

## Research Article

# Effect of a Polymeric Protective Coating on Optical and Electrical Properties of Poly(*p*-phenylene vinylene) Derivatives

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The resistance to photodegradation of poly[(2-methoxy-5-*n*-hexyloxy)-*p*-phenylene vinylene] (OC<sub>1</sub>OC<sub>6</sub>-PPV) films was significantly enhanced by the use of poly(vinyl alcohol) 99% hydrolyzed as protective coating. The deposition of poly(vinyl alcohol) onto OC<sub>1</sub>OC<sub>6</sub>-PPV films did not affect the absorption and the emission spectra of the luminescent polymer. The protected film showed 5% drop on the absorbance at 500 nm after 270 hours of light exposure while the unprotected film completely degraded in the same conditions. The conductivity of the protected film remained stable (around  $7 \times 10^{-10}$  S/m) while the value for the unprotected one dropped around two orders of magnitude after 100 hours of light exposure.

## 1. Introduction

Poly(*p*-phenylene vinylene), PPV, derivatives have been widely explored for applications in optoelectronics such as photoluminescent devices, light-emitting diodes, and sensors [1–3]. Despite their wide range of possible applications, the PPV derivatives are highly susceptible to photodegradation, by the combined action of light and oxygen. The photodegradation reaction involves mainly the vinyl group, leading to the formation of carbonyl groups, reducing the conjugation length and, in further stages, leading to chain scission [4–14]. The photodegradation occurs in solution or in the solid state, causing a decay in the absorbance intensity and a blue shift in the absorbance and, consequently, in the emission spectrum of the polymer. In solid state, the photodegradation is thickness dependent due to mainly two factors. The first factor is the difference in the light intensity through the thickness of the material due to the light absorption. The light intensity should be maximum at the surface and decrease exponentially with the increase in thickness (Lambert's law) [15]. The second factor is

the oxygen concentration throughout the material, which depends on the oxygen diffusion through the film [11]. Some approaches have been used in order to prevent or at least try to minimize the photodegradation in the PPV derivatives. An alternative is the use of different encapsulations [16–21]. In a previous paper [16], we presented some results on the use of polymer protective layers aiming to reduce the effects of the photodegradation PPV derivatives. We observed that, among the several polymers tested, poly(vinyl alcohol) (PVA) which is 99% hydrolyzed and deposited onto films of poly(2-methoxy-5-hexyloxy-*p*-phenylene vinylene) (OC<sub>1</sub>OC<sub>6</sub>-PPV) remarkably reduced the photodegradation of these films. However, PVA is water soluble and can absorb water at room conditions. Then, the effect of this protective layer on the electrical properties of OC<sub>1</sub>OC<sub>6</sub>-PPV has to be explored prior to its use in conductivity-based devices. In this paper, thin films and single layer devices fabricated with OC<sub>1</sub>OC<sub>6</sub>-PPV and coated with PVA were submitted to continuous white light exposure and their optical and electrical properties, such as conductivity and electroluminescence, were explored.

## 2. Experimental

Cast films of  $\text{OC}_1\text{OC}_6\text{-PPV}$  (ca. 300–400 nm thickness) were deposited onto glass substrates, indium tin oxide (ITO) or interdigitated chromium-gold array at room temperature in the dark [22] from chloroform solutions (0.3 mg/mL). The PVA coatings were prepared by dipping the samples into a 2 wt% solution of PVA 99% hydrolyzed in ethanol-water mixture and drying them under reduced pressure at 40°C, yielding  $a \approx 1 \mu\text{m}$  layer. The gold array was prepared by lift-off lithography with 100 lines of 5 mm length electrodes with 100 nm of thickness, separated by 10  $\mu\text{m}$  of distance. Photodegradation experiments were performed with a white light from a halogen lamp (50 W, 12 V-Osram) placed at a fixed distance from the samples, yielding 17 mW/cm<sup>2</sup> of power at the sample surface. These irradiations were performed at room atmosphere at 25°C. UV-Vis absorption measurements were carried out in a HITACHI U-2001 spectrophotometer in the range between 400 and 650 nm. The emission spectra of the film ( $\lambda_{\text{exc}} = 490 \text{ nm}$ ) and the emission spectra of the device (current applied = 6 mA) were recorded in a Shimadzu 5301 PC spectrofluorimeter. All films used in the photodegradation measurements presented the same optical density in order to avoid the effect of film thicknesses on photodegradation. The device used to record the electroluminescence spectra was ITO/ $\text{OC}_1\text{OC}_6\text{-PPV}$ /Al; the  $\text{OC}_1\text{OC}_6\text{-PPV}$  active layer was made of cast film from 0.25 mg/mL chloroform solution (ca. 300 nm). In this case, the PVA layer was applied over the aluminum layer. A 90 nm thick Al cathode was vacuum evaporated ( $10^{-6}$  Torr) and with an active area for the devices of 0.12 cm<sup>2</sup>. The electrical behavior was carried out by measuring the current versus voltage at room conditions with a Keithley 238 high voltage source-measure unit.

## 3. Results

The characteristic current versus electrical field curves do not show significant differences with the use of PVA as coating, as shown in Figure 1. The onset voltage of the device coated with PVA was around 5 V, which is similar to other devices of  $\text{OC}_1\text{OC}_6\text{-PPV}$  made from cast films and the same configuration [23–25].

The absorption in the visible region of the cast films with and without the PVA coating showed no significant differences, and the maximum wavelengths of absorption are at 500 nm (Figure 2). The same result was obtained for the photoluminescence (PL) and electroluminescence (EL) spectra of these films, as also shown in Figure 2 and its inset. The emission wavelength of the zero-phonon transition was about 590 nm for all samples. It is worth to note that the values of absorbance, PL and EL, of protected film are nearly the same of the neat film since the protective coating is completely transparent and does not absorb or have emission on the visible range and all the film production and the coating processes are performed in dark. Extreme care should be taken to reproduce intensity values of the photo- and electroluminescence spectra of  $\text{OC}_1\text{OC}_6\text{-PPV}$  because even

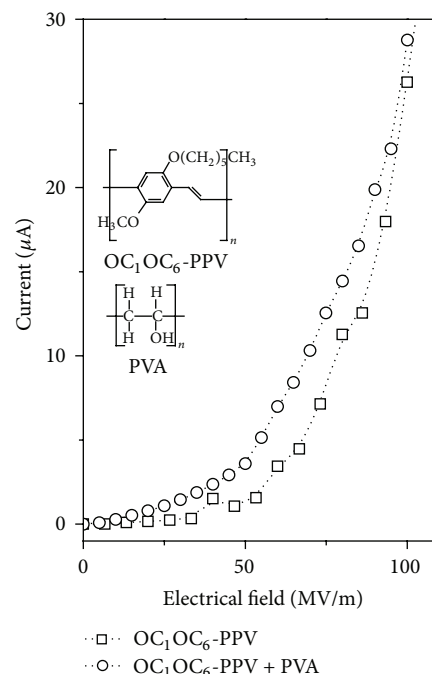


FIGURE 1: Current versus electrical field of ITO/ $\text{OC}_1\text{OC}_6\text{-PPV}$ /Al, neat and coated with PVA.

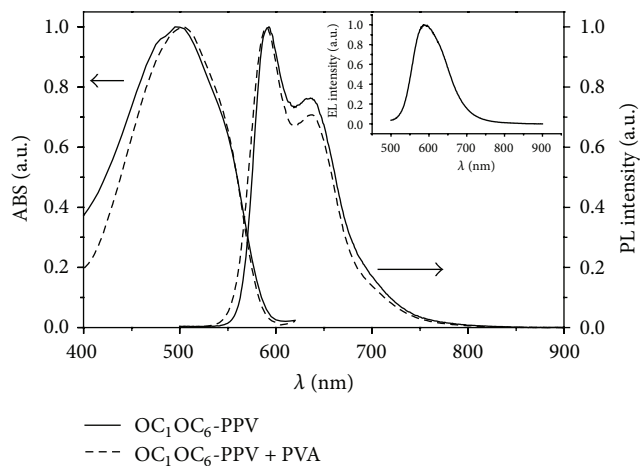


FIGURE 2: Visible, photoluminescence, and electroluminescence spectra of  $\text{OC}_1\text{OC}_6\text{-PPV}$  films with and without a PVA coating. The electroluminescence spectra were carried out onto ITO/ $\text{OC}_1\text{OC}_6\text{-PPV}$ /Al (neat and coated with PVA).

the ambient light degrades the neat film. Also, very short exposures to the excitation light have to be used to record the photoluminescence spectra of these films in ambient conditions.

The electroluminescence of two single layer devices of  $\text{OC}_1\text{OC}_6\text{-PPV}$  (ITO/ $\text{OC}_1\text{OC}_6\text{-PPV}$ /Al), neat and coated with poly(vinyl alcohol) over the aluminum layer (as in inset of Figure 3), was recorded continuously for 300 seconds at ambient conditions as shown in Figure 3. After the turn-on, the devices presented some instability due to the electrical

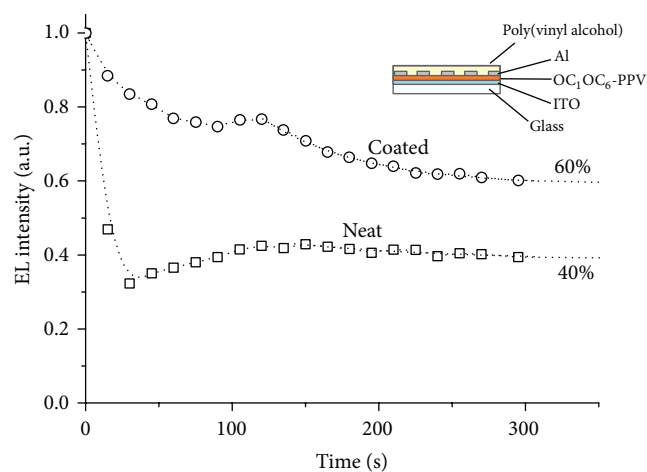


FIGURE 3: Normalized electroluminescence decay for the ITO/OC<sub>1</sub>OC<sub>6</sub>-PPV/Al cast film and ITO/OC<sub>1</sub>OC<sub>6</sub>-PPV/Al cast film coated with PVA. The lines are only to guide the eyes.

contacts. After 150 seconds of stabilization, the coated device presented 60% of the initial emission intensity while the neat one presented just 40%. Studies on the effects of the luminance and lifetime of the devices are subject of future works. For single layer devices, interface and Joule effects are more pronounced in long-term experiments which is required for lifetime studies, turning the results more complicated to analyze properly. Build-up of multilayer devices can introduce more variables in the analysis turning the system even more complicated to reach a clear conclusion. Therefore, long-term experiments of light exposure were performed only with optical and conductivity measurements and not with the devices.

The absorption spectra of OC<sub>1</sub>OC<sub>6</sub>-PPV cast film without the poly(vinyl alcohol) coating, taken after several periods of exposure to the white light, showed a behavior similar to the one observed in earlier reports [13, 14]. The absorbance initially decreases without changing the line shape of the spectra or the wavelength of maximum absorbance and, in a further step of the degradation, the spectra are blue shifted while continuously decreasing the maximum absorbance values [14]. However, when the cast film is coated with poly(vinyl alcohol), the changes in the spectra are drastically reduced, and, in the same period of irradiation, the decrease in the absorbance values was about 5%, while in the same period the nonprotected OC<sub>1</sub>OC<sub>6</sub>-PPV film was completely degraded. This effect is clearly seen by plotting the normalized absorbance values at 500 nm (wavelength of maximum absorption of the nondegraded OC<sub>1</sub>OC<sub>6</sub>-PPV) in function of the irradiation time as shown in Figure 4. This figure shows the results of the film coated with poly(vinyl alcohol) in function of the continuous exposure of the film to the white light till 620 hours, showing a total decrease of ca. 12% of the absorbance values. The inset of Figure 4 shows the kinetic plot from which the photodegradation rates could be estimated, being two orders of magnitude lower for the coated film: ca.  $4 \times 10^{-2} \text{ h}^{-1}$  and  $2 \times 10^{-4} \text{ h}^{-1}$ , respectively, for the neat film and the film coated with PVA. It is very important

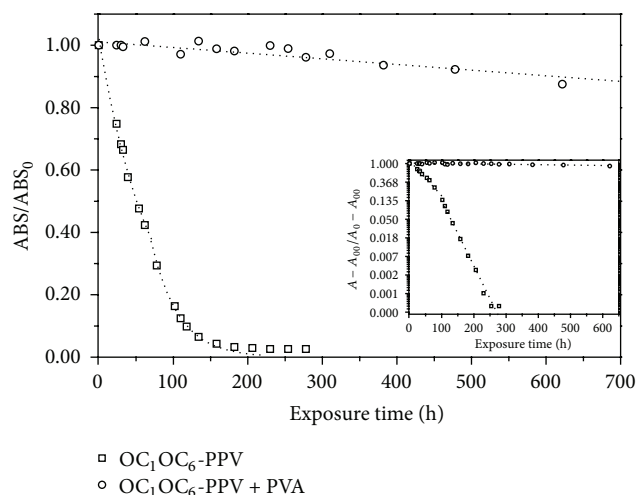


FIGURE 4: Normalized absorbance decay for the OC<sub>1</sub>OC<sub>6</sub>-PPV cast film and OC<sub>1</sub>OC<sub>6</sub>-PPV cast film coated with PVA, irradiated with white light. The inset shows the kinetic plot ( $y$ -axis in log scale) for the same samples. The lines are only to guide the eyes.

to emphasize that these estimated values are only valid for samples with thicknesses of ca. 300–400 nm since there is a strong dependence between the absorbance decay rates and the film thickness.

Similar protecting effect of the PVA coating against OC<sub>1</sub>OC<sub>6</sub>-PPV photodegradation can also be seen in the photoluminescence characterization. The PL intensity of the pure film drops 50% in the first 40 minutes of exposure, while the intensity for the coated one remains the same.

For the conductivity measurements, a constant voltage of 6 V was applied for several hours at room conditions while exposing the films under the electrodes to the white light and measuring the current at different time intervals. The conductivity measurements showed that the cast films coated with PVA presented a more stable conductivity than that observed for neat OC<sub>1</sub>OC<sub>6</sub>-PPV films (Figure 5). The conductivity values obtained for the PVA-protected OC<sub>1</sub>OC<sub>6</sub>-PPV film deposited onto an interdigitated chromium-gold array under the illumination remain constant (around  $7 \times 10^{-10} \text{ S/m}$ ) for at least 100 hours of continuous light exposure. For the unprotected OC<sub>1</sub>OC<sub>6</sub>-PPV, the conductivity decreased two orders of magnitude in the same exposure period (from  $4.5 \times 10^{-10} \text{ S/m}$  to  $2.5 \times 10^{-12} \text{ S/m}$ ).

## 4. Conclusions

In conclusion, the use of coatings of poly(vinyl alcohol) onto OC<sub>1</sub>OC<sub>6</sub>-PPV films was successful in minimizing the photodegradation, probably due to its low oxygen permeation, showing only 12% of absorbance decay after 30 days of continuous exposure to a 50 W halogen lamp. The coating did not affect the optical properties, such as emission and absorption spectra, of the OC<sub>1</sub>OC<sub>6</sub>-PPV. The conductivity of the protected OC<sub>1</sub>OC<sub>6</sub>-PPV film showed remarkable stability under the exposure to light. This method of coating allows fabrication of stable devices which, after the proper

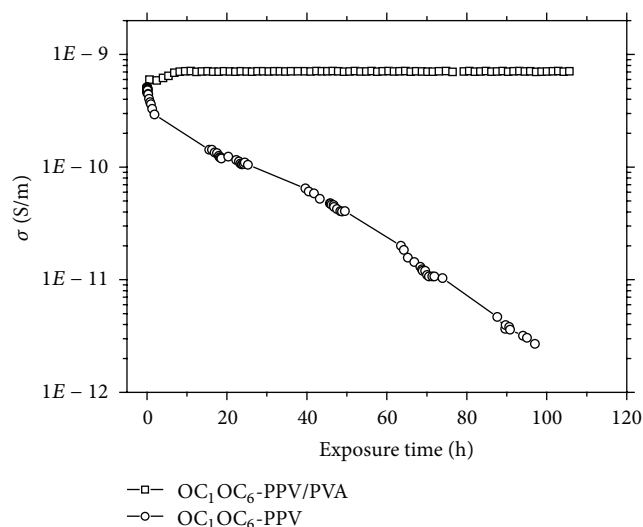


FIGURE 5: Conductivity values of the OC<sub>1</sub>OC<sub>6</sub>-PPV cast film and OC<sub>1</sub>OC<sub>6</sub>-PPV cast film coated with PVA, measured in an interdigitated electrode and irradiated with white light. The lines are only to guide the eyes.

optimization of fabrication, can be used in applications such as sensors and FETs, among others.

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## References

- [1] J. H. Burroughes, D. D. C. Bradley, A. R. Brown et al., "Light-emitting diodes based on conjugated polymers," *Nature*, vol. 347, pp. 539–541, 1990.
- [2] N. C. Greenham, S. C. Moratti, D. D. C. Bradley, R. H. Friend, and A. B. Holmes, "Efficient light-emitting diodes based on polymers with high electron affinities," *Nature*, vol. 365, no. 6447, pp. 628–630, 1993.
- [3] F. Hide, M. A. Díaz-García, B. J. Schwartz, M. R. Andersson, Q. Pei, and A. J. Heeger, "Semiconducting polymers: a new class of solid-state laser materials," *Science*, vol. 273, no. 5283, pp. 1833–1836, 1996.
- [4] B. H. Cumpston and K. F. Jensen, "Photo-oxidation of electroluminescent polymers," *Trends in Polymer Science*, vol. 4, no. 5, pp. 151–157, 1996.
- [5] G. H. Gelinck and J. M. Warman, "The effect of photo-oxidation on the photo-conductivity of isolated polyphenylenevinylene chains," *Chemical Physics Letters*, vol. 277, no. 4, pp. 361–366, 1997.
- [6] F. J. J. Janssen, L. J. Van IJendoorn, H. F. M. Schoo et al., "Degradation effects in poly para-phenylene vinylene derivatives due to controlled oxygen exposure," *Synthetic Metals*, vol. 131, no. 1–3, pp. 167–174, 2002.
- [7] W. Holzer, A. Penzkofer, M. Pichlmaier, D. D. C. Bradley, and W. J. Blau, "Photodegradation of some luminescent polymers," *Chemical Physics*, vol. 248, no. 2–3, pp. 273–284, 1999.
- [8] H. Y. Low, "Photo and photo-oxidative degradations of poly(phenylene vinylene) derivatives," *Thin Solid Films*, vol. 413, no. 1–2, pp. 160–166, 2002.
- [9] B. H. Cumpston and K. F. Jensen, "Photo-oxidation of polymers used in electroluminescent devices," *Synthetic Metals*, vol. 73, no. 3, pp. 195–199, 1995.
- [10] G. D. Hale, S. J. Oldenburg, and N. J. Halas, "Effects of photo-oxidation on conjugated polymer films," *Applied Physics Letters*, vol. 71, no. 11, pp. 1483–1485, 1997.
- [11] A. Alba García, H. Schut, L. D. A. Siebbeles, and A. Van Veen, "Depth profiling of the degradation of OC1OC10-PPV monitored by positron beam analysis," *Synthetic Metals*, vol. 138, no. 1–2, pp. 43–47, 2003.
- [12] R. F. Bianchi, D. T. Balogh, M. Tinani, R. M. Faria, and E. A. Irene, "Ellipsometry study of the photo-oxidation of Poly[(2-methoxy-5-hexyloxy)-p-phenylenevinylene]," *Journal of Polymer Science, Part B*, vol. 42, no. 6, pp. 1033–1041, 2004.
- [13] F. M. Marconi, R. F. Bianchi, R. M. Faria, and D. T. Balogh, "Solvent effects on the photodegradation of a PPV derivative," *Molecular Crystals and Liquid Crystals Science and Technology Section A*, vol. 374, pp. 475–480, 2002.
- [14] C. A. Olivati, M. Ferreira, R. F. Bianchi, R. M. Faria, O. N. Oliveira Jr., and D. T. Balogh, "The influence of preparation method of OC1OC6-PPV films on the photo-oxidation process," *Polymer Degradation and Stability*, vol. 91, no. 10, pp. 2342–2346, 2006.
- [15] F. H. Lohman, "The mathematical combination of Lambert's law and Beer's law," *Journal of Chemical Education*, vol. 32, no. 3, p. 155, 1955.
- [16] V. C. Gonçalves, A. J. F. Carvalho, and D. T. Balogh, "Polymeric coatings for photostability enhancement of poly(p-phenylene vinylene) derivative films," *Polymer International*, vol. 59, no. 5, pp. 637–641, 2010.
- [17] H.-C. Lee, T.-W. Lee, Y. T. Lim, and O. O. Park, "Improved environmental stability in poly(p-phenylene vinylene)/layered silicate nanocomposite," *Applied Clay Science*, vol. 21, no. 5–6, pp. 287–293, 2002.
- [18] B. H. Cumpston and K. F. Jensen, "Photooxidative stability of substituted poly(phenylene vinylene) (PPV) and poly(phenylene acetylene) (PPA)," *Journal of Applied Polymer Science*, vol. 69, no. 12, pp. 2451–2458, 1998.
- [19] P. Le Rendu, T. P. Nguyen, and L. Carrois, "Cellulose acetate and PVDC used as protective layers for organic diodes," *Synthetic Metals*, vol. 138, no. 1–2, pp. 285–288, 2003.
- [20] J. S. Lewis and M. S. Weaver, "Thin-film permeation-barrier technology for flexible organic light-emitting devices," *IEEE Journal on Selected Topics in Quantum Electronics*, vol. 10, no. 1, pp. 45–57, 2004.
- [21] G. H. Kim, J. Oh, Y. S. Yang, L.-M. Do, and K. S. Suh, "Encapsulation of organic light-emitting devices by means of photopolymerized polyacrylate films," *Polymer*, vol. 45, no. 6, pp. 1879–1883, 2004.
- [22] C. De Almeida Olivati, R. F. Bianchi, F. M. Marconi, D. T. Balogh, and R. M. Faria, "Photoconduction effect on PPV and MH-PPV structures," *Molecular Crystals and Liquid Crystals Science and Technology Section A*, vol. 374, pp. 451–456, 2002.
- [23] C. A. Olivati, M. Ferreira, A. J. F. Carvalho et al., "Polymer light emitting devices with Langmuir-Blodgett (LB) films: enhanced

- performance due to an electron-injecting layer of ionomers,” *Chemical Physics Letters*, vol. 408, no. 1–3, pp. 31–36, 2005.
- [24] C. A. Olivati, A. J. F. Carvalho, D. T. Balogh, and R. M. Faria, “Electrical properties of polymer/metal interface in polymer light-emitting devices: electron injection barrier suppression,” *Journal of Materials Science*, vol. 41, no. 10, pp. 2767–2770, 2006.
- [25] C. A. Olivati, A. J. F. Carvalho, D. T. Balogh, H. von Seggern, and R. M. Faria, “Effect of ion concentration of ionomer in electron injection layer of polymer light-emitting devices,” *Journal of Non-Crystalline Solids*, vol. 352, no. 9–20, pp. 1686–1690, 2006.



