Device Performance and Polymer Morphology in Polymer Light Emitting Diodes: Morphology Dependent Emission Spectra

Y. Shi, J. Liu, and Y. Yang*

Department of Materials Science and Engineering, University of California-Los Angeles, Los Angeles, CA 90066, USA

SUMMARY: Polymer thin films for the light-emitting devices (LEDs) are usually obtained by spin-casting from slightly viscous solutions. The performance of polymer light-emitting diodes is strongly influenced by the thin film morphology. It is known that the polymer thin film morphology (or aggregation) is determined by the solvents used for obtaining polymer solutions. In this manuscript, we demonstrate that the polymer aggregation can also be controlled by the concentration of the polymer solution and the rotational speed used during spin-casting of the films. The correlation between the film morphology and emission spectra for polymer light-emitting diodes fabricated using poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV) has been studied. Our findings indicate that there is a strong correlation between the "vibronic structure" observed in the emission spectra of the MEH-PPV devices and the aggregation of the polymer chains.

Introduction

Conducting and semiconducting plastics have attracted a lot of research due to their lightweight, flexibility and ease of processing, coupled with their unique electrical and photonic semiconducting characteristics. Since some of these materials can be obtained in solution-form, spin-casting has become the most common processing technique for polymers. Spin-casting is an easy and low-cost processing technique for obtaining uniform thin films of these materials. It is also rather easy to control the film thickness by simply adjusting the rotational

speed of the spinner. The thickness of the films obtained are a function of the rotational speed and the viscosity of the solution, with higher spinning rates usually yielding thinner films and vise versa. It is often noticed that emission, both photoluminescence (PL) and electroluminescence (EL), of polymer films are somewhat different when the film thickness varies. This observation is often associated with the microcavity effect,[1,2,] which is purely an optical effect, while the differences in the film morphology and polymer chain aggregation, primarily controlled by the spin-casting process conditions (solvent, solvent evaporation rate, spin speed, etc) are usually ignored.

In this manuscript, we produce evidence to show that the change of PL and EL emission spectra of MEH-PPV thin films, prepared from polymer solutions with different concentrations and/or with different spin-speeds, have a strong correlation with the different aggregation states of the polymer chains. The aggregation of polymer chains favors the formation of an excimer-like excited state which red-shifts the emission spectrum almost to a red emission. At high spin-speeds and low polymer concentrations, the aggregation in the polymer films are less and the emissions are yellow. This observation is reproducible with the polymer solutions prepared from different solvents and is independent of the polymer film thickness. The detailed experimental approach and results are discussed below.

Experimental

The LEDs discussed in this manuscript consist of a polymer active layer sandwiched between a cathode and an anode. For this study, calcium was used as the cathode, and ITO/PEDOT (3,4-polyethylenedioxythiophene-polystyrenesulfonate) was used as the anode. Poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV) was chosen as the active material in our study.[3] Unless otherwise indicated, cyclohexanone is the solvent used in this study. The ITO substrates underwent a routine cleaning procedure, which included sonication in detergent followed by repeated rinsing with de-ionized water, acetone and isopropanol and finally treated with UV-ozone. PEDOT was first spin-cast onto ITO/glass substrate at a spin speed of 4000 rpm, corresponding to 85nm thick, and baked at 120 °C for 2 hours before spin-casting the MEH-PPV film. The cathode of the polymer LED was formed by the thermal evaporation of Ca and Al from tungsten boats at a

pressure of around 1×10^{-6} torr. The thickness of the calcium and the aluminum protective layer was approximately 200Å and 1000 Å, respectively. The diode area was 12 mm^2. MEH-PPV solutions were prepared and spin-cast in a nitrogen gas environment. The EL and PL emission spectra were obtained from a S2000 fiber optic spectrometer by Ocean Optic Inc.. The UV-Vis absorption spectra were recorded on a HP 8453 spectrophotometer. The film thickness data was measured using an Alphastep profilometer.

Results and Discussion

It is observed that the UV-Vis absorption spectrum of the polymer film depends on the concentration of the polymer solution as well as the spin speed. The λ_{max} of a polymer film obtained from a more dilute solution and/or spin-cast at a higher spin speed is significantly red-shifted, and vice versa. Figure 1 shows the absorption spectra of a thinner film spin-cast using 0.3wt% MEH-PPV solution and a thicker film using 1wt% solution with the same spin speed (8000 rpm). Also shown for comparison is a normalized spectrum-a. It can be easily seen from Figure 1 that the emission of the polymer film from the more dilute solution is significantly red-shifted (λ_{max} = 510 nm) as compared to that obtained from the more concentrated solution (λ_{max} = 496 nm). Similar spectral shift can also be demonstrated by using the same solution (of medium concentrations, e.g. 0.5-0.8wt%) but different spin speeds. For example, spin-casting a 0.8wt% solution at 1500 rpm leads to λ_{max} = 499 nm (OD = 0.75) while at 8000 rpm λ_{max} = 509 nm (OD = 0.35). At higher ($\geq$ 1wt%) or lower ($\leq$ 0.2wt%) concentrations, however, no spin speed dependence is observed. Similar effects can also be observed in other solvents such as tetrahydrofuran (THF) and *p*-xylene. It is known that many polymers can exist in aggregated and un-aggregated forms in solutions. Many research groups[4] have showed the evidence for aggregate formation in thin films of different polymers. The above spectral shift observed in MEH-PPV films suggests that the MEH-PPV chains in thin films also exist in two (or more) different aggregation states, i.e. the un-aggregated form and the aggregated form. The fact that no spin speed dependence was

observed for films prepared with concentrations $\geq$ wt1% suggests that the polymer chains form strong aggregates (so strong that spinning at 8000 rpm is not sufficient to break the aggregates apart) at these concentrations. As the concentration decreases, the chains become less aggregated and the aggregates also become smaller and looser. It is therefore expected that such aggregates can be torn apart more easily by the centrifugal force. When more dilute solutions (e.g. < 0.2wt%) are used, the λ_{max} of the resulted films is usually closed to 510 nm and is independent of the spin speed within the range of 1000-8000 rpm. This is expected since the amount of aggregates in highly dilute solutions, if any, should be very little. In addition, such polymer films are usually so thin that they dry almost instantly without allowing the formation of large amounts of polymer chain aggregates. On the other hand, the centrifugal force also tends to stretch the polymer chains to the more extended conformation and thus results in a better conjugation and a red-shifted absorption spectrum. It is thus expected that the un-aggregated polymer chains in a spin-cast film should be more "stretched" while the aggregated chains should be more curled.
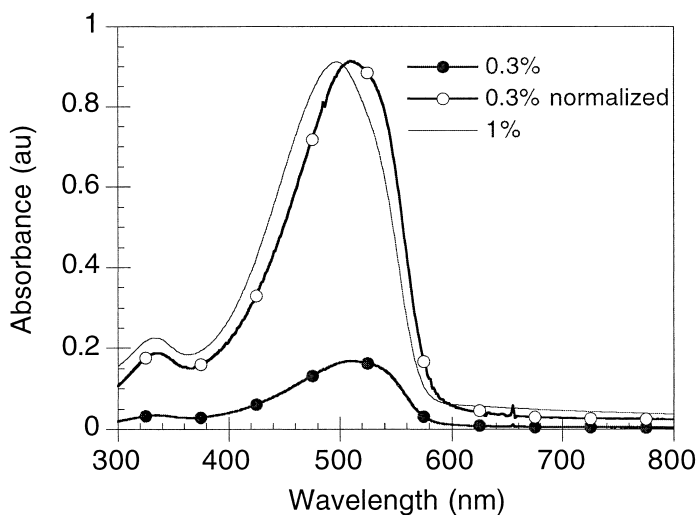
Figure 1. Absorption spectra for MEH-PPV films spin-cast on glass plates using 0.3wt% and 1wt% MEH-PPV solutions. The spin speed used was 8000 rpm.

The electroluminescence spectra of thin films prepared using spin-casting technique is also morphology dependent. Figure 2 shows the spin-speed dependent electroluminescence (EL) spectra for some MEH-PPV LEDs fabricated using this technique. When the polymer solution is cast at high speeds (8000 rpm, 0.7wt%), the resulting devices have a strong yellow emission at (λ_{max} = 575 nm) and a shoulder at red (~630 nm, Figure 2). A similar photoluminescence (PL) spectrum was observed in dilute solutions of MEH-PPV and was assigned to the un-aggregated chains.[5] As discussed above, it is expected that at high spin speed the films comprise mostly of the more "stretched" un-aggregated polymer chains. We thus assign the yellow emission (~575 nm) to the un-aggregated form. As the spin speed decreases, the relative intensity of the yellow emission to the red emission decreases, accompanied by a red-shift of the yellow emission (Figure 2). Similar spectral changes were also observed by Swager and co-workers[6] when they compared a poly(p-ethynylene) thin film prepared by Langmuir-Blodgett technique with that prepared using the spin-casting technique. They suggested that these spectral changes were the result of interactions (π-stacking) between the polymer backbones in thicker films. Cornil et al[7] showed by quantum
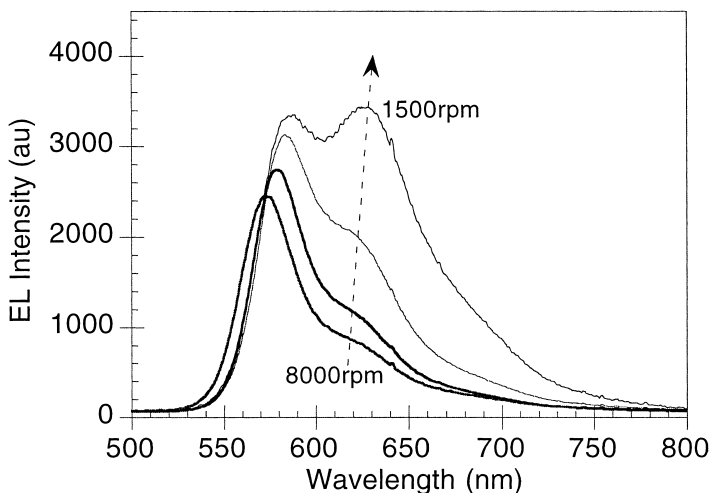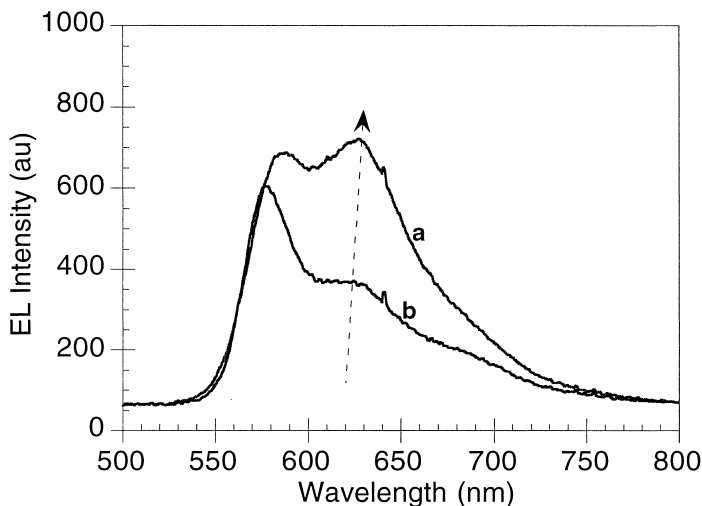
Figure 2. EL emission spectra for MEH-PPV films spin-cast at different spin speeds. The arrow indicates the decrease of spin speed, 8000, 4000, 2500, and 1500 rpm. The relative height of the curves do not reflect the actual intensities.

mechanic calculations that the π-stacking of polymer backbones could red-shift the absorption spectrum. If this explanation also applies to MEH-PPV, a spectral red-shift in the absorption spectrum is expected as the thickness of the film increases. However, this prediction is in contradiction to our experimental observations in which the absorption spectrum of a thicker film (assigned to the aggregate species) is blue-shifted. In order to account for this contradiction, we suggest that the π-stacking of the polymer backbones of MEH-PPV is hindered in the ground state, probably due to the bulky ethylhexyl side chains, and such interactions become more pronounced only in the excited state. In other words, the red emission is due to an excimer- and/or exciplex-like excited state resulted from interchain (between an excited molecule and a ground state molecule) and/or intrachain (between the different conjugation segments of the same molecule in the excited state) π-electron interactions. The above argument so far tends to suggest that the emission spectra shown in

Figure 2 are thickness dependent. As discussed earlier, the film morphology also varies with spin speed. As the spin speed decreases, more and more "loose" aggregates can survive the centrifugal force, while the film also becomes thicker, leading to a slower evaporation rate of the solvent. Both these effects favor the formation of aggregates. It is thus possible that the spectral changes shown in Figure 2 are morphology dependent. In order to clarify this point, the emission spectra of a "single layer" device and a "multi-layer" device with similar thickness were compared. These devices were prepared using the same solution but the polymer films were coated differently. In the "single-layer" device, the polymer film was formed by a single spin-casting procedure at a lower spin speed (1000 rpm, 0.7wt%, film thickness ~ 900 Å). For the "multi-layer" device, the film was obtained by nine consecutive spin-castings using the same polymer solution at higher spin speed (7000 rpm, film thickness ~950 Å). It was observed that in the "multi-layer" device the red emission (~635 nm) is significantly suppressed (by ~50%) and the yellow emission (~575 nm) is relatively enhanced. Similar results can also be demonstrated by comparing the EL spectra (Figure 3) of the above "single layer" device (curve-a) and a "double layer" device (curve-b) with different thickness. For the double layer device, the first layer was coated under exactly the same conditions as the "single layer" device. After the first layer was dried, a second layer of polymer was coated on top of the first layer using the same solution but a higher spin speed (4000 rpm). The thickness of the "double layer" device was approximately 1400 Å, ~ 50% thicker than the "single layer" device. According to the previous discussion, it is expected that the second layer should contain more "stretched" (un-aggregated) chains and thus one should expect to see more intense yellow emission (575 nm) and weaker red emission (635 nm) in the "double layer" device. This is exactly what was observed experimentally. It can be seen from Figure 3 that the relative intensity of the yellow to the red is significantly enhanced in the "double layer" device although the polymer film is thicker. These results strongly suggest that the observed spectral changes are strongly correlated to polymer morphology. We therefore assign the red emission (635 nm) to the aggregated species. Since the "second layer" is right beneath the cathode, the fact that the red emission in the "double layer" device is substantially suppressed may also imply that the electron-hole recombination

region is near the cathode. More detailed studies are currently being carried out in order to clarify this hypothesis.

Figure 3. El emission spectra for a "single layer" (curve a) and a "double-layer" (curve b) device. Curve a: the polymer film was formed by a single spin-casting from a 0.7% MEH-PPV solution at 1000 rpm. The resultant film thickness is approximately 900 Å. Curve b: the film was first spin-cast using the above conditions. After the film was dried, a second spin-casting was performed at 4000 rpm using the same polymer solution. The final thickness of the film is approximately 1400 Å.

It can also be seen from Figure 3 that the emission spectrum of the "double layer" device shows a shoulder at ~680 nm. We have investigated this emission band by using different solvent systems and the "multi-layer" device fabrication technique.[8] All the evidence that has been collected so far indicates that this band is probably due to the formation of excimers between the un-aggregated polymer chains or between the aggregated and un-aggregated species. Schwartz and co-workers[5] also observed a similar emission band (~660 nm) in

solution (solvent: THF). In dilute solutions, they observed very similar photoluminescence excitation (PLE) spectra at 552 nm and 660 nm, suggesting both bands to be due to the excitation of the same species. As the polymer concentration increases, they observed a wavelength dependent PLE spectrum at 660 nm and thus assigned this emission band to the aggregate species. More recently, Rothberg and co-workers[9] also reported a similar species (λ_{max} = 700 nm) observed in the PL spectra of the polymer films and assigned it to the aggregate emission. On considering results from these groups, we suggest that the 660 nm emission observed in solution is more likely due to a minor aggregate species consisting of the more "extended" chains. In reality, the polymer chains can exist in the more extended un-aggregated form, the curled /aggregated form, as well as any other possible intermediate conformations in between. The relative amounts of these species will depend on the concentration as well as the solvent. It is therefore not surprising that more than one kind of aggregate species are observable.

It is known that the microcavity effect can also change the emission spectrum of a thin film LED device. This effect has been applied to devices color turning in thin film light-emitting diodes, known as microcavity devices.[1,2, 10, 11] These devices usually need electrodes with good reflectivity (e.g. using gold electrodes) in order to achieve a pronounced microcavity effect. Wittmann et al [1] indicated that the microcavity effect is less significant in devices using ITO electrodes. More recently, So and Choi [12] have demonstrated microcavity effect in ordinary OLEDs with only one reflective electrode. In both cases, these microcavity devices are characterized by their thickness dependent emission spectra. Since we have already shown (*vide supra*) that the spectral changes reported here are thickness independent, the microcavity effect can be excluded. However, this does not rule out the possibility that the microcavity effect may have a minor contribution. In order to check for this possibility, the photoluminescence of polymer films coated on transparent glass plates was studied. Since there are no reflective electrodes available in these cases, microcavity effect, if any, should be very small. Not surprisingly, the photoluminescence spectra of such films spin-cast at different spin speed and/or using different concentrations showed a similar trend as was

observed in the electroluminescence shown in Figure 2. These results further confirmed that these spectral changes are not the result of a microcavity effect.

Conclusion

In summary, we have demonstrated that MEH-PPV can exist in two major aggregation states, the un-aggregated and aggregated forms, in spin-cast films. The un-aggregated form is more "stretched" and the aggregated species is more curled. The interchain and intrachain $\pi-\pi$ interaction in the ground state is so weak that the aggregates do not show a spectral red-shift in the absorption spectrum as commonly observed in many polymers. In contrast, formation of the curled aggregates breaks the conjugation of the polymer backbones and thus results in a blue-shift of the absorption spectrum. The emission spectrum of the polymer film consists of two major components, the yellow (λ_{max} = 575 nm) due to the un-aggregated species and the red (λ_{max} = 635 nm) due to the aggregated species. The relative intensity of the two bands and thus the color of the device depend on the relative amounts of the un-aggregated and the aggregated emitting species in the film, which can be controlled by "multi-layer" device fabrication technique or by varying the concentration of the polymer solution. Due to the spectral overlapping and the complexity of the film morphology, however, we can not completely resolve these two spectra at this time.

Acknowledgement

References

1. H. F. Wittmann, J. Grüner, R. H. Friend, G. W. C. Spencer, S. C. Moratti, A. B. Holmes, *Adv. Mater*. **7**, 541 (1995).

2. V. Cimrová, D. Neher, *J. Appl. Phys*. **79**(6), 3299 (1996).

3. F. Wudl, G. Srdanov, U.S. Patent No. 5,189,136 (1993).

4. For example, J. W. Baltchford, S. W. Jessen, L.-B. Lin, T. L. Gustafson, D.-K. Fu, H.-L. Wang, T. M. Swager, A. G. MacDiarmid, A. J. Epstein, *Phys. Rev. B* **54**, 9180 (1996); J. W. Baltchford, T. L. Gustafson, A. J. Epstein, D. A. Vanden Bout, J. Kerimo, D. A. Higgins, P. F. Barbara, D.-K. Fu, T. M. Swager, A. G. MacDiarmid, *Phys. Rev. B* **54**, R3683 (1996); T. Pauck, R. Hennig, M. Perner, U. Lemmer, U. Siegner, R. F. Mahrt, U. Scherf, K. Müllen, H. Bässler, E. O. Göbel, *Chem. Phys. Lett*. **244**, 171 (1995); U. Lemmer, S. Heun, R. F. Mahrt, U. Scherf, M. Hopmeier, U. Siegner, E. O. Göbel, K. Müllen, H. Bässler, *Chem. Phys. Lett*. **240**, 373 (1995); R. F. Mahrt, T. Pauck, U. Lemmer, U. Siegner, M. Hopmeier, R. Hennig, H. Bässler, E. O. Göbel, *Phys. Rev. B* **54**, 1759 (1996).

5. T.-Q Nguyen, V. Doan, B. J. Schwartz, *J. Chem. Phys.* **110**(8), 4068 (1999).

6. I. A. Levitsky, J. Kim, T. M. Swager, *J. Am. Chem. Soc*. **121**, 1466 (1999).

7. J. Cornil, D. A. dos Santos, X. Crispin, R. Silbey, J. L. Bredas, *J. Am. Chem. Soc*. **120**, 1289 (1998).

8. Unpublished results from this group.

9. R. Jakubiak, C.J. Collison, W.C. Wan, L.J. Rothberg *J. Phys. Chem. A* **103**, 2394 (1999).

10. A. Dodabalapur, L. J. Rothberg, T. M. Miller, E. W. Kwock, *Appl. Phys. Lett.* **64** (19), 2486(1994).

11. A. Dodabalapur, L. J. Rothberg, T.M. Miller, *Appl. Phys. Lett.* **65**(18), 2308 (1994).

12. S. K. So, W. K. Choi, *Appl. Phys. Lett*. **74**, 1939 (1999).