



Optoelectrochemical properties of copolymer of terthiophene with 3,4-ethylenedioxy pyrrole

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ABSTRACT

A copolymer of 2,2':5',2''-terthiophene and 3,4-ethylenedioxy pyrrole was synthesized as a new electrochromic polymer and its spectroelectrochemical properties were investigated. This copolymer shows multicolor electrochromism, switching between dark blue, light brown, and orange-red. Three different electrochromic materials were evaluated using the electrochromic copolymer. Double potential step chronoamperometry experiments showed that this copolymer film has good stability, fast switching time and high optical contrast.

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1. Introduction

Electrochromism is defined as the property inherent in some materials which enable them to electrochemically switch between different colored states as a result of redox reaction. Typical electrochromic behavior leads to switching between a transparent or bleached state and a colored state or between two different colored states. Many different types of organic and inorganic materials, such as inorganic metal oxides, mixed-valence metal complexes, organic small molecules and conducting polymers, exhibit electrochromic behavior. Among these electrochromic materials, conducting polymers (CPs) have received a great deal of attention due to their outstanding electrochromic properties, such as their short switching time, good stability, coloration efficiency, and wide range of colors. CPs are represented by polyheterocycles such as polypyrrole (PPy), poly(3,4-ethylenedioxythiophene) (PEDOT) and their derivatives. Several discoveries brought CPs to full commercialization with applications in electrochromic rearview mirrors [1,2], windows [3,4], thin-film transistors [5], displays [6], sensors [7], polymer light-emitting diodes [8,9], photovoltaics [10], and electrochromic devices [11–14]. Recently, research into CPs has mostly focused on their optical properties in the visible [15,16]

and near infra-red (NIR) [17–20] spectral regions. Poly(thiophene) derivatives have been most widely studied materials, since they exhibit fast switching times, outstanding stability and high contrast ratio in the visible and NIR regions. The earliest electrochromic materials in the visible region were the inorganic compounds, tungsten trioxide (WO_3) and iridium dioxide (IrO_2) [21]. Due to their increased versatility, organic materials, such as viologens, metallophthalocyanines and conducting polymers [22,23], have recently received the brunt of attention for potential electrochromic applications [24]. Among the various organic materials, conjugated polymers have several advantages over small molecules and inorganic solids, viz. their outstanding coloration efficiency, fast switching times [25,26], multiple colorations with the same material [16], fine-tunability of the band gap [27], high stability [28,13], thin-film flexibility and cost effectiveness. The electrochromism of conducting polymers is related to the doping–undoping process. The doping process modifies the polymer's electronic structure, producing new electronic states in the band gap, which cause color changes. The electronic absorption shifts bathochromically upon doping, and the color contrast between the undoped and doped states is related to the polymer band gap [29]. A major focus in the study of electrochromic polymeric materials has been that of controlling their colors by main-chain and pendant group structural modification and copolymerization. Indeed, it has been observed that the color of copolymers based on carbazole, thiophene and pyrrole derivatives can be controlled by

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altering the ratio of the respective monomers [30]. For instance, the electrochemical copolymerization of 2,2'-bis(3,4-ethylenedioxythiophene) (BiPEDOT) and 3,6-bis(2-(3,4-ethylenedioxy)thienyl)-*N*-methylcarbazole (BEDOT-NMeCz) was studied by Gaupp et al. [31]. This research work revealed that by modifying the monomer ratios of BiPEDOT and BEDOT-NMeCz, during the electrochemical copolymerization, it is not only possible to obtain a broad color palette for the neutral polymer, but also to obtain materials which show electrochromic behavior (e.g., reddish-purple, blue and green) in the case of particular compositions.

Recently, Argun et al. [32] published an interesting review including different multicolored electrochromic copolymers based on PEDOT. Very recently, Kraft et al. [33] reported a new electrochromic polymer (*N*-ethyl substituted poly(3,4-ethylenedioxythiopyrrole)) which displays switching between green, violet and gray.

Additionally, Song et al. [34] reported an interesting strategy to achieve multicolor electrochromism from polypyrrole, by doping this conducting polymer with a molecular electrochromogen (2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonate)).

In the case of PEDOT, the 3,4-alkylenedioxy substitution pattern facilitates its electrochemical polymerization by lowering the monomer oxidation potential (E_p) and directing polymerization through the 2- and 5-positions, yielding regiosymmetric polymers with a low degree of main-chain imperfections. This is not the case with PPy, which exhibits structural defects arising from β -couplings, resulting in conjugation breaks [35]. The substitution of pyrrole at the β -positions prevents these unwanted couplings, leading to more regular materials. At the same time though, PPy exhibits quite a low oxidation potential (-0.2 V vs. SCE) [36] and can be produced in the form of highly conductive (near metallic) and stable films [37]. Moreover, its redox properties are compatible in aqueous electrolytes, making it useful in biological systems [38]. It is evident that a combination of the electron-rich pyrrole heterocycle with the 3,4-alkylenedioxy substituent in 3,4-ethylenedioxythiopyrrole (EDOP) would provide a stable conducting polymer (as reported in a single patent by Savage et al. [39]) and is the focus of our recent efforts with regard to the use of electroactive polymers as aqueous compatible biomaterials [40].

With this view in mind, we synthesized a copolymer of 2,2':5',2''-terthiophene (TT) with 3,4-ethylenedioxythiopyrrole (EDOP). The electrochemical polymerization of P(TT-co-EDOP) was achieved in acetonitrile (MeCN) using tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. The resultant polymer was characterized via cyclic voltammetry, SEM, FTIR spectroscopy and conductivity measurements. The optoelectrochemical and electrochromic properties of the copolymer, such as its relative luminance, change of color upon redox switching, and long-term switching stability, were determined. The resulting multichromic polymer showed up to three different colors (dark blue, light brown and orange-red) and is therefore a promising polymer for organic electronic displays.

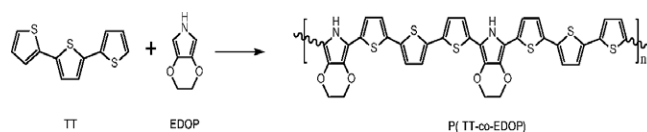
2. Experimental

2.1. Chemicals

EDOP, TT, MeCN and TBAP were purchased from Aldrich and used without further purification. All other reagents used were of analytical grade. High purity argon was used for deaeration. All experiments were carried out at room temperature.

2.2. Instrumentation

Cyclic voltammetry (CV) was performed with a three-electrode potentiostat [Bioanalytical Systems (BAS) 100B/W] in a grounded



Scheme 1. Synthesis of copolymer.

Faraday cage. A platinum-wire electrode was used as the auxiliary electrode. An Ag/AgCl electrode supplied by BAS was used as the reference electrode. The P(TT-co-EDOP) modified ITO (size 4 cm \times 0.9 cm, sheet resistance 12 Ω /sq.) electrode was used as the working electrode. All potentials were reported with respect to the Ag/AgCl electrode at room temperature under an argon atmosphere. The FTIR spectra were recorded on a Varian 660 FTIR spectrometer. The field emission scanning electron microscopy (FESEM) images of the modified electrode were obtained on a JSM-7500F field emission scanning electron microanalyzer (JEOL, Japan). A UV-vis spectrophotometer (Jasco-530 V) was used to conduct the spectroelectrochemical experiments and to characterize the devices. The colorimetry measurements were performed using a Minolta CS-100 spectrophotometer.

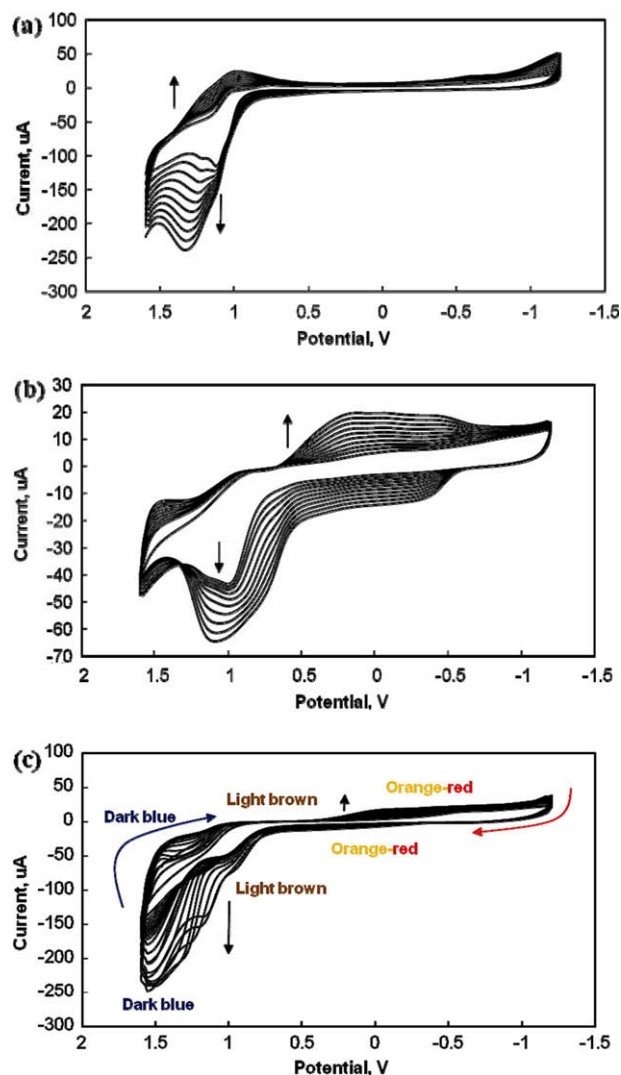


Fig. 1. Cyclic voltammograms of TT (a), EDOP (b) and TT/EDOP (c) using ITO-coated glass as working electrode, Ag/AgCl as reference electrode, Pt as counter electrode, 0.1 M TBAP/MeCN at a scan rate of 100 mV/s and 10 cycles.

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