

STUDY OF THICKNESS EFFECT ON ABSORPTION, PHOTO AND ELECTROLUMINESCENCE SPECTRA IN ROPPV POLYMER FILMS

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Abstract. The study of EL in thin films is of vital interest both for fundamental and technological reasons. Research in case of organic polymers as the active semiconductors in light-emission has advanced rapidly, and prototype devices now meet realistic specifications for applications. The ROPPV films of various thicknesses have been prepared using solution casting technique by dissolving different amounts of ROPPV granules in DMF. Their absorption, photo and electroluminescence spectra have been studied. The films are found to be transparent in the visible region and absorption peaks are obtained only in the ultraviolet range. The thickness of polymer layer was measured by Fizeau fringes technique. The ROPPV films thicknesses were varied between 200 to 400 nm. Absorption spectra were taken by Perkin – Elmer – Lambda -12 spectrometer. Photo luminescence has been studied by monochromator. The electroluminescence (EL) of ROPPV films have been studied by sandwiching them between SnO₂ coated conducting glass plate and aluminum electrodes. Result of absorption spectra shows that the peaks are obtained only in the ultraviolet region. Thick films show only one peak at 310 nm, whereas decreasing the thickness it is divided in two or three peaks. Thin films show only one peak at 310 nm indicating the HOMO level, whereas increasing the thickness, other higher energy orbital is also revealed. The PL spectrum of ROPPV films was excited through violet filter. It has been observed that peaks are obtained at wavelength 380 nm, 450 nm, and 510 nm by violet filter. For lower thickness the PL intensity is less. The EL brightness is found to increase with increasing thickness of ROPPV emissive layer. It is observed that higher threshold voltage is required for the thicker films. The EL spectrum shows two main peaks one at 450 and the other at 510 nm. The intensity of peak at 510 nm increases linearly with the emissive layer thickness; whereas no systematic variation has been observed in the intensity of the peak at 450 nm. The results are analyzed on the basis of energy levels and recombination profile of ROPPV.

1. Introduction

Since the discovery of electroluminescence (EL) at low voltage in semi conducting polymer in 1990, considerable progress has been made in understanding the electronic and optical properties of the emissive materials. There have been several studies on the effect of solvent and annealing condition on the polymer film morphology. Few systematic studies have been made on understanding the changes in the optical properties (Burn, 1992) [1]. An alternating current thin film electroluminescent (ACTFEL) device is an electro-optic device in which electrical energy (in the form of some type of AC voltage waveform) is applied as

an input, and visible light constitutes the desired output. In this paper, we explore the absorption and electroluminescence characteristics of ROPPV films of various thicknesses.

2. Experimental

For absorption measurement films are made by solution casting technique. The absorption spectra for the various thicknesses (200 nm to 400 nm) materials studied. For recording the absorption spectra of ROPPV films, UV/VIS Perkin Elmer Lambda-12 spectrometer is used. For measurement of the absorption of the samples, several pieces of approximately the same size were cut from the grown polymer film. The polymer films were placed at the sample position and reference position was left as it is, taking air as reference. The absorption spectra of all the ROPPV films of different thickness were recorded.

The schematic diagram of the experimental set up used for the study of PL is shown in Fig. 1. The main units are Picoammeter, constant deviation spectrometer (CDS), color filters, light source, PMT and power supply (750 V). PL was excited by monochromatic light of using a mercury lamp and optical filters. The spectrum of emitted light was obtained by a constant deviation spectrograph. Photomultiplier tube was used to measure the intensity of light whose output is connected to a picoammeter.

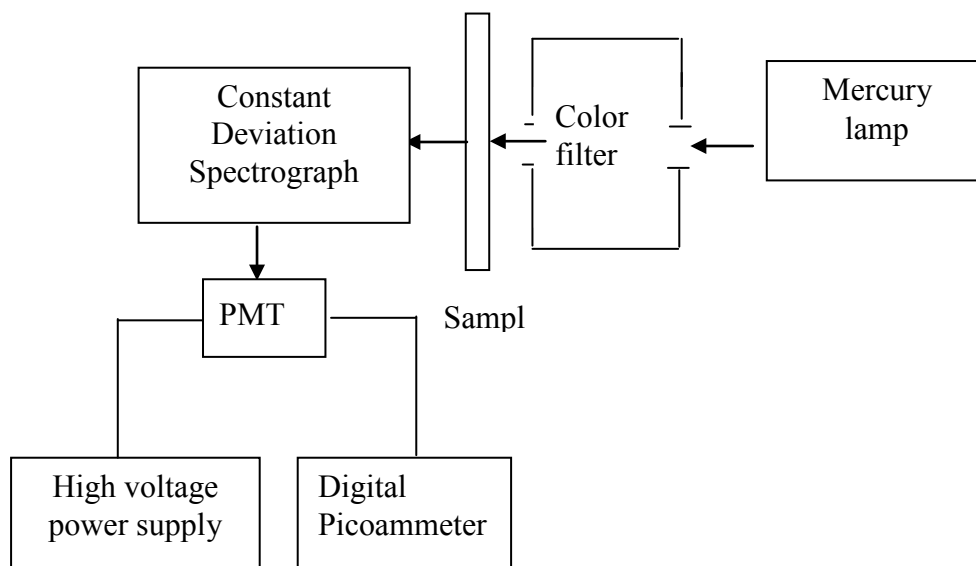


Fig. 1. PL set up diagram.

The emission spectrum was obtained with the help of CDS. By rotating the drum of CDS, the wavelength at the exit slit has been varied from 300 nm to 800 nm. The photoluminescence (PL) studies of polymer films were carried out using mercury lamp with different excitation wavelength violet filter.

The EL cell with single polymer layer was fabricated. The EL setup is shown in Fig. 2. Electroluminescence measurements were performed with the help of an audio-oscillator coupled to a wide band amplifier (for high frequency excitation). The light output was recorded by a photomultiplier tube which was operated by a high voltage power supply. The EL emission spectra were recorded by using a grating monochromator.

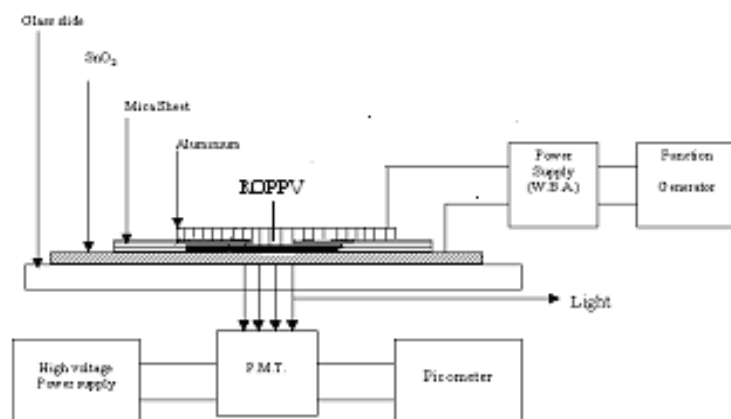


Fig. 2. Set-up for recording the emission spectra.

3. Result and Discussion

Table 1 shows that when the ROPPV granule increases in DMF, the thickness of film increases.

Table 1. Concentration and film thickness of ROPPV.

Sr. no.	Concentration (ROPPV / 10 ml DMF)	Thickness of films (Å)
1	200 mg	2473
2	300 mg	2561
3	400 mg	2862
4	500 mg	3400
5	600 mg	4012

The absorption spectra of the ROPPV films are shown in Fig. 3. The ROPPV films are found to be transparent in visible region. Result of absorption spectra shows that the peaks are observed only in the ultraviolet region. Thick films show only one peak at 310 nm indicating the HOMO level, whereas decreasing the thickness, other higher energy orbital is also revealed.

Figure 3 represents absorption spectrum for different thickness of polymer films. The changes in absorption may be related to the process involved in the formation of thin films. The ROPPV emissions are found to behave almost similar to that of other polymer like PPV, MEH-PPV, and MEH-CN-PPV. According to energy levels diagram Fig. 4, it is shown clearly the possible transitions in 600 mg film are $n-\pi^*$ (310 nm) and 400, 500 mg films shows two possible transition $n-\pi^*$ (310 nm), $\pi-\pi^*$ (280 nm), 300, 200 mg films shows three possible transitions $n-\pi^*$ (310 nm), $\pi-\pi^*$ (280 nm), $n-\sigma^*$ (260 nm) and other small peaks are not identified. It may be due to some defect or impurities. ROPPV can therefore absorb light of those different wavelengths: the pi bonding to pi anti-bonding absorption peaks at 280 nm; the non-bonding to sigma anti-bonding absorption peaks at 260 nm; the non-bonding to pi anti-bonding absorption peaks at 310 nm.

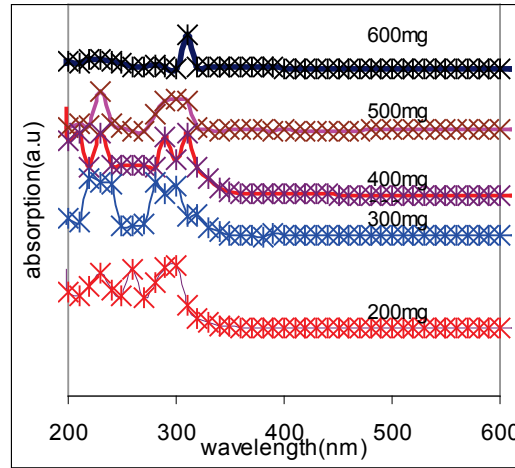


Fig. 3. Absorption spectrum for different thickness of polymer films.

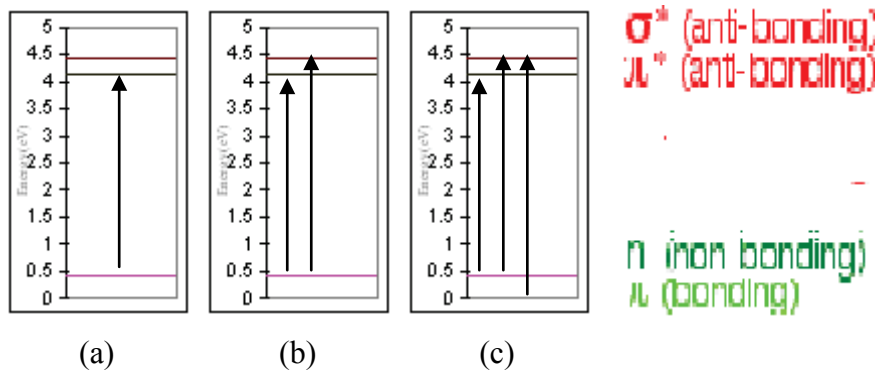


Fig. 4. (a) Energy levels for 600 mg; (b) Energy levels for 500 mg, 400mg; (c) Energy levels for 300 mg, 200 mg of ROPPV films.

The intensity and spectral content of photoluminescence is a direct measure of various important material properties as shown in Fig. 5.

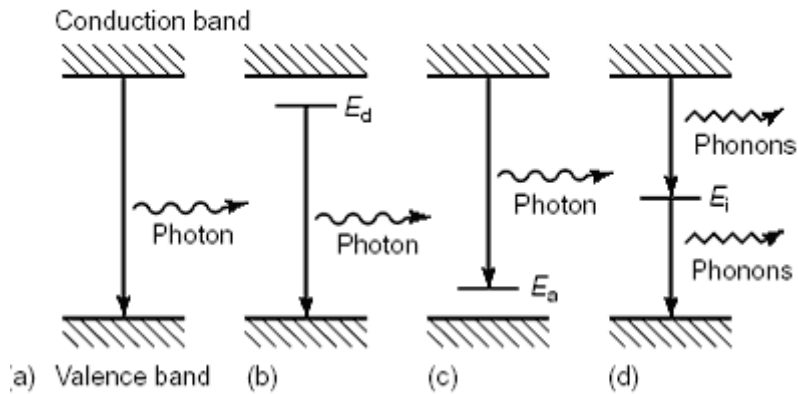


Fig. 5. (a-c) Radiative recombination paths: (a) band-to- band; (b) donor to valance band; (c) conduction band to acceptor. (d) Non-radiative recombination via an intermediate state.

Photo-excitation causes electrons within the material to move into permissible excited states. When these electrons return to their equilibrium states, the excess energy is released and may (a radiative process) or may not (a nonradiative process) include the emission of light. The PL emission originates from the recombination of the localized electrons (LE) and delocalized holes (DH) in valence band. When the applied energy increases, the LE tends to be delocalized and excited to the higher energy localized states, which leads to an increase in recombination energy. Due to the strong localization, it is generally difficult to observe the emission corresponding to the delocalized carrier's transition between band-band (BB), instead only one emission involving localized states is visible.

In the photoluminescence spectrum shown in Fig. 6, the emission peak of films observed at 380 nm, 450 nm, 510 nm may be associated with acceptor levels. However, in the ROPPV films band gap decreases due to thickness of film increases and hence the emission energy is also affected correspondingly. At higher concentration of polymer in DMF shows higher emission. Since the observed result shows a broader peak, the emission cannot be related directly to transitions. It may be related to combination of defect and also generated by more traps. Thus, both of these may correspond to transition in the energy levels. Additional peaks in the red region are observed. It should be noted that films show excess surface defects. The maximum photoluminescence (PL) appeared at 510 nm. These values are similar to those of poly (2, 5-dialoxy-p-pnylenevinylene) (ROPPV) as observed by Kalinowaski (Kalinowaski, 1998) [2]. Photoluminescence due to radiative recombination of singlet excitons is observed at energies just below the onset of the $\sigma^*-\pi^*$ absorption band at 2.25 eV. Photoinduced absorption shows bands peaking at {3.26, 2.69, and 2.25 eV}. The features at 3.26 and 2.25 eV are associated with the same excited state, which we propose is a doubly charged bipolaron, while the third at 2.69 eV is unrelated. We assign this 2.69 eV absorption to a triplet-triplet transition of a triplet exciton.

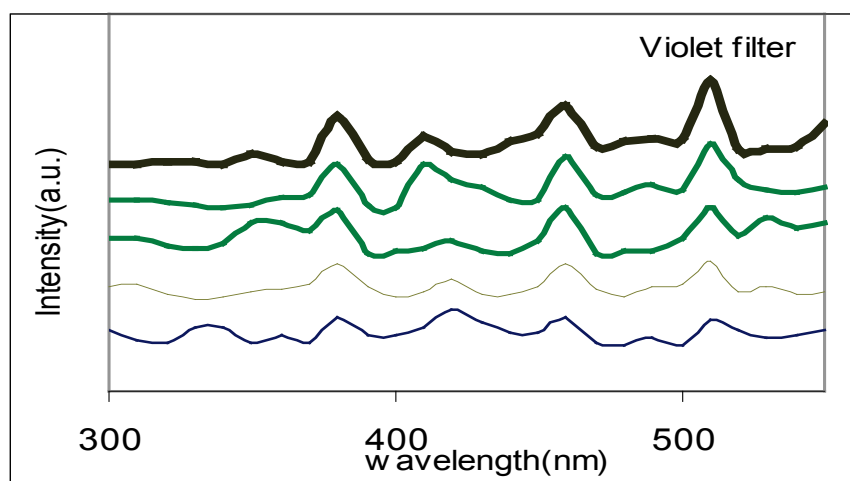


Fig. 6. Photoluminescence spectrum for different thickness of polymer films.

For different concentration of ROPPV and DMF (200 - 600 mg / 10 ml), voltage-brightness and EL spectrum are shown in Fig. 7 and Fig. 8. The EL brightness is found to increase with increasing thickness of the emissive layer seen from Fig. 7. It is observed that higher threshold voltage is required for thicker films. The thicker line indicate V-B curve for thick films and vice-versa. The threshold voltages obtain between the ranges 325 - 425 V. Initially thick films show low value of brightness after apply high voltage near 400 V it shows high brightness as shown in graph.

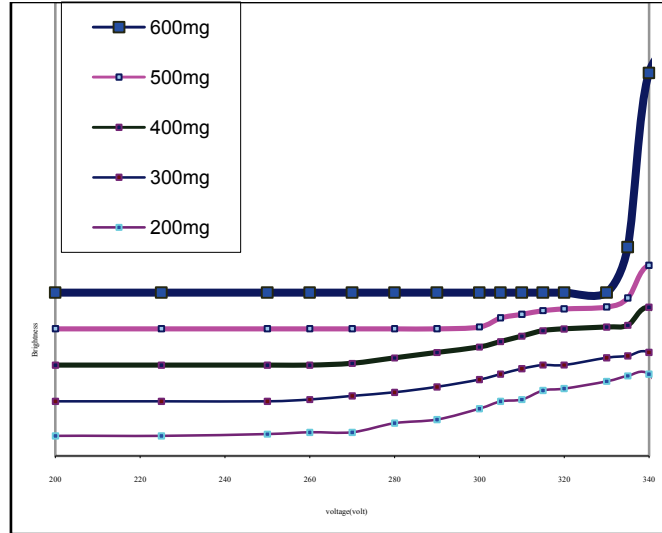


Fig. 7. Voltage - Brightness plot for ROPPV films.

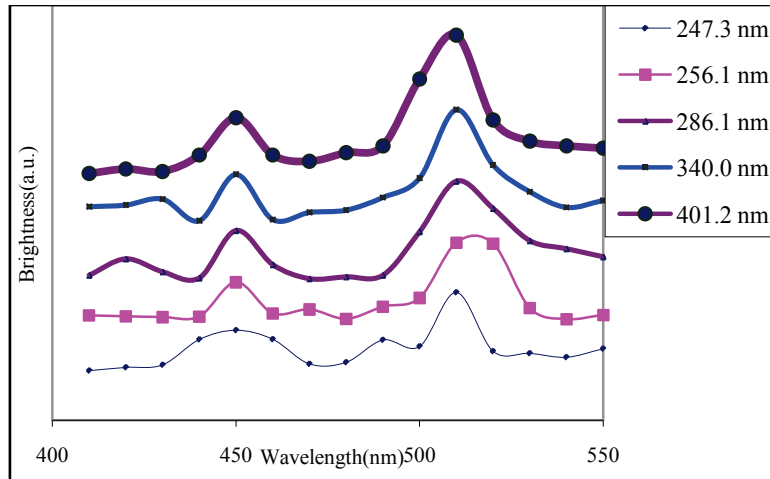


Fig. 8. EL spectrum of ROPPV films.

In the EL spectrum 450 nm and 510 nm peaks are observed at constant voltage (380 V) and frequency (1 kHz) for different thickness. When the thickness of films increases, the intensity of both peaks at 510 nm and 450 nm increases. It seems that the 510 nm emission corresponds to the direct excitation of luminescence center at higher voltage. The 510 nm peak is intense which is attributed to radiative exciton decay. The other peak is weaker. This is probably due to recombination of injected charge carriers. It has been found that the EL brightness increases with increasing thickness of the emissive layer. Above a particular threshold voltage the brightness (B) increases rapidly with increasing voltage (V) and the dependence of B on V follows the following relation:

$$B=B_0\exp (-b/V^{1/2}), \tag{1}$$

where, B_0 and b are parameters, which depend on the temperature, frequency of alternating voltage and also on the material and other details of constructing EL cell. In fact, equation (1) is based on the acceleration-collision mechanism of EL excitation.

Figure 9 shows graph between $\log B$ versus $1000 / V^{1/2}$ for sample (500 mg / 10 ml) at different frequency. We obtained a straight line with negative slope. This dependence was ractilinear when plotted in the co-ordinate $\log B$ and $V^{1/2}$. In other words, the dependance could be described by the formula $B \propto \exp(-\text{constant} / V^{1/2})$.

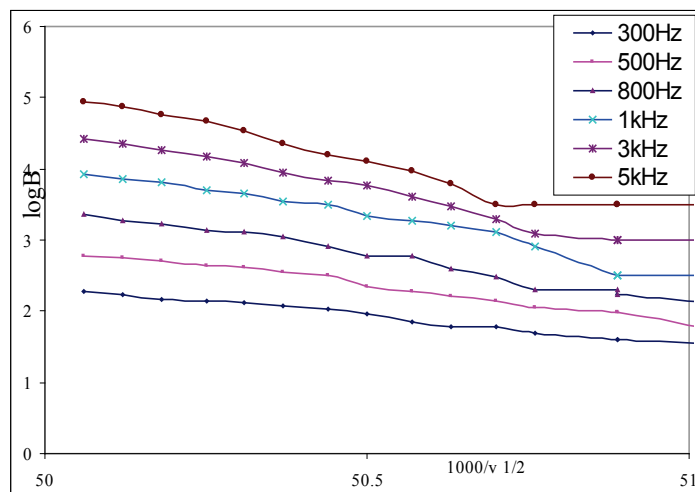


Fig. 9. Log B versus $1000 / V^{1/2}$ graph for ROPPV (500 mg / 10 ml).

This dependence can be explained by impact ionization on the assumption that the field in a film is related to the external voltage by $E \propto V^{1/2}$.

When the field is connected in a Mott-Schottky depletion barrier, the effective field is related to the external voltage by $E \propto V^{1/2}$. This is a consequence of a uniform distribution of the space charge across the barrier width, since the contact of our samples were ohmic. This results suggests the existance of Mott - Schottky barrier and indicates the mechnaism of EL excitation should be of acceleration – collision type.

It is found that the brightness of 510 nm band is less affected by the increase of thickness of the film. At lower thickness the electrons captured in traps have less chance to escape and therefore the numbers of electron taking part in the radiative transition are relatively small and hence the brightness level is low. As the thickness is increased the number of excited electron at the available frequency increase hence the brightness increases.

From the voltage-brightness curve for sample 500 mg / 10 ml DMF at different frequency shown in Fig. 10, it is seen that the EL emission starts at a threshold voltage and it increases rapidly with voltage. The EL brightness increases with increasing frequency of the applied electric field and it attains saturation at higher frequencies. The brightness does not increase linearly with the frequency for different voltages as shown in Fig. 11. Thornton, by considering that the recombination rate to be determined by field-controlled release of electrons from traps, has reported the following relation between EL brightness and frequency

$$B = N_0 f [1 - \exp(-A/f)], \quad (2)$$

where, N_0 represents constant number of the excited centers for each half cycle, A is a factor which increases with increase in voltage and f is the frequency of applied field. This formula quite satisfactorily explains the starting and the saturation parts of frequency dependence [3].

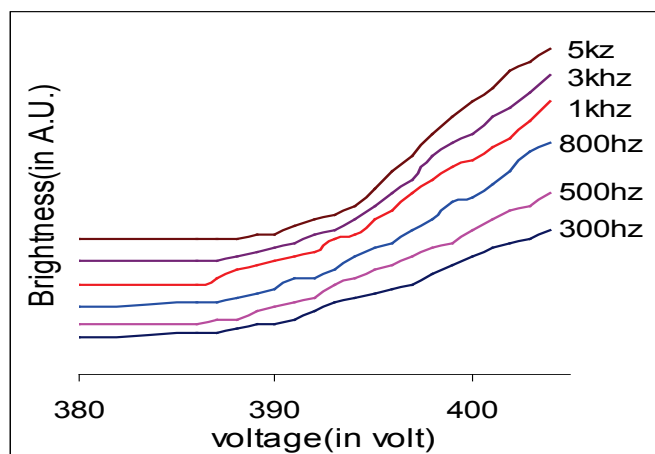


Fig. 10. Voltage and brightness graph for different frequency at thickness 340 nm of polymer film.

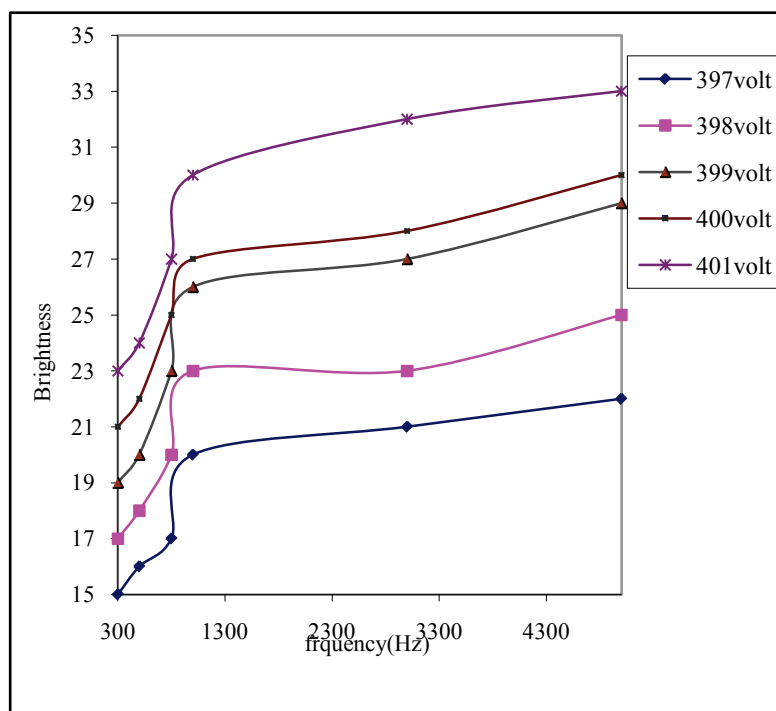


Fig. 11. F - B curve of Polymer ROPPV.

The EL brightness increases with increasing frequency of the applied electric field and it attains saturation at higher frequencies as shown in graph. At very high frequency, near to 3-5 kHz, the brightness increases slowly and attains maximum value and then falls down due to dielectric heating of samples. When the frequency increases continuously, at very high frequency the available time for the exhaustion of the trapped electron is decreased, requiring higher frequency to make the traps empty. The thickness dependent behavior at fixed frequency and voltage shows that the intensity of emission normally increases with the

increase of thickness for both transitions. The increase in EL brightness with frequency can also be understood on the basis that emptying and refilling of EL center take place more rapidly, with the increase in frequency but when time period of applied AC cycle becomes comparable with lifetime of the excited electrons, the electron does not have enough time to emerge out from trap. Therefore, the brightness will not increase linearly with the frequency. So thicker film would lead to stronger contributions from defect related luminescence emission and the actual charges present in sample determine the intensity as the emission peak [4-8]. In ROPPV sample, it is found that EL brightness decreases at very high frequency. This is probably due to emission from defect states and impurities. In the crystalline material, charge carriers can be trapped at defect site or dopant ions.

The trapped charge carriers at the surface are also affected by the presence of molecules or ions from the solute.

The total brightness and brightness of peaks 510 nm, 450 nm are found to increase with increasing thickness of the films as shown in Fig. 12. That graph also shows thickness versus threshold voltage curve, which is increasing as the thickness increases.

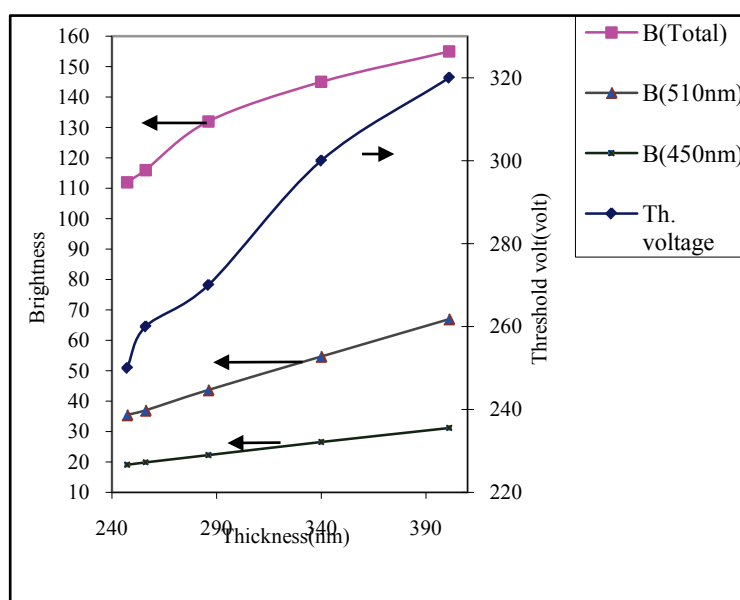


Fig. 12. Threshold voltage and brightness graph for different thickness of polymer films.

References

- [1] P.L. Burn, A.B. Holmes, A. Kraft, D.D.C. Bradley, A.R. Brown, R.H. Friend, R.W. Gymer R.W. // *Nature* **356** (1992) 47.
- [2] J. Kalinowski, G. Giro, P. Di Marco, V. Fattori, E. Di-Nicoló // *Synthetic Metals* **98** (1998) 1.
- [3] J.L. Bredas, J.P. Calbert, D.A. da Siva Filho, J. Cornil // *Proc. Natl. Acad. Sci. USA* **99** (2002) 5804.
- [4] S. Bushuk, V. Douglas, K. Kal'vinkovskaya, L. Klapshina, B. Bushuk, A. Rubinov, V. Semenov, A. Stupak // *Journal of Applied Spectroscopy* **71** (2004) 863.
- [5] Akihiko Fujii, Tetsuya Takashima, Naoki Tsujimoto, Takashi Nakao, Yuichi Yoshida, Masanori Ozaki // *Japanese Journal of Applied Physics* **45** (2006) L833.
- [6] Serap Günes, Karolina P. Fritz, Helmut Neugebauer, Niyazi Serdar Sariciftci, Sandeep Kumar, Gregory D. Scholes // *Solar Energy Materials and Solar Cells* **91** (2007) 420.

- [7] Q.L. Song, H. Yang, H.R. Wu, F.Y. Li // *Journal of Luminescence* **119-120** (2006) 142.
- [8] A. Staudte, D. Pavičić, S. Chelkowski, D. Zeidler, M. Meckel, H. Niikura, M. Schöffler, S. Schössler, B. Ulrich, P.P. Rajeev, T.H. Weber, T. Jahnke, D.M. Villeneuve, A.D. Bandrauk, C.L. Cocke, P.B. Corkum, R. Dörner // *Phys. Rev. Lett.* **98**, (2007) 073003.