J Mater Sci (2011) 46:2644–2648
DOI 10.1007/s10853-010-5119-7

Decreased degradation of poly(*p*-phenylene vinylene) films at the indium–tin oxide interface

L. C. Poças · S. L. Nogueira · R. S. Nobuyasu ·
Gustavo G. Dalkiranis · M. J. M. Pires ·
José R. Tozoni · R. A. Silva · Alexandre Marletta

Received: 18 October 2010 / Accepted: 26 November 2010 / Published online: 14 December 2010

Abstract This article discusses a strategy to reduce the degradation of a poly(*p*-phenylene vinylene) (PPV) film at the interface with an indium–tin oxide (ITO) electrode. It consists of using a less aggressive leaving group, the sodium dodecylbenzenesulfonate salt (DBS), in the chemical synthesis of PPV starting with the polymer precursor, and performing the thermal conversion into PPV at a lower temperature (100 °C) than in the conventional synthesis. The absorbance spectrum for an ITO/PPV + DBS film indicated that the polymer is less degraded and has the emission efficiency increased by ca. 4.5 times in comparison to ITO/PPV films obtained with the conventional procedures, i.e., with thermal conversion at 200 °C, in vacuum, during 2 h. The main reason for the enhanced performance of the route reported in this article is a decrease in the oxygen concentration at the ITO/PPV interface, as inferred with X-ray Photoelectron Spectroscopy which corroborates the optical properties.

Introduction

The conjugated, light-emitting poly(*p*-phenylene vinylene) (PPV) is promising for use in optoelectronic applications, such as polymer light-emitting diodes (PLEDs) [1] and photocells [2, 3]. This possible use is due to the significant progress in finding new routes to synthesize PPV from a soluble, non-conjugated polymer precursor, namely poly (xylylidenetetrahydrothiophenium chloride) (PTHT) [4]. PTHT films are converted into PPV films through a thermal treatment in which the tetrahydrothiophenium lateral group is eliminated, generally at high temperatures (>200 °C). This procedure is not compatible with PLED fabrication, where materials with different thermal properties may have to be employed. Moreover, during the PTHT thermal treatment, chemical sub-products (hydrochloric acid, HCl) react with the hole-injector transparent electrode (indium-tin oxide, ITO) forming indium chloride ($InCl_3$) [5–7]. This sub-product degrades the ITO film and diffuses to the ITO/PPV interface, forming an oxidized layer [8]. This non-intentional doping causes the interface to behave as a Schottky barrier, thus leading to a hetero-layer device, regardless of the work function of the hole-injector metal [9]. The degradation at the ITO electrode decreases the charge injection efficiency and the electroluminescence quantum yield [9, 10]. The main effects on the transparent electrode (ITO) have been analyzed using X-ray photoelectron spectroscopy (XPS) experiments [8, 11], scanning electron microscopy (SEM), and dispersive X-ray spectroscopy (EDXS) [8, 11, 12].

As an alternative to the conventional chemical synthesis, PPV can be obtained at a lower temperature by using the dodecylbenzenesulfonate (DBS) anion as counter-ion of the PTHT polymer. The DBS anion may act as a less aggressive leaving group [13], thus reducing the electrode degradation

---

L. C. Poças
Universidade Tecnológica Federal do Paraná/UTFPR,
Campus Apucarana, Rua Marcílio Dias, 635, Apucarana,
PR CEP 86812-460, Brazil

S. L. Nogueira · R. S. Nobuyasu · G. G. Dalkiranis ·
J. R. Tozoni · R. A. Silva · A. Marletta (✉)
Instituto de Física, Universidade Federal de Uberlândia,
CP 593, Uberlândia, MG 38400-902, Brazil
e-mail: marletta@ufu.br

M. J. M. Pires · R. A. Silva
Divisão de Metrologia de Materiais, Instituto Nacional de
Metrologia, Normalização e Qualidade Industrial, Duque de
Caxias, RJ 25250-020, Brazil

during the PPV conversion process, as suggested by Brütting et al. [9]. The low conversion temperature opens the possibility of using PPV as an active layer in multi-layer organic semiconductor devices. In this article, the authors have utilized this new chemical route to investigate the effect on absorbance and emission properties of the PPV layer deposited on ITO-substrate, when a less aggressive leaving group, the DBS anion, is used as a counter-ion for PTHT. XPS was used to probe the ITO/PPV interface.

Experimental section

Ultra-thin PPV films were deposited onto glass substrates coated with ITO. The substrates were washed using the RCA procedure [14], dipped into a solution containing H_2O (Milli-Q):H_2O_2:NH_4OH in the proportion of 5:1:1 (v/v) at 80 °C for 30 min. Then, the substrates were rinsed with ultrapure water (Milli-Q) in order to remove chemical residues. The PPV precursor (PTHT) was synthesized by using the chemical route as developed by Bradley [4]. PTHT + DBS spin-coating films were processed from aqueous solutions with concentrations of 11.77 and 58.85 mmol L^{-1} 1:1 (mol/mol) for PTHT and DBS, respectively, and thermally converted into PPV + DBS at 100 °C (DBS100), and 200 °C (DBS200) for 2 h in vacuum (0.1 atm). For comparison purposes, the PPV spin-coated film was processed from a PTHT aqueous solution with concentration 11.77 mmol L^{-1} without DBS, being thermally converted at 200 °C (PPV200) for 2 h in vacuum (0.1 atm). Spin-coating deposition was performed at approximately 2,000 rpm, leading to a thickness of ca. 10 nm for the films.

Ultraviolet–visible (UV–Vis) absorption measurements were performed with an Ocean Optics USB2000 spectrometer and a deuterium-tungsten lamp. The photoluminescence (PL) spectra were obtained at room temperature using the 458 nm line of an Ar^+ laser as the excitation source. The spectral analysis of the photoluminescence was carried out with a USB2000, Ocean Optics. The samples were kept in a cryostat in vacuum (1×10^{-3} mbar). The XPS experiment was carried out on an Omicron ESCAplus P analyzer using a MgKα X-ray source in ultra high vacuum with the pressure of the chamber at 5×10^{-10} mbar. The pass energy was 50 eV to obtain wide scan spectra, while 20 eV were used, depending on the signal intensity, for scans of the O 1s, C 1s, in 3d and Sn 3d binding energy regions.

Results and discussion

The absorbance spectra in Fig. 1a for the spin-coated PTHT and PTHT + DBS films display two bands for stilbene moieties at 320 nm and aggregated stilbene units at 360 nm [15]. The addition of the DBS leaving group decreased the band intensity assigned to the aggregated stilbene, as indicated in the spectrum for PTHT + DBS. It was noted that this spectral range corresponds to the absorbance of the PPV units with lower conjugation degrees ($n < 3$). Figure 1b shows well-defined bands in the bandgap region for spin-coated PPV, DBS100, and DBS200 films, with the absorption of the PPV + DBS film displaying a trend for decreasing intensity below 450 nm. This decrease is generally associated with the reduced concentration of PPV segments with low conjugation degrees. The reduction in the effective conjugation length for the PPV layer is attributed to breaks in the conjugation caused by structural defects incorporated during the conventional thermal conversion [16]. The defects are

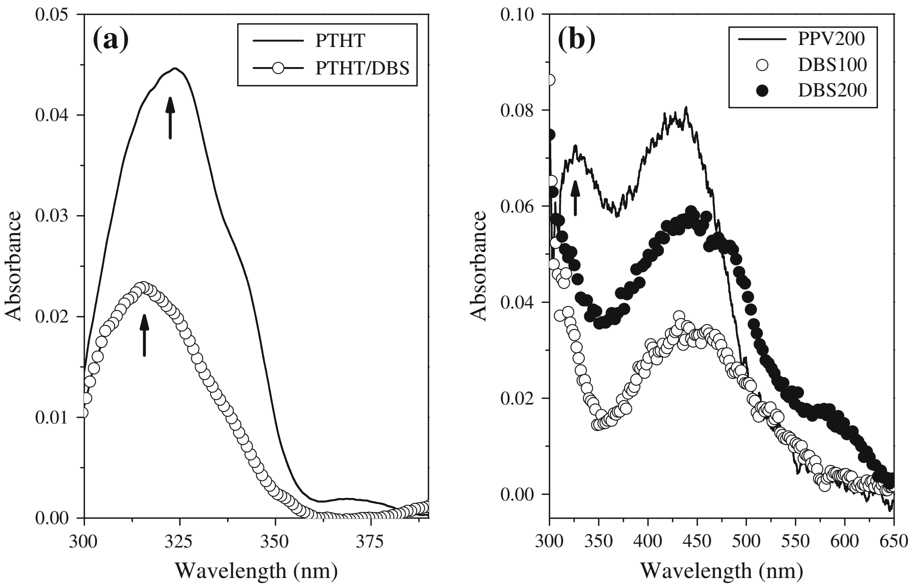


Fig. 1 Absorbance spectra of spin-coated films of PPV200, DBS100, and DBS200 on ITO substrates

probably caused by carbonyl groups (C=O) attached to the polymeric chain because of the polymer thermal oxidation which occurs above 150 °C [17]. In subsidiary experiments (results not shown), the authors observed that the absorption of ITO was little affected by thermal treatment or exposure to a pH 5 of HCl solution. Therefore, the degradation of ITO should be a surface effect, being restricted to small distances from the polymer/electrode interface, as mentioned in the literature [5–8]. However, this effect is sufficient to increase the Schottky barrier for the hole-injector metal (ITO), as a non-intentional hetero-junction was produced [9]. To probe this surface effect, the authors resorted to XPS (see below), as the UV–Vis spectroscopy could not provide detailed information.

Upon absorbing light, radiative processes, energy transfer, and/or charge diffusion take place in PPV. In particular, PL is observed because of the PPV segments with the highest conjugation degrees ($\pi^* \rightarrow \pi$ transition). Figure 2 shows the PL spectrum normalized by power absorbed (Pot) at room temperature for all the samples. Here, Pot $= 1 - 10^{-A(\lambda)}$ and A(λ) is the absorbance intensity for the excitation wavelength at 458 nm. Well-resolved vibronic structures are seen in all spectra, with almost the same spectral shape and peak position for the zero-phonon emission at 508 nm. Therefore, these spectra confirm that the thermal conversion of PPV was achieved. The PL peaks in the lower energy range in Fig. 2 are related to the phonon replicas transitions [18, 19]. The difference in energy between the zero-phonon peak ($\lambda_1 \sim 508$ nm) and the first vibrational mode ($\lambda_2 \sim 538$ nm) is 1,235 cm^{-1}, which agrees with infrared and/or Raman spectroscopy results [16]. One feature that distinguishes the PL curves is a small blue-shift ($\sim$5 nm) and narrow line width in the sample DBS100. This indicates a decrease in the aggregation of PPV species, and is consistent with the narrow width in the absorbance spectrum for the PTHT + DBS film in Fig. 1a. For higher conversion temperatures, the PL spectra for DBS200 and PPV200 samples are red shifted and the line width is increased, thus confirming the increase in polymeric aggregation. This dependence on the temperature is probably associated with the fact that the glass/vitreous transition for PPV is ca. 200 °C. Therefore, a thermal treatment at this temperature should increase the entanglement of polymer chains.

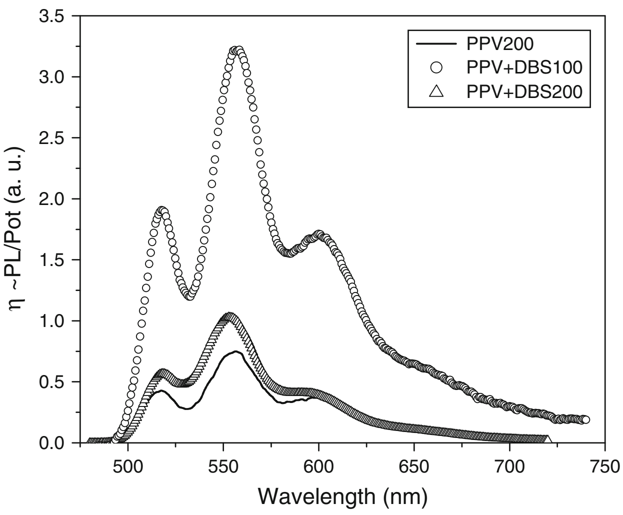


Fig. 2 Normalized photoluminescence spectra for spin-coated films of PPV200, DBS100, and DBS200 on ITO substrates

Using the Franck–Condon's factor for the emission spectrum, one may estimate the Huang-Rhys' parameter S by calculating the ratio I_1/I_0, where I_0 is the zero-phonon peak intensity and I_1 is the first phonon-peak intensity [20]. The values of S are given in Table 1 for all samples. It is important to stress that the absorbance intensity is very low in the emission range and, therefore, self-absorption is not significant. As obtained previously for bulk PPV films, the parameter S for PPV increases with the thermal conversion temperature, due to oxidative processes [13]. The best result in terms of relative emission efficiency was obtained for the PPV + DBS film converted at 100 °C (see Table 1). This sample has an emission efficiency ca. 4.5 times the value for the film obtained with the conventional thermal conversion process (PPV200). The relative emission efficiency (η) was calculated from the area of the curves in Fig. 2. This effect is a consequence of the small number of defects incorporated, mainly carbonyl groups, during the low temperature conversion [13]. Therefore, the thermal degradation of PPV is decreased when DBS is used as counter-ion for the PPV precursor and the conversion process is performed at low temperatures. This finding is consistent with the study of Brütting et al. [9], where a less aggressive leaving group of PTHT was used, i.e., a derivative from a weak acid. In addition, upon using a long counter-ion chain, as the DBS used here, the aggregation is also reduced, as indicated by the PL line shape in Fig. 2 for the DBS100 sample and the absorption spectrum for PTHT + DBS in Fig. 1a, in comparison to the DBS200 and PPV200 samples [21]. In conclusion, two effects can be associated with a decreased emission efficiency: oxidation and aggregation.

The hypothesis of incorporation of structural defects as being responsible for decreasing emission efficiency in the PPV films converted with the conventional procedures

Table 1 Huang-Rhys' parameter S and relative emission efficiency η of spin-coated films of PPV200, DBS100, and DBS200 on ITO substrates

Film	$S \sim I_1/I_0$	$\eta \sim$ PL/Pot (arb. unit)
PPV200	1.82	0.75
DBS100	1.62	3.22
DBS200	1.89	1.03

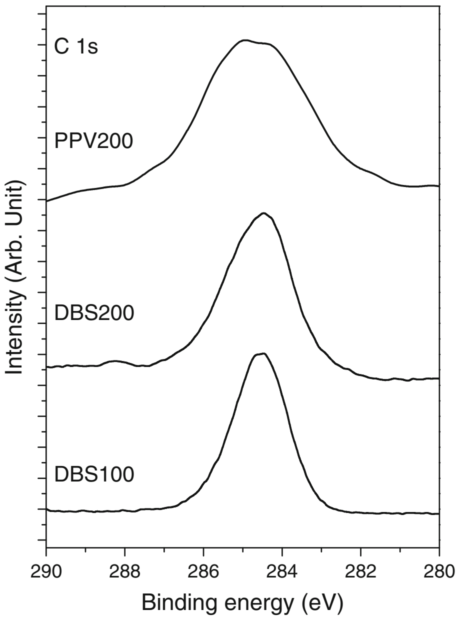


Fig. 3 XPS spectra at the beginning (before sputtering) for DBS100, DBS200, and PPV200 samples for the C 1s binding energy

could be confirmed by studying the ITO/PPV interface with XPS measurements. The latter were performed with polymer layers being successively removed through cathodic erosion with Argon ions. It was noted that the low energy used in the sputtering did not degrade the polymer chemical structure. Figure 3 displays C 1s spectra recorded along the film surface in the initial sputtering; the energy of the main peak for C 1s was 284.5 eV [8]. The XPS restricted spectra had the peaks fitted after subtraction of a Shirley background using Gaussian–Lorentzian line shapes obtained from the CasaXPS software package. Figure 4a and c shows the experimental and fitting curves for C 1s bands with energy levels at 284.5, 285.5, and 288.0 eV for the initial and after sputtering measurements. The two lower energy bands are attributed to C–C and C–H bindings for PPV, respectively; the higher energy band corresponds to C=O [8]. Table 2 shows the atomic percentages of carbon and oxygen elements for the samples in the beginning (initial) and after sputtering (sputt.). Significantly, the initial amount of carbonyl for PPV200 is twice the value for the DBS100 and DBS200 films. The formation of carbonyl groups in polymeric films is responsible for introducing structural defects along the PPV main chain, and these defects represent non-radiative channels that cause the emission efficiency to decrease [16].

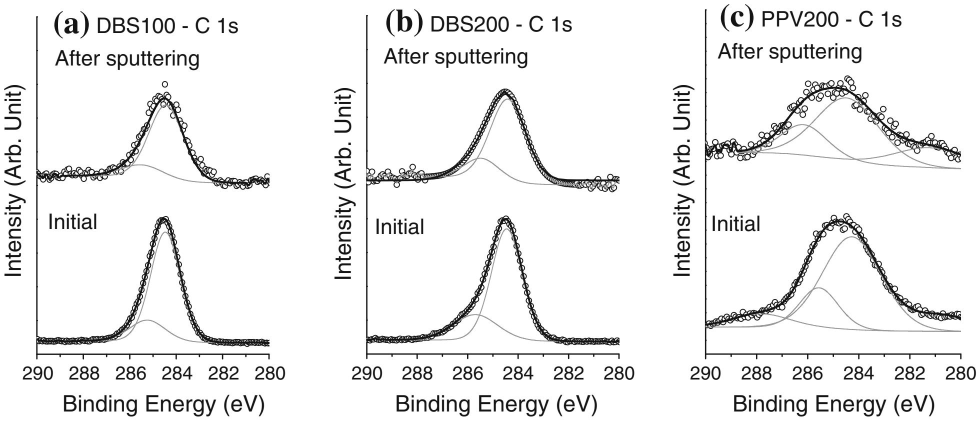
The number of carbonyl groups generated during the thermal conversion into PPV may be diminished by replacing the Cl counter-ion of PTHT with DBS and by using lower conversion temperatures (<150 °C) [13]. This is precisely what occurred in this results, as confirmed by the percentage of oxygen in Table 2. The DBS counter-ion decreases the attack by hydrochloric acid released during thermal conversion of PTHT into PPV on the ITO/PPV interface [4]. Indeed, the percentage of oxygen for the DBS200 sample is lower than for the conventional sample (PPV200), indicating that DBS practically does not react with ITO. Furthermore, when DBS is incorporated in the PTHT matrix, sodium chloride (NaCl) is formed which assists in controlling the pH and hampering an acid attack to the ITO layer.

Table 2 Atomic percentages for oxygen and carbon atoms obtained from the XPS spectra in Fig. 4 for the samples at the beginning (initial) and after sputtering (sputt.)

Sample	Atomic percentages ± 2%	
	C	O
PPV200 (initial)	36	41
PPV200 (sputt.)	25	44
DBS100 (initial)	70	19
DBS100 (sputt.)	24	38
DBS200 (initial)	69	18
DBS200 (sputt.)	30	34

The uncertainties are ± 2%

Fig. 4 XPS spectra for the beginning and after sputtering for **a** DBS100, **b** DBS200, and **c** PPV200 samples at the C 1s binding energy. The fits are also shown



Conclusion

In this article, the authors have studied the influence from the thermal conversion process on the PPV emission efficiency at the interface between ITO and a PPV thin film. The authors adopted the alternative strategy to obtain PPV, in which a less aggressive chemical leaving group (DBS) was used in the polymer precursor, and thermal conversion was performed at lower temperatures than in the conventional synthesis. The sample DBS100 obtained with this strategy exhibited an increased PL emission efficiency (ca. 4.5), which was attributed to a significant reduction in the oxidative process at the ITO/PPV interface, in addition to less chemical and/or thermal degradation of PPV. The results with three types of PPV samples could be summarized as follows. The sample DBS200 had higher efficiency than the PPV film produced in the conventional method (PPV200) because of the lower number of defects. Its efficiency is lower than for the DBS100 because of a larger degree of aggregation [22]. Finally, XPS experiments were used to demonstrate that less structural defects, mainly represented by carbonyl groups, were generated with the use of DBS and lower conversion temperatures. Therefore, in PLEDs, a considerable decrease is expected for both the Schottky barrier at the electrode/polymer interface and the device operating voltage.

Acknowledgements The authors would like to acknowledge the financial support granted by the Brazilian agencies: Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), Fundação de Apoio à Pesquisa do Estado de Minas Gerais (FAPEMIG), and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq). We also thank the Dr. Osvaldo N. Oliveira Jr. for manuscript revision.

References

1. Parker ID (1994) J Appl Phys 75:1656
2. Benten H, Ogama M, Ohkita H, Ito S (2008) Adv Funct Mater 18:1563
3. Ogawa M, Kudo N, Ohkita H, Ito S, Benten H (2007) Appl Phys Lett 90:223107
4. Bradley DDC (1987) J Phys D 20:1389
5. Karg S, Meier M, Riess W (1997) J Appl Phys 82:1951
6. Brütting W, Meier M, Herold M, Karg S, Schwoerer M (1998) Chem Phys 227:243
7. Herold M, Gmeiner J, Drummer C, Schwoerer M (1997) J Mater Sci 32:5709. doi:10.1023/A:1018661516099
8. Nguyen TP, de Vos S (1996) Vacuum 47:1153
9. Brütting W, Meier M, Herold M, Karg S, Schwoerer M (1997) Synth Met 91:163
10. Lemmer U, Karg S, Scheidler M, Deussen M, Rie W, Cleve B, Thomas P, Bässler H, Schwoerer M, Göbel EO (1994) Synth Met 67:169
11. Sheats JR, Roitman DB (1998) Synth Met 95:79
12. Nguyen TP, Spiesser M, Garnier A, de Kok M, Tr VH (1999) Mater Sci Eng B 60:76
13. Marletta A, Gonçalves D, Oliveira Jr ON, Faria RM, Guimarães FEG (2000) Adv Mater 12:69
14. Kern WW (1984) Semicond Int 7:94
15. Aguiar M, Akcelrud L, Pinto MR, Atvars TDZ, Karasz FE, Saltiel J (2003) J Photosci 10:149
16. Cumpston BH, Jensen KF (1996) Trends Polym Sci 4:151
17. Marletta A, Castro FA, Borges CAM, Oliveira ON Jr, Faria RM, Guimaraães FEG (2002) Macromolecules 35:9105
18. Yu J, Fann WS, Kao FJ, Yang DY, Lin SH (1994) Synth Met 66:143
19. Yu J, Hayashi M, Lin SH, Liang KK, Hsu JH, Fann WS, Chao CI, Chuang KR, Chen SA (1996) Synth Met 82:159
20. Cornil J, Beljonne D, Heller CM, Campbell IH, Laurich BK, Smith DL, Bradley DDC, Mullen K, Bredas JL (1997) Chem Phys Lett 278:139
21. Marletta A, Akcelrud L (2009) J Lumin 129:672
22. Tozoni JR, Guimarães FEG, Atvars TDZ, Nowacki B, Akcelrud L, Bonagamba TJ (2009) Eur Polym J 45:2467