

Photophysical Studies of Polyvinylcarbazole Polymer Films

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ABSTRACT: Polyvinylcarbazole (PVK) films have been prepared by solution method. Their absorption spectra, photoluminescence, and electroluminescence have been studied. Absorption in pure PVK is found to be high at lower wavelengths in UV region and decreases in visible range. In case of I₂ doped PVK, absorption is observed in visible region also. The photoluminescence is obtained in pure PVK when excited by violet or blue light but in case of I₂ doped PVK, similar excitation gives low intensity peaks in yellow–green region. The results indicate that I₂

levels in PVK causes absorption in 400–600 nm wavelength range and makes the deexcitation of the molecules nonradiative. Light emission by application of ac voltage from mains up to 100 V has been studied. Nonlinear increase in emission intensity has been observed with increasing voltage. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 722–726, 2007

Key words: PVK film; absorption spectra; photoluminescence; electroluminescence

INTRODUCTION

Polymeric materials have found wide-spread applications in many diversified areas. Some polymers have been found to exhibit high fluorescent yield.¹ Polyvinylcarbazole (PVK) appeared to be much more efficient emitting polymer because of its optically active carbazole groups. Intensive studies of pure and doped PVK films have been initiated with a series of works by Partridge.² Polymers exhibit a number of attractive characteristics for the understanding of physical process in organic electroluminescence (EL) as well as their practical use for low cost full color flat panel display and other emissive devices.³ To be useful, these devices must have high brightness and efficiency while requiring a low operating voltage. The device efficiency is highly dependent on both carrier recombination efficiency and photoluminescence (PL) quantum yield of the emitting material. Visible light emission has been reported to from P3OT/PVK films.⁴ Present investigations are based on the optical characteristic of PVK and reports absorption, photoluminescence, and electroluminescence of pure and iodine (I₂) doped PVK films.

EXPERIMENTAL

Film of PVK has been prepared by solution technique. The granules of PVK are dissolved in Dimethyl form-

amide (DMF) by heating up to 90°C. A small amount of I₂ was added in case of doped samples. The prepared transparent waxy solution of PVK was spread on petry dish and air-dried at room temperature for 24 h. The dried thin film of PVK was taken out of the dish and used for the PL and absorption studies.

The absorption spectra of the PVK films were obtained with the help of Perkin Elmer λ -12 spectrometer. PL of the films was studied using mercury lamp, and various color filters for excitation and HM-104 monochromator and photomultiplier tube (PMT) for obtaining the spectra. The set up for PL studies is shown in Figure 1.

EL was investigated using a single layer structure EL device. The PVK emission layer was placed between two electrode layers. One of the electrodes was SnO₂ coated transparent glass plate and aluminum was used as second electrode deposited by vacuum coating method.

The SnO₂ coated transparent electrode has been prepared by depositing thin film of SnO₂ by chemical vapor deposition on clean glass substrate. SnCl₂·2H₂O was thermally decomposed in atmosphere into Sn and Cl₂, which after reaction, forms SnO₂ layer on heated glass slides. Polymer film is deposited on half portion of this conducting glass plate by spreading a small amount of waxy solution of PVK in DMF as mentioned earlier and air dried for 24 h. Over a portion of the PVK film, aluminum is coated by vacuum coating, which was used as second electrode for the EL cell. The thickness of the aluminum electrode was of the order of 1 μ m.

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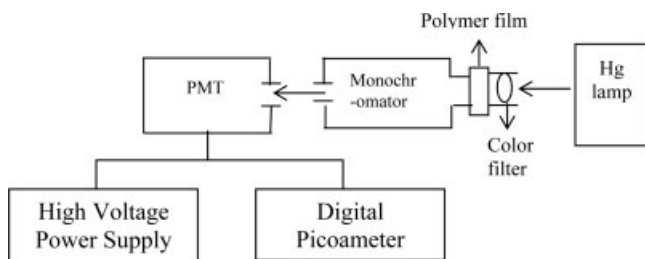


Figure 1 Setup for PL spectra.

The light emission was observed from EL cell by applying 50 Hz ac voltage obtained from mains and the emitted light intensity was measured by PMT, which was connected to intensity recorder (Fig. 2). EL intensity was measured by increasing the applied voltage up to 100 V with the help of a variac.

RESULTS

The pure PVK films were translucent and I₂ doped films appeared purple in color. Figures 3 and 4 shows the absorption spectra of pure and I₂ doped PVK films. In both cases the absorption is high at low wavelength ~ 250 nm and decreases as the wavelength increases up to ~ 325 nm but the decrease is slow in case of I₂ doped sample. After 325 nm, there is a sudden decrease in absorption and it remains low up to 390 nm. At 390 nm, I₂ doped sample show a narrow peak and plateau up to 500 nm and after that gradual decrease in absorption, whereas in case of pure PVK absorption remains low and practically constant for 400 nm and above. Thus there is greater absorption in I₂ doped PVK in the wavelength range 390–600 nm.

From the PL spectra of polymer films it is observed that a number of PL peaks are obtained when pure PVK is excited by violet or blue light (Fig. 5). Excitation by green or yellow light gives peaks at the incident wavelength (Fig. 6), whereas excitation by red light do not show any luminescence, rather low intensity peaks are observed in the wavelength range 500–680 nm over background intensity at other UV or IR wavelengths. In case of I₂ doped PVK, no high intensity luminescence peaks are obtained as can be seen from Figure 7. Only low intensity peaks in the wavelength range 500–680 nm over background intensity are observed. This indicates that I₂ doped PVK is not giving any luminescence as in case of excitation of pure PVK by red light.

Figure 8 shows the EL intensity versus voltage graph of pure and I₂ doped PVK films. Light green emission was observed from pure PVK and I₂ doped PVK emitted light of sky blue color. The EL intensity is found to increase nonlinearly with increasing voltage. It is seen that light emission starts at higher voltage in case of pure PVK, but increase in intensity with increasing voltage is quite large. For I₂ doped samples light emission is obtained at lower voltage but net emission remains low even at high voltages. Thus, much higher intensity is obtained from pure PVK.

DISCUSSION

A general feature of the disorder-affected spectra is their extended long wavelength tail due to a high density of defects resulting from spectral inhomogeneities. These features are obtained in PL and absorption studies of PVK film by Zhang et al.⁵ Since polymers are high molecular weight organic solids, it is

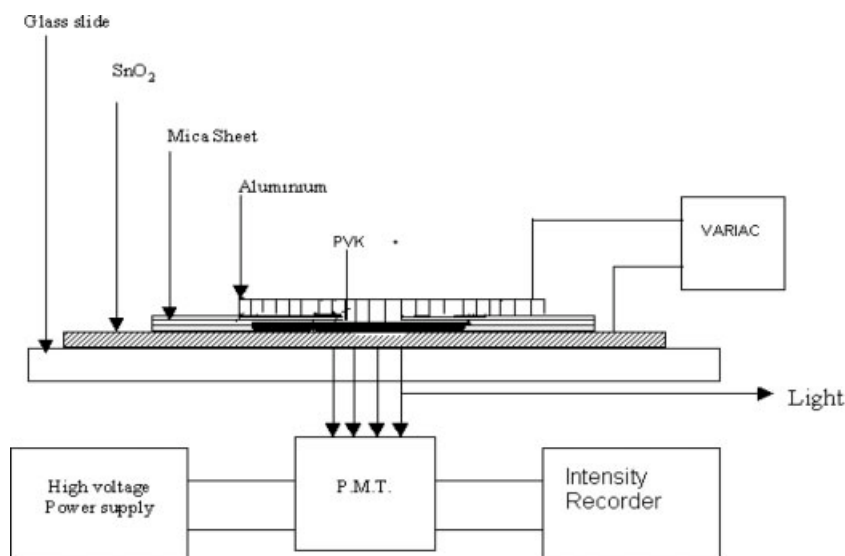


Figure 2 Setup for electroluminescence.

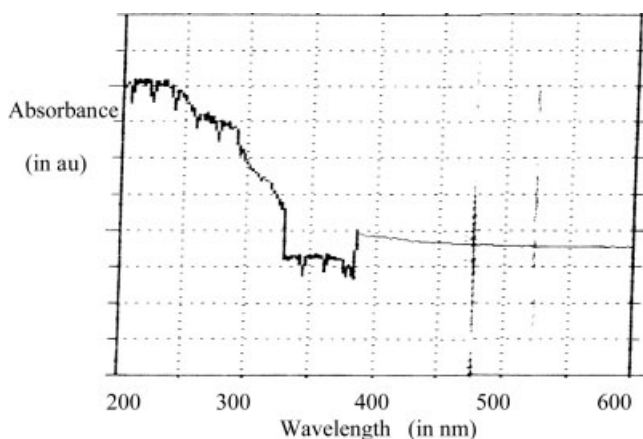


Figure 3 Absorption spectrum of PVK (pure) film.

easily conceivable and experimentally confirmed that a large group of organic solids displays an intermediate degree of disorder characterized by the presence of aggregates whose structure is similar to the crystal structure. The absorption spectrum of PVK in DMF solution is the same as it is in solid state, showing that the carbazole chromophores of the polymers act as individual molecules in DMF solution and in the solid state, where the oscillator strength of similar transitions are essentially equal.

The broad absorption and PL emission peaks suggested that the emission is excimeric in nature. The intermolecular interaction impose a communal response upon the molecular behavior of organic solids, leading to a collective electronic excitation called molecular or small radius (Frankel Type) excitons. Its energy levels may split into as many components (Davydov Splitting) as there are individual molecules per unit cell.⁶ This splitting is in addition to the level splitting produced by the interaction between two adjacent identical molecules. The splitting $[\Delta = 2|L_{12}(K = 0)|]$ depends upon the resonance interaction between molecules that are transitionally inequivalent whereas the mean energy displacement downward (L_{11}) depends on resonance interaction between equivalent molecules. The exciton band dispersion can thus be expressed as

$$\varepsilon_{(k)} = \varepsilon_q - D - L_{11}(k) \pm L_{12}(k) \quad (1)$$

where D is the gas (ε_q) to crystal shift arising from the nonresonant interaction between an excited molecules and its surrounding medium. The Davydov splitting as small as 10 cm^{-1} for triplet states because of the short range of exchange interactions, can vary from a few hundred to several thousands cm^{-1} for highly excited singlet states. In addition to this spectral splitting, the Davydov bands have different polarization properties. The presence of Davydov components can be observed in the absorption or emission spectrum

of organic solids, although their identification is not necessarily straight forward because of an overlap with vibronic bands and disorder broadening of the bands.

The luminescence of pure PVK can be ascribed to excimer sites, each formed by a pair of carbazole groups in close proximity to one another. They all formed by the migration of singlet excitons along the polymer chain and from one polymer chain to another. The mean free path of the singlet exciton is $40\text{--}80 \text{ \AA}$, the chromophores forming the excimer sites are separated by an interplaner carbazole molecules of size $\approx 3 \text{ \AA}$.⁷

The photoluminescence studies of pure and I_2 doped PVK have indicated that pure PVK gives a number of PL peaks in the whole visible spectrum when excited by high energy photons but exposure to low energy photons do not give any luminescence. I_2 doped PVK films also show similar spectra as obtained for pure PVK exposed to red light when excited even with violet or blue light (Fig. 7). These observations may be explained as follows:

1. Violet/Blue light excites the PVK molecules from highest occupied molecular orbitals (HOMO) to lowest unoccupied molecular orbitals (LUMO) and deexcitation is also radiative giving luminescence peaks in violet/blue region. Also there are some defect/impurity levels below the LUMO. Radiative deexcitation to these levels cause emission in IR region and radiative transition from these defect levels to HOMO give emission in green/yellow region.
2. Green/Yellow light cause excitation from LUMO to the defect levels only and radiative relaxation gives the same light.
3. Red light is not able to cause any excitation and hence no luminescence is obtained. The low intensity peaks in $500\text{--}680 \text{ nm}$ range may be due to absorption of background light exciting the molecules from HOMO to defect levels.

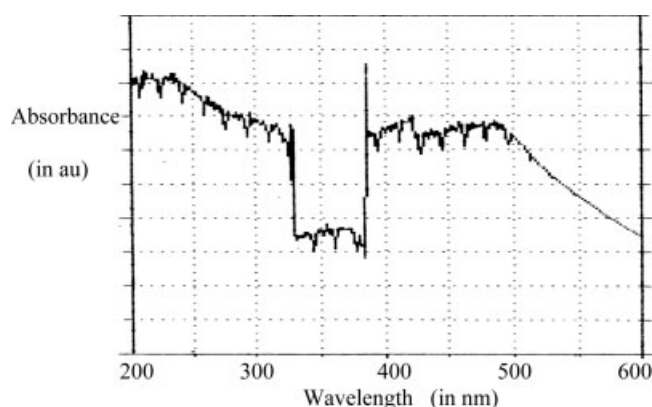


Figure 4 Absorption spectrum of PVK (I_2 doped) film.

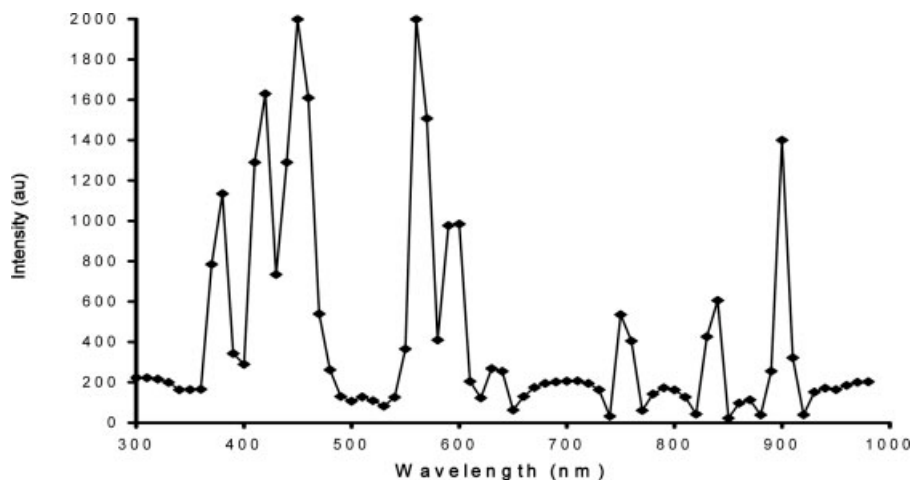


Figure 5 Photoluminescence spectrum of PVK (pure) film excited through violet filter.

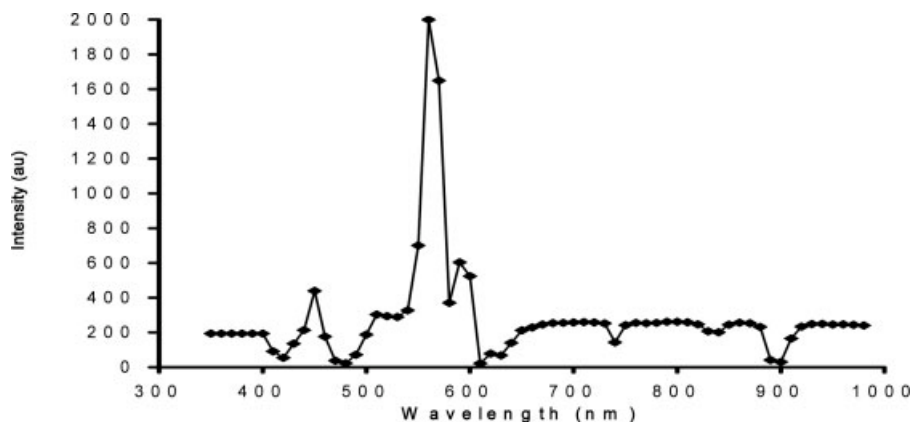


Figure 6 Photoluminescence spectrum of PVK (pure) film excited through green filter.

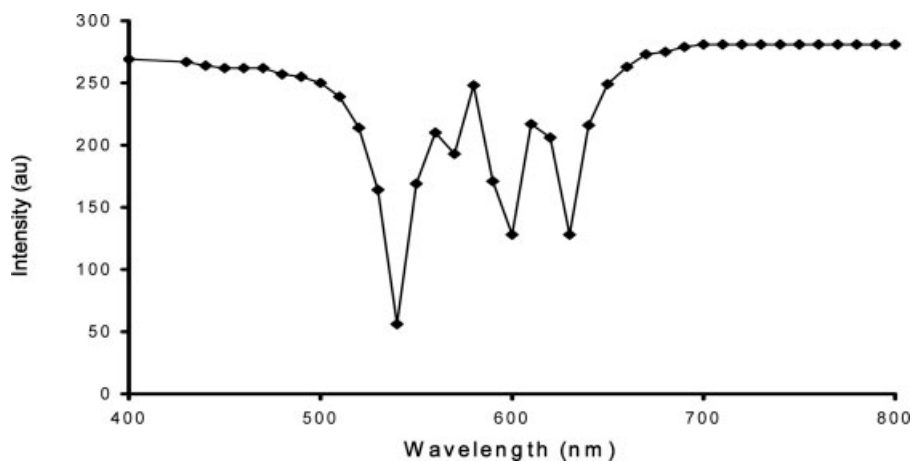


Figure 7 Photoluminescence spectrum of PVK (I₂ doped) film excited through violet filter.

4. When I₂ is mixed in PVK, the color of films becomes violet and no high intensity peaks are obtained in PL studies. Hence it can be said that I₂ produces energy levels close to or within

LUMO increasing the absorption in violet/blue/green region and make the deexcitation nonradiative. Therefore only low intensity peaks in 500–700 nm range are obtained because of ab-

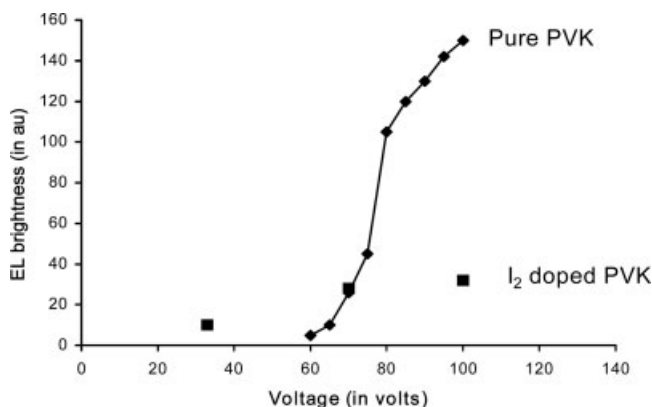


Figure 8 EL intensity of PVK (pure and I₂ doped) as a function of applied voltage.

sorption of background light exciting the PVK molecules from HOMO to defect levels.

Kalinowski⁶ have compared the PL and EL spectra of PVK films and their resemblance suggested that the EL emission is excimeric in nature and that the aluminum layer is impenetrable for exciton and holes, therefore confining them to the emitting PVK layers.

In an attempt to find the mechanism of EL excitation, plot between $\log \phi_{EL}$ vs. $1/\sqrt{v}$ was considered. The straight line nature shows the the voltage dependence of the EL brightness may be given by⁶

$$\phi_{EL} = \phi_{EL}^{\infty} \exp(-b/\sqrt{v}) \quad (2)$$

where ϕ_{EL} = EL intensity, v is voltage, ϕ_{EL}^{∞} is the intensity at higher voltages, and b is constant. This suggested that carrier injection current is governed by the hot carriers.

The value of the constant b and ϕ_{EL}^{∞} has been calculated for EL of pure and I₂ doped PVK by plotting the $\log \phi_{EL}^{\infty}$ vs. $1/\sqrt{v}$ curves. In case of pure PVK, two different slopes are obtained; for voltage below 80 V value of constant b is 66.67 and for voltage above 80 V it is 15. The value of constant b in case I₂ doped PVK has been obtained as 10. The calculation give the value of ϕ_{EL}^{∞} for pure PVK as ~ 5000 arb. units and for I₂ doped PVK as ~ 400 arb. units.

Excimers produced by the electron-hole recombination process in EL have a larger binding energy than those formed under optical excitation in PL. The light green emission from pure PVK shows that the EL is generated by the recombination process from the impurity centers. Because of the spin statistics during recombination events and singlet triplet intersystem crossing transition at the impurity centers, triplet excitations could be efficiently produced giving characteristic phosphorescence emission. However, direct electron-collision excitation of lower energy triplet states of the structural defects of carbazole and impurity molecules cannot be completely excluded if the electric field at the crystal boundary is not sufficient to cause ionization. Also the excitation mechanism cannot be firmly concluded on the basis of the voltage and frequency dependence of the EL brightness.

CONCLUSIONS

The studies have revealed that PVK is a good luminescent material and shows PL as well as EL. Addition of small amount of I₂ makes it purple in color. I₂ levels causes absorption in 400–600 nm wavelength range and gives nonradiative path for relaxation of excited molecules. This reduces the luminescence efficiency in case of photoluminescence as well as electroluminescence.

References

1. Drexhage, K. H. In *Topics in Applied Physics: Dye Lasers*; Schafer, F. P., Ed.; Springer: New York, 1997; Vol. 1, p 144.
2. Partridge, Rh. *Polymer* 1983, 24, 733.
3. Luchikawa, M.; Amagi, J.; Horiba, Y.; Koyarana, T. *J Appl Phys Lett* 2003, 9, 12.
4. Wang, G.; Yuan, C.; Wu, H.; Yu, W. *Jpn J Appl Phys* 1995, 34, L182.
5. Zhang, Z.-L.; Jiang, X.-Y.; Xu, S.-H.; Nagatomo, T. In *Organic Electroluminescent Materials and Devices*; Miyata, S., Nalwa, H. S., Eds.; Gordon and Breach: Amsterdam, 1997; Chapter 5.
6. Kalinowski, J. *J Phys D: Appl Phys* 1999, 32, R179.
7. Pope, M.; Swenberg, C. E. *Electronic Process in Organic crystals*; Calrendon: New York, 1982.