

Article

Applications of Tris(4-(thiophen-2-yl)phenyl)amine- and Dithienylpyrrole-based Conjugated Copolymers in High-Contrast Electrochromic Devices

Tzi-Yi Wu * and Hsin-Hua Chung

Department of Chemical and Materials Engineering, National Yunlin University of Science and Technology, Yunlin 64002, Taiwan; k309798@yahoo.com.tw

* Correspondence: wuty@yuntech.edu.tw; Tel.: +886-5-534-2601 (ext. 4626)

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Abstract: Tris(4-(thiophen-2-yl)phenyl)amine- and dithienylpyrrole-based copolymers (P(TTPA-co-DIT) and P(TTPA-co-BDTA)) were electropolymerized on ITO electrode by applying constant potentials of 1.0, 1.1, and 1.2 V. Spectroelectrochemical investigations revealed that P(TTPA-co-DIT) film displayed more color changes than P(TTPA-co-BDTA) film. The P(TTPA-co-DIT) film is yellow in the neutral state, yellowish-green and green in the intermediate state, and blue (1.2 V) in highly oxidized state. The ΔT_{\max} of the P(TTPA-co-DIT) and P(TTPA-co-BDTA) films were measured as 60.3% at 1042 nm and 47.1% at 1096 nm, respectively, and the maximum coloration efficiency (η) of P(TTPA-co-DIT) and P(TTPA-co-BDTA) films were calculated to be $181.9 \text{ cm}^2 \cdot \text{C}^{-1}$ at 1042 nm and $217.8 \text{ cm}^2 \cdot \text{C}^{-1}$ at 1096 nm, respectively, in an ionic liquid solution. Dual type electrochromic devices (ECDs) consisting of P(TTPA-co-DIT) (or P(TTPA-co-BDTA)) anodic copolymer, ionic liquid-based electrolyte, and poly(3,4-(2,2-diethylpropylenedioxy)thiophene) (PProDOT-Et₂) cathodic polymer were constructed. P(TTPA-co-BDTA)/PProDOT-Et₂ ECD showed high ΔT_{\max} (48.1%) and high coloration efficiency ($649.4 \text{ cm}^2 \cdot \text{C}^{-1}$) at 588 nm. Moreover, P(TTPA-co-DIT)/PProDOT-Et₂ and P(TTPA-co-BDTA)/PProDOT-Et₂ ECDs displayed satisfactory optical memory and long term switching stability.

Keywords: electrochemical polymerization; optical contrast; spectroelectrochemistry; coloration efficiency; electrochromic devices

1. Introduction

Functional conjugated polymers (CPs) have attracted an increasing attention due to their potentials for unique optical and electrochemical properties, multiple color exhibitions, and high optical contrast ability. In recent years, several kinds of CPs are promising candidates for a large number of advanced technological applications in electrochromic devices (ECDs) [1–3], automotive rear-view mirrors [4], light-emitting diodes [5], architectural energy-saving windows [6], catalysts [7–9], displays [10], and sensors [11,12]. Especially, CPs-based electrochromic materials, such as polyanilines [13], polycarbazoles [14], polypyrroles [15], polyindoles [16], polythiophenes [17–19], poly(3,4-ethylenedioxythiophene)(PEDOT) [20], and polytriphenylamine [21], have been extensively investigated for using as anodic (or cathodic) layers in ECDs. Among these materials, polytriphenylamine possesses hole conducting properties and can be easily oxidized to form polarons, the redox process exhibits obvious color variations. Hsiao *et al.* reported that triphenylamine-containing polyamides displayed good electrochemical stability and multicolor electrochromic behaviors upon applying potentials [22], the percent transmittance change and coloration efficiency of triphenylamine-containing polyamides are 58% and $209 \text{ cm}^2 \cdot \text{C}^{-1}$ at 929 nm,

respectively. Polythiophenes and their derivatives are promising organic CPs for commercial electrochromic applications due to their potential to combine with other electrochromic materials to display multichromic behaviors. However, most polythiophenes are insoluble in general solvents and the E_{onset} of polythiophenes is high (ca. 1.5 V vs. Ag/AgCl) [23], the attachment of alkyl and alkoxy groups to polythiophenes gives rise to good solubility and processability of the polymer in general solvents. Moreover, the incorporation of electron donating substituents to the 3- and 4-positions of polythiophenes decreases the E_{onset} of polythiophenes. Poly(2,5-dithienylpyrrole)s (PSNS) are one of the promising polythiophenes derivatives due to their low oxidation potential (ca. 0.7 V vs. Ag/AgCl) and exhibit multichromic behaviors (yellow, green and blue) upon applying potentials. The incorporation of substituents to the nitrogen atom of central pyrrole unit in PSNS backbone gives rise to tunable band gap of PSNS and makes possible modifications to properties. Recently, a number of SNS derivatives have been reported and displayed specific electrochromic properties. Camurlu *et al.* synthesized anthracene- and pyrene-containing thienylpyrrole derivatives (SNS-Anth [24] and SNS-pyrene [25]) and reported their multichromic properties. Koyuncu *et al.* reported the synthesis and electrochromic characterizations of a novel polymer (PSNS-PDI) consisting of SNS-donor and PDI-acceptor units [26]. PSNS-PDI has a high optical contrast ($\Delta T = 45\%$ at 900 nm), a short response speed (0.5 s), and a high coloration efficiency ($254 \text{ cm}^2 \cdot \text{C}^{-1}$). Shim *et al.* incorporated 3-pyridinyl and 1,10-phenanthroline units in the central pyrrole ring of PSNS, which were named polyPTPy and polyPhenTPy [27], and the ΔT of polyPTPy and polyPhenTPy were 42% and 31%, respectively. Furthermore, copolymers provide an effective method for controlling the properties of CPs, copolymerization is a facile way to combine (or change) the electrochromic properties of individual homopolymers. Toppare *et al.* synthesized a copolymer (P(FFTP-*co*-EDOT)) using FFTP and EDOT electrochemically [28], P(FFTP) has only two colors in its reduced and oxidized states (yellow and blue), while its copolymer with EDOT shows five colors (light gray, green, purple, red, and blue), indicating the incorporation of specific units in copolymer backbone gives rise to multichromic behaviors.

In the present work, two tris(4-(thiophen-2-yl)phenyl)amine- and 2,5-dithienylpyrrole-based conducting copolymers (P(TTPA-*co*-DIT) and P(TTPA-*co*-BDTA)) were prepared using electrochemical copolymerizations. The chemical structure of indene is similar to 1,2,5-thiadiazole, and both of them were introduced to the central pyrrole ring of the SNS unit. The two $-\text{C}=\text{N}-$ groups in 1,2,5-thiadiazole group increase the electron-withdrawing ability, decrease the lowest unoccupied molecular orbital (LUMO) level, and reduce the band gap of the SNS unit, thereby expand absorbance to longer wavelength region. Moreover, tris(4-(thiophen-2-yl)phenyl)amine (TTPA) unit combines the individual properties of triphenylamine and thiophene moieties. Although the oxidation potential of polythiophenes is ca. 1.5 V vs. Ag/AgCl [23], the incorporation of a triphenylamine unit among three thiophene groups increase the electron-donating ability of entire TTPA unit. Consequently, poly(tris(4-(thiophen-2-yl)phenyl)amine) shows lower oxidation potential than that of polythiophenes. It was interesting to incorporate the TTPA unit in the copolymer backbone and explore their spectroelectrochemical and electrochromic behaviors. Moreover, the electrochromic devices (ECDs) were constructed using P(TTPA-*co*-DIT) and P(TTPA-*co*-BDTA) as the anodic materials of coloring electrodes, PProDOT-Et₂ as the cathodic material of complementary electrodes, and an ionic liquid and poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP) composite films as the electrolyte membranes. The spectroelectrochemical properties, such as percent transmittance changes, electrochromic switching, coloration efficiency, and stability of the ECDs were systematically and comprehensively investigated.

2. Materials and Methods

2.1. Materials and Electrochemical Synthesis

Tris(4-(thiophen-2-yl)phenyl)amine, 1-ethyl-3-propylimidazolium bis(trifluoromethanesulfonyl) imide (EPIDIL), SNS derivatives, and ProDOT-Et₂ were prepared from previously published

procedures [29–32]. P(TTPA-co-DIT) and P(TTPA-co-BDTA) films were prepared potentiostatically at 1.0, 1.1, and 1.2 V on ITO glass electrodes with an applied charge density of $30 \text{ mC} \cdot \text{cm}^{-2}$. The ITO is conductive with an electrical resistivity of $10^{-4} \Omega \cdot \text{cm}$. The active area of polymer films on ITO glass was 1.8 cm^2 . Film thicknesses of deposited polymers were obtained with an Alpha-Step profilometer (KLA Tencor D-120, KLA-Tencor, Milpitas, CA, USA). The thicknesses of P(TTPA-co-DIT) and P(TTPA-co-BDTA) films were about 45 and 50 nm, respectively, for the CV and spectroelectrochemical experiments. P(TTPA-co-DIT) and P(TTPA-co-BDTA) films were prepared using feed molar ratio of TTPA/DIT (or TTPA/BDTA) at 1/1.

2.2. Construction of ECDs and Spectroelectrochemical Characterizations

Electrolyte membranes were prepared by a casting solution containing PVDF-HFP, EPIDIL, DMF solvent, and propylene carbonate. The weight ratio of PVDF-HFP:EPIDIL:propylene carbonate = 1:3:2. ECDs were constructed using P(TTPA-co-DIT) (or P(TTPA-co-BDTA)) as the anodic material and PProDOT-Et₂ as the cathodic material. The PProDOT-Et₂ film was electrodeposited onto ITO glass at +1.4 V. ECDs were constructed using anodic and cathodic polymer films facing each other to be separated by an electrolyte membrane.

Electrochemical experiments were carried out in a three-component cell with a CHI660a electrochemical analyzer (CH Instruments, Austin, TX, USA). ITO glass plate, platinum wire, and Ag/AgCl electrode were used as working, counter, and reference electrodes, respectively. Spectroelectrochemical experiments were studied with a V-630 JASCO UV-Visible spectrophotometer (JASCO International Co., Ltd., Tokyo, Japan) to record *in situ* UV-Vis spectra and were done in a quartz cuvette of 1 cm path length assembled as an electrochemical cell with an ITO working electrode, a platinum wire, and an Ag/AgCl reference electrode.

3. Results and Discussion

3.1. Electrochemical Polymerization

The polarization curves of neat TTPA, DIT, and BDTA monomers, and the mixture of two monomers (TTPA + DIT and TTPA + BDTA) in 0.1 M LiClO₄/ACN are shown in Figure 1. P(TTPA) showed E_{onset} and oxidation peak at 0.79 and 1.16 V, respectively (Figure 1a). On the other hand, the E_{onset} of PDIT and PBDTA films were 0.68 and 0.73 V, respectively, and the oxidation peaks of PDIT and PBDTA films were 0.90 and 0.97 V, respectively (Figure 1b,c). When the CVs were scanned in 0.1 M LiClO₄/ACN solution containing two monomers (2 mM TTPA + 2 mM DIT and 2 mM TTPA + 2 mM BDTA), the CVs' shape and redox peaks observed in Figure 1d,e are different to those of P(TTPA), PDIT, and PBDTA homopolymer films, demonstrating the formation of copolymers. The electrochemical routes of P(TTPA-co-DIT) and P(TTPA-co-BDTA) are shown in Figure 2.

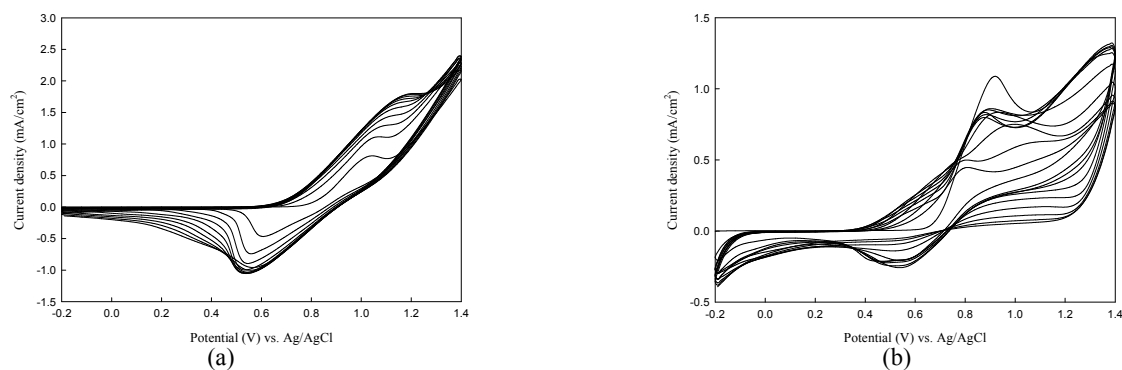


Figure 1. Cont.

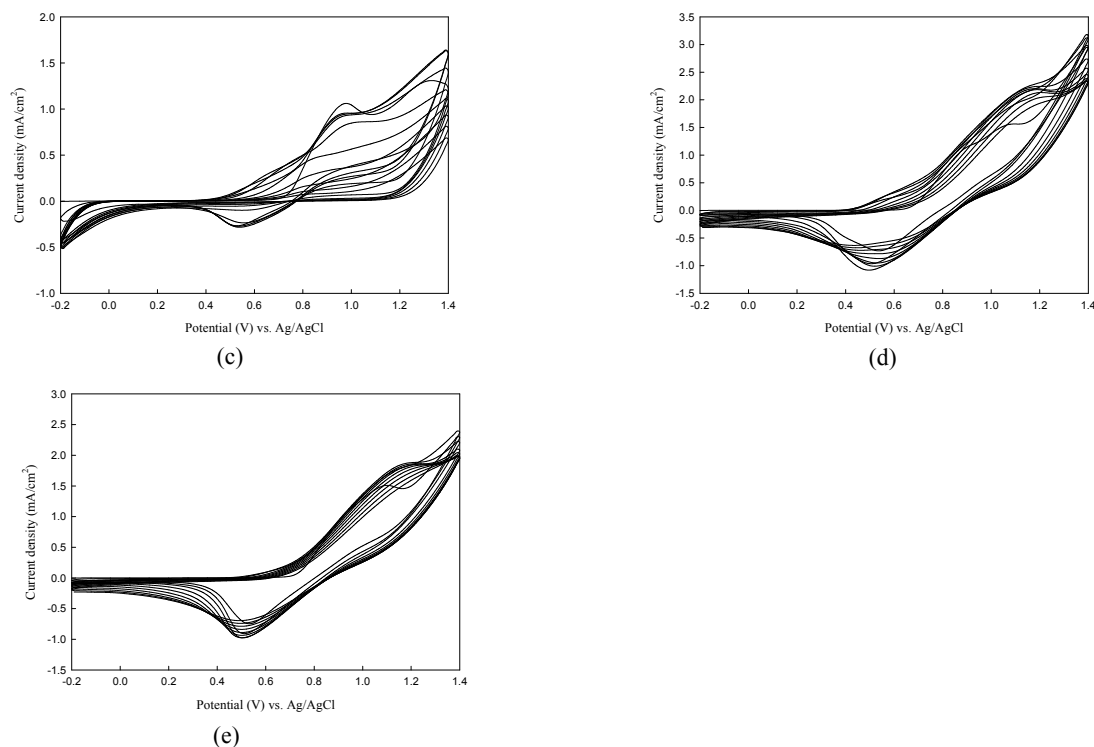


Figure 1. Cyclic voltammograms of: (a) 2 mM tris(4-(thiophen-2-yl)phenyl)amine (TTPA); (b) 2 mM 1-(2,3-dihydro-inden-4-yl)-2,5-di(thiophen-2-yl)-pyrrole (DIT); (c) 2 mM 4-(2,5-di(thiophen-2-yl)-pyrrol-1-yl)benzo[c][1,2,5]thiadiazole (BDTA); (d) 2 mM TTPA + 2 mM DIT; and (e) 2 mM TTPA + 2 mM BDTA in 0.1 M LiClO₄/ACN at a scan rate of 100 mV s⁻¹ on ITO working electrode.

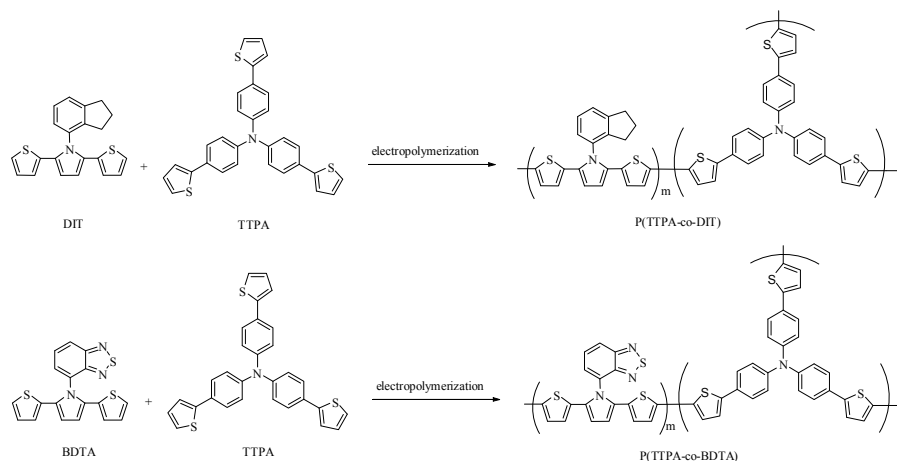


Figure 2. The electrochemical copolymerization of dithienylpyrrole (SNS) derivatives and tris(4-(thiophen-2-yl)phenyl)amine.

Copolymer films P(TTPA-co-DIT) and P(TTPA-co-BDTA) prepared by constant potential deposition at 1.0 V were scanned at different rates in the range from 25 to 200 mV · s⁻¹ in 0.1 M LiClO₄/ACN solution. As can be seen in Figures 3a and 4a, the P(TTPA-co-DIT) and P(TTPA-co-BDTA) presented two well-defined redox peaks, the current density response increased with the increasing of the scan rate, indicating that the copolymer films had good electrochemical activity and were adhered well to the electrode. With the increasing scan rate, the anodic and cathodic peak current densities

showed a linear dependence on the scan rate as illustrated in Figures 3b and 4b, demonstrating that the redox process of the copolymers were not limited by diffusion control [33].

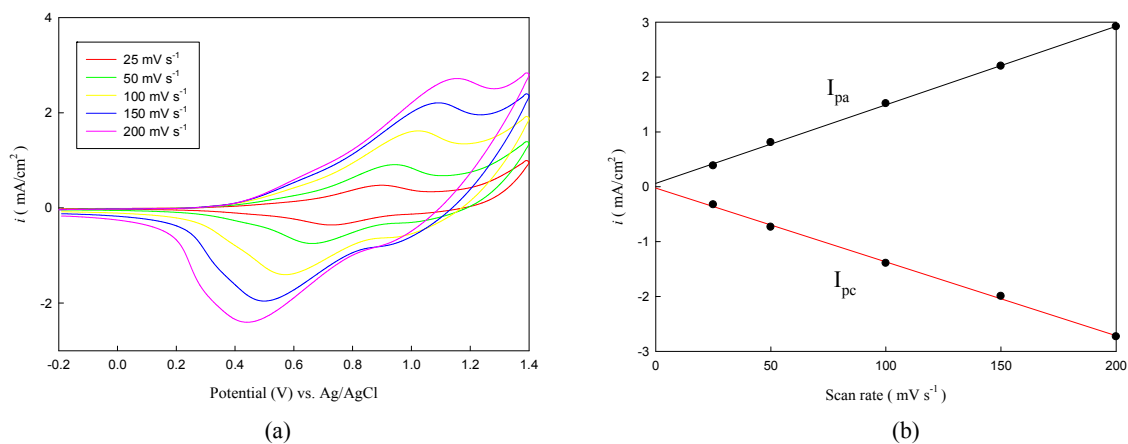


Figure 3. (a) CV curves of the P(TTPA-co-DIT) film at various scan rates between 25 and 200 $\text{mV} \cdot \text{s}^{-1}$ in 0.1 M $\text{LiClO}_4/\text{ACN}$ solution. P(TTPA-co-DIT) film was prepared potentiostatically at 1.0 V; (b) Relation between peak current density and scan rate of the P(TTPA-co-DIT) film in 0.1 M $\text{LiClO}_4/\text{ACN}$ solution.

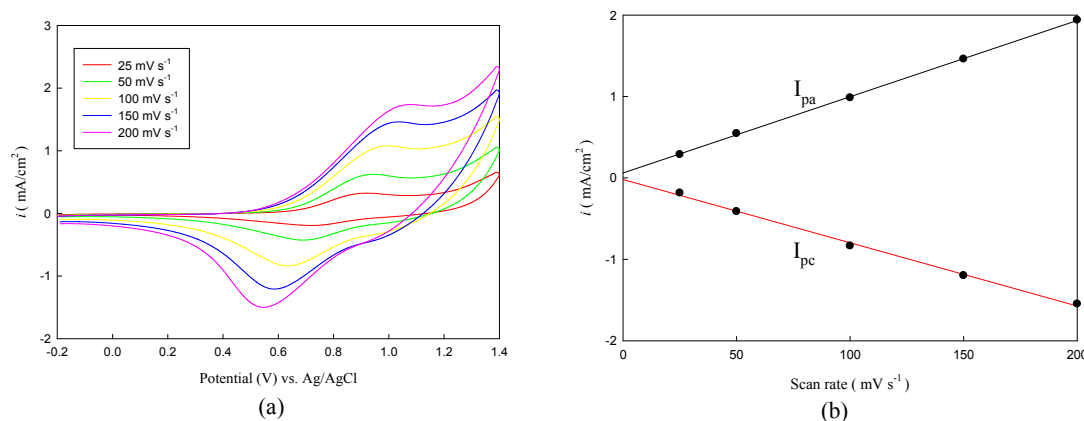


Figure 4. (a) CV curves of the P(TTPA-co-BDTA) film at various scan rates between 25 and 200 $\text{mV} \cdot \text{s}^{-1}$ in 0.1 M $\text{LiClO}_4/\text{ACN}$ solution. P(TTPA-co-BDTA) film was prepared potentiostatically at 1.0 V; (b) Relation between peak current density and scan rate of the P(TTPA-co-BDTA) film in 0.1 M $\text{LiClO}_4/\text{ACN}$ solution.

3.2. Electrochromic Properties of the Copolymer Films

Spectroelectrochemistry combines electrochemical and spectroscopic methods for investigating the changes in the absorption spectra upon applying of an external electrical potential. Spectroelectrochemistry of P(TTPA-co-DIT) and P(TTPA-co-BDTA) copolymer films coated on ITO electrode was studied in an ionic liquid solution. Figure 5 displayed the spectroelectrochemical spectra of P(TTPA-co-DIT) film at various potentials in EPIDIL solution. The copolymer films were prepared potentiostatically at 1.0 V, 1.1 V, and 1.2 V (see Figure 5a–c, respectively). As shown in Figure 5a and Table 1, the peak of P(TTPA-co-DIT) film in the neutral state was found at 388 nm, which corresponded to the $\pi-\pi^*$ transition of P(TTPA-co-DIT) in EPIDIL solution. Upon applying more than 0.8 V, the absorbance of $\pi-\pi^*$ transition peak of P(TTPA-co-DIT) decreased gradually and charge carrier bands appeared in higher wavelength region, which corresponded to the development of polaron and bipolaron bands [34]. When the P(TTPA-co-DIT) film was prepared potentiostatically at 1.1 V and 1.2 V, the $\pi-\pi^*$ transition of P(TTPA-co-DIT) film did not shift significantly. However,

the position of polaron peak with maximal absorbance changes shifted conspicuously upon applying various potentials, this can be ascribed to adherent polymer films undergo configuration changes during electrochemical overoxidation [35]. The π - π^* transition of P(TTPA-co-BDTA) film in EPIDIL solution located at similar position with P(TTPA-co-DIT) film, whereas the polaron peak positions of P(TTPA-co-BDTA) film with maximal absorbance shifted bathochromically relative to those of P(TTPA-co-DIT) film upon applying various potentials (Figure 6), which could be attributed to an electron-withdrawing 1,2,5-thiadiazole unit in BDTA unit showed narrower band gap in EPIDIL solution than that of DIT unit.

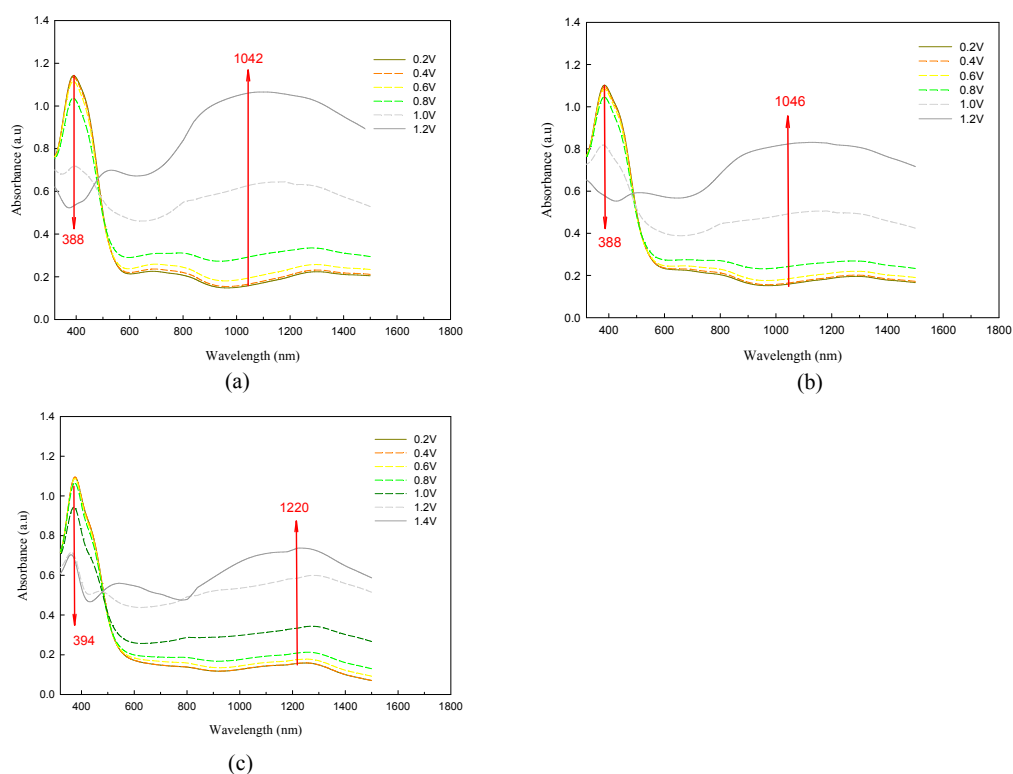


Figure 5. Spectroelectrochemical spectra of P(TTPA-co-DIT) films on ITO electrode at various potentials in an ionic liquid solution. The copolymer films were prepared potentiostatically at: (a) 1.0 V; (b) 1.1 V; and (c) 1.2 V on ITO glass electrodes.

Table 1. Absorption peaks of polymer films in ionic liquid solution.

Polymer films	$\lambda(\pi$ - π^* peak)/nm	λ (polaron peak)/nm
P(TTPA-co-DIT)-1.0 V	388	1,042
P(TTPA-co-DIT)-1.1 V	388	1,046
P(TTPA-co-DIT)-1.2 V	394	1,220
P(TTPA-co-BDTA)-1.0 V	394	1,096
P(TTPA-co-BDTA)-1.1 V	392	1,194
P(TTPA-co-BDTA)-1.2 V	388	1,304

Table 2 shows the photographs and colorimetric values (L^* , a^* , b^*) of the copolymer films at various potentials in EPIDIL solution. The P(TTPA-co-DIT) film was yellow (0.2 V) in the neutral state, yellowish-green (0.8 V) and green (1.0 V) in the intermediate state, and blue (1.2 V) in highly oxidized state. The P(TTPA-co-BDTA) film showed less color changes than those of P(TTPA-co-DIT) film, P(TTPA-co-BDTA) film was yellow (0.2 V) in the neutral state, bluish-green (1.0 V) in the intermediate state, and blue (1.2 V) in highly oxidized state, indicating the incorporation of DIT unit into copolymer backbone gives rise to more color changes than that of BDTA unit.

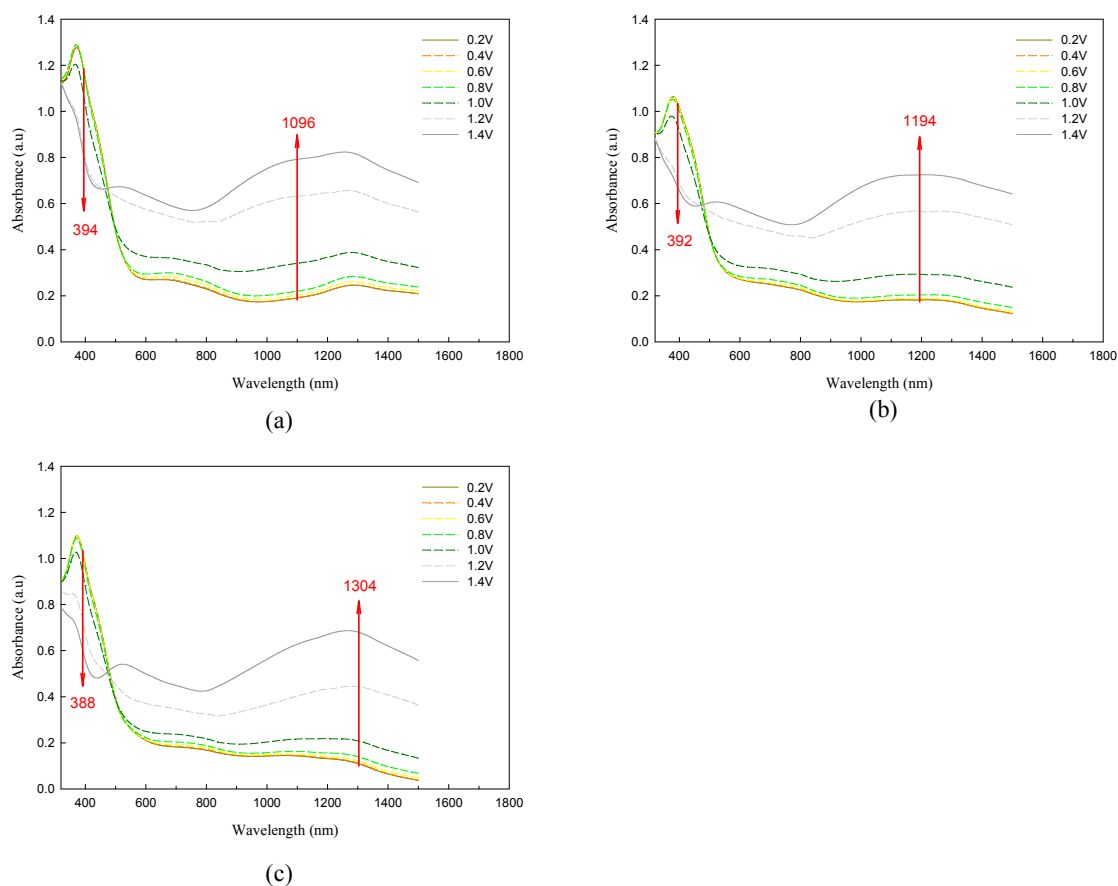


Figure 6. Spectroelectrochemical spectra of P(TTPA-co-BDTA) films on ITO electrode as applied potentials between 0.2 V and 1.4 V in an ionic liquid solution. The copolymer films were prepared potentiostatically at: (a) 1.0 V; (b) 1.1 V; and (c) 1.2 V on ITO glass electrodes.

Table 2. Electrochromic photographs and colorimetric values (L^* , a^* , b^*) of the copolymer films at various potentials in ionic liquid solution.

Polymer films	E/V	Photographs	L^*	a^*	b^*
P(TTPA-co-DIT)-1.0 V	0.2		77.29	-4.24	56.58
	0.8		73.53	-6.66	43.36
	1.0		63.02	-1.3	14.59
	1.2		52.53	5.36	-7.73
	0.2		74.32	-5.14	45.18
P(TTPA-co-BDTA)-1.0 V	1.0		68.96	-5.45	29.7
	1.2		57.32	0.71	6.57
	1.4		54.12	2.65	1.14

A square-wave potential step technology coupled with a UV-Visible spectrophotometer was used for analysis of switching kinetics and optical contrast of the copolymer films [36]. The P(TTPA-co-DIT) and P(TTPA-co-BDTA) films were stepped by repeated potential between neutral state (0.2 V) and oxidized state (+1.2 V) with a time interval of 5 s in an ionic liquid solution. The *in situ* transmittance–time profiles of P(TTPA-co-DIT) and P(TTPA-co-BDTA) films in EPIDIL solution are displayed in Figure 7, and the optical contrast (ΔT) estimated at 1st, 50th, and 100th cycles are summarized in Table 3. For P(TTPA-co-DIT) film prepared potentiostatically at 1.0 V, 1.1 V, and 1.2 V, the ΔT of P(TTPA-co-DIT)-1.0 V, P(TTPA-co-DIT)-1.1 V, and P(TTPA-co-DIT)-1.2 V films at first cycle are 60.3, 55.6, and 49.4%, respectively, and P(TTPA-co-DIT) film prepared potentiostatically at 1.0 V shows the highest ΔT . For the ΔT of copolymer films at different switching cycles, the ΔT of P(TTPA-co-DIT)-1.0 V film from the bleaching state to the coloration state in EPIDIL solution was 60.3, 58.8 and 57.1%, respectively, at 1st, 50th, and 100th cycle. However, the ΔT of P(TTPA-co-DIT)-1.2 V film from the bleaching state to the coloration state in EPIDIL solution was 49.4, 43.2 and 42.6%, respectively, at 1st, 50th, and 100th cycle. The stability of P(TTPA-co-DIT)-1.0 V and P(TTPA-co-DIT)-1.2 V films at the 100th cycle was 94.7 and 86.2%, respectively, and the P(TTPA-co-DIT)-1.0 V film shows higher stability than that of P(TTPA-co-DIT)-1.2 V film at high switching cycles, which can be attributed to an overoxidation of the copolymer takes place when electropolymerization at high potential (*i.e.*, in highly oxidized state). The ΔT of P(TTPA-co-DIT)-1.0 V and P(TTPA-co-BDTA)-1.0 V films from the bleaching state to the coloration state in EPIDIL solution were 60.3 and 47.1%, respectively, at the first cycle, implying P(TTPA-co-DIT) film shows higher ΔT than that of P(TTPA-co-BDTA) film. The stability of P(TTPA-co-DIT)-1.0 V and P(TTPA-co-BDTA)-1.0 V films at the 100th cycle was 94.7 and 85.6%, respectively, revealing the P(TTPA-co-DIT) film shows higher stability than that of P(TTPA-co-BDTA) film at high switching cycles.

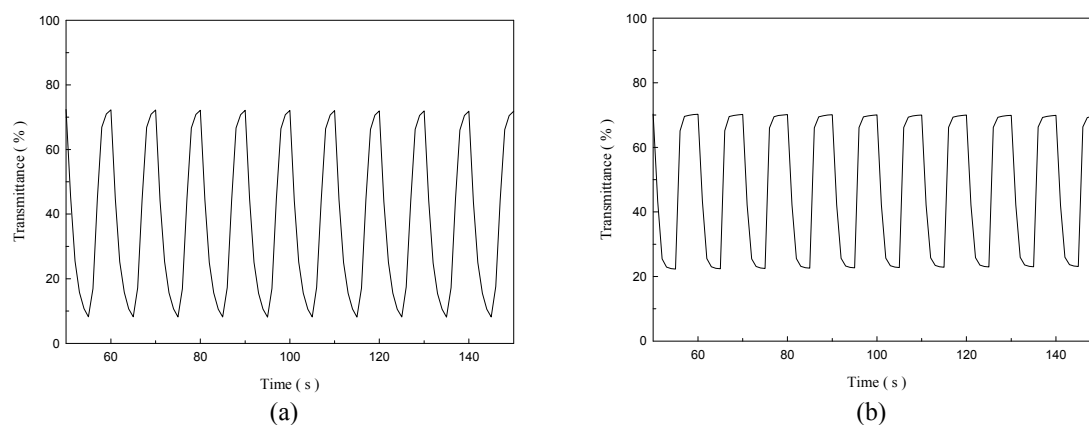


Figure 7. *In situ* transmittance of: (a) P(TTPA-co-DIT); and (b) P(TTPA-co-BDTA) films as a function of time in EPIDIL electrolyte, the time interval is 5 s. The copolymer films were prepared potentiostatically at 1.0 V on ITO electrodes and were stepped by repeated potential between 0.2 V and +1.2 V.

The coloration switching time (τ_c) and the bleaching switching time (τ_b) of copolymer films estimated at 1st, 50th, and 100th cycles are also summarized in Table 3. The switching time was estimated at 90% of the full-transmittance variation. P(TTPA-co-BDTA) film shows shorter τ_c and τ_b than those of P(TTPA-co-DIT) film, revealing that P(TTPA-co-BDTA) film exhibits fast switching speeds from the dedoped to the doped state and from the doped to the dedoped state when we employ EPIDIL as a supporting electrolyte. The ΔT_{\max} of P(TTPA-co-DIT)-1.0 V and P(TTPA-co-BDTA)-1.0 V films are higher than that reported for P(TTPA-co-EDOT) [37], and higher than those reported for PSNS derivatives (PTEPA [38], PSNS-1-NAPH [39], and P(SNS-Fc-co-EDOT) [40]). This could be ascribed to the fact that ΔT_{\max} of P(TTPA-co-DIT)-1.0 V and P(TTPA-co-BDTA)-1.0 V

films were estimated in long wavelength region (1042–1096 nm) when we employed EPIDIL as a supporting electrolyte.

Table 3. Electrochromic photographs and colorimetric values (L^* , a^* , b^*) of the copolymer films at various potentials in ionic liquid solution.

Polymer films	λ/nm	Cycle No.	Optical contrast/%			τ/s		Stability (100 cyc)
			T_b	T_c	ΔT	τ_c	τ_b	
P(TTPA-co-DIT)-1.0 V	1042	1	70.9	10.6	60.3	2.64	2.42	94.7
		50	69.5	10.7	58.8	2.48	2.31	
		100	68	10.9	57.1	2.37	2.23	
P(TTPA-co-DIT)-1.1 V	1046	1	68.3	12.7	55.6	2.45	2.27	93
		50	65.4	13	52.4	2.16	2.67	
		100	65	13.3	51.7	2.11	2.54	
P(TTPA-co-DIT)-1.2 V	1220	1	63.9	14.5	49.4	2.07	2.35	86.2
		50	62.7	19.5	43.2	1.81	1.74	
		100	62.4	19.8	42.6	1.79	1.58	
P(TTPA-co-BDTA)-1.0 V	1096	1	69.8	22.7	47.1	1.82	0.99	85.6
		50	68.9	25.9	43	1.64	0.92	
		100	68.3	28	40.3	1.58	0.88	
P(TTPA-co-BDTA)-1.1 V	1194	1	72.1	28.9	43.2	2.15	1.72	62.7
		50	70.9	36.6	34.3	2.07	1.93	
		100	68.6	41.5	27.1	2.32	2.36	
P(TTPA-co-BDTA)-1.2 V	1304	1	78.3	35.7	42.6	1.56	1.61	48.4
		50	77.1	47.1	30	1.22	1.65	
		100	74.5	53.9	20.6	1.26	1.23	

ΔOD is the discrepancy of optical density, which can be estimated using the transmittance of the oxidation state (T_{ox}) and neutral state (T_{neu}) using the following equation:

$$\Delta\text{OD} = \log \left(\frac{T_{\text{ox}}}{T_{\text{neu}}} \right) \quad (1)$$

The $\Delta\text{OD}_{\text{max}}$ of P(TTPA-co-DIT)-1.0 V film at 1042 nm and P(TTPA-co-BDTA)-1.0 V film at 1096 nm in EPIDIL solution are 80 and 49%, respectively. Similar to ΔT_{max} , P(TTPA-co-DIT)-1.0 V film showed higher $\Delta\text{OD}_{\text{max}}$ than that of P(TTPA-co-BDTA)-1.0 V film.

The coloration efficiency (η) at a specific wavelength can be defined as the ΔOD for the charge (q) consumed per unit electrode area (A):

$$\eta = \frac{\Delta\text{OD}}{q/A} \quad (2)$$

As shown in Table 4, the η_{max} of P(TTPA-co-DIT)-1.0 V film at 1042 nm and P(TTPA-co-BDTA)-1.0 V film at 1096 nm in EPIDIL solution are 181.9 and 217.8 $\text{cm} \cdot \text{C}^{-1}$, respectively, which were higher than those reported for PTEPA [38] at 448 nm and PSNS-1-NAPH [39] at 423 nm.

Table 4. Summary of ΔT_{max} and η_{max} for various polymer films.

Polymer films	Electrolyte	λ/nm	$\Delta T_{\text{max}}/\%$	$\Delta\text{OD}_{\text{max}}/\%$	$\eta_{\text{max}}/\text{cm}^2 \cdot \text{C}^{-1}$	Ref.
P(TTPA-co-EDOT)	0.2 M NaClO ₄ /ACN/DCM	460	30.6	-	-	[37]
P(TTPA-co-EDOT)	0.2 M NaClO ₄ /ACN/DCM	800	45	-	-	[37]
PTEPA	0.2 M NaClO ₄ /ACN/DCM	448	26.84	-	152	[38]
PSNS-1-NAPH	0.1 M LiClO ₄ /ethanol	423	18.2	25	102	[39]
P(SNS-Fc-co-EDOT)	LiClO ₄ /ACN	415	20.9	-	-	[40]
P(TTPA-co-DIT)-1.0 V	EPIDIL	1042	60.3	80	181.9	This work
P(TTPA-co-BDTA)-1.0 V	EPIDIL	1096	47.1	49	217.8	This work

3.3. Spectroelectrochemistry of ECDs

Dual type ECDs consisting of electrochemically deposited P(TTPA-co-DIT)-1.0 V/PProDOT-Et₂ and P(TTPA-co-BDTA)-1.0 V/PProDOT-Et₂ were constructed and their spectroelectrochemical behaviors were studied by recording the optical absorbance spectra at various potentials. ECDs showed a reversible response in a potential range of −0.4 V and 1.2 V, as depicted in Figure 8. At −0.4 V, P(TTPA-co-DIT)-1.0 V/PProDOT-Et₂ and P(TTPA-co-BDTA)-1.0 V/PProDOT-Et₂ ECDs revealed well defined transitions at *ca.* 382 and 424 nm, respectively, which are in accordance with the spectral behaviors of P(TTPA-co-DIT)-1.0 V and P(TTPA-co-BDTA)-1.0 V films in reduced state. However, in this situation, the complementary PProDOT-Et₂ layer is expected to be in oxidized state and it does not show significant transition in UV spectrum. Upon increasing the potential gradually, P(TTPA-co-DIT)-1.0 V and P(TTPA-co-BDTA)-1.0 V films begin to oxidize and a new absorption band at 588 nm appeared due to neutralization of the PProDOT-Et₂ layer, and the ECDs were blue in the potential range of +0.8 and 1.2 V for P(TTPA-co-DIT)-1.0 V/PProDOT-Et₂ ECD and in the potential range of +1.0 and 1.4 V for P(TTPA-co-BDTA)-1.0 V/PProDOT-Et₂ ECD (Table 5).

Table 5. Electrochromic photographs and colorimetric values (L*, a*, and b*) of the ECDs. The P(TTPA-co-DIT) and P(TTPA-co-BDTA) films were prepared potentiostatically at 1.0 V on ITO glass electrodes.

ECDs	E/V	Photographs	L*	a*	b*
P(TTPA-co-DIT)/ PProDOT-Et ₂	−0.4		85.82	2.95	32.99
	0.2		84.21	0.62	29.04
	0.4		81.66	1.2	24.51
	0.6		78.26	0.54	18.34
	0.8		74.76	−0.04	12.22
	1.0		73.54	−0.09	9.24
P(TTPA-co-BDTA)/ PProDOT-Et ₂	1.2		73.06	−0.18	7.31
	−0.4		75.43	−5.99	31.89
	0.6		75.57	−6.16	31.99
	0.8		75.46	−6.27	31.78
	1.0		73.87	−5.83	29.33
	1.2		56.54	0.21	4.25
	1.4		50.25	−2.73	−6.74

The transmittance–time profiles of P(TTPA-co-DIT)-1.0 V/PProDOT-Et₂ and P(TTPA-co-BDTA)-1.0 V/PProDOT-Et₂ ECDs were shown in Figure 9, which were stepped by repeated potential in the range of neutral (− 0.2 V) and oxidized states (+1.2 V) with a time interval of 5 s, and the

ΔT , τ_c , and τ_b estimated at different double-step potential cycles are summarized in Table 6. The ΔT of P(TTPA-co-DIT)-1.0 V/PProDOT-Et₂ and P(TTPA-co-BDTA)-1.0 V/PProDOT-Et₂ ECDs is 43.5 and 48.1% at the first cycle, respectively, implying P(TTPA-co-BDTA) film is a promising electrochromic material to increase the ΔT when we employ P(TTPA-co-BDTA) film as anodic copolymer layer in ECDs. For P(TTPA-co-BDTA) film was prepared potentiostatically at 1.0 V, 1.1 V, and 1.2 V, the ΔT of P(TTPA-co-BDTA)-1.0 V/PProDOT-Et₂, P(TTPA-co-BDTA)-1.1 V/PProDOT-Et₂, and P(TTPA-co-BDTA)-1.2 V/PProDOT-Et₂ ECDs at first cycle are 48.1, 35.6, and 30.1%, respectively, and P(TTPA-co-BDTA) film prepared potentiostatically at 1.0 V shows the highest ΔT . The stability of P(TTPA-co-DIT)-1.0 V/PProDOT-Et₂ and P(TTPA-co-DIT)-1.2 V/PProDOT-Et₂ ECDs at the 100th cycle was 96.3 and 90.8%, respectively, indicating the P(TTPA-co-DIT)-1.0 V/PProDOT-Et₂ ECD shows higher stability than that of P(TTPA-co-DIT)-1.2 V/PProDOT-Et₂ ECD at high switching cycles. Moreover, the stability of P(TTPA-co-BDTA)-1.0 V/PProDOT-Et₂ ECD is higher than P(TTPA-co-DIT)-1.0 V/PProDOT-Et₂ ECD, and the stabilities of ECDs are high than those of copolymer films in an ionic liquid solution. For the optical switching time of P(TTPA-co-DIT)/PProDOT-Et₂ and P(TTPA-co-BDTA)/PProDOT-Et₂ ECDs, the τ_c and τ_b of the ECDs were shorter than those of copolymer films in EPIDIL solution, displaying the ECDs changed color faster upon applying potentials than the copolymer films in EPIDIL solution.

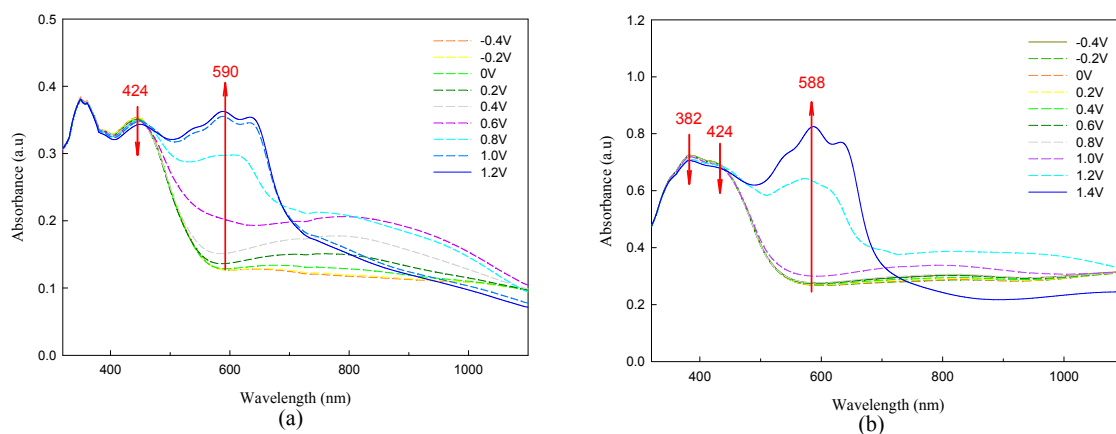


Figure 8. Spectroelectrochemical spectra of: (a) P(TTPA-co-DIT)/PProDOT-Et₂; and (b) P(TTPA-co-BDTA)/PProDOT-Et₂ ECDs as applied potentials between -0.4 V and 1.2 V. P(TTPA-co-DIT) and P(TTPA-co-BDTA) films were prepared potentiostatically at 1.0 V.

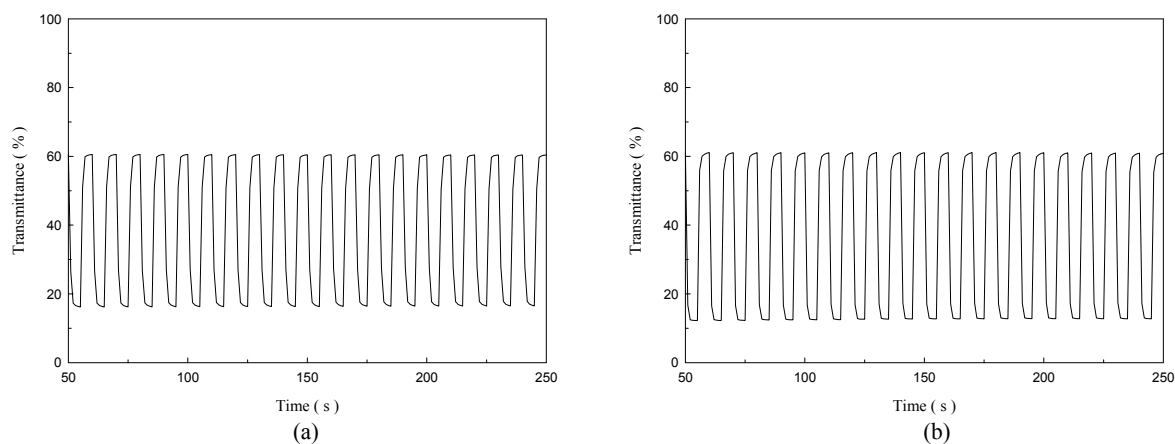


Figure 9. *In situ* transmittance of: (a) P(TTPA-co-DIT)/PProDOT-Et₂ ECD (590 nm); and (b) P(TTPA-co-BDTA)/PProDOT-Et₂ ECD (588 nm) as a function of time, the time interval is 5 s. The ECDs were stepped by repeated potential between -0.2 V and $+1.2$ V.

Table 6. Color–bleach switching time of ECDs.

ECDs	λ/nm	Cycle No.	Optical contrast/%			τ/s		Stability (100 cyc)
			T_b	T_c	ΔT	τ_c	τ_b	
P(TTPA-co-DIT)-1.0 V/ ProDOT-Et ₂	590	1	60	16.5	43.5	1.52	1.52	96.3%
		50	59.8	17.3	42.5	1.61	1.48	
		100	59.5	17.6	41.9	1.61	1.55	
P(TTPA-co-DIT)-1.1 V/ PProDOT-Et ₂	590	1	54.9	20.8	34.1	0.91	0.83	96.2%
		50	54.6	21	33.6	0.91	0.87	
		100	54.1	21.3	32.8	0.9	0.86	
P(TTPA-co-DIT)-1.2 V/ PProDOT-Et ₂	590	1	54.8	24.2	30.6	0.86	0.85	90.8%
		50	54.2	24.3	30	0.83	0.84	
		100	52.4	24.6	27.8	0.82	0.88	
P(TTPA-co-BDTA)-1.0 V / PProDOT-Et ₂	588	1	60.5	12.4	48.1	0.93	0.91	97.1%
		50	60.2	13	47.2	0.96	0.97	
		100	59.7	13	46.7	1.04	1.08	
P(TTPA-co-BDTA)-1.1 V / PProDOT-Et ₂	590	1	58.7	23.1	35.6	1.82	1.59	96.9%
		50	58.4	23.5	34.2	1.69	1.54	
		100	58.2	23.7	34.5	1.67	1.51	
P(TTPA-co-BDTA)-1.2 V / PProDOT-Et ₂	592	1	58.6	28.5	30.1	1.82	1.4	96.7%
		50	58.4	28.7	29.7	1.31	1.21	
		100	58	28.9	29.1	0.86	0.83	

Table 7 shows the ΔT_{max} , ΔOD_{max} , and η_{max} of P(TTPA-co-DIT)/PProDOT-Et₂ and P(TTPA-co-BDTA)/PProDOT-Et₂ ECDs and reported dual-type ECDs, P(TTPA-co-DIT)/PProDOT-Et₂ and P(TTPA-co-BDTA)/PProDOT-Et₂ ECDs show higher ΔT_{max} than those reported for P(SNS-HE)/PEDOT [41], PTEPA/PEDOT [38], P(TTPA-co-BT)/PEDOT [42], P(TTPA-co-EDOT)/PEDOT [37], and P(Cz4-co-CIn1)/PProDOT-Me₂ [43] ECDs. In another aspect, P(TTPA-co-BDTA)/PProDOT-Et₂ ECD shows higher η than that of P(TTPA-co-DIT)/PProDOT-Et₂ ECD. P(TTPA-co-BDTA)/PProDOT-Et₂ ECD shows higher η than those reported for PTEPA/PEDOT [38], P(TTPA-co-EDOT)/PEDOT [37], and P(Cz4-co-CIn1)/PProDOT-Me₂ ECDs [43], whereas P(TTPA-co-BDTA)/PProDOT-Et₂ ECD shows lower η than that reported for P(SNS-HE)/PEDOT [41] ECD.

Table 7. The optical contrast, changes of the optical density and coloration efficiency of ECDs.

ECDs	λ/nm	$\Delta T_{\text{max}}/\%$	$\Delta OD_{\text{max}}/\%$	η of $\Delta OD_{\text{max}}/\text{cm}^2 \cdot \text{C}^{-1}$	Ref.
P(SNS-HE)/PEDOT	570	14.1	-	741	[41]
PTEPA/PEDOT	628	24.72	-	277	[38]
P(TTPA-co-BT)/PEDOT	630	30.58	-	-	[42]
P(TTPA-co-EDOT)/PEDOT	650	24	-	545	[37]
P(Cz4-co-CIn1)/PProDOT-Me ₂	575	32	24.6	372.7	[43]
P(TTPA-co-DIT)-1.0 V /PProDOT-Et ₂	590	43.5	56	373.3	This work
P(TTPA-co-BDTA)-1.0 V /PProDOT-Et ₂	588	48.1	69	649.4	This work

3.4. Open Circuit Memory of ECDs

The open circuit memory test of P(TTPA-co-DIT)-1.0 V/PProDOT-Et₂ and P(TTPA-co-BDTA)-1.0 V/PProDOT-Et₂ ECDs were monitored at 590 and 588 nm, respectively, as a function of time by applying potential for 1 s for each 200 s time interval. The test potentials for P(TTPA-co-DIT)-1.0 V/PProDOT-Et₂ ECD were -0.4 and 1.2 V in neutral and oxidized states, respectively, for P(TTPA-co-BDTA)-1.0 V/PProDOT-Et₂ ECD were -0.2 and 1.2 V in neutral and oxidized states, respectively. It can be seen in Figure 10a,b that these ECDs show less than 5% transmittance change in oxidized state and less than 2% transmittance change in neutral state, indicating the presence of good optical memories for the ECDs.

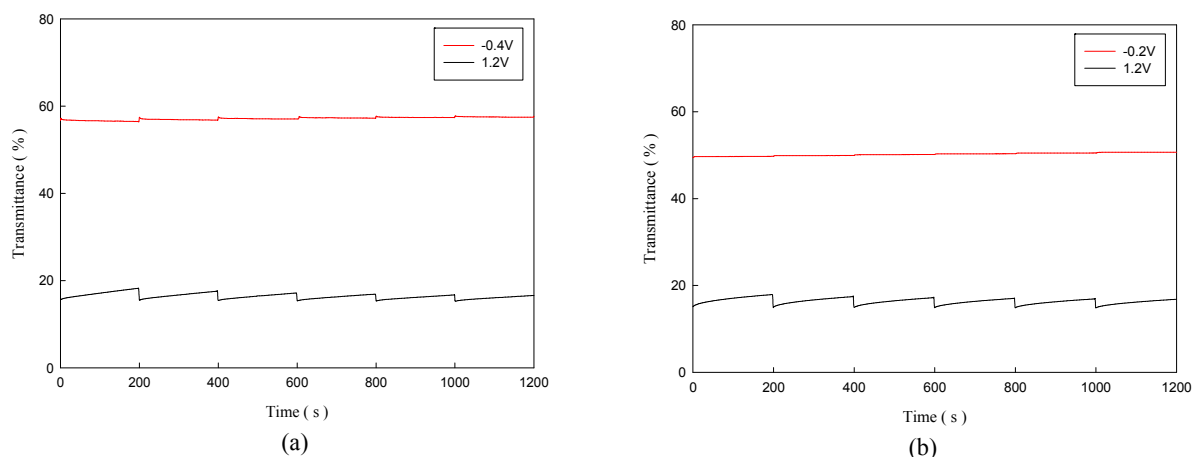


Figure 10. Open circuit stability of the: (a) P(TTPA-co-DIT)-1.0 V/PProDOT-Et₂ ECD monitored at 590 nm; and (b) P(TTPA-co-BDTA)-1.0 V/PProDOT-Et₂ ECD monitored at 588 nm.

3.5. Stability of ECDs

Stability upon repeatedly applied potentials between neutral and oxidized states is a way to estimate the electrochromic lifetime of ECDs [44]. Stabilities of the P(TTPA-co-DIT)-1.0 V/PProDOT-Et₂ and P(TTPA-co-BDTA)-1.0 V/PProDOT-Et₂ ECDs were verified by 1000 cycles CV measurements of the applied potential between -1.0 V and 1.4 V with $100 \text{ mV} \cdot \text{s}^{-1}$ scan rate. As shown in Figure 11a,b, the electrochromic switch between neutral and oxidized states of P(TTPA-co-DIT)-1.0 V/PProDOT-Et₂ and P(TTPA-co-BDTA)-1.0 V/PProDOT-Et₂ ECDs, 92% and 96%, respectively, of electroactivity was maintained after 500 cycles, and 88% and 93%, respectively, of electroactivity was retained after 1000 cycles, implying these ECDs exhibited reasonable environmental and redox stability after 1000 cycles.

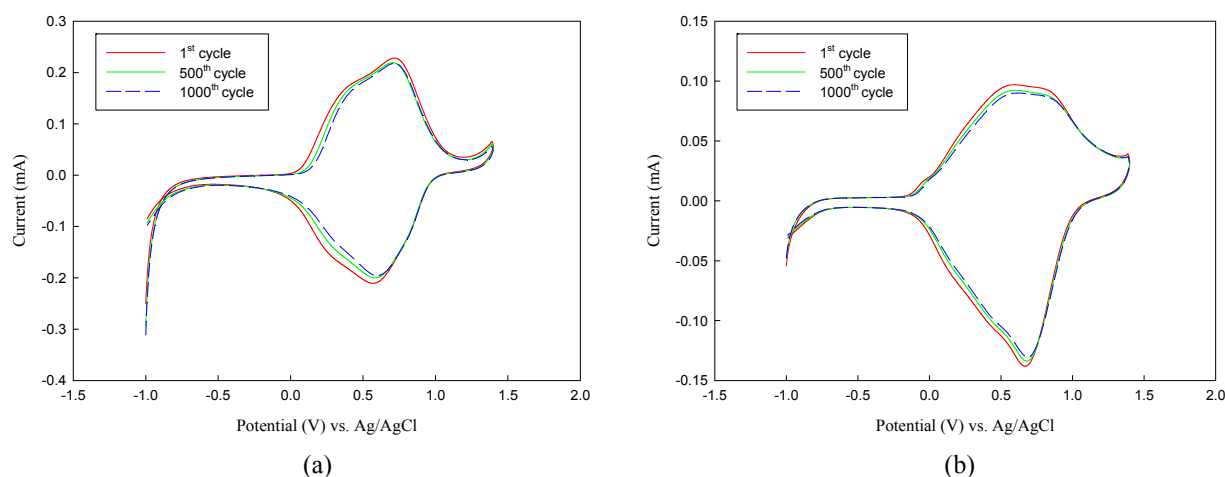


Figure 11. Cyclic voltammogram of: (a) P(TTPA-co-DIT)-1.0 V/PProDOT-Et₂ ECD; and (b) P(TTPA-co-BDTA)-1.0 V/PProDOT-Et₂ ECD as a function of repeated scans at $100 \text{ mV} \cdot \text{s}^{-1}$.

4. Conclusions

Copolymers based on tris(4-(thiophen-2-yl)phenyl)amine and SNS derivatives were electrochemically synthesized and characterized in an ionic liquid solution. Spectroelectrochemical studies exhibited that P(TTPA-co-DIT) and P(TTPA-co-BDTA) films have distinct electrochromic behaviors from neutral state (yellow) to the oxidized state (blue) upon applying various potentials. Electrochromic switching characterizations of copolymer films indicate that P(TTPA-co-DIT)-1.0 V film has higher ΔT_{max} (60.3% at 1042 nm) than the P(TTPA-co-BDTA)-1.0 V film (47.1% at 1096 nm),

whereas P(TTPA-co-BDTA)-1.0 V film has higher η_{\max} ($217.8 \text{ cm}^2 \cdot \text{C}^{-1}$ at 1096 nm) than the P(TTPA-co-DIT)-1.0 V film ($181.9 \text{ cm}^2 \cdot \text{C}^{-1}$ at 1042 nm) in an ionic liquid solution. Dual type ECDs employing P(TTPA-co-DIT) (or P(TTPA-co-BDTA)) as anodic layer and PProDOT-Et₂ as cathodic layer were fabricated. The stability of P(TTPA-co-BDTA)-1.0 V/PProDOT-Et₂ ECD was higher than P(TTPA-co-DIT)-1.0 V/PProDOT-Et₂ ECD, and the stabilities of ECDs were higher than those of copolymer films in an ionic liquid solution. The ΔT_{\max} and η_{\max} of P(TTPA-co-BDTA)-1.0 V/PProDOT-Et₂ ECD are 48.1% and $649.4 \text{ cm}^2 \cdot \text{C}^{-1}$ at 588 nm, respectively, which are higher than those of P(TTPA-co-DIT)-1.0 V/PProDOT-Et₂ ECDs. In addition, the stabilities for the color-bleach switching of ECDs at 100th cycles are higher than those of copolymer films characterized in an ionic liquid solution. In view of the above results, the P(TTPA-co-DIT)-1.0 V and P(TTPA-co-BDTA) films could be useful as the active layers in ECDs.

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Conflicts of Interest: The authors declare no conflict of interest.

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