



Electrochemical characterization of newly synthesized polyterthiophene benzoate and its applications to an electrochromic device and a photovoltaic cell

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ABSTRACT

A novel conjugated polymer bridged a benzene ring between polymer backbone and carboxylic acid, poly(2,2':5',2''-terthiophene-3'-*p*-benzoic acid) (pTTBA) has been synthesized and applied to an electrochromic device and a polymer-sensitized solar cell. The pTTBA is characterized as a photo sensitizer on a TiO₂ layer, and the cell performance is compared with that of poly(5,2':5',2''-3'-carboxylic acid) (pTTCA), which does not contain the benzene ring. The conductivity of pTTBA is determined to be 0.24 S cm⁻¹ at 1.4 V. The spectroelectrochemical study shows that pTTBA switches to an opaque dark-blue in its oxidized state from transmissive yellow in its reduced state with a contrast of 53%. The polymer film exhibits a good optical switching time within 0.82 s. The pTTBA film has a band gap energy of 1.98 eV. The impedance results show that the pTTBA is the enhanced electron transfer process in the TiO₂/polymer/electrolyte interface in comparison with that of pTTCA. A photovoltaic cell is assembled with pTTBA coated on the TiO₂ electrode as an anode and Pt-counter electrode as a cathode. The electrolyte is used a propionitrile solution containing I⁻/I₃⁻ as a redox couple. The higher energy conversion efficiency was achieved with the pTTBA based dye solar cell (3.97%) (active layer = 0.24 cm²).

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1. Introduction

Of the various π -conjugated polymers, polythiophene (PT) is one of the most important and widely studied polymers because of its high stability in air and potential applications [1,2]. PTs have been used in a variety of applications such as organic field-effect transistors (OFETs) [2], polymer light-emitting diodes (PLEDs) [3], solar cells [4], and chemical sensors [5], because of their ability to be processed, environmental stability, thermal stability, and good electronic properties. However, the high oxidation potential of the monomers and the α - β coupling between the thiophene rings during polymerization cause these polymers to have poor chemical and physical properties. To overcome this limitation, 3-substituted and 3,4-disubstituted PTs have been synthesized using different functional groups [6,7]. However, the resultant structures must contain large numbers of thiophene ring that are twisted far out of conjugation as a result of steric hindrance between 3- or/and 3,4-substituents (functional groups). To avoid such problems, we tried to synthesize terthiophenes containing a functional group as a unit of polymer backbone instead of thiophene. These compounds can be easily applied for use in the electrochromic devices,

solar cell electrode materials, and other various applications. We previously studied the applications of 3'-substituted terthiophene derivatives [8–11]. These polymers show chemical stability in their oxidized states, high optical contrast values, and fast switching times between redox states. The electrochemical and spectroscopic properties of these polymers also vary significantly according to the degree of extended conjugation between the consecutive repeated units. Controlling the band gap of conjugated polymers, one important property, is an essential application for the electrochromism devices and solar cell systems. The band gap is controlled by five contributions *via* bond-length alternation, aromaticity, conjugation length, substituent effects, and intermolecular interactions related to the conjugated polymer backbone [12]. Since the emitted light (color) depends on the band gap of the π - π^* transition; therefore, the modification of the structure will affect the electronic properties, which will consequently change the emitted color and intensity.

It has been previously demonstrated that PTs can be applied in electrochromic devices (ECDs) on the basis of their well-defined electrochromic behaviors [13]. Most ECDs materials can be applied in a variety of photovoltaic devices. Thus, it is interesting to apply these polymers for use in the electrochromic devices and dye sensitized solar cells (DSSCs) [10,14,15]. Of the available solar cells, DSSCs based on nanocrystalline TiO₂ is an essential type of photovoltaic cell, since the properties of photosensitizers, such as the absorptivity of photons in the visible region (absorption color) and

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the electron-transfer rate are important factors in determining the photovoltaic cell performance. Recently, the interest in polymer-sensitizers, such as polythiophenes, is increasing because of their various advantages, including their diverse of molecular structure, and high molar extinction coefficient. To date, the highest energy conversion efficiency of these polymer dye cells is approximately 2.32% using pTTCA [10]. Although the energy conversion efficiency of these cells is lower than that of ruthenium complex dyes [16], it has potential applicability to the solar cell because of the increasing efficiency through the change of structure of these polymers [10,14,17]. Thus, we tried to improve the low energy conversion efficiency of the cells using a polyterthiophene backbone bearing a carboxylic acid bridged with a conjugated benzene ring. The role of the carboxylic acid groups was very strongly absorbed onto the TiO₂ layer through the covalent C–O–Ti bond formation [18]. The TTBA consists of the terthiophene backbone moiety acting as an electron donor and carboxylic acid moiety acting as an acceptor, and the two functional groups are connected by a π -conjugated benzene ring. A conjugated benzyl moiety can help enhance electron transfer from terthiophene backbone moiety to carboxylic acid moiety. Furthermore, this configuration is expected to be more reactive with resonance effect, significantly reduces steric hindrance with bulky group of terthiophene moiety, and avoids the aggregation of conjugate polymer dye on the TiO₂ surface, which contributes the enhancement of the electron transfer property.

In the present study, we synthesized and characterized a 3'-substituted polyterthiophene derivative (pTTBA) containing an electro-withdrawing *p*-benzoic acid group as a potential material for solar cells. The structure of the monomer was analyzed by ¹H NMR, ¹³C NMR, FT-IR and mass spectroscopy. The resulting polymer film was electrochemically and spectroelectrochemically characterized by cyclic voltammetry (CV), conductivity, *in situ* UV-vis spectroscopy, and electrochromic behavior studies. The solar cell performance of pTTBA was compared with pTTCA, which does not contain the benzyl moiety in the polymer backbone structure. Electrochemical impedance spectroscopy (EIS) was also employed to investigate the charge-transfer processes of polymer dye solar cells. We have studied its performance both as a polymer photovoltaic cell and as an electrochromic display function.

2. Experimental

2.1. Chemicals

All chemical reagents were purchased from Sigma–Aldrich Co. (USA), and were used as received. All aqueous solutions were prepared in double distilled water, which was obtained from a Milli-Q water-purifying system (18 M Ω cm). 3'-Bromo-2,2':5,2''-terthiophene (BTT) was synthesized by the method in the literature [13]. All reactions and manipulations were carried out under N₂ with the use of standard inert atmosphere and Schlenk techniques. Chromatography for product separation and purification was carried out using silica gel for flash columns, 70–230 mesh. The fluorine-doped SnO₂ (FTO, 2.2 mm 15 Ω sq⁻¹), TiO₂ (Ti-Nanoxide HT), the electrolyte (Iodolyte PN-50), the Pt paste (platisol), and the hot-melt film (SX 1170-60) were purchased from Solaronix (Switzerland).

2.2. Measurements

The ¹H and ¹³C NMR spectra were obtained in deuterated chloroform (CDCl₃) using a Bruker Advance 300. Chemical shifts are given in parts per million (ppm) with tetramethylsilane (TMS) as an internal standard. Mass spectra were recorded on a JMS-700 double focusing mass spectrometer (JEOL, Japan) The FT-IR

spectrum was recorded using a JASCO FT-IR spectrometer. The absorption spectrum was recorded in a dilute dichloromethane solution with a Shimadzu UVPC-3101 spectrometer. The emission spectrum was measured in a dilute dichloromethane solution with a PerkinElmer LS50B Fluorescence spectrophotometer. The atomic force microscopy (AFM) images were obtained in ambient conditions using a Multimode AFM device (Veeco Metrology) equipped with a Nanoscope IV controller (Veeco). The cyclic voltammetry (CV) was performed using a potentiostat/galvanostat, Kosentech, Model PT-2 (South Korea). A quartz crystal microbalance (QCM) experiment was conducted using a SEIKO EG&G model QCA 917 and a PAR model 263A potentiostat/galvanostat. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of a platinum (Pt) working electrode, a platinum wire counter electrode, and Ag/AgCl reference electrode. The solvent in all experiments was dichloromethane, and the supporting electrolyte was 0.1 M tetrabutylammonium perchlorate (TBAP) dried at a vacuum oven (1.33 \times 10⁻³ Pa). *In situ* UV-vis spectroscopic spectra were obtained from a UV-vis spectrometer assembled to a CCD detector, a xenon flash lamp, and a bifurcated optical fiber from Ocean Optics Co. An electrochemical cell with a quartz window was used for the *in situ* experiment. The method for obtaining the absorption spectra was the same as the one previously report in the literature [19]. The impedance spectra were measured with the EG&G Princeton Applied Research PAR-STAT 2263 at an open circuit voltage from 100 kHz to 100 mHz at a sampling rate of five points per decade (AC amplitude: 10 mV). The photovoltaic measurement was performed using an air mass (AM) 1.5 solar simulators that were equipped with a 150 W xenon lamp (Model 92251A, Newport). The power of the simulated light was calibrated to 100 mW cm⁻² using a reference Si photodiode, which was measured at the solar-energy institute (NREL, USA). The short-circuit photocurrent of the reference Si solar cell was calibrated to the average data from NREL under the one-sun condition. Curves I–V were obtained by measuring the generated photocurrent using a Keithley Model 2400 digital source meter.

2.3. Synthesis of monomer

3'-Bromo-2,2':5,2''-terthiophene (BTT) was prepared according to a previously reported method [13]. A degassed diethyl ether solution (15 mL) of BTT (3.27 g, 10.0 mmol) was slowly reacted with tetramethylethylenediamine (TMEDA) (1.8 mL, 12.0 mmol) and 1.6 M *n*-BuLi (7.5 mL, 12.0 mmol) under N₂ atmosphere at –83 °C. The reaction mixture was stirred for 1 h at –83 °C, and trimethyl borate (2.2 mL, 20.0 mmol) diluted in diethyl ether (30 mL) was added. The mixture was allowed to warm to room temperature and was stirred for 4 h after 2 M HCl (20 mL) was added. After 1.5 h of additional stirring, crude 2,2':5,2''-terthiophene-3'-boronic acid (TTB) was precipitated out in white solids, washed with water and dried under reduced pressure. The crude TTB, 4-bromobenzonitrile (1.7 g, excess), Pd(PPh₃)₄ (0.116 g, 1.0 mol%), toluene (20 mL) and a nitrogen degassed aqueous solution of 2 M K₂CO₃ (8 mL, 16.0 mmol) were added and stirred for 10 min under N₂. The mixture was heated at 80 °C for 24 h and monitored *via* thin layer chromatography (TLC) for reaction completion. Toluene was then evaporated using a rotary evaporator and the product was extracted with dichloromethane, washed with water, and dried over MgSO₄. The removal of the solvent afforded the crude product as brown oil, which was then precipitated out in methanol. The residue was purified by chromatography on silica gel eluted with *n*-hexane/dichloromethane (2:1) to yield 1.98 g (48%) of BNIT as a yellow-green solid. IR (KBr): 2215, 1495 cm⁻¹; ¹H NMR (CDCl₃): 5.34 (s, 2H), 6.96–6.99 (m, 1H), 7.02–7.08 (m, 3H), 7.20–7.24 (m, 3H), 8.34 (s, 2H); ¹³C NMR (CDCl₃): 120.2, 124.2, 125.0, 125.9, 126.4,

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