

Synthesis and Characterization of Polymer Films Based on Bis(EDOT)-Substituted Benzenes

Kalya Eaiprasertsak^{*}, Manu Fuengfoong and Tawee Chim-oye

Physics Department, Faculty of Science & Technology, Thammasat University, Rangsit Campus, Pathum Thani, 12121 Thailand

^{*}Correspondence : E-mail : keaipra@tu.ac.th

Richard V. Gregory

Department of Chemistry and Biochemistry, College of Sciences, Old Dominion University, Norfolk, VA, 23529 USA.

Abstract

A series of polymers based on 2,5-bis[(3,4-ethylenedioxy)thien-2-yl]-substituted benzene monomers were electropolymerized. Thin polymer films exhibit electrochromism and their photoluminescence (PL) is in the orange and red regions. Cyclic voltammetry (CV), infrared (IR), UV-vis-NIR and PL spectroscopy were employed to investigate and characterize the properties of these new polymers.

Keywords: BEDOT, PBEDOT-Bs, Cyclic voltammetry, Photoluminescence.

1. Introduction

The past few decades have seen a rapid growth in the application of semiconducting conjugated polymers for use as optoelectronic materials for LEDs, thin-film organic transistor and non-linear optic applications, and fluorescence sensors for chemical and biological applications, etc.[1] Co-polymers of these systems have been used as the emissive layer in polymeric LEDs (PLEDs) [2]. This has led to a renewed focus on π -conjugated oligomers based on thiophenes with specifically tuned molecular properties, because their chemical structures can be well defined and their physical properties can be molecularly tuned with relatively ease [3,4]. Extensive research has been done on poly(3,4-ethylenedioxythiophene) (PEDOT) [5,6], however, in contrast to

other thiophene base systems, 3,4-ethylenedioxythiophene (EDOT) systems have received less attention [7].

We have synthesized a relatively low-oxidation potential electropolymerizable 2,5-bis[(3,4-ethylenedioxy)thien-2-yl]-3-substituted benzenes (BEDOT-Bs) monomers including 2,5-bis[(3,4-ethylenedioxy)thien-2-yl]-toluene (BEDOT-TOL), 2,5-bis[(3,4-ethylenedioxy)thien-2-yl]-2-butoxybenzene (BEDOT-BOB), and 2,5-bis[(3,4-ethylenedioxy)thien-2-yl]-2-fluorobenzene (BEDOT-FB) [7]. These monomers exhibit photoluminescence with blue emission characteristics and have quantum yields ranging from 7% to 10% that made them candidates for either electrochromic or luminescent applications. The electrochemical behavior of the monomers and the polymers on a glassy carbon electrode had been reported [7].

In this paper, we report the electropolymerization of these monomers onto ITO-coated glass substrate and the properties of the resultant polymers were investigated using IR, UV-vis-NIR, and photoluminescence (PL) spectroscopy.

2. Experimental Details

BEDOT-TOL, BEDOT-BOB, and BEDOT-FB monomers were synthesized as described previously [8]. The electrochemical experiments were carried out using a Bioanalytical systems C2 Cell Stand Electrochemical Analyser model BSA 100A. A non-aqueous cell was used for the electrochemical analysis consisting of acetonitrile (ACN) as the solvent, tetrabutylammonium hexafluorophosphate (TBAPF₆) as the electrolyte (0.1M). The TBAPF₆ was used for a supporting electrolyte. The TBAPF₆ was recrystallized from ethanol and dried under vacuum (25 °C, 48 h). The ACN was distilled over CaH₂ under a N₂ atmosphere, and was degassed with N₂ prior to use. The three electrodes used were a Pt auxiliary electrode, a Ag/Ag⁺ reference electrode and ITO-coated glass substrate working electrode. The reference electrode solution was 0.01 M AgNO₃ in the 0.1 M electrolyte solution. Monomer solutions of 1.0 mM were prepared from BEDOT-TOL, BEDOT-BOB, and BEDOT-FB in 0.1 M TBAPF₆/ACN. Polymer films of these materials were deposited by a repeated potential scanning method with scan rate of 50 mV/s.

UV-vis-NIR spectra were obtained on a Shimadzu UVPC-3101 spectrometer using a slow scanning speed and 0.8 nm slit width. Photoluminescence spectra were obtained on a Perkin Elmer LS 50B. The surface of the film was 30° to the incident beam. The PL spectra were collected with 450 nm excitation wavelength. A scan rate of 100 nm/min was used to collect emission spectra of all samples.

The IR spectra of all polymers (doped, intermediate, and undoped states) were recorded using a Nicolet Magna-IR™ 550 FT-IR spectrometer in the reflection mode. The spectra were collected from 4000 to 600 cm⁻¹.

3. Results and Discussion

3.1 Electrochemical Properties

The cyclic voltammograms of all polymer films show one anodic wave followed by a broad plateau as shown in Figure 1(a) for PBEDOT-TOL, which is generally representative of the materials reported in this study. Large anodic and cathodic currents of nearly constant value are observed over a potential range on the order of 1 V. The large peak separation is essentially not a function of the potential sweep rate. This fact points to a chemical reaction charge transfer. The most probable and plausible explanation is that upon oxidation the polymer chains stabilize themselves from a twisted to a partially planar structure with better conjugation due to overlap and delocalization of electrons. In the case of aromatic polymers this is the transition from a more benzenoid structure to a quinoid structure [8]. This also indicates that the polymers are stable over a broad potential window.

For each polymer film, cyclic voltammetry as a function of scan rate was performed with the scan rate between 10 and 300 mV/s. Cyclic voltammetry of each polymer at various scan rates shows the general shape of the voltammograms to be similar and exhibit a low anodic wave peak. For these polymers, the peak current shows a linear relation to the square root of scan rate (i_p vs. $v^{1/2}$). The proportionality of current to $v^{1/2}$ clearly indicates a diffusion controlled process [9]. The peak current varies linearly with scan rate as expected for electroactive species that are surface bound. This indicates that the electroactive polymer is well-adhered to the electrode surface.

3.2 Optical and Electronic Properties

During potential cycling, these polymers exhibit electrochromism. The color of the oxidation (doped) state and neutral (undoped) state of each polymer is shown in Figure 2. The color change is reversible in electropolymerization. Polymer films in the oxidized or neutral state can be obtained depending on the potential at which polymerization is stopped.

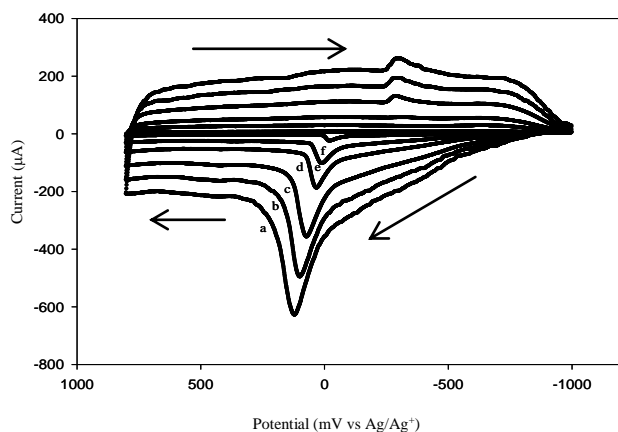
Figure 3 (A) shows the UV-vis-NIR spectra of those films in both oxidized and neutral states, as well as chemically reduced films of PBEDOT-Bs. The optical band gap for each polymer was obtained from the onset of the π - π^* transition.

UV-vis-NIR absorption spectra of PBEDOT-TOL show the π - π^* transition at 2.30 eV (538 nm) with the band gap at 1.73 eV (ca.723 nm) while PBEDOT-BOB shows the band gap at 1.85 eV and PBEDOT-FB shows the band gap at 1.76 eV. The highly doped state of these polymers exhibits the characteristic of a

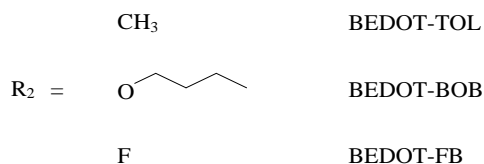
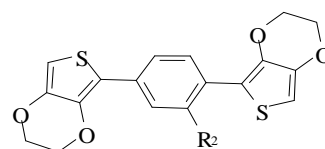
charge carrier tail with no well defined peak.

3.3 Photoluminescence Spectra

Figure 3(B) shows the photoluminescence (PL) emission spectra of PBEDOT-TOL, PBEDOT-BOB and PBEDOT-FB. The PL emission, maxima at 611, 632 and 626 nm for PBEDOT-TOL, PBEDOT-BOB and PBEDOT-FB, respectively, is in the orange-red region. The emission spectra of PBEDOT-BOB and PBEDOT-FB appear more symmetrical, while the extended long wavelength tail appears in PBEDOT-TOL spectra. This tail in PBEDOT-TOL spectrum is most likely due to structural inhomogeneities [10] caused by differences in conjugation length from the presence of doping segments in the undoped films. Evidence of this is the persistence of the low energy absorption peak at around 900 nm in the UV-vis-NIR spectra of PBEDOT-TOL in the undoped state.



(a)



(b)

Figure 1. (a) Scan rate dependence of the cyclic voltammogram of PBEDOT-TOL thin film on GCE in 0.1 M TBAPF₆/ACN, scan rate (a) 400, (b) 300, (c) 200, (d) 100, (e) 50, and (f) 10 mV/s.

(b) Chemical structure of PBEDOT-Bs.

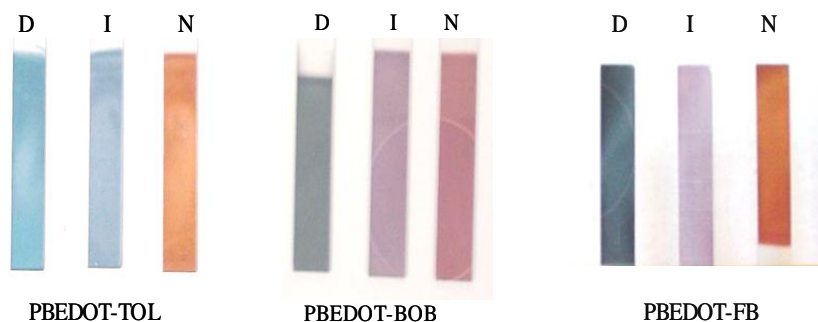


Figure 2. Color of PBEDOT-TOL, PBEDOT-BOB and PBEDOT-FB films electrochemical polymerization deposited on ITO-coated glass by repeated potential scanning method. D = doped, I = intermediate states, N = neutral (undoped).

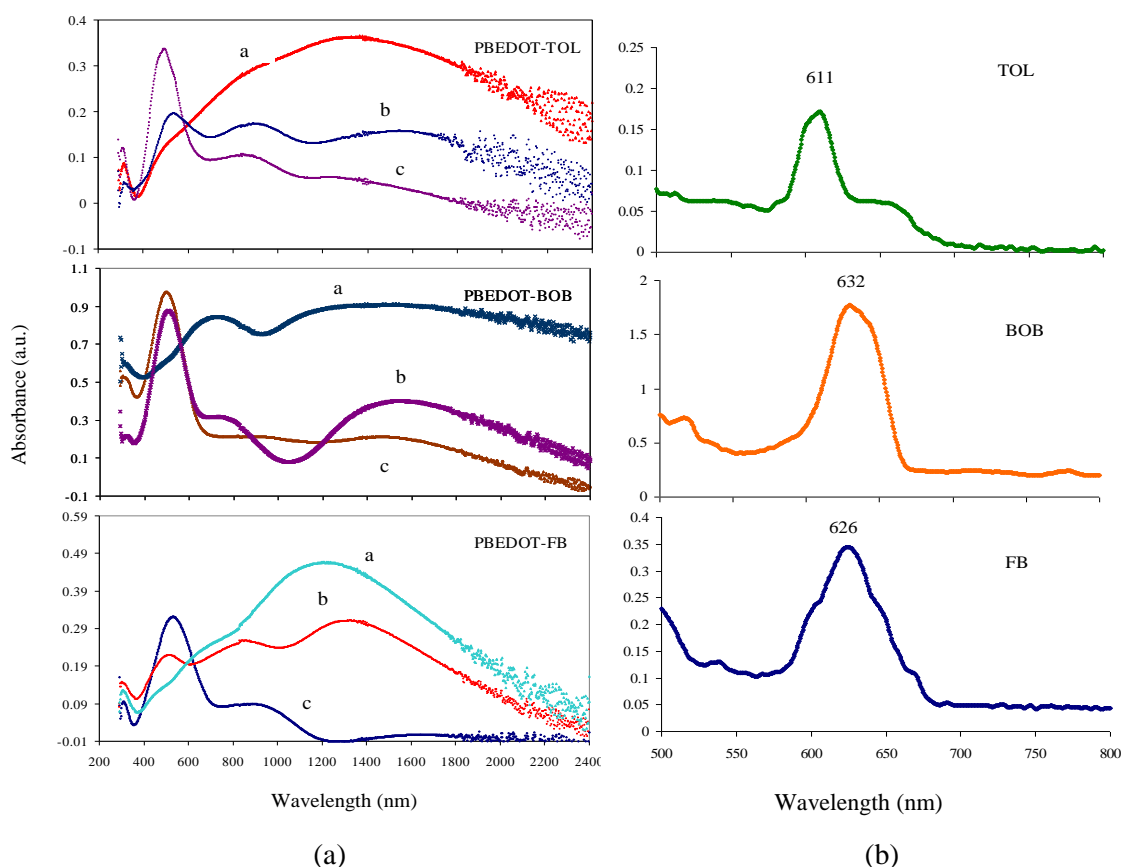


Figure 3. (A) UV-vis-NIR spectra of PBEDOT-TOL, PBEDOT-BOB and PBEDOT-FB films deposited on ITO-coated glass (a) doped, (b) intermediate, and (c) neutral states.

(B) PL spectra of PBEDOT-TOL, PBEDOT-BOB and PBEDOT-FB films deposited on ITO-coated glass.

3.4 Infrared Spectra

Infrared spectra of these polymers were obtained from the same films used for

UV-vis-NIR measurement. All polymers showed similarity in IR spectra compare to those of corresponding monomers. The IR

absorption bands showed the influence of the aromatic structure both in the vicinity of 830-840 cm^{-1} and above 3000 cm^{-1} [11].

4. Conclusion

Cyclic voltammetry studies of these polymers shows that if the electron donating ability of the substituent group increases, the oxidation potential of that polymer is lowered compared to others in the same series. Moreover, the larger potential in the plateau area of PBEDOT-Bs suggests that PBEDOT-Bs are more planar and are better conjugated than that of PEDOT and its derivatives [12]. The large potential plateau also indicates that the polymers are stable over a broad potential window where they can be used as conductors, for both electrode and transport layers.

IR data showed that there is no change in the structure of these polymers from that of the monomers. This may imply that polymerization takes place at the BEDOT α -position, with no opening of the central ring.

All polymers exhibited electrochromism with a spectrum of colors in the undoped state, ranging from red purple to reddish, and their photoluminescence in the orange and red regions. It appeared that PBEDOT-TOL, PBEDOT-BOB and PBEDOT-FB were stable in both doped and undoped states in ambient atmosphere. This property makes them good candidates for use in electroluminescence devices either in the undoped form for an emissive layer, or in the doped form for a transport layer or as injection electrodes. The success in electropolymerization of these new polymers, with unique properties, in thin films, and that their thickness can be controlled by controlling deposition charges has opened the door for using these polymers in the area of optoelectronic devices.

5. Acknowledgement

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