



# Synthesis of polyether-bridged bithiophenes and their electrochemical polymerization to electrochromic property



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## ABSTRACT

The polyether-bridged 2,2'-bithiophenes were designed with a single methylene between the thiophene ring and the first oxygen atom in polyether, and synthesized by the Williamson reaction and the Suzuki coupling reaction. The electrochemical polymerization of as-synthesized monomers were investigated. The as-prepared polymers of polyether-bridged 2,2'-bithiophenes (P(BT-E-BT)) show a better electrochemical activity with a high-quality film on electrodes compared to the polymers of polyether-bridged thiophenes (T-E-T) in a neutral media. The P(BT-E-BT) exhibited broad absorption in near infrared region with the band gaps (2.03–2.05 eV) and the good thermal stability. The versatile coloration change for P(BT-E-BT) films on a ITO glass electrode were achieved from salmon pink (neutral state) to blue–green and transmissive rusty red (oxidized states). Further electrochromic investigation implied that the polymer P(BT-E-BT) films showed moderate to high contrast ratios, good coloration efficiencies, low switching voltages, fast response times, excellent stabilities and colour persistence as potential electrochromic materials.

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## 1. Introduction

Polythiophene and its derivatives, an important class of five-membered unsaturated heterocyclic polymers with excellent environmental stability and electroactivity, have attracted great attention in the field of organic electron devices such as the field-effect transistors, electroluminescent devices, solar cells, photochemical resists, chemical sensors and so on [1–4]. Over the past decades, the considerable interest have focused on the polymerization of thiophene with the modification of different functional groups. Since the functionalization can not only improve the solubility and processability of conjugated polythiophene, but also achieve the structure control on a molecular level for electronic and electrochemical properties [5–7].

Presently, thiophene modified by different terminal  $\alpha$  and  $\beta$  substituents such as alkyl, alkyl sulphonate, and polyether chains have been synthesized and their polymers show superior electrochemical activity in previous reports [8–10]. The polythiophene  $\beta$ -substituted by polyether chains is one of the most

important parts as the promising electroactive materials for solid-state batteries and ion-selective electrodes [9,11]. Initially, the polyether functionalized polythiophenes are of special interest in ionophoric resins [12]. The introduction of polyether chains with appropriate length in polythiophene effectively minimize the steric hindrance leading to the good conjugation of polymer backbone [11,13]. However, the oxygen atoms in polyether chains badly affect the polymerization of monomers and the properties of the resulting polymers. Roncali et al. pointed out that the electron-withdrawing effect of oxygen in polyether group increased the oxidation potential of the monomer and lowered the polymer yield, leading to the formation of large amounts of soluble products and the low conductivity [14]. Taking into account of the drawbacks, the introduction of ether groups requires a double methylene spacer between the thiophene ring and the first oxygen atom to neutralize its electron-withdrawing effect on the conjugated system [11,14]. Furthermore, bithiophenes bridged by polyether were developed and used to produce the highly conjugated structural polymers by electrochemical method with a low oxidation potential [9,13]. Additionally, the introduction of polyether is easy to leads to the formation of cavity structures for the polymers of bithiophene. It is expected for polymers that the cavities are capable of interacting with guest species potentially and resulting in a good electroactivity consequently [9].

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As we know, thiophene group is recognized as an important unit in conjugated polymer electrochromic devices. However, most of polyether bridged thiophene polymers are limited to the electrochemical properties and chemical sensors [15]. For polythiophene modified by polyether, one of the most distinguished feature is its large electrochemical active surface area due to easy formation of cross-linking structure [16]. Compared with chemical polymerization routes, the facile electrochemical polymerization has been proved to be one of the most useful approaches for the produce of high quality conducting polymer films [17–19]. Additionally, it combines polymerization and deposition into one step and bypasses polymer isolation and purification. Polythiophenes prepared by electrochemistry good electrochromic materials due to their excellent stability, high conductivity, swift change of color with potential and low band gap [20]. Recently, enormous efforts have been devoted to the design and synthesis of novel conducting polymer electrochromic materials [21]. The band gap project has attracted great attention on tuning the electrochromic property by introduction of donor and acceptor group in the main chain, which leads to the various color change [22,23]. Therefore, the polythiophene derivatives modified by polyether chains as donor are expected to possess some novel color and superior electrochromic properties.

In this work, we designed and synthesized the various length polyether chains bridged thiophene (T-E-T) and 2,2'-bithiophene (BT-E-BT) groups using the common reaction of Williamson and Suzuki coupling reactions [24], respectively. The electrochemical polymerization were performed and the electrochemical performance of the corresponding polymer films were investigated in 0.2M LiClO<sub>4</sub>/ACN solution. The morphology and structure of polymer films were characterized using FT-IR spectra, scanning electron microscope (SEM), and *in-situ* spectroelectrochemistry. Based on their versatile color change, we investigated the electrochromic parameters including the optical contrast ratio ( $\Delta T\%$ ), response time, and coloration efficiency (*CE*) of as-prepared polymer films in detail. The polymer of polyether bridged 2,2'-bithiophene P(BT-E-BT) exhibited the acceptable electrochromic performance.

## 2. Experimental

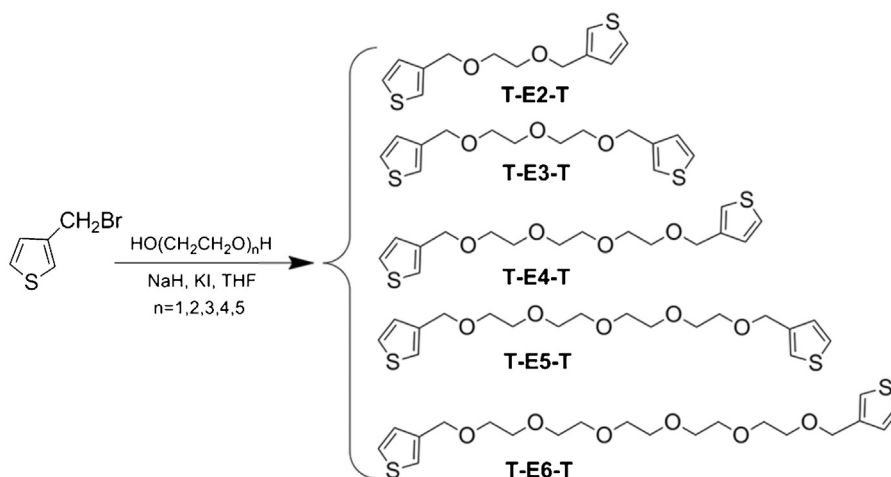
### 2.1. Materials

3-Bromomethylthiophene (98%), ethylene glycol (99.5%), diethylene glycol (99%), triethylene glycol (99%), tetraethylene glycol (98%), pentaethylene glycol (98%), 2-thiopheneboronic acid (95%), tetrakis(triphenylphosphine) palladium (Pd(PPh<sub>3</sub>)<sub>4</sub>, 99%), anhydrous Na<sub>2</sub>CO<sub>3</sub>, and sodium chloride were purchased from Shanghai J&K Scientific Ltd. Sodium hydride (NaH, 60%), potassium iodide (KI, 99.5%; Tianjin Damao Chemical Reagent Factory), sodium hydroxide ( $\geq 99.5\%$ ; Shantou Xilong Chemical Industry Co. Ltd.), N-bromosuccinimide (NBS, 99%; Energy Chemical) were used without further purification. Chloroform (CHCl<sub>3</sub>), dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), acetic acid (CH<sub>3</sub>COOH), acetone and diethyl ether were obtained from Beijing Chemical Reagents Company with their purity being of analytical grade. Acetonitrile (ACN), boron fluoride ethyl ether (BFEE) and tetrahydrofuran (THF) were purified by distillation over calcium hydride and sealed storage before use; Tetra-n-butylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>, 98%; Engy Chemical) and lithium perchlorate (LiClO<sub>4</sub>, 99%; Acros Organics) was dried under vacuum at 60 °C for 24 h before used.

### 2.2. Monomer synthesis

#### 2.2.1. Polyether-bridged thiophene groups (T-E-T, Scheme 1)

The thiophene groups linked with different length of polyether chain were synthesized as precursors by the common Williamson reaction. Ethylene glycol/diethylene glycol/triethylene glycol/tetraethylene glycol/pentaethylene glycol (5 mmol), KI (0.17 g, 1 mmol), and NaH (60%, 0.52 g, 13 mmol) were added into a three-necked flask and dissolved in THF (10 mL) with stirring. This flask was kept in an ice bath, and then a solution of 3-bromomethylthiophene (2.22 g, 12.5 mmol) in THF (10 mL) was injected slowly within an hour. After that, the reaction was performed at 50 °C with continuous stirring and kept for 10 h under a nitrogen atmosphere. After cooling to room temperature, 20 mL H<sub>2</sub>O was added. The resultant mixture was extracted with ethyl acetate (3 × 30 mL). The organic phase was separated washed with brine solution (3 × 100 mL), dried with anhydrous MgSO<sub>4</sub>, and filtered. After evaporation of the solvent, the remaining crude product was isolated by flash chromatography using petroleum ether/ethyl acetate as an eluent on silica gel. Eventually, the yellow oily liquid



Scheme 1. Synthetic routes of T-E-T.

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