylthiophene monomers with FeCl_3 .¹⁹ While, Pol(3-hexylthiophene) (PHeT) was purchased from sigma Aldrich.

PhotoLuminescence Excitation (PLE) measurements and Photoluminescence Quantum Yield efficiencies (QY) are obtained on a Jobin-Yvon Fluorolog 3 spectrometer using a Xenon lamp (450 W) at room temperature. We have estimated the QY using the method of de Mello et al.²¹ in an integrating sphere of 3 inches in diameter. Signals were recorded from the empty sphere, from the sphere with the sample inside not directly illuminated (off-axis geometry) and from the sample inside the sphere directly in the exciting beam (on axis-geometry). We estimated the errors for QY to be 20% of the measured value. QYs were measured at 3.1 eV ($\lambda_{\text{exc}} = 400 \text{ nm}$).

Time-resolved photoluminescence (TRPL) experiments, at room temperature, were carried out with a regenerative amplified femtosecond Ti:Sapphire laser system (Spectra Physics Hurricane X). This setup generates 100 fs pulses at 800 nm with a repetitive rate of 1 kHz and a power of 1 W. Two wavelengths of excitation are delivered by the setup: 266 and 400 nm. The laser line is frequency-doubled with a thin BBO crystal to obtain an excitation line $\lambda_{\text{exc}} = 400 \text{ nm}$ (3.1 eV). The pump energy pulse is controlled to ensure that the excitation density in the sample did not exceed 10^{17} cm^{-3} then to avoid bimolecular annihilation process and sample photodegradation. The transient signals were spectrally dispersed into an Oriel MS260i imaging spectrograph (150 grooves/mm, $f = 1/4$) designed to minimize stray light with high spectral resolution. 3D-map is obtained with energy emission versus time (range 0-1 ns) and intensity in false color. The emission spectra were temporarily resolved with a high dynamic

range Hamamatsu C7700 streak camera with a temporal resolution $<20 \text{ ps}$.

RESULTS AND DISCUSSIONS

Optical investigations of the neutral PVK-3MeT graft copolymer

PLE spectrum of PVK-3MeT in solution for a maximum emission peak located at 560 nm (λ_{em}) is shown in Figure 1(a). It can be seen that a maximum centred at around 410 nm is observed. This latter is related to the High Occupied Molecular Orbital (HOMO) to Low Unoccupied Molecular Orbital (LUMO) π - π^* electronic transition, found in the optical absorption spectrum of PVK-3MeT solution [Fig. 1(b)], with the strongest calculated oscillator strength.²⁰ However, optical absorption spectrum of PVK-3MeT present absorption bands in the UV part at 330, 270, and 230 nm and a large band centred at around 410 nm in chloroform solution [Fig. 1(b)]. This means that only visible wave-lengths are radiative excitations. Therefore, we can deduce that only the excitation wavelength $\lambda_{\text{exc}} = 400 \text{ nm}$ among the wavelengths delivered by the setup system recording good experimental conditions of emission.

3D-maps TRPL in false colors on PVK-3MeT are presented in Figure 2. In this case the 3D-map colors going from blue to red represent the increase of the PL intensity. The prompt view of these maps shows qualitatively that the PL intensity changes according to the physical phases of PVK-3MeT, whereas the width of PL spectra remains similar. From these 3D-maps, TRPL spectra, and decay times on PVK-3MeT in different physical morphologies are obtained and then shown in Figures 3 and 4.

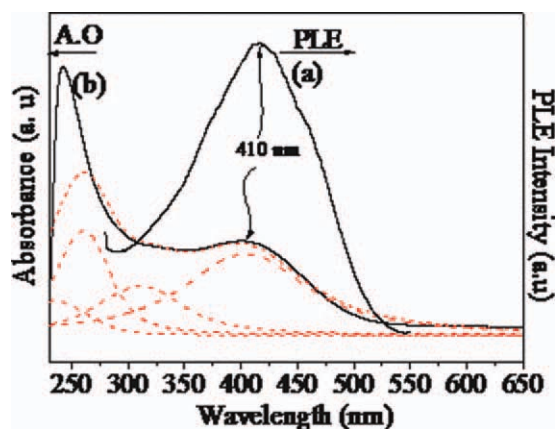


Figure 1 (a) Normalized Photoluminescence excitation (PLE) spectra of PVK-3MeT in chloroform solution. (b) Optical absorption spectra (A.O.) of PVK-3MeT in chloroform solution, deconvolution of the optical absorption spectrum into Lorentzian profiles (...). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

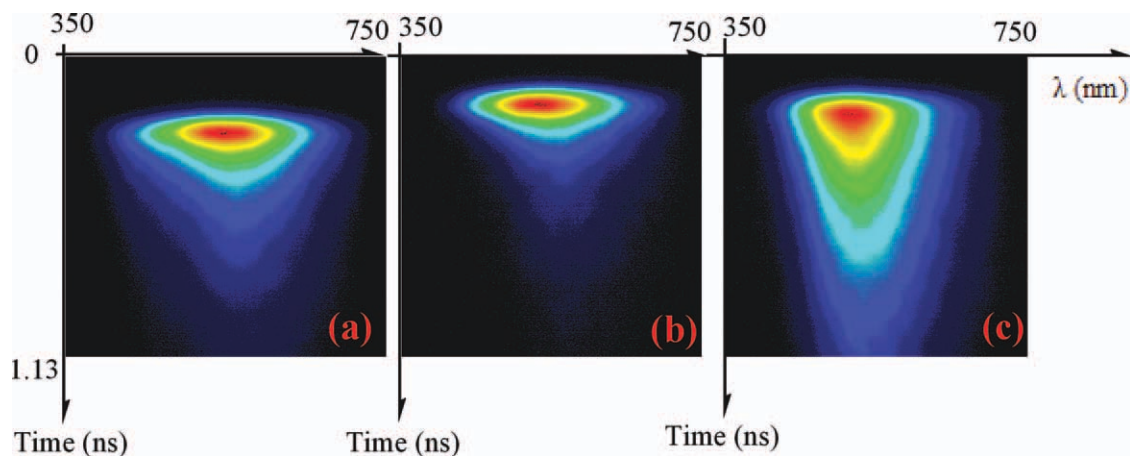


Figure 2 Transient photoluminescence contour maps in the false colour of PVK-3MeT graft copolymer: (a) film, (b) powder, (c) solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Furthermore, the collected PL spectra (Fig. 3) of different samples are quite similar to those recorded in steady state PL spectra already published in our previous article.¹⁹ Their profiles are structureless and their PL maxima are localized at 550 nm in the case of PVK-3MeT powder, at 560 nm for PVK-3MeT in solution and 600 nm for PVK-3MeT in film state. Those maxima are the result of the radiative electronic transition $S1 \rightarrow S0$ with strongest calculated oscillator strength of 2.62.²⁰ whereas, the red-shift of the emission in PVK-3MeT films involving the extent of its conjugation is related to the improvement of the macromolecular organization according to the parallel direction of the substrate. Contrarily to PVK-3MeT film, the solution has individual polymer chains coiled to varying degrees which interrupt the conjugation, and the short and

isolated conjugated segments become predominant inducing a decrease of the effective conjugation length going from film to solution.^{22,23} Concerning PVK-3MeT powder, the blue shift of the emission can be interpreted by its compact and amorphous structure. Compared to PPV, PVK-3MeT in the solid state has no crystallized domains. In fact, its amorphous and compact structure seem be the result of a fast evaporation of the solvent, leaving the solute in coil which can interact creating more disorder. This can explain the decreasing of conjugation inducing a blue shift of the emission compared with PVK-3MeT solution.

To underline the effect of physical morphology of samples on the excited states dynamics, we plot the TRPL decays. Figure 4 shows the normalized PL decay dynamics on a logarithmic scale in the range of 0–1 ns

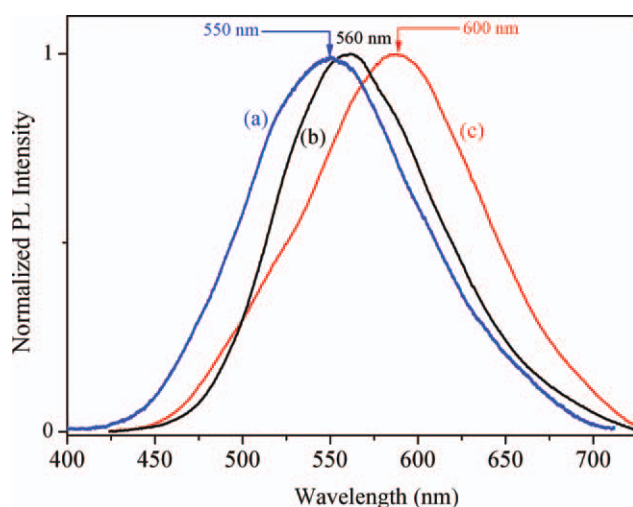


Figure 3 Normalized Time integrated transient photoluminescence emission of PVK-3MeT (a) powder, (b) solution, and (c) film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

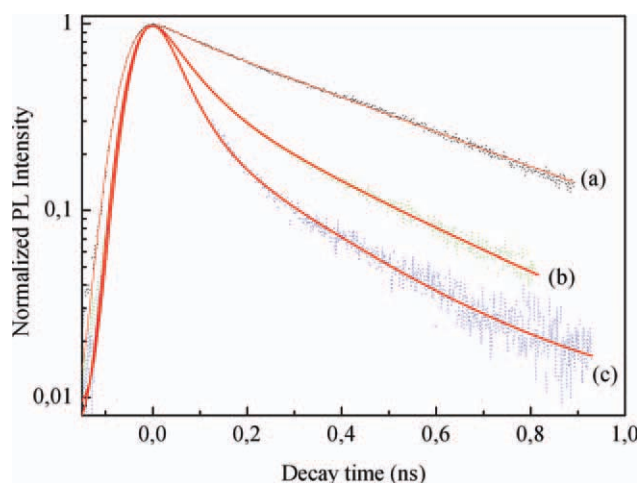


Figure 4 Integrated transient photoluminescence decays of the PVK-3MeT at different morphological sites (a) solution, (b) film, and (c) powder. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
PL Quantum Yield (QY), (τ_1 , τ_2 , τ_{mean}), Radiative, and Nonradiative Lifetimes (τ_r and τ_{nr}), Pre-Exponential Factor (A_1 , A_2) and Percentage Contributions P1, P2 to Emission of Levels 1 and 2 and PL Maximum Peak Listed For the Transient PL of the Different Samples Investigated

Samples	QY (%)	τ_1 (ns) (A_1) (P_1 %)	τ_2 (ns) (A_2) (P_2 %)	τ_{mean} (ns)	τ_r (ns)	τ_{nr} (ns)	PL maximum (nm)
PVK-MeT Thin film	13	0.069 (12.46) (46)	0.332 (2.94) (53)	0.18	1.38	0.2	600
PVK-MeT Powder	–	0.0484 (13.94) (59)	0.253 (1.83) (40)	0.13	–	–	550
PVK-MeT Solution	–	0.0559 (8.97) (14)	0.456 (6.46) (85)	0.39	–	–	565
PMeT Powder	–	0.0185 (12.22) (57)	0.123 (1.36) (42)	0.063	–	–	620
PHeT Thin film	1	0.0163 (6.9) (80)	0.083 (1.3) (19)	0.019	1.9	0.02	650/680

for PVK-3MeT in different states: in chloroform solution [Fig. 4(a)], film [Fig. 4(b)] and in powder [Fig. 4(c)].

A single monoexponential fit cannot reproduce these data for temporal window of 0–1 ns. This suggests the presence of several decay mechanisms. This kinetics is well reproduced with two coupled exponential decays convoluted with the contribution of apparatus function given by the Gaussian temporal dependence $G(t)$ of the laser pulse according to the following rate equations:

$$\frac{dn_1}{dt} = P(t) - n_1k_1, \quad \frac{dn_2}{dt} = n_1k_1 - n_2k_2 \quad (1)$$

In eq. (1); n_1 and n_2 are the populations of the excited states levels 1 and 2, respectively; k_1 and k_2 are the inverse of the lifetimes τ_1 and τ_2 . In this simple model²³ n_1 and n_2 are coupled in order to account indirectly for a migration process from the short to the long segments. Photogenerated charges populating the higher energy level 1 migrate toward defects and fast relax on the lower energy state 2 with lifetime τ_1 . At longer time, the photogenerated charges on level 2 are less mobile and consequently survive longer with a slower time constant τ_2 . Furthermore, n_1 and n_2 represent the total populations of photogenerated charges in the energy states 1 and 2. These populations include photogenerated charges recombining radiatively and nonradiatively.

The decaying population is $n = A_1n_1 + A_2n_2$, where A_1 and A_2 are proportional to the PL intensity from levels 1 and 2 respectively. We define below [eq. (2)] an average decay time called τ_{mean} in order to show the average trend of the photogenerated charge migration time.

$$\tau_{\text{mean}} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2} \quad (2)$$

For clarity, the weight corresponding to the relative population of photogenerated charges contribut-

ing to each of the decay times (A_i , τ_i) is calculated by the following formula:

$$P_i(\%) = \frac{A_i\tau_i}{\sum A_i\tau_i} \quad (3)$$

Results are summarized in Table I where P_i is reported in parentheses for each decay component. In this same Table I, we present the wavelength of PL peak maximum for each sample as well as radiative (τ_r) and non radiative (τ_{nr}) lifetime obtained from QY and τ_{mean} by the following relations:

$$\tau_r = \frac{\tau_{\text{mean}}}{\text{QY}} \quad \text{and} \quad \tau_{nr} = \frac{\tau_{\text{mean}}}{1 - \text{QY}}$$

QY has been measured for the PVK-3MeT graft copolymer in film and the value of QY concerning to P3HT film is extracted from literature.²³

On the one hand, according to Table I, PVK-3MeT film exhibits $\tau_{\text{mean}} = 0.18$ ns, $\tau_r = 1.38$ ns, and $\tau_{nr} = 0.2$ ns. For this sample the radiative lifetime τ_r is in the order of nanosecond consistent with a fully allowed transition of a strongly absorbing molecule. This is characteristic of an emission process resulting mainly from singlet intrachain excitons.²⁴ As in the case of PPV films, this is the photogeneration of singlet intrachain excited states^{24,25} that seems to be the dominant product of the photoexcitations in this copolymer film.

On the other hand in Figure 4, we can also see that the decay times are more and more slowly when going from PVK-3MeT powder to PVK-3MeT film and to PVK-3MeT solution. These features are confirmed by the increase of τ_2 and τ_{mean} (Table I). These trends make us believe that the nonradiative process become less important in film and in solution compared to that in powder. In fact, focused studies on the optical properties of various PPV derivatives in different morphologic states (film, nanofiber...), show that the increase of the decay

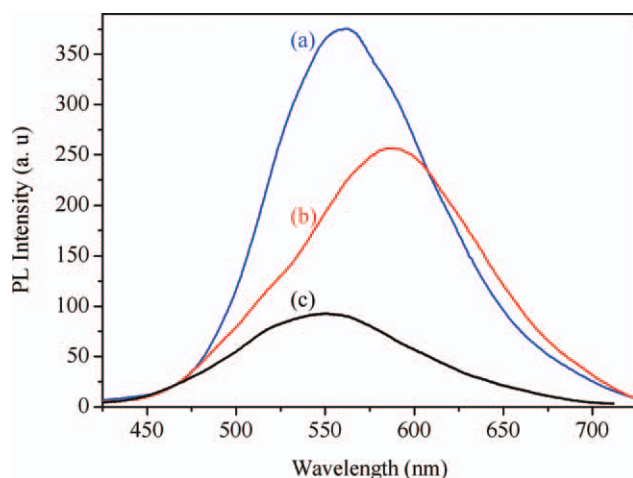


Figure 5 Time integrated transient photoluminescence emission of PVK-3MeT (a) solution, (b) film, (c) powder. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

times is accompanied by the increasing of the QY efficiency,^{24,25} and followed with an increase in the PL intensity. The some phenomena are observed in our case when going from PVK-3MeT powder to PVK-3MeT film and solution (Fig. 5).

Indeed, the strong macromolecular interactions in PVK-3MeT powder become less high in film and negligible in solution. Consequently, in solution, the migration of the emitting species created mainly on short conjugated segments is inexistent inducing a high luminescence. Whereas in film, macromolecules have a distribution of conjugated segments, the migration of excitons created on short segments to longer segment becomes possible, therefore a quenching of luminescence intensity is observed.^{24,26} In PVK-3MeT powder a weak quenching was observed in PL spectra (Fig. 5) with a faster decays time. This could be related to the fast migration process of the photogenerated species in the excited state, or the formation of nonemissive interchain species in powder.

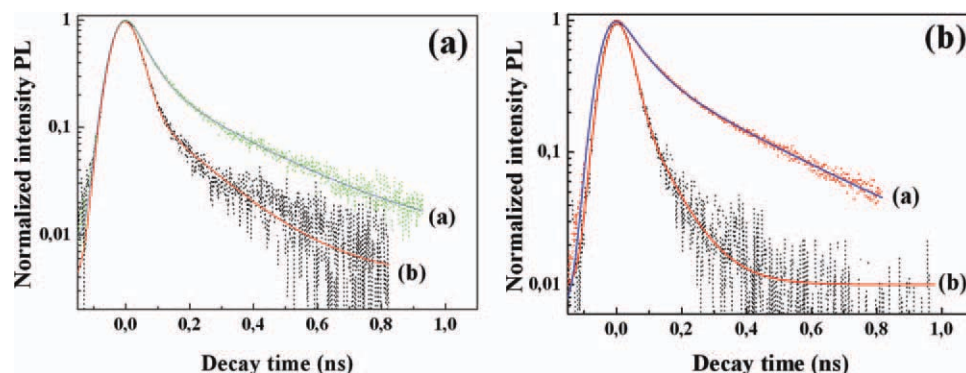


Figure 6 (a) Integrated transient photoluminescence decays of (a) PVK-3MeT powder, (b) PMeT powder. (b) Integrated transient photoluminescence decays of (a) PVK-3MeT film, (b) Poly(3-hexylthiophene) (PHT) film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

As said before, we are interested in comparing the optical properties of PVK-3MeT graft copolymer to those of PMeT and PHeT homopolymer. Normalized decays dynamics spectra on a logarithmic scale in the range of 0–1 ns of PVK-3MeT, PMeT, and P3HT are represented in Figure 6(a,b). It is clearly seen that the PL lifetime of the PVK-3MeT graft copolymer is longer compared with that of PMeT or PHeT. Going from PMeT or PHeT homopolymer to PVK-3MeT graft copolymer, τ_2 and τ_{mean} increase with the increase of the QY efficiencies from 1% in PHeT film to 13% in PVK-3MeT film which is in accordance with the increasing of the TRPL intensity going from PMeT and PHeT homopolymer to PVK-3MeT copolymer (Fig. 7). Indeed, in comparing τ_r and τ_{nr} (Table I) of PVK-3MeT film and those of PHeT film, we can deduce that the radiative pathway is more important in the graft copolymer. This means that the radiative channel is enhanced by using PVK in the PVK-3MeT synthesis. To make an explanation of this effect, we present in Figure 8 XRD pattern of PMeT homopolymer [Fig. 8(a)] and that of the PVK-3MeT graft copolymer [Fig. 8(b)]. It can be seen that the use of PVK in the PVK-3MeT synthesis reduces the crystalline phases in the prepared copolymer compared with those of the homopolymer PMeT. So, the weight of isolated and short segments forming the amorphous part of the polymer is increased in PVK-3MeT graft copolymer compared to those in polyalkylthiophenes. These results are in good agreement with the optical observation and explain the enhancement of the radiative pathway in the copolymer compared with that in polyalkylthiophenes. In fact polythiophenes are photoluminescence conjugated polymers with low QY efficiencies in films, due to the long conjugation length and the high interchain interaction in the solid state.^{12,23,27} These trends could be enhanced by the enhancement of the regio-regularity of the polymer.^{12,23} In addition, in the excited state the conformation of polythiophenes tend to be coplanar structure, allowing the

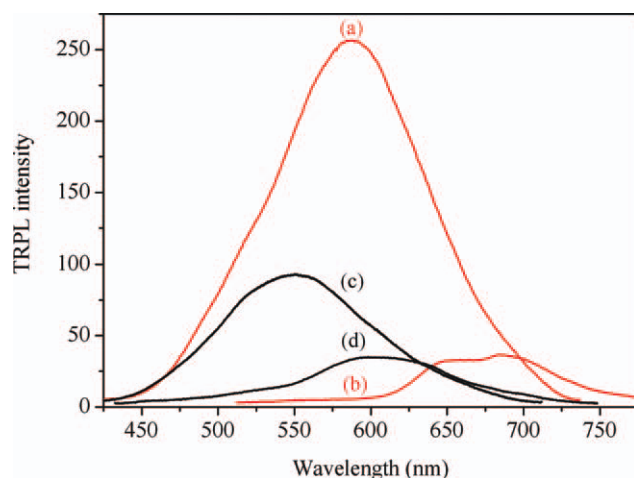


Figure 7 Time-integrated transient photoluminescence emission of (a) PVK-3MeT film, (b) PHeT film, (c) PVK-3MeT powder, and (d) PMeT powder. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

formation of the nonemissive excimers species in the excited state.^{12,23} In our synthesized copolymer the system is rich in short and isolated segments. Added to that, upon excitation the chemical structure presents a noncoplanar conformation.²⁰ So, the probability of the formation upon photo-excitation of the nonemissive excimers is reduced, while, the photo-generation of the intrachain excitons with higher fluorescence efficiencies and longer fluorescence lifetime^{24,26,28} is favored in our copolymer. Conse-

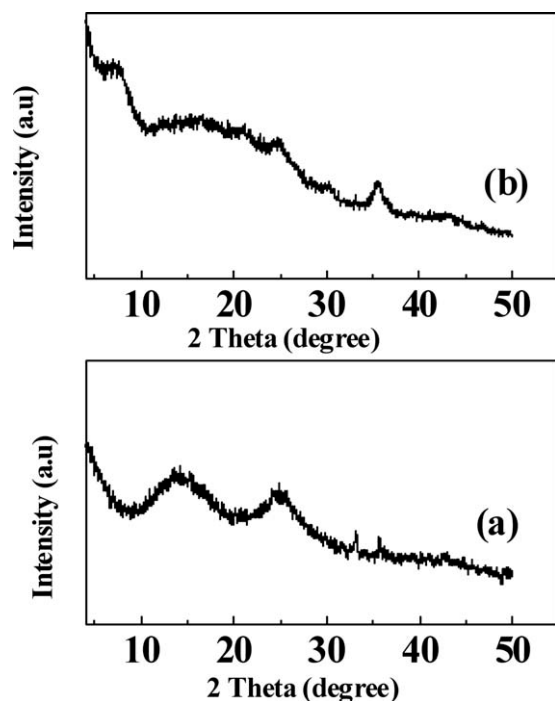


Figure 8 XRD pattern of (a) PMeT homopolymer, (b) PVK-3MeT graft copolymer.

quently we notice an increase of the radiative pathway in our synthesized copolymer compared to that in polythiophenes systems.

CONCLUSION

The combination of QY and TRPL lifetime measurements is a powerful tool to understand the nature of the photoexcitations generated in conjugated polymer. In contrast with the polythiophenes family, in PVK-3MeT graft copolymer, the predominant photoexcitations species are the emissive generated single intrachain excitons. Consequently, we observe an enhancement of the QY of the prepared copolymer compared with that of polythiophenes with a most slowly radiative recombination life time. The use of PVK in the chemical synthesis allowed the development of a new conjugated polymer with better optical properties which constitute a good candidate for OLEDs applications.

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