



A blue-light dosimeter which indicates the dose accumulation by a multicoloured change of photodegraded polymer

C.K.B. de Vasconcelos, R.F. Bianchi*

Laboratório de Polímeros e Propriedades Eletrônicas de Materiais – LAPPEM, Departamento de Física da Universidade Federal de Ouro Preto – UFOP, Campus Morro do Cruzeiro, CEP 35.400-000, Ouro Preto, MG, Brazil

ARTICLE INFO

Article history:

Received 26 November 2008

Received in revised form 27 August 2009

Accepted 8 September 2009

Available online 19 September 2009

Keywords:

Sensor

OLED

Hyperbilirubinemia

Jaundice

Semiconducting polymer

Photooxidation

ABSTRACT

Luminescent polymers are commonly employed in light-emitting displays because of their good processability and higher luminance with low power consumption. However, even though they are candidates for lighting applications, they are susceptible to photooxidation processes which dramatically change their colour with light exposure. In this work we use the light instability of luminescent polymers in order to design a blue-light dosimeter which indicates dose accumulation by multicoloured changes of photodegraded poly(2-methoxy-5(2'-ethylhexyloxy)-*p*-phenylenevinylene) (MEH-PPV). Photoluminescence and absorbance spectra measurements were carried out on MEH-PPV solutions under the effect of blue-light provided by phototherapy systems. All measurements were done maintaining chief conditions of jaundice treatments. It is observed that changes from orange-red to yellow clearly on colour solutions, while its peak position emission shifts from orange-red to blue and decreases in intensity with increasing radiation exposure time. Experiments performed with oxygen enriched solutions were shown to improve these effects, which is mainly caused by the competition between two possible mechanisms: a light induced polymerization of MEH-PPV and replacement of C=C by C=O bonds on the polymer backbone. Analyses of the relation between the irradiance produced by phototherapy systems and CIE (1931) chromatic diagram of MEH-PPV reveal this polymer as an easy to operate blue-light dosimeter, and the results reported here clearly demonstrated the possibility to produce self-adhesive patch of luminescent polymers in order to attach such organic dosimeter safely and placed closer to the skin of jaundiced infants.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

In the past years, conjugated polymers have been appeared as very promising materials for use in next generations of displays, not only because of their good processability in solutions and lightweight, but also due to their higher luminance with low power consumption [1,2]. However, even though they are good candidates for lighting applications, they still have major problems in terms of stability [3]. Because of their conjugated nature, they are highly susceptible to degradation processes [3–5] which dramatically change the emission colour and reduce the efficiency and durability of their devices. Apart from the degradation processes due to electrical and/or thermal effects, there is also a need for suitable polymers which are inherently resistant to photooxidation process [6]. This result reveals, on the one hand, the low reliability of polymer devices, and on the other reflects the possibility to design and develop dosimeters where the effects of visible radiation on the optical properties of conjugated polymers are more important

than improving the luminance and lifetime of the light-emitting devices made from them. Moreover visible dosimetry is desired especially in medical applications where phototherapy is used, for example, in the treatment of preterm infants with jaundice [7,8], which is one of the most common reasons for hospital readmissions of newborn infants and where a strong relationship exists between the rate of decline in serum bilirubin level of infant's skin and the intensity, irradiance, irradiated area and spectral qualities of the light source provided by commercial systems [9–11]. However, evidence has been gathering from several studies [12–14] that bilirubin is potentially toxic to the central nervous systems and it is clear that it needs to be controlled to prevent neurological damages in newborn infants. A good review of some of the bilirubin metabolism during phototherapy can be found in Ref. [13]. More recently, Maisels et al. [13] also have reported that no single standardized method or radiometers are general used for reporting the correct phototherapy dosages in the clinical literature. As a consequence, the need for an effective management of the radiation doses planning before treatment of jaundice is therefore obvious.

In this work we investigated the changes on colour, photoluminescence and absorbance behavior of poly(2-methoxy-5(2'-ethylhexyloxy)-*p*-phenylenevinylene) (MEH-PPV) solutions under

* Corresponding author. Tel.: +55 31 3559 1742; fax: +55 31 3559 1667.
E-mail address: bianchi@iceb.ufop.br (R.F. Bianchi).

the effect of blue-light radiation usually used to treat preterm infants with jaundice. Emphasis is placed on the irradiance and on the effects of oxygen enriched solutions and polymer concentration on the optical performance of a blue-light dosimeter which indicates the dose accumulation by a multicoloured change of photodegraded polymer. In the design of such device, it has been amply demonstrated that luminescent polymers are potential candidates for film-based sensor for easy readout.

2. Experimental procedures

The poly(2-methoxy-5(2'-ethylhexyloxy)-*p*-phenylenevinylene) (MEH-PPV) was purchased from Sigma–Aldrich. 2 ml of chloroform solutions were prepared and transferred to glass ampoules which were then flame-sealed. Since oxygen plays an important role on the photooxidation process of MEH-PPV [4,5], the solutions were also enriched with oxygen or nitrogen gases during 15 min. We assumed here the nitrogen enriched solution as an almost free-oxygen system. Photodegradation experiments were performed by illuminating the solutions with a commercial phototherapy system (Bilitron® 3006, 460 nm focus). Irradiation was performed at room temperature and placed at 30 cm, 32 cm and 36 cm from the samples, yielding an estimated central peak irradiance of $40 \mu\text{W}/(\text{cm}^2 \text{ nm})$, $37 \mu\text{W}/(\text{cm}^2 \text{ nm})$ and $34 \mu\text{W}/(\text{cm}^2 \text{ nm})$, respectively, in order to investigate the importance of irradiance and the sensibility of the MEH-PPV solutions under phototherapy conditions [11]. The photoemission spectra were recorder using an USB2000 Ocean Optics spectrophotometer, while a blue LED ($\lambda_{\text{max}} = 460 \text{ nm}$, $0.15 \mu\text{W}/(\text{cm}^2 \text{ nm})$) was used as excitation source. It is being considered here that the low central peak irradiance of such blue LED and the short period of PL measurements ($<1 \text{ s}$) do not play a significant role for photooxidation mechanism of MEH-PPV solutions. Finally, absorption spectra were carried out in the 300–800 nm range using a Shimadzu UV 1650 equipment, while the colour coordinates of CIE (1931) diagram chromatics were recorded using a Pantone® Colour Cue® 2 and a Pantone GoeGuide™ colours (the international printing, publishing and packaging colour language). All measurements were done at room temperature.

It is important to remark that the radiation exposure time instead of radiation dose is used in this work since it is the usual controller parameter applied in phototherapy treatments, and the results presented in this paper are divided in two sections: fundamental investigations on the effect of blue-light on the optical properties of MEH-PPV, and the design and development of an organic dosimeter to determine the dose from the polymer colour.

3. Results and discussions

Fig. 1 shows the photoemission (PL) spectra obtained from MEH-PPV solutions ($50 \mu\text{g}/\text{ml}$) enriched with N_2 (Fig. 1a) and O_2 (Fig. 1b) and also exposed to the commercial phototherapy system from $t_0 = 0 \text{ min}$ to 480 min. The spectra of both non-irradiated solutions ($t_0 = 0$) are characteristic of poly(*p*-phenylenevinylene)–PPV derivatives showing a main emission peak (λ_{max}) assigned as an excitonic emission [15] at about 560 nm with a small shoulder at 590 nm. The maximum PL intensity at about 560 nm is then significantly increased from 0.9 to 1.0 with $t_0 = 60 \text{ min}$ and 20 min for N_2 and O_2 enriched solutions, respectively, while the peak at 560 nm became dominant and the peak at 590 nm disappeared. From t_0 higher than 60 min (Fig. 1a) and 20 min (Fig. 1b), it is observed that: (i) the polymer solution changes from orange-red to yellow clearly, (ii) λ_{max} shifts towards lower wavelength and (iii) PL intensity decays surprisingly. Moreover, the inset in Fig. 1b shows the λ_{max} vs. t_0 curves of both exposed solutions and it is clear that

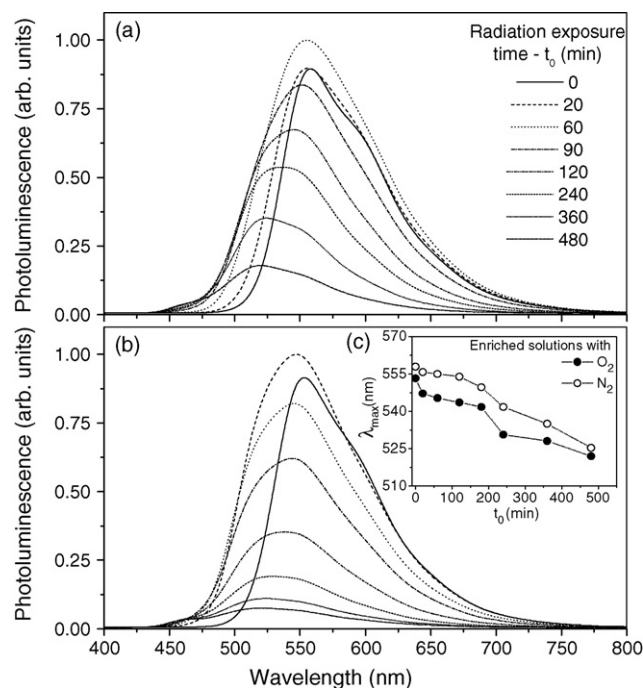


Fig. 1. Photoemission spectra obtained from MEH-PPV solutions ($50 \mu\text{g}/\text{ml}$) enriched with (a) N_2 and (b) O_2 and also exposed to the commercial phototherapy system from $t_0 = 0 \text{ min}$ to 480 min. The inset in (b) shows the λ_{max} vs. t_0 curves of both exposed solutions. The lines are only guiding the eyes.

role of photooxidation mechanism is less pronounced in N_2 enriched solution. The observed MEH-PPV optical behavior is consistent with the replacement of vinyl group ($\text{C}=\text{C}/970 \text{ cm}^{-1}$) by carbonyl groups ($\text{C}=\text{O}/1670 \text{ cm}^{-1}$) on MEH-PPV backbone due to photooxidation process [5,16]. This is confirmed by monitoring the FTIR spectra of cast films obtained from irradiated N_2 enriched solution (Fig. 2) using the same equipment and procedure as described in Ref. [5]. This effect reduces the average effective polymer conjugation length and usually acting as quenching centers for excitonic emission [16]. It was established here that the basic principle behind the PL enhancement of MEH-PPV dilute solutions may involve a competition between two possible mechanisms: (i) a light induced polymerization of MEH-PPV, as pointed out by the increase of vinyl groups on FTIR measurements and (ii) also an efficient spectral diffusion of excited carries into no degraded polymer chains by Förster energy transfer consistent with earlier reports [17]. However, these assumptions should urge further investigations on MEH-PPV dilute solutions under the effect of blue LED light source.

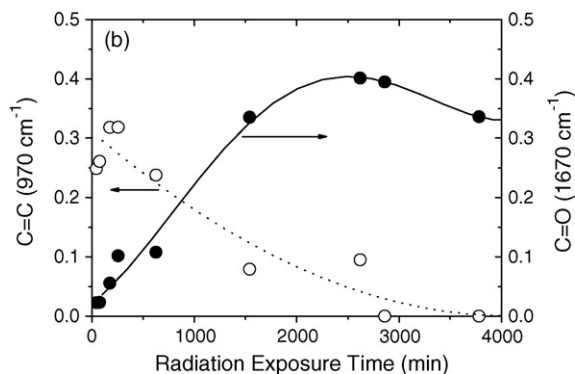


Fig. 2. Absorption values of $\text{C}=\text{C}$ (970 cm^{-1}) and $\text{C}=\text{O}$ (1670 cm^{-1}) groups obtained from MEH-PPV solutions exposed to the commercial phototherapy system. The lines are only guiding the eyes.

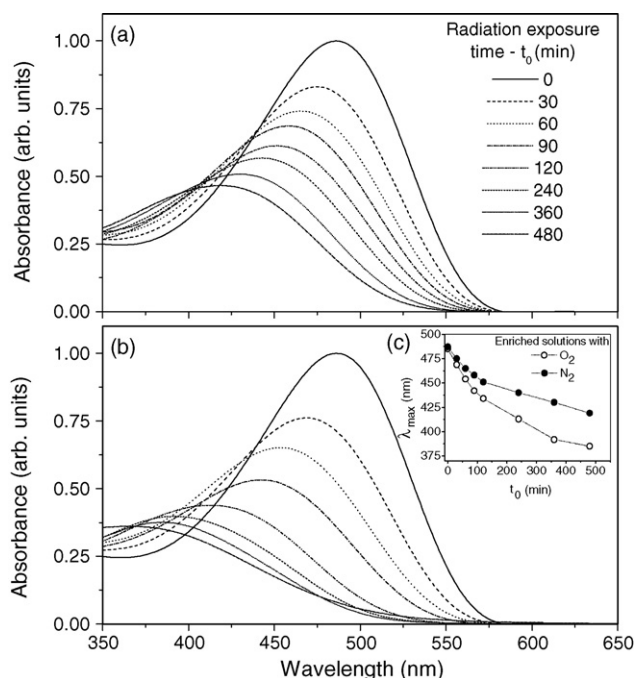


Fig. 3. Absorbance spectra obtained from MEH-PPV solutions (50 $\mu\text{g/ml}$) enriched with (a) N_2 and (b) O_2 and exposed to the commercial phototherapy system from $t_0 = 0$ min to 480 min. The inset in (b) shows the λ_{max} vs. t_0 curves of both exposed solutions. The lines are only guiding the eyes.

Fig. 3 shows the absorbance spectra obtained from MEH-PPV solutions (50 $\mu\text{g/ml}$) enriched with N_2 (Fig. 3a) and O_2 (Fig. 3b) and also exposed to the commercial phototherapy system from $t_0 = 0$ min to 480 min. Again, the spectra of the non-irradiated solutions ($t_0 = 0$) are characteristic of poly(*p*-phenylenevinylene)–PPV derivatives showing a main absorption peak (λ_{max}) at 490 nm, with decreases in intensity and position with increasing radiation exposure time. The inset in Fig. 3b shows the λ_{max} vs. t_0 curves of both solutions where the role of photoxidation mechanism is more pronounced in O_2 enriched solution.

Fig. 4 shows the time to reach the maximum PL intensity of MEH-PPV solutions enriched with N_2 and O_2 gases and with different mass concentrations (50 $\mu\text{g/ml}$, 100 $\mu\text{g/ml}$, 250 $\mu\text{g/ml}$ and 500 $\mu\text{g/ml}$). We note on the results shown in Fig. 4 that the higher is the polymer concentration for N_2 enriched solutions, higher is t_0 . This concentration-dependence seems to obey a linear behavior.

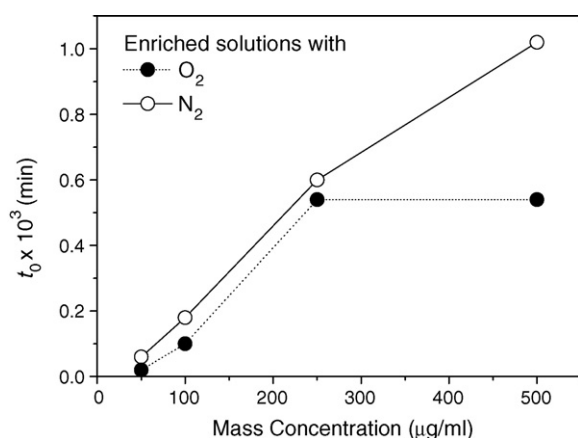


Fig. 4. Time to reach the maximum PL intensity of MEH-PPV solutions enriched with N_2 and O_2 gases with different mass concentrations (a) 50 $\mu\text{g/ml}$, (b) 100 $\mu\text{g/ml}$, (c) 250 $\mu\text{g/ml}$ and (d) 500 $\mu\text{g/ml}$. The lines are only guiding the eyes.

ior. On the other hand, a plateau at around 475 min is observed to occur at about 250 $\mu\text{g/ml}$ for O_2 enriched solution, indicating a saturation value. Within the limits of experimental errors, the only change in the curves was the change of t_0 and thus t_0 dependence on the PL intensity of N_2 enriched solutions is an important key to the fundamental investigations on the effects of blue-light on the MEH-PPV photooxidation in which for $t \leq t_0$, the integrated PL intensity increases slowly with t , while for $t \geq t_0$, it decreases considerably. In practice, there is no implication of the increase in the PL spectra for the design of light sensors, but the decrease in the PL and in the absorbance spectra have been the subject of a great deal of research in the development of a system to determine the dose from the polymer colour.

The advantage of MEH-PPV as radiation detector is also manifested from the dramatic colour change of CIE (1931) chromatic diagram and the PL emission shown in Figs. 5 and 6, respectively. The chromatic diagrams were obtained from N_2 enriched solutions with different mass concentration (25 $\mu\text{g/ml}$, 50 $\mu\text{g/ml}$, 100 $\mu\text{g/ml}$ and 250 $\mu\text{g/ml}$), while the PL were obtained from N_2 enriched solutions (50 $\mu\text{g/ml}$). All the solutions were exposed to the commercial phototherapy system from 0 min to 240 min. From Fig. 5, it is also observed that the colour changes occur in opposite directions as function of mass concentration probably associated with the different degradation rates of low and high polymer mass concentration solutions. Moreover, it is applicable in practice using two or more solutions with different mass concentration to avoid indeterminacy in reading the radiation dose, in which the same value of PL intensity may correspond to different irradiation times. It is important to remark here that 120 min is the time-interval between breastfeeding and thus when the phototherapy may be interrupted.

Finally, from the results shown in Fig. 5 it is made possible to design a standardized colour chart for blue-light phototherapy management based on the colour changes of MEH-PPV solutions exposed to radiation in order to represent easily the optical response of organic solutions and thus the radiation dose prescription usually used in management of neonatal jaundice. Fig. 7 shows a standardized colour chart for blue-light phototherapy management obtained from colour of MEH-PPV solutions exposed up to 240 min of radiation. This colour chart was easily obtained from the colour comparison between the MEH-PPV solution and a Pantone GoeGuide™ colours. A check against the colour comparison standardized colour chart (Fig. 7) easily supplied allows the dose to be determined. This figure also present the Pantone GoeGuide™ colours Code hence this organic system is applicable as a simple and low cost dosimeter (<US\$ 0.10) for manages the radiation doses planning before treatment of jaundice of neonates. The colour change shown in Fig. 5 are used to design a novel indicator-dosimeter. Fig. 8 shows the CIE (1931) chromatic diagram obtained from N_2 enriched solutions (50 $\mu\text{g/ml}$) exposed to 40 $\mu\text{W}/(\text{cm}^2 \text{ nm})$, 37 $\mu\text{W}/(\text{cm}^2 \text{ nm})$ and 34 $\mu\text{W}/(\text{cm}^2 \text{ nm})$ from 0 min to 240 min. Under these conditions, the sensibility of the device is directly proportional to the radiation dose in agreement with the importance to control the incident dose in neonates treat with phototherapy [11]. Our analysis shows that the colour of the polymer sensor can provide the dose irrespectively of the illumination power. These results, which to our knowledge are new for phototherapy of neonatal jaundice, have enable a quantitative analysis to be made of how the polymer colour is modified by the dose provided by blue LEDs.

4. Final remarks

The colour and PL behavior of MEH-PPV under the effect of blue-light source described in this work possesses many attractive features for novel radiation dosimeter for phototherapy applica-

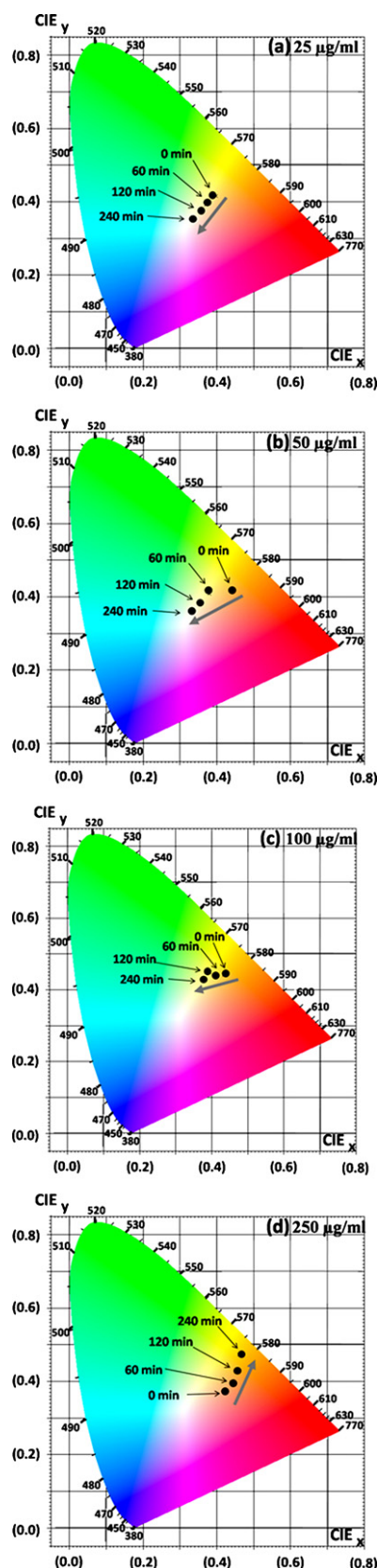


Fig. 5. CIE (1931) chromatic diagram showing the influence of blue-light radiation on the colour coordinates of MEH-PPV chloroform solutions with different mass concentrations (a) 50 $\mu\text{g/ml}$, (b) 100 $\mu\text{g/ml}$, (c) 250 $\mu\text{g/ml}$ and (d) 500 $\mu\text{g/ml}$.



Fig. 6. PL images of N_2 enriched solutions (50 $\mu\text{g/ml}$) exposed to the commercial phototherapy system from (a) 0 min, (b) 60 min, (c) 120 min, (d) 180 min and (e) 240 min.

tions in which the needs of control of dose absorption of infant's skin is extremely important not only for medical investigations and prescriptions, but also for medical controller and inspections. As can also be seen for the results shown in Figs. 1 and 3, the roles of the oxygen and the polymer concentrations are important keys to improve the dose–response of the MEH-PPV dosimeter since these parameters were found to be very useful for investigating the sensibility response of the sensor [18].

In summary, we are motivated by our goal to provide a novel indicator-dosimeter to manage the radiation doses to newborn infants in blue-light phototherapy procedures using the light instability of colour and luminescent polymers commonly used as active material for light-emitting displays. Advantages of the use of this organic solution as the indicator-dosimeter are: low cost, easy to make, easy to read, easy to operate and accuracy for individual monitoring which indicates the dose accumulation by a multi-coloured change of photo-degraded polymer. Moreover, in order to improve the optical properties and performance of the indicator-dosimeter in the range relevant for the considered applications, and thus the efficiency of the overall effects, the influence of light doses and the possibility to produce self-adhesive patch of MEH-PPV in order to attach the polymer dosimeter safely and placed closer to the skin of the infant are still under development and investigation.

RADIATION EXPOSURE TIME (MIN)					
	0	60	120	240	
MASS CONCENTRATION (μg/ml)	25	PANTONE 608C	PANTONE 7485C	PANTONE ClGy1C	PANTONE 663C
	50	PANTONE 7509C	PANTONE 808C	PANTONE 621C	PANTONE ClGy1C
	100	PANTONE 156C	PANTONE 7403C	PANTONE 127C	PANTONE 600C
	250	PANTONE 1625C	PANTONE 721C	PANTONE 7508C	PANTONE 610C

Fig. 7. A standardized colour chart for blue-light phototherapy management based on the colour changes of MEH-PPV solutions exposed to radiation and the Pantone GoeGuide™ colours Code.

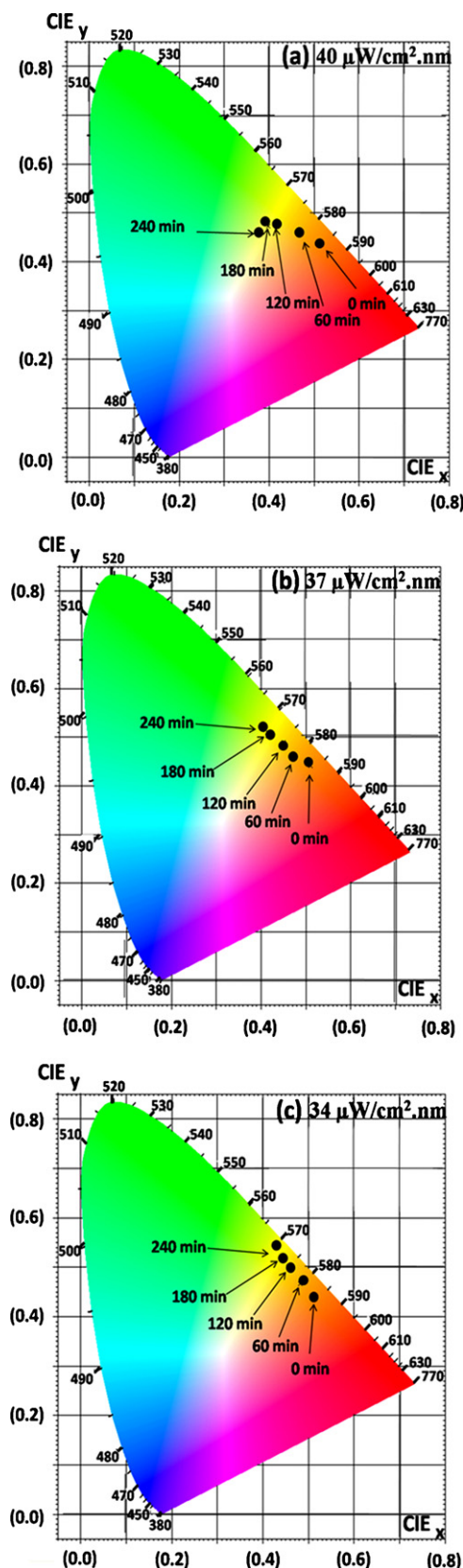


Fig. 8. CIE (1931) chromatic diagram obtained from N₂ enriched solutions (50 μg/ml) exposed to 40 μW/(cm² nm), 37 μW/(cm² nm) and 34 μW/(cm² nm) from 0 min to 240 min.

Acknowledgement

This work was supported by FAPEMIG, CNPq and INEO/CNPq (Brazil).

References

- [1] J.N. Bardsley, J.N. Bardsley, International OLED technology roadmap, *IEEE J. Sel. Top. Quant. Electron.* 10 (2004) 3–9.
- [2] F. So, B. Krummacher, M.K. Mathai, D.S. Poplavskyy, A. Choulis, V.E. Choong, Recent progress in solution processable organic light emitting devices, *Appl. Phys.* 102 (2007) 091101.1–091101.21.
- [3] G.R. Chaji, C. Ng, A. Nathan, A. Wemer, J. Birnstoch, O. Schneider, J. Blochwitz-Nimoth, Electrical compensation of OLED luminance degradation, *IEEE Electron. Dev. Lett.* 28 (2007) 1108–1110.
- [4] C.A. Olivati, M. Ferreira, R.F. Bianchi, R.M. Faria, O.N. Oliveira, D.T. Balogh, The influence of preparation method of OC1OC6-PPV films on the photo-oxidation process, *Pol. Deg. Stab.* 91 (2006) 2342–2346.
- [5] R.F. Bianchi, D.T. Balogh, M. Tinani, R.M. Faria, E.A. Irene, Ellipsometry study of the photo-oxidation of poly[[2-methoxy-5-hexyloxy]-p-phenylenevinylene], *J. Pol. Sci. B: Pol. Phys.* 42 (2004) 1033–1041.
- [6] M. Atreya, S. Li, E.T. Kanga, K.G. Neoh, Z.H. Ma, K.L. Tan, W. Huang, Stability studies of poly[2-methoxy-5-[2'-ethyl hexyloxy]-p-phenylene vinylene] [MEH-PPV], *Pol. Deg. Stab.* 65 (1999) 287–296.
- [7] H.J. Vreman, R.J. Wong, D.K. Stevenson, R.K. Route, S.D. Reader, M.M. Fejer, R. Gale, D.S. Seidman, Light-emitting diodes: a novel light source for phototherapy, *Pediatr. Res.* 44 (1998) 804–809.
- [8] A. Madan, Phototherapy: Old questions, new answers, *Acta Paediatr.* 94 (2005) 1360–1362.
- [9] J.E. Colletti, S. Kothori, D.M. Jackson, K.P. Kilgore, K. Barringer, An emergency medicine approach to neonatal Hyperbilirubinemia, *Emerg. Med. Clin. N. Am.* 25 (2007) 1117–1118.
- [10] M.J. Maisels, E. Kring, J. DeRidder, Randomized controlled trial of light-emitting diode phototherapy, *J. Perinatol.* 27 (2007) 565–567.
- [11] G. Hart, R. Cameron, The importance of irradiance and area in neonatal phototherapy, *Arch. Dis. Child. Fetal Neonatal Ed.* 90 (2005) F437–F440.
- [12] J.F. Watchko, Neonatal hyperbilirubinemia—what are the risks? *N. Engl. J. Med.* 354 (18) (2006) 1947–1949.
- [13] M.J. Maisels, A.F. McDonagh, Phototherapy for neonatal jaundice, *N. Engl. J. Med.* 358 (9) (2008) 920–928.
- [14] L.I. Grossweiner, *The Science of Phototherapy: An Introduction*, Springer, Netherlands, 2005 (Chapter 13).
- [15] M. Segal, M.A. Baldo, R.J. Holmes, S.R. Forrest, Excitonic singlet-triplet ratios in molecular and polymeric organic materials, *Phys. Rev. B* 68 (2003) 075211.1–075211.14.
- [16] B.H. Cumpston, K.F. Jensen, Photooxidation of polymers used in electroluminescent devices, *Synth. Met.* 73 (1995) 195–199.
- [17] M. Anni, G. Gigli, R. Cingolani, Y.G. Gobato, A. Vercik, A. Marletta, F.G.E. Guimarães, R.M. Faria, Defect-assisted photoluminescence intensity enhancement in poly[p-phenylene vinylene] films probed by time-resolved photoluminescence, *Phys. Rev. B* 68 (2003) 035215.1–035215.6.
- [18] G.R. Ferreira, C.K.B. de Vasconcelos, R.F. Bianchi, Design and characterization of a novel indicator dosimeter for blue-light radiation, *Med. Phys.* 36 (2) (2009) 642–644.

Biographies



Cláudia Karina Barbosa de Vasconcelos was born in Pouso Alegre, MG, Brazil, on March 10, 1985. She received her physics undergraduate degree from Federal University of Ouro Preto - UFOP in 2008. She is a graduate student at UFOP in Material Science Engineering.

Rodrigo Fernando Bianchi was born in São Carlos, SP, Brazil, on January 24, 1973. He received his physics undergraduate degree from Institute of Physics at University of São Paulo—USP, São Carlos—SP, Brazil, in 1995, and his master and Ph.D. in material science engineering from USP in 1997 and 2002, respectively. Bianchi began his professional teaching career at Polytechnic School—USP in 2004 and was appointed Professor of Physics at UFOP in 2006. Nowadays he is the supervisor of Laboratory of Polymers and Electronic Properties of Materials - LAPPEM at UFOP (www.fisica.ufop.br/lappem) that aims at providing a stimulating scientific atmosphere for graduate and undergraduate students. LAPPEM carries out the basic research in the field of experimental and theoretical charge transport of materials. It presents chemical, electrical and optical facilities in order to produce organic thin films and electronic devices (diodes, transistors, photovoltaic cells, dosimeters and sensors), as well as their fundamental characterizations.