

Light-emitting diodes from partially conjugated poly(*p*-phenylene vinylene)

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We report the effect of conversion conditions on the device characteristics of poly(*p*-phenylene vinylene) (PPV) light-emitting diodes. Both electroluminescence and photoluminescence intensities decrease with increasing degree of conversion. Partial conjugation enhances the electroluminescence intensity and gives an efficiency (with Ca as electron-injecting contact) as high as 0.75% photons per electron, about two orders of magnitude more efficient than from similar devices prepared from fully converted PPV. The results of constant current stress measurements suggest that the partially conjugated PPV diode is relatively stable at room temperature.

I. INTRODUCTION

Initial results from semiconducting polymers employed in light-emitting diodes (LEDs) have demonstrated various colors (red, yellow, green, and blue) with impressive efficiency, brightness, and uniformity.¹⁻¹¹ Flexible light-emitting structures, which take unique advantage of the processing advantages and mechanical properties of polymers, have also been fabricated.¹²

Poly(*p*-phenylene vinylene) (PPV) was first used as the light-emitting layer in a light-emitting diode by Burroughes *et al.*¹ The efficiency (photons emitted per injected electron) was 0.01% in a sandwich device configuration of aluminum/polymer/indium-tin oxide. Recently, a significant increase in efficiency was reported when a polymer with both conjugated and nonconjugated sequences was used as the light-emitting layer.⁴ The efficiencies rise to 0.8% photons/electron with an electron-transporting layer placed between PPV emitting layer and the negative electrode.⁵

Thin films of semiconducting PPV are made by first spin casting the precursor polymer, and then converting (either completely or partially depending on time and temperature) to the conjugated form by a thermal elimination reaction. We summarize the results of a study of the effect of the conversion conditions on the device characteristics of LEDs made with PPV as the active luminescent layer. We find that a major improvement in electroluminescence intensity is obtained when partially conjugated PPV is used as the light-emitting layer. The efficiency is as high as 0.75% photons/electron for a sandwich device configuration using calcium as the electron-injecting contact (calcium/PPV/indium-tin oxide). Both electroluminescence and photoluminescence decrease with increasing conjugation length. The partially conjugated PPV LEDs are quite stable at room temperature.

II. EXPERIMENTAL DETAILS

PPV was synthesized, as shown in Fig. 1, via a solution processable precursor polymer in the form of a tetrahydrothiophenium polyelectrolyte.¹³ This precursor polymer is conveniently prepared from α,α' -dichloro-*p*-xylene,

through polymerization of the sulphonium salt intermediate. We carried out the polymerization in water in the presence of base under nitrogen flow and, after termination, dialysed the reaction mixture against distilled water. The solvent was removed and the precursor polymer redissolved in methanol. For both photo- and electroluminescence measurements thin films with three to eight layers of the precursor were spin coated from 1.2% methanol solution onto suitable substrates. Each precursor layer was heated on a hotplate at 160 °C for 3 min before the next layer was applied. After thermal conversion at different temperatures, ranging from 160 to 300 °C, the partially to fully conjugated PPV films are homogeneous, dense and uniform with green to yellow color.

The LED structure consists of a metal contact (Ca) on the front surface of a PPV film on a glass substrate, partially coated with a layer of indium/tin-oxide (ITO), the hole-injecting contact. Electron-injecting calcium contacts are deposited on the top of the polymer films by vacuum evaporation at pressure below 4×10^{-7} Torr yielding active areas of 0.1 cm². All processing steps are carried out in a nitrogen atmosphere. Indium solder is used to connect wires to the electrodes.

Spectroscopic measurements use a single-grating monochromator (Spex 340S) with a Photometrics CCD camera (Tektronix TK512 CCD) as a detector. Electroluminescence (EL) spectra were recorded while applying a steady current of 2.5 mA. For photoluminescence (PL) spectra, the polymer is excited with UV light at 365 nm.

III. RESULTS AND DISCUSSION

The forward bias current is obtained when the ITO electrode is positively biased and the Ca electrode grounded. Figure 2 shows the current and light intensity versus voltage characteristics measured from a partially conjugated PPV device in which the PPV precursor was heated at 160 °C for 2 h. The forward current increases with increasing forward bias voltage and the reverse bias current remains small; the rectification ratio is in the range 10^2 – 10^3 . Light emission first becomes visible at a bias of just under 10 V at which point the current density is ~ 100

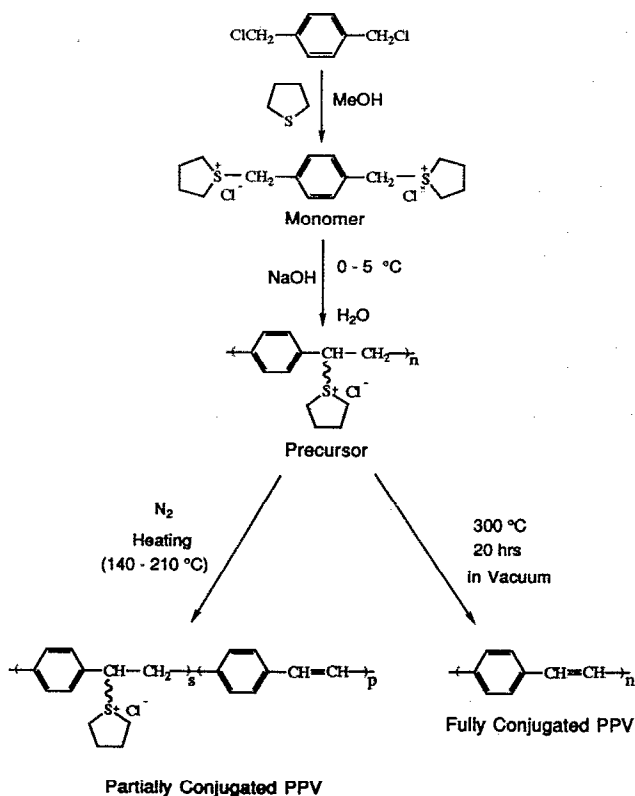


FIG. 1. Synthetic route to partially and fully conjugated PPV.

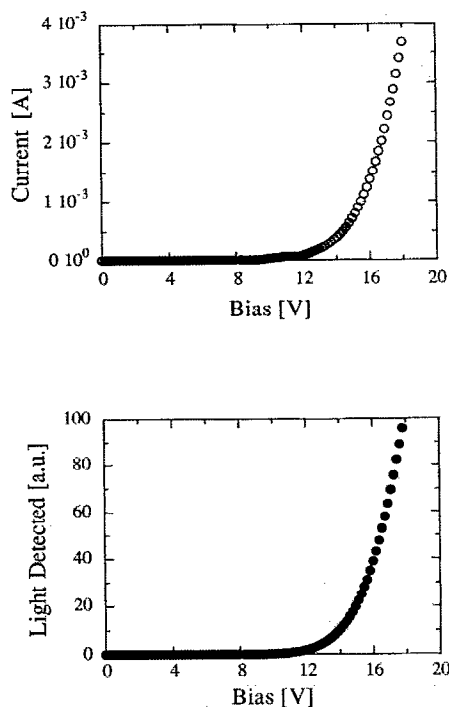


FIG. 2. Current and light emission vs voltage plots for a partially conjugated (conversion condition: $160\text{ }^\circ\text{C}$ for 2 h) PPV diode, ($\text{Ca}/\text{PPV}/\text{ITO}$).

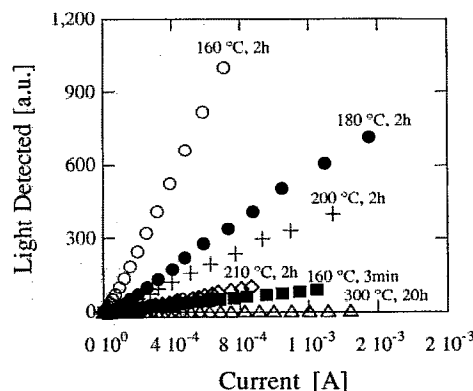


FIG. 3. Emitting light intensity recorded by calibrated Si photodiode vs current following through PPV LEDs ($\text{Ca}/\text{PPV}/\text{ITO}$) prepared at different conversion conditions.

$\mu\text{A}/\text{cm}^2$. Above 14 V ($4\text{ mA}/\text{cm}^2$), the green light emission is visible under normal laboratory lighting.

Figure 3 compares the emission intensity dependence on current for PPV devices prepared under different conversion conditions. The emission intensities increase linearly with increasing injected currents. The highest emission intensities are obtained from the device in which PPV was converted at $160\text{ }^\circ\text{C}$ for 2 h . As conversion temperature increases, from 160 to $300\text{ }^\circ\text{C}$, the emitted light intensity becomes weaker.

Figure 4 shows the emission efficiency dependence on conversion temperature for PPV devices prepared under different conditions. The efficiency increases with increasing conversion temperature when the temperature is below $160\text{ }^\circ\text{C}$. When the conversion temperature is above $160\text{ }^\circ\text{C}$, the efficiency decreases with increasing conversion temperature. The efficiency is as high as 0.75% photons per electron for the device in which the PPV light-emitting layer was converted at $160\text{ }^\circ\text{C}$ for 2 h . The efficiencies of devices prepared at conversion temperature of $300\text{ }^\circ\text{C}$ for 20 h in vacuum are 0.003% and lower. The efficiency of the device prepared at $160\text{ }^\circ\text{C}$ for 2 h is about 250 times greater than that at $300\text{ }^\circ\text{C}$ for 20 h , and 10 times greater than that of $140\text{ }^\circ\text{C}$ for 2 h . Brown *et al.* reported that the efficiency was

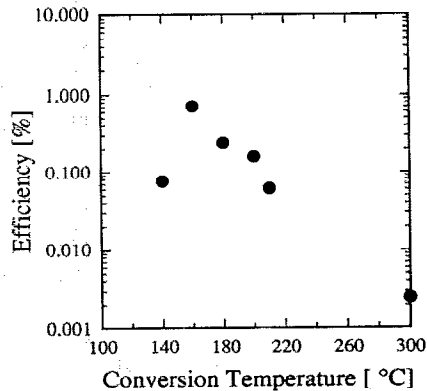


FIG. 4. Dependence of electroluminescent efficiency on the conversion temperature of PPV films.

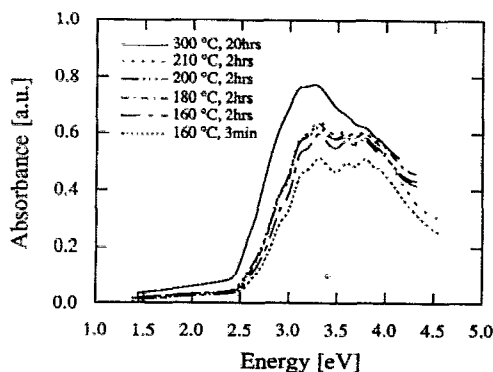


FIG. 5. Room-temperature absorption spectra of PPV thin films prepared at different conversion conditions.

0.1% for a sandwich device configuration of a calcium/PPV/ITO.⁵ That efficiency is much higher than our device prepared at 300 °C for 20 h in vacuum, but close to that prepared at 210 °C for 2 h in nitrogen (0.06%). The difference could result from reaction conditions for preparation of the monomer and/or the precursor polymer, and the details of the device fabrication conditions.

The absorption spectra of PPV obtained at different conversion temperature are shown in Fig. 5. As the conversion temperature increases, the band gap shifts to lower energy, implying that the conjugation length of PPV increases with increasing conversion temperature.

Figures 6 and 7 show room-temperature electroluminescence (EL) and photoluminescence (PL) spectra of PPV prepared at different conversion temperatures. The EL yield decreases with increasing conjugation length. The highest efficiency EL was obtained from PPV converted at 160 °C for 2 h, the lowest EL from PPV converted at 300 °C for 20 h in vacuum, in agreement with the decrease in PL intensity as the conjugation length increases.¹⁴ Thus, the EL and PL both decrease in intensity as the conjugation length increases. One explanation proposed for this result was that an increase in conjugation length leads to a larger excitation mobility resulting in more rapid motion

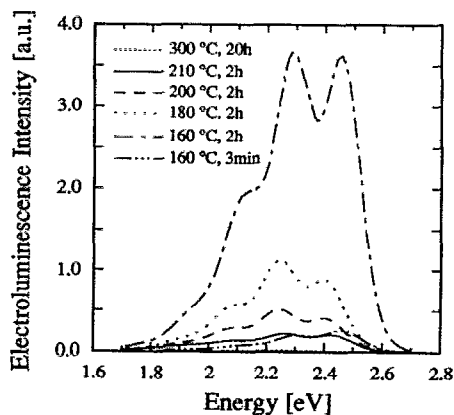


FIG. 6. Room-temperature electroluminescence intensity vs photon energy for PPV devices (Ca/PPV/ITO) prepared at different conversion conditions.

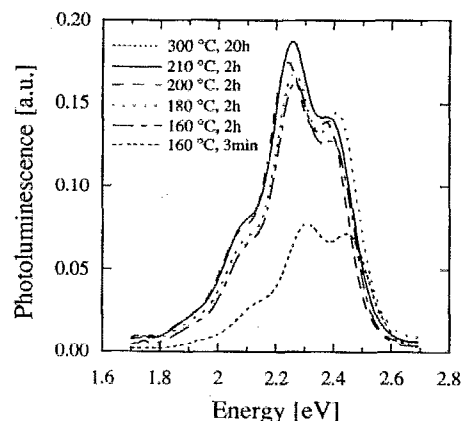


FIG. 7. Room-temperature photoluminescence spectra of PPV thin films prepared at different conversion conditions.

and greater possibility of interactions, e.g., with quenching sites, that lead to nonradiative decay.³ Because the PL and EL spectra reported to date are virtually identical, it is believed that the same excited states give rise to both PL and EL emission.^{1,7}

The data of Figs. 6 and 7 confirm that the PL and EL both cover the same energy range, and that they exhibit similar vibronic features. Nevertheless, they are not precisely identical. Although both decrease in intensity with increasing conjugation length, the PL of different conjugation lengths are almost identical in peak positions and shapes. This difference is not fully understood, but it is likely that different emission centers dominate the PL and EL spectra. Photogenerated emission does not rely on carrier mobility in the sense that excitations generated in portions of the film with low mobility can contribute to the emission. In fact, such regions of the film might dominate the PL because of enhanced nonradiative recombination in high mobility regions, as noted above. For EL, oppositely charged carriers must move sufficiently close that they can recombine radiatively, so the EL spectra might be more characteristic of the regions of the film with higher mobility. Since the longer conjugated segments should have higher mobility, they would produce the observed EL behavior.

The effect of self-absorption should be considered. These PL measurements use thin films illuminated from the same side of the film as the detector; so carriers are generated throughout the sample, and self-absorption is minimal. The EL emission requires that carrier injected from opposite electrode recombine. If asymmetric injection leads to more EL emission on one side of the sample than the other, the effect of self-absorption would act to enhance or diminish the highest-energy features, near the onset of the absorption band. That the highest-energy (zero phonon) peaks in the EL spectra are stronger than those in the PL spectra suggests that there is less self-absorption in the EL than the PL. Reduced self-absorption would indicate that the EL emission prefers the front surface of the film, which is the edge near the ITO electrode, and would imply that the ITO/PPV interface dominates carrier injection.

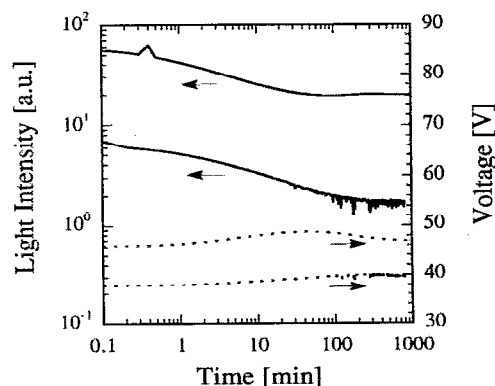


FIG. 8. Emitting light intensity (solid) and bias voltage (dashed) vs time of a partially conjugated PPV device (conversion condition: 160 °C, 2 h) at constant current in a dry box: lower curves, 0.1 mA; upper curves, 1 mA.

It was found that LEDs prepared from partially conjugated PPV were quite stable at room temperature. Figure 8 shows stability data of a partially conjugated PPV device prepared at 160 °C. The emitted light intensity and bias voltage were recorded as a function of time at 0.1 and 1.0 mA constant current. The brightness drops by only a factor of 3 or 4, and the device allows stable operation for 14 h in nitrogen dry box. Because the partially converted PPV is thermodynamically unstable, tending toward the fully conjugated form, the performance of devices made from the partially converted materials would be expected to gradually diminish over time. The conversion is, however, relatively gradual; after four months storage in a nitrogen dry box, the specific device with characteristics shown in Figs. 2 and 3 was remeasured. The current versus voltage characteristics showed a drop in current by about a factor of 3 at any given bias, and the efficiency of light output had dropped in half.

In conclusion, relatively high efficiency LEDs were made by using partially conjugated PPV as the light-

emitting layer. Both the electroluminescence and the photoluminescence decrease with increasing conjugation length. Constant current stress measurements show that the partially conjugated PPV device is quite stable at room temperature.

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- ¹J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, and A. B. Holmes, *Nature* **347**, 539 (1990).
- ²D. D. C. Bradley, A. R. Brown, P. L. Burn, J. H. Burroughes, R. H. Friend, A. B. Holmes, K. D. MacKay, and R. N. Marks, *Synth. Met.* **43**, 3135 (1991).
- ³P. L. Burn, A. B. Holmes, A. Kraft, A. R. Brown, D. D. C. Bradley, and R. H. Friend, *Proceedings of the MRS Autumn Meeting, Boston, 1991*.
- ⁴P. L. Burn, A. B. Holmes, A. Kraft, D. D. C. Bradley, A. R. Brown, and R. H. Friend, *J. Chem. Soc., Chem. Commun.* **32** (1992).
- ⁵A. R. Brown, D. D. C. Bradley, J. H. Burroughes, R. H. Friend, N. Greenham, P. L. Burn, A. B. Holmes, and A. Kraft, *Appl. Phys. Lett.* **61**, 2793 (1992).
- ⁶P. L. Burn, A. B. Holmes, A. Kraft, D. D. C. Bradley, A. R. Brown, R. H. Friend, and R. W. Gymer, *Nature* **356**, 47 (1992).
- ⁷D. Braun, A. J. Heeger, and H. Kroemer, *J. Electron. Mater.* **20**, 945 (1991).
- ⁸D. Braun, G. Gustafsson, D. McBranch, and A. J. Heeger, *J. Appl. Phys.* **72**, 564 (1992).
- ⁹Y. Ohmori, M. Uchida, K. Muro, and K. Yoshino, *Solid State Commun.* **80**, 605 (1991).
- ¹⁰Y. Ohmori, M. Uchida, K. Muro, and K. Yoshino, *Jpn. J. Appl. Phys.* **30**, L1941 (1991).
- ¹¹G. Grem, G. Leditzky, B. Ullrich, and G. Leising, *Adv. Mater.* **4**, 36 (1992).
- ¹²G. Gustafsson, Y. Cao, G. M. Treacy, F. Klavetter, N. Colaneri, and A. J. Heeger, *Nature* **357**, 477 (1992).
- ¹³Robert W. Lenz, Chien-chung Han, John Stenger-Smith, and Frank E. Karasz, *J. Polym. Sci. Part A* **26**, 3241 (1988).
- ¹⁴K. S. Wong, D. D. C. Bradley, W. Hayes, J. F. Ryan, R. H. Friend, H. Lindenberger, and S. Roth, *J. Phys. C* **20**, L187 (1987).