

SYNTHESIS AND CHARACTERIZATION OF POLYMER FILMS BASED ON BIS(EDOT)-SUBSTITUTED THIOPHENES

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ABSTRACT

A series of polymers based on 2,5-bis[(3,4-ethylenedioxy)thien-2-yl]-substituted thiophene monomers have been electropolymerized. Thin polymer films exhibited 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.

INTRODUCTION

The past few decades have seen a rapid growth in the application of semiconducting conjugated polymers for use as optoelectronic materials for LED, thin-film organic transistor and NLO applications, 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 a specifically tuned molecular properties, because their chemical structures can be well defined and their physical properties can be molecularly tuned with a relatively ease [3,4]. Extensive research has been done on poly(3,4-ethylenedioxythiophene) (PEDOT) [5], however, in contrast to other thiophene base system, 3,4-ethylenedioxythiophene (EDOT) systems have received less attention [6].

Recently, we have synthesized a relatively low-oxidation potential electropolymerizable of 2,5-bis[(3,4-ethylenedioxy)thien-2-yl]-3-substituted thiophenes (BEDOT-Ts) monomers including 2,5-bis[(3,4-ethylenedioxy)thien-2-yl]-3-butylthiophene (BEDOT-3BT), 2,5-bis[(3,4-ethylenedioxy)thien-2-yl]-3-octylthiophene (BEDOT-3OT), 2,5-bis[(3,4-ethylenedioxy)thien-2-yl]-3-(butylthio)thiophene (BEDOT-3TBS) and 2,5-bis[(3,4-ethylenedioxy)thien-2-yl]-3-(4'-methoxyphenyl)-thiophene (BEDOT-3MPT) [7]. These monomers exhibit photoluminescence with blue emission characteristics and have quantum yields ranging from 3% to 5% that made them candidate for either electrochromic or luminescent applications. The electrochemical behaviors of the monomers and the electrochemical synthesis polymers onto 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 result polymers were investigated using IR, UV-vis-NIR, and photoluminescence (PL) spectroscopy.

EXPERIMENTAL DETAILS

BEDOT-3BT, BEDOT-3OT, and BEDOT-3TBS monomers were synthesized as described previously [7]. 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 as the solvent, tetrabutylammonium hexafluorophosphate as the electrolyte (0.1M). 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 of BEDOT-3BT, BEDOT-3OT, and BEDOT-3TBS. Polymer films of these materials were deposited by 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-IRTM 550 FT-IR spectrometer in the reflection mode. The spectra were collected from 4000 to 600 cm⁻¹.

RESULTS AND DISCUSSION

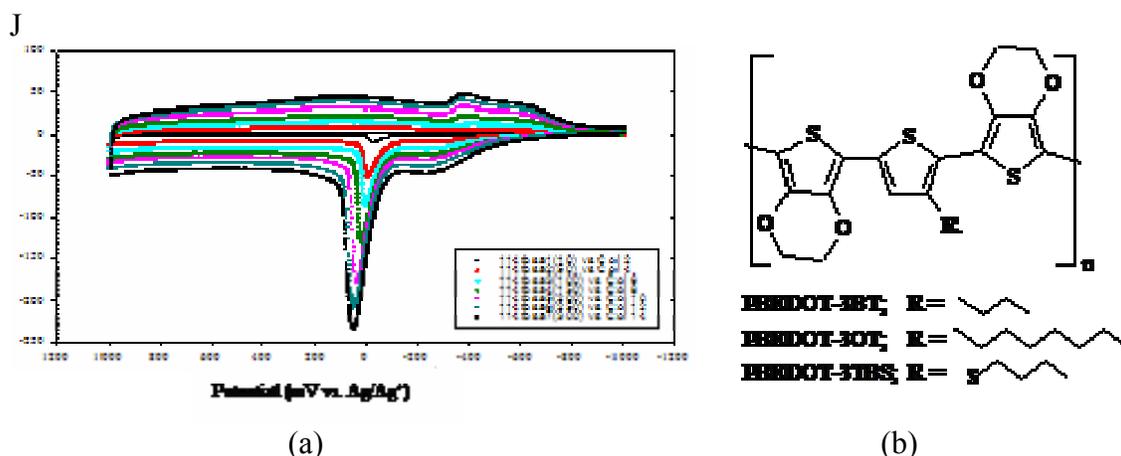


Figure 1: (a) Scan rate dependence of the cyclic voltammogram of PBEDOT-3TBS thin film on GCE in 0.1 M TBAPF₆/ACN, scanned at 10, 50, 100, 150, 200, 250, and 300 mV/s. (b) Chemical structure of PBEDOT-Ts.

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 changed is reversible in electropolymerization. The polymer films in the oxidized or neutral state can be obtained depending on the potential at which polymerization is stopped.

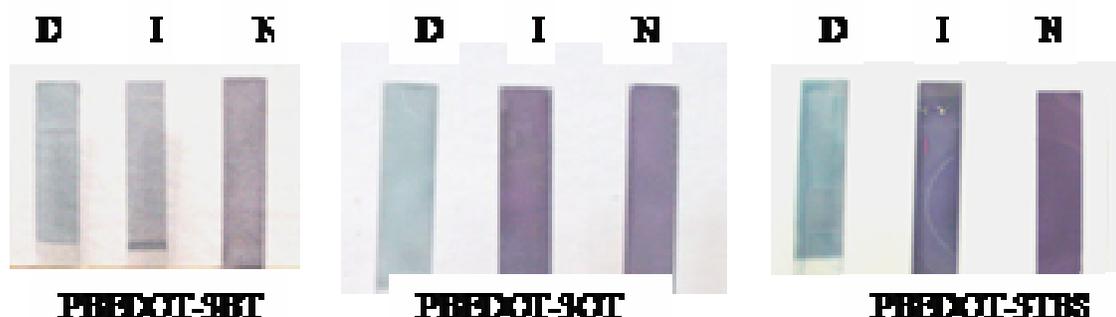


Figure 2: Color of PBEDOT-3BT, PBEDOT-3OT and PBEDOT-3TBS films electrochemical polymerization deposited on ITO-coated glass by repeated potential scanning method.
D = doped, N = neutral (undoped), I = intermediate states.

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-Ts. The optical band gap for each polymer was obtained from the onset of the $\pi-\pi^*$ transition.

UV-vis-NIR absorption spectra of PBEDOT-3BT show the $\pi-\pi^*$ transition at 2.21 eV (560 nm) with the band gap at 1.71 eV (ca.723 nm) while PBEDOT-3OT shows the band gap at 1.69 eV and PBEDOT-3TBS shows the band gap at 1.76 eV. The highly doped state of these polymers exhibits the characteristic of charge carrier tail with no well defined peak.

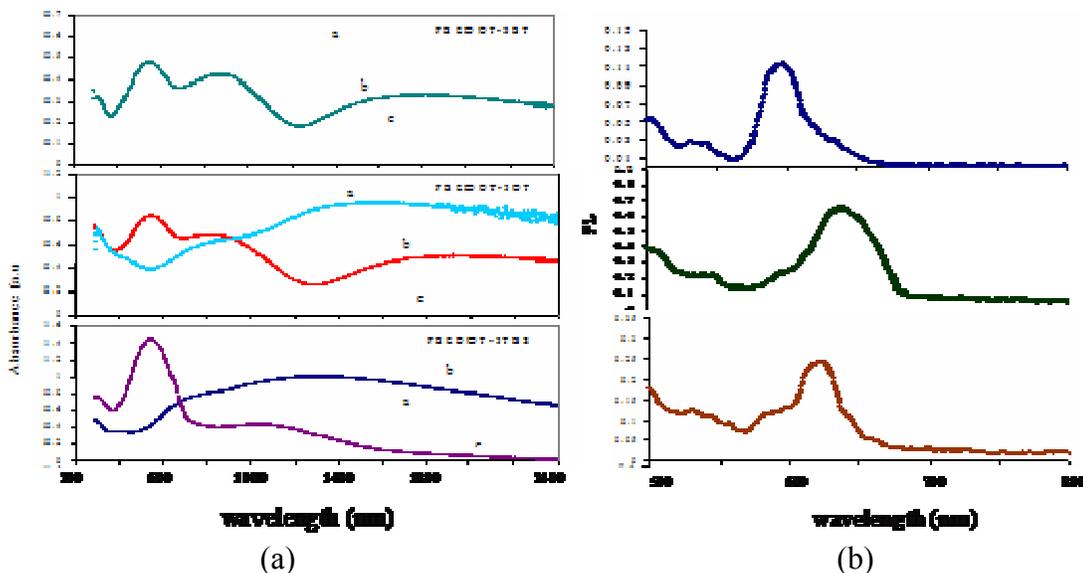


Figure 3: (a) UV-vis-NIR spectra of PBEDOT-3BT, PBEDOT-3OT and PBEDOT-3TBS films deposited on ITO-coated glass (a) neutral, (b) intermediate, and (c) doped states. (b) PL spectra of PBEDOT-3BT, PBEDOT-3OT and PBEDOT-3TBS films deposited on ITO-coated glass.

These polymers are somewhat unstable at the highest doping level during prolonged exposure to the laboratory environment since the spectra show reappearance of the absorption peak at the $\pi-\pi^*$ transition.

Infrared Spectra

Infrared spectra were obtained from the same films using for UV-vis-NIR measurement. All polymers show similarity in IR spectra. The most striking difference in IR absorption peaks of PBEDOT-Ts is the relative intensity of the peak at 822-843 cm^{-1} to 910-980 cm^{-1} . The intensity increases with increased doping levels corresponding probably due to the structure changed from benzenoid to quinoid at the thiophene ring. In spite of reducing in hydrazine monohydrate, the band at 800s cm^{-1} do not totally disappear. This may explain why the PBEDOT-Ts could not be fully undoped, consistent with the UV-vis-NIR spectra of these polymers. From the IR spectra, it has been shown that the electrochemical polymerization of BEDOT-Ts monomers occur at the end of polymer chains and does not open up the central ring.

Photoluminescence Spectra

Figure 3(B) shows the photoluminescence emission spectra of PBEDOT-3BT, PBEDOT-3OT and PBEDOT-3TBS. The PL emission, maxima at 598, 611, 624 and

584 nm for PBEDOT-3BT, PBEDOT-3OT and PBEDOT-3TBS respectively, is in the orange-red region. The spectra of these polymers show the extended long wavelength tail. This feature is due to a high density of defects resulting from structural inhomogeneities [10] disorder-affected spectra.

The low intensity of PL spectra of these polymers is most likely caused by the quenching sites from doped segment that are still left in the polymer. The evidence of the absorption peak at lower energy is shown in the UV-vis-NIR spectra of undoped polymer films.

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-Ts suggests that PBEDOT-Ts are more planar and are better conjugated. This may be one of the reasons that the bandgaps of PBEDOT-Ts are slightly low. 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 should take place at the BEDOT □-position, with no opening of the central ring.

All polymers exhibited electrochromism and a spectrum of colors in the undoped state, ranging from light to deep-purple and their photoluminescence in the orange and red regions.

It appeared that PBEDOT-3BT, PBEDOT-3OT and PBEDOT-3TBS were stable in the intermediate (partially doped) form. The color of doped polymer films is changed from blue to purple-blue, and UV-vis-NIR spectra show that the absorption intensity of the carrier tail decreased with the appearance of two new absorption peaks. The success in electropolymerization of these new polymers, with unique properties, in thin films and that their thickness could be controlled by controlling deposition charges has opened the door for using these polymers in the area of optoelectronic devices.

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