



Methyl blue dyed polyethylene oxide films: Optical and electrochemical characterization and application as a single layer organic device



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ABSTRACT

A single layer organic device employing methyl blue (MB) dyed polyethylene oxide (PEO) film has been fabricated and studied. The cyclic voltammetry was used to estimate the redox potential and energy band diagram of the device. The polymer film with highest concentration of the dye in PEO (PMB2%) possessing highest conductivity exhibited energy band gap of 2.62 eV with HOMO and LUMO values of 5.34 and 2.72 eV respectively. Based on cyclic voltammetry data, the electron affinity, ionization potential and energy band diagram of the device are discussed.

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1. Introduction

Organic light emitting diodes (OLEDs) and polymer solar cells (PSCs) based on conjugated polymers have acquired significant interest due to their low cost and ease of processing for flexible device applications [1–6]. The main aim is to develop the high-performance OLEDs having good emission intensity and charge transportation with improved multifunctional properties. Hence, the preparation, characterization, design and fabrication of electrochemically active devices are still under the foreground of research activity in electrochemistry. Even though there is a significant improvement in the efficiency as well as stability of PLEDs and PSCs, further enhancement is still required for their commercial applications. The pioneering work of inverted structure was approached with the fabrication of OLED which was referred to as an “upside-down” structure initially [7,8]. In inverted structure, the top metal electrode is a high work function electrode such as silver or gold (Ag or Au) and the bottom electrode is a transparent electron conducting layer of oxides such as indium tin oxide (ITO), zinc oxide (ZnO) or titanium oxide (TiO_x). The performance of inverted structure was even better than that of the standard one with reactive cathode materials like Ca or LiF [9–11]. The main advantages of inverted structure are working with air stable cathode materials like Ag or Au and thus eliminating the problem of

oxidation, while the acidic problem was eliminated by using transparent electron conducting layers.

The motive is focussed on understanding the behavior of these systems, specifically on the charge transportation mechanism involved in the redox reactions of polymer system and their promising applications in the field of electronic devices, energy storage, photoelectrochemistry, electroanalysis, sensors, electrochromic displays, microelectronic devices, rechargeable batteries, solar cells, etc. [12–17]. Generally, as per the band theory in particular, the gap between the conduction and valance bands play crucial role in the determination of the intrinsic properties of these polymers.

Consequently the knowledge of the positions of highest occupied molecular orbital (HOMO, π^*) and lowest unoccupied molecular orbital (LUMO, π) levels are key factors in determining current density under applied potential. The cyclic voltammetry (CV) is an important technique to understand the electrochemical behavior of a system in terms of band gaps, electron affinities and work functions of various polymers. It can also be interpreted that reduction process represents the electron addition to the LUMO energy level, whereas the oxidation cycle corresponds to removal of charge from HOMO energy level. The difference between the two onset potentials gives the energy band gap and is directly compared with the optical band gap which gives useful information about polymers that should be used in the fabrication of the devices [18].

Various solid polymer electrolytes can be used for constructing solid state photo-electrochemical systems. Polyethylene oxide (PEO) is the most widely used polymer due to its high solvating power over a variety of metal salts to form polymeric electrolytes

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exhibiting good processability and outstanding mechanical properties [19].

The optical and electrochemical properties of a polymer can be suitably modified by the addition of dopants. Dye molecules are frequently used materials for organic optical gain in photonic applications, such as optical amplification and light emission. In the recent years, extensive interest has been focused on the fabrication of dye-doped active polymers for potential applications [20]. Dye doped polyethylene oxide films were widely used in the polymer dye lasers and dye sensitized solar cells [21–26]. Many reports are available on the electrical properties of the PEO based polymer electrolyte systems [27–29]. On the other hand, investigation of the optical and electrochemical properties of these composite systems is still limited and only a few reports are available on PEO-based electrolytes intended to be p-type inorganic materials and organic hole conductors [30–35].

This report is concerned with the optical and electrochemical properties of polyethylene oxide films doped with methyl blue dye (PEO/MB). The solid-state single layer organic device of methyl blue dye doped PEO was fabricated on ITO with Ag as top metal electrode and characterized for electrochemical applications.

2. Experimental methods

2.1. Preparation of dyed polymer films

Polyethylene oxide (PEO) ((C₂H₄O)_n, Mol wt.: 5 × 10⁶) was purchased from M/S Sigma Aldrich, USA, methyl blue (MB) dye (C₃₇H₂₇N₃Na₂O₉S₃) from Merck chemicals. PEO and the desired amount of MB (different concentrations 0.2%, 1% and 2%) were dissolved in methanol (CH₃OH, 0.790–0.793 g wt. per ml) separately and then mixed by using magnetic stirrer to get the homogeneous viscous solution. The solution was casted on a petri dish to obtain the films. Films thickness was estimated by using thickness gauge and is in the range of 0.15–0.2 mm.

2.2. Fabrication of the device

The inverted structure type device was fabricated on a cleaned indium tin oxide (ITO) coated glass substrate. PEO:MB (PMB2%) exhibiting highest conductivity was chosen as active layer for the device fabrication. A thin layer of PMB2% mixture was deposited on ITO glass substrate by dip coating. For the top metal electrode silver paste was applied by doctor blading technique with an effective area of 1 cm².

2.3. Characterization techniques

Thermogravimetry (TG) and differential thermal analysis (DTA) were performed with SDT Q600 TG/DTA thermal analyzer under nitrogen stream from temperature 30–650 °C at a heating rate of 10 °C min⁻¹. FTIR measurement was done by using Perkin Elmer-8800 IR spectrophotometer in KBr medium in the spectral range 4000–600 cm⁻¹. The surface micrographs of the films were obtained with OLYMPUS BX-51 system microscope and Nanosurf Atomic Force Microscope (AFM). A computer aided Perkin-Elmer LAMBDA-35 double-beam UV-Visible spectrometer was used to record optical absorbance in the wavelength range 190–900 nm with a slit width of 0.5 nm and a scanning interval of 1 nm. A fluorescence spectrum was recorded using Hitachi F-7000 fluorescence spectrophotometer. DC electrical conductivity measurement was conducted with the help of Wayne Kerr 6500B Precision impedance analyzer in the frequency range from 20 Hz to 1 MHz at room temperature. Cyclic Voltammetry measurement was done by using CHI660E electrochemical work station.

3. Results and discussion

3.1. Thermal analysis

In order to ascertain the thermal decomposition and stability, the PEO and PMB films were subjected to TG/DTA analysis and shown in Fig. 1(a–d). In Fig. 1(a) the curve shows an endothermic peak at 72.4 °C which is the melting point of PEO and it has increased to 74.6 °C, 75.8 °C and 78.04 °C for PMB0.2%, 1% and 2% films respectively and are shown in Fig. 1(b–d). At a temperature of 100 °C the weight loss on the TG curve was due to dehydration of the films, and it is also ascribed to the presence of volatile impurities in the samples [36].

The onset of complete decomposition of the films starts at 190 °C, which indicates, the film is stable up to 190 °C. A continuous one step weight loss was observed in the interval of 190–450 °C on the TG curve accompanied by an exothermic peak with maxima at 345 and 377 °C on DTA curve for PEO and PMB0.2% films respectively. In the DTA curves of PMB1% and 2% films two exothermic peaks were observed at 382, 408 °C and 391, 416 °C respectively depicting the thermal decomposition of the organic matter of the films [37,38]. The changes in TG/DTA curves of the films indicate the enhanced thermal stability in PEO due to addition of MB dye.

3.2. Fourier transform infrared spectroscopy

The FTIR spectra of PEO, MB dye and PMB films are given in Fig. 2(a). The characteristic peaks of PEO observed at 2926, 1463, 1348 cm⁻¹ are attributed to C–H stretching, CH₂ wagging and CH₂ bending respectively. The C–O–C stretching vibrations observed at 1084 cm⁻¹ in the spectra of PEO represents semi crystalline phase of PEO.

The two peaks 952 and 843 cm⁻¹ are ascribed to CH₂ rocking modes [39]. In the spectra of MB dye the characteristic band of S=O is observed at 1053 cm⁻¹ and a broad peak observed at 3460 cm⁻¹ corresponds to N–H stretch vibrations possessed by methyl blue dye [40].

In PMB films the C–O–C stretching band was shifted to 1091, 1096 and 1100 cm⁻¹ for PMB 0.2%, 1% and 2% films, but there was significant decrease in the intensity of these peaks. Furthermore, the CH₂ rocking modes of PEO almost disappeared when the MB concentration was increased. This indicates that the dye is dissociated uniformly in the polymer host and thereby interrupts the crystallization process leading to an enhancement in the amorphous phase. On the other hand, the peak at 1463 cm⁻¹ in PEO is slightly shifted to higher wavenumbers at 1464, 1467 and 1469 cm⁻¹ for PMB 0.2%, 1% and 2% respectively, as observed from Fig. 2b. These observations confirm the existence of (NH...O) group due to intermolecular interaction between NH group from MB dye and oxygen from the PEO [41].

3.3. Surface morphology

Fig. 3 shows the optical micrographs of PEO and PMB films. In Fig. 3(a) the PEO displayed large semicrystalline, different sized rough spherulites.

It is also observed that a number of platelets or lamellae are formed from folded chains and are radiating from a nucleating center; the dark region between the platelets within the spheres represents the amorphous phase [42].

Fig. 3(b–d) displays the optical micrographs of PMB films at different concentrations of MB dye. For PMB films the characteristic Maltese-cross pattern of polymer spherulites were observed under cross polarisers. MB dye act as a nucleation agent and thus increase

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