

Electrochemical Synthesis of the Copolymer Poly(2-methoxy-5-bromo-*p*-phenylenevinylene)/(2,5-dicyano-*p*-phenylenevinylene) (MB-PPV/DCN-PPV): Tuning Properties

Karine C. C. W. S. Klider,^a Fábio S. Santos,^a Laura O. Péres,^b Karen Wohnrath^a and Jarem R. Garcia^{*a}

^aState University of Ponta Grossa (UEPG), Chemistry Department,
Av. Gal. Carlos Cavalcanti, 4748, 84030-900 Ponta Grossa-PR, Brazil

^bFederal University of São Paulo (UNIFESP), Campus Diadema,
R. Artur Riedel, 275, 09972-270 Diadema-SP, Brazil

Descreve-se um método eletroquímico para a preparação do copolímero poli(2-bromo-5-metoxi-*p*-fenileno-2,5-diciano-*p*-fenileno) (*cop*-MB-PPV/DCN-PPV). Este copolímero foi proposto por apresentar uma estrutura D-A, produzida pela presença do grupo elétron-doador metoxi e do grupo elétron-retirador diciano. O copolímero foi sintetizado eletroquimicamente por redução catódica dos materiais de partida convenientes dissolvidos em DMF/LiClO₄ usando um poço de mercúrio como eletrodo de trabalho. O copolímero foi caracterizado por medidas de espectroscopia no infravermelho (IR), no UV-Vis e de fluorescência (FL) e por medidas de voltametria cíclica (CV). Todos os resultados foram comparados com o homopolímero MB-PPV. A análise dos resultados indica que o *cop*-MB-PPV/DCN-PPV foi obtido através da formação de blocos contendo unidades de DCN-PPV ligadas por blocos contendo unidades de MB-PPV. A caracterização da estrutura eletrônica, obtida por meio de medidas de CV, UV-Vis e FL mostraram que a banda de condução é mais estabilizada no copolímero em comparação ao homopolímero. Além disso, os espectros de FL indicaram que a emissão de luz do *cop*-MB-PPV/DCN-PPV em solução de clorofórmio ocorre por meio da formação de excímeros.

The present work describes an electrochemical method to produce the copolymer poly(2-methoxy-5-bromo-*p*-phenylenevinylene)/(2,5-dicyano-*p*-phenylenevinylene) (*cop*-MB-PPV/DCN-PPV). This copolymer was proposed due to its D-A characteristic produced by the presence of the electron-donating methoxy moiety and the electron-withdrawing dicyano moiety. The copolymer was electrochemically synthesized by cathodic reduction of the convenient starting materials dissolved in a DMF/LiClO₄ using a mercury pool acting as working electrode. The copolymer was characterized by infrared (IR), UV-Vis and fluorescence (FL) spectroscopy and cyclic voltammetry (CV). All the results were compared to the MB-PPV homopolymer. The analysis of electrochemical measurements and IR indicated that the *cop*-MB-PPV/DCN-PPV was obtained through the formation of blocks containing DCN-PPV units linked by blocks containing MB-PPV units. The electronic structure, performed by CV, UV-Vis and FL showed that the conduction band is more stabilized in the copolymer than in homopolymer. Furthermore, the FL spectra indicated that the light emission of the *cop*-MB-PPV/DCN-PPV in chloroform solution occurs by means of excimer formation.

Keywords: PPV-like copolymer, donor-acceptor structure, polymeric solar cell, electrochemical polymerization

Introduction

During the last two decades, bulk heterojunction polymer solar cells (PSCs) have been widely studied regarding the possibility of developing efficient and renewable energy sources through the low cost devices production.¹⁻³ Due to massive research efforts there has been significant progress in the field of organic solar cells and within about 25 years higher efficiencies and lifetimes were achieved and power conversion efficiencies (PCEs) higher than 10% have been reported.⁴ Nevertheless, before commercialization, additional improvements, particularly in the power conversion efficiency, are required. One of the reasons for the low efficiency of the PSCs is the lack of acceptor polymers which present properties such as high electron affinity, high electron mobility, and higher sunlight absorption. The former requirement could be overpassed if the absorption spectra of the conjugated polymers match the solar spectrum, and for this the polymers must present band gap (E_g) values close to 1.75 eV.⁵⁻⁹ One of the most useful methods to obtain a low band gap polymer is the production of a copolymerized donor-acceptor (D-A) structure.¹⁰ In these types of structure the proper combination of donor (D) and acceptor (A) units in the copolymer gives the possibility of tuning the electronic energy levels and produce a broadening in the photoactive material absorption. For this purpose, a vast diversity of D-A copolymers¹¹ based on different donor units and acceptor units have been synthesized and applied to PSCs.^{6,10-12} Another important feature that must be taken into account concerning the production of organic semiconductors suitable for PSC application is the possibility of molecular ordering, since higher aggregation states could result in higher mobility. In this context, diketopyrrolopyrrole polymeric systems (PDPP) have been prepared and studied as activity material for a series of devices based on organic electronics.¹³⁻¹⁵ This class of polymer has presented some of the highest mobility values assigned to the remarkable aggregation properties of the DPP moieties.¹⁵

Based on what has been discussed above the present paper describes the electrochemical synthesis of the copolymer poly(2-methoxy-5-bromo-*p*-phenylenevinylene)/(2,5-dicyano-*p*-phenylenevinylene) (*cop*-MB-PPV/DCN-PPV) as shown in Scheme 1. This copolymer was proposed due to the fact that it contains the electron-donating methoxy-phenylene units (the MB-PPV units) as the donating group (D) and the electron-withdrawing dicyano-phenylene units (the DCN-PPV units) as the acceptor (A) group. In this way, the MB-PPV/DCN-PPV copolymer was electrochemically synthesized by the cathodic reduction of a mixture of compounds **1** and **2** (as shown in Scheme 1) dissolved in a DMF/LiClO₄ electrolytic solution using a mercury pool as working electrode. This approach allows the production of a soluble fraction of the copolymer. This soluble copolymer was characterized by infrared (IR), UV-Vis and fluorescence emission spectroscopies. The electronic characteristics of the films were measured by cyclic voltammetry. All the results were compared to the MB-PPV homopolymer.

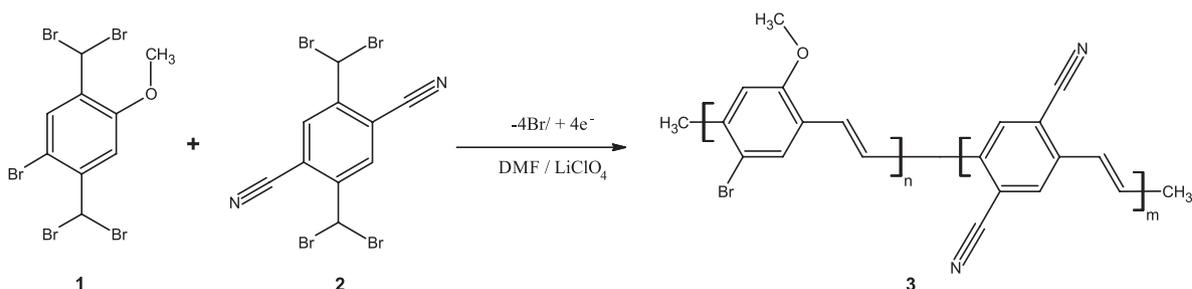
Experimental

Solvents and electrolyte

N,N-dimethylformamide (DMF) (Vetec 99.8%) was heated under reflux over copper sulfate for 36 h before distillation under reduced pressure. It was stored over freshly baked 4 Å molecular sieves. Lithium perchlorate (LiClO₄) (Merck, 99%) was held in a dessicator with phosphorus pentoxide overnight before use. All other chemicals were commercial grade and used as received.

Equipment

The electrotheses were carried out using an OMNI 101 Potentiostat/Galvanostat. Fourier transform infrared spectra (FTIR) were measured on KBr pellets on a Shimadzu FTIR-8400 spectrophotometer; UV-Vis



Scheme 1.

spectra were obtained by transmission on a Hitachi U-321 spectrophotometer. Emission spectra were recorded on an Ocean Optics HR-4000 fluorimeter. Electrochemical characterizations were carried out using a Palm Sens Potentiostat/Galvanostat.

Starting material

The MB-PPV starting material (compound **1** from Scheme 1) was obtained as described below: In a three neck round-bottom flask, 46.7 mmol of 2,5-dimethylanisole and 47 mL of CCl_4 were mixed. In round-bottom flask a reflux condenser and a dropping funnel with 0.2 mol of previously dried Br_2 were connected. This mix was heated with constant stirring and lighted by an IR incandescent lamp of 500 W. The Br_2 in dropping funnel was added dropwise in flask, and a new drop was only added after decolorization of the solution. After finished reaction, the mix was cooled overnight. The solid obtained was filtered and recrystallized in CHCl_3 . The DCN-PPV starting material (compound **2** from Scheme 1) was obtained as described by Garcia *et al.*¹⁶

Electropolymerization

The electrochemical synthesis of the MB-PPV/DCN-PPV copolymer was carried out on a stirred mercury pool working electrode, using Ag/AgCl as reference electrode and graphite sheet as counter electrode. Starting materials were used on a mass proportion of 7:3 of compound **1** and **2**, respectively, from a total mass of 0.6 g of starting material dissolved in 50 mL of distilled DMF and 0.1 mol L^{-1} of LiClO_4 . Syntheses were performed using potentiostatic methods by passing a total charge of 4.4 F mol^{-1} . Using this approach the copolymerization was completed after 5 hours. It was also produced the homopolymer MB-PPV using a similar procedure as described above, but in the absence of compound **2**. Purification of the copolymer and the homopolymer occurred by water addition followed by filtration of the solid polymers and Soxhlet extraction of the soluble fraction with CHCl_3 . Obtained copolymer and homopolymer were submitted to FTIR, UV-Vis and emission fluorescence spectroscopies.

Film preparation and electronic characterization

Films of MB-PPV and *cop*-MB-PPV/DCN-PPV were obtained by drop casting method. Soluble portion of separated materials dissolved on CHCl_3 were dropped over indium tin oxide (ITO) transparent substrate and the solvent was evaporated. Cyclic voltammetry measurements

were performed on an H format electrochemical cell using ACN/ LiClO_4 as a solvent/electrolyte system. A graphite sheet was used as the counter electrode and Ag/AgCl as reference electrode. N_2 was bubbled through the system, shortly before measurements, in order to remove any dissolved O_2 .

Results and Discussion

Electrochemical polymerization

The *cop*-MB-PPV/DCN-PPV was synthesized by application of -2.0V (*vs.* Ag/AgCl) potential and the MB-PPV by application of -1.8V (*vs.* Ag/AgCl) potential. The more negative potential used to synthesize the copolymer was necessary because it was demonstrated that the formation of the DCN-PPV occurs in less negative potential values in relation to MB-PPV.¹⁶ For this reason the preparation of copolymer MB-PPV/DCN-PPV was held through the application of a more negative potential value in order to increase the amount of MB-PPV units in the copolymeric chain since the formation of DCN-PPV would be predominant in less negative potentials. The polymer formation was accompanied using chronoamperometric measurement technique and the current profiles as a function of time for the electrochemical formation of the two polymers are shown in Figure 1.

The behavior of the current with the elapsed time shows interesting information about the electropolymerization process, for example, in the case of the MB-PPV formation (Figure 1a) the current value remains practically constant during the time in which the starting compound is present in the reaction medium. This kind of profile indicates that the rate of the polymer formation is the same while the charge transfer process is possible. This homogeneity on electropolymerization kinetics is possible due to mechanical agitation of the solution during the process. In the case of the preparation of *cop*-MB-DCN-PPV (Figure 1b) the current profile as a function of time shows that the current value is greater at the beginning of the process and decreases with increasing time. It is observed that the current profile form three levels with values of ca. 35, 28 and 25 mA, respectively.

This behavior indicates that the rate of polymerization is higher at the beginning and decreases during the polymer formation. This suggests that the copolymer formation occurs mainly by the preferential formation of blocks of DCN-PPV due to the fact that the overpotential for electropolymerization of the DCN-PPV is lower than for the MB-PPV.^{16,17} In this way, the consumption of the monomer for the DCN-PPV is greater at the beginning, and its concentration decreases favoring the increase of

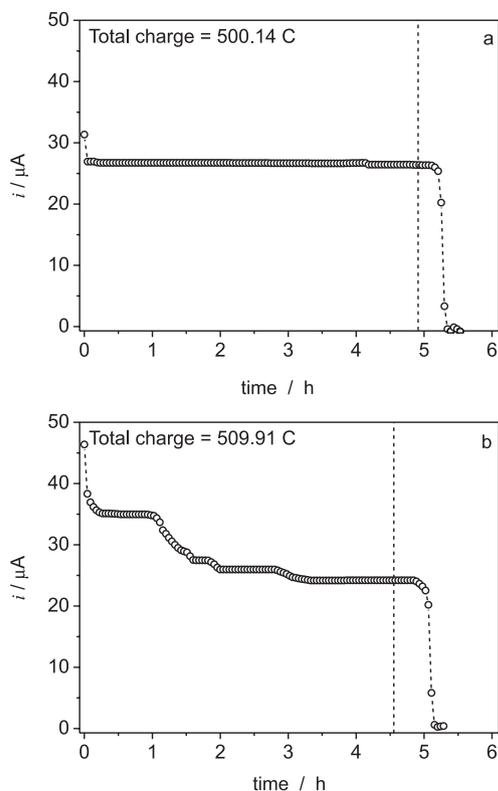


Figure 1. Profile of the current as a function of time for the potentiostatic electropolymerization of a) MB-PPV ($-1.8 \text{ V vs. Ag/AgCl}$) and b) $\text{cop-MB-PPV/DCN-PPV}$ ($-2.0 \text{ V vs. Ag/AgCl}$) in an electrolytic solution of $0.1 \text{ mol L}^{-1} \text{ LiClO}_4$ in DMF using a mercury pool as working electrode.

the reduction of the monomer of the MB-PPV, diminishing the reduction velocity due to the increase of the required overpotential for the reaction.¹⁶⁻¹⁸

Spectroscopic analysis

The electrochemical polymerization of the MB-PPV homopolymer and the $\text{cop-MB-PPV/DCN-PPV}$ over the mercury pool allows the production of a soluble and an

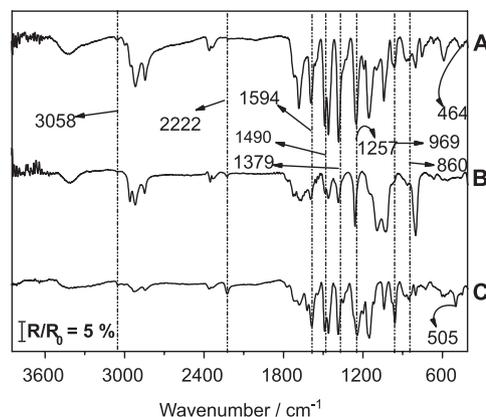


Figure 2. FTIR spectra of A) MB-PPV; B) $\text{cop-MB-PPV/DCN-PPV}_{\text{sol.fr.}}$ and C) $\text{cop-MB-PPV/DCN-PPV}_{\text{insol.fr.}}$

insoluble fraction. The IR spectra of MB-PPV and $\text{cop-MB-PPV/DCN-PPV}$ insoluble fraction are shown in Figure 2.

Both the soluble and insoluble fractions of the $\text{cop-MB-PPV/DCN-PPV}$ presents typical $\text{C}\equiv\text{N}$ band at 2222 cm^{-1} , although it should be noted that the ratio of the intensity of this band related to the other characteristic bands of the copolymer (for example in ca. 1594 , 1490 and 1379 cm^{-1}) is smaller for the spectrum of the soluble fraction than for the spectrum of the insoluble fraction. Furthermore, only the insoluble fraction of this copolymer presents the typical DCN-PPV band at 505 cm^{-1} .¹⁶ These two observations can be an indication that, in condition of preparation used in this study, the insoluble fraction of the $\text{cop-MB-PPV/DCN-PPV}$ contains more units of DCN-PPV than the soluble fraction. This could be explained by the higher insolubility of the DCN-PPV compared to the MB-PPV units.¹⁶⁻¹⁹

The observations described above corroborate the discussions of the behavior of the current profile observed during the electrochemical production of the $\text{cop-MB-PPV/DCN-PPV}$ where the higher current value at the beginning of the reaction was assigned to the preferential formation of DCN-PPV blocks. Table 1 shows the band assignments

Table 1. Assignments for the main IR bands observed for MB-PPV and cop-MB-PPV/DCNPPV at soluble and insoluble fraction

MB-PPV bands / cm^{-1}	$\text{cop-MB-PPV/DCN-PPV}_{\text{sol.fr.}}$ bands / cm^{-1}	$\text{cop-MB-PPV/DCN-PPV}_{\text{insol.fr.}}$ bands / cm^{-1}	Assignment ^a
3058	3058	3058	$\nu_{\text{C-Harom.}}$
–	2222	2222	$\nu_{\text{C}\equiv\text{N}}$
1594	1594	1594	$\nu_{\text{C}=\text{Carom.}}$
1490	1490	1490	$\nu_{\text{C}=\text{Carom.}}$
1379	1379	1379	$\nu_{\text{C}=\text{Carom.}}$
1257	1257	1257	$\nu_{\text{assym.C-O-C}}$
969	969	969	$\delta_{\text{C-Htrans-vinylene O-o-p}}$
860	860	860	$\delta_{\text{C}=\text{Carom.}}$
–	–	505	aromatic 1,4-disubstituted
464	464	464	$\delta_{\text{C-Br O-o-p}}$

^ao-o-p: out-of-plane.

for the principal absorptions in the FTIR spectra of the studied polymers.¹⁶

The UV-Vis spectra of solutions of the soluble fraction of MB-PPV and *cop*-MB-PPV/DCN-PPV prepared in chloroform are shown in Figure 3a and 3b, respectively. Both spectra present a main absorption band around 320 nm and a shoulder at 395 nm. According to Brédas *et al.*¹⁹ the transition in ca. 320 nm could be assigned to the localized transitions $l \rightarrow \pi^*$ and $\pi \rightarrow l^*$ (where l represents localized levels and π represents delocalized levels). On the other hand the shoulder at 395 nm could be assigned to the strongly delocalized $\pi \rightarrow \pi^*$ electronic transition.

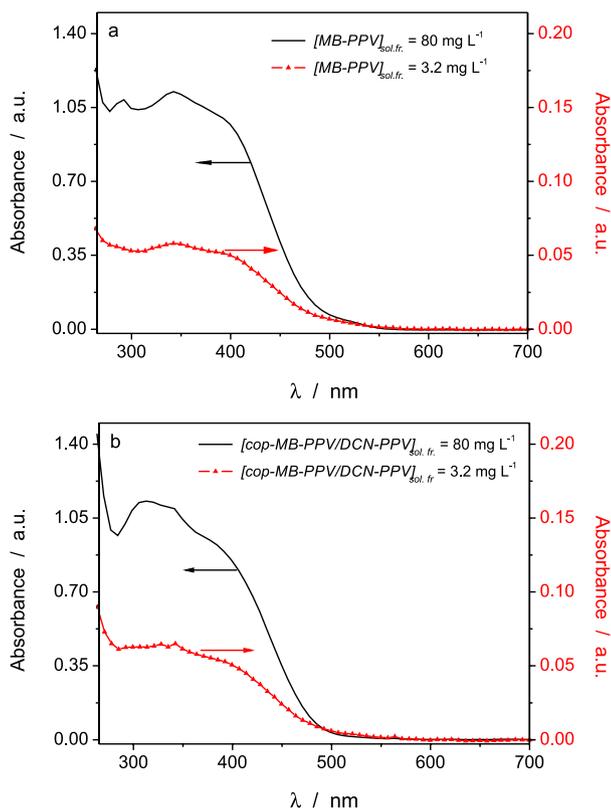


Figure 3. UV-Vis spectra of soluble fraction of a) MB-PPV (-1.8 V vs. Ag/AgCl) at 80 mg L^{-1} and 3.2 mg L^{-1} and b) *cop*-MB-PPV/DCN-PPV (-2.0 V vs. Ag/AgCl) at 80 mg L^{-1} and 3.2 mg L^{-1} .

The predominance of non-delocalized transitions is an indication that the polymers formed have a short average chain length. In fact, the method of electropolymerization in Hg pool produces the conjugated polymer in one step, and for this reason, the major chains formed remain in the insoluble form. However, the addition of O-CH₃ (methoxy) group increases the solubility, as can be seen when comparing polymers DCN-PPV and PPV obtained by Péres *et al.*^{20,21} with the polymers obtained in this work.

Fluorescence emissions were also investigated in order to get information about the electronic structure of

polymers as well as data about the process of radiation emission. Figure 4 shows fluorescence emission spectra of the soluble fraction in chloroform solution of MB-PPV and *cop*-MB-PPV/DCN-PPV, both containing 3.2 mg L^{-1} . The emission of the polymers was evaluated at four different wavelengths of excitation, 350, 400, 450 and 500 nm. It may be noted in Figure 4 that the emission spectra for the first three wavelengths of excitation present similar format with a small displacement of the emission maximum to the red region as excitation radiation is also shifted to red. This behavior is a strong indication that the emission process should occur from entities like aggregates or excimers formed by strong interactions between the polymer molecules. These entities have a tendency to emit at longer wavelengths than the isolated molecules.

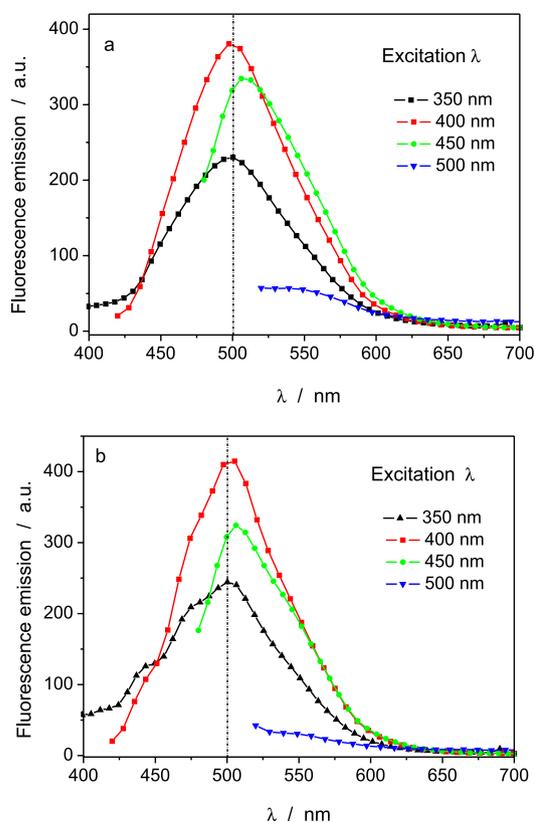


Figure 4. Emission spectra of soluble fraction of a) MB-PPV (-1.8 V vs. Ag/AgCl) at 3.2 mg L^{-1} and b) *cop*-MB-PPV/DCN-PPV (-2.0 V vs. Ag/AgCl) at 3.2 mg L^{-1} .

The excitation spectra obtained for both polymers also indicate that the maximum of excitation does not match the maximum absorption of the UV-Vis spectrum (Figure not shown). These characteristics are typical of exciton emissions, which could be formed between chains, such as excimer and aggregates. Excimers are groups of two or more segments of molecules with a coplanar arrangement having a repulsive interaction in the ground state, which

becomes attractive when one of these molecules is excited. Aggregates are arrangements of molecules that form entities through attractive interactions in both the ground state and excited state.¹⁸ The formation of aggregates or excimers requires basically the same conditions. In the case of the excimer, the distance between the two parallel units must be between 3 to 4 Å to enable a π orbital overlap. For the formation of aggregates the space between the forming units must be smaller than in the case of excimer in order to provide a sufficiently large interaction to form a stable association in the ground state.^{18,19} Thus it can be inferred that the observed emission behavior of the polymers evaluated in this paper occurs due to the formation of excimers since the excitation spectra for both polymers does not match the absorption of the UV-Vis spectra.

Cyclic voltammetry of films

The cyclic voltammograms of the films of the soluble fraction of the polymers obtained in this work are shown in Figure 5. These measurements were performed by cycling the potential from 0.0 V (*vs.* Ag/AgCl) toward positive potentials until 1.5 V (*vs.* Ag/AgCl) in the limit range allowed by the solvent/electrolyte system used. In this case no current increase was observed concerning the oxidation of the MB-PPV or the *cop*-MB-PPV/DCN-PPV.

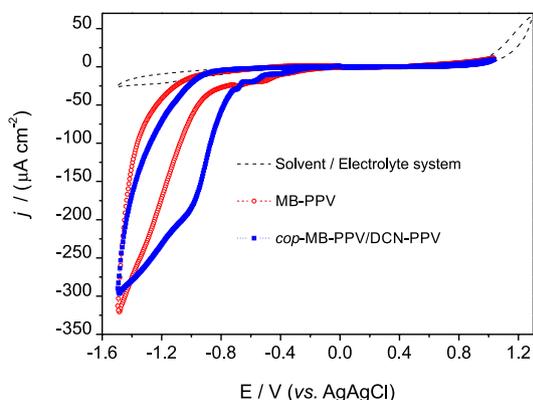


Figure 5. Cyclic voltammograms of the polymer films obtained with the soluble fraction of - - ○ - - MB-PPV (-1.8 V *vs.* Ag/AgCl) and - - ■ - - *cop*-MB-PPV/DCN-PPV (-2.0 V *vs.* Ag/AgCl) at 80 mg L⁻¹. The films were obtained by drop casting of the polymeric solution in CHCl₃ over ITO substrate, scan rate = 50 mV s⁻¹. The black dash line shows the voltametric profile of the bare ITO surface on an ACN/LiClO₄ 0.1 mol L⁻¹ solution used as solvent/electrolyte system in all the voltametric characterization.

On the other hand, toward negative potential values it was observed that the *cop*-MB-PPV/DCN-PPV reduction process starts at less negative values in comparison with MB-PPV reduction process. The use of electrochemical data to estimate parameters of the electronic structure requires that the charge transfer

process be reversible, which is not true for the processes noted above.^{22,23} However it can be observed that the reduction to *cop*-MB-PPV/DCN-PPV begins to flow through the system in less negative potentials compared to MB-PPV. These results indicate that the copolymer presents a more stable conduction band than MB-PPV, which is consistent with the presence of DCN-PPV blocks formed during electropolymerization process, as already shown by IR results. This observation indicated that the *cop*-MB-PPV/DCN-PPV formed at the Hg pool presented a D-A characteristic, and for this reason is a good candidate to be used as active layer in photovoltaic devices.

Conclusions

The electrochemical method has been effective for preparing soluble PPV-like polymer and copolymer, containing units with -O-CH₃ groups and/or -CN groups attached to the aromatic ring. The analysis of electrochemical measurements and infrared spectroscopy indicated that the copolymer *cop*-MB-PPV/DCN-PPV was obtained through the formation of blocks containing DCN-PPV units linked by blocks containing units of MB-PPV. The characterization of the electronic structure of the obtained polymers, performed by cyclic voltammetry measurements, UV-Vis and fluorescence spectroscopy allowed verifying that the conduction band of the copolymer is more stabilized than the conducting band of the homopolymer MB-PPV. Furthermore, the measurements of emission and excitation spectra indicated that the process of light emission in the case of dilute solutions of the copolymer prepared in chloroform occurs by means of the formation of excimers. The production of the *cop*-MB-PPV/DCN-PPV opens the possibility of using the electrochemical methods to produce interesting materials as PPV-like polymers with good properties to be used in photovoltaic devices with improved processability due to the increase of solubility caused by the presence of the -O-CH₃ moieties.

Acknowledgments

K. C. C. W. S. K and F. S. S. are grateful for the fellowship granted from CAPES. The authors also thank the financial support provided for this research by the Brazilian Agencies CNPq, CAPES, Fapesp (07/50742-2) and Fundação Araucária (Paraná State).

References

1. Scharber, M. C.; Sariciftci, N. S.; *Prog. Polym. Sci.* **2013**, *38*, 1929.

2. Chiechi, R. C.; Havenith, R. W. A.; Hummelen, J. C.; Koster, L. J. A.; Loi, M. A.; *Mater. Today* **2013**, *16*, 281.
3. Heeger, A. J.; *Adv. Mater.* **2014**, *26*, 10.
4. Li, W.; Hendriks, K. H.; Roelofs, W. S. C.; Kim, Y.; Wienk, M. M.; Janssen, R. A. J.; *Adv. Mater.* **2013**, *25*, 3182.
5. Janssen, R. A. J.; Nelson, J.; *Adv. Mater.* **2013**, *25*, 1847.
6. Wang, L.; Jiang, P.; Zhang, Z.-G.; Fu, Q.; Li, Y.; *Macromol. Chem. Phys.* **2013**, *214*, 1772.
7. Marin, K.; Lutsen, L.; Vanderzande, D.; Maes, W.; *Org. Biomol. Chem.* **2013**, *11*, 5866.
8. Lyons, D. M.; Kesters, J.; Maes, W.; Bielawski, C. W.; Sessler, J. L.; *Synt. Metals* **2013**, *178*, 56.
9. Kesters, J.; Ghooos, T.; Penxten, H.; Drijkoningen, J.; Vangerven, T.; Lyons, D. M.; Verreet, B.; Aernouts, T.; Lutsen, L.; Vanderzande, D.; Manca, J.; Maes, W.; *Adv. Energ. Mater.* **2013**, *3*, 1180.
10. Lei, T.; Dou, J.-H.; Cao, X.-Y.; Wang, J.-Y.; Pei, J.; *J. Am. Chem. Soc.* **2013**, *135*, 12168.
11. Shin, S. A.; Kim, J.-H.; Park, J. B.; Kang, I.-N.; Park, M.-J.; Hwang, D.-H.; *Macromol. Chem. Phys.* **2013**, *214*, 1780.
12. Van Mierloo, S.; Hadipour, A.; Spijkman, M.-J.; Van den Brande, N.; Ruttens, B.; Kesters, J.; D'Haen, J.; Van Assche, G.; de Leeuw, D. M.; Aernouts, T.; Manca, J.; Lutsen, L.; Vanderzande, D.; Maes, W.; *Chem. Mater.* **2012**, *24*, 587.
13. Wienk, M. M.; Turbiez, M.; Gilot, J.; Janssen, R. A. J.; *Adv. Mater.* **2008**, *20*, 2556.
14. Bijleveld, J. C.; Zoombelt, A. P.; Mathijssen, S. G. J.; Wienk, M. M.; Turbiez, M.; de Leeuw, D. M.; Janssen, R. A. J.; *J. Am. Chem. Soc.* **2009**, *131*, 16616.
15. Nielsen, C. B.; Turbiez, M.; McCulloch, I.; *Adv. Mater.* **2013**, *25*, 1859.
16. Garcia, J. R.; Peres, L. O.; Fernandes, M. R.; Gruber, J.; Nart, F. C.; *J. Solid. State Electrochem.* **2004**, *8*, 122.
17. Peres, L. O.; Varela, H.; Garcia, J. R.; Fernandes, M. R.; Torresi, R. M.; Nart, F. C.; Gruber, J.; *Synth. Met.* **2001**, *118*, 65.
18. Garcia, J. R.; Gehlen, M.; de Oliveira, H. P. M.; Nart, F. C.; *J. Braz. Chem. Soc.* **2008**, *19*, 1306.
19. Brédas, J. L.; Cornil, K.; Meyers, F.; Beljonne, D.; *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R., eds.; Marcel Dekker: New York, USA, 1998, ch. 1.
20. Lima, J. R.; Péres, L. O.; Garcia, J. R.; Gruber, J.; Hümmelgen, I. A.; *Solid-State Electr.* **2000**, *44*, 565.
21. Péres, L. O.; Aguiar, M.; Akcelrud, L.; Garcia, J. R.; Gruber, J.; Fugihara, M. C.; Hümmelgen, I. A.; *J. Lumin.* **2002**, *96*, 219.
22. Micaroni, L.; Nart, F. C.; Hümmelgen, I. A.; *J. Solid State Electrochem.* **2002**, *7*, 55.
23. Valaski, R.; Moreira, L. M.; Micaroni, L.; Hümmelgen, I. A.; *Braz. J. Phys.* **2003**, *33*, 392.

Submitted: October 31, 2013

Published online: February 7, 2014

FAPESP has sponsored the publication of this article.