Photoluminescence of Solution Processed Poly *n*-Vinyl Carbazole Films

P. S. Chung, P. H. Holloway

Department of Materials Science and Engineering, University of Florida, Gainesville, Florida 32611-6400

ABSTRACT: The photoluminescence (PL) of poly *n*-vinyl carbazole (PVK) films formed by solution processing was investigated. PVK films were formed by spincasting onto bare glass or glass covered by films of indium tin oxide (ITO) and poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate)ethylene (PEDOT : PSS). Some of the spincast films were redissolved in chloroform solvent and redried both in the absence or presence of an electric field (6000 V/cm). The broad aggregate PL peak near 410 nm exhibited both blue and red shifts dependent upon the processing conditions. These shifts in PL were attributed to changes in the excimer populations associated with the molecular conformation of adjacent carbazole groups. The PL data were deconvoluted into two component peaks representing two excimers associated with overlap of only one (partial or P) or full overlap (F) of both aromatic rings on adjacent carbazole groups. It was concluded that the excimer population was dependent on the amount of residual solvent left in the film after processing and upon the type of substrate. The mechanism(s) controlling the molecular configurations was discussed. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 1–9, 2009

Key words: luminescence; thin films; solid-state structure; photophysics; atactic

INTRODUCTION

Organic electronic materials have advanced tremendously over the past several decades as active device materials. Organic materials were widely known for their high electrical resistivities and low carrier mobilities, thereby limiting their uses in electrical circuits to insulators. The first report of a highly conductive form of polyacetylene was published in 1977.[1] Using halogen dopants to provide extrinsic carriers, charge mobilities as high as 1 cm^2/V s were achieved, compared to $\sim 10^{-7}$ cm^2/V s for more typical polymers.[1] This showed that semiconducting polymers can play active roles in electronic applications, such as light emitting devices (LED), field-effect transistors, and photovoltaic devices.[2–5]

An advantage of using polymers is the ability to solution process. For example, spincasting eliminates the need for costly vacuum instrumentation, can be performed in air and can be scaled for manufacturing. Processing of inorganic semiconductors frequently requires stringent vacuum controls to achieve the desired functionality. With the exception of light emitting displays,[6] polymer-based electronics are still in the research stage due to inferior device performance. For example, the best terrestrial photovoltaic devices composed of silicon and III-V compounds have efficiencies of 20–30%.[7,8] In contrast, the best organic photovoltaic device has yet to exceed 5%.[9]

One of the main problems facing organic devices is control of the structure of molecules and polymers. Charge carriers in polymers do not move through a periodic three dimensional lattice as they do in inorganic materials, but rather they are constrained by two dimensional bonding paths and nearest neighbor bond length and angles. As a result, carrier mobilities of organic materials, including solution-processed materials, are relatively poor compared to conventional semiconductor materials. In general, solution- processed polymers are amorphous and disordered, contributing to the already complex nature of charge transport. The objective of this research was to investigate the optical and electronic properties of poly *n*-vinyl carbazole (PVK) processed in solution. To accomplish this objective, photoluminescence (PL) and PL excitation (PLE) data will be reported below from PVK films on glass substrates, or glass coated first with indium tin oxide (ITO) and coated second with poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT-PSS). The chemical structures of PVK, PEDOT, and PSS are shown in Figure 1.

For PL from PVK, two distinct excimer states have been reported to result in two peaks at different wavelengths dependent upon the relative position of the carbazole side groups.[10] One PVK excimer state is associated with a partially eclipsed conformation,
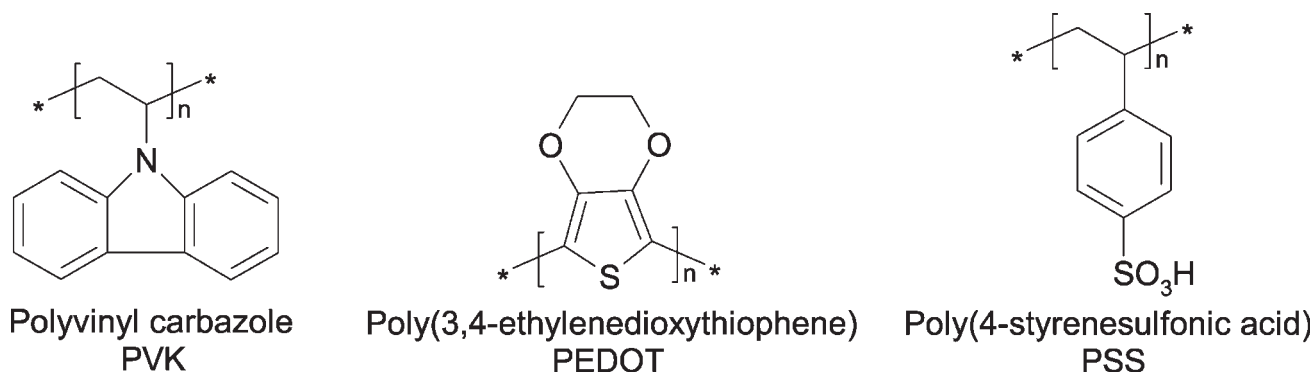
Figure 1 Chemical structure for polymers used in this research.

where one benzene ring overlaps a single benzene ring with no overlap of the second benzene ring of adjacent carbazole groups (Fig. 2). This excimer state results in an optical transition centered at $\sim$ 370 nm (3.182 eV),[11] and will be referred to as the partially eclipsed excimer "P". A second excimer state, referred to as fully eclipsed excimer "F", is where both benzene rings on adjacent carbazole groups overlap (Fig. 2), and its optical transition is centered at $\sim$ 420 nm (2.954 eV).[11] The area of each emission peak provides a measure of the excimer population, which results from short-range structural changes[12] and therefore can be used to measure the conformation of adjacent carbazole groups.

EXPERIMENTAL

PVK polymer ($M_w \sim$ 90,000 g/mole, PDI $\sim$ 2.5) was obtained from Scientific Polymer Products Inc. The polymer was synthesized by free radical polymerization, which generally produces an atactic configuration. The glass transition temperature, 215°C, measured with differential scanning calorimetry, was similar to that reported for atactic PVK (227°C).[11] The glass transition temperatures of syndiotactic and isotactic PVK were reported to be 276 and 126°C, respectively. The polymer was dissolved in chlorobenzene at a 50 mg/mL concentration. Before use in making films, all solutions were syringe filtered through a 0.2 μm nylon filter from Gelman®.

The substrates used in this research were bare glass or glass coated with ITO. Corning 2947 microscope slide glass or ITO on unpolished float glass (sheet resistance = 8–12 Ω per square, nominal thickness = 1200–1500 Å) were purchased from Fisher Scientific and Delta Technologies, respectively. To facilitate electrical testing, the ITO-coated glass was patterned by etching it with heated aqua regia for 5 to 10 min. The etch was terminated when the resistance of the etched area was on the order of 1 MΩ.

Substrates were cleaned in several steps. The initial steps included sonication for 20 min, first in an aqueous solution of Alconox detergent, followed sequentially by deionized water, acetone, and isopropanol. After this series of sonication steps, the substrates were blow dried with nitrogen. The glass substrates were then ready for polymer film deposition. ITO-coated substrates were exposed for 25 min to an oxygen plasma to increase the ITO work function and enhance the hole transport for conjugated polymers.[13] Before coating with PVK, ITO-coated glass substrates were also spin coated with poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) in an aqueous dispersion (PEDOT-PSS) purchased from HC-Starck. The PEDOT-PSS solution, consisting of a 1 : 20 weight ratio of PEDOT to PSS, was first syringe filtered through a 0.2 μm nylon filter from Gelman® before spincasting 400 μL of solution at 4000 rpm for 30 s. After spincasting, the resulting films were baked in a vacuum oven (0.03 atm produced by an oil sealed rotary vane mechanical pump) at 150°C for 4 h, resulting in a film thickness of 50 nm. PEDOT-PSS is commonly used as a hole transport layer for organic optoelectronic devices.[14]

After filtration and substrate cleaning, 50 mg/mL PVK/chloroform solutions were processed into films by spincasting with a CHEMAT Technologies model KW-4A spin coater. A fixed volume of solution was dropped onto the stationary bare glass or glass/
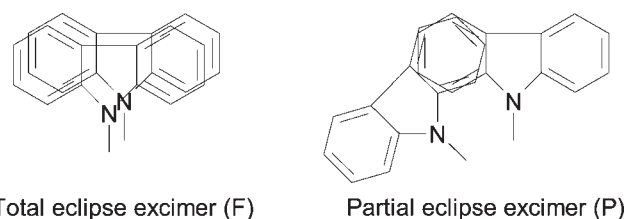

Figure 2 Spatial diagram showing the benzene ring overlap for adjacent carbazole groups for the two excimer states "F" and "P." View is along the chain axis.

ITO/ PEDOT-PSS substrate, which was immediately rotated at 3000 rpm for 30 s. The PVK-coated substrates were heated in a 0.03 atm vacuum oven to 60°C for 2 h to reduce the residual solvent, although some solvent still remains in the films (see below). The resulting spin cast PVK film thickness was 200 nm.

After spin casting and vacuum baking, some films were further processed in the presence of an electric field using a custom apparatus. A 0–10 kV high voltage source from Physical Electronic Industries was used to supply a DC voltage between two parallel metal plates placed 0.5 cm apart, producing applied electric fields ranging up to 20,000 V/cm (2 V/μm). The top plate was negative and held by a rubber insulated clamp, and the grounded bottom plate rested on a grounded heater plate. To prevent arcing between the parallel plates, a polyimide film was placed on the bottom electrode to prevent dielectric breakdown of air.

The substrates were placed on the grounded bottom electrode. Before any electric field was applied, the PVK film was redissolved in 150 μL of chlorobenzene. The film was then dried in room temperature air either without or with an applied electric field (6000 V/cm) until the droplet was no longer visible. Drying times were between 2 and 3 h, after which the samples were annealed in the vacuum oven at 60°C for 2 h to minimize the remaining solvent. Annealing the films at temperatures greater than 70°C caused the PVK polymer films to become brittle and flake off the substrates.

PL and photoluminescence excitation (PLE) data were collected from PVK layers on glass. An Oriel Cornerstone™ 260 1/4 m monochromator was used to select wavelengths from the excitation source (Oriel model 63,358 QTH W lamp) for PLE. An Oriel MS257 monochromator with a Si-based photomultiplier detector (Oriel 77,345) was used to measure the PL emission vs. wavelength. For PLE data, the PL monochromator was set at the wavelength of the maximum emission peak, and the excitation monochromator scanned to generate the PLE spectrum.

RESULTS

The redissolution process caused a physical redistribution of polymer in the film, resulting in the center of the film decreasing in thickness and the edges of the film increasing in thickness. All data reported below were taken from the center of the film. Redissolution of PVK films without and with the electric field yielded film thicknesses of ~ 66 nm and ~ 35 nm, respectively.

PL data are shown in Figure 3 from PVK films spincast onto glass from the 50 mg/mL solution concentration using three different subsequent process-
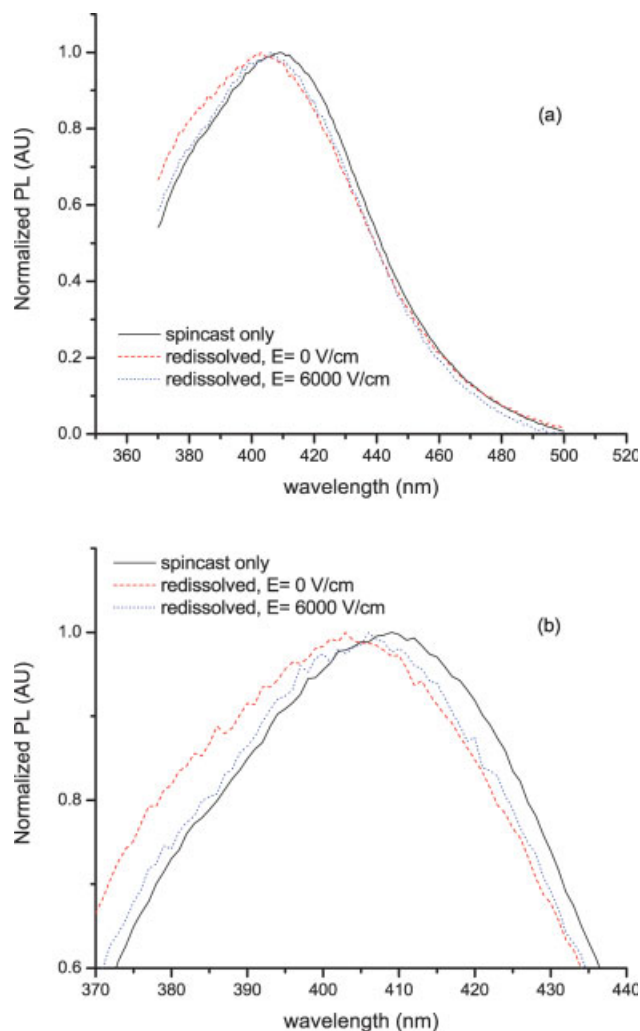

Figure 3 PL spectra of PVK films spincast on glass from a 50 mg/mL solution: (a) normal view (b) enlarged view of (a). The solid lines represent the spincast films only, the dashed lines represent the redissolved and unexposed films ($E = 0$ V/cm), and the dotted lines represent the redissolved films with $E = 6000$ V/cm during drying. All spectra are normalized to their maximum value and the excitation wavelength was fixed at 335 nm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ing conditions: (1) a spincast only film (no further processing), (2) a film that was redissolved with 150 μL of chlorobenzene solvent and subsequent dried in ambient air between the parallel plates without applying an electric field, and (3) process (2) but the electric field was applied during the redissolution and subsequent ambient air drying. After drying in ambient air, redissolved films were dried in a vacuum oven at 60°C for 2 h. The excitation wavelength for PL was 335 nm and the PL spectra were normalized to their maximum emission peak value. For spincast only films, the broad peak was centered at 407 nm. When the film was redissolved without being exposed to the electric field (the second
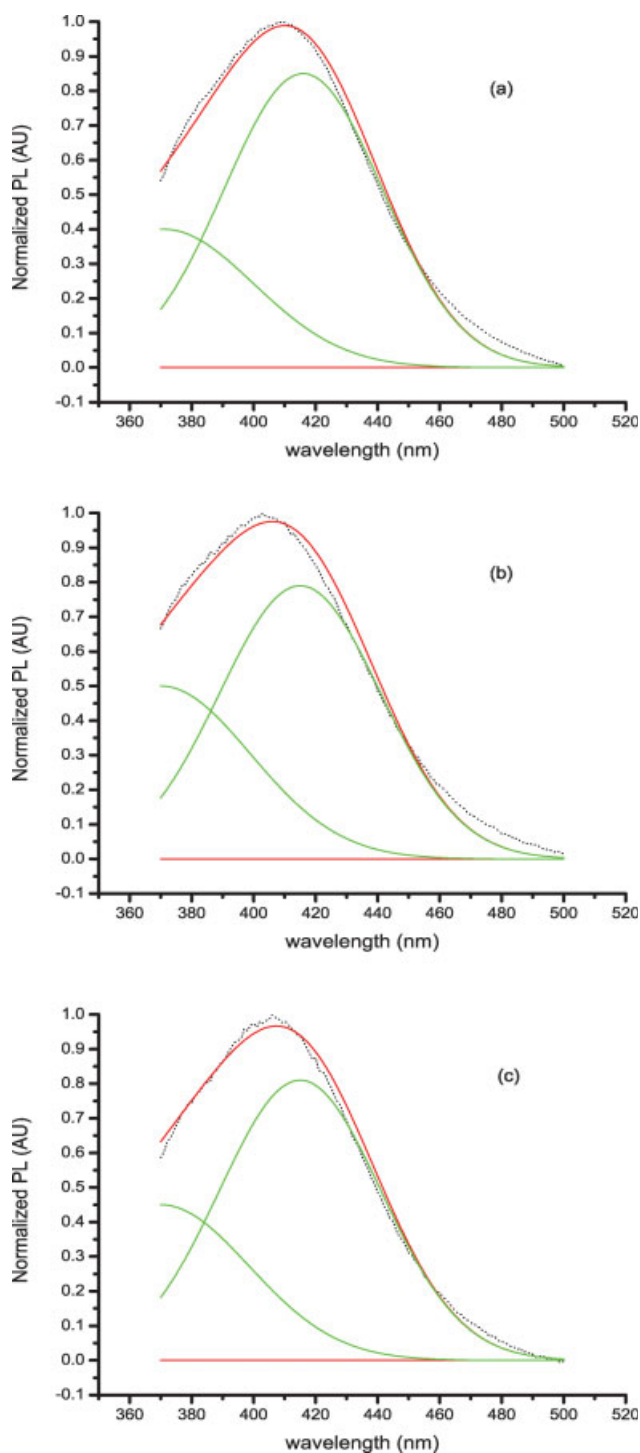
Figure 4 PL curve fitting for 50 mg/mL concentration spincast films on glass with three processing conditions: (a) spincast only, (b) redissolved with $E = 0$ V/cm, and (c) redissolved with $E = 6000$ V/cm. The solid black lines are the experimental data, the dashed lines are the summation of the peaks fitted for excimers P and F (dotted lines). Note the changing area between the peaks from excimer P and F vs. processing condition. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

control condition), the peak exhibited a blue shift of 4 nm relative to spincast only, in addition to the appearance of a high energy shoulder at $\sim$ 380 nm. When the redissolved film was exposed to a 6000 V/cm electric field, the film showed a red shift of 3 nm relative to the peak from the redissolved, zero field second control film.

Curve fits using peaks from excimers P at 370 nm (3.354 eV) and F at 420 nm (2.954 eV) for the PL spectra on glass substrates are shown in Figure 4. The peak from excimer "P" is terminated at 370 nm to avoid interference from the tail of the excitation peak at 335nm. For spincast films, and redissolved films without and with an electric field, the P/F peak area ratios were 0.28 $\pm$ 0.01, 0.35, and 0.32, respectively. The relative area of each peak is shown in Figure 5 vs. processing conditions. Error bars on the measurements were estimated to be $\pm$1.4%.

PLE spectra for the three processing conditions are shown in Figure 6 for PL emission at 410 nm. The PLE peaks at $\sim$ 295 and $\sim$ 340 nm from excimers "P" and "F," respectively, were both prominent for spincast only films. The $\sim$ 295 nm peak height increased relative to the 340 nm peak, and a more pronounced shoulder was observed at $\sim$ 265 nm after redissolution with or without a field.

The same process conditions used to spincast films on glass were also used to create PVK films on glass/ITO/PEDOT : PSS substrates, and Figure 7 shows the PL spectra from PVK films spincast from 50 mg/mL solutions. For spincast only films, the PL features are identical to the PL spectra for films deposited on glass, with the peak maximum at 407 nm. When the film was redissolved without an electric field, the peak blue shifted to 400 nm and the PL intensity at 370 nm was 80% greater (relative to the normalized maximum at 407 nm) compared to the
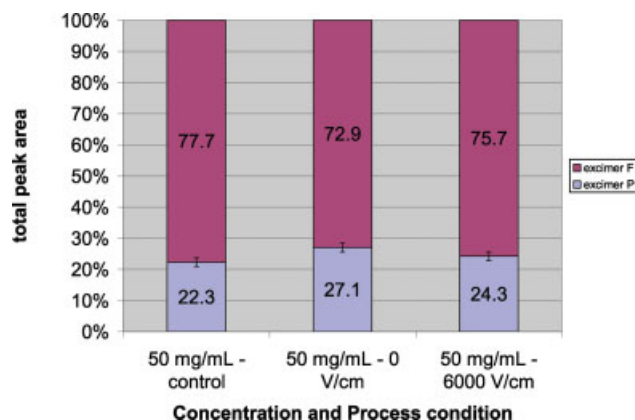

Figure 5 Percent peak area corresponding to excimer P and excimer F vs. processing conditions for PVK films on glass. The error bars are $\pm$1.4%. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]
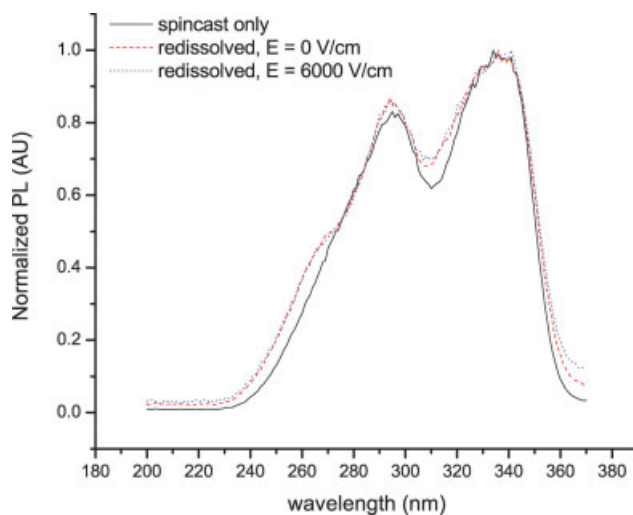
Figure 6 PLE spectra from PVK films from a 50 mg/mL solution concentration. All spectra are normalized to the maximum value at ∼ 345 nm and the detected PL wavelength was fixed at 410 nm. The solid lines represent the spincast films only, the dashed lines represent the redissolved films (*E* = 0 V/cm), and the dotted lines represent the redissolved films (*E* = 6000 V/cm). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

spincast only condition. When an electric field was applied during the redissolution process, the high energy shoulder decreased and the main peak shifted to 403 nm.

Curve fits for the "P" and "F" excimer peaks at 370 and 420 nm, respectively, to the PL the 50 mg/mL PVK film on glass/ITO/PEDOT : PSS are shown in Figure 8. The P/F peak area ratio for the spincast only films was 0.29 ± 0.01, which is statistically the same as the P/F area ratio for the spincast films on glass (0.28) reported above. When the film was redissolved without an electric field, the P/F area ratio increased significantly from 0.29 to 0.88. When the electric field was applied to the redissolved film, the ratio decreased to 0.57. The percentage of the total peak area attributed to excimer P and F are summarized in Figure 9 vs. processing conditions.

PLE spectra from PVK films on glass/ITO/ PEDOT : PSS from 50 mg/mL solutions are shown in Figure 10, and the prominent peaks at 345 and 295 nm are similar to the spectra for 50 mg/mL films on glass. For films on ITO/PEDOT : PSS, the peak height at 295 nm was slightly smaller than that of the film on glass (∼ 0.7 compared to ∼ 0.8). A slight shoulder feature on the high energy sides of the main peak was observed for redissolved films, both with and without the electric field.

The greater intensity of the peak at ∼ 380 nm in the PL data for the films on ITO/PEDOT : PSS compared to those on glass (compare Figures 4 and 7)

warranted an additional experiment. PVK films were spincasted onto glass or glass/ITO/PEDOT : PSS substrates from a more dilute solution of 10 mg/mL. The PL spectra of the spincast only films [Fig. 11(a)] show that this film from a dilute solution on ITO/PEDOT : PSS exhibited a single peak at ∼ 380 nm, whereas the film on glass showed a second maximum at ∼ 430 nm. In the PLE spectra [Fig. 11(b)], the films on both substrates exhibited a peak maximum around 330 nm, but the film on glass/ ITO/PEDOT : PSS exhibited a smaller FWHM than the film on glass. When the films were redissolved with solvent and exposed or not to the electric field, no appreciable change in the PL and PLE spectra
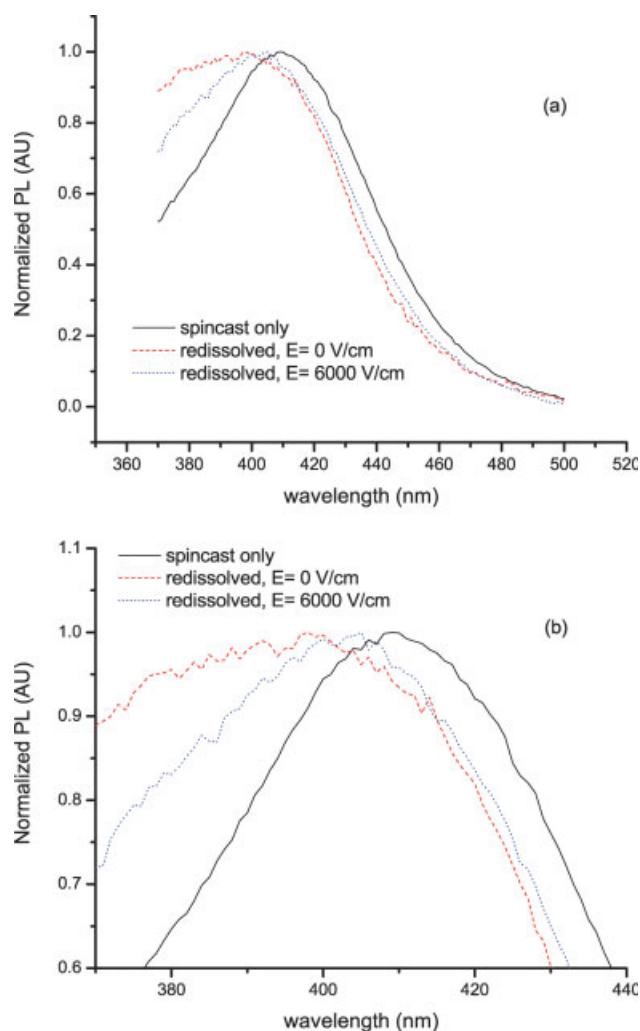

Figure 7 PL spectra of 50 mg/mL PVK films on glass/ ITO/PEDOT : PSS. (a) Regular view, (b) enlarged view of (a). The solid lines represent the spincast films only, the dashed lines represent the redissolved films (*E* = 0 V/cm), and the dotted lines represent the redissolved films (*E* = 6000 V/cm). All spectra are normalized to their maximum value and the excitation wavelength was fixed at 335 nm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
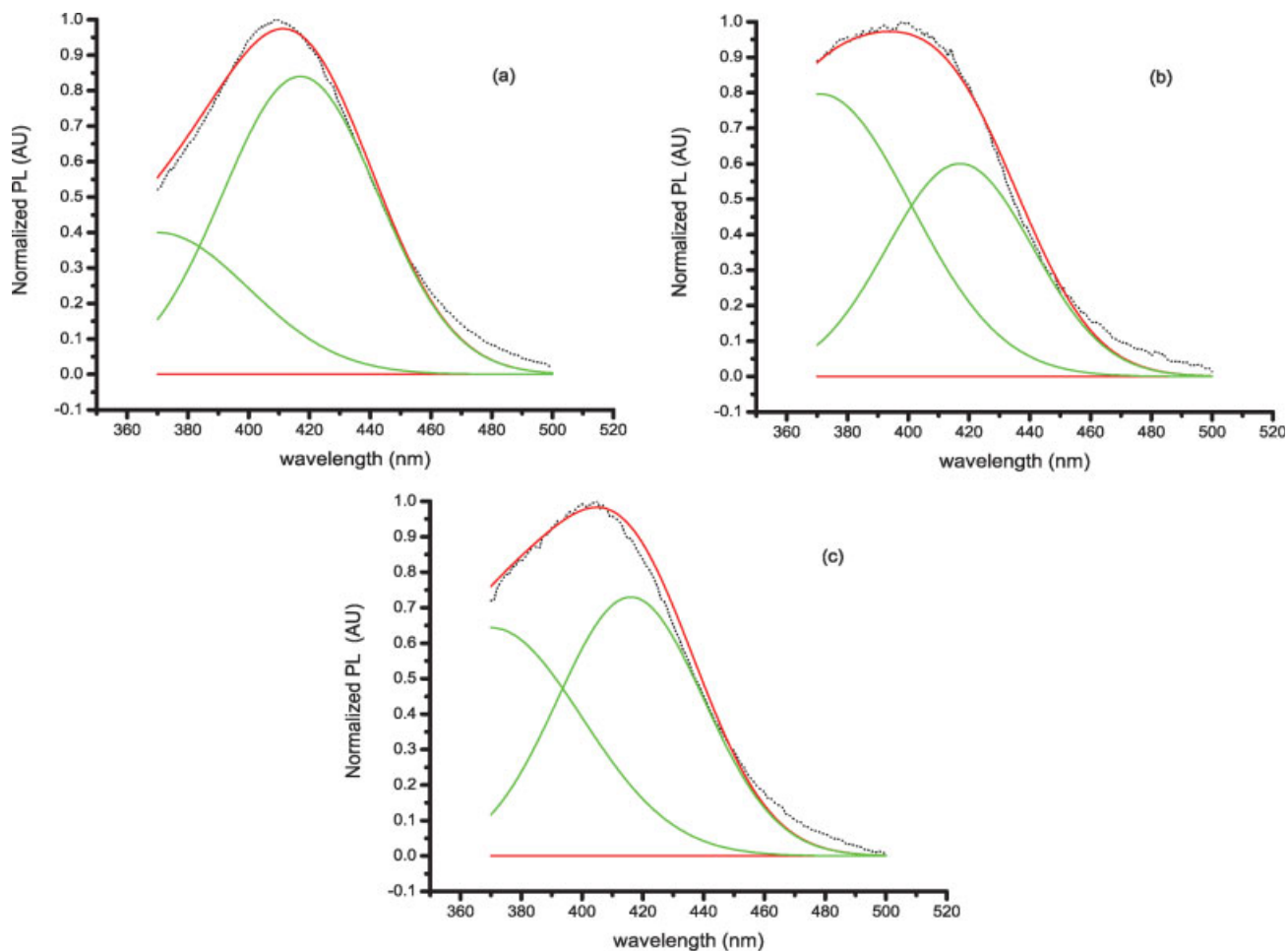
Figure 8 Excimer P and F fits to the aggregate PL peak from 50 mg/mL PVK films on glass/ITO/PEDOT : PSS for different processing conditions: (a) spincast only, (b) redissolved, $E = 0$ V/cm, and (c) redissolved, $E = 6000$ V/cm. The solid black lines are the experimental data, the dashed lines are the summation of the peaks fitted for excimers P and F (dotted lines). All spectra are normalized to their maximum value. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

was observed (data not shown) vs. the spincast only data shown in Figure 11.

DISCUSSION

The PL data reported above were analyzed by resolving them into the constituent peak areas associated with excimer P or F. The blue and red shifts in the aggregate peak position results from a change in relative population of P and F excimers, which result from overlap of one or both of the benzene rings on adjacent carbazole groups, respectively. It should be noted that not all the carbazole groups participate in excimer formation. Because the chain is typically amorphous and atactic, carbazole groups in nonlinear portions of the chain are unable to attain the conformations necessary for excimer emission. Nevertheless, excimer emissions at ~ 380 and ~ 430 nm are indicative of the amount of carbazole units that are aligned in a particular geometric

arrangement, that of the fully eclipsed (F excimer) or the partially eclipsed (P excimer) conformations[11] (Fig. 2). Several trends were evident in the PL data. For spincast films, a PL blue shift was observed in going from the spincast only to redissolved films with $E = 0$ V/cm [Figs. 4 and 8 (a,b)]. The blue shift results from an increase in the relative concentration of the high energy P excimer conformation relative to the low energy F excimer. On the application of an electric field to the redissolved films, a red shift (relative to the $E = 0$ V/cm sample) in PL was evident, indicating an increased relative concentration of the fully eclipsed F excimer.

The changes in the relative concentrations of molecular conformations and therefore excimers are attributed to the presence of residual solvent in the processed PVK films. A predominance of the partially eclipsed P excimer has been reported for solutions, whereas the fully eclipsed F excimer dominates in solid films.[10] The mechanism of
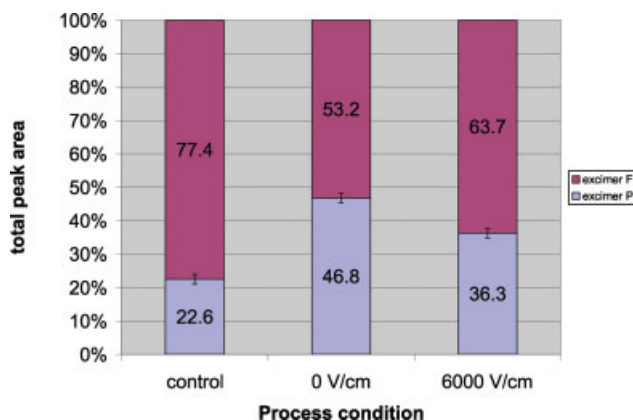
Figure 9 Percent peak area from excimer P and F for 50 mg/mL PVK films on ITO/PEDOT : PSS for spincast only (control), or redissolved with $E = 0$ V/cm or $E = 6000$ V/cm. The error bars are $\pm 1.4\%$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

dissolution of PVK in chlorobenzene is based on the interaction between the aromatic rings on the solvent and on the carbazole groups. When the carbazole groups are fully eclipsed (i.e., excimer F), the close proximity of neighboring side groups prevents the solvent from interacting with carbazole groups. On rotation about the carbon backbone (i.e., excimer P), solvent-carbazole interactions can occur more easily.[15]

In the current study, the annealing temperature in the vacuum oven (60°C, 0.03 atm) was selected to
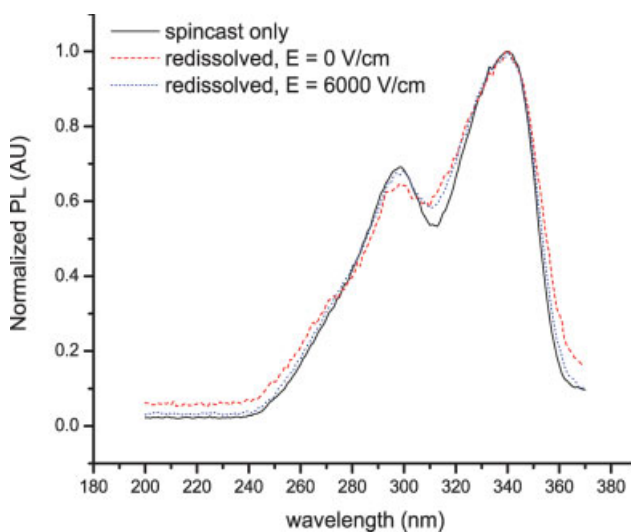

Figure 10 PLE spectra from 50 mg/mL PVK films on glass/ITO/PEDOT : PSS. All spectra are normalized to their maximum value and the PL wavelength was fixed at 410 nm. The solid lines represent the spincast only films, the dashed lines represent the redissolved films ($E = 0$ V/cm), and the dotted lines represent the redissolved films ($E = 6000$ V/cm). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

remove most of the chlorobenzene solvent from the film. The boiling temperature of chlorobenzene at atmospheric pressure is $\sim 130°C$.[16] By Trouton's rule, which describes the boiling temperature for solvents in relation to pressure, the boiling temperature of chlorobenzene is predicted to be $\sim 30°C$ at 0.03 atm.[17] The vacuum heating was thus initially assumed to remove all of the solvent, but the presence of C—Cl stretching peaks in FTIR data from the films (data not shown) suggest that solvent is still present in the films even after vacuum baking.

Figure 12 shows the effect on PL of vacuum heating time after the solvent has redissolved a 50 mg/mL film, followed by ambient air drying for 2 h without the application of an electric field, then heating under vacuum at 60°C for either 2 or 6.5 h. The spincast only data are shown for a reference. It is obvious that the high energy shoulder increased on
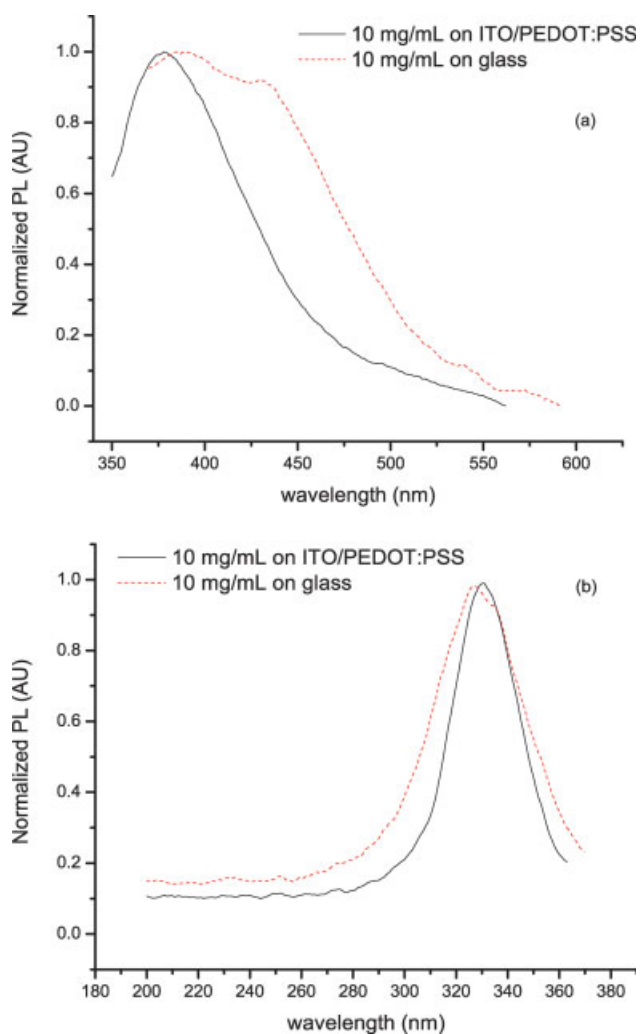

Figure 11 (a) PL and (b) PLE spectra from a 10 mg/mL spincast only film of PVK on glass or on glass/ITO/PEDOT : PSS. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
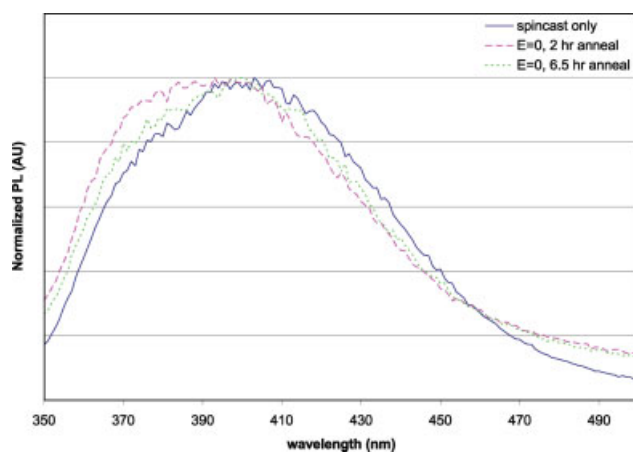
Figure 12 PL spectra from 50 mg/mL PVK films on glass/ITO/PEDOT : PSS with annealing times of 2 (dashed line) or 6.5 h (dotted line) after redissolution without an electric field applied ($E = 0$ V/cm). The spectrum from a spincast only film (solid line) is shown for comparison. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

heating, which represents an increase in the concentration of partially eclipsed P excimer. The PL spectra from the spincast only film resemble the solid state PL spectrum reported by Klöpffer[10] with a larger fraction of F excimers. Because of the nature of the spincasting process, the bulk of the solution is flung off the substrate, leaving a small amount of solvent in the film. When the film is redissolved with solvent, dried in the ambient air, and then annealed in the vacuum oven (60°C at 0.03 atm) for 2 h the high energy shoulder increases, indicating an increase in the P excimer, consistent with a dominance of P excimers for PVK in solution.[10] Increasing the heating time from 2 to 6.5 h causes the high energy P excimer shoulder to decrease and the PL spectra more closely resembles the solid state form due to less solvent remaining in the film, i.e., more solvent has been driven out due to the longer annealing time.

These results suggest that the original annealing treatment (2 h at 60°C at 0.03 atm) was not sufficient to completely remove the solvent molecules reintroduced by the redissolution process, and residual solvent causes the shifts in excimer population and therefore PL spectra. As discussed above, the majority of the solution is flung off the substrate during spin casting and more of the solvent evaporates due to the rapid rotation of the spincasting process. By the time the film is annealed, very little solvent remains in the film. Because the distribution of excimers is dependent on the tacticity of the polymer, complete removal of solvent does not guarantee the presence of only fully eclipsed F excimers. The PVK used in this study was determined to be atactic, thus both P and F excimers should be present in a film

without any residual solvent. On redissolution and drying without an electric field, more solvent was residual in the film as evidenced by an increased intensity for the high energy shoulder (relative to spincast only, Fig. 12). This larger shoulder indicates a larger population of the partially eclipsed P excimer, due to the larger interaction of the P conformation with the solvent. When an electric field was applied during redissolution, the PL peak red shifted relative to those without an applied field due to a decreased intensity of the high energy shoulder. Because these films were typically thinner than redissolved zero field films, the solvent molecules had less distance to travel to the film surface and evaporate. Because the annealing vacuum, time and temperature were constant, a thinner film would have less residual solvent than a thicker film. This conclusion is supported by the fact that films cast from the dilute solutions (10 mg/mL, Fig. 11) yielded thinner films that did not exhibit any changes in PL when redissolved with solvent. FTIR data also confirmed the presence of an absorption assigned to the C—Cl stretching frequency of chlorobenzene in an annealed film.

An initial objective of this research was to test whether an electric field of 6000 V/cm could reorient electric dipoles on PVK and thereby change the molecular configuration. Chung[18] has discussed the dipoles expected for PVK and how it creates an ~ 100 meV lower energy state for the F excimer vs. the higher energy P excimer configuration. This is consistent with the energy differences reported for isotactic and syndiotactic dyads of 99.7 and 69.3 meV, respectively.[15] Based on the dipole estimated for PVK, an electric field of 6 kV/cm was not sufficient to change the molecular orientation or configuration.

The data show that the substrate also affects the PL spectra, e.g. glass (Fig. 3) vs. glass/ITO/PEDOT : PSS (Fig. 7). Redissolution of the spincast film on glass caused a PL blue shift vs. the spincast only film in the absence of an electric field, because the P peak area increased slightly from 0.22 to 0.27 (Fig. 5) due to an increased concentration of P excimers. The PL spectra from redissolved PVK on the glass/ITO/PEDOT : PSS substrate (Fig. 7) exhibits a prominent higher energy shoulder, which is indicative of a greater number of P excimers. The change in P peak area from spincast only to redissolved without the electric field increased from 0.23 to 0.47 (Fig. 9). Figure 11 shows that the fully eclipsed F excimer centered at 420 nm is absent from the PL spectra of a 10 mg/mL spincast only film on glass/ITO/PEDOT : PSS, whereas both P and F excimers are prominent in the PL spectra from the glass substrate. It is speculated that an aromatic ring on PEDOT : PSS can interact with an aromatic ring on the carbazole group, similar to the chlorobenzene interaction

with the carbazole groups, as discussed above. Therefore, the partially eclipsed excimer P would be favored over fully eclipsed excimer F. Because of the lack of aromatic structures on the surface of a glass substrate, the carbazole units adopt the fully eclipsed F excimer form. The excimer distribution for the spincast only film was the same for both substrates (0.22 vs. 0.23 for the relative P peak area) suggesting that the forces exerted by the spincasting process minimizes the aromatic interaction. The influence of aromatic interaction was increased by the redissolution process.

CONCLUSIONS

PL spectra from PVK films were deconvoluted into two peaks representing P and F excimer states known to occur in PVK when one or both carbazole groups, respectively, are aligned on adjacent neighbors. In solid films, the fully eclipsed F excimer centered at 420 nm is favored, whereas the partially eclipsed P excimer with a peak at 380 nm is favored in solutions. Changes in the aggregate peak wavelength and shape from spincast and redissolved films were due to changes in the relative emission intensities of P and F excimers. Changes in the ratio of emission for P and F excimers for films that were spincast only vs. redissolved with chloroform and subsequently dried were attributed to the presence of residual solvent in the film. FTIR data confirmed that solvent was residual in the film. These differences in the relative P and F excimer populations were attributed to the fact that fully eclipsed F excimer precludes carbazole-solvent interactions, therefore the partially eclipsed P excimer is favored in solution or for higher residual solvent concentrations. Application of a 6000 V/cm electric field decreased the redissolved film thickness (from 66 to 35 nm) which increased the fraction of F excimers due to lower concentrations of residual solvent. Films spincast from lower concentration solutions (10 vs. 50 mg/mL) yielded thicknesses less than 50 nm and exhibited no change in PL under the same redissolution process conditions. Finally, films deposited on glass vs. glass/ITO/PEDOT : PSS substrates showed a lower fraction of partially eclipsed P excimers when redissolved with solvent. It was speculated that the PEDOT : PSS aromatic rings could interact with the aromatic rings on the carbazole groups and increase the fraction of the P excimer.

References

1. Chiang, C. K.; Fincher, C. R.; Park, Y. W.; Heeger, A. J.; Shirakawa, H.; Louis, E. J.; Gua, S. C.; Macdiarmid, A. G. Phys Rev Lett 1977, 39, 1098.
2. Weinberger, B. R.; Gau, S. C.; Kiss, Z. Appl Phys Lett 1981, 38, 555.
3. Chen, S. N.; Heeger, A. J.; Kiss, Z.; Macdiarmid, A. G.; Gau, S. C.; Peebles, D. L. Appl Phys Lett 1980, 36, 96.
4. Ozaki, M.; Peebles, D. L.; Weinberger, B. R.; Chiang, C. K.; Gau, S. C.; Heeger, A. J.; Macdiarmid, A. G. Appl Phys Lett 1979, 35, 83.
5. Grant, P. M.; Tani, T.; Gill, W. D.; Krounbi, M.; Clarke, T. C. J Appl Phys 1981, 52, 869.
6. Eastman Kodak Company, Displays, October 2004. Available at: http://www.kodak.com/US/en/corp/display/applications.jhtml. Accessed December 2004.
7. Kazmerski, L. Elevator Talking Points About Solar Electricity; NREL in-house publication: Golden, Colorado.
8. National Renewable Energy Laboratory, Table of Photovoltaic Performance, n.d. Available at: http://www.pv.unsw.edu.au/eff/Effic.%20Table%20(Table%201(V18).pdf. Accessed January 2005.
9. Nelson, J. Mater Today 2002, 5, 20.
10. Klöpffer, W. J Chem Phys 1969, 50, 2337.
11. Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R.;Handbook of Conducting Polymers, Dekker: New York, 1998.
12. De Schryver, F. C.; Vandendriessche, J.; Toppet, S.; Demeyer, K.; Boens, N. Macromolecules, 1982, 15, 406.
13. Wu, C. C.; Wu, C. I.; Sturm, J.; Kahn, A. Appl Phys Lett 1997, 70, 1348.
14. Koch, N.; Elschner, A.; Schwartz, J.; Kahn, A. Appl Phys Lett 2003, 82, 2281.
15. Sundararajan, P. R. Macromolecules 1980, 13, 512.
16. University of Massachusetts, Department of Chemistry, Solvent Physical Properties, n.d. Available at: http://xray.chem.umass.edu/solvent.html. Accessed October 2006.
17. University of Cambridge, Boiling Points. Available at: http://www.ch.cam.ac.uk/magnus/boil.html. Accessed October 2006.
18. Chung, P. S. Effects On Photoluminescence and Photovoltaic Properties of Solution-Processed Poly N-Vinylcarbazole. Doctoral Dissertation, University of Florida, Gainesville, FL, 2007.