

Change in electrical characteristics of poly(*p*-phenylene vinylene)-based self-assembled devices by addition of ionic salt to poly(sodium 4-styrenesulfonate)

Jinhan Cho^a, Kookheon Char^{a,*}, Sun-Young Kim^a, Jong-Dal Hong^b,
Dong Young Kim^c, Ki-Bong Lee^d

^aSchool of Chemical Engineering, Seoul National University, San 56-1, Shinlim-dong, Kwanak-gu, Seoul 151-742, South Korea

^bDepartment of Chemistry, University of Incheon, Dowha-dong, Namgu, Incheon 402-749, South Korea

^cPolymer Materials lab, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 130-650, South Korea

^dDepartment of Physics, Pohang University of Science and Technology, San 31, Hyoja-dong, Nam-gu, Pohang 790-784, Kyungbuk, South Korea

Received 27 January 2001; received in revised form 9 April 2001; accepted 9 April 2001

Abstract

A systematic study was performed on the effect of added salt on the effective conjugation lengths poly(*p*-phenylene vinylene)s (PPVs) formed by heat-treatment of PPV precursors in self-assembled films based on the layer-by-layer deposition between PPV and poly(sodium 4-styrenesulfonate) (PSS). It was demonstrated that the increased adsorbed amount of negatively charged PSS layer by adding NaCl salt to the PSS solution caused a blue spectral shift in electroluminescence and at the same time yielded a high turn-on voltage. The changes of electrical properties of PPV in the self-assembled films were mainly attributed to the restricted growth of conjugation bond length of PPVs induced by the increase of binding sites with the adsorbing PSS and the subsequent formation of sulfonic ester group during the thermal elimination reaction. Consequently, it is shown that the electrical properties of PPV can be simply tuned by the variation of physical parameters for the fabrication of self-assembled films without a change of PPV chemistry. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Poly(*p*-phenylene vinylene) (PPV); Multilayer; Self-assembly method; Electroluminescence (EL); Ionic salt

1. Introduction

Conjugated polymers have attracted much interest for their potential applications, particularly as materials for solid-state light-emitting devices (LED) [1,2]. In order for these materials to be applicable to LED devices, emission color control is a crucial requirement [3]. In addition, for the fabrication of a multilayer structure to improve device performance, various organic or inorganic layers with unique electrical properties such as hole transporting, electron transporting or hole blocking characteristics are inserted in the electroluminescence (EL) devices for balanced recombination of holes and electrons [3–6].

First described by Decher et al. in 1992 [7], a layer-by-layer self-assembly method based on the electrostatic attraction between opposite charges has been successfully employed to include a wide variety of conjugated polymers or inorganic materials with novel electrical and optical

properties for the EL devices [8,9]. Rubner and his collaborators have reported that in self-assembled multilayer films prepared with PPV and polyanion, the polyanion influences the amount of conjugated PPV deposited per bilayer, the thickness of each layer, and eventually the electrical properties of the films [10]. They also showed that using different kinds of polyanions such as poly(sodium 4-styrenesulfonate) (PSS) and poly(methacrylic acid) (PMA), it was possible to tune the wavelength of light emitted by the device without chemically modifying the PPV structure as typically done. We have previously reported on the blue shift of UV–VIS absorption and photoluminescence (PL) spectra of self-assembled (PPV/PSS) films with increasing the amount of ionic salt in the PSS deposition solution [11]. It was clearly shown that the conjugation bond length of PPV could be adjusted by the ionic strength of the polyanion solution.

In present work, the objective is to extend the optical characteristics reported previously to electrical characteristics of the self-assembled PPV devices. Instead of changing the type of polyanion used in the self-assembled PPV

* Corresponding author. Tel.: 82-2-880-7431; fax: +82-2-888-7295.
E-mail address: khchar@plaza.snu.ac.kr (K. Char).

devices, we systematically investigate, by way of changing the adsorbed amount of PSS interlayers by the addition of ionic salt to PSS solution, the changes in electrical properties such as EL and turn-on voltage of the self-assembled (PPV/PSS) films.

2. Experimental section

2.1. Materials

PPV precursor was prepared by the polymerization of a bis-sulphonium salt of *p*-xylene using the method given by Lenz et al. [13]. The reaction product was dialysed with a molecular weight cut-off at 12,000 and the concentration of PPV precursor in aqueous solution was estimated by gravimetry to be 0.013 monomol/l. Poly(sodium 4-styrenesulfonate) (PSS, $M_w = 70,000$) was obtained from Aldrich and used without further purification.

2.2. Film deposition

The polyelectrolytes were deposited onto negatively charged quartz or silicon substrates as described previously [11,12]. In order to investigate the ionic salt effect, the ionic strength of the dipping PSS solution is controlled by adjusting NaCl concentration. The ionic strengths were fixed at 0.0, 0.1 and 2.0 M of NaCl; the corresponding samples were denoted by $F_{0.0}$, $F_{0.1}$ and $F_{2.0}$. In addition, self-assembled films fabricated by a simple increase of the number of bilayer deposition without the addition of NaCl salt were prepared and denoted by N_{20} for 20, N_{40} for 40 and N_{50} for 50 bilayers, respectively, for comparison with the self-assembled films containing ionic salts.

2.3. Electroluminescence measurement

LEDs based on the self-assembly were prepared in a similar fashion on indium tin oxide (ITO) coated glasses (obtained from Samsung Corning Co.). The thickness of ITO layer is about 1850 Å and the sheet resistance is 10–20 Ω cm. The ITO substrates were cleaned by sonication in isopropyl alcohol for 1 h, followed by immersion in $H_2O/H_2O_2/NH_3$ (5/1/1) for 1 h. The fabrication of self-assembled multilayer films on the ITO substrates is identical to the procedure adopted on the quartz glasses. After thermal conversion of the PPV precursor to a conjugated form of PPV, an aluminum counter electrode was evaporated onto the PPV multilayer film. The thickness of Al electrode was about 1500 Å and the active area for light emission is 16 mm².

EL spectra were obtained using a Jobin Yvon U-1000 Double Monochromator with a Stanford Research SR 400 Photon Counter. *I*–*V*–*L* characteristics were also recorded. A Keithly 236 source/detector unit was used to obtain the voltage-current relationship and a Newport SIS-SL

photodiode was used for measuring the voltage-electroluminescence intensity relationship.

3. Results and discussion

It is well known that the adsorption behavior depends strongly on the ionic strength of polyelectrolyte solution as schematically shown in Fig. 1 [11,14]. In an adsorbed state shown in Fig. 1(a), a negatively charged PSS layer without containing ionic salt, which is in a stretched conformation, is collapsed onto a positively charged PPV precursor surface. On the other hand, the addition of ionic salt such as NaCl in the PSS solution increases the adsorbed amount of the PSS layers in a coiled conformation due to the screening of negative charge repulsion between sulfonic acid groups. This adsorption behavior of the PSS layers increases the binding sites per unit area for the adsorption of PPV precursor onto the PSS layer and thus induces more adsorption of PPV precursors as shown in Fig. 1(b). As a result, the binding sites between the cationic PPV precursor and the anionic PSS are significantly increased due to the addition of ionic salt in the PSS solution and give rise to the increased amount of sulfonic ester groups reducing the conjugation bond length during the thermal treatment as evidenced in the blue shift in the PL spectra shown in Fig. 1(c) [9]. This suggests that the respective sandwiched PPV precursor layer is significantly confined between the thicker PSS layers by the addition of ionic salt.

When the PSS aqueous solutions contain 0, 0.1 and 2 mol of NaCl electrolyte, we note that the bilayer thickness of PPV precursor and PSS is drastically increased from 8 Å to about 27 Å. As the increase of thickness by the ionic salt addition is believed to be due to the electrostatic interaction between the sulfonium group of PPV precursor, which should be eliminated after thermal conversion, and the sulfonic acid group of PSS, the increase of the conjugation bond length for fully conjugated PPVs is strongly restricted despite a high temperature treatment at 230°C. In order to systematically investigate the EL behavior of the sandwiched PPVs by the increase of binding sites between PPV precursor and PSS, we fabricated three different EL devices of ITO/(PPV/PSS)₂₀/Al by changing the ionic strength of the PSS solution. Fig. 2 shows the EL spectra of this structure (after thermal conversion at 230°C for 1 h in vacuum) as a function of ionic strength in the PSS solution. As shown in the Fig. 2, the increase of the amount of NaCl salt added to the PSS solution causes the blue shift in the EL maxima of PPV (i.e. $\lambda_{max} = 504$ nm for $F_{0.0}$, 492 nm for $F_{0.1}$ and 484 nm for $F_{2.0}$, respectively). Since the EL spectra of self-assembled PPV devices depend on the energy band gap of PPV, the blue spectral shift observed in this case implies that a larger band gap of PPV was obtained due to the shorter conjugation bond length of a PPV layer sandwiched between PSS layers with a large amount of NaCl in the PSS solution. This trend is also consistent with the results of blue shifted

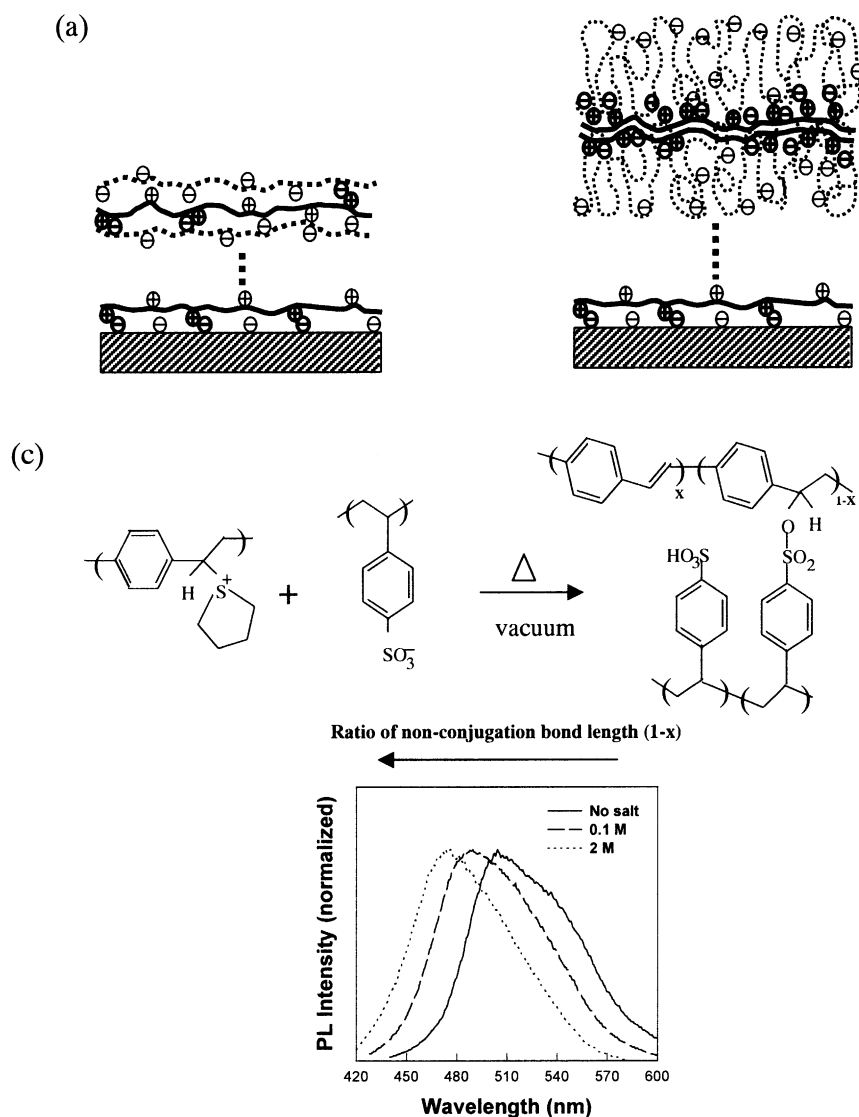


Fig. 1. Schematic of the conformational change of PSS and PPV precursor layer due to the addition of ionic salt to PSS solution: (a) without the addition of ionic salt; (b) with the addition of ionic salt (solid lines: PPV precursor chains, dotted lines: PSS chains); (c) The formation of conjugated PPV polymer and sulfonic ester group in a self-assembled film during thermal conversion and PL spectra as a function of salt amount added to PSS solution.

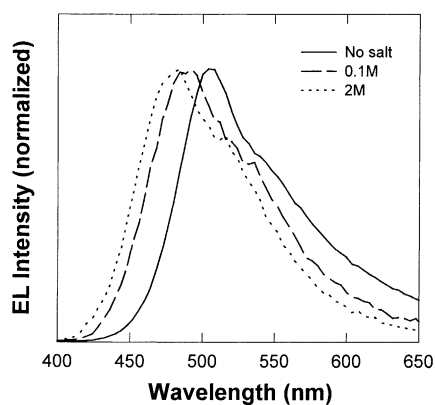


Fig. 2. The change of EL spectra of 20 bilayers of PPV/PSS sandwiched between ITO and Al with the addition of NaCl to PSS solution.

PL spectra upon addition of salt to the PSS solution, as shown in Fig. 1(c) [11]. Furthermore, we can also think that the shorter conjugation bond length of PPV and thicker PSS layers have a significant effect on the charge injection characteristics of the self-assembled devices.

In order to support this idea, we measured the current–voltage–light (I – V – L) characteristics for two different types of self-assembled PPV devices: the simple increase of the number of bilayers and the increase of ionic strength in PSS solution using a salt additive. In the case of a self-assembled PPV device containing no ionic salt in the PSS, the respective devices composed of 20, 40 and 50 bilayers start to emit light and to rapidly increase current flow at about 3 V as shown in the $\log I$ – $\log V$ and $\log L$ – $\log V$ curves of Fig. 3. This voltage is defined as the turn-on voltage, which depends

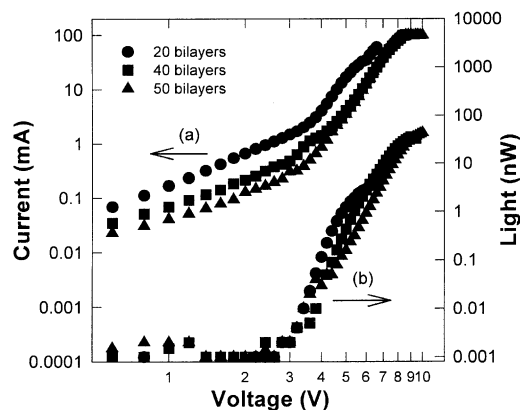


Fig. 3. (a) $\log I$ – $\log V$ and (b) $\log L$ – $\log V$ characteristics of ITO/(PPV/PSS)_n/Al devices. The number of (PPV/PSS) bilayers was increased from 20 to 50 bilayers without the addition of NaCl salt in PSS solution.

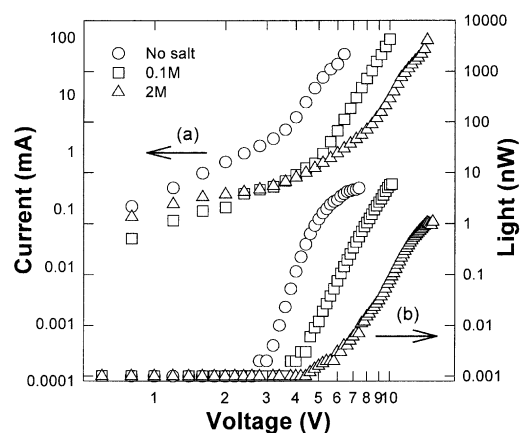


Fig. 4. (a) $\log I$ – $\log V$ and (b) $\log L$ – $\log V$ characteristics of ITO/(PPV/PSS)₂₀/Al devices. The ionic strength of PSS solution was varied by the addition of NaCl.

only upon the bandgap of polymer and should be independent of polymer thickness [15]. This means that the conjugation bond length of the self-assembled PPVs with different numbers of bilayers is identically maintained.

On the other hand, Fig. 4 shows the $\log I$ – $\log V$ and $\log L$ – $\log V$ curves of respective EL devices when the adsorbed amount of PSS layer is increased by the addition of NaCl salt in the PSS solution. In this case, the current flow and light emission for given devices of F_{0,0}, F_{0,1}, and F_{2,0} start to rapidly increase at 3, 3.5 and 4.8 V, respectively. The changes of turn-on voltages of the self-assembled EL devices prepared with different amounts of ionic salt concentration in the PSS solution have a few important implications. First, the binding between cyclic sulphide cations of PPV precursor and sulfonic anions of PSS is increased by the increase of salt (NaCl) concentration in the PSS dipping solution. The binding sites later give rise to the formation of sulfonic ester during thermal treatment [9] and contribute to

the decrease of the conjugation bond length as schematically shown in Fig. 1(c). Second, the growth of conjugation bond length of PPV is more strongly suppressed due to the esterification reaction between PSS and PPV precursor for a larger amount of salt added to the PSS solution, yielding a larger band gap and a higher turn-on voltage of the self-assembled PPV device.

Since it is shown that the conjugation bond length of a self-assembled PPV is easily varied by the change of the number of binding sites between PPV precursor and PSS layers due to the addition of ionic salt to the PSS solution, it is possible to properly control the energy gap and charge injecting characteristics of EL devices with this type of simple physical treatment.

4. Summary

We have demonstrated that the increased amount of adsorbed PSS interlayers strongly influences the electrical properties of self-assembled PPV devices. Thus, the simple variation of ionic strength in the PSS dipping solution can be utilized for systematically tuning the bandwidth of PPV without resorting to the chemical modification of PPV structure as is typically done. We understand that the relationship between the amount of adsorbed PSS layers and the bandwidth of PPV arises from the suppression of conjugation bond growth of PPV due to the increase of binding sites between PPV precursor and PSS and further conversion to the sulfonic ester during thermal conversion.

The dependence of turn-on voltage on the variation of salt concentration in the PSS dipping solution as evidenced from the $\log I$ – $\log V$ and $\log L$ – $\log V$ plots of multilayer self-assembled systems, shows strong potential for tuning both bandwidth and charge injecting characteristics of the PPV. We believe that our physical concept for controlling the electrical properties in EL devices can be utilized to establish a suitable method for fabricating stable and improved EL devices.

Acknowledgements

This work was supported by the Ministry of Education through the Brain Korea 21 Program and also by Inter-University Semiconductor Research Center (ISRC 96-E-4044) at Seoul National University. We are also very grateful to Samsung Corning Co. for its generous donation of ITOs.

References

- [1] T. Virgili, D.G. Lidzey, D.D.C. Bradley, *Adv. Mater.* 12 (2000) 58.
- [2] Y. He, J. Kanicki, *Appl. Phys. Lett.* 76 (2000) 661.
- [3] E.-C. Chang, S.-A. Chen, *J. Appl. Phys.* 85 (1999) 2057.
- [4] C. Giebeler, H. Antoniadis, D.D.C. Bradley, Y. Shirota, *J. Appl. Phys.* 85 (1999) 608.

- [5] H. Mattoussi, L.H. Radzilowski, B.O. Dabbousi, D.E. Fogg, R.R. Schrock, E.L. Thomas, M.F. Rubner, M.G. Bawendi, *J. Appl. Phys.* 86 (1999) 4390.
- [6] Y.-E. Kim, H. Park, J.-J. Kim, *Appl. Phys. Lett.* 69 (1996) 599.
- [7] G. Decher, J.-D. Hong, J. Schmitt, *Thin Solid Films* 210/211 (1992) 831.
- [8] V. Bliznyuk, B. Ruhstaller, P.J. Brock, U. Scherf, S.A. Carter, *Adv. Mater.* 11 (1999) 1257.
- [9] K.H.P. Ho, M. Granstroem, R.H. Friend, C.M. Greenham, *Adv. Mater.* 10 (1998) 769.
- [10] A.C. Fou, O. Onitsuka, M. Ferreira, M.F. Rubner, *J. Appl. Phys.* 79 (1996) 7501.
- [11] J.-D. Hong, D.S. Kim, K. Char, J.-I. Jin, *Synth. Met.* 84 (1997) 815.
- [12] J. Cho, K. Char, S.-Y. Kim, J.-D. Hong, S.K. Lee, D.Y. Kim, *Thin Solid Films* 379 (2000) 188.
- [13] D.R. Gagnon, J.D. Capistran, F.E. Karasz, R.W. Lenz, S. Antoun, *Polymer* 28 (1987) 570.
- [14] Y. Lvov, G. Decher, H. Mohwald, *Langmuir* 9 (1993) 481.
- [15] I.D. Parker, *J. Appl. Phys.* 75 (1994) 1656.