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LEDs based on conjugated PPV block copolymers

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Abstract

A way to control the bandgap in semi-conducting polymers is by preparing polymers with a partially conjugated backbone. In our laboratory, three conjugated copolymers containing PPV trimers as light emitting chromophores have been synthesized, which emit in the blue, green and orange wavelength region. The copolymers have a well defined conjugated backbone consisting of regularly alternating terphenylene and *p*-phenylene-vinylene blocks. The desired control of conjugation length is achieved through steric interaction induced by the side-chains in the terphenyl blocks of the copolymer. In this paper we evaluate the electrical and optical properties of LED devices based on these conjugated PPV block copolymers.

Keywords: Poly(*p*-phenylene vinylene) block copolymer, Diodes, Electroluminescence

1. Introduction

The introduction of Light Emitting Diodes (LEDs) based on poly[*p*-phenylene vinylene] (PPV) in 1990 [1,2] triggered intensive research in the field of semiconducting conjugated polymers. This led to the elaboration of various other polymer light emitting diodes with high efficiencies [3] and color tuning [4,5]. In organic systems, light emission is established by radiative decay of mobile π - π^* singlet excitons [6]. The bandgap is roughly determined by the extent of delocalization of the π -electrons, the so called effective conjugation length. In fully conjugated polymers like PPV and poly[*p*-phenylene] (PP), the actual conjugation length is an average value determined principally by random conformational or chemical defects in the polymer backbone and is difficult to control. A way to control the conjugation length or bandgap is by preparing partially conjugated polymers [7-11].

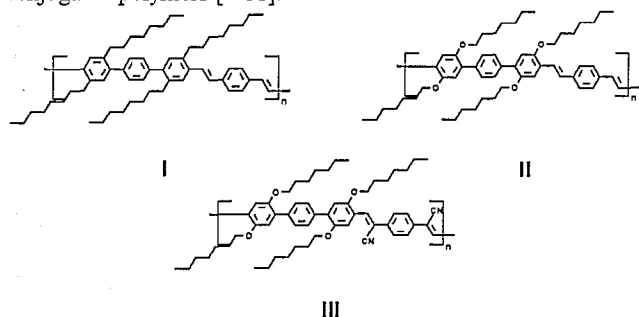


Fig. 1. Chemical structure of the copolymers

In our laboratory, three novel copolymers containing PPV trimers as active chromophores were synthesized (figure 1), which emit in the blue, green and orange wavelength region. The copolymers have a well defined conjugated backbone

consisting of regularly alternating terphenylene and *p*-phenylene-vinylene blocks. The desired control of conjugation length was achieved through steric interactions induced by the side-chains within the terphenyl part of the copolymer. The alkyl or alkoxy side chains in these polymers serve a dual role: (1) interrupting the conjugation and (2) providing solubility. The middle rings in the terphenyl units are twisted out of plane and the π -orbital overlap is effectively interrupted. The absorption and photoluminescence (PL) spectra of the copolymers are nearly identical with those of the PPV trimer model compounds, which confirms the effective blocking of the conjugation [9,10]. The luminescence properties of these copolymers are excellent, PL quantum yields as high as $\Phi_F \sim 0,9$ were obtained in solution for copolymer I [9].

In this paper we evaluate the electrical and optical properties of LED devices based on these conjugated PPV block copolymers.

2. Experimental

The synthesis and characterization of the conjugated block copolymers have been described [9,10]. Light-emitting diodes were fabricated by spincoating the polymers from filtered (0.2 μ m-filters) chloroform solutions (3% w/w) onto ITO-covered glass slides. By varying the rotation speed in the range of 700 - 2500 rpm film thicknesses of 50 - 175 nm were obtained. Al or Au top electrodes (area 6 mm²) were deposited by vacuum evaporation. Dektak 3030ST surface profiler was used to determine the layer thickness, and IV-measurements were taken with a Keithley 236 SMU. EL spectra of the devices were recorded on a SLM-Aminco SPF500C spectrofluorometer. The quantum efficiencies (%ph/el) of the devices were determined by measuring the light output vs. current with a calibrated photodiode mounted on an integrated sphere. A Stanford SR400 photon counter was used to measure the photodiode output.

3. Results and discussion

Polymer I in which the chromophore is an alkyl substituted distyrylbenzene unit emits in the blue (440 nm, see figure 2). The change of the type of side chains from alkyl to alkoxy (II) shifts the emission wavelength to the green (490 nm), due to the increased electron density of the π -system induced by the electron donating alkoxy group. Introduction of electron accepting cyano substituents on the vinylene-bond in combination with alkoxy side groups (polymer III) results in a red shift to the orange part of the spectrum (570 nm).

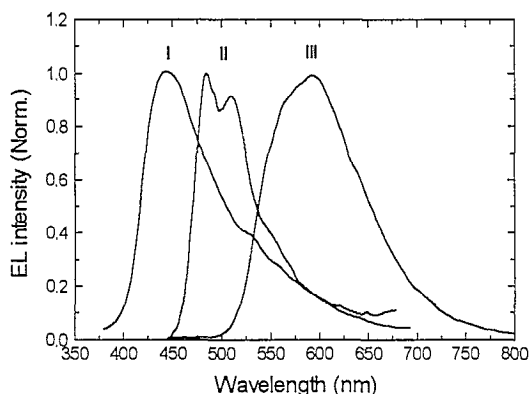


Fig. 2. Electroluminescence spectra of the copolymers.

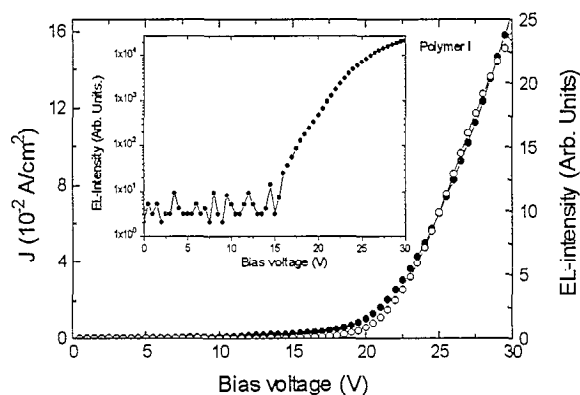


Fig. 3. $J(V)$ and $EL(V)$ characteristics of a single layer ITO/polymer I/Al device (solid circles: current density, open circles: EL-intensity). Inset: semilog plot of $EL(V)$.

In figure 3 the IV and LV characteristics are shown for a single layer ITO/polymer I/Al device with a layer thickness of 100 nm. Forward bias is defined as the positive voltage on ITO. The LEDs turned on at approximately 17 Volts (turn-on voltage is defined here as the voltage at which the luminescence starts exceeding the back-ground detection).

The IV-characteristics of the devices scale with the layer thickness of the emitting polymer indicating that the electric field is uniformly distributed across the device. The observed rectification in our devices indicates that charge injection from the electrodes is one of the limiting factors for device performance [12]. A change of the electron injecting metal from

Al ($\phi = 4.3$ eV) to Au ($\phi = 5.2$ eV) resulted in no light emission in forward bias, which supports the conclusion that electron injection determines the emission properties of the devices.

The turn-on voltages of polymers I, II and III are equal to 17, 13 and 10 Volts, respectively (table 1). This lowering is mainly caused by the reduced band gap which results in a lower barrier for electron injection. The field dependence of the I-V characteristics were analyzed using Fowler-Nordheim (FN) tunnelling theory [12]. The hole injection barrier height for copolymer I is determined to be approximately 0.1 - 0.2 eV higher than for the copolymers II and III.

Table 1

Electrical properties and efficiencies

Polymer	V_{to} (Volts) ^{a)}	Φ_{holes} (eV) ^{b)}	Ext. eff ($10^{-2}\%$)
I	17	0.40 ± 0.05	2,0
II	13	0.22 ± 0.05	0,9
III	10	0.26 ± 0.05	2,3

^{a)} forward bias ^{b)} Fowler-Nordheim analysis

The external EL quantum efficiencies of all polymers are in the range of 10^{-2} % ph/el, which are reasonable high values for non-optimized single layer devices with Aluminium top-electrode.

4. Conclusion

LED devices based on a series of conjugated PPV block copolymers were studied. The performance of the polymers were examined in non optimized single layer devices with Al as electron injecting contact. Electroluminescence in the spectral range from blue to orange was achieved with reasonably high efficiencies. Device optimization is currently in progress.

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