

SYNTHESIS, STRUCTURE AND ELECTRICAL PROPERTIES OF POLY(PHENYLENE VINYLENE) FILM DOPED WITH FERRIC CHLORIDE*

LI Wenguang (李文广) and WAN Meixiang** (万梅香)

(*Institute of Chemistry, Academia Sinica, Beijing 100080*)

ABSTRACT

Poly(phenylene vinylene) (PPV) film was synthesized via a soluble precursor polymer. Strong fluorescence at 500–600 nm was observed in both precursor and PPV film. Room-temperature conductivity of PPV film doped with FeCl_3 depends on the elimination temperature, the concentration of FeCl_3 and doping time. The maximum conductivity of doped PPV at room-temperature can reach about $40 \text{ S}\cdot\text{cm}^{-1}$. The temperature dependence of conductivity was controlled by 1D-VRH (1 Dimension Variable Range Hopping) model with T_0 value of $3.9 \times 10^3 \text{ K}$. Non-Ohmic conductivity resulting from Schottky effect was observed and the value of converted voltage from Ohmic region into non-Ohmic region at the current-voltage characteristic was found to be dependent upon the work function of electrodes.

INTRODUCTION

Poly(phenylene vinylene) (PPV) is a typical conducting polymer like polyacetylene (PA), polypyrrole (PPY), polythiophene (PTH) and polyaniline (PANI). Compared with those conducting polymers, PPV has attracted much attention because of its unique properties. Firstly, PPV can perform both p-type^[1–5] and n-type doping^[1,6] like PA, whereas, most other conducting polymers, such as PPY, PTH and PANI, can only carry out p-type doping. Thus, PPV film can form p-n junction, which can be used as rectifying diode. Secondly, most conducting polymers, such as PA, PPY, PTH and PANI were usually synthesized directly from their monomers, and the resulting conducting polymers were insoluble in common organic solvent. Instead, PPV was synthesized by thermal treatment of its precursor polymer^[7],

* This research was financially supported by the National Natural Science Foundation of China and the Chinese Academy of Sciences

** To whom the correspondence should be addressed

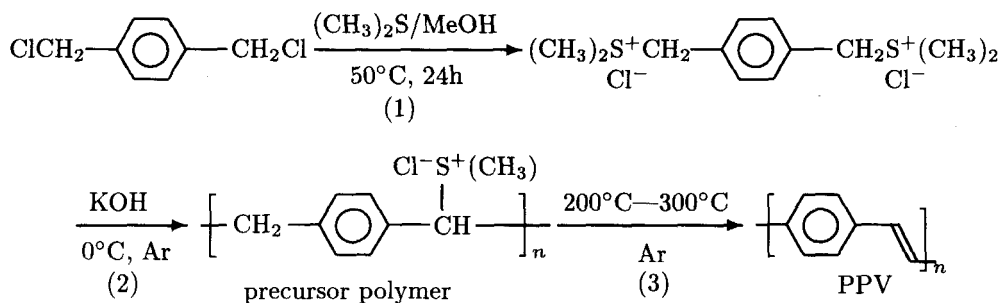
Received January 16, 1996

which is soluble in water or organic solvent. As a result, the precursor polymer can be easily purified, modified or stretched before the formation of PPV, and consequently the properties of PPV can be modified indirectly. Thirdly, PPV is a good electroluminescence material for light emitting diode (LED)^[8-13], which can be used in display technology. In comparison with inorganic LED, LED made of PPV shows the following advantages: (1) The fabrication of LED is relatively simple, (2) the emission color can be adjusted by using different conjugated structure, copolymer or polymer blend^[8,9,11], thus the full spectra of color (red, yellow, green and blue) for such polymer LED can be made, and (3) it is possible to make flexible LED with larger size. However, the LED made of PPV still faces a main difficulty that the life of LED and its light emitting efficiency^[8-10] are poor. Based on the emission mechanism, the emission process for such LED is mainly controlled by the following parameters: the injection of charge carriers such as electron or hole from electrode to semiconductor, which is determined by the work function of electrode and semiconductor, transportation of electrons and holes in semiconductor, and the efficiency of the combination of electrons and holes. It is presumed that all these are related to the conduction and transportation properties of charge carriers. Therefore, it is necessary to investigate the electrical and transportation properties of PPV in more detail.

In this article, PPV was synthesized via thermal treatment of soluble precursor polymer, and was doped with FeCl₃. The structure of resulting precursor polymer and PPV was characterized by elemental analysis, IR, XPS, UV-Vis. spectra, fluorescence spectra, X-ray diffraction, and SEM. The electrical properties of PPV doped with FeCl₃ were measured as a function of elimination temperature, doping time, and the concentration of FeCl₃. Besides its conduction mechanism was discussed.

EXPERIMENTAL

PPV was synthesized with a method reported by Lenz et al.^[7]. The procedure of PPV synthesis is given as follows:



The precursor polymer solution obtained from reaction (2) was purified by dialysis in water, then it was cast on glass substrate to form precursor film. The precursor film was treated at temperature between 180 and 380°C in Ar atmosphere for about 3 h. A free standing film with 10–30 μm in thickness was obtained. The resulting PPV film was doped with a solution of anhydrous FeCl_3 in dry CH_3NO_2 . The concentration of FeCl_3 solution varied between 0.2 mol·dm⁻³ and 0.62 mol·dm⁻³. PPV was characterized with IR spectra (Bruker, IFS-113 V), XPS (Kratos, ES-300), UV-Vis. spectra (UV-3100 spectrophotometer), fluorescence spectra (Hitachi, MPF-4), X-ray diffraction (M-18 XHF), and SEM (Hitachi, S-530). The conductivity of PPV film doped with FeCl_3 at room-temperature was measured by four probe method, using Keithley 196 SYSTEM DMM Digital Multimeter, and ADVANTEST R6142 Programmable DC voltage/current Generator as current source. The temperature dependence of conductivity was measured at temperatures between 150 and 300 K. The current-voltage (I-V) characteristic at room-temperature was measured with different electrodes separately. In the measurement of I-V curve, PPV film was sandwiched between two Al or Cu electrodes, which were made by vacuum evaporation.

RESULTS AND DISCUSSION

1. Structural characterization

It was found that the composition of PPV film depends on the elimination temperature. The elimination reaction from precursor to PPV film took place at temperature between 150 to 250°C. Two strong peaks at 2913 and 1421 cm⁻¹ in the IR spectra of precursor polymer which can be assigned to stretching and bending vibration of C—H bond of CH_3 and CH_2 groups^[14] were observed, and the intensity of these peaks decreases with the increase of the elimination temperature. Moreover, the peaks at 3021 and 960 cm⁻¹ were observed in PPV, and can be assigned to stretching and bending vibration of C—H bond of *trans*-ethylene^[14], respectively. The intensity of these two peaks increases with increasing the elimination temperature. The variation of IR spectra with the elimination temperature suggests that the degree of conjugation of PPV film is enhanced after thermal treatment, which is consistent with the results reported by Murase et al.^[4]. Furthermore, it also supports that the elimination temperature higher than 210°C is enough for conversion from precursor into PPV film, which is in agreement with the results of elemental analysis.

UV-Vis. spectra of the precursor solution, precursor film, and PPV obtained at different elimination temperature are shown in Fig. 1. In UV-Vis spectra of the

precursor solution, two peaks at 229.0 nm and 317.0 nm were observed. The intensity of the former is stronger than that of the latter, and the peak at 317.0 nm is assigned to the longer conjugated structure in the precursor polymer. This indicates that there are a few phenylene vinylene units in the precursor solution. For the precursor film, there is a peak at 326 nm, in comparison with the spectra of precursor solution, which shows a red shift and whose intensity is relatively enhanced. This corresponds to a color change from colorless precursor solution to yellow-green precursor film, and indicates the increase of longer conjugated structure in precursor film. After thermal treatment, three peaks at 200, 240 and 360 nm were observed. The position of the peak at 200 nm, which is the absorption of benzene ring, is independent of the elimination temperature. In addition, a red shift of the peak at 360 nm, which is related to conjugated degree, was observed when the elimination temperature increased, and it indicates that the conjugated length of PPV is enhanced by thermal treatment.

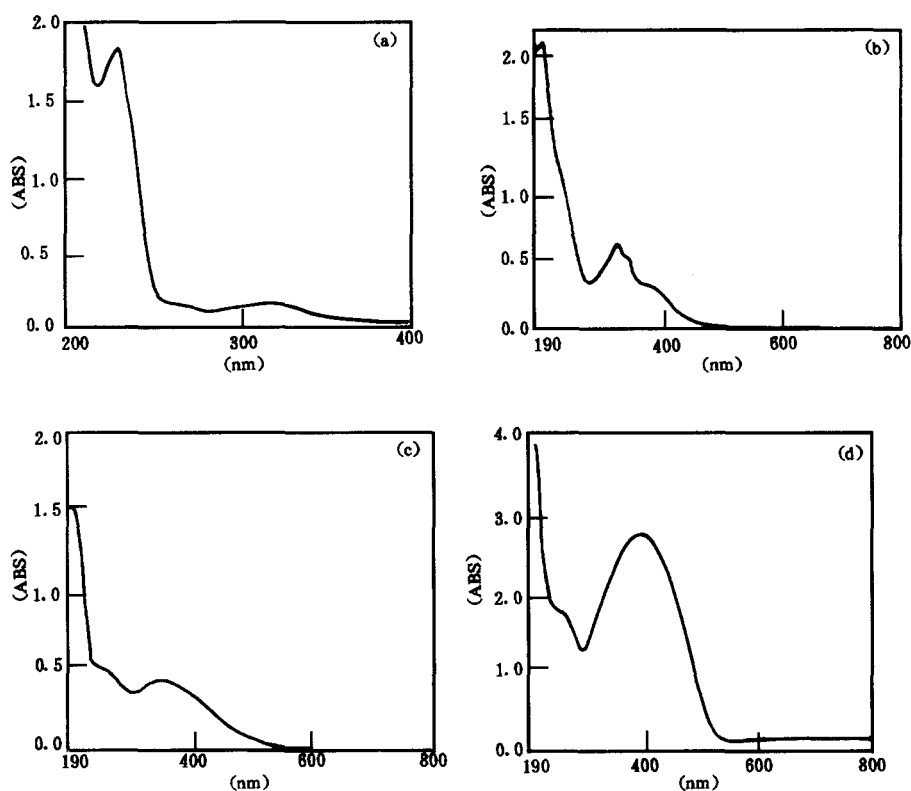


Fig. 1 UV-Vis. spectra for precursor polymer and PPV obtained by thermal treatment at different temperatures

(a) precursor solution; (b) precursor film; (c) PPV, $T_e = 250^\circ\text{C}$; (d) PPV, $T_e = 340^\circ\text{C}$

In our experiment, a strong fluorescence was observed in both precursor polymer and PPV film as shown in Fig. 2. For the precursor solution, there is a peak at 370 nm in the emission spectra of fluorescence. For the precursor films, however, the emission peak becomes broader and appears at 500—520 nm, as if there are two peaks at 500 nm and 520 nm overlapping each other, and their positions are independent of the excitation wavelength. The fluorescence peak of PPV film is similar to that of precursor film, but it splits into two clear peaks at 500 and 520 nm, whose position is also independent of the excitation wavelength and elimination temperature. Therefore, it is reasonable that the fluorescence in both precursor film and PPV may be emitted by the same structure. However, the origin of fluorescence observed in both precursor polymer and PPV film is not yet understood. The intensity of fluorescence diminishes obviously at high elimination temperature ($T_e = 340^\circ\text{C}$). The reason for this may be due to some defects on the chain of PPV, which was produced by thermal treatment at high temperature, and trapped the exciton. Moreover, the fluorescence can be quenched by doping process.

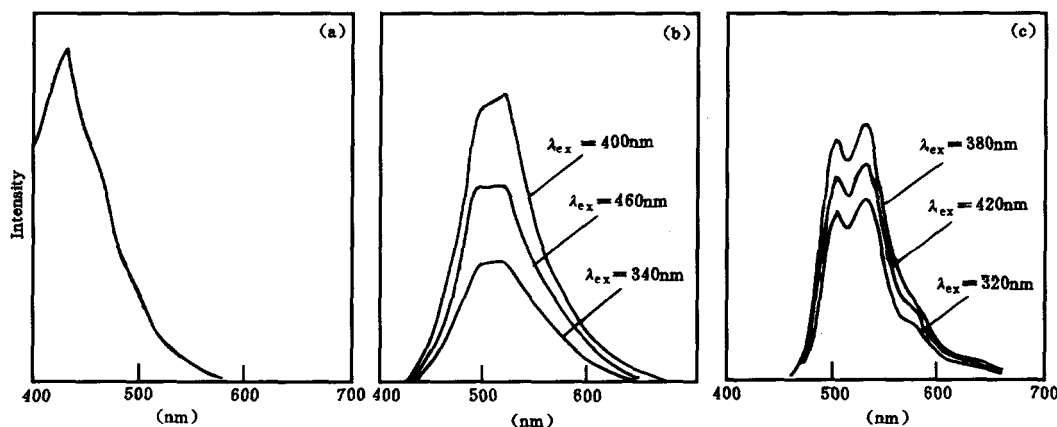


Fig. 2 Fluorescence spectra of precursor polymer and PPV (a) precursor solution; (b) precursor film; (c) PPV, $T_e = 250^\circ\text{C}$; (T_e is the elimination temperature)

2. Doping of PPV film with FeCl_3

The color of PPV film changed from yellow to dark-blue after it was doped with FeCl_3 . By means of XPS, the Fe and Cl elements were detected in doped PPV, and the content of Cl element was much higher than that of Fe element. The binding energy of $\text{Fe}_{2p3/2}$ is 711.6 eV, which corresponds to Fe^{3+} . In addition, Cl_{2p} consists of two peaks at 200.6 eV and 198.8 eV, respectively, which may be attributed to Cl^- and Cl binding with FeCl_3 to form FeCl_4^- . Thus, it is reasonable to postulate that both Cl^- and FeCl_4^- are counter-ions in the doped PPV film, FeCl_4^- as counter-ion

has been demonstrated by Mössbauer measurement^[15]. There is another evidence to demonstrate that the PPV film can be doped with FeCl_3 ($[\text{FeCl}_3]=0.5 \text{ mol}\cdot\text{dm}^{-3}$) because the electronic structure of PPV was changed after doping as shown in Fig. 3.

Before doping there are three peaks at 200, 240 and 340 nm, while the doped PPV has a new peak at 600 nm and its intensity increased with increasing doping time. Most peaks were weak after the doping time exceeding 1 minute. A corresponding change in IR spectra of PPV film was also observed after doping. Most of the characteristic peaks of PPV disappeared, instead, some new peaks at 1457 , 1318 and 1278 cm^{-1} appeared.

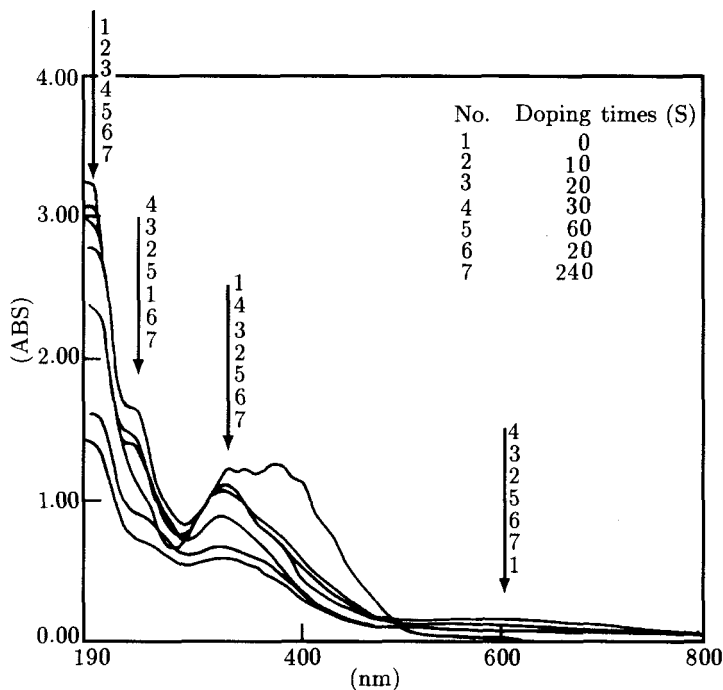


Fig. 3 Variations of UV-Vis. spectra of PPV with doping time

X-ray diffraction patterns of PPV exhibit only one broad peak at about $2\theta = 21^\circ$ ($d = 0.42 \text{ nm}$), which indicates that PPV is amorphous. After doping, the peak appears at about 18° ($d = 0.49 \text{ nm}$), and becomes broader. This suggests that the interchain distance increases after doping. On the other hand, the morphology of PPV doped and undoped is similar, and shows particles about 200–500 nm in diameter.

The conductivity of doped PPV film measured at room-temperature is dependent strongly on the elimination temperature, doping time and the concentration of FeCl_3 as shown in Fig. 4, Fig. 5 and Table 1. At low elimination temperature

($T_e < 200^\circ\text{C}$), the room-temperature conductivity of doped PPV film increases with the increase of the elimination temperature, but increases slowly with the elimination temperature at higher elimination temperature ($T_e > 200^\circ\text{C}$). This behavior is consistent with the fact that the elemental content of the doped PPV varies with the elimination temperature. As shown in Fig. 5, for different concentration of FeCl_3 , a similar variation of conductivity with doping time was observed. Conductivity exhibits a fast initial increase with doping time to reach a plateau and then decreases. The more concentrated the solution of FeCl_3 is, the faster PPV can be doped, and the lower conductivity of doped PPV can reach. The maximum room-temperature conductivity of doped PPV can reach about $40 \text{ S}\cdot\text{cm}^{-1}$ in our experiment. When the doped PPV is exposed to air, its conductivity decreases exponentially with time, and lowers to one tenth of the initial conductivity after 40 days, as shown in Fig. 6.

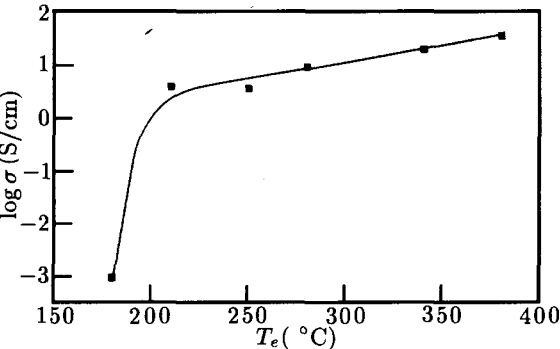


Fig. 4 Dependence of room-temperature conductivity of the doped PPV film on the elimination temperature

Table 1 Effect of concentration of FeCl_3 on conductivity of PPV doped with FeCl_3

$[\text{FeCl}_3]$ (mol·dm ⁻³)	σ_{max} (S·cm ⁻¹)	t_e (min)*
0.20	39.7	40
0.50	28.0	5
0.62	0.20	0.8

* t_e is the doping time needed to reach the maximum conductivity (σ_{max})

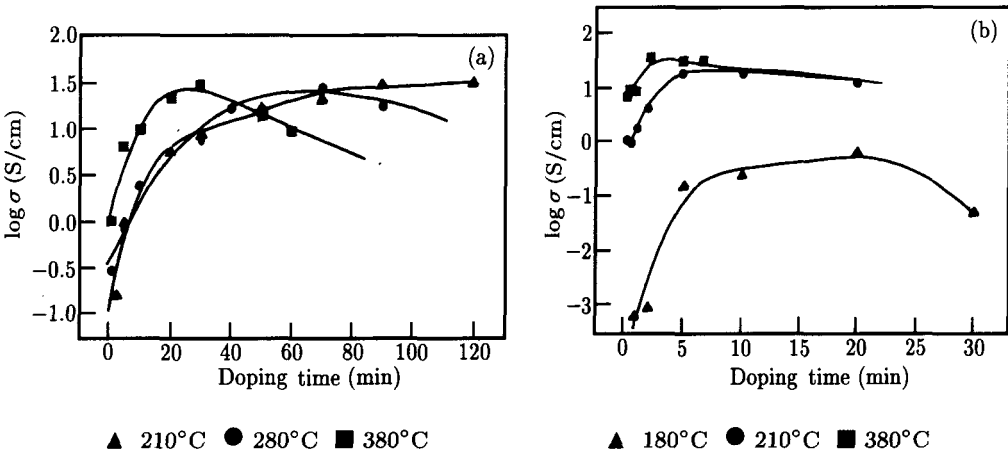


Fig. 5 Effect of the doping time on the room-temperature conductivity of the doped PPV film (a) $[\text{FeCl}_3]=0.20 \text{ mol}\cdot\text{dm}^{-3}$; (b) $[\text{FeCl}_3]=0.50 \text{ mol}\cdot\text{dm}^{-3}$

3. Electrical conduction mechanism

In order to understand the mechanism of the electrical conduction of doped PPV film, its electrical properties were measured as a function of temperature, electrical field and work function of electrode. The temperature dependence of conductivity of PPV film doped in different doping time is shown in Fig. 7. The best fit of conductivity (σ) vs. temperature (T) can be described by Mott's one dimensional Variable Range Hopping (1D-VRH) model^[16]:

$$\sigma(T) = \sigma_0 \exp \left[- \left(\frac{T_0}{T} \right)^{\frac{1}{2}} \right] \quad (1)$$

where $T_0 = 3.9 \times 10^3$ K, which was calculated from the slope of the line plotted in Fig. 7, represented the hopping energy of charge carrier. This result is different from the result published by Mertens et al.^[17].

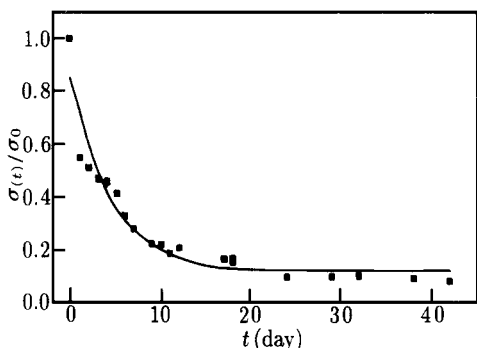


Fig. 6 Stability of PPV doped with FeCl_3 in air

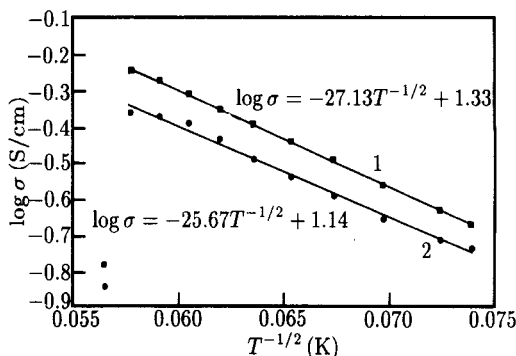


Fig. 7 Temperature dependence of conductivity of doped PPV film for different doping time

Sample 1: $[\text{FeCl}_3] = 0.20 \text{ mol} \cdot \text{dm}^{-3}$; doping time = 40 min. Sample 2: $[\text{FeCl}_3] = 0.20 \text{ mol} \cdot \text{dm}^{-3}$; doping time = 90 min.

Current-voltage characteristic of the doped PPV film is shown in Fig. 8. Non-Ohmic conducting behavior was observed in doped PPV when the applied field was higher than $10^3 \text{ V} \cdot \text{cm}^{-1}$. The converted voltage, V_t , from Ohmic into non-Ohmic conductivity depends on the work function of electrode, i.e. the value of V_t for Al and Cu electrode was estimated to be about 1.06 V and 0.64 V, respectively. It is obvious that the value of V_t for Al electrode is higher than that of Cu electrode due to the oxidation of Al in air. Non-Ohmic conductivity in the region of high applied electrical field can be expressed by Schottky effect^[18], that is

$$\sigma = \sigma_0 \exp \left(\frac{\beta}{K T l^{\frac{1}{2}}} \right) V^{\frac{1}{2}} \quad (2)$$

where $\beta = \left(\frac{e^3}{4\pi\epsilon_0\epsilon} \right)^{\frac{1}{2}}$, ϵ_0 and ϵ are the dielectric constants of vacuum and the sample, l is the thickness of sample, respectively. The β value can be calculated from the slope of $\ln \sigma$ vs. $E^{1/2}$ plot, and $\beta = 6.64 \times 10^{-5} \text{ eV (V}\cdot\text{m}^{-1})$ for doped PPV film was obtained. The Schottky effect observed from doped PPV film is the fundamental condition for LED because the injection of charge carrier from electrode into semiconductor is the first step of light-emitting.

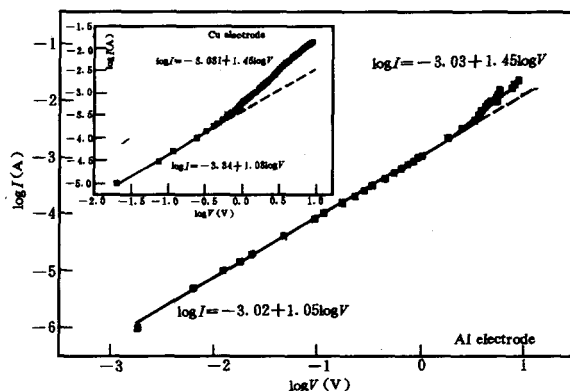


Fig. 8 Current-voltage characteristic of doped PPV film

CONCLUSION

1. A strong fluorescence between 500 and 600 nm emitted by both precursor and PPV polymer was observed.
2. The room-temperature conductivity of PPV doped with FeCl_3 depends on the eliminating temperature, concentration of FeCl_3 and doping time. The maximum room-temperature conductivity of doped PPV can reach 40 S/cm.
3. The transportation mechanism of doped PPV is mainly controlled by 1D-VRH model. The hopping energy of charge carriers was estimated to be $3.9 \times 10^3 \text{ K}$.
4. Non-Ohmic conductivity for PPV doped with FeCl_3 was observed at high applied electrical field, and the converted voltage from Ohmic into non-Ohmic conductivity depends on the work function of electrode. The observed non-Ohmic conductivity results from Schottky effect.

Keywords:

PPV; Fluorescence; Conductivity; Schottky effect; Light emitting diode (LED)

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