

Electrochemical copolymerization of benzothiophene with thiophene

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ABSTRACT

Copolymerization of benzothiophene (BTh) with thiophene (Th) was successfully achieved electrochemically by potentiodynamic methods. BTh and Th were also both copolymerized separately with pyrrole (Py) for comparison. The electrochemical properties of copolymers obtained at different monomer concentrations, scan rates and scan numbers were characterized by voltametric, electrochemical impedance spectroscopy (EIS), ATR-FTIR, spectroelectrochemical and conductivity measurements. Results suggested that optical band gaps and oxidation potentials can be decreased by copolymerization and this advantage makes copolymers suitable for electrochromic and photovoltaic applications. Conductivity of copolymers generally lies in between that of homopolymers and specific capacitance value of BTh could be raised from 18.9 mF/cm² to 138.3 mF/cm² by copolymerization with Py. A proper mechanism for copolymerization was suggested.

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1. Introduction

Polythiophenes (PTh) are a large family that has been studied extensively during the last decades by researchers due to their satisfying chromic [1] and fluorescent properties [2] and also their stability on environmental and operational conditions [3]. BTh however has been the subject to a few publications concerning the electrochemical polymerization [4–6]. It has been reported that relatively transparent, highly-conducting polymeric film was obtained electrochemically if appropriate supporting electrolyte, solvent and current density were selected [6]. It has been electrochemically polymerized in acetonitrile or benzonitrile [6], in boron trifluoride diethyl etherate (BFEE) in which the oxidation potentials of aromatic monomers are considerably lowered [7,8]. It has been also reported that the electrochemical polymerization of BTh most probably occurs at 2, 4, and 7 positions that is consistent with the previous literature reports. Although the current efficiency is low and the film quality is rather poor, PBTh had been shown as a potential material for commercial applications such as lasers due to its strong fluorescence in the blue light region [7].

A lot of studies have been reported on copolymerization of thiophene (Th) and pyrrole (Py) derivatives in order to obtain even much better featured copolymers [9–13]. On the other hand there are only a few studies on the copolymerization of BTh. Seki et al. has reported electrochemical copolymerization of BTh with Py in acetonitrile and reported flexible and transparent conductive poly-

mer with a rough and brittle surface [14]. In the same research it was also reported that the conductivity reaches a gentle maximum when benzothiophene composition is about 40–50 mol%.

So in the light of literature, in this study BTh was electrochemically copolymerized with Th and Py in tetrabutylammonium hexafluorophosphate (TBAPF₆) containing dichloromethane (DCM) and P(BTh-co-Py) and P(BTh-co-Th) were obtained. In order to understand the optic and electrochromic properties of the copolymers, in situ spectroelectrochemical and electrochemical impedance spectroscopy, electrical conductivity and SEM measurements of them were performed and the copolymerization mechanism was suggested.

2. Experimental

2.1. Materials

Py (from Fluka with a purity of 97%); Th (from Sigma Aldrich with a purity of 99%) and BTh (from Aldrich with a purity of 95%) were used as supplied. Tetrabutylammonium hexafluorophosphate (TBAPF₆ from Fluka) and dichloromethane (DCM) (Merck) were analytical grade chemicals of the highest purity and used without further purification.

2.2. Measurements

All electrochemical experiments were performed at room temperature (25 °C ± 1) using a PARSTAT 2263 model potentiostat connected to a computer. The electrochemical impedance software PowerSine was used to carry out impedance measurements

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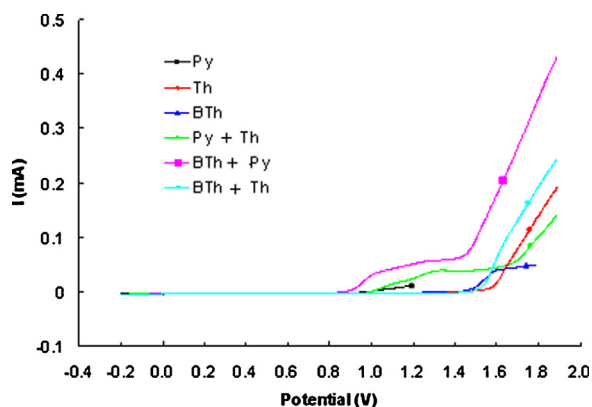


Fig. 1. The anodic polymerization curves of 4.92×10^{-3} M Py, 0.1 M Th, 0.1 M BTh and Py+Th, BTh+Py, BTh+Th ($n_{\text{Py}}/n_{\text{Th}} = 1:1$, $n_{\text{BTh}}/n_{\text{Py}} = 1:1$, and $n_{\text{BTh}}/n_{\text{Th}} = 1:1$) in 0.1 M TBAPF₆ in DCM. (Scan rate = 50 mV/s).

between 10 mHz and 10 kHz (amplitude of 10 mV). Specific capacitance (C_{sp}) was obtained from the slope of imaginary component of the impedance (Z_{im}) versus inverse of the reciprocal frequency (f) using the following equation [15].

$$C_{\text{sp}} = (2\pi \cdot f \cdot Z_{\text{im}})^{-1}$$

FTIR spectra were recorded on a JASCO FTIR 5300 Fourier transform infrared spectrometer using KBr pellets prepared from polymers or copolymer powders. A Shimadzu UV-160 UV Visible Spectrophotometer was used for spectroelectrochemical measurements of the polymers deposited on indium-tin-oxide (ITO) coated glass (8 mm × 50 mm × 1.1 mm). In order to obtain the polymers

in the oxidized form, in a monomer free solution 1.2 V, 1.9 V, 1.7 V, 1.4 V and 1.7 V were applied for PPy, PTh, P(Py-co-Th), P(BTh-co-Py) and P(BTh-co-Py) respectively. The electrochemical un-doping and re-doping processes of polymers were performed by applying constant potentials of -1.0 V and 1.0 V respectively.

Solid state electrical conductivity measurements were performed from pellets (the thickness was c.a 0.8 mm) by using Keithley 2400 model current source, Keithley 2000 multimeter, Lucas labs 302 model probe holder and SP4-180-TFS type probe and calculated from the following equation as suggested in literature [16]:

$$\sigma = V^{-1} I \left(\frac{\ln 2}{\pi d_n} \right)$$

where V is the potential in volts, I is current in ampere, and d_n is the thickness in cm.

The morphological studies of the polymer films were performed with a JEOL JSM-T330 scanning electron microscope (SEM).

2.3. Electrochemical synthesis

The synthesis of all homopolymers and copolymers was performed electrochemically by potentiodynamic method on Pt button electrode (area = 0.022 cm²). Counter electrode was Pt wire and a pseudo reference electrode was Ag wire and calibrated externally using a 5 mM solution of ferrocene/ferrocenium (Fc/Fc⁺) couple (0.35 V vs. Ag/AgCl) in the electrolyte and the potentials are reported versus Ag/AgCl. Prior to each examination, electrodes were carefully polished and cleaned with deionized water and acetone then dried in air. The polymerization solution consisted of 0.1 M TBAPF₆ in DCM as an electrolyte and monomers (4.92×10^{-3} M Py, 0.1 M Th and 0.1 M BTh) or monomer mixtures

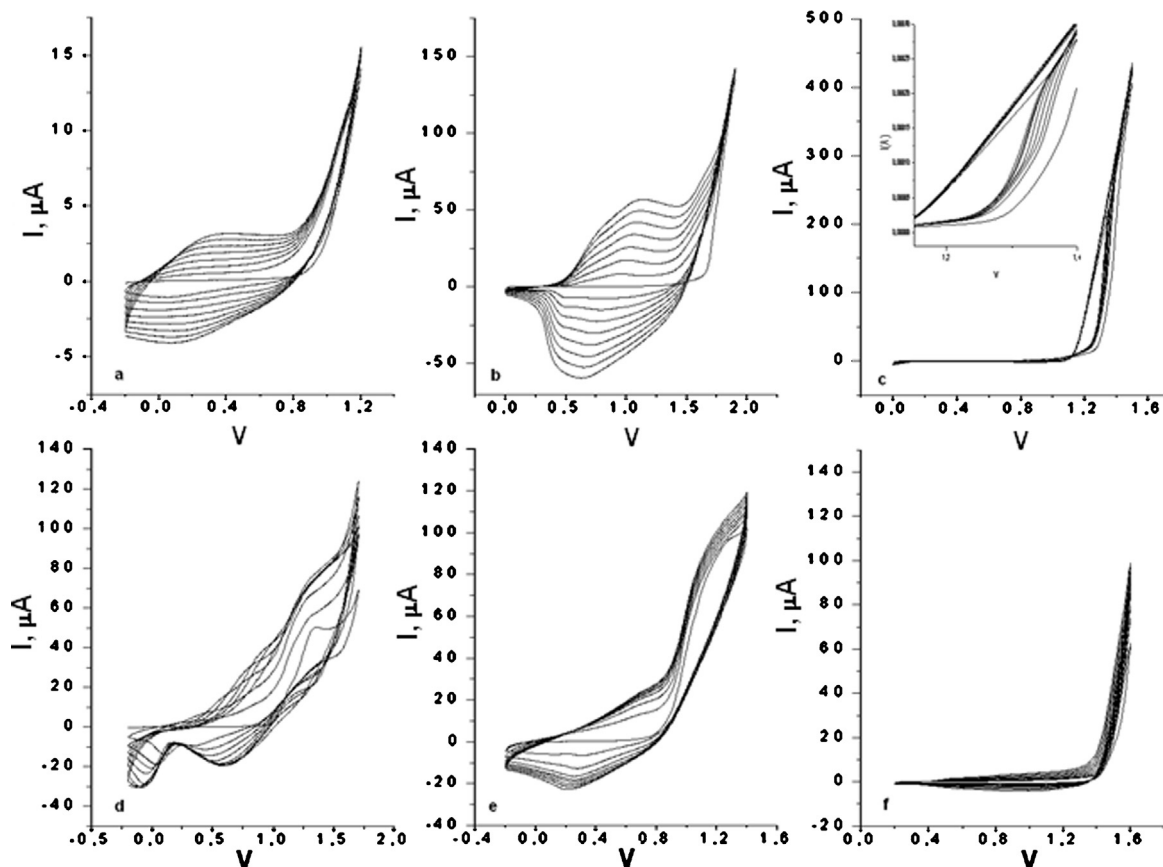


Fig. 2. The CV of (a) PPy at 50 mV/s, (b) Th at 100 mV/s, (c) PBTh at 20 mV/s, (d) P[Py-co-Th] at 50 mV/s, (e) P[BTh-co-Py] at 50 mV/s and (f) P[BTh-co-Th] at 50 mV/s in 0.1 M TBAPF₆ in DCM.

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