Synthesis, electrochemical, and spectroelectrochemical properties of conductive poly-[2,5-di-(2-thienyl)-1H-pyrrole-1-(p-benzoic acid)]

Yung Hyun Kim 1, Jaeyoung Hwang 1, Jung Ik Son, Yoon-Bo Shim *

Department of Chemistry, Pusan National University, Geumjeong-gu, Busan 609-735, South Korea

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Poly(ter-heteroaromatic(thiophene-pyrrole-thiophene)), PDPB, was electrochemically prepared from the 2,5-di(2-thienyl)-1H-pyrrole-1-(p-benzoic acid) (DPB) monomer using the Paal-Knorr pyrrole condensation reaction. The structure of the monomer was confirmed using 1H-, 13C NMR, FT-IR and mass spectroscopy. The maximum UV–visible absorption and PL emission bands of PDPB were observed at 330 nm and 500 nm, respectively. The cyclic voltammograms (CVs) recorded for the electrochemically polymerized DPB revealed a set of redox peaks at 0.65/0.53 V. The conductivity monotonically increased with respect to the applied potential from 0.0 V to 1.0 V, exhibiting a maximum conductivity of 0.18 S/cm at +0.80 V. The in situ UV–visible spectroelectrochemical analysis of PDPB revealed electronic transitions at 420 nm, 654 nm, and 870 nm corresponding to the \( \pi-\pi^* \) transition, polaron, and bipolaron states, respectively. The optical band-gap (\( E_g \)) of PDPB was 2.16 eV. The color of the PDPB film transitioned yellow (at 0.0 V) to blue (at 1.0 V) when the potential was switched between the reduced and oxidized states with a good electrochromic response time (0.95 s).

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1. Introduction

\( \pi \)-Conjugated polymers [1,2] have intensively been investigated due to their potential applicability as sensors [3–6], electrochromic materials [7,8], etc. The \( \pi \)-conjugated polymers that belonging to the family of polyheteroaromatics, such as polypyrroles and polythiophenes are analogous to the polymer backbone structure. Since, these polymers are insoluble and infusible, numerous substituted derivatives of these polymers have been developed in order to overcome these problems [9]. Synthesized electroactive processable polymeric materials with a linear combination of thiophenes as the external units and \( N \)-substituted pyrrole as the central unit (2,5-di(2-thienyl)-1H-pyrrole derivatives) have attracted interest. These derivatives are easily synthesized using the Paal-Knorr pyrrole condensation reaction [10] and are cheaper and more easily processable than thiophene derivatives. Additionally, the oxidation potential of the 2,5-di(2-thienyl)-1H-pyrrole derivative is lower than the thiophene derivative, and poly-[2,5-di-(2-thienyl)-1H-pyrrole] films can easily be formed on an electrode using various solvents [11,12].

The 2,5-di(2-thienyl)-1H-pyrrole derivative, [(2,5-di-(2-thienyl)-1H-pyrrole)-1-(p-benzoic acid)] (DPB) was chosen as a model compound because, in this system, the carboxylic acid group of benzoic acid is one of the most useful units to further incorporate functional groups into the polymer backbone. In particular, specific biological species including enzymes, antibiotics, DNA, receptors, and even whole cells, can be grafted onto the monomer units through the carboxylic group of DPB, which can be electropolymerized on an electrode in order to construct conducting polymer biosensors [4,13–15].

In the present study, DPB was synthesized using the Paal-Knorr pyrrole condensation reaction. The structure of the 2,5-di(2-thienyl)-1H-pyrrole derivative (DPB) was analyzed using 1H-, 13C NMR, FT-IR and mass spectroscopy. The spectroscopic and luminescence behavior of DPB was investigated using UV–visible and photoluminescence (PL) spectroscopy. This study presented a simple preparation method for PDPB using as a monomeric block and electropolymerization. The resulting polymer was analyzed using cyclic voltammetry (CV) and in situ UV–visible spectroscopy and the electrochromic and electrical properties were characterized.

2. Experimental

2.1. Materials

Thiophene, aluminium chloride (\( \text{AlCl}_3 \)), succinyl chloride, 4-aminobenzonitrile, and p-toluenesulfonic acid (PTSA) were purchased from the Sigma–Aldrich Co. (USA). Column chro-
matography was performed on a silica gel 60 (70–230 mesh). Tetrabutylammonium perchlorate (TBAP, electrochemical grade) was obtained from the Fluka Co. and dried under a vacuum (10⁻⁵ Torr). Dichloromethane (99.8%, anhydrous, sealed under N₂ gas) was purchased from the Sigma–Aldrich Co. (USA). All of the aqueous solutions were prepared from doubly distilled water, which was obtained from a Milli-Q water-purifying system (18 MΩ cm).

2.2. Instruments

The 1H and 13C NMR experiments were conducted using a Bruker Advance 300 FT-NMR with CDCl3 as the solvent unless otherwise stated. The chemical shifts (in ppm) were observed downfield from tetramethylsilane (TMS). The FT-IR spectrum was recorded using a JASCO FT-IR spectrometer. The absorbance spectrum was obtained using a Shimadzu UVPC-3101 spectrometer and the photoluminescence spectrum was obtained using a PerkinElmer LS50B.

The cyclic voltammetry (CV) was performed using a Kosentech Model PT-2 (S. Korea) and a Princeton Applied Research, Model 273 (USA) potentiostat/galvanostat. A Pt working electrode, a platinum wire counter electrode and Ag/AgCl reference electrode were used in the three-electrode system. The Pt electrode was polished with 1.0 µ, 0.5 µ, and 0.05 µ alumina/water slurries until the surface exhibited a mirror finish and then sonicated following by rinsed with distilled water. After polishing, the electrode was electrochemically pretreated through potential cycling between +1.5 V and −1.4 V in 0.1 M H₂SO₄. The in situ UV–visible spectroscopic data were obtained using a UV–visible spectrometer that was assembled with a CCD detector, a Xenon flash lamp, and a bifurcated optical fiber from the Ocean Optics Co. An electrochemical cell with a quartz window was used for the in situ experiments. The absorption spectra were principally obtained using a previously method [16].

2.3. Synthesis of 1,4-di(2-thienyl)-1,4-butanedione (1)

The starting material, 1,4-di(2-thienyl)-1,4-butanedione was synthesized according to the method described in previous literature [11]. A solution of thiophene (9.6 mL, 0.12 mol) and succinyl chloride (5.5 mL, 0.05 mol) in CH₂Cl₂ (100 mL) was added dropwise to a suspension of AlCl₃ (16 g, 0.12 mol) in CH₂Cl₂ (15 mL). The mixture was stirred at 18–20 °C for 4 h and poured into ice. Then concentrated HCl (5 mL) was added and the resulting dark green organic phase was washed with concentrated NaHCO₃ (3 × 25 mL), and dried over MgSO₄. After the solvent was evapo-

2.4. Synthesis of 1-(benzonitril)-2,5-di(2-thienyl)-1H-pyrrole (BTP) (2)

1,4-Di(2-thienyl)-1,4-butanedione (1.25 g, 5 mmol), 4-aminobenzonitrile (0.66 g, 7 mmol), p-toluenesulfonic acid (1.03 g, 5.4 mmol), and toluene (15 mL) were mixed in a round bottom flask equipped with a nitrogen inlet and a magnetic stirrer. The resulting mixture was stirred and refluxed for 24 h under a nitrogen atmosphere. Then toluene was evaporated, and then flash column chromatography (SiO₂ column, elution with dichloromethane) was carried out in order to obtain the desired compound as a white solid (82%). Scheme 1 shows the synthetic route of 1-(benzonitril)-2,5-di(2-thienyl)-1H-pyrrole. IR(KBr): 3100 cm⁻¹ (aromatic C–H), 2227 cm⁻¹ (C≡N), 1510 cm⁻¹, 1407 cm⁻¹ (C–S in thiophene); 1H NMR: (300 MHz; CDCl₃) 6.51–6.53 (m, 4H), 6.84 (dd, 2H), 7.13 (dd, 2H), 7.36 (d, 2H), 7.66(d, 2H); 13C NMR: (300 MHz; CDCl₃) 111.21, 112.50, 118.11, 125.05, 125.52, 127.13, 129.66, 130.59, 132.91, 133.96, 133.96, 142.41.

Fig. 1. UV absorption (solid line) and photoluminescence (PL) spectrum (dash line) of DPB in dichloromethane solution (excitation wavelength: 330 nm).
2.5. Synthesis of (2,5-di(2-thienyl)-1H-pyrrole-1-yl)-1-(p-benzoic acid) (DPB) (3)

A stirred solution of BTP (2.73 g, 10 mmol) and potassium hydroxide (1.0 g, 17.8 mmol) in ethoxyethanol–water (5:1) was refluxed for 5 h and acidified with excess hydrochloric acid (12 M). The mixture was allowed to cool, and the yellow precipitates formed were filtered and washed with water. Then, these precipitates were recrystallized from ethanol to form 2.69 g (92%) of yellow needles. Scheme 1 shows the synthetic route of (2,5-di(2-thienyl)-1H-pyrrole-1-yl)-1-(p-benzoic acid). Mp: 268.5–269.5 °C. IR (KBr) 3430–3187 cm⁻¹ (br, OH), 1660 cm⁻¹ (C=O), 1510 cm⁻¹, 1417 cm⁻¹ (C–S in thiophene); ¹H NMR (CDCl₃) 6.50–6.53 (m, 4H), 6.89 (dd, 2H), 7.16 (dd, 2H), 7.38 (d, 2H), 7.69 (d, 2H); MS (EI) m/z = 351 (M⁺, 100%); HRMS (ES+) calcd. for C₁₉H₁₃NO₂S₂ [M+1]⁺ 352.0464, found 352.0458.

3. Results and discussion

3.1. Preparation and characterization of DPB

The monomer (DPB) was synthesized from 1,4-di(2-thienyl)-1,4-butanedione (1) using a two-step process. In the first step, 1,4-di-(2-thienyl)-1,4-butanedione (1) was refluxed with PTSA in toluene to produce an 85% yield of BTP (2). Then, the resulting BTP (2) was hydrolyzed with a KOH aqueous solution to produce a 90% yield of the desired DPB. The products were characterized using spectroscopic methods (FT-IR, ¹H-, ¹³C NMR, and mass spectroscopy).

The behavior of the DPB monomer was investigated using UV–visible and photoluminescence (PL) spectroscopy in dichloromethane as shown in Fig. 1. The maximum absorption was observed at 330 nm for DPB and was attributed to the π−π* transition of the π-conjugated segments and the ter-heteroaromatic (thiophene-pyrole-thiophene) units. When DPB was excited at 330 nm, the same PL spectrum exhibited a λem,max = 500 nm. These results suggested that intramolecular energy was transferred from the benzoic acid group to the ter-heteroaromatic unit.

3.2. Electrochemical polymerization of DPB

Fig. 2(A) shows the CVs that were recorded during the polymerization in a 1 mM DPB/0.1 M TBAP solution containing dichloromethane, where the potential was cycled between 0.0 V and +1.0 V versus Ag/AgCl (saturated KCl) six times at 100 mV/s. The monomer was oxidized at +0.9 V, and then the polymer.
film immediately grew on the electrode surface. As the potential cycling continued between 0.0 V and +1.0 V, CV peaks appeared at +0.56/0.9 V, corresponding to redox peaks of the polymer formed on the electrode surface. The peaks became gradually larger, and the anodic peak potentials shifted in the positive direction as the number of potential cycle increased, which indicated the formation and growth of the polymer as previously reported for other conducting polymers [1,3–6]. Fig. 2(B) shows the CVs that were recorded during the redox cycles of the polymer film in a 0.1 M TBAP blank solution. In Fig. 2(C), the peak current was directly proportional to the scan rate, indicating that the surface adsorbed species were involved in the polymer redox reaction. Therefore, the thickness of the film was smaller than the diffusion layer thickness of the counter anions on this cyclic voltammetric time scale. Thus, the anions diffused in and out during the doping and dedoping processes. The oxidation peaks shifted in the positive direction at higher scan rates above 10 mV/s because of the quasi reversibility of the redox process. PDPB displayed a noticeably lower oxidation potential compared to poly(5,2′:5′,2″-terthiophene-3′-carboxylic acid) (polyTTCA) [6,17] because the molecules of the benzoic acid group were better stabilized by resonance than the mono carboxylic acid group.

![Fig. 4. Stability of PDPB film via cyclic voltammetry with a scan rate of 100 mV/s.](image)

The tapping-mode AFM images were obtained to investigate the morphology of the polymer film deposited onto the electrode. The polymer film was grown through two cycles in a 0.1 M TBAP/CH2Cl2 solution containing 1 mM DPB. From the topological surface 3D images in Fig. 3, a rough surface was observed for the randomly distributed morphologies of the PDPB monolayer with a height and depth of 12.5 nm and 12.3 nm, respectively. A good degree of polymerization without defects was observed in the AFM image.

The long-term stability of the redox activity for the corresponding PDPB polymer film was also investigated a 0.1 M TBAP/dichloromethane solution (Fig. 4). The CV showed that 700 cycles occurred between 0.0 V and +1.0 V at a scan rate of 100 mV/s.

![Fig. 5. (A) In situ UV–visible absorption spectra recorded during the oxidation of 1 mM monomer on the platinum electrode. The spectrum of the polymer film that grown with the potential cycling from 0.0 V to 1.0 V five times in a 0.1 M TBAP/dichloromethane solution without a monomer. DCVA curves for the data shown in Fig. 6(A) for polymer film growth in CH2Cl2 at (B) 420 nm, (C) 654 nm, and (D) 870 nm. The potential scan rate was 5 mV/s.](image)

![Fig. 6. Resistance and conductivity as function of applied potential for PDPB film in dichloromethane containing 0.1 M TBAP.](image)
In Fig. 4, the current exchange charge did not change much after 700 cycles.

3.3. Spectroelectrochemistry of PDPB

The PDPB film was further investigated using in situ UV–visible spectroelectrochemistry. First, the polymer film was deposited onto the platinum electrode, and its absorption spectra was obtained in 0.1 M TBAP/dichloromethane while the potential was scanned from 0.0 V to +1.0 V at a scan rate of 5 mV/s. Each spectrum was recorded at a 20 mV interval over 2.0 V potential span so that one hundred spectra were collected. The spectrum recorded at the 100th wavelength scan (store number) corresponded to the first spectrum when the potential was reversed, i.e., +1.0 V. Fig. 5 illustrates the in situ UV–visible spectral behavior of the polymer film during the switch from the reduced to the fully oxidized state. In the reduced state, the color of the polymer film was yellow, and a single broad absorption band was present at 420 nm with an onset of 574 nm. The spectroelectrochemical analysis revealed that the polymer had an optical band-gap ($E_g$) of 2.16 eV from the onset of the $\pi-\pi^*$ transition. In Fig. 5, a very strong absorption band appeared at 420 nm, which corresponded to the $\pi-\pi^*$ transition of the PDPB film. The intensity of this band gradually decreased as the applied potential increased from 0.0 V to +1.0 V. Therefore, the absorption band at 420 nm was related to the electronic transition of the polymer film in the neutral state. The intensity of the absorption band at 654 nm clearly increased as the potential went from +0.7 V to +0.86 V. However, the intensity of this band decreased as the applied potential went over +0.86 V to +1.0 V. Therefore, the first oxidized state was observed between +0.70 V and +0.86 V which corresponded to the formation of the radical cation (polaron) on the PDPB backbone. A new absorption band was clearly visible at about 870 nm as the potential went to +1.0 V, indicating the formation of the dication (bipolaron) of the polymer film.

3.4. In situ conductivity measurement of PDPB

The conductivity of the PDPB film was measured using an in situ technique [18], with an applied potential in a non-aqueous solution. The resistance was measured for the dication (bipolaron) of the polymer film. Moreover, the DCVA curve at 870 nm in Fig. 5(D) revealed that this band was caused by a different species than the band observed at 654 nm. Therefore, the absorption band at 870 nm was associated with the chemical species formed at a potential of around +0.82 V (the average value of the cathodic and anodic peaks), corresponding to the dication (bipolaron) of the polymer film.

3.5. Fast optical switching property of PDPB

For electrochromic applications, the polymer must exhibit a rapid switching ability and a striking color change. The electrochromic properties of the polymer film grown on a Pt electrode...
were examined in a 0.1 M TBAP/CH₂Cl₂ solution. The polymer film was obtained by cycling the potential from 0.0 V to 1.0 V ten times at a scan rate of 100 mV/s. Fig. 7(A) shows the colors of the films obtained in the 0.1 M TBAP/CH₂Cl₂ solution. The color of the films coated on the Pt electrode changed from yellow at 0.0 V to bright blue at over +1.0 V. When a double step pulse potential was applied to the polymer film between +1.0 V and 0.0 V, the color completely switched after 0.95 s, which was quite fast compared to the switching time of other polymers. This time was determined to be 95% of the signal at the maximum value (t95) with a measured wavelength of 420 nm, in Fig. 7(B).

4. Conclusion

Conductive PDPB was electrochemically polymerized from a newly synthesized DPB monomer in dichloromethane. The in situ conductivity of polyDPB was 0.18 S/cm at +0.80 V. The spectroelectrochemical data for the PDPB film clearly distinguished the neutral, oxidized states (polaron (+0.71 V), and bipolaron states (+0.82 V)) of the absorption bands at 420 nm, 654 nm, and 870 nm, respectively. PDPB had an optical band-gap (Eg) of 2.16 eV and therefore, could be used in electron transporting materials. The PDPB film exhibited a good switching time (0.95 s) and good stability. Considering these results, PDPB is a promising candidate for both electrochromic devices and the construction of conducting polymer biosensors.

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