

# Study of conduction mechanism in poly(9-vinylcarbazole) pure and doped with ferrocene

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**Abstract**— Measurements of dc-conduction in poly (9-vinylcarbazole) (PVK) pure and doped with ferrocene has been studied. Various mechanism of conduction (Poole-Frenkel, Space-charge limited current, Richardson-Schottky emission, hopping) can cause non-linear characteristics. Analysis the current-electric field dependence proved that the mechanism responsible for conduction in poly(9-vinylcarbazole) doped with ferrocene was bulk limited and Poole-Frenkel mechanism is prevalent. The dependence of current on electrode material, temperature, field and dopant concentration is studied. The role of doping molecular concentration in the polymer matrix and change in conduction characteristics are also studied. Lowering of the activation energy due to doping was observed. The conductivity was found to increase with an increase in the ferrocene concentration in the composite.

**Index Terms**— Activation energy, conduction mechanisms, dc-conduction, dopant concentration, ferrocene, Poole-Frenkel mechanism, PVK.

## 1 Introduction

Charge transport in different polymers has been studied extensively during the past few decades to understand the nature of charge carriers in these materials [1-3]. Poly (9-vinylcarbazole) (PVK) seems to be the least studied polymer as for as dc-conductivity study and its dependent on different doping material is concerned. Most of the studies on PVK have been focused on photo conductivity property and fabrication of light emitting diode (LED) [4-6].

Therefore in the present study we have taken up pure PVK and ferrocene doped PVK in thin films form. The main aim of the study is to understand the nature of charge carriers and trap distribution within these polymers. For this purpose dc-conduction properties of these polymers are studied in detail. The dependence of dc-current on electric field, temperature, electrode materials and the concentration of the dopant material is studied extensively and the results of these studies are reported in this paper. Various conduction mechanisms such as Poole-Frenkel emission [7-9], Schottky emission [10, 11], Tunneling [12], Space charge limited current [13] and hopping conduction [14, 15] are reported in the literature for this purpose. In the present study it has been found that the conduction mechanism is bulk limited and Poole-Frenkel mechanism seems to be prevalent for dc-conduction and charge carriers responsible for conduction were controlled by the dopants rather than the main chain of polymer [16].

## 2 Experimental

### 2.1 Sample preparation

Poly(9-vinylcarbazole) supplied by Aldrich Chemical Co., USA, having a glass transition temperature ( $T_g$ )~ 200C, molecular weight average  $M_w$ ~ 1,100,000 product no. 182605, CAS Number 25067-59-8, refractive index 1.683 and density 1.2g / ml at 25C was obtained. The structure of macromolecule of PVK and ferrocene are given as below figure (2.1).

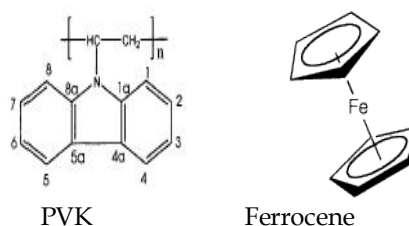


Fig.(2.1): (a). Structure of PVK (b) Structure of Ferrocene

For the preparation of the films, polymer obtained was used as such, without any further purification /recrystallization. Dopant ferrocene used was of MERCK make. In the present study thin films of pure PVK and ferrocene doped were grown by isothermal solution casting technique. The PVK and PVK doped with Ferrocene, is soluble in chloroform, dichloromethane, dioxan, Dichlorobenzene and pyridine. In this study chloroform (AR-Grade) was used as a solvent for preparation of thin films. The thickness of film varies was monitored as per selection of concentration of solution. The solution was prepared in a glass beaker by first dissolving 100mg PVK in 2ml chemically pure chloroform at

room temperature and this was continuously stirred with a Teflon-coated magnetic stirrer for 30 minute. Thereafter it was stirred and heated to 40°C to yield a homogeneous solution. For maximum dispersion, solution was stirred at a constant temperature approximately for 2 to 3 hours. The thin films of polymer composite (PVK & Ferrocene), were prepared in the laboratory by weight percent method, with an accuracy of 0.0001g, Electronic single pan balance, Adiardutt-180 was used for weighing purpose, 99mg of PVK along with 1mg of ferrocene was dissolved in 2ml chloroform (AR-Grade).

The solution was kept at constant 40°C temperature for two hours to allow polymer to dissolve completely to yield a clear solution. An optically flat glass plate thoroughly cleaned with hot water and then with acetone was used as a substrate. To achieve perfect leveling and uniformity in the thickness of the film, a pool of mercury was used in a glass tray in which glass plate was freely floating [17].

The solution was poured on the glass plate and allowed to spread uniformly in all directions on the substrate. The whole assembly was placed in a dust free chamber maintained at a constant temperature 40°C. In this way, the film was prepared by isothermal evaporation technique [18].

The film was subjected to drying for 12 hours at constant 40°C temperature, and for another 12h at room temperature to remove traces of solvent. For obtaining pinhole free and smooth film, precaution was taken to reduce the rate of vaporization, because solvent chloroform has high rate of vaporization, so for controlling it, whole assembly (tray filled with mercury and solution poured glass plate) was partially covered with another glass plate. This resulted in slow vaporization rate of chloroform solvent and after some time a smooth pinhole free uniform thin film was obtained. Finally the film was removed from glass plate. It was cut into small pieces of suitable size, which were washed with ethyl alcohol to remove the surface impurities and the dried films were ready for different studies.

## 2.2 Experimental procedure

DC-Conductivity measurement experimental setup configuration, consist of high voltage power supply (EHT-11), Digital Picoammeter (DPM-111), digital temperature controlled oven (temperature range room temp. to 250°C), sample holder, variac (for current controlling), circular disk shaped silver, aluminum electrodes, conducting paste, Teflon coated crocodile switch attached leads. For better results, a well earthing system is required. Experimental setup assembly is shown in figure (2.2). All measurements are taken at constant temperature (313 to 393 K) with step of 10 K, as a function of voltage 5 to 230 V for each sample.

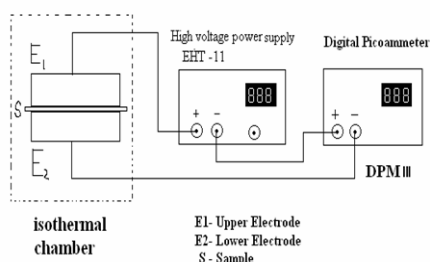


Fig.(2.2):Experimental Setup for DC-Conductivity

## 3 Results

### 3.1 Current-voltage characteristics

The isothermal I-V characteristics,  $\ln I$  vs  $\ln V$  plots of ferrocene doped poly(9-vinylcarbazole) (PVK) thin films at various temperatures shown in figure (3.3), exhibit almost similar nature for all temperatures from 40-120°C. I-V characteristics curves show two distinct parts, one at low field region (1- 14 kV/cm or 5 – 70 Volts) and other at high field region (14 – 46 kV/cm or 70 – 230 Volts). In these two regions, the curve exhibits approximate linear relationship, separately. Figure (5.3) exactly show that the magnitude of current increases with applied field, from 313° K to 343° K, rather slowly but from 363° K to 393° K current vs voltage curves were more dispersive.

### 3.2 Schottky Plots

Figure (3.4), shows the variation of current density as a function of square root of electric field at different temperatures for ferrocene doped poly (9-vinylcarbazole) (PVK) thin films. All plots show the similar nature ins temperature range 3130 K to 3930 K. Current density increases with applied electric field at different temperatures. These plots show perfect linearity in higher field region.

### 3.3 Poole-Frenkel Plots

Figure (3.5), show the Poole-Frenkel plots in the form of logarithm of conductivity ( $\ln \sigma$ ) Vs square root of electric field ( $E^{1/2}$ ) in the temperature range 3130 K to 3930 K for ferrocene doped poly (9-vinylcarbazole) (PVK) thin films. All the curves display similar nature showing a decreasing trend in the beginning and increasing afterwards. At given temperature range all curves show the linearity at higher field with positive slope, but at some points show deviations from linearity.

### 3.4 Fowler-Nordheim Plots

Fowler-Nordheim plots in the form of  $\ln J/V^2$  Vs  $1000/V$  plots is expected to be a linear straight line relation with a -ve slope. In present case Figure (3.6),  $\ln J/V^2$  Vs  $1000/V$  plots, show nearly straight lines with a +ve slope for higher as well as lower values of V. All the curves display similar nature in the temperature range (313 – 393° K).

### 3.5 Arrhenius Plots

Variation of conductivity with temperature at different fields show Arrhenius plots, in the form of  $\ln \sigma$  Vs  $103/T$  is shown in figure (3.7). All plots show temperature dependent conductivity. All curves show similar nature with positive slope, their slopes give the corresponding values of activation energy of ferrocene doped poly (9-vinylcarbazole) thin film. All curves are of similar nature with nearly similar slopes.

### 3.6 Activation energy Plot

The variation of activation energy with field is shown in Figure (3.8) for ferrocene doped poly (9-vinylcarbazole) (PVK) thin film samples. Plot displays decreasing trend with field.

## 4 Discussion

The observed behaviour of I-V characteristics shown non-linearity with applied voltage and does not follow a

power law,  $I = kV^m$ , where  $k$  and “ $m$ ” are constants. The increasing trends of current with temperature exhibited the negative resistance temperature coefficient, which proves the semiconductor nature of ferrocene doped poly(9-vinylcarbazole) material. At low field (0.9 – 10.9 kV/cm) the value of “ $m$ ” is less than or nearly equal to unity, but at high fields the value of “ $m$ ” reaches the value greater than unity or equal to 1.5, approximately for all temperatures. This type of behaviour shows that in lower fields, Ohm’s law is obeyed and the probability of space charge limited conduction recommended at higher field.

Regarding space charge limited conduction; it follows that electrical conduction may occur through the movement of either electrons or ions. The polymeric subgroup falls at low conductivity end. In most polymeric materials it is very difficult to observe any electronic conductivity and the observed conductivity may be due to the movement of adventitious ions. Because of feeble charge carrier density, space charge limited conduction seems to be a remote possibility.

The other likely processes of conduction at high fields are tunneling or Fowler-Nordheim mechanism [19], or field emission and field enhanced thermoionic emission over an interfacial barrier (Richardson-Schottky mechanism)[20-22] or from localized coulombic traps within the polymer matrix ( Poole-Frenkel mechanism) [23].

In present case, the  $\ln(J/V^2)$  vs  $1000/V$  plots for ferrocene doped poly(9-vinylcarbazole) (PVK) sample are presented in figure (5.6), which are nearly straight lines with a +ve slope for higher as well as lower values of applied voltage, indicating the absence of tunneling current as suggested by Fowler-Nordheim relation which requires straight line with negative slope. In this case the film thickness was very high (55  $\mu\text{m}$ ), the conduction mechanism by tunneling is ruled out, which requires the

film thickness to be very thin ( $\leq 50 \text{ \AA}$ ).

Let us subject Richardson-Schottky and Poole-Frenkel mechanism on trial. The  $\ln J$  vs  $E^{1/2}$  Schottky plots of ferrocene doped PVK show perfect linearity above high field region shown in figure (3.4). This show that the linear behaviour of the  $\ln J$  vs  $E^{1/2}$  plots may be due to electronics-type conduction i.e. the conduction process may be governed by Richardson-Schottky (RS) or Poole-Frenkel (PF) mechanism. To determine the actual conduction mechanism, the value of  $\beta$ -factor, at different temperatures, calculated from the slope of plots of  $\ln J$  vs  $E^{1/2}$  figure (3.4), were compared with the theoretically calculated value of  $\beta$ , based on the assumption that one of the mechanisms was operating. The theoretical expression for  $\beta$  according to Poole-

Frenkel mechanism is  $\beta_{PF} = \left(\frac{e^3}{\pi\epsilon_0\epsilon}\right)^{1/2} J(\text{m/V})^{1/2}$  or  $\beta_{PF} = \left(\frac{e}{\pi\epsilon_0\epsilon}\right)^{1/2} eV(\text{m/V})^{1/2}$ . Theoretical value of  $\beta$ , at

dielectric constant of ferrocene doped PVK,  $\epsilon = 3$ ,  $\beta_{PF} =$

$$\left(\frac{e}{\pi\epsilon_0\epsilon}\right)^{1/2} = 4.38 \times 10^{-5} \text{ and } \beta_{RS} = \frac{\beta_{PF}}{2} = 2.19 \times 10^{-5} \text{ has}$$

been calculated and given in table (3.1). The experimental value of  $\beta$  obtained from the slopes of plots  $\ln J$  vs  $E^{1/2}$  are also given in table (3.1). For experimental values of  $\beta$  were found out with the help formula,  $\beta = \text{Slope} \cdot kT$ , where the value of Boltzmann constant  $k = 8.615 \text{ eV/degree Kelvin}$ . Experimental values of  $\beta$  for temperature range (313 to 393<sup>o</sup> K) are found out to be  $3.48 \times 10^{-5}$  to  $5.11 \times 10^{-5}$ . In present case, the experimental values of  $\beta$  given in table (3.1), were close to the theoretically arrived values of  $\beta_{PF}$  based on the assumption that P-F was the particular mechanism that was operating. To get the supportive results for specifying the conduction mechanism, the effect of nature of different electrode materials like aluminum and silver was studied. The current remains practically unchanged when polarities are reversed. This is suggestive of Poole-Frenkel mechanism, which does not depend on the potential barriers between the electrode and the bulk of the solid. We observed no considerable change in the current on using the asymmetric structure of the electrodes of different work functions. This justifies that the conduction mechanism is essentially the Poole-Frenkel type which is known to be electrode independent mechanism.

Thus we found that the variation of the current density with the square root of the applied electric field for Al-film-Al sandwich structure is independent of the polarities of different electrodes. The theoretical values show a close relationship with the experimental values for this mechanism at higher field and the linear positive slope indicates that the Poole-Frenkel mechanism governs the conduction mechanism in ferrocene doped poly (9-vinylcarbazole). **El Tayan and Khogali [24]**, found the similar results with poly (9-vinylcarbazole) doped with ferric chloride.

This mechanism is also justified by the Poole-Frenkel plots for the complex samples as shown in figure (3.5). These plots are characterized and justified by the linearity of

$\ln \sigma$  versus  $E^{1/2}$  plots with positive slope using equation

$$\sigma = \sigma_0 \exp\left[\frac{\beta_{PF} E^{1/2}}{2kT}\right] \text{ or } \ln \sigma = \ln \sigma_0 + \left[\frac{\beta_{PF} E^{1/2}}{2kT}\right].$$

In the present case the linear positive slope indicates that the Poole-Frenkel mechanism is operative in the conduction process in ferrocene doped poly (9-vinylcarbazole) films.

In present case Richardson-Schottky conduction mechanism has been rejected because the experimental value of  $\beta_{RS}$ , does not tally with the theoretical value of  $\beta$ .

The temperature dependence of conductivity of poly (9-vinylcarbazole) doped with ferrocene thin film is presented in the form of Arrhenius plots shown in figure

(3.7),  $\ln \sigma$  versus  $10^3/T$ , plots show nearly straight line

with negative slope. From the slope of straight line, the activation energy is calculated using equation

$$\sigma = \sigma_0 \exp\left(\frac{-E_{ac}}{kT}\right) \quad \text{or} \quad \ln\sigma = \ln\sigma_0 + \frac{-E_{ac}}{kT},$$

where  $\sigma_0$ , is the maximum conductivity and  $E_{ac}$  is the activation energy. Activation energy is found to be in between 0.207 to 0.195 eV and may be due to the typical electronic conduction [25], as the values less than 0.8 eV are normally considered to be due to electronic conduction mechanism, while the activation energies above 1 eV, are attributed to ionic conduction.

Figure (3.1) shows the AFM images of pure and ferrocene doped PVK polymer. The smoothness of the film surface increases with doping concentration. Figure (3.2) shows the X-ray diffraction analysis of pure and ferrocene doped PVK, prove amorphous nature of material.

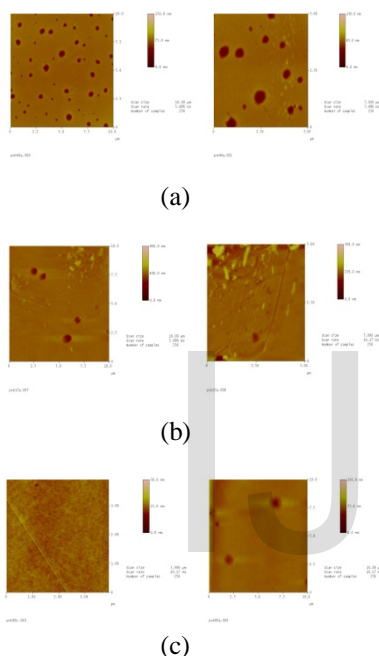


Fig.(3.1): (a) AFM of Pure PVK thin film (b) AFM of 1% ferrocene doped PVK (c) AFM of 2% ferrocene doped PVK.

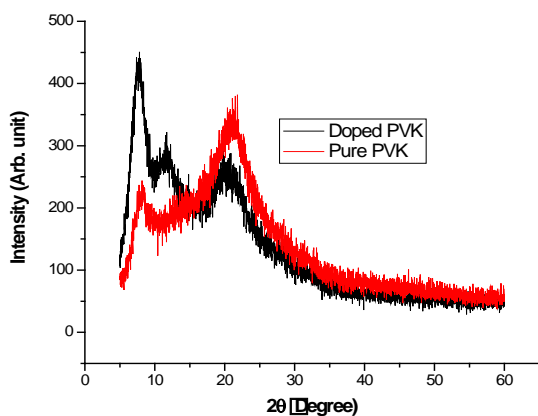


Fig.(3.2): X-ray diffraction pattern of pure and ferrocene doped PVK thin films.

Table (3.1): Comparisons of theoretical and experimental value of  $\beta$  for 2% ferrocene doped PVK thin film material

Temp. (K)	$\beta_{RS}$ (Theoretical) $V^{-1/2} m^{1/2}$	$\beta_{PF}$ (Theoretical) $V^{-1/2} m^{1/2}$	$\beta$ (Experimental) $V^{-1/2} m^{1/2}$
313	$2.19 \times 10^{-5}$	$4.38 \times 10^{-5}$	$3.48 \times 10^{-5}$
323	$2.19 \times 10^{-5}$	$4.38 \times 10^{-5}$	$3.73 \times 10^{-5}$
333	$2.19 \times 10^{-5}$	$4.38 \times 10^{-5}$	$3.76 \times 10^{-5}$
343	$2.19 \times 10^{-5}$	$4.38 \times 10^{-5}$	$3.93 \times 10^{-5}$
363	$2.19 \times 10^{-5}$	$4.38 \times 10^{-5}$	$4.47 \times 10^{-5}$
373	$2.19 \times 10^{-5}$	$4.38 \times 10^{-5}$	$4.46 \times 10^{-5}$
383	$2.19 \times 10^{-5}$	$4.38 \times 10^{-5}$	$4.95 \times 10^{-5}$
393	$2.19 \times 10^{-5}$	$4.38 \times 10^{-5}$	$5.11 \times 10^{-5}$

Table (3.2): Activation Energy of 2% ferrocene doped PVK thin film material

Voltage (Volts)	Activation Energy (eV)
100	0.20704
120	0.20196
140	0.20578
160	0.19996
180	0.19998
200	0.1957
220	0.195

Table (3.3): Slope "m" of 2% ferrocene doped PVK thin film material

Temp. (K)	Slope (5-60 V) or Low field (0.9-10.9) kV/cm	Slope (60-230 V) or High field (10.9-41.8) kV/cm
313	1.08	1.52
323	0.97	1.48
333	1.01	1.37
343	1.02	1.29
353	0.98	1.3
363	0.9	1.2
373	0.78	1.06
383	0.8	1.12
393	0.68	1.01



thin film.

(POOLE-FRENKEL PLOTS)

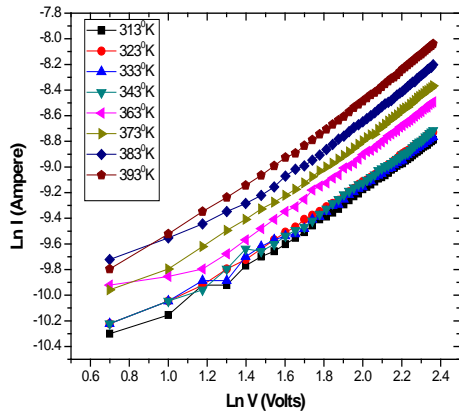


Fig 3.3: Variation of current (I) as a function of voltage, for 2% ferrocene doped PVK thin film.

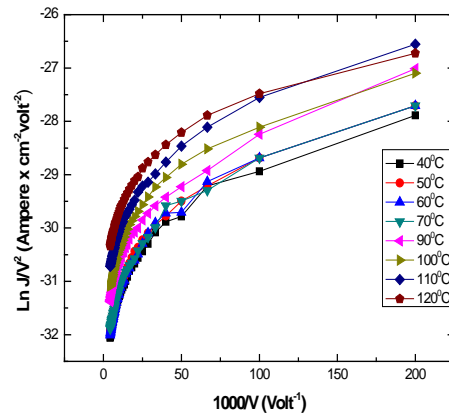


Fig 3.6: Variation of conductivity ( $\sigma$ ) as a function of square root of electric field for 2% ferrocene doped PVK thin film.  
 (FOWLER-NORDHEIM PLOTS)

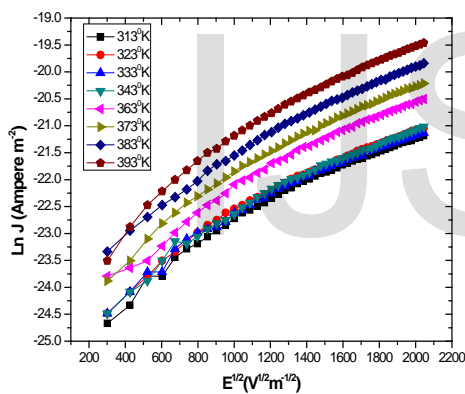


Fig 3.4: Variation of current density (J) as a function of square root of electric field for 2% ferrocene doped PVK thin film.

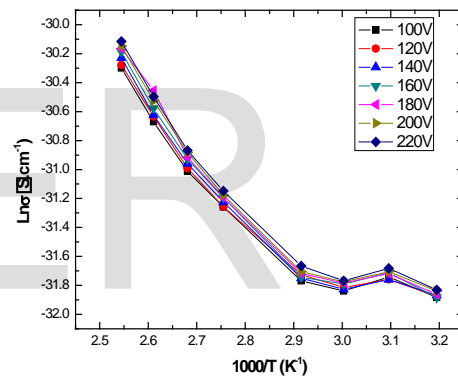


Fig 3.7: Variation of logarithm of conductivity ( $\sigma$ ) as a function of inverse of temperature for 2% ferrocene doped PVK thin film.

(SCHOTTKY PLOTS)

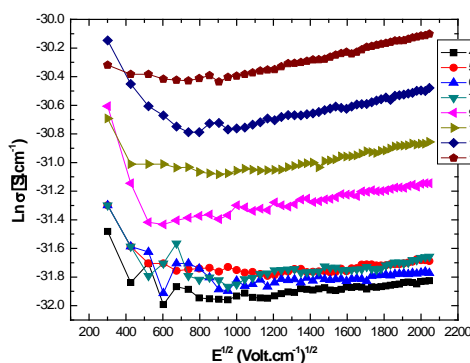


Fig 3.5: Variation of conductivity ( $\sigma$ ) as a function of square root of electric field for 2% ferrocene doped PVK thin film.

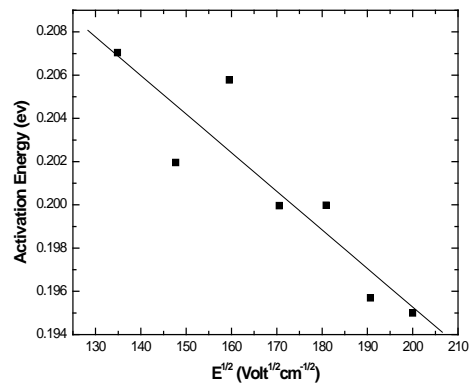


Fig.3.8: Activation Energy ( $E_a$ ) vs Square root of electric field for 2% ferrocene doped PVK thin film.

## 5 Conclusions

After studying electrical conduction with doped and pure samples, it is suggested that-

(i) In the lower field region (0.9 – 10.9 kV/cm) conduction through metallic electrode sandwich ferrocene doped PVK thin films obeys the Ohm's law.

(ii) At high field region (10.9 – 40.8 kV/cm) conduction process is bulk limited and electrode independent, governed by Poole-Frenkel mechanism.

(iii) The activation energy for DC conduction is about 0.207-0.195 eV, which is suggestive of typical electronic conduction.

(iv) The presence of ferrocene molecules in poly (9-vinylcarbazole) enhances conductivity and 2% ferrocene doping was optimum. The conductivity of pure poly (9-vinylcarbazole) (PVK) thin films is reported to be very weak.

(v) The enhancement in conductivity due to formation of charge transfer complexes (C-T-C) between ferrocene and poly (9-vinylcarbazole) has been attributed to the creation of excess charge cloud and formation of localized levels.

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