Blue Electroluminescent Copolymers by Parylene-Based Chemical Vapor Deposition

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ABSTRACT: Copolymerization of chemically vapor deposited poly(*p*-phenylenevinylene) and parylene-N is explored as a method for color-tuning the polymer photoluminescence. A significant blue shift in peak photoluminescence from that of pristine poly(*p*-phenylenevinylene) is observed in the vapor-deposited copolymer, the magnitude of which is controlled by the delivery rates of each of the monomers, with peak photoluminescence wavelengths ranging from 525 nm for low parylene-N incorporation to 470 nm for high parylene-N incorporation. These copolymers are successfully integrated into single-layered light-emitting diodes exhibiting blue light output, which is the first demonstration of color-tuning poly(*p*-phenylenevinylene) prepared by parylene-based chemical vapor deposition.

Introduction

Conjugated polymers with band gaps in the visible region such as poly(*p*-phenylenevinylene) (PPV) and its derivatives have generated a large amount of interest over the past decade, due to their potential as low-cost materials for optoelectronic devices such as light-emitting diodes (LEDs)[1] and lasers.[2,3] One of several advantages of these electroluminescent (EL) polymer systems is that, with the wide variety of solution-based methods known for modifying the chemical structure of polymers, it is fairly easy to control the emission color of the material.[4] Shifting the characteristic green-yellow photoluminescence (PL) color of pristine PPV to the red or blue has been realized by two major routes: increasing or decreasing the band gap of the polymer by placing substituents on the polymer backbone that alter the electronic structure of the material[5,6] and reducing the effective conjugation length of the polymer (for a blue shift only). The latter of the two methods can be achieved by forcing the polymer backbone to twist out of plane with bulky side chains[7] or kinked linkages[8,9] or by disrupting the conjugated structure of the polymer through copolymerization with a second unconjugated monomer.[10−12]

An alternate method to solution-processing for synthesis of PPV is chemical vapor deposition (CVD) from *p*-xylene derivatives such as 1,9-dihalo[2.2]paracyclophanes[13] or α,α′-dihalo *p*-xylenes,[14] in a manner analogous to CVD of parylenes.[15,16] The potential advantages of synthesizing the polymer film by CVD, as compared to solution processing, include better control of impurity incorporation and layer thickness during film deposition and a greater amount of flexibility in the fabrication of complex structures such as graded compositions and stacked layers. To date, the emission colors of EL polymers prepared with parylene-based CVD chemistry have been from the green-yellow part of the visible spectrum.[14,17,18] In principle, the same types of approaches used to tune the emission color of solution-processed EL polymers could also be used for fabrication of CVD PPV derivatives. In practice, it is not straightforward to implement these schemes, since the chemistry of vapor polymerization processes is not as well understood as solution polymerization chemistries. Most attempts at CVD of PPV derivatives have focused on fabrication of substituted homopolymers via pyrolysis of α,α′-dihalo-*p*-xylylenes with ring group substituents, but none have proven successful due to difficulties in monomer sublimation and excessive monomer fragmentation.[14] Fabrication of phenyl-substituted PPV with a hybrid CVD/solution process has been demonstrated, but use of solvents is undesirable with CVD since it adds complexity to film processing.[19]

Our previous work with PPV CVD revealed that incorporation of a small amount of aliphatic groups (which form as side products during monomer pyrolysis) into the polymer backbone resulted in a small blue shift in peak PL[20] from the polymer. This suggests that a possible approach for blue-shifting the peak photoluminescence of CVD PPV in a controlled manner is deliberate copolymerization with an unconjugated monomer, which would have the effect of shortening the PPV conjugation length. This has been demonstrated previously with solution-processed PPV,[10] but to our knowledge, color-tuning of CVD PPV-based EL polymers by copolymerization is relatively unexplored. However, use of copolymerization to tailor the properties of unconjugated CVD parylenes has been reported previously.[21−23] This approach has the potential to be quite flexible, since the *p*-xylylene reactive intermediate of the process can be either copolymerized with another *p*-xylylene or used as a radical initiator for an unsaturated monomer. The resulting material of this deposition is a statistical copolymer, where the polymer composition is controlled by the reactivity and delivery rates of each monomer.[22]

In this paper, we report our preliminary results on CVD copolymerization of PPV and parylene-N for fabrication of blue light-emitting polymers (Scheme 1). A significant blue shift in peak luminescence is observed from the copolymer, the magnitude of which is controlled by the monomer delivery rates. These copolymers are incorporated into functional single-layered LEDs exhibiting measurable brightnesses.

Experimental Section

Polymer Synthesis. The system used for polymer CVD has been described previously.[18] The temperatures used for monomer pyrolysis and deposition were 675 and 25 °C, respectively.

Scheme 1. Chemistry for Copolymerization of CVD PPV and Parylene-N from α,α′-Dichloro-*p*-xylenes and [2.2]Paracyclophanes
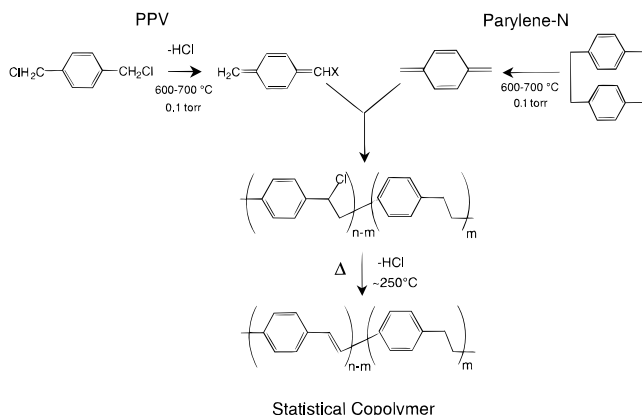
Copolymerization was performed with α,α′-dichloro-*p*-xylene (Aldrich), a typical CVD PPV monomer, and [2.2]paracyclophane (Aldrich), the monomer used for CVD of parylene-N. The monomer delivery rates were controlled by the temperature of the monomer boat, and film deposition rates ranged from 5 to 15 Å/s. Thermal conversion of the polymer films was performed at 250 °C and 10^{-6} Torr for several hours.

Polymer Characterization and Device Fabrication. Infrared reflection−absorption spectroscopy (IRRAS) was performed with a Nicolet infrared spectrometer on silicon surfaces metallized with 1000 Å of aluminum. All PL measurements ($\lambda_{excite} = 325$ nm) were performed with a SPEX Fluorolog fluorimeter. LEDs consisted of a glass substrate with indium tin-oxide (ITO) strips, a copolymer layer (950 Å), and an aluminum cathode (1500 Å). Other details of device fabrication and testing have been reported elsewhere.[24,25]

Results and Discussion

The magnitude of the blue shift in peak PL from the CVD PPV/parylene-N copolymer is controlled by the amount and distribution of parylene-N incorporation into the PPV backbone, with a higher number of interruptions resulting in a greater blue shift in film luminescence. This is in turn controlled by the relative delivery rates and reactivities of each of the *p*-xylylene CVD monomers. IRRAS spectra of three CVD PPV/parylene-N copolymers prepared at different monomer delivery rates are shown in Figure 1. As the rate of [2.2]-paracyclophane delivery is increased (copolymer **1a** to **1c**), the signal at 965 cm^{-1} characteristic of the trans-substituted double bond of PPV decreases, and the aliphatic hydrocarbon signal at 2900 cm^{-1} characteristic of parylene-N increases. An estimate of the amount of parylene-N incorporation into the CVD copolymer can be obtained from the intensity of the IRRAS peak at 965 cm^{-1}, corresponding to the trans-substituted vinyl bond characteristic of PPV, normalized to the intensity of the ring mode at 1420 cm^{-1}, characteristic of both PPV and parylene-N. From this analysis, we estimate that the fraction of parylene-N in copolymers **1a**, **1b**, and **1c** is 0.15, 0.6, and 0.8, respectively.

Integration of parylene-N into CVD PPV did have a significant influence on the peak in PL from the resulting polymer (Figure 1). As the parylene-N incorporation increased, the peak emission wavelength of the CVD copolymer blue-shifted with respect to that of pristine CVD PPV (545 nm), ranging from blue-green (525 nm, copolymer **1a**) to blue (470 nm, copolymer **1c**). Since parylene-N is not a luminescent polymer in the visible spectrum, integration of parylene-N segments must
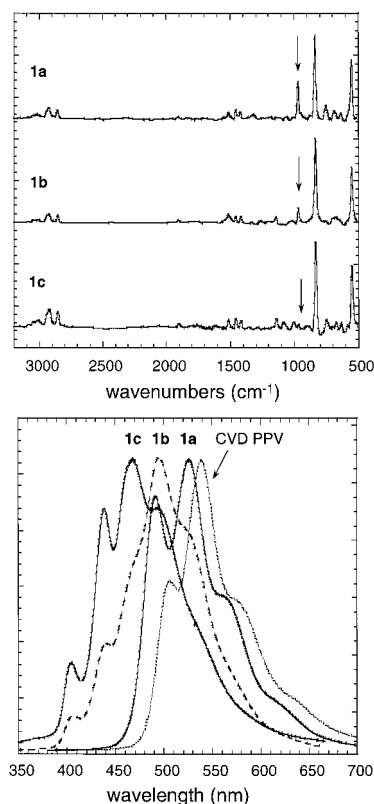

Figure 1. IRRAS (left) of three CVD copolymer films prepared at PPV//parylene-N monomer delivery rates of 10 Å/s//5 Å/s (**1a**), 10 Å/s//10 Å/s (**1b**), and 10 Å/s//15 Å/s (**1c**). The arrow highlights the trans-substituted vinyl bond stretch at 965 cm^{-1}. Photoluminescence spectra of the three copolymers and pristine CVD PPV are shown in the lower figure.
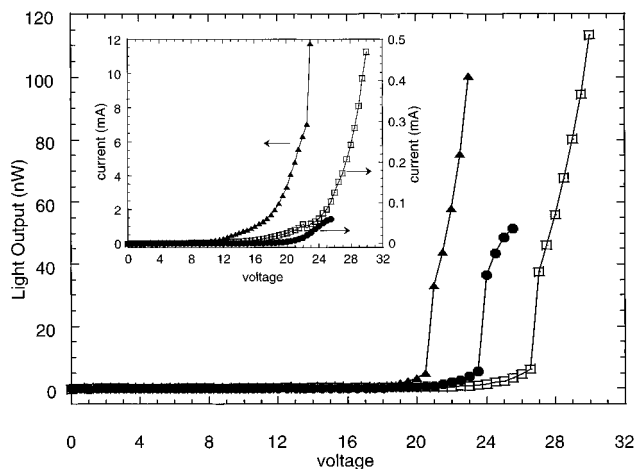

Figure 2. Luminance vs voltage scans for single-layered LEDs fabricated with CVD copolymer **1a** (filled triangles), **1b** (filled circles), and **1c** (open squares). The current vs voltage scans are shown in the inset of the figure.

sufficiently disrupt the conjugated structure of CVD PPV so as to confine the electron−hole pair to a smaller segment along the backbone, producing the blue shift in polymer luminescence.

All of the CVD PPV/parylene-N copolymers shown in Figure 1 were successfully incorporated into single-layered LEDs, the current−luminance−voltage characteristics of which are shown in Figure 2. Unlike single-layered CVD PPV LEDs,[24] which typically exhibit smoothly varying luminance−voltage traces similar to solution-processed EL polymer devices, the light emis-
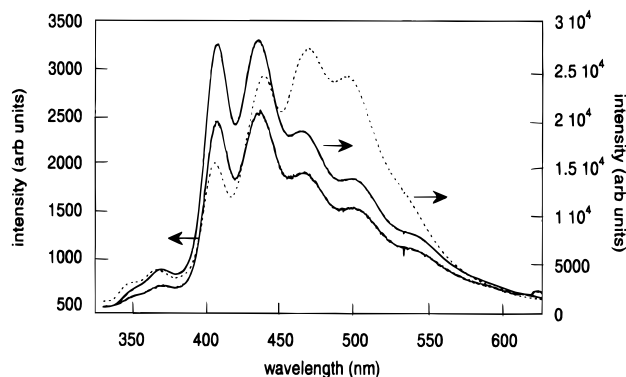
Figure 3. Photoluminescence (dashed line) and electroluminescence (solid lines) from copolymer **1c** single-layered LED. Electroluminescence is shown at two operating voltages: 20 V (left *y*-axis) and 28.5 V (right *y*-axis).

sion from the copolymer devices increases slowly until a certain threshold voltage, at which point the light output changes rapidly. Note that the LED threshold voltage is higher with greater parylene-N incorporation into the copolymer. However, the sharp increase in light output is not accompanied by a similar change in device current at the threshold voltage (see inset). This current−luminance−voltage behavior was found to be very reproducible over multiple voltage scans and appears to be a characteristic of the CVD PPV/parylene-N copolymer system. The light output from these devices could easily be seen in a well-lit room, with device external quantum efficiencies of 0.00054, 0.049, and 0.014% respectively for copolymers **1a**, **1b**, and **1c**, the latter two of which are actually higher than what is typical for CVD PPV with the same electrode materials and device geometries (∼0.002%).[24] This type of enhancement in electroluminescence efficiency has been observed previously with solution processed PPV copolymers exhibiting blue light emission.[10−12]

The spectrally resolved EL output from an LED prepared with copolymer **1c** is shown in Figure 3, along with the PL spectra for comparison. The structures of the EL spectra from the device above and below the threshold voltage (27 V) are very similar, which would suggest that the sharp increase in device luminescence is primarily due to improved charge injection into polymer layer at higher voltages. The phonon placement of the EL spectra is in good agreement with the PL, but the relative intensities of the 0−0 and 0−1 transitions are higher in EL, resulting in an overall blue shift in peak EL emission (to 420 nm from 470 nm). This trend in EL structure was also observed with LEDs of copolymer **1b**, but the PL and EL from the LED made from copolymer **1a** were in good agreement.

Incorporation of the PPV/parylene-N copolymers into single-layered devices is, to our knowledge, the first report of blue EL from a CVD PPV polymer. Although the efficiencies of LEDs fabricated with copolymers **1b** and **1c** are higher than that of pristine CVD PPV, the turn-on voltages of the LEDs are an order of magnitude higher than what is typical for pristine CVD PPV (<10 V), with higher turn-on voltages observed with higher parylene-N incorporation. This is not completely unexpected, since shortening the effective conjugation length of PPV with unconjugated parylene-N segments would also reduce the electrical conductivity of the polymer. We also note that, for solution-processed EL polymers, the device performance can be improved by using a

cathode material with a higher work function than aluminum, such as calcium, and by inserting buffer layers at both the anode/polymer and cathode/polymer interfaces. It is likely that these CVD copolymer devices could benefit from similar device optimization approaches. Despite the high turn-on voltages, the fact that observable light output could be realized with the CVD statistical copolymers suggests that, with appropriate monomer design and optimization, this method could be a viable approach for color-tuning CVD EL polymers fabricated with parylene chemistry.

Conclusions

Copolymerization of PPV and parylene-N prepared by CVD is explored as a method for controlling the luminescence properties of vapor-deposited EL polymers. A significant blue shift in peak luminescence is observed from the copolymer, the magnitude of which is controlled by the delivery rates of each monomer. These copolymers are successfully integrated into single-layered LEDs exhibiting blue light output, which is the first demonstration of color-tuning PPV prepared with parylene-based CVD chemistry. Although only blue shifts in CVD PPV luminescence are presented here, a red shift in PL could also be realized through copolymerization with appropriate selection of comonomer, such as α,α′-dihalomethylthiophenes. The studies presented here suggest that such copolymerization approaches could be a viable method for color-tuning CVD EL polymer luminescence.

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