

STRUCTURAL AND OPTICAL STUDIES OF MEH-PPV USING TWO DIFFERENT SOLVENTS PREPARED BY SPIN COATING TECHNIQUE

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ABSTRACT

Spin coating technique is commonly used to obtain uniform thin films. Conducting unsaturated polymer of red colour poly [2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV), can be easily dissolved in non-aromatic and aromatic solvents to exhibit different optical and structural properties. The MEH-PPV solutions in the two types of solvents were prepared at concentration of 8 mgml⁻¹. They were then spin coated onto glass and calcium difluoride (CaF₂) substrates at 4 krpm for 10 seconds. The spun films of MEH-PPV on glass substrates were used for investigating the optical properties by using UV-Visible-NIR (UV-VIS-NIR) and Photoluminescence (PL) spectroscopy. The structural properties of the films were investigated by Fourier Transform Infrared (FTIR) spectroscopy. The structural transformations of the films when annealed at 76 °C and 140 °C were also studied by analysing and comparing the FTIR spectra of the films at that specific temperature.

INTRODUCTION

Poly [2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene (MEH-PPV) is an electroluminescent polymer, widely utilized in the fabrication of Polymer Light Emitting Diodes (PLEDs). The application of this polymer is mainly focused on display such as Light Emitting Diode (LEDs), field effect transistor and photovoltaic cells [1]. Recent studies on the material have shown that the polymer morphology as well as the polymer processing condition such as the type of solvent, spin coating speed, solution concentration and annealing temperature are important factors in determining the final physical properties of the polymer thin films and subsequently the performance of the device made from the polymer [2].

MEH-PPV is one of derivatives with alkoxy on phenyl groups [3] and exhibits superior solubility in common organic solvent such as tetrahydrofuran (THF), chloroform, xylene, chlorobenzene (CB), and toluene. It can be solution-soluble at room temperature into uniform, thin films with large area and display optical-quality properties [4] by spin coating technique. Spin coating technique is one of the easiest techniques to produce uniform films onto large area. This paper focuses on the study of spin coated thin films of MEH-PPV prepared from chloroform and toluene solutions with the same concentration.

Thuc-Quyen Nguyen et al [4] found that various conformations of MEH-PPV chains occurred in aromatic solvent such as chlorobenzene (CB), as the polymer has open conformation. The conformation in non-aromatic solvent is however, much more

restricted and as a result chains tend to form tighter coils. Orientation of the molecular chain has also been investigated using Fourier Transform Infrared (FTIR) spectroscopy [2,10].

EXPERIMENTAL DETAILS

MEH-PPV used in this work has purity of >99% and it was purchased from H.W. Sands. The molecular weight of the MEH-PPV is $200,000 \text{ g mol}^{-1}$ (PS standard). Figure 1 shows the molecular structure of the MEH-PPV. The material was dissolved in two different solvents, chloroform (HPLC grade) and toluene at concentration of 8 mg ml^{-1} . Before coating the polymer on glass substrate and calcium difluoride (CaF_2), both of these types substrates were sonicated in foam (DECON TM) for 15 minutes and then rinsed with deionised water, acetone and ethanol respectively, and rinsed again in deionised water. Finally the substrates were dried with nitrogen gas.

The glass substrate on which the polymer layer was spin coated has dimension of $1 \text{ mm} \times 2 \text{ mm}$. The spin coating was carried out at speed 4krpm for 10 seconds. The films were dried in vacuum chamber for 2 hours at 50°C to ensure complete evaporation of solvents. Optical and structural characterizations were carried out at room temperature, 27°C . The Sample coated on CaF_2 substrate was then annealed at 76°C and 140°C using Carbolite furnace.

The absorption spectra of the films were measured from wavelength range, 200 nm to 2500 nm using a JASCO V570 UV-VIS-NIR spectrophotometer. Photoluminescence (PL) spectra were measured with PERKIN ELMER LS50B luminescence spectrometer which was attached with xenon excitation lamp (200-500nm). Determination of orientation chain of MEH-PPV coated on CaF_2 substrate was measured using Fourier Transform Infrared (FTIR) spectroscopy.

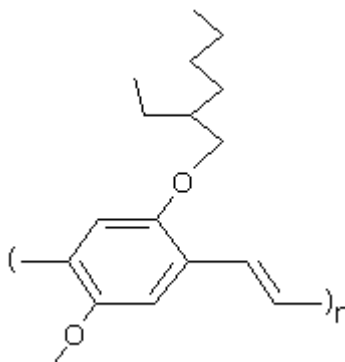


Figure 1: Molecular structure of MEH-PPV

RESULTS AND DISCUSSION

Figure 2 shows different peaks absorbance from the thin films prepared from two different solvents of the same concentration of 8 mg ml^{-1} . The figure indicates that, the absorption spectra of the thin film prepared from the two solvents are not exactly the same. The MEH-PPV film prepared from chloroform and toluene absorb weakly at 326

nm and 332 nm respectively. However at higher wavelength the thin films absorb quite significantly. The maximum absorption for the thin films prepared from chloroform and toluene solvents are 502 nm and 510 nm respectively which are similar to that reported in reference [5] and can be ascribed to the π - π^* transition of the MEH-PPV polymer [6]. The optical band gap of this polymer in chloroform and toluene are 2.48 eV and 2.43 eV respectively. These data show high energy is required for the polymer to excite from π - π^* in non-aromatic solvent. A polymer chain tends to coil and becomes rigid in toluene and the conformation of the main chain changes [7-9] significantly in toluene compared to that in chloroform. As a result, the absorption spectrum in toluene is significantly red-shifted compared to that in chloroform. The maximum absorption is located at 510 nm for toluene solution and at 502 nm for chloroform solution.

The PL spectra as shown in Figure 3 of MEH-PPV thin films dissolved in the two solvents are also different. MEH-PPV dissolved in chloroform shows broader PL spectrum compared to the films dissolved in toluene. From the PL graph the maximum wavelength ($\lambda_{\max}$) of the film in toluene is 585 nm while that of the film in chloroform is 592 nm and the emission energy for both are 2.12 eV and 2.10 eV respectively. The difference between the emission energies of the two films are small that is only 0.02 eV. MEH-PPV film prepared from chloroform is more red-shifted compared to that of MEH-PPV film prepared from toluene.

Figure 4 (a) and (b) show FTIR spectra for MEH-PPV films dissolved in toluene and chloroform solvent respectively. The molecular orientation can be found

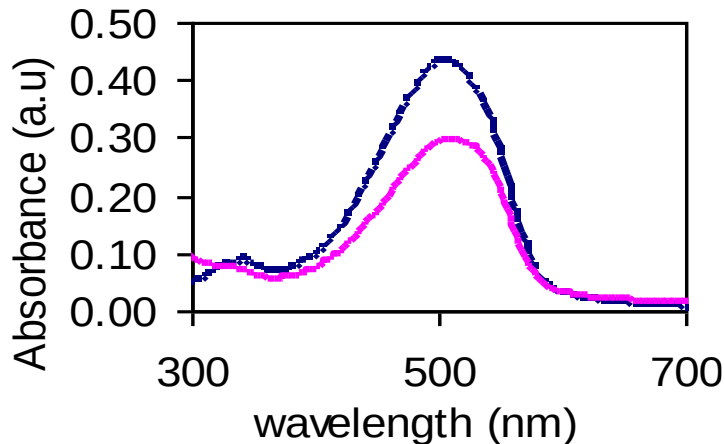


Figure 2: (a) Absorption peak of 8mgml⁻¹MEH-PPV in CHCl₃ and toluene at 4k rpm speed

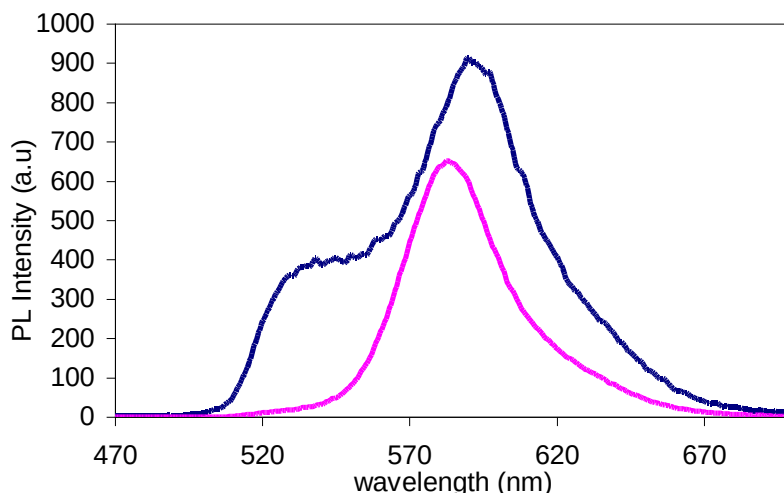


Figure 3: (b) PL peak of 8mgml^{-1} MEH-PPV in CHCl_3 and toluene at 4k rpm speed

from the peak of the spectra. The thermal annealing process was carried out for 1 hour for each sample and the measurement was taken under atmospheric pressure. The results indicate that the temperature could change the structure of the thin films dramatically, which can be observed by comparing the intensity of the transmission spectra. At room temperature, 27°C , the transmission peak at 965 cm^{-1} of the thin film prepared from chloroform solvent has higher intensity compared to that of the films prepared from toluene. When the temperature increases, the intensity of the peak for the film prepared from toluene does not show significant changes. The intensity of the peak for the thin film prepared in chloroform is however, decreases with temperature. The transmission peak at 850 cm^{-1} is assigned to the out-of-plane phenyl C-H wagging and the 965 cm^{-1} peak is assigned to the trans-double bond C-H wagging (vinyl group). Jie Liu et al [10] have reported that transitions at 850 and 965 cm^{-1} have dipoles normal to the phenyl-vinyl plane. The intensities of the two peaks are expected to be higher when the phenyl-vinyl planes are aligned parallel to the sample surface compared to that when they are aligned perpendicular to the substrate surface. Symmetrical and asymmetrical C (aromatic)-O-C stretching vibration modes are located at 1040 cm^{-1} and 1205 cm^{-1} respectively. The intensity of the transmission peaks at 1040 cm^{-1} and 1205 cm^{-1} , decrease when the annealing temperature increases which may indicate that, the phenyl rings becomes more parallel to the substrate plane upon thermal annealing. This result is similar to that report in reference [10]. Figure 5 shows the peak of the spectrum in high frequency regime. The transmission peaks at 3050 cm^{-1} , 2955 cm^{-1} , 2930 cm^{-1} , 2870 cm^{-1} and 2857 cm^{-1} correspond to $-\text{CH}$ stretching vinyl, $-\text{CH}_3$ asymmetric stretching, $-\text{CH}_2$ asymmetric stretching, $-\text{CH}_3$ symmetric stretching and $-\text{CH}_2$ -symmetric stretching respectively. Intensity of the transmission peaks markedly change for MEH-PPV thin film prepared from two types of solvents. Thus, it indicates the structural properties of MEH-PPV depend on the type of solvent used [10].

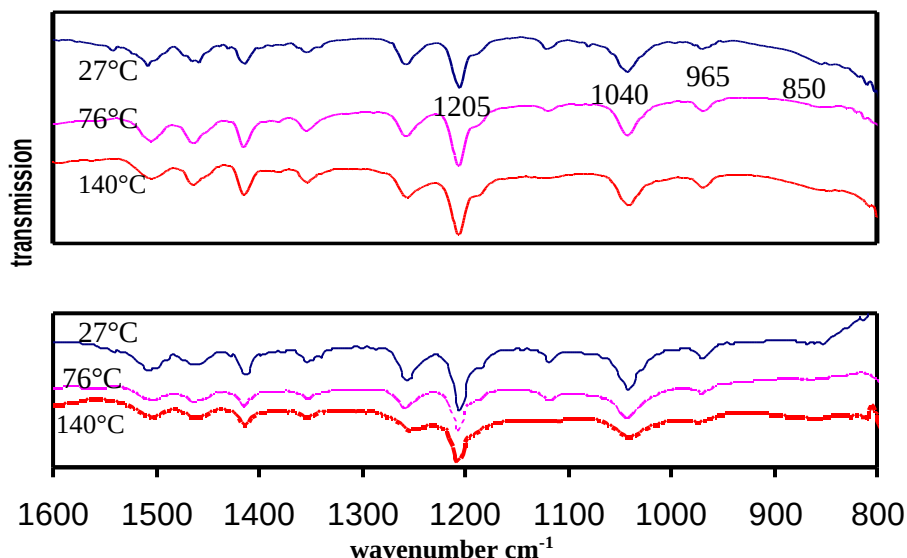


Figure 4: The transmission FTIR spectra of MEH-PPV spun from a) toluene b) chloroform solvents.

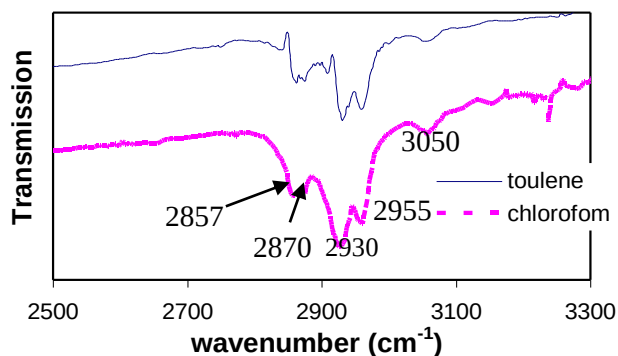


Figure 5: Transmission peaks at high frequency regime

CONCLUSION

Toulene and chloroform are examples of an aromatic and non-aromatic solvent which can be used to dilute MEH-PPV powder to produce uniform spun films by using spin coating technique. The concentration of the solution and spun speed are fixed at 8mgml^{-1} and 4 krpm respectively. The absorption from UV-visible spectra shows that the maximum wavelength (λ_{max}) in toluene is 510 nm while that in chloroform, the maximum wavelength (λ_{max}) is 502 nm. The absorption spectrum of the thin film prepared in toluene is red-shifted compared to that of the thin film prepared in chloroform. The PL spectrum for chloroform is observed to be broader compared to that in toluene due to the rigid conformation of the MEH-PPV in non-aromatic solution. The

emission energy obtained from PL graph for the MEH-PPV thin film prepared in toluene and chloroform are 2.12 eV and 2.10 eV respectively which are derived from the maximum intensity peak which occur at 585 nm for the toluene solution and 592 nm for the chloroform solution. The orientation of the polymer chain is described by the peak of the FTIR spectrum obtained for thin films diluted in toluene and chloroform before and after annealing treatment. Intensity of the assignment peaks for the transmission spectra before and after heating significantly changes. This maybe due to the changes in the conformation of the MEH-PPV polymer as it is annealed from 27°C to 140°C.

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