Surface Morphology and Optical Characterization of $OC_1 OC_6$-PPV Films

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We report optical and morphological properties of poly(2-methoxy-5-hexyloxy-p-phenylenevinylene) (OC_1OC_6-PPV) films processed by casting, spin-coating (SC) and Langmuir-Blodgett (LB) techniques. The absorption spectra are practically the same, with an absorption maximum at approximately at 500 nm. For the photoluminescence (PL) spectra at low temperature (T=10K), a small but significant difference was noted in the cast film, in comparison with the LB and SC films. The zero-phonon transition shifted from 609 nm for the LB film to 615 and 621 nm for the SC and cast films, respectively. At room temperature, the PL spectra are similar for all films, and blue shifted by ca. 25 nm in comparison with the spectra at low temperature due to thermal disorder. Using atomic force microscopy (AFM) we inferred that the distinctive behavior of the cast film, probably associated with structural defects, is related to the large thickness of this film. The surface roughness, which was surprisingly higher for the LB film, apparently played no role in the emission properties of OC_1OC_6-PPV films.

Keywords: MH-PPV; Processing effect; Optical and topological properties

I. INTRODUCTION

Conjugated polymers are potential materials for polymer light emitting diodes (PLEDs) [1] and one main challenge is to identify polymers that are solution processable. The phenylene-based OC_1OC_6-PPV, or poly(2-methoxy-5-hexyloxy-*p*-phenylenevinylene), meets this criterion, as it is soluble in organic solvents and may be easily processed in thin-solid films [2]. The optimization of the emission properties, however, requires investigation of the processing conditions. For example, polymer-polymer interactions introduce structural defects causing the emission quantum efficiency to decrease [3-4]. In addition, electronic properties and the structural arrangement of the polymer main chain may be strongly associated with the polymer-film processing technique.

In this work we investigate the effects from the film-forming techniques on the optical properties, absorption and emission, of OC_1OC_6-PPV films. Three techniques are used, namely casting, spin-coating (SC) and Langmuir-Blodgett (LB). Atomic Force Microscopy (AFM) is used to study the film morphology, and the data are analyzed with first-order statistics.

II. EXPERIMENTAL

Figure 1 shows the chemical structure of OC_1OC_6-PPV synthesized as described in Ref. 2. All films were processed onto glass substrates, previously cleaned using the RCA procedure [5], from polymer solutions in chloroform. The cast film was produced from a 0.5 mg/ml solution of OC_1OC_6-PPV. The SC film was obtained using a photo-resist spinner (Hedway Research Inc-model:1-EC101DT-R484) at 2000 rpm during 90s and with a polymer solution of 0.5 mg/ml. The LB film was obtained following the procedure of Ref. [6],

with a polymer solution of 0.2 mg/ml. The films were dried and stored at room temperature, and protected from light to avoid photodegradation.

The photoluminescence (PL) spectra were recorded using a SPEX-750M monochromator equipped with a Joban-Yvon CCD-detector (2000×800-3) in the temperature range between 10 and 300K. Excitation was performed with the 457.8 nm line of an Ar^+ laser. The samples were kept in a closed helium cryostat at 10^{-4} torr. The UV-VIS. spectra were obtained with a Hitachi U-2001 spectrophotometer. AFM experiments were performed with a Nanoscope®IIIa Multimode^{TM}of Digital Instruments. The images were obtained under ambient conditions in the tapping mode. A commercial Si cantilever with a spring constant of 20 to 100 N/m was used, with free oscillation in the range between 250 and 300 KHz. The scanned area for the images was 10x10 μm^2 and the scan rate was 0.7 Hz
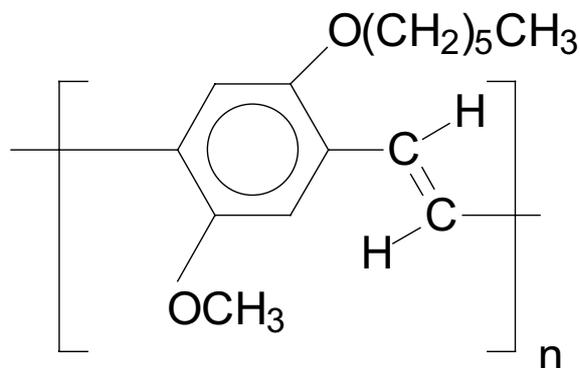

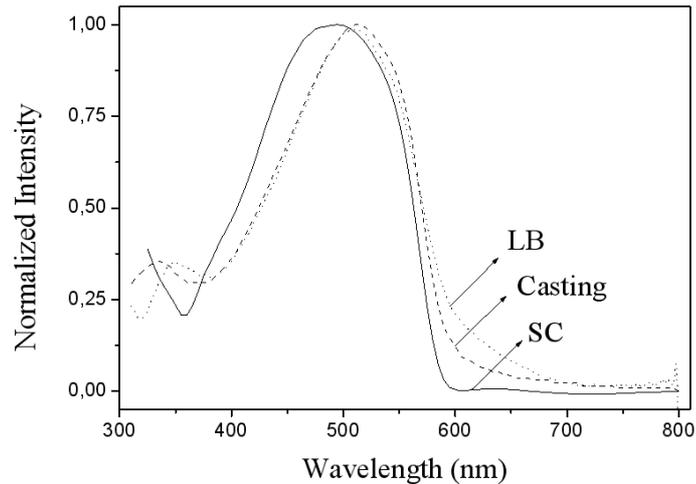FIG. 1: Chemical structure of OC_1OC_6-PPV.

FIG. 2: Absorbance of cast, SC and LB film of OC_1OC_6-PPV at room temperature.
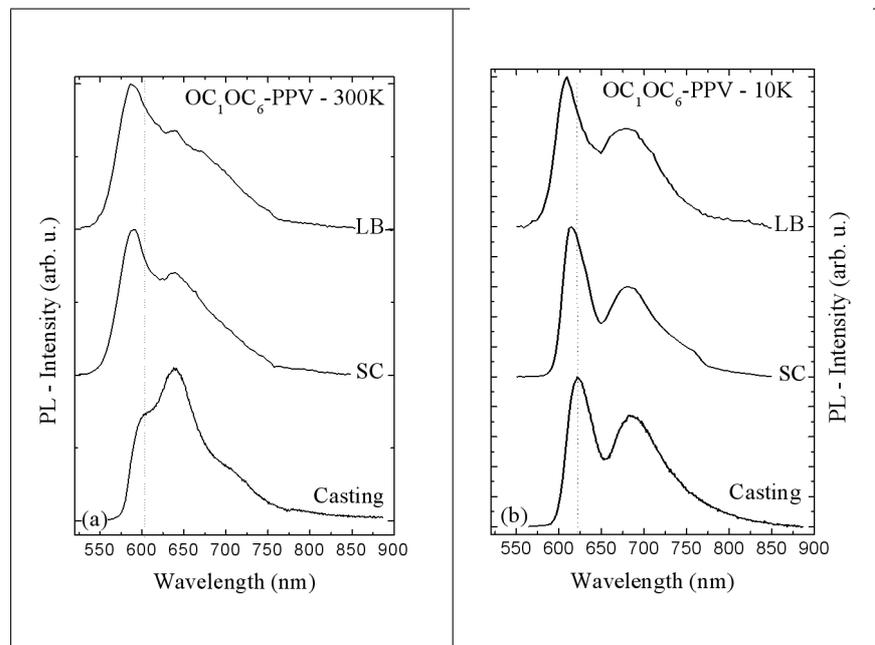

FIG. 3: Photoluminescence spectra at 300K (a) and 10K (b) for Cast, SC and LB OC_1OC_6-PPV Films.

III. RESULTS AND DISCUSSION

Figure 2 shows the absorbance spectra of OC_1OC_6-PPV cast, SC and LB films. The curves were normalized taking the peak intensity as one. For all films, the extended band above 350 nm is related to non-localized states (HOMO-LUMO transitions). The spectra for the cast and LB films were red shifted by ca. 10 nm at the maximum and by 3 nm at the band edge, in comparison to the SC film. According to the effective conjugation model, these results indicate that the SC

film possesses a distribution with slightly lower conjugation lengths than the other two films [7].

The PL spectrum of OC_1OC_6-PPV displays a peak correlated to the zero-phonon transition (I_0) at 601 nm and two electron-vibrational coupling modes (phonon-replicas, I_1 and I_2) at 635 and 706 nm at 300K, for the cast film (Fig. 3a). In this case, the zero-phonon transition is attributed to the interchain transition [3]. For the SC and LB films, the spectra are blue shifted, with increased line width and increased intensity of the zero-phonon peak. At low temperature (Fig. 3b),
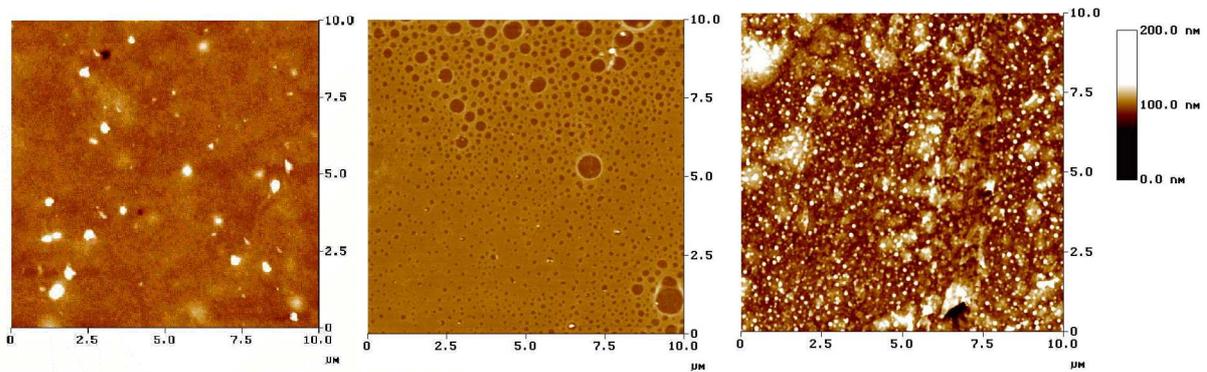
FIG. 4. AFM images of OC_1OC_6-PPV films processed via (a) casting, (b) SC and (c) LB technique.

the thermal disorder decreases and the PL spectra are similar for all films [8]. The shift to lower energy for the cast film is correlated to the interchain interaction due to the structural disorder.

According to the molecular exciton model and the effective conjugation degree [9], emission occurs at the long polymer segments. We therefore conclude that emission for SC and LB films takes place under basically the same polymer-polymer environment, i.e. with similar interchain interactions. [10]. That is to say, the molecular packing appears not to be influenced by the polymer solution concentration. The low value of the electron-phonon coupling ($S{\sim}I_1/I_0$) [11] shows that the polymer chain is more rigid in these films. At low temperature (Fig. 3b), all films present the same S, as structural disorder becomes less important.

The small but significant difference in the PL spectrum for the cast film may be associated with morphological features. We have checked this hypothesis by obtaining AFM images, shown in Figures 4a-c. Using first-order statistics [12], we obtained the mean square roughness (σ_{RMS}) for the images, yielding the results in table 1. Though the LB film exhibits a higher roughness, which can be inferred from a visual inspection of the AFM images, the main feature distinguishing the films is the thickness of the cast film. The higher thickness may have led to structural disorder affecting the emission properties of the cast film (cf. Figure 3). On the other

hand, the organization that could be induced by the LB technique [13] appears neither to lead to smooth films or affect the emission properties in comparison with the cast films.

TABLE I: AFM parameters of OC_1OC_6-PPV films.

	Cast	SC	LB (41 layers)
σ_{RMS} (nm)	7.3	4.5	12.6
Thickness (nm)	230.2	8.6	70.5

IV. CONCLUSIONS

It has been demonstrated that the film morphology for OC_1OC_6-PPV depends strongly on the film processing technique. For the systems investigated, the morphological feature that affected most the luminescence properties was the thickness, with the thick cast film displaying a distinct PL spectrum at room temperature, at which structural disorder plays an important role.

Acknowledgements

[1] I. D. Parker, J. Appl. Phys. **75**, 1656 (1994).
[2] F. M. Marconi, R. F. Bianchi, R. M. Faria, and D. T. Balogh, Mol. Cryst. Liq. Cryst. **374**, 475 (2002)
[3] Y. Shi, J liu, Y. Yang, J. Appl. Phys. **87** (2000) 4254
[4] J. Liu, Y. Shi, Y. Yang, Appl. Phys. Lett. **79** (2001) 578
[5] W. Kern, Semicon. Int. 94-98 (1984).
[6] M. Ferreira, C. J. L. Constantino, C. A. Olivati, A. L. Vega, D. T. Balogh, R. F. Aroca, R. M. Faria, and O. N. Oliveira, Langmuir **19**(21), 8835 (2003).
[7] A. Marletta, F. E. G. Guimarães, and R. M. Faria, Braz. J. Phys **32**(2), 570 (2002).
[8] H. S. Woo, O. Lhos, S. C. Grahan, D. D. C. Bradley, R. H. Friend, C. Quattrocchi, J. L. Bredas, E. Schenk, and K. Mullen,

Synth. Met. **59**(1), 13 (1993).
[9] R. Chang, J. H. Hsu, W. S. Fann, K. K. Liang, C. H. Chiang, M. Hayashi, J. Yu, S. H. Lin, E. C. Chang, K. R. Chuang, and S. A. Chen, Chem. Phys. Lett. **317**(1-2), 142 (2000).
[10] A. Marletta, V. C. Gonçalves, and D. T. Balogh, J. Lum, **116**, 87 (2006).
[11] O. Narwark, A. Gehard, S. C. J. Meskers, S. Brocke, E. Thorn-Csanyi, and H. Bassler, Chem. Phys. **294**(1), 17 (2003).
[12] T. R. Thomas, "*Rough surface*" Imperial College Press (1999).
[13] C. A. Olivati, M. Ferreira, A. J. F. Carvalho, D. T. Balogh, O. N. Oliveira, H. von Seggen, and R. M. Faria, Chem. Phys. Lett. **408**(1-3), 31 (2005).