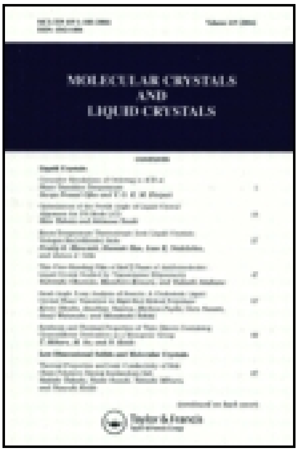

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Polyaniline as Transparent Carrier Injection Electrode Compatible with Low Temperature Poly(p-Pheniline Vinylene) Conversion Process

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To cite this article: Silmar A. Travain, Luiz H. Libardi, Alexandre Marletta, JosÉ A. Giacometti, Francisco E. G. Guimarães & Roberto M. Faria (2002): Polyaniline as Transparent Carrier Injection Electrode Compatible with Low Temperature Poly(p-Pheniline Vinylene) Conversion Process, Molecular Crystals and Liquid Crystals, 374:1, 439-444

To link to this article: http://dx.doi.org/10.1080/713738250

Mol. Cryst. Liq. Cryst., Vol. 374, pp. 439-444
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1058-725X/02 $12.00 + .00

Polyaniline as Transparent Carrier Injection Electrode Compatible with Low Temperature Poly(p-Pheniline Vinylene) Conversion Process

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ABSTRACT

A light-emitting diode (LED) using polyaniline (PAni) as transparent hole-injector electrode was fabricated. The PAni layer was deposited "in situ" onto indium-tin oxide (ITO) coated glass and over it a layer of non-conjugated polymer precursor of poly(*p*-phenylene vinylene) (PPV) was spin-coated. The low temperature thermal conversion was used to convert the precursor into the PPV layer. This (ITO/PAni/PPV/Al) LED structure exhibited an operation voltage 3 times lower when compared with the conventional (ITO/PPV/Al) structure. The low temperature conversion procedure opens the possibility of using PPV as active layer in heterostructures devices leading to enhancement of their optical and the electrical properties.

Keywords: LED; heterostructures devices, poly(*p*-phenylene vinylene); polyaniline

INTRODUCTION

Conjugated poly(*p*-phenylene vinylene) is a promising candidate to be used as an active polymer in commercial electroluminescent devices.

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The preparation of PPV films via precursor route is nowadays possible after a significant progress in the synthesis and because of the easy processibility of the polymeric materials.[1] Films prepared from non-conjugated precursors are usually converted into PPV by thermal elimination of substituting leaving groups at elevated temperatures (>300 °C), during ~6 h under vacuum. However, a conversion at such high temperature is incompatible with LEDs devices fabrication processes. Also, it is not possible to use the PAni as injecting electrode since it degrades at such high temperatures.[2] Recently, we developed an alternative approach that consists in substituting the chloride counterion of the PPV precursor[3], poly(xylylidene tetrahydrothiophenium chloride) (PTHT), by a long chain dodecylbenzenesulfonate (DBS) ion (hereafter PPV-DBS), which showed the advantage of converting the spin-casted PPV films at 115 °C within few minutes under the atmospheric pressure. This PPV-DBS polymer compared with traditional PPV has also a high conjugation length keeping its optical properties.[3]

The use of PAni as hole injecting layer in LEDs heterostructures was demonstrated[4] using poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) (for MEH-PPV the conversion process used for PPV is not required). The performance of such LED was increased to ~30%-40% and its operation voltage decreased about 30%-50% when compared with the LED without the PAni layer. Thus, the use of a PAni layer could bring a large advantage to built LEDs.

In this work, we report the enhancement of the electrical properties of a PPV-LED using a PAni layer deposited by the "in situ" polymerization process[5] and using the low temperature PPV conversion process. We show that the operating voltage will decrease about 30% when compared with the traditional PPV-LED.

EXPERIMENTAL DETAILS

The PPV-precursor (PTHT) solution was prepared as described in the literature.[6] The PAni films were obtained by "in situ" polymerization process[5] and they were deposited onto ITO glass slides in aqueous-HCl solution media, at 0 °C. The resulting films are in form of emeraldine salt, with thickness of ~200 nm.[5] The spin-casted precursor of the PPV layer (~400 nm) was obtained by mixing PTHT and DBS at a 10:1 w/w in water. After the layer deposition, it was thermal converted to PPV-DBS at 150 °C under vacuum for 2 hours.

Finally, a 100 nm aluminum electrode of area equal to 3 mm^2 was vacuum deposited on the PPV layer to act as the cathode. Aiming to compare results a conventional LEDs structure (ITO/PPV/Al) was also produced using the same experimental conditions. Measurements of device characteristics were performed in vacuum at room temperature. UV-Vis spectroscopy measurements were performed using a Hitachi U-2001 spectrophotometer.

Photoluminescence (PL) properties were also studied and the light signal was measured using a photomultiplier mounted on a 0.5 m monochromator (in 480 - 700 nm range) and using a lock-in amplifier. The current-voltage (I-V) characteristic was measured using an I-V Tecktronics tracer.

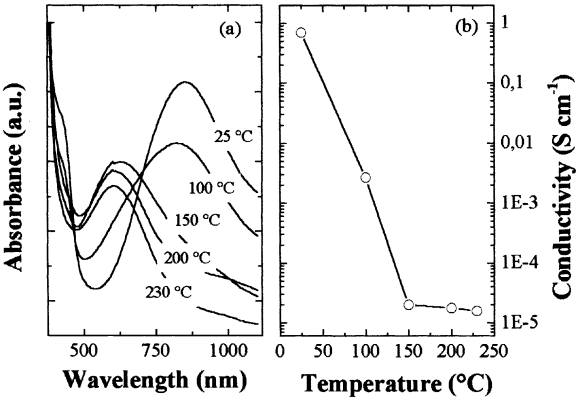

Figure 1. (a) Absorbance and (b) conductivity of PAni 200 nm layer films for various temperature of treatment, during 2 hours under vacuum.

RESULTS

Optical and electrical PAni layer characteristics are shown in Figure 1. Absorbance spectra in the UV-Vis range of PAni films thermall treated at different temperatures are shown in Fig. 1a. Increasing the temperature of treatment produces a blue shift in the delocalized (π-π^*) band (850 nm), indicating a dedoping process. For doped PAni the weak absorption in between 500 nm and 650 nm (Fig. 1a) opens a window for the emitted light from the active luminescent PPV layer. However, the thermal treatment at high temperatures (230 °C), during 2 hours, increases the absorption, destroying such optical window. In addition, the thermal treatment decreases its electric conductivity as from 0.5 S/cm at 25 °C to 2.10^{-5} S/cm for the treatment at 150 °C, as shown in Fig. 1b.

Aiming the use of PAni/PPV films in LEDs it is important to keep the electric conductivity as high as possible without changes in the optical window. As mentioned the PPV requires a conversion procedure made by thermal treated at temperatures of the order of 200 °C. Even under such a severe thermal treatment during 3 hours no morphological degradation was observed.[2] This result indicates that, in principle, PAni can be used as transparent electrode in LEDs based on PPV.

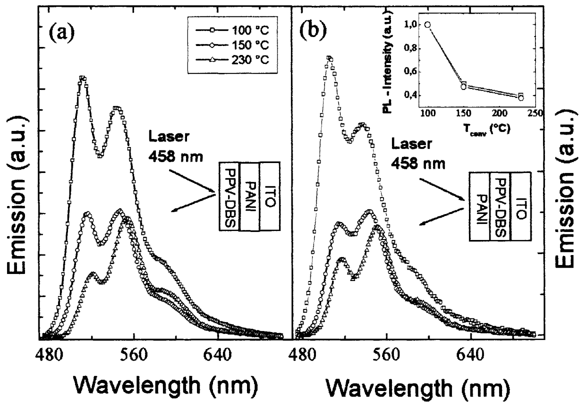

Figure 2. Photoluminescence at room temperature of ITO/PAni/PPV-DBS for different PPV-DBS conversion temperatures (100, 150 e 230 °C). In Fig. 2(a) the excitation was made directly through the PPV-DBS layer side and in 2(b) through ITO/PAni side. In the insert of Fig. 2(b) it is shown the integrated PL spectra.

Figure 2 shows the photoluminescence spectra of ITO/PAni/PPV-DBS structure with different conversion temperatures (100, 150 and 230 °C). Figure 2a shows PL curves of the PPV-DBS layer excited directly on the top surface, while in Figure 2b the excitation was performed through the ITO/PAni layer (the PL spectra was collected in the same side of excitation). It is worth noting that results are independent of the excitation side indicating that the PAni layer does not affect the PL line shape. Increasing the conversion temperature a spectral red shift was observed. This spectral shift does not change for conversion temperatures higher than 150 °C. However, there is an increase of vibrational progression of the spectra as the conversion temperature increases. The insert of Figure 2b displays the PL integrated signal as function of treatment temperature for excitations performed in the two side of the device. The similar behavior for both kinds of excitations confirms that the PAni layer does not affect the luminescence from PPV.

It is shown in Figure 3 current-voltage (I-V) curves obtained from ITO/PAni/PPV-DBS/Al and ITO/PPV-DBS/Al devices. The operating voltage in ITO/PAni structure is significant lower, typically 30% when compared with device without the PAni layer, in good agreement with results obtained for ITO/PAni/MEH-PPV/Ca LEDs.[4]

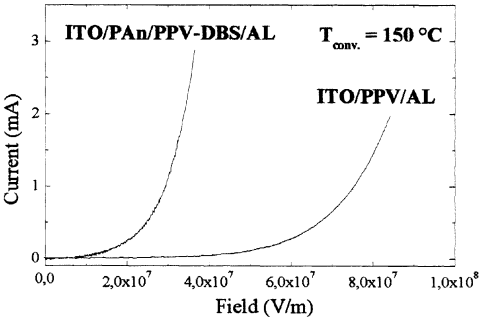

Figure 3. Current-voltage curves obtained with the ITO/PAni/ PPV/Al and ITO/PAni/ PPV-DBS/Al devices. The thickness of active polymer layer film is 400 nm. The PPV was converted at 150 °C during 2 hours.

CONCLUSIONS

In the present work it was demonstrated that the ITO/PAni structure could be used, as transparent anode for hole-injection and it is compatible with the low temperature conversion process of PPV obtained by thermal treatment. The I-V characteristics showed a decrease of about 30% in the operation voltage of the device when compared with the traditional LED without the active PAni layer. At our knowledge this is the first time that the enhancement of electrical properties of PPV-LED device is reported, similarly to that obtained using a LED based on PAni/MEH-PPV built by Yang and Heeger.[4] Measurements of electroluminescence characteristics of such devices are under way in order to evaluate the efficiency of our ITO/PAni LEDs, which it is expected to increase as already observed in the PAni/MEH-PPV device.

ACNOWLEDGMENTS

The authors would like to thank the financial assistance from the Brazilian agencies FAPESP, CNPq and CAPES.

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