Efficient Light Emitting Diodes from Ternary Blends of PPV-Based Copolymers

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ABSTRACT: Light emitting diodes (LEDs) were prepared using ternary blends of block copolymers emitting in the blue (**I** and **II**) and green (**III**) regime. These blends were studied in terms of their absorbance, photoluminescence (PL), and electroluminescence (EL) spectra. The PL spectra in dilute solution and in the solid state were compared. Förster energy transfer from **I** and **II** to **III** was studied in the solid state. The EL device made using a ternary blend with the ratio (1 : 1 : 1) showed the highest EL quantum efficiency. Differential scanning calorimetry (DSC) measurements have been made to investigate the phase separation in these copolymer blends. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 2509–2511, 2006

Key words: light emitting diode; photoluminescence; electroluminescence; polymer blends

INTRODUCTION

Polymer blends have been used as chromophores and it has been demonstrated that emission colors can be varied as a function of voltage[1] while combinations of polymers with blue, red, and green emissions can be used in a blend to obtain a white light-emitting diode.[2] Polymer blends also provide a platform with which to combine two polymers with different properties, such as hole transport or emission efficiencies with each other as opposed to preparing a multilayer device.[3] Polymer blending can be used as a tool to increase the efficiency of devices[4,5] by improving charge injection[6] and localization. Energy transfer between the components in polymer blends leads to an enhancement in the PL efficiency of films and EL efficiency in resulting devices.[7,8] DSC measurements have also been studied on a series of electro-optically active alternating block copolymers and their blends.[9]

We report the utilization of a ternary polymer blend system consisting of three conjugated polymers, which are blue emitting (**I, II**) and green emitting (**III**). Förster energy transfer in the photoluminescence and electroluminescence of the blends was studied. The devices based on the 1 : 1 : 1 weight ratio blend showed optimally enhanced external quantum efficiency and higher brightness compared to pure copolymers and other blends studied. Glass transition temperatures of these copolymers and copolymer blends were also measured to assess the nature of phase separation in these copolymers.

EXPERIMENTAL

Chloroform (Aldrich) and poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT : PSS) (Bayer) were used as purchased. The PPV-based copolymers as shown in Figure 1 were synthesized as described previously.[10–12] Solutions of polymer blends were prepared (10 mg/mL in chloroform) in selected proportions of copolymers (**I : II : III**) (1 : 1 : 1), (1 : 1 : 2), (1 : 2 : 2), (2 : 1 : 2), (2 : 2 : 1) filtered through 0.2 μm millex FGS Filters (Milipore). Thin films for optical absorption and photoluminescence measurements were spin-cast onto glass slides. All the films were dried in vacuum at room temperature for 1 h to remove residual solvent. Optical absorption spectra were taken on a Hitachi U-3010 UV–visible spectrophotometer. PL spectra were recorded on a PerkinElmer LS 50B luminescence spectrometer using a xenon discharge lamp for excitation.
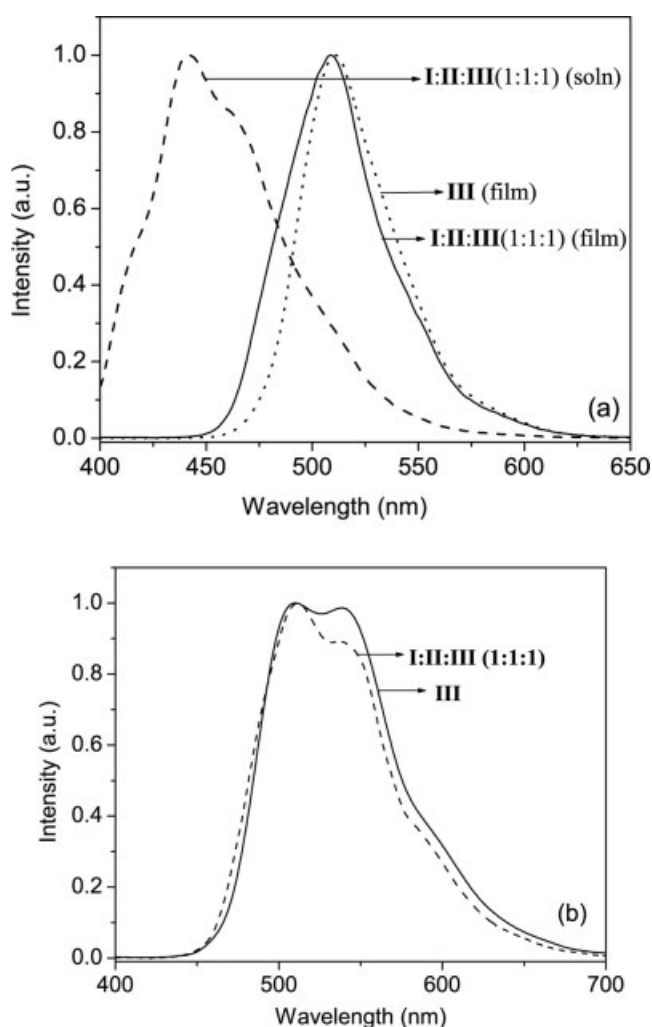
Double-layer PLEDs with the configuration ITO/PEDOT : PSS/polymer/Ca/Al were fabricated on ITO-coated glass slides cleaned in ultrasonic baths of water and acetone. A hole injection layer of PEDOT:PSS was spin-coated on top of the ITO and dried at 100°C for 1 h under vacuum. A 100 nm layer of the copolymers and of their blends were spin-coated from the respective chloroform solutions onto the PEDOT : PSS layer under nitrogen. A 400 nm thick calcium electron-injecting cathode was deposited on the polymer film through a 6 mm^2 mask by vacuum evaporation at a pressure less than 2×10^{-6} Torr, followed by a protective coating of aluminum. The devices were characterized using a sys-
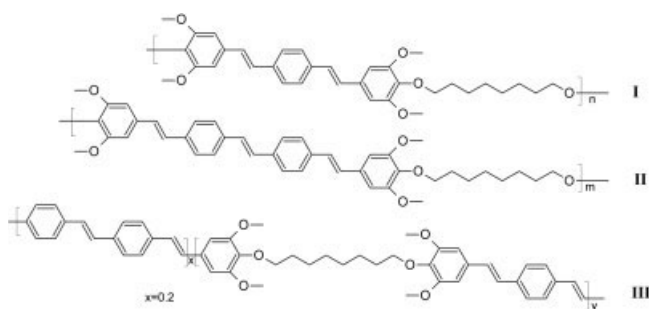
Figure 1 Chemical structures of polymers **I–III**.

tem described previously.[13] The thermal properties of all the copolymers and their blends were measured by differential scanning calorimetry (DSC PerkinElmer Model 7 using Pyris Software). Temperature calibration was performed using indium ($T_m = 156.6°C$). The samples, 15–20 mg, were heated from −50 to 200°C with the heating rate 20°C min^{-1}. The glass transition temperature was taken as injection point from the second scan.

TABLE I
LED Characteristics

Composition (I : II : III)	λ^{EL}_{max}	Turn on voltage (V)	Maximum luminance efficiency (cd/A)
2 : 2 : 1	510	3	2.09
2 : 1 : 2	510	4	1.81
1 : 1 : 1	512	3	4.83
1 : 1 : 2	512	3.5	2.84
1 : 2 : 2	512	4	1.78

RESULTS AND DISCUSSION

Excitation energy transfer in blended systems needs intimate mixing and good spectral overlap between the emission of the host material and the absorption of the guest material. The PL spectra of **I** and **II** overlap with a major portion of the absorption spectrum of **III**.
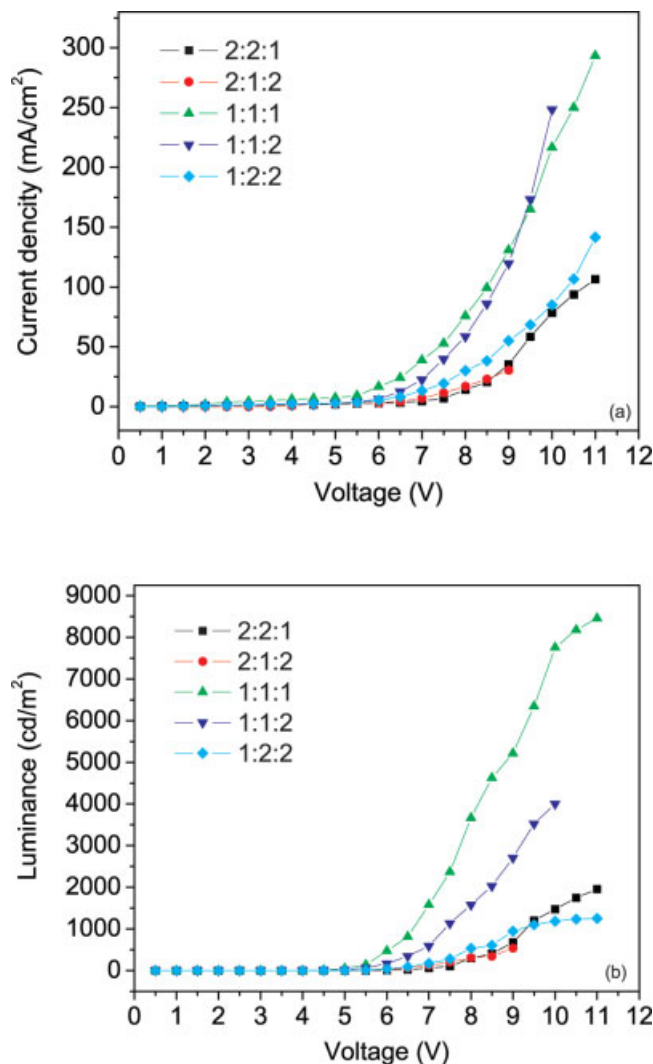

Figure 2 (a) PL spectra of ternary blend in chloroform and in the solid-state and polymer **III**. (b) EL spectra of polymer **III** and ternary blend.

Figure 3 (a) Current density-voltage; (b) luminance-voltage characteristics for the **I : II : III** blend LEDs. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
DSC Results of Electroluminescent Block Copolymers and Their Blends

Composition (I : II : III)	M_w (10^{-3})	T_g (°C)
I	27.3	80.9
II	8.63	78.7
III	18.3	76.8
2 : 2 : 1		80.1
2 : 1 : 2		79.7
1 : 1 : 1		79.1
1 : 1 : 2		79.4
1 : 2 : 2		78.9

Thus, Förster intermolecular energy transfer from **I** and **II** to **III** is expected to be efficient in these blends provided that the respective phase domains are small.

Solution photoluminescence spectra were recorded with excitation wavelengths corresponding to the solution absorption peak wavelengths of the samples. The solid-state PL spectra were obtained by exciting the samples with 370 nm light. Pure polymers **I–III** in chloroform showed fluorescence maxima at 440, 442, and 460 nm, respectively. In the PL spectra of the blends in solution, the contribution from each polymer can be observed [Fig. 2(a)]. The comparison of the film fluorescence spectra with the corresponding solution spectra shows major differences. The shape changes for PL spectra and the red shifts are due to intermolecular interactions in the films. In the solid state, all the blends display only green emission of 509–514 nm with the characteristics of polymer **III**, showing Förster energy transfer from the blue polymer **I** and **II** to the green polymer **III**.

The EL spectra for the double-layer LEDs are shown in Figure 2(b). The operating conditions, characteristics, and performance of LEDs are listed in Table I. The EL spectra of **III** and the blend in Figure 2(b) and the corresponding solid-state PL spectra in Figure 2(a) are similar, suggesting that both PL and EL originate from the same radiative decay process of the singlet exciton. The EL spectrum corresponds to that of pure **III** with a peak at 505–515 nm and a shoulder at 535–545 nm associated with the 0–1 and 0–0 transitions, respectively. The presence of **I** and **II** improves devices performance with optimal LED performance from the blend with a 1 : 1 : 1 (**I** : **II** : **III**) weight ratio, which exhibited a very high luminance efficiency (4.83 cd/A) at 8 V and a high brightness (8500 cd/m^2). In comparison, an ITO/PEDOT/**III**/Ca/Al device showed a brightness of about 2700 cd/m^2.[5] Figure 3 shows the current density-voltage-luminance characteristics of the optimal ITO/PEDOT : PSS/blend/Ca/Al devices. The current density and luminance increase exponentially with increasing forward bias voltage above the turn-on voltage, and all devices exhibit robust diode characteristics. The turn-on voltage for the devices using blends studied varies between 3 and 4 V. The existence of one glass transition temperature for all blends shows the miscible nature of this system (Table II).

CONCLUSIONS

PL studies showed that efficient Förster energy transfer from the higher energy band gap polymers (**I** and **II**) to the lower energy band gap polymer (**III**) can achieved in the solid state due to intermolecular interactions, whereas in dilute solution, energy transfer was not observed. Only a green emission was obtained in the solid-state PL and EL of the blends, suggesting a complete Förster energy transfer process in the blends. The LEDs of copolymer blends (1 : 1 : 1) exhibit significantly better performance than the device using **III** because of energy transfer.

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