

# Polymer Light Emitting Diodes\*

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Polyphenylene vinylene-based conjugated-nonconjugated alternating block copolymers form the active chromophores in a series of light emitting diodes (LEDs). The quantum efficiency and brightness of these devices can be improved by several orders of magnitude by incorporation of appropriate carrier transport layers and by rational choice of electrodes. Further improvements can be gained by blending of the active chromophores with high or low molecular weight species.

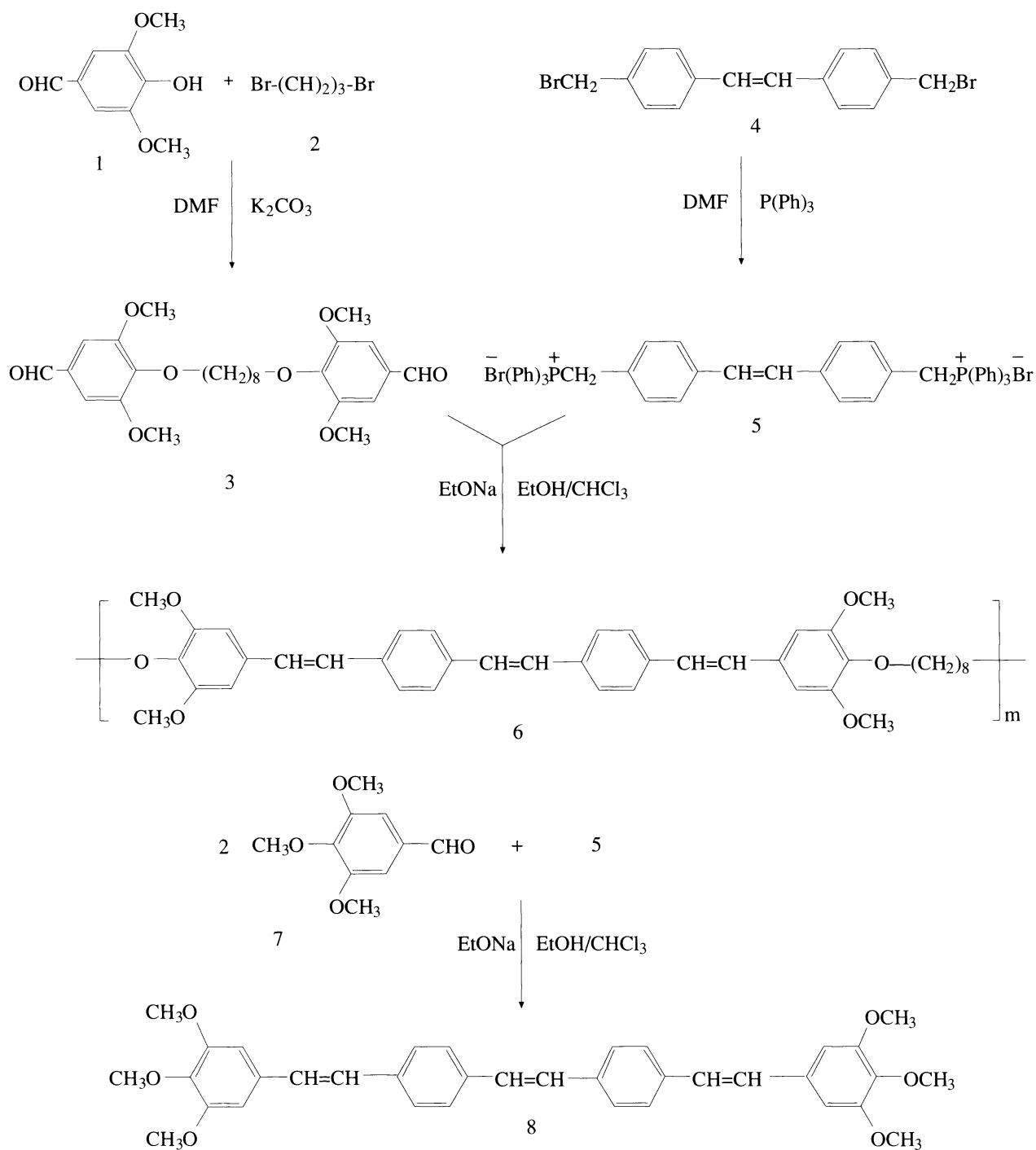
Polymer light-emitting diode (LED) devices have been reported using a variety of conjugated polymers, following Burroughes et al. who first demonstrated the light-emitting capability of poly(p-phenylene vinylene) (PPV)<sup>1</sup>. LED devices have also been made using organic low molar mass molecules dispersed or dissolved in an inert polymeric matrix<sup>2</sup>. We have reported on a series of conjugated-nonconjugated copolymers (CNCPs) containing multiple uniformly alternating conjugated rigid and nonconjugated flexible blocks which exhibit blue electroluminescence with a spectral maximum at 465 nm<sup>3</sup>. It may be noted that CNCPs have unique advantages in that the conjugated rigid blocks may be of specified and uniform conjugation length, factors which are crucial for tailoring the electronic transition band gap which in turn determines the spectral properties of the light-emitting chromophore. The flexible blocks, on the other hand, contribute to the solubility and the film forming properties of the system. The advantage of the block copolymer structure over blends of small molecules in an inert polymeric matrix is that it is necessarily homogeneous (on a nanometer scale) and obviates the problem of recrystallization or elution of the small molecules in the matrix.

We have shown that a modification of the molecular structure in the conjugated blocks of the copolymers provides convenient color tuning in the polymer LED without change of the other properties. In an earlier report we demonstrated for example that changing the aromatic ring structure in the conjugated blocks of a given CNCP causes band-gap shifts in which light emission changed from blue to yellow to red<sup>4</sup>. Thus simply extending the conjugation length in the conjugated block of the previously described copolymer by one phenylene vinylene unit yields a copolymer with a red-shifted UV absorption, photoluminescent (PL) and electroluminescent spectra. This copolymer emits green light with maximum intensity at 513 nm. It was synthesized using a Wittig reaction and characterized with elemental analysis. FTIR, NMR, GPC, UV, photoluminescent spectroscopy and DSC. The synthetic strategy shown in Fig. 1 outlines the chemical reaction scheme and the structure of the resultant copolymer and of a model low molar mass analog.

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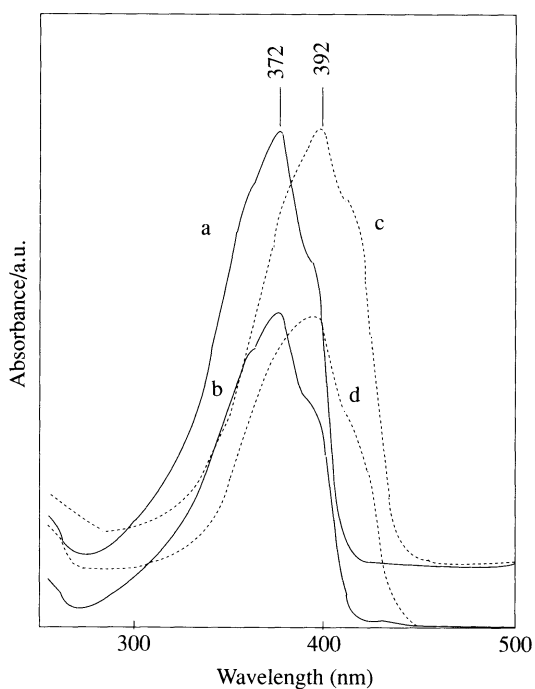
The high solubility and excellent film forming properties of the copolymer enabled us to readily fabricate LED devices. The emission brightness of the resulting device permitted direct observation in a brightly lit room. The polymer forms highly transparent greenish-yellow, free-standing films of which can be cast from a chloroform solution while spin-coating of the same solution produces substantially pinhole-free thin films on substrates. DSC measurement show a glass transition at 343 K, and it was also noted that the polymer exhibited some flow at temperatures in excess of 420 K. No other transitions attributable to crystalline or liquid crystalline behavior were observed in the temperature range of 300 to 530 K, and it is concluded that the copolymer is essentially amorphous.



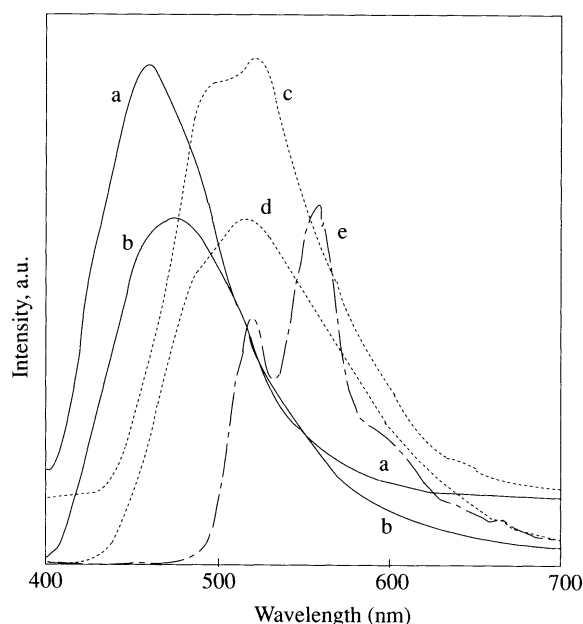
**Figure 1.** Synthesis of “green” copolymer and model compound.

Figure 2 shows the UV-vis spectra of this copolymer and of the analogous model compound and (for further comparison) of the previously synthesized "blue" copolymer and its related model compound. It is obvious that both copolymers have absorption spectra very similar to those of their respective model compounds as a result of the similarity in chromophores. The absorption peaks of two copolymers are themselves qualitatively similar though clearly the new material has a maximum absorption at a relatively longer wavelength because of the extended conjugation length of its conjugated blocks.

The red-shifted absorption of the copolymer correlates with the red-shifted photoluminescent (PL) and electroluminescent (EL) spectra. Figure 3 displays the PL and EL spectra of the two copolymers and for comparison, the EL of PPV. The PL spectra were obtained at excitation wavelength 360 nm and did not depend on the excitation wavelength. Both exhibit relatively blue shifted PL and EL spectra when compared to those of PPV. In this case it is obvious that the different conjugation lengths play a major role; the longer the conjugated lengths, the longer is the wavelength of the emitted light. Thus tuning the observable color by chemical modification is, therefore, not only feasible in this system but also rather facile in terms of chemical synthesis. In the case of the phenylene vinylene structure the long wavelength limit which can be reached by simple extension in the absence of additional substituents on the conjugated backbone may be in the yellow portion of the spectrum. The reason is that the nominally fully conjugated PPV chain may be distorted from the perfectly coplanar, and certainly possesses structural defects originating from a variety of causes.



**Figure 2.** Absorption spectra of "green copolymer (c) and model compound (d), and of "blue" copolymer (b) and model compound (a). The "blue" species contain one fewer phenylene vinylene units.

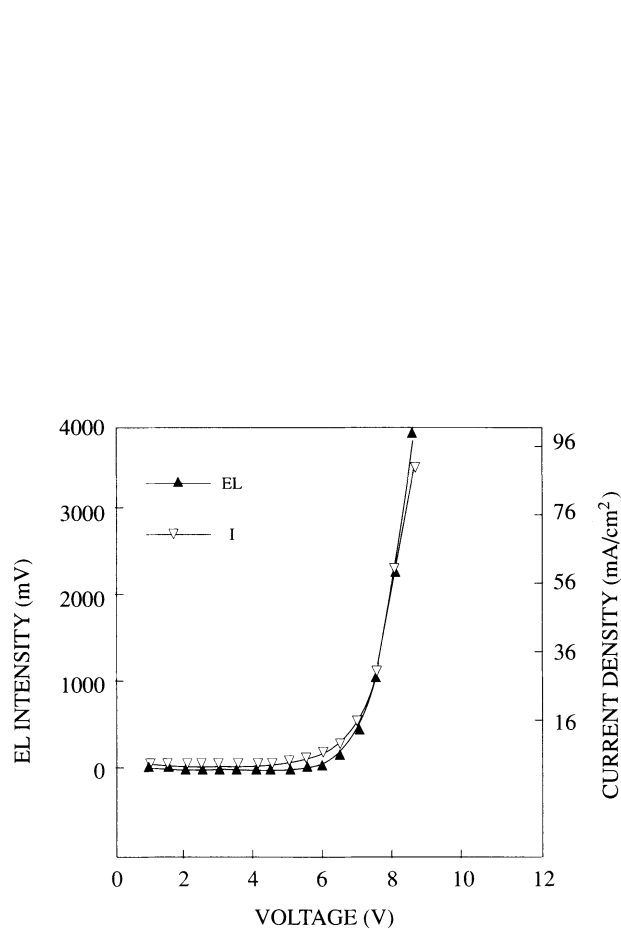


**Figure 3.** Solid state photoluminescent spectra of "blue" copolymer (a) and of "green" copolymer (c), and corresponding electroluminescent spectra, (b) and (d). EL spectrum of PPV (e) also shown.

Figure 4 shows the typical room temperature current and relative light emission as a function of applied voltage in a single layer LED with ITO anode and Al cathode. These data are correlated with an active layer thickness of the order of 80 nm and has a threshold point at ca. 13 volts. Above this point, the current and brightness increase rapidly with increase in voltage until breakdown occurs. The green light emitted can be easily seen in a brightly lit room.

Further improvement in brightness and quantum yield can be gained by a number of design strategies, the most important of which are a) chromophore blending, b) incorporation of carrier transport layers and c) optimization of band gaps, work functions and electron affinities of the constituent components.

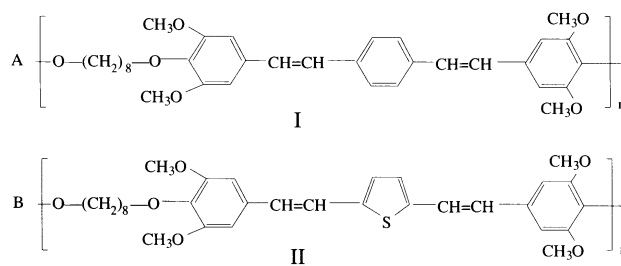
Figure 5 shows the electroluminescent spectra of two copolymers, of the alternating type discussed above, in their respective pure states and in a 1:1 blend. It is clear that the spectrum of the blend closely resembles that of the lower energy emitter; the intensity of the corresponding device is at least one order of magnitude greater. With lower relative blend concentration of the lower energy emitter this strategy may also be used to modulate the emission wavelength.



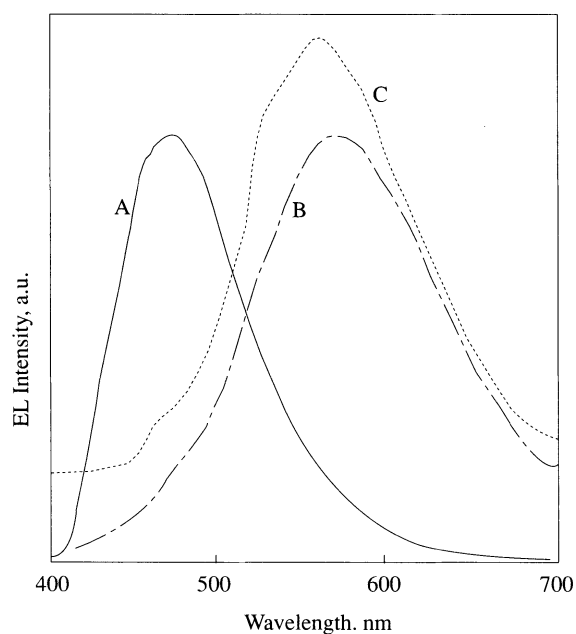
**Figure 4.** EL output and current,  $i$ , as a function of forward bias voltage for ITO/copolymer/Al single layer device.

The beneficial effect of an electron transport (i.e. hole-blocking) layer on EL intensity is seen in Fig. 6 in which EL intensity vs. current results are shown for two standardized devices using the carbazole modified PPV block copolymer, PCPV, with and without an electron transport layer of the widely used diazole derivative PBD.

Electroluminescence in  $\pi$ -conjugated polymers and device construction thus involves a number of materials issues, including a) processibility of chromophores and carrier transport layers, which in practice means facile film formation, b) stability, both chemical and physical, c) intrinsic breakdown strength and d) color tunability. Mechanistic questions also arise namely a) the details of electron-hole recombination i.e. of the photophysics of the process and b) carrier confinement by blocking layers and/or by polymer structure and morphology in copolymers and blends. Optical design factors to maximize the external photonic yield

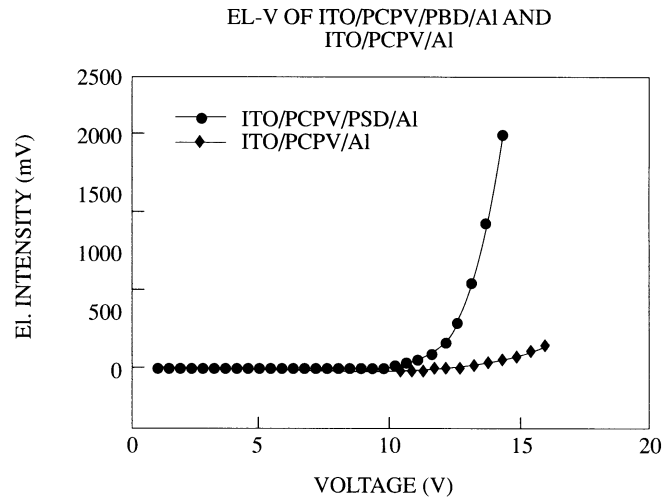


C BLEND I:II=1:1



**Figure 5.** EL spectra of copolymers and copolymer blend shown.

and to provide a polarized output, if desired, must also be considered. If these issues are successfully resolved polymer LEDs have the promise of yielding versatile, efficient, large or small area devices with low cost manufacturability.



**Figure 6.** EL output as a function of forward bias voltage for comparable LED devices with and without an electron transport layer of PBD.

## Acknowledgement

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