Available online at www.sciencedirect.com
SCIENCE DIRECT®

Polymer 45 (2004) 8567–8571

polymer

www.elsevier.com/locate/polymer

Enhanced electroluminescence from a conjugated polymer/ionomer blend

Tae-Ho Kim, Jong Hyeok Park, Tae-Woo Lee, O Ok Park*

Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, 373-1, Guseong-dong, Yuseong-gu, Daejeon 305-701, South Korea

Received 13 April 2004; received in revised form 20 September 2004; accepted 6 October 2004
Available online 27 October 2004

Abstract

Poly [2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) and poly (sodium 4-styrenesulfonate) ionomer (PSS-ionomer) blends were used as emitting layers in polymer light-emitting diodes (LEDs). The polymers were blended in various ratios, and their luminescent properties were compared with those of a MEH-PPV/polystyrene (PS) blend system. The MEH-PPV/PSS-ionomer and MEH-PPV/PS devices showed a much higher luminescent efficiency when compared with pure polymer devices, due to the dilution effect. The MEH-PPV/PSS-ionomer blend device achieved a more enhanced luminescent efficiency as compared with that of the MEH-PPV/PS device, due to polar groups in the PSS-ionomer, which may enhance the electron injection from the cathode to the emitting molecules. In addition, the turn-on voltage of the MEH-PPV/PSS-ionomer based on LEDs was also dramatically decreased.

Keywords: Luminescent efficiency; Poly(sodium 4-styrenesulfonate) ionomer; Dilution effect

1. Introduction

Since the electroluminescence (EL) of poly (*p*-phenylene vinylene) (PPV) polymers was discovered in 1990, polymer light emitting diodes (PLED) based on π-conjugated electroluminescent polymers have attracted much attention, because of their possible applicability in the flat panel displays [1–3]. Until now, the researches that used synthesized polymers, polymer blends, or polymer bilayer into emitting layer in PLED for improving the efficiency of EL devices have been actively studied [4–6]. For elevating the quantum yield, electron injection should be enhanced in the PLED because a hole is the major carrier in the emitting layer. In order to do that, several attempts have been reported [7–9].

In a recent study it was reported that ionomers, as an electron injecting layer, increase the affinity with electrons and, thus, effectively lower the turn-on voltage and the driving voltage, which makes EL devices more efficient [10–13]. Ionomers are thermoplastic resins that contain metal ions, as well as organic ionic molecules, as the pendant group in the polymer chain. These polymers usually have a small mole fraction of ionic groups of under roughly 15 mol%. The morphology of ionomers was studied and reported in the literatures [14,15].

In this study, we investigated the optical properties and the current–voltage–luminance (*I*–*V*–*L*) characteristics of devices that utilize the blends of the light-emitting conjugated polymer and the ionic polymer. The merits of this blended electroluminescent device include effective electron injection and expectations of the dilution effect. A previous study investigated the dilution effect of the inert polymer polystyrene (PS) blend with MEH-PPV [16]. The interchain interaction between the polymer chains was decreased to improve the luminance intensity and the luminescent stability of the MEH-PPV/polystyrene (PS) blend at the high temperature [16].

Similar to the blend system, it is quite natural to expect the dilution effect in the case of a blend of MEH-PPV and poly (sodium 4-styrenesulfonate) ionomer (PSS-ionomer). The thermal stability and mechanical property of the PSS-ionomer are excellent, and its thermoplastic processability is also good. Moreover, a MEH-PPV and PSS-ionomer blended system may enhance the electron injection.

Counter ions of the ionomer can attract the electrons

---

* Corresponding author. Tel.: +82 42 869 3923; fax: +82 42 869 3910.
E-mail address: ookpark@kaist.ac.kr (O O. Park).

0032-3861/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2004.10.008

from the cathode to the emitting layer effectively, so that EL efficiency is improved considerably and the turn-on voltage and the operating voltage of the EL devices are decreased remarkably. In order to distinguish from the effect of dilution, we compared a MEH-PPV and PSS-ionomer blend system with a MEH-PPV and PS blend system.

2. Experimental

2.1. Materials

Polystyrene with a weight-averaged molecular weight of 230,000 and number-averaged molecular weight of 140,000 was purchased from Aldrich Co. The sulfonation of polystyrene and the synthesis of the PSS-ionomer was performed using a method described elsewhere [13]. The sulfonate content in the sulfonated polystyrene can be ranged from about 3.5 to 15.4 mol%. For optimum properties, we selected an ionic concentration of 6.7 mol%, which exhibited the highest EL intensity and quantum efficiency as reported in previous work [13]. The chemical structures of MEH-PPV and the prepared ionomers are shown in Fig. 1(a) and (b). The morphology of the PSS-ionomer is shown in Fig. 1(c). Many circular ionic groups are distributed in the morphology, and the diameter of the ionic clusters is about 5–6 Å. MEH-PPV ($M_w \sim 12{,}500$) was purchased from Aldrich Co.

MEH-PPV and the PSS ionomer were dissolved in chlorobenzene, separately. Then, the two solutions were mixed, at various ratios. The ratio of the blended polymer is 30/70, 40/60, 50/50, 60/40, 70/30. This mixture, dissolved in chlorobenzene, was spin coated to a 100 nm thickness on indium-tin-oxide coated glass substrates.

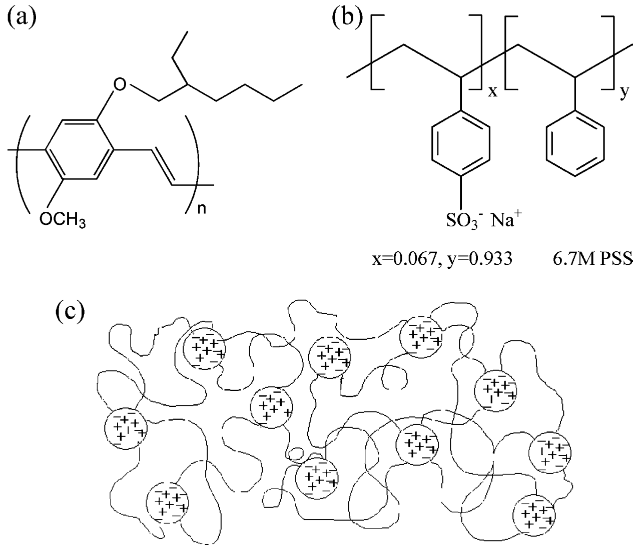

Fig. 1. Chemical structures of (a) MEH-PPV, (b) a PSS-ionomer, and (c) the morphology of the PSS-ionomer.

2.2. Fabrication of the EL device

The EL devices of the MEH-PPV and PSS-ionomer blend were fabricated as follows. Indium-tin-oxide (ITO) coated glass substrates were sonicated sequentially in acetone for 10 min, in methanol for 10 min, and in chloroform for 10 min, and then dried with a nitrogen gun. The MEH-PPV and PSS-ionomer blend dissolved in chlorobenzene was spin-coated at thickness of 100 nm onto the ITO-coated glass substrate. The thickness was measured with an alpha-step. LiF (Lithium Fluoride) was deposited to a 1 nm thickness, and then an Al cathode was deposited to a 150 nm thickness by means of a thermal evaporator, under a pressure of 1×10^{-6} Torr.

2.3. Measurement

In order to investigate the electrical characteristics of the device, the current–voltage (*I–V*), the luminance–voltage (*L–V*), and the luminance–current (*L–I*) were measured with a current and voltage source measurement unit (Keithley 238) and a luminance meter (LS100). In addition, the photoluminescent and electroluminescent spectra of the device were measured by means of fluorospectroscopy (ISS Photon Counter Meter).

3. Results and discussion

At the outset, we needed to identify those optical properties that were based on the dilution effect, before investigating the opto-electrical properties of the devices blended with the PSS-ionomer. We investigated the photoluminescent properties of the MEH-PPV/PSS-ionomer blend films to identify the effect caused by dilution, except for the effect that was dependent on the electron injection of an ionomer, and we compared these films with the MEH-PPV/PS polymer blend film to identify the electrical and optical properties of these devices.

Fig. 2(a) shows the PL spectra of the MEH-PPV/PS polymer blend films, which have the same film thickness as the various blended ratios. The blended films had higher PL efficiency than the pure MEH-PPV film, and the PL efficiency of the MEH-PPV(50%)/PS(50%) film was double that of the pure MEH-PPV film. Polystyrene, as an inert polymer, decreases the interchain interaction of the conjugated polymer and diminishes the exciton quenching, due to the packing of the conjugated polymer chains, thereby increasing the luminescent efficiency.

When blending with MEH-PPV with the PSS-ionomer, the PL spectra showed similar aspects as those of the MEH-PPV/PS blended films (Fig. 2(b)). The PL intensity of the blended films was greatly increased by the dilution effect, which decreases the interchain interaction of MEH-PPV. The efficiency of the MEH70/PSS-ionomer30 film was lower than that of the 50/50 film, because the film was not

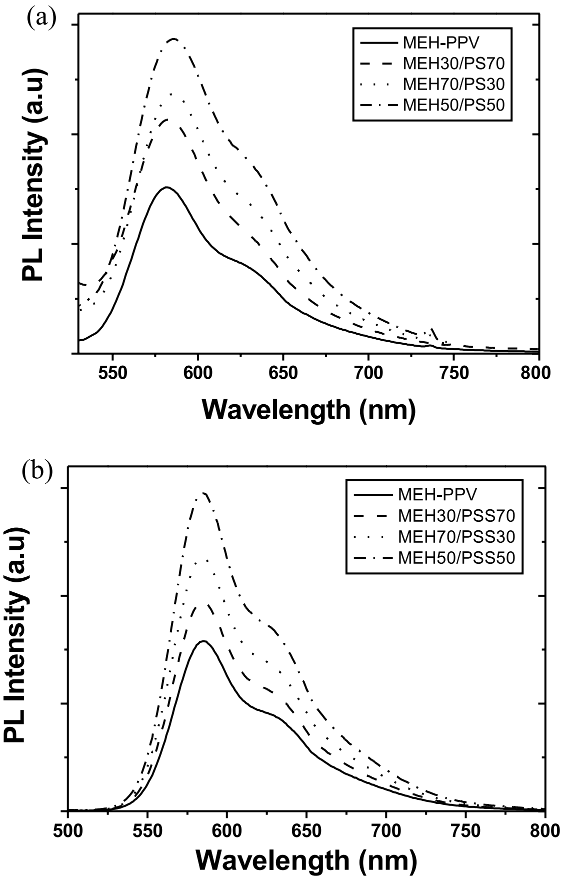

Fig. 2. Photoluminescent spectra of (a) MEH-PPV and its blends with PS and (b) MEH-PPV and its blends with PSS-ionomer.

diluted sufficiently. The efficiency of the MEH30/PSS-ionomer70 film was also low due to the small concentration of MEH-PPV. Both the MEH-PPV/PS and the MEH-PPV/PSS-ionomer film had a maximum PL intensity in the blending ratio of 50:50. Therefore, the most suitable blending ratio for a good dilution effect is 50/50.

Fig. 3 shows the luminance versus the voltage curve of the blended EL devices, at various blended ratios. The luminance of the film blended in the ratio of MEH50/PSS-ionomer50 is the brightest among those of the various blended ratios. While the EL intensity of the MEH50/PS50 film roughly doubled that of the pure MEH-PPV film, due to dilution effect similarly with its PL spectrum, the EL intensity of the MEH50/PSS-ionomer50 device was more than 4 times brighter, when compared with the pure MEH-PPV device. Moreover, the turn-on voltage and the working voltage were decreased significantly. The driving voltage corresponding to the maximum EL intensity of the devices were decreased from 10.8 to 6–6.5 V, and the threshold voltage was also decreased from 4 to 2.1 V, in the case of the 50/50 blended device. It is because band bending occurs, which lowers the energy band of MEH-PPV, so that ionic groups of ionomer can induce electron injection into an emitting layer from the cathode.

In Fig. 4 the current density is plotted against the voltage. We can identify the electron injection and the mobility of carrier in Fig. 4. Under the electric field, local dipoles form in the emitting layer composed of the PSS-ionomer and MEH-PPV near the cathode. The local dipoles are arranged continuously from local dipoles formed near the cathode to the anode. These local dipoles strongly attract electrons and the injected electrons move into the anode quickly in the blended polymer layer. Consequently, recombination probability with holes is improved and luminescent efficiency is also improved, by decreasing the quenching near the cathode. Therefore, while the currents flows plentifully, the luminance of the devices become brightened gradually, as the current density increases.

After exceeding the ratio of PSS-ionomer 50%, the brightness became reduced, due to the decrease of concentration of MEH-PPV, even though electrons were injected. In the case of the MEH50/PS50 device, polystyrene is an electrically insulating material, so it blocks the injection of electrons under low voltage, and the current density increases beyond a certain critical voltage.

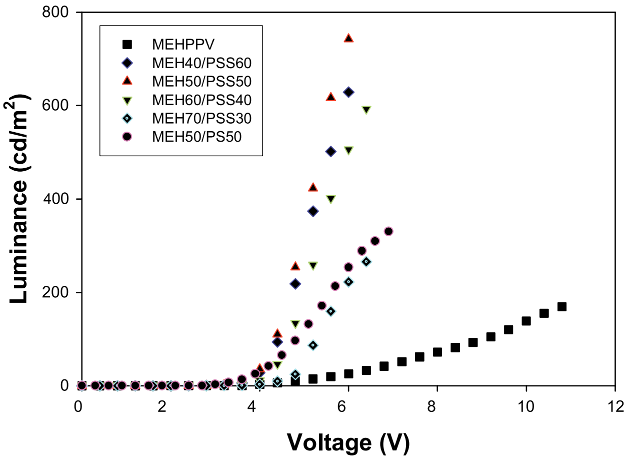

Fig. 3. Luminance vs. voltage of EL devices of MEH/PSS-ionomer blend at various blending ratios, MEH50/PS50 blend, and pure MEH-PPV.

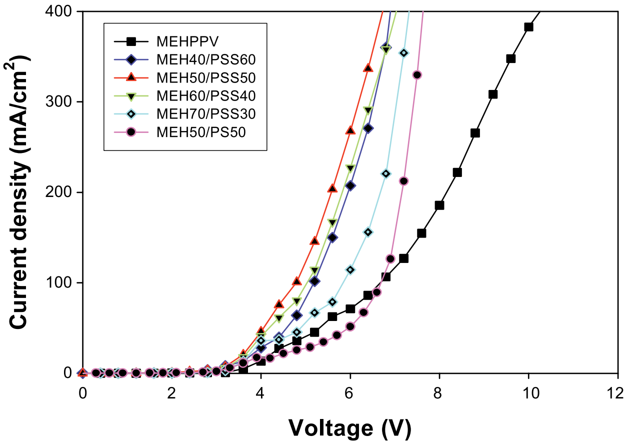

Fig. 4. Current density vs. voltage of the EL devices of MEH/PSS-ionomer blend at various blending ratios, MEH50/PS50 blend, and pure MEH-PPV.

In Fig. 5(a) and (b), both the luminance and the EL quantum efficiency are plotted against the current density for the blended polymer LED. The MEH50/PSS-ionomer50 device is the brightest and the most efficient. The device has the highest luminance when compared with the others, at a current level that can drive the devices. Moreover, its maximum EL quantum efficiency is 0.13%, which is 10 times higher than that of the pure MEH-PPV device.

The PSS-ionomer and PS are thermally and mechanically stable polymers. Therefore, when we blend these polymers with conjugated polymers and fabricate EL devices, we can expect improved thermal stability of the devices. The investigations of the normalized PL spectra after annealing MEH-PPV, MEH50/PSS-ionomer50, and MEH50/PS50 devices at 100 °C during 3 h in a vacuum oven are presented in Fig. 6. The MEH-PPV and PSS-ionomer blend film maintains nearly its original form at high temperatures, without transformation, as contrasted with pure MEH-PPV film. Because the glass transition temperature (T_g) of the PSS-ionomer (roughly 104 °C) is much higher than that of MEH-PPV (roughly 70 °C), the PSS-ionomer chains prevent the packing and the aggregation of the MEH-PPV chains at high temperatures. Therefore, a stable PL spectrum is maintained. It indicates that the devices can be stable against heat generated in a long-time drive when we apply the devices composed of conjugated polymers blended with the PSS-ionomer to EL display.

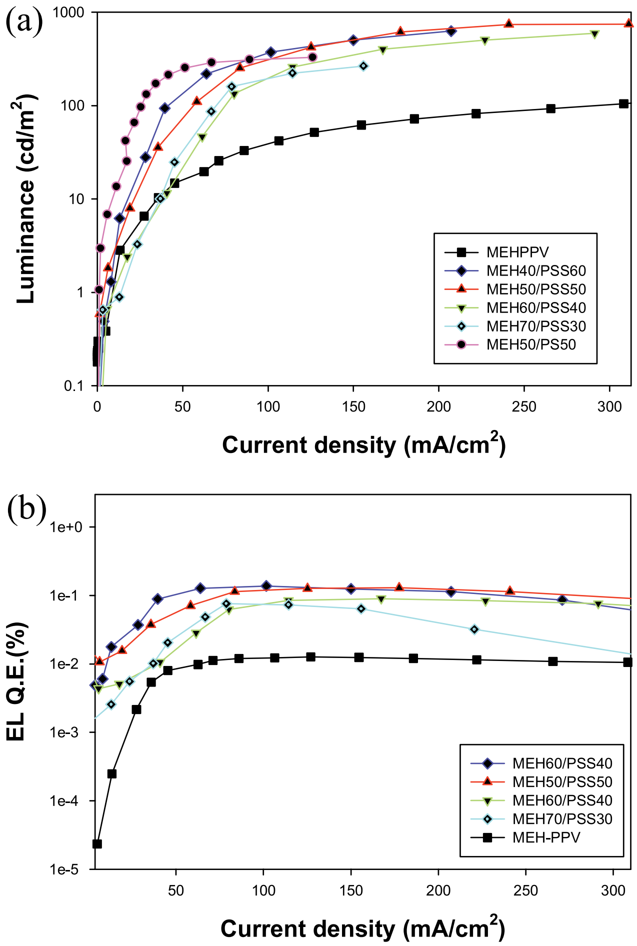

Fig. 5. (a) Luminance vs. current density and (b) EL quantum efficiency vs. current density of EL devices of MEH/PSS-ionomer blend at various blending ratios and pure MEH-PPV.

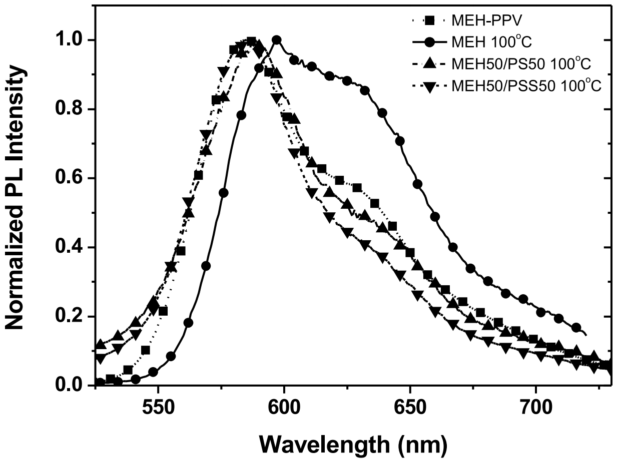

Fig. 6. PL spectra of pure MEH-PPV film (■), MEH-PPV film annealed at 100 °C (●), MEH50/PS50 blended film annealed at 100 °C (▲), and MEH50/PSS-ionomer50 blended film at 100 °C (▼) during 3 h in vacuum.

4. Conclusions

We studied the effects of ionomer in devices with a conjugated polymer, MEH-PPV, blended with PSS-ionomer. The PSS-ionomer decreased the interchain interaction of MEH-PPV by means of the dilution effect and increased the PL intensity of the blended devices. Moreover, ionic clusters in the ionomer formed local dipoles near the cathode, which attracted electrons from the cathode. Because of the enhanced electron injection, the turn-on voltage and the operating voltage are decreased significantly and the EL intensity of the 50/50 blended device is increased more than 4 times, when compared with the pure MEH-PPV film. We believe that this effect is due to the synergy effect caused by the enhancement of electron injection and to the dilution effect. Moreover, the thermal stability of these devices can be improved with the presence of PSS-ionomer.

Acknowledgements

This work was supported by the Brain Korea 21 Project, and the Center for Advanced Functional Polymers through KOSEF.

References

[1] Burroughes JH, Bradley DDC, Brown AR, Marks RN, Mackay K, Friend RH, Burns PL, Holmes AB. Nature 1990;347:539.

[2] Braun D, Heeger AJ. Appl Phys Lett 1991;58:1982.

[3] Yang W, Huang J, Liu CZ, Niu YH, Hou Q, Yang RQ, Cao Y. Polymer 2004;45:865.

[4] Vestweber H, Bassler H, Gruner J, Friend RH. Chem Phys Lett 1996;256:37.

[5] Park JH, Lee KJ, Park OO, Yu JW, Kim YC, Kim JK. Chem Phys Lett 2004;386:101.

[6] Kim SW, Shim SC, Jung BJ, Shim HK. Polymer. 2002;43:4297.

[7] Parker ID. J Appl Phys 1994;75:1659.

[8] Jenekhe SA, Zhang X, Chen XL, Choong VE, Gao Y, Hsieh BR. Chem Mater 1997;9:409.

[9] Fukuda T, Kanbara T, Yamamoto T, Ishikawa K, Takezoe H, Fukuda A. Appl Phys Lett 1996;68:2346.

[10] Lee HM, Choi KH, Hwang DH, Do LM, Zyung T, Lee JW, Park JK. Appl Phys Lett 1998;72:2382.

[11] Yoon J, Kim JJ, Lee TW, Park OO. Appl Phys Lett 2000;76:2152.

[12] Lee TW, Park OO. Appl Phys Lett 2000;76:3161.

[13] Lee TW, Park OO, Do LM, Zyung T, Ahn T, Shim HK. J Appl Phys 2001;90:2128.

[14] Eisenberg A. Macromolecules 1970;3:147.

[15] Marx CL, Caufield DF, Cooper SL. Macromolecules 1973;6:344.

[16] He G, Li Y, Liu J, Yang Y. Appl Phys Lett 2002;80:4247.