Spectroelectrochemical and electrochromic behaviors of newly synthesized poly[3′-(2-aminopyrimidyl)-2,2′:5′,2″-terthiophene]∗

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**ABSTRACT**

The functionalized conductive polymer precursor of the terthiophene derivative, 3′-(2-aminopyrimidyl)-2,2′:5′,2″-terthiophene (PATT) was firstly synthesized and confirmed with FT-IR, 1H NMR, 13C NMR, and mass spectroscopy. The electrochemical and electronic properties of polyPATT film are investigated and compared with that of poly(3,4-ethylenedioxythiophene)-3′-p-carboxylic acid (PEDOT:PSS), which has an electron-accepting group. The cyclic voltammograms (CVs) recorded for electrochemically grown polyPATT reveal the redox peaks at +1.1/+0.96 V, and the conductivity increases monotonically as the applying potential goes to the positive direction (0.11 S cm−1 at +1.4 V). The spectrotoclectrochemical analysis of polyPATT reveals the absorption bands at 456, 825 and 643 nm corresponding to the π–π* transition, polaron, and bipolaron formations, respectively. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the polyPATT film bearing an electron donating group are to be 3.60 and 5.54 eV, respectively. The polyPATT film shows reversible multiple color transition within 0.6 s (from brownish-yellow (at 0.0 V) to blue (at +1.4 V)) when the potential switches between the reduced and oxidized states.

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1. Introduction

The π-conjugated polymers [1,2] have currently received much attention because of their various potential applications in the fields of batteries [3,4], electrochromic display devices [5–7], sensors [8–13], and organic electrical devices [14–16]. Common classes of conjugated polymers include poly(aniline)s, poly(pyrrrole)s, poly(furan)s, and especially poly(thiophene) etc. Of these, poly(thiophene) derivatives have been widely studied, due to the potential for combining the typical features of organic polymers, i.e. low specific weight and resistance to corrosion, and the typical features of inorganic semiconductors, i.e. electrical conductivity. Additionally, the polythiophene derivatives and oligothiophenes substituted with donor/acceptor groups have been extensively investigated. These compounds are often used as energy transfer and light-harvesting systems and as optical and electronic devices [17–19].

Pyrimidine derivatives, a class of heterocycles of great importance, possess a remarkable biological activity, and have been widely used in fields ranging from the medicinal to industrial applications [19–21]. The amino (-NH2) group substituted in the pyrimidine rings are acidic components in the hydrogen bonding between the base pairs of nucleic acid responsible for the formation of the double helices in DNA and RNA [21]. Moreover, the complexing ability of 2-aminopyrimidine with transition metal ions is of great interest [22], and it is also possible to have a specific interaction to organic species.

Generally, the substituted groups and monomer backbones have considerable influence over the polymerization processes. The electrochemical oxidation of these resonance-stabilized heterocyclic systems has become one of the principal methods for preparing the conjugated, electronically conducting polymers, attributed to electronic and steric considerations [23]. Terthiophenes substituted at the 3′-position can often undergo electropolymerization to produce conducting polymers, since the 2′- and 5′-positions remain available for the monomer coupling [23,24]. The electrochemical behavior of a wide range of 3′-substituted thiophenes has been investigated, and the 3′-substituted thiophenes are generally more suitable because of their high stability and ease of preparation [23]. The properties of the products formed by electrochemical oxidation highly depend on the substituent, with some reactions producing conducting polymers and others, insulating layers or soluble species.
In the present study, a new terthiophene derivative (3′-(2-amino pyrimidinyl)-2,2′:5′,2′-terthiophene (PATT)) was synthesized through the Suzuki coupling reaction, which consisted of a 2-aminopyrimidyl group as an electron donating moiety. The electrochemically formed–polymer film is characterized via several techniques, such as cyclic voltammetry (CV), atomic force microscopy (AFM), in situ conductivity measurements, and electrochemical impedance spectroscopy (EIS). The in situ spectroelectrochemical and electrochromic properties of the polymer film are also studied and compared with poly(2,2′:5′,2′-terthiophene-3′-p-benzoic acid) (poly(TBBA)) [25] that contains the benzyl moiety in the polymer backbone structure.

2. Experimental

2.1. Chemicals

2,3,5-Tribromothiophene, 2-bromothiophene, tetramethylenediamine (TMEDA), Mg, trimethyl borate, tetrakis(triphenylphosphine)palladium(0) (Pd(PPh3)4), and 2-amino-5-bromopyrimidine were used as received. All of the other chemicals were purchased from the Sigma–Aldrich Co. (USA), and used as received. Column chromatography was performed on the silica gel 60 (70–230 mesh). Tetrabutylammonium perchlorate (TBAP, electrochemical grade) was obtained from the Fluka Co. (USA), and dried under 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 in doubly distilled water, which was obtained from a Milli-Q water-purifying system (18 MΩ cm).

2.2. Instruments

A Bruker Advance 300 Spectrometer was used to record the 1H NMR and 13C NMR spectra in CDCl3. The chemical shifts were given in ppm downfield from tetramethylsilane (TMS). The FT-IR spectrum was recorded on a JASCO FT-IR spectrometer. The absorbance spectra were obtained at a slow scanning speed and the slit width of 5 nm using a Schimadzu UVPC-3101 spectrophotometer. The photoluminescence spectrum was obtained on a PerkinElmer LS50B. 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 made by Kosentech, Model PT-2 (South Korea). The CV system was a three-electrode system with a glassy carbon working electrode, platinum wire counter electrode and Ag/AgCl reference electrode that was internally calibrated vs. the chemical redox couple of ferrocyanide/ferri cyanide. The Pt electrode was polished with 1.0, 0.5, and 0.05 μm alumina/water slurries followed by sonication and rinsing with distilled water. After polishing, the electrochemical pretreatment of the electrode was carried out by potential cycling between +1.5 and −1.4 V in 0.1 M H2SO4. The in situ conductivity measurements were carried out on the electrolyte solution using the method reported by Wrighton et al. [26]. We used gold interdigitated electrodes (~10 μm gap) as the working electrode, where the gap between the two split gold electrodes was bridged by growing the polyPATT film. The current was then monitored according to the potential applied across the polymer bridge on the Au interdigitated electrodes, and the resistances were calculated from them. The impedance spectra were measured with EG&G Princeton Applied Research PARSTAT 2263 at a given potential from 100 kHz to 100 mHz, at a sampling rate of five points per decade. The in situ UV–vis spectroscopic spectra were obtained from the assembly of a charge-coupled device (CCD) detector, a Xenon flash lamp and a bifurcated optical fiber made by the 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 principally the same as the previous one [27,28].

2.3. Synthesis of 3′-(pyrimidyl-2-amino)-2,2′:5′,2′-terthiophene (PATT)

3′-Bromo-2,2′:5′,2′-terthiophene (BTT) was synthesized according to a previously reported method [24]. Tetramethylethylenediamine (TMEDA) (2.77 mL, 18.33 mmol) and 1.6 M n-Buti (11.46 mL, 18.34 mmol) were slowly added to a degassed diethyl ether solution (11.50 mL) of BTT (5.0 g, 15.28 mmol) under a N2 atmosphere at −83 °C. The reaction mixture was stirred for 1 h at −83 °C, and trimethyl borate (5.20 mL, 30.56 mmol) diluted in diether ether (30 mL) was added. The mixture was allowed to warm up to room temperature, and stirred for 4 h, after which 2 M HCl (4.2 mL) was added. After 1.5 h of additional stirring, crude 2,2′:5′,2′-terthiophene-3′-bromonic acid (TTB) was precipitated out as a white solid, which was washed with water and dried under reduced pressure. The crude TTB, NaHCO3 (8.4 g), 2-amino-5-bromopyrimidine (1.7 g, excess) and Pd(PPh3)4 (116 mg, 1 mol%) were combined in a two-phase solution (60 mL) of toluene/water (5:1). The mixture was refluxed for 2 h. Dichloromethane was added, and the separated organic layer was washed with water. After further removal of the solvent, a green–yellow solid remained which was purified using column chromatography with n-hexane/ethyl acetate (100:1). Recrystallization from ethanol provided 2.05 g of a green–yellow solid. IR (KBr): 3315, 3169, 1663, 1495 cm⁻¹; 1H NMR (CDCl3): 5.34 (s, 2H), 6.96–6.89 (m, 1H), 7.02–7.08 (m, 2H), 7.20–7.24 (m, 3H), 8.34 (s, 2H); 13C NMR (CDCl3): 120.2, 124.2, 125.0, 125.9, 126.4, 126.9, 127.5, 128.0, 131.1, 133.0, 134.8, 136.3, 136.4, 158.2, 162.1; MS 341(M⁺, 100%), exact MS calculated for C16H11N2S2: 341.0115. Found: 341.0110.

3. Results and Discussion

3.1. Synthesis and spectroscopic properties of PATT

The starting material, 3′-bromo-2,2′:5′,2′-terthiophene (BTT), was prepared from 2,3,5-tribromothiophene by the one step procedure illustrated in Scheme 1. Then, BTT was treated with n-Buti and trimethyl borate in Et2O under a N2 atmosphere at −83 °C to get 2,2′:5′,2′-terthiophene-3′-bromonic acid (TTB). The Suzuki coupling of TTB with 2-amino-5-bromopyrimidine in a refluxing two-phase solution of THF/water (5:1) in the presence of NaHCO3 and Pd(PPh3)4 formed 3′-(2-aminopyrimidinyl)-2,2′:5′,2′-terthiophene (PATT) with an overall yield of 39.3%. In the FT-IR spectrum, the intense band at 3300 and 3143 cm⁻¹ was the characteristic absorptions of the N–H stretch mode of amine in the pyrimidyl group. The N–H bend mode of the pyrimidyl group was present at 1648 and 1589 cm⁻¹. In the 1H NMR spectrum, PATT exhibited the aromatic–N3H proton and pyrimidine proton peaks at 5.34 and 8.31 ppm, respectively. Additionally, the peaks between 6.96 and 7.24 ppm in the spectrum of PATT arose from the protons in terthiophene. The mass spectroscopic data of the PATT corresponded with the expected formula.

Before characterization of the polymers, the spectroscopic and luminescence behavior of PATT monomer was investigated using UV–vis and photoluminescence (PL) spectroscopy. The UV–vis absorption and PL emission spectra of the PATT monomer, recorded in dichloromethane (see supplementary materials S1). The maximum absorption was observed at 350 nm for PATT along with a shoulder peak at the low-wavelength side (280 nm), which was attributed to the π–π transition of the π-conjugated segments and pyrimidine units. PATT showed a blue fluorescence with an
emission peak at 455 nm (excitation wavelength: 350 nm) with a large Stokes shift of about 105 nm, which may be due to the possibility of an excited-state intramolecular proton transfer as observed in thiophene based terthiophene [29].

To get an insight for the electron distribution in the molecular structures of PATT and TTBA, their geometries have been optimized using the density functional theory (DFT) calculation at DFT/B3LYP/6-31G* level of theory using a gauss view (5.0.8) program. Comparison of the electron distribution on PATT and TTBA structures using DFT shows the role of an electron-donating substituent with respect to an electron-accepting one attached on the polymer backbone. The frontier orbital of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of PATT and TTBA [25] are shown in Fig. 1. As shown in Fig. 1(A), the electrons at the HOMO orbital of PATT are delocalized over all the π system of the terthiophene backbone and 2-aminopyrimidinyl substituent. The LUMO orbital of PATT shows localized π electrons in the terthiophene backbone only that informs the electron donating property, while an electron accepting property of p-benzoic acid of the TTBA has that tends to be more rich in electrons (Fig. 1(B)). Thus, they can be used for effective electron transporting materials in photovoltaic cells. Whereas, this shows that the PATT monomer with an efficient electron-accepting moiety can be applied for an electrochemical sensor for anionic species based on the electrostatic interaction.

3.2. Electropolymerization and characterization of polyPATT and polyTTBA

In Fig. 2(A), the CVs were recorded during the electropolymerization of PATT and TTBA monomers, separately, in dichloromethane containing 0.1 M TBAP by the potential cycling between 0.0 and +1.4 V vs. Ag/AgCl. The PATT monomer is oxidized at +1.25 V to immediately form a polymer film at the electrode surface, while TTBA is oxidized at 1.3 V and the reverse scan shows a cathodic peak at +0.9 V as shown in the inset of Fig. 2(A). The shift in the redox peaks and the increase in the oxidation current are resulted from reducing of the ohmic potential drop due to the formation of long conjugated polymer chain on the electrode surface, where the polymer film grows as the number of potential cycling increases. The CVs recorded for polyPATT in a blank solution revealed a set of redox peaks at +1.1/+0.96 V, while a pair of
redox peaks of polyTTBA is observed at +1.1/+0.75 V. In Fig. 2(B), the peak currents of polyPATT at +0.96 and +1.1 V increase as the cycle number increases, indicating the formation and growth of a polymer. The color of the polymer film formed on the Pt electrode surface was blue, beyond the potential of +1.1 V at the anodic scan. As shown in the inset of Fig. 2(B), the CVs are recorded at different scan rates for the oxidation of polyPATT film in a blank 0.1 M TBAP solution. The peak current was directly proportional to the scan rate, indicating the involvement of the surface adsorbed species. This suggested that the thickness of the film was thinner than the diffusion layer thickness of the counter anions on the cyclic voltammetric time scale, and therefore, the anions diffused in and out during the doping and dedoping processes. The oxidation peaks shifted to a more positive potential at the scan rates higher than 10 mV s\(^{-1}\) due to the quasi reversibility of the redox process. Similar results were observed for the polyTTBA film.

The morphologies of the polymer films after electropolymerization were observed by atomic force microscopy (AFM) using the tapping mode. It shows homogeneous composition of small particles of polymer film. The particle size of polymer film was determined to be 41.5 ± 6.6 nm for polyPATT, and 73.2 ± 22.3 nm for polyTTBA. The difference in the root mean square (RMS) surface roughness between the polyPATT films is not very large, as depicted in Fig. 2(C). The RMS roughness of polyPATT is 1.35 nm, which is less than that of polyTTBA (1.75 nm). As can be seen in Fig. 2(D), a cross-section SEM image of the polyPATT, and polyTTBA films obtained in the same growing condition shows that the thickness of the polyPATT and polyTTBA layer is about 0.42 and 3.2 μm, respectively.

3.3. In situ conductivity and impedance spectroscopic behaviors of polyPATT

The in situ conductivity measurements were performed in a dichloromethane solution at various applied potentials. At first, the resistances were measured for the polymer bridged across a
value decreased as the applied potential became 1.4 V through 0.6 V. This is coincident with the in situ conductivity result. In this case, although the conductivity of polyPATT is higher than that of polyTTBA at the neutral state (0.0 V), one of the polyTTBA increases more largely compared with that of polyPATT as the electrochemical doping state goes high (>0.6 V). This indicates that the conductivity concerns with the degree of the conjugated structure of polymers due to the polaron/bipolaron formation. The Warburg response indicates that the electron transfer might be controlled by the diffusion of counter anions through the polyPATT film. The conductivity of the polyPATT film in the fully doped state was 0.09 S cm⁻¹ at +1.4 V, while the polyTTBA was 0.19 S cm⁻¹ at +1.4 V. The conductivities from the EIS method agree with the ones of the in situ conductivity measurement within an error range.

3.4. In situ spectroelectrochemical behavior of polyPATT

Fig. 4(A) shows a series of in situ UV–vis absorption spectra recorded from the polymer film in a 0.1 M TBAP solution without a monomer. This film was grown on the platinum electrode with potential cycling from 0.0 to 1.4 V five times. Altogether, 108 spectra were recorded over a potential span of 2.8 V during the scan, with the individual spectra being recorded at intervals of 0.026 V. In Fig. 4, a very strong absorption band appears at 456 nm, which corresponds to the π–π⁺ transition of polyPATT, where it shifts to the longer wavelength than that of monomer (at 350 nm) due to the polymerization. The intensity of this band gradually decreases as the applying potential goes more positive than around +1.0 V, which indicates that the absorption band at 456 nm is due to the electronic transition of the polymer film in the neutral state by absorption of photons. When the applied potential goes to +1.0 V, the intensity of the band at 825 nm increases and then it decreases as the applied potential goes over +1.0 V, which indicates this band corresponds to the formation of polaron at +1.0 V. An absorption band at 643 nm is observed as the potential reaches to +1.2 V, indicating the formation of a bipolaron, where another major bipolaron band over 1000 nm is not observed for polyPATT film in this experimental condition [1]. On the other hand, spectra of poly TTBA showed the absorption bands at 472, 847, and 993 nm, which corresponded to the π–π⁺ transition in neutral state, polaron, and bipolaron formation, respectively.

The derivative technique, called the derivative cyclic voltammetry (DCVA) curve, where the derivative absorption signal could easily discriminate the polaron/bipolaron species generated in the conducting polymer film [27,28]. Since the in situ UV–vis absorption spectra shown in Fig. 4(A) are highly crowded and, it is difficult to see how each band is affected during the potential sweep, we obtained the rates of increase/decrease in absorbance units (dA/dt) at given wavelengths and plotted them as a function of the scanning potential. The DCVA curves recorded at 456, 643 and 825 nm are shown in Fig. 4 along with the corresponding CVs. As the applied potential increased in the positive direction, the π–π⁺ transition band at 456 nm disappeared. As shown in Fig. 4(B), as the potential sweeps in the positive direction, the dA/dt value obtained at 456 nm decreases. The band at 456 nm is generated at the potential at which the polyPATT is in the neutral state and matched well with the CV of the polyPATT film. For the DCVA curve at 643 nm in Fig. 4(C), the dA/dt value increases, as the potential sweeps in the positive direction, which indicates that a new species forms and absorbs photons at 643 nm. The neutral polymer film is converted into another oxidation form having anodic and cathodic peak potentials at around +0.93 and +1.1 V, respectively. Therefore, the absorption band at 643 nm is related to the species formed at the potential of +1.0 V (the average value of the cathodic and anodic peaks), which corresponds to the formation of the dication (bipolaron) in the polyPATT film. Moreover, the DCVA curve at 825 nm
Fig. 4. (A) The in situ UV–vis spectra of the polymer film, the potential cycling from 0.0 to 1.4 V in a 0.1 M TBAP/dichloromethane solution without a monomer. The potential scan rate was 5 mV s⁻¹. DCVA curves for the polymer film during potential cycling in dichloromethane at (B) 456 nm, (C) 643 nm, and (D) 825 nm. The potential scan rate was 5 mV s⁻¹.

as shown in Fig. 4(D) corresponds to a different species compared to the absorption band at 643 nm. During the oxidation of the polymer film, the DCVA curve obtained at 825 nm shows two transition processes. In this DCVA, two anodic peaks appear around +0.85 and +1.3 V during the oxidation of the polyPATT, and the corresponding cathodic peaks appear around +0.94 and +1.1 V. When the potential sweeps in the more positive direction, the dI/dt curve shows two sets of peaks. The first oxidation process at +0.9 V (the average value of the anodic and cathodic peaks) is associated with the transition to the polaron state and the second process at +1.2 V (the average value of the anodic and cathodic peaks) with transition to a new chemical species. Therefore, the absorption band at 825 nm is related to the chemical species formed at the potential of around +1.2 V, which corresponds to the dication (bipolaron) of the polymer film. In Fig. 4(D), this new species (bipolaron) appears at +1.2 V before the polaron disappears.

The HOMO energy level of polyPATT was estimated by measuring the oxidation potential with respect to ferrocene using cyclic voltammetry [30]. The onset potential (E_onset) for the oxidation of polyPATT was observed at +1.10 V. The HOMO level was calculated using the following empirical equation, HOMO = (−4.44 + E_onset), HOMO = (−4.44 + 1.10) = −5.54 eV. The LUMO level was calculated from the band gap (E_g) of the polymer, which was determined from the maximum absorption band of the absorption edge. The band gap of the polymer was estimated to be 1.91 eV from the onset potential of the oxidation processes, and was consistent with the results from the absorption edge. According to the equations, the HOMO and LUMO of polymer were estimated to be −5.54 and −3.63 eV, while the HOMO, LUMO, and band gap energy of the polyTBA were determined to be −5.53, −3.55, and 1.98 eV, respectively. The band gap was lower than that of polyliophene, which had a band gap (E_g) value of about 2.1–2.3 eV [1]. The electrochemical data from the CV indicated that the introduction of the electron donating 2-aminopyrimidyl functionality led to a significant increase in the electron affinity demonstrating the effectiveness of the 2-aminopyrimidyl group in improving the charge injection property of the polymer.

3.5. Electrochromic behavior of polyPATT

The electrochromic properties of the polymer film grown on a Pt disk were investigated in a 0.1 M TBAP/CH₂Cl₂ solution. The polymer film was obtained by cycling the potential from 0.0 to 1.4 V at a scan rate of 100 mV s⁻¹ ten times. Fig. 5(A) shows the colors of the film obtained at the redox potentials in a 0.1 M TBAP/CH₂Cl₂ solution. The color of the film coated on the Pt disk changes from brownish-yellow at 0.0 V to blue at +1.4 V. The spectroelectrochemical results demonstrate that the polymer film switches between the oxidized and the reduced forms with an accompanying color change. The switching time of color change, which is defined as the time required for switching between two colored states, is one of the most important characteristics of electrochromic devices. When the double step pulse potential from 0.0 to +1.4 V was applied to the polyPATT film, the response switching time was 0.6 s in the forward and reverse directions. This calculation was performed at 95% of the switch time, which was determined from the comparison between the signal and the maximum values in Fig. 5(B), where the measuring wavelength was 750 nm. The polyPATT film shows
Fig. 5. (A) The polymer film grown on the Pt electrode showing an electrochromic switching between yellow at 0.0 V and blue at 1.4 V. (B) Electrochromic response of the polymer in a 0.1 M TBAI/dichloromethane solution (Double step pulse was applied between 0.0 and 1.4 V). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

a faster switching time than the polyTTBA (0.82 s), which indicates a fast electronic state transition.

4. Conclusion

The PATT monomer was synthesized and characterized, which bears a 2-aminopyrimidyl group as an electron donating moiety. We also compared the polyPATT having an electron donating group with polyTTBA bearing an electron-accepting one. By introducing different functional groups in the thiophene backbone, we can control the spectroelectrochemical properties of conducting polymer. The results show that polyPATT and polyTTBA are promising candidates for electrochromic devices, photovoltaic cell, and the construction of conducting polymer biosensor. The cyclic voltammetry, DFT calculation, in situ UV-vis, and in situ conductivity measurements of the polyPATT film reveal the unique properties of a conducting polymer. The in situ conductivity of polyTTBA was better than that of polyPATT. The in situ UV-vis spectra showed the absorbance bands at 456 nm due to the π–π* transitions and the charge carrier bands at around 825 and 643 nm which were attributed to the formation of polaron and bipolaron bands, respectively. The polyPATT film has a low band-gap ($E_g$) of 1.91 eV with respect to polyTTBA (1.98 eV), which is useful for an electron transporting material. The spectroelectrochemical results of the polymer film showed the color change from blue in the oxidized form to brownish-yellow in the reduced one, where the switching time was within 0.6 s.

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Appendix A. Supplementary data

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References


