

Synthesis and optoelectrochemical properties of a magenta-to-transmissive electrochromic polymer based on 3, 4-dioxythiophene

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ABSTRACT

A new magenta-to-transmissive electrochromic polymer, poly(3,4-bis(3-bromopropoxy)thiophene) (PBBrPOT) was synthesized by electrochemical polymerization and its electrochromic properties were characterized in detail. Compared with the representative “large-volume alkyl substituents” strategy, herein we use bromines as the end-capping groups of two propoxyl substituents on the 3- and 4- position of the thiophene ring to introduce more steric repulsion within the polymer chains, and therefore obtain a magenta neutral state of the polymer. The PBBrPOT film shows a set of reasonable electrochromic features, including low driving potentials (−0.1 V and 0.9 V), appropriate transmittance change (38% at 556 nm), but a relatively longer response time in bleaching process ($t_{95} = 6.5$ s).

1. Introduction

Electrochromism is noticed in reversible redox systems which display telling optical changes by the effect of externally applied potentials [1]. As one of the most popular electrochromic materials, conjugated polymers feature a number of superior electrochromic properties such as low driving potentials, high transmittance changes, short switching times and tunable colors [2].

Generally colored neutral states will be exhibited by conjugated polymers because they intrinsically possess extended delocalization of π electrons along the backbone, making their optical absorption be well localized in the visible region [3]. The oxidation of conjugated polymers (the removal of π -electrons from the valence band) creates half-filled polaron levels that are symmetrical about the bandgap center, causing the emergence of new electronic transitions at lower energies and a shift of the absorption to higher wavelengths, and therefore, the electrochromism occurs. [4]

Among various well noted electrochromic polymers, dioxythiophene-based π -conjugated polymers show particularly intriguing electrochromic properties as most of them feature a highly transmissive oxidized state which is highly essential for some popular real-world applications such as electrochromic windows and displays. The reason accounting for the transmissive oxidized state of polydioxythiophenes is documented by Nishinaga et al that the electron donating nature of dioxy-substituents stabilizes a closed-shell bipolaron structure in high p-doping levels [5].

A large number of representative works on colored-to-transmissive

electrochromic polymers based on dioxythiophene have been published by Reynolds' group [6–11], Toppare's laboratory [12] and other researchers [13–15] including us [16,17] in the last 15 years. Based on these pioneering studies, electrochromic polymers with additive primary colors (red, green, blue), subtractive primary colors (cyan, magenta, yellow) and even black color have been successfully developed, making progressive steps towards full color electrochromic applications.

Compared with red, green, blue and black, electrochromic polymers with subtractive primary colors, i.e. cyan, magenta and yellow neutral states are relatively rare. Among them, to the best of our knowledge, magenta-to-transmissive electrochromic polymer could be found in only a few papers [18,19]. Therefore, more polymers with different structures to realize magenta-to-transmissive electrochromic feature need to be developed.

Since the representative polydioxythiophenes such as polyethylenedioxythiophene (PEDOT) and polypropylenedioxythiophene (PProDOT) generally have blue neutral states due to the absorptions localized at the red region of the visible light [20,21], the most popular strategy to design magenta-to-transmissive electrochromic polymer is that introduce large-volume alkyl side chains such as 2-ethylhexyl or octadecyloxymethyl in polydioxythiophene derivatives to induce more steric hindrance [18,19], as a result the conjugation length of the polymer decreases and the bandgap increases, then consequently the absorption localized at the red region of the spectrum will shift to relatively shorter wavelength. That means a part of red light will be transmitted and combined with the blue light, producing a magenta

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color.

Having considerations based on above results, as a continuation of our efforts toward developing novel electrochromic polymeric materials [16,17], herein, we reported a new magenta-to-transmissive electrochromic polymer derived from dioxothiophene, poly(3,4-bis(3-bromopropoxy)thiophene) (PBBrPOT). In the study on electropolymerization of 3,4-dibromothiophene reported by Waltman et al. [22], they found that the bulky bromine substituents at the 3- and 4-positions of thiophene ring may hinder chain propagation by steric crowding, giving rise to a more severely twisted polymer. In the present work we hope that, with bulky bromines as the end capping groups of two propoxyl substituents on the 3- and 4- position of the thiophene ring, more steric repulsion between the side chains of PBBrPOT will be introduced, resulting in the decrease of the conjugation length to a specific extent, therefore, realizing a magenta-to-transmissive electrochromic polymer, as presented in the following results in this paper.

2. Experimental

2.1. Materials

3,4-Di(methoxy)thiophene (DMOT) was synthesized according to the procedure reported by Beaujuge and Reynolds et al. [23]. 3-Bromo-1-propanol and lithium perchlorate (LiClO_4 , 99%, anhydrous) were bought from Aladdin Industrial Inc. All other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd. All reagents were used as received without further purified unless otherwise noted.

2.2. Instruments

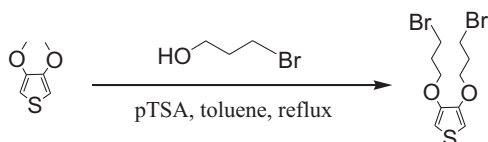
NMR spectra were obtained on a 400 MHz Bruker Avance 400 spectrometer in deuteriochloroform (CDCl_3). Mass spectra were obtained on a Electrostatic Field Orbital Trap Mass Spectrometer (Thermo, Orbitrap XL ETD). Cyclic voltammetry, spectroelectrochemistry and colorimetry experiments were carried out on CHI600E electrochemical analyzer (CH Instruments Ins.) and T6 New Happy UV-Vis-NIR spectrometer (Beijing Persee General).

2.3. Synthesis of 3,4-bis(3-bromopropoxy)thiophene (BBrPOT)

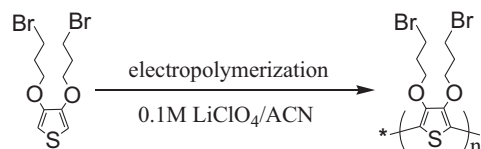
The pathway of the synthesis of the monomer BBrPOT is depicted in Scheme 1. 3,4-di(methoxy)thiophene (50 mmol), p-toluenesulfonic acid (5 mmol), 3-bromo-1-propanol (150 mmol) and 300 mL toluene were combined in a round bottom flask equipped with a Soxhlet extractor with type 4 Å molecular sieves. The mixture was refluxed for 12 h, cooled and washed with deionized water for multiple times. The toluene was removed through rotary evaporation under vacuum. The residue was subjected to column chromatography (hexane / chloroform = 8 : 1, v / v) to give the final product as a white solid. ^1H NMR (400 MHz, CDCl_3 , δ): 6.25 (s, 2H), 4.12 (t, 4H), 3.59 (t, 4H), 2.34 (t, 4H). ^{13}C NMR (100 MHz, CDCl_3 , δ): 29.98, 32.21, 67.92, 97.93, 146.95. HRMS m/z = 357.9135 $[\text{M} + \text{H}]^+$, calc. for $\text{C}_{10}\text{H}_{14}\text{Br}_2\text{O}_2\text{S}$ = 357.91.

2.4. Synthesis of PBBrPOT

The electropolymerization was performed in an one-compartment cell with three electrodes (Pt wire as the counter electrode, Ag wire as the pseudo-reference electrode and an ITO-coated glass slide as the



Scheme 1. The synthesis of BBrPOT.sc1.



Scheme 2. The synthesis of PBBrPOT. sc2.

working electrode). The electrolytic solution consists of 0.03 M BBrPOT and 0.1 M LiClO_4 / ACN electrolyte-solvent couple. The solution was deaerated by dry nitrogen and maintained under a minor overpressure during the polymerization to circumvent the effect of oxygen. The polymer was directly deposited on ITO / glass potential dynamically through cyclic voltammetry scan between 0 V and 1.9 V for 10 segments (5 cycles). After polymerization, the polymer film was repeatedly washed with ACN to remove the electrolyte, monomers and oligomers. The synthetic route is shown in Scheme 2.

2.5. Electrochemical and spectroelectrochemical experiments

The electrochemical and spectroelectrochemical experiments were carried out in a quartz cuvette consisting of an ITO / glass (4 cm \times 0.7 cm) as the working electrode, a Pt wire as the counter electrode and an Ag wire as the pseudo-reference electrode. All measurements were performed in monomer-free lithium perchlorate (LiClO_4) – propylene carbonate (PC) electrolytic medium as PC is a good solvent to dissolve and dissociate lithium salts which has been documented by Haregewoin et al [24]. Ag wire pseudo reference electrode was calibrated externally using 5 mM solution of ferrocene (Fc/Fc^+) in the same electrolyte ($E_{1/2}(\text{Fc}/\text{Fc}^+) = 0.36$ V versus Ag wire in 0.1 M LiClO_4 / PC). The potentials are reported versus Ag wire according to the suggestion of Toppare [25]. Following the suggestion of Silva and Ribeiro et al. [26], CIE (Commission Internationale de l'Éclairage) 1931 color coordinates (x , y) and relative luminance were calculated from UV-Vis-NIR spectroscopy using a Spectra Lux Software [27] and a Microsoft Excel spreadsheet developed by Mortimer and Varley [28].

3. Results and discussion

3.1. Electrochemical polymerization

The electropolymerization was carried out using successive cyclic voltammetry (CV) of BBrPOT (0.03 M) in 0.1 M LiClO_4 / ACN solution between 0 and 1.9 V for 5 cycles at a potential scan rate of 100 mV/s and the resulting polymer was deposited on indium tin oxide (ITO) coated glass slides.

As shown in Fig. 1, the first cycle of the CV test is attributed to the oxidation of BBrPOT monomer. The onset oxidation potential is at

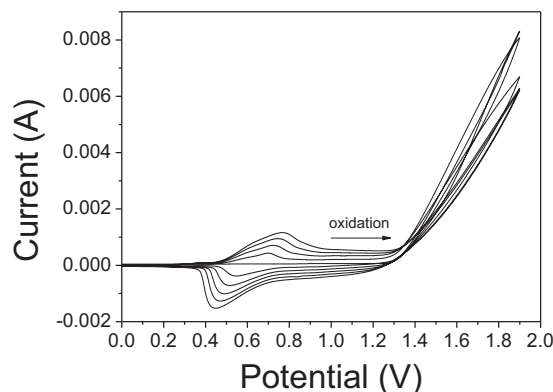


Fig. 1. Successive cyclic voltammogram of 0.03 M BBrPOT between 0 and 1.9 V at 100 mV/s in 0.1 M LiClO_4 in ACN.

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