

# Electrosynthesis and Characterization of a New Multielectrochromic Copolymer of 1,4-Bis(2-thienyl) Benzene with 3,4-Ethylenedioxythiophene

Chuansheng Cui, Lianyi Xu, Jinsheng Zhao, Qingpeng He, Bin Wang

Shandong Key Laboratory of Chemical Energy Storage and Novel Cell Technology, Liaocheng University, Liaocheng 252059, People's Republic of China

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**ABSTRACT:** A copolymer based on 1,4-bis(2-thienyl) benzene (BTB) and 3,4-ethylenedioxythiophene was electrochemically synthesized in acetonitrile containing sodium perchlorate (NaClO<sub>4</sub>). Cyclic voltammetry, ultraviolet–visible spectroscopy, and Fourier transform infrared analyses confirmed that the resulting polymer was a copolymer rather than a blend or a composite of the respective homopolymers. Poly(1,4-bis(2-thienyl) benzene) has only two colors; it switches between yellow in the neutral state and green in the oxidized state, whereas the poly[1,4-bis(2-thienyl) benzene-co-3,4-ethylenedioxythiophene] (PBTBE) film exhibited five different colors (brown–red, orange–yellow, yellowish green, green, and blue). This revealed distinct electrochromic prop-

erties from that of the BTB homopolymer film. The maximum optical contrast ( $\Delta T$  %) and response time of the copolymer film were measured to be 27.8% and 0.51 s, respectively, at 780 nm. An electrochromic device (ECD) based on PBTBE and poly(3,4-ethylenedioxythiophene) was also constructed and characterized. This ECD showed a  $\Delta T$  % value of 22.2% in the visible region with a response time of 0.43 s at 616 nm. The coloration efficiency of the device was calculated to be 129 cm<sup>2</sup>/C at 616 nm. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** conducting polymers; conjugated polymers; copolymerization; differential scanning calorimetry (DSC)

## INTRODUCTION

$\pi$ -Conjugated polymers have been considered to be promising materials, holding unique optical and electrical properties,<sup>1</sup> and have been widely applied in the fields of polymer solar cells,<sup>2</sup> electrochromic devices (ECDs),<sup>3,4</sup> sensors,<sup>5</sup> polymer light-emitting diodes,<sup>6</sup> and so on. These electroactive and photoactive polymers are usually based on thiophene, pyrrole, phenylene, fluorene, or carbazole moieties.<sup>7,8</sup> Recently, electrochromic (EC) polymers have drawn a lot of attentions because of their outstanding coloration efficiency (CE),<sup>9</sup> fast switching times,<sup>10</sup> multiple colorations in the same material,<sup>11</sup> fine-tunability

of the band gap (and the color),<sup>12</sup> high stability,<sup>13</sup> thin-film flexibility, and cost effectiveness,<sup>14</sup> and they have been widely used in the fields of displays,<sup>15</sup> energy-saving smart windows,<sup>16</sup> and memory devices.<sup>17</sup>

For EC polymers, the electrochromism is related to the changing of band gaps during the doping–dedoping process.<sup>18</sup> The doping process modifies the polymer electronic structure and generates new electronic states in the band gap, which can cause color changes. The electronic absorption shifts bathochromically upon doping, and the color contrast between the dedoped and doped states is related to the polymer band gap.<sup>19</sup> However, most electroactive polymers are limited to two colors, where only few show multiple color states.<sup>20</sup> Although there have been some reports on multichromic materials,<sup>21,22</sup> it is still important to achieve materials that display distinctive color changes that cover the entire visible region upon an applied potential.

The EC properties of conducting polymers can be varied over a wide range through the control of the band gap of the polymer via proper choice of the heteroaromatic ring and its substituents. Blending and copolymerization are among the methods frequently used to tune the EC properties of materials. Copolymerization is an easy, facile method to combine the EC properties of the comonomers.<sup>20,22</sup>

Additional Supporting Information may be found in the online version of this article.

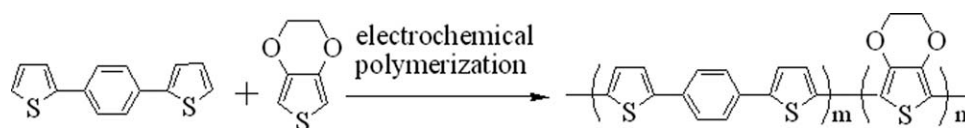
Correspondence to: J. Zhao (j.s.zhao@163.com).

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**Scheme 1** Synthetic routes of the copolymer.

The copolymerization of distinct monomers or the homopolymerization of hybrid monomers containing several distinct units can lead to an appealing combination of the properties of the parent polymers.

Many polybithiophenes with alternating aromatic units have been synthesized and characterized.<sup>23,24</sup> It has been shown that the introduction of an aromatic bridge in the bithiophene polymer main chains can result in changed highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) band gap polymers compared with both homopolymers.<sup>24</sup> Among those poly(1,4-bis(2-thienyl) benzene) (PBTB) has been shown to exhibit color changes between yellow and green.<sup>24</sup> 3,4-Ethylenedioxythiophene (EDOT) is a popular choice as a comonomer for copolymer synthesis because it produces a low-band-gap polymer with a high stability and good conductivity.<sup>25</sup>

In this study, we electrochemically synthesized a copolymer of 1,4-bis(2-thienyl) benzene (BTB) with EDOT, and the basic structure of poly[1,4-bis(2-thienyl) benzene-co-3,4-ethylenedioxythiophene] (PBTBE) is illustrated in Scheme 1. The copolymer revealed multichromism throughout the entire visible region. To explore the use of this material in ECDs, we constructed an absorptive/transmissive type ECD with an indium tin oxide (ITO)-coated glass/copolymer/gel electrolyte/poly(3,4-ethylenedioxythiophene) (PEDOT)/ITO configuration, where the copolymer and PEDOT functioned as the anodically and cathodically coloring layers, respectively. Characterizations of the EC behavior of the copolymer and the device were achieved by spectroelectrochemistry and kinetic and colorimetry studies.

## EXPERIMENTAL

### Materials

The BTB monomer was synthesized as reported previously by our group.<sup>24</sup> EDOT (98%) was purchased from Aldrich Chemical (Oregon, USA) and was used as received. Commercial high-performance-liquid-chromatography-grade acetonitrile (ACN; Tedia Co., Inc.) was used directly without further purification. Sodium perchlorate ( $\text{NaClO}_4$ ; Shanghai Chemical Reagent Co., 98%) was dried *in vacuo* at 60°C for 24 h before use. All other reagents were used as received without further treatment.

### Instrumentation

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 5700 FTIR spectrometer from Thermo Nicolet Analytical Instruments (Madison, WI, USA), where the samples were dispersed in KBr pellets. Scanning electron microscopy (SEM) measurements were taken with a JEOL JSM-6380LV SEM instrument. The photographs of the EC films were taken with a Fujifilm Shot (FinePix F200EXR) digital camera.

### Electrochemistry

The electrochemical syntheses and experiments were carried out in a one-compartment cell with a CHI 760 C electrochemical analyzer from Shanghai Chenhua Instrument Co. Ltd (Shanghai, China), under computer control with a platinum wire with a diameter of 0.5 mm as a working electrode, a platinum ring as a counter electrode, and a silver wire (Ag wire) as a pseudo-reference electrode. The working and counter electrodes were placed 0.5 cm apart during the experiments. The electrolytic solution consisted of 0.2M  $\text{NaClO}_4$  in ACN solution. The electrodeposition was performed in a 0.2M  $\text{NaClO}_4$ /ACN solution containing monomers or a monomer mixture potentiodynamically at a scan rate of 100 mV/s or potentiostatically at 1.30 V versus Ag wire. The pseudo-reference was calibrated externally with a 5 mM solution of ferrocene ( $\text{Fc}/\text{Fc}^+$ ) in the electrolyte [ $E_{1/2}(\text{Fc}/\text{Fc}^+) = 0.20$  V versus Ag wire in 0.2M  $\text{NaClO}_4$ /ACN, where  $E_{1/2}$  is the half-wave potential].<sup>10</sup>  $E_{1/2}$  of  $\text{Fc}/\text{Fc}^+$  measured in the 0.2M  $\text{NaClO}_4$ /ACN solution was 0.28 V versus a saturated calomel electrode. Thus, the potential of Ag wire was assumed to be 0.08 V versus the saturated calomel electrode. Cyclic voltammetry (CV) of polymer was carried out with the same electrode setup in monomer-free electrolyte solution. The PBTB, PBTBE, and PEDOT films used for the FTIR spectral measurements were deposited on the ITO ( $0.8 \times 2.1 \text{ cm}^2$ ) surface potentiostatically at 1.3, 1.3, and 1.4 V, respectively, and dedoped potentiostatically at  $-0.1$ ,  $-0.8$ , and  $-0.8$  V, respectively. All of the electrochemistry experiments were carried out at room temperature under a nitrogen atmosphere.

### Spectroelectrochemistry

The spectroelectrochemical data were recorded on a PerkinElmer Lambda 900 ultraviolet–visible (UV–

vis) near-infrared spectrophotometer from Perkin-Elmer Co. Ltd (Mount Holly, New Jersey, USA) connected to a computer. A three-electrode cell assembly was used, where the working electrode was an ITO-coated glass slide (sheet resistance <math>< 10 \Omega/\text{cm}</math>, Shenzhen CSG Display Technologies, China), the counter electrode was a stainless steel wire, and an Ag wire was used as pseudo-reference electrode. The potentials are reported versus Ag wire. The polymer films for spectroelectrochemistry were prepared by potentiostatic deposition on ITO-coated glass slides (active area =  $2.1 \times 0.8 \text{ cm}^2$ ).

### Preparation of the gel electrolyte

A gel electrolyte based on poly(methyl methacrylate) (molecular weight = 350,000) and  $\text{LiClO}_4$  was plasticized with propylene carbonate to form a highly transparent and conductive gel. ACN was also included as a high-vapor-pressure solvent to allow easy mixing of the gel components. The composition of the casting solution by weight ratio of ACN to propylene carbonate to poly(methyl methacrylate) to  $\text{LiClO}_4$  was 70 : 20 : 7 : 3. The gel electrolyte was used for construction of the polymer ECD cell.<sup>9</sup>

### Construction of ECDs

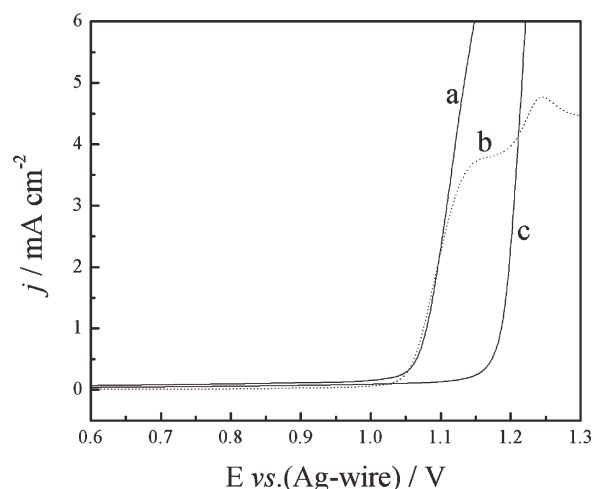
ECDs were constructed with two complementary polymers, namely, PBTBE as the anodically coloring material and PEDOT as the cathodically coloring material. Both the PBTBE and PEDOT films were electrodeposited onto two ITO-coated glass slides ( $1.8 \times 2.4 \text{ cm}^2$ ) at 1.3 and 1.4 V, respectively, with both polymerization charges at  $4.7 \times 10^{-2} \text{ C}$ . The electrical capacity of this ECD was also calculated, and its value was  $2.4 \times 10^{-3} \text{ C}$ . We built the ECD by arranging the two polymer films (one oxidized and the other reduced) facing each other and separated by a gel electrolyte.

## RESULTS AND DISCUSSION

### Electrochemical polymerization and characterization of PBTBE

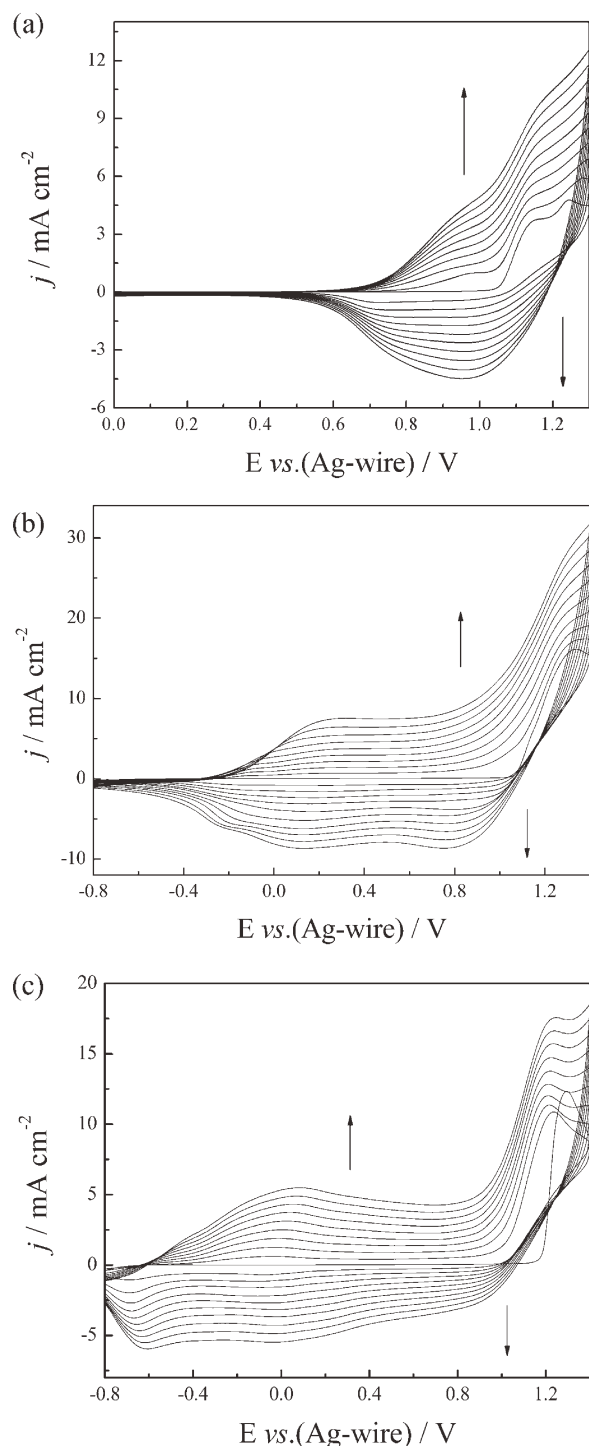
#### Electrochemical polymerization

It is well known that the onset oxidation potential ( $E_{\text{pa onset}}$ ) of the starting monomers is relatively close with intention to prepare copolymer chains with alternating monomer units.<sup>26,27</sup> To ensure the copolymerization of BTB and EDOT in  $0.2 \text{ M NaClO}_4/\text{ACN}$ , the electrochemical experiments were classified into different groups on the basis of the feed ratios of the two monomers. Figure 1 shows the typical anodic polarization curves of the monomers and monomer mixtures taken in  $0.2 \text{ M NaClO}_4/\text{ACN}$



**Figure 1** Anodic polarization curves of (a) 0.004M BTB and 0.01M EDOT, (b) 0.004M BTB, and (c) 0.01M EDOT in  $0.2 \text{ M NaClO}_4/\text{ACN}$ . Scanning rate =  $100 \text{ mV/s}$ . E denotes the potential.

at a potential scanning rate of  $100 \text{ mV/s}$ . As shown in Figure 1, the  $E_{\text{pa onset}}$  of EDOT [ $E_{\text{pa onset}} = 1.19 \text{ V}$ , Fig. 1(c)] was higher than that of BTB [ $E_{\text{pa onset}} = 1.05 \text{ V}$ , Fig. 1(b)]. The difference of the  $E_{\text{pa onset}}$  values between BTB and EDOT was  $0.14 \text{ V}$ . From this point, it seemed that it was hard to achieve the electrochemical copolymerization of EDOT and BTB. To realize the copolymerization successfully, we tried to solve this problem with the diffusion method established by Kuwabata et al.<sup>28</sup> Under the diffusion-limited conditions, the copolymerization strategy was to oxidize BTB at potentials where EDOT oxidation occurred. To confirm the suitable feed ratios of BTB and EDOT, a series of experiments with different feed ratios were carried out (the successive CV curves of different EDOT/BTB ratios are shown in Fig. 1). When the concentration of EDOT was too low, the cyclic voltammograms of copolymerization were similar to those of BTB. However, when the concentration of EDOT was too high, the CV was very similar to EDOT. For this purpose, the concentrations of EDOT and BTB were chosen as  $0.01$  and  $0.004 \text{ M}$ , respectively. The anodic polarization curve of this mixture is shown in Figure 1(a). It can be seen that the  $E_{\text{pa onset}}$  of this mixture was  $1.06 \text{ V}$ , which is intermediate between those of EDOT and BTB. However, the superposition of curves b and c did not add up to curve a. This may have been partly due to some changes of the electrochemical environment caused by successive deposition of the two monomers during the anodic polarization,<sup>28</sup> this indicated the existence of the interaction between the two monomers in  $0.2 \text{ M NaClO}_4/\text{ACN}$ .<sup>29</sup> The latter experimental results also indicated that the copolymerization between EDOT and BTB with  $0.01 \text{ M EDOT}$  and  $0.004 \text{ M BTB}$  was feasible under this feed ratio.



**Figure 2** Successive CV curves of (a) 0.004M BTB, (b) 0.004M BTB and 0.01M EDOT, and (c) 0.01M EDOT in 0.2M NaClO<sub>4</sub>/ACN. Scanning rates = 100 mV/s. E denotes the potential.

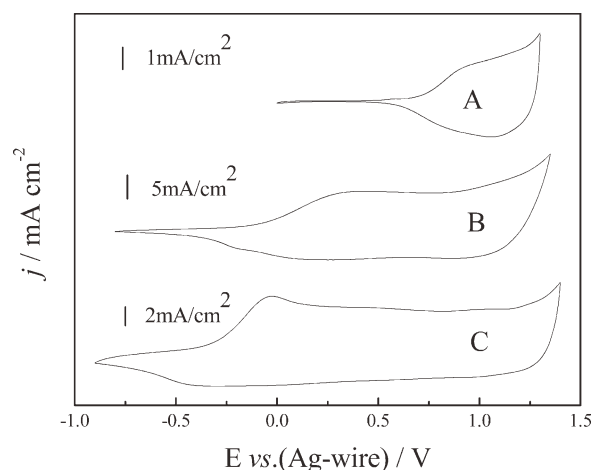
The successive CV curves of 0.004M BTB, 0.01M EDOT, and the BTB/EDOT mixture (0.004M BTB and 0.01M EDOT) in 0.2M NaClO<sub>4</sub>/ACN are illustrated in Figure 2. As shown in Figure 2(a), the polymerization of BTB presented unsymmetrical redox peaks, and the cathodic peak potential of the

oligomer of BTB was at 0.95 V, whereas the corresponding oxidation waves of the oligomer at about 1.3 V overlapped with the oxidation waves of the BTB monomer and could not be observed clearly.<sup>30</sup> The CV curves of EDOT showed a broad oxidation peak at 0.07 V and two successive reduction peaks at 0.60 and 0.045 V [Fig. 2(c)]. However, the CV curve of the BTB/EDOT mixture exhibited an anodic peak around 0.32 V and two well-defined cathodic peaks at 0.13 and 0.76 V, respectively [Fig. 2(b)], which were different from those of BTB and EDOT and indicated the formation of a new copolymer (PBTBE) consisting of both the BTB and EDOT units.<sup>31</sup> In addition, as can be seen from Figure 2, there was an obvious increase in the peak current density (*j*) of the BTB/EDOT mixture compared with those of EDOT and BTB; this also implied the formation of a copolymer.<sup>32</sup>

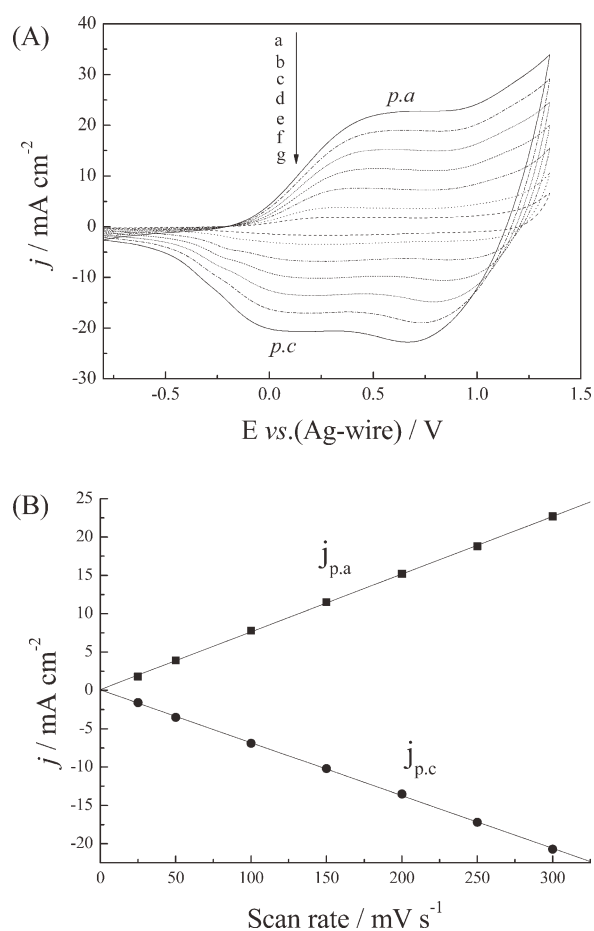
#### Electrochemistry behavior of the PBTBE films

We prepared films of PBTB, PBTBE, and PEDOT on platinum wires by sweeping the potentials for 10 cycles, and their CV curves in 0.2M NaClO<sub>4</sub>/ACN are given in Figure 3. As shown in Figure 3(A), the PBTB film exhibited one main reduction peak around 1.06 V, although the PEDOT film displayed one main oxidation peak around -0.03 V and a broad reduction peak around -0.31 V, as depicted in Figure 3(C). The PBTBE film exhibited an intensive CV response with two reversible redox processes over a wide potential range and main redox peaks around 0.28 and 0.44 V [Fig. 3(B)]; this was attributed to the existence of BTB and EDOT units in the copolymer chain.<sup>33</sup>

Figure 4 shows the electrochemical behavior of the PBTBE film (prepared on platinum wires by the



**Figure 3** Cyclic voltammogram curves of (A) PBTB, (B) PBTBE, and (C) PEDOT films in monomer-free solution of 0.2M NaClO<sub>4</sub>/ACN at a scanning rate of 100 mV/s. E denotes the potential.



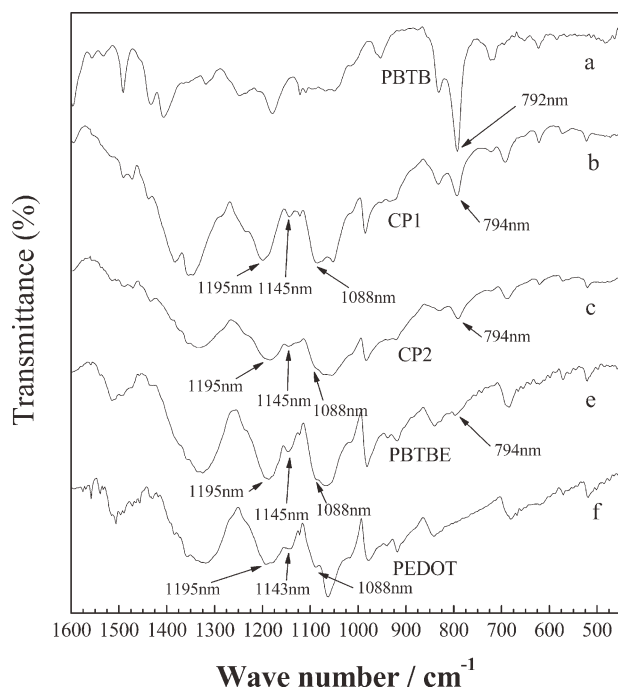
**Figure 4** (A) CV curves of the PBTBE film at different scanning rates between 25 and 300 mV/s in monomer-free 0.2M NaClO<sub>4</sub>/ACN. Scanning rates: (a) 300, (b) 250, (c) 200, (d) 150, (e) 100, (f) 50, and (g) 25 mV/s. (B) Scan rate dependence of the PBTBE film. E denotes the potential, p.a and p.c denote the anodic and cathodic peaks, respectively.

sweeping of the potentials from  $-0.8$  to  $1.4$  V for 10 cycles) at different scan rates between 25 and 300 mV/s in 0.2M NaClO<sub>4</sub>/ACN. The  $j$  response increased with increasing scan rate; this indicated that the obtained copolymer film had good electrochemical activity and adhesion.<sup>32,34</sup> The scan rate dependence of the anodic peak current density ( $j_{p.a}$ ) and cathodic peak current densities ( $j_{p.c}$ ; the anodic peak at 0.73 V and the cathodic peak at 0.13 V, respectively) presented a linear dependence on the scan rate, as illustrated in Figure 4(B). The  $j$  values were proportional to the potential scan rates, which indicated that the electrochemical processes of PBTBE seemed to be reversible and not diffusion-limited.<sup>29,35</sup>

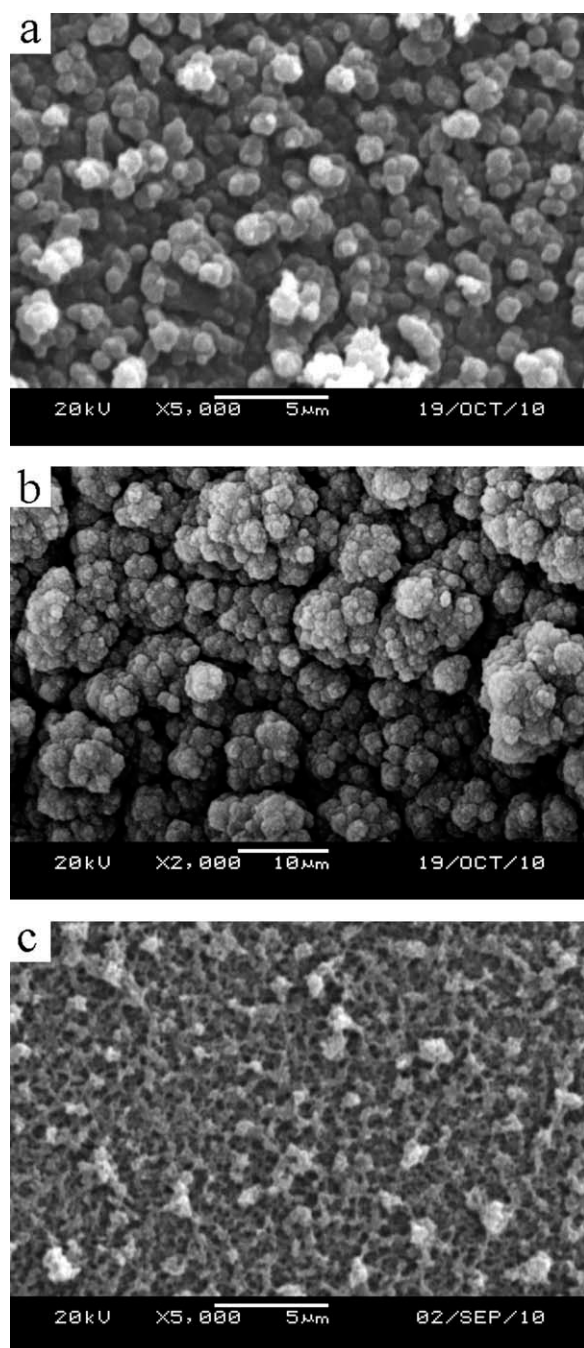
FTIR spectra of PBTBE, PBTB, and PEDOT

To obtain sufficient amounts of polymers for FTIR spectral characterization, the ITO glasses were

employed as working electrodes. The polymers were synthesized potentiostatically in a solution of 0.2M NaClO<sub>4</sub>/ACN containing BTB or EDOT monomer or their mixtures. Figure 5 shows the FTIR spectra of PBTB, CP1, CP2, PBTBE, and PEDOT [the copolymers PBTB, CP1, CP2, PBTBE, and PEDOT were prepared in a 0.2M NaClO<sub>4</sub>/ACN solution with 0.004M BTB (PBTB), 0.004M BTB/0.004M EDOT (CP1), 0.004M BTB/0.006M EDOT (CP2), 0.004M BTB/0.01M EDOT (PBTBE), and 0.01M EDOT (PEDOT), respectively]. According to the spectrum of PBTB [Fig. 5(a)], the absorption bands at  $792\text{ cm}^{-1}$  were due to the out-of-plane C—H bonds in the  $\beta$  position of the 2,5-disubstituted thiophene rings.<sup>36</sup> In the spectrum of PEDOT [Fig. 5(e)], the bands at 1195, 1143, and  $1088\text{ cm}^{-1}$  were assigned to the stretching of the C—O—C bond in the EDOT ring.<sup>37</sup> The aforementioned bands of PBTB and PEDOT could also be found in the FTIR spectra of CP1 [Fig. 5(b)], CP2 [Fig. 5(c)], and PBTBE [Fig. 5(d)]. Compared with corresponding homopolymers, the band at  $794\text{ cm}^{-1}$  in the spectra of copolymers CP1, CP2, and PBTBE originated from the out-of-plane C—H bond in the  $\beta$  position of the 2,5-disubstituted thiophene rings; this indicated the presence of BTB units in the copolymers, although the bands at 1195, 1145, and  $1088\text{ cm}^{-1}$  in the copolymers could also be ascribed to the stretching of the C—O—C bond in the EDOT monomer. All of these features indicated that the



**Figure 5** FTIR spectra of (a) PBTB obtained at 1.3 V, (b) CP1 obtained at 1.3 V, (c) CP2 obtained at 1.3 V, (d) PBTBE obtained at 1.3 V, and (e) PEDOT obtained at 1.4 V potentiostatically from 0.2M NaClO<sub>4</sub>/ACN solution, respectively.



**Figure 6** SEM images of (a) PBTB, (b) PBTBE, and (c) PEDOT deposited potentiostatically on an ITO electrode.

copolymers CP1, CP2, and PBTBE contained both BTB and EDOT units.

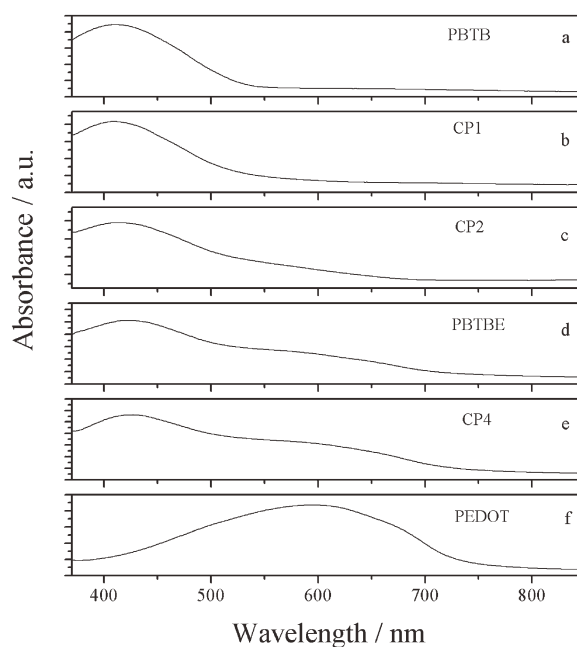
#### SEM

SEM of the polymers provided their clear surface and bulk morphologies, which were closely related to their optical and electrical properties. PBTB, PBTBE, and PEDOT were deposited potentiostatically on the ITO electrode ( $0.5 \times 0.5 \text{ cm}^2$ ) at 1.3, 1.3, and 1.4 V, respectively, from the 0.2M  $\text{NaClO}_4/\text{ACN}$

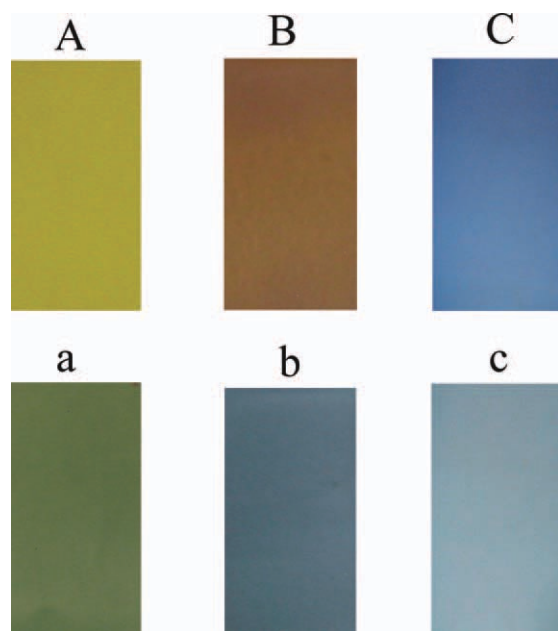
solution and dedoped for 60 s. Their scanning electron micrographs are shown in Figure 6. In this case, the PBTB film exhibited a compact structure, and globulelike droplets were dispersed on the side of the film [Fig. 6(a)]. PEDOT exhibited a network structure with a great number of slots [Fig. 6(c)]. Although PBTBE showed a crowded morphology with huge amounts of granules stacked together [Fig. 6(b)], this was significantly different from the two corresponding homopolymers. The difference in morphology between PBTBE and the homopolymers also confirmed the occurrence of copolymerization between BTB and EDOT.

#### UV-vis spectra of PBTBE, PBTB, and PEDOT

The solubility of the homopolymers and copolymers was investigated in detail in common organic solvents, including dichloromethane, *N,N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). The results show that all of the polymers were insoluble in dichloromethane solvent, and the homopolymers were also insoluble in DMF and DMSO, whereas the resulting copolymers were partially soluble in DMF and DMSO. It was interesting that the copolymers dissolved in DMF and DMSO emitted a strong blue-green fluorescence when they were exposed to UV irradiation at 365 nm. These solubility properties of the resulting polymers indicated a new copolymer formation based on the BTB and EDOT units.



**Figure 7** UV-vis spectra of (a) PBTB at 1.3 V, (b) CP1 at 1.3 V, (c) CP2 at 1.3 V, (d) PBTBE at 1.3 V, (e) CP4 at 1.4 V, and (f) PEDOT at 1.4 V deposited on ITO in the neutral state. The polymer films were prepared potentiostatically from the 0.2M  $\text{NaClO}_4/\text{ACN}$  solution.



**Figure 8** Colors of the polymer films: (a) green, (b) blue, and (c) light blue were the doped films, and (A) yellow, (B) brown red, and (C) blue were the dedoped films of PBTB, PBTBE, and PEDOT, respectively. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

The UV-vis spectra of PBTB, PEDOT, and their copolymers CP1, CP2, PBTBE, and CP4 deposited on the ITO electrode with a polymerization charge of  $3.0 \times 10^{-2}$  C are shown in Figure 7 [the copolymers CP1, CP2, PBTBE, and CP4 were prepared in a 0.2M NaClO<sub>4</sub>/ACN solution with 0.004M BTB/0.004M EDOT (CP1), 0.004M BTB/0.006M EDOT (CP2), 0.004M BTB/0.01M EDOT (PBTBE), and 0.004M BTB/0.014M EDOT (CP4), respectively]. In the neutral state, the PBTB film exhibited an absorption peak at 411 nm due to the  $\pi$ - $\pi^*$  transition [Fig. 7(a)]. On the other hand, the neutral state PEDOT exhibited the  $\pi$ - $\pi^*$  electron transition peak at about 599 nm [Fig. 7(f)]. However, as presented in Figure 7(d), a well-defined maximum absorption band centered at 423 nm with a shoulder located around 550 nm was observed; this was attributed to the  $\pi$ - $\pi^*$  transi-

tion of the neutral state of the PBTBE copolymer. Compared with the maximum absorption peak of the PBTB film, there was a gradual redshift of the absorption peaks of the copolymers obtained with the increase of the feed ratio of the EDOT/BTB monomers in the 0.2M NaClO<sub>4</sub>/ACN solution due to the introduction of more EDOT units into the copolymer backbone [Fig. 7(b-e)]. This further confirmed the occurrence of the copolymerization of BTB with EDOT.

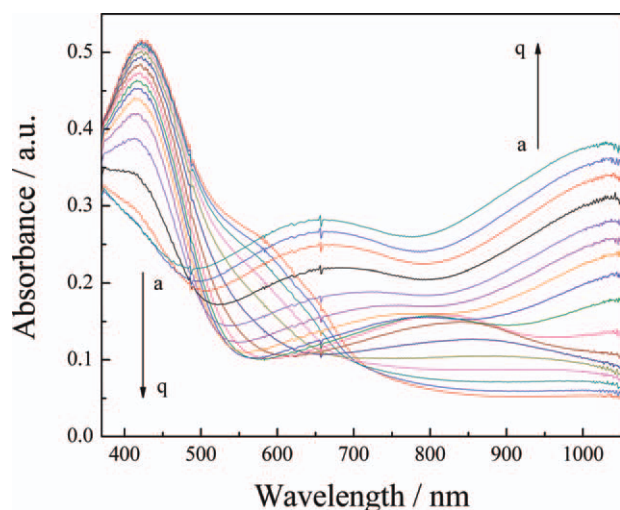
The colors of the polymers films of PBTB, PBTBE, and PEDOT potentiostatically electrodeposited on ITO were also recorded, as shown in Figure 8. PBTB was green in its doped state and yellow in its dedoped state [Fig. 8(a,A)], PEDOT was a light blue and blue polymer in its doped and dedoped states [Fig. 8(c,C)], respectively, and PBTBE changed color from blue in the doped state [Fig. 8(b)] to brown-red in the dedoped state [Fig. 8(B)]. The electrochromism phenomenon of PBTBE was significantly different from those of the two individual homopolymers. This further confirmed the formation of a copolymer consisting of both BTB and EDOT units and indicated the generation of a new EC material consisting of BTB and EDOT moieties.

Table I summarizes the electronic absorption, the onset oxidation potential ( $E_{\text{onset}}$ ), and the optical band gap ( $E_g = 1240/\lambda_{\text{edge}}$ , where  $\lambda_{\text{edge}}$  is the low-energy edge of the absorption spectrum) of PBTB, CP1, CP2, PBTBE, CP4, and PEDOT quite clearly. Their HOMO energy levels ( $E_{\text{HOMO}}$ 's) were calculated with the formula  $E_{\text{HOMO}} = -e(E_{\text{onset}} + 4.48)$  ( $E_{\text{onset}}$  vs Ag wire), and their LUMO energy levels ( $E_{\text{LUMO}}$ 's) were calculated by the subtraction of  $E_g$  from the HOMO levels.<sup>38,39</sup>  $\lambda_{\text{edge}}$  of PBTB was 535 nm, which corresponded to an  $E_g$  of 2.31 eV. For PEDOT, it was observed at 737 nm, which corresponded to a band gap of 1.68 eV.  $\lambda_{\text{edge}}$  of PBTBE was 718 nm, which corresponded to a band gap of 1.73 eV. This was lower than that of PBTB (2.31 eV) and higher than that of PEDOT (1.68 eV). Similar results can also be found in Table I for the band gaps of CP1, CP2, and CP4. The effect of copolymerization between BTB and EDOT led to an obvious decrease in  $E_g$  compared with that of PBTB and

**TABLE I**  
 $E_{\text{onset}}$ ,  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$ , and  $E_g$  Values of PBTB, CP1, CP2, PBTBE, CP4, and PEDOT

Compound	$E_{\text{onset}}$ versus Ag wire (V)	$\lambda_{\text{max}}$ (nm)/ $\lambda_{\text{edge}}$ (nm)	$E_g$ (eV)	HOMO (eV)	LUMO (eV) <sup>a</sup>
PBTB	0.72	411/535	2.31	-5.20	-2.89
CP1	0.55	412/546	2.27	-5.03	-2.76
CP2	0.05	413/682	1.82	-4.53	-2.71
PBTBE	-0.06	423/718	1.73	-4.42	-2.69
CP4	-0.07	427/725	1.71	-4.41	-2.70
PEDOT	-0.31	599/737	1.68	-4.17	-2.41

<sup>a</sup> Calculated by the subtraction of  $E_g$  from the HOMO level.



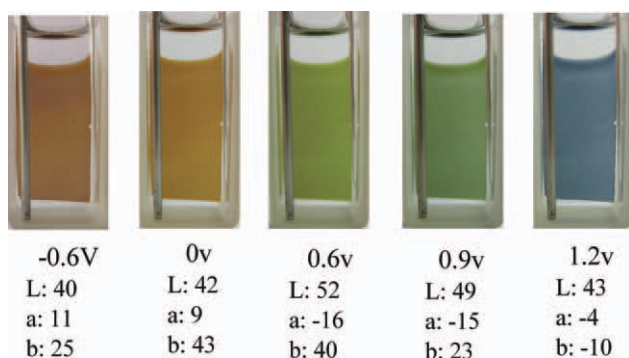
**Figure 9** Spectroelectrochemical spectra of PBTBE with applied potentials between  $-0.6$  and  $1.2$  V in monomer-free  $0.2M$   $NaClO_4/ACN$ . The applied potentials were the following: (a)  $-0.6$ , (b)  $-0.3$ , (c)  $-0.2$ , (d)  $-0.1$ , (e)  $0$ , (f)  $0.1$ , (g)  $0.2$ , (h)  $0.3$ , (i)  $0.4$ , (j)  $0.5$ , (k)  $0.6$ , (l)  $0.7$ , (m)  $0.8$ , (n)  $0.9$ , (o)  $1.0$ , (p)  $1.1$ , and (q)  $1.2$  V. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

indicated that the introduction of EDOT units into PBTB reduced the  $E_g$  values of the copolymers.

### EC properties of PBTBE

#### Spectroelectrochemical properties of PBTBE

Spectroelectrochemistry was used to obtain information about the electronic structure of PBTBE and to examine the spectral changes that occurred during redox switching. PBTBE-coated ITO (prepared potentiostatically at  $1.30$  V vs Ag wire) was switched between  $-0.6$  and  $1.20$  V in a  $0.2M$   $NaClO_4/ACN$  solution to obtain the *in situ* UV-vis spectra (Fig. 9). In the neutral state, polymer film exhibited an absorp-



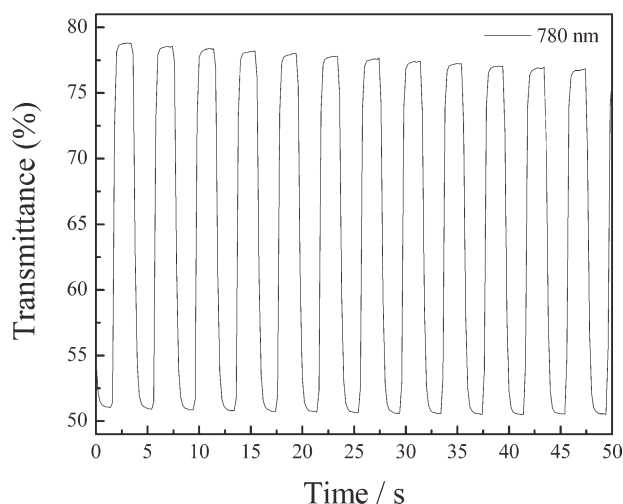
**Figure 10** Images of the PBTBE film at  $-0.6$  V (the neutral state),  $0$  V (the intermediate doped state),  $0.6$  V (the intermediate doped state),  $0.9$  V (the intermediate doped state), and  $1.20$  V (the fully doped state). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

tion band at  $423$  nm with a weak shoulder around  $550$  nm due to the  $\pi-\pi^*$  transition. As shown in Figure 9, the intensity of the PBTBE  $\pi-\pi^*$  electron transition absorption decreased, whereas three charge carrier absorption bands located at  $656$ ,  $800$ , and  $1031$  nm increased dramatically upon oxidation. The appearance of three charge carrier bands was attributed to the evolution of polaron and bipolaron bands. According to the spectroelectrochemical properties of PBTB reported by our group,<sup>24</sup> the polymer film in the neutral state exhibited an absorption peak at  $411$  nm due to the  $\pi-\pi^*$  transition. Upon oxidation, the intensity of the  $\pi-\pi^*$  transition of PBTB decreased, and a simultaneous increase in the absorbance at  $610$  nm was observed.

The PBTB film presented two colors in the doped and dedoped states, as shown in Figure 8(a,A), whereas the PBTBE film had distinct multielectrochromic properties and displayed five different colors (brown-red, orange-yellow, yellowish green, green, and blue at  $-0.6$ ,  $0$ ,  $0.6$ ,  $0.9$ , and  $1.2$  V, respectively). This could have been related to the formation of EDOT- and BTB-rich domains within the copolymer (or rather block copolymer). The colors of the EC materials were defined accurately by colorimetry measurements. The Commission Internationale de l'Eclairage system is used as a quantitative scale to define and compare colors. Three attributes of color, hue ( $a$ ), saturation ( $b$ ), and luminance ( $L$ ), are measured and recorded. These colors and their corresponding  $L$ ,  $a$ , and  $b$  values are given in Figure 10.

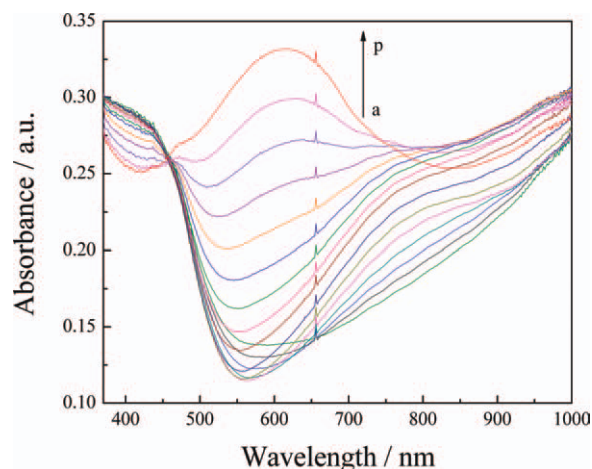
#### EC switching of the PBTBE film in solution

It is important that the polymers could switch rapidly and exhibit striking color changes, revealing



**Figure 11** EC switching ( $780$  nm) for the PBTBE film monitored in  $0.2M$   $NaClO_4/ACN$  solution under an applied square voltage signal between  $-0.6$  and  $1.20$  V with a residence time of  $2$  s.





**Figure 12** Spectroelectrochemical spectra of the PBTBE/PEDOT device at various applied potentials from  $-0.8$  to  $1.4$  V. The applied potentials are the following: (a)  $-0.8$ , (b)  $-0.6$ , (c)  $-0.4$ , (d)  $-0.2$ , (e)  $0$ , (f)  $0.2$ , (g)  $0.4$ , (h)  $0.6$ , (i)  $0.7$ , (j)  $0.8$ , (k)  $0.9$ , (l)  $1.0$ , (m)  $1.1$ , (n)  $1.2$ , (o)  $1.3$ , and (p)  $1.4$  V. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

superior results in EC applications. A double-step chronoamperometry technique was used to monitor the changes in the electro-optical responses during switching.<sup>40,41</sup> The dynamic EC experiment for PBTBE was carried out at  $780$  nm to investigate the switching ability of PBTBE between its neutral and fully doped state (Fig. 11). The potential was interchanged between  $-0.6$  V (the neutral state) and  $1.2$  V (the oxidized state) at regular intervals of  $2$  s. One important characteristic was the *maximum optical contrast* ( $\Delta T$  %), which could be defined as the transmittance difference between the redox states.  $\Delta T$  % of PBTBE was found to be  $27.8\%$  at  $780$  nm, as shown in Figure 11. It has to be noted that the stability of PBTBE in the dedoped state was not satisfactory because the transmittances in the dedoped state were reduced by  $2\%$  during 10 cycles in the EC switching experiment of PBTBE.

CE was also an important characteristic for the EC materials. CE was calculated with the following equations:<sup>42</sup>

$$\Delta OD = \lg\left(\frac{T_b}{T_c}\right)$$

and

$$\eta = \frac{\Delta OD}{\Delta Q}$$

where  $T_b$  and  $T_c$  are the transmittances before and after doping, respectively;  $\Delta OD$  is the change in optical density, which is proportional to the amount of created color centers;  $\eta$  denotes the CE; and  $\Delta Q$  is the amount of injected charge per unit sample area. CE of the PBTB film was measured as  $64 \text{ cm}^2/\text{C}$  (at  $780$  nm) in the fully doped state, which had a reasonable CE.

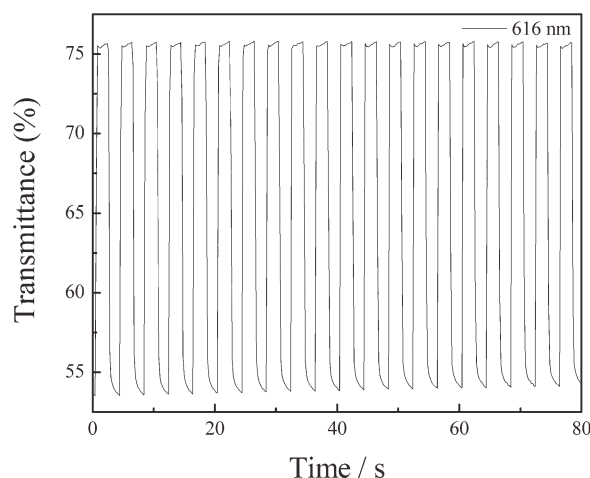
The *response time*, one of the most important characteristics of EC materials, is the time needed to perform a switching between the neutral state and the oxidized state of the materials.<sup>35</sup> The time required to attain a  $95\%$  total transmittance difference was found to be  $0.51$  s from the reduced to the oxidized state and  $0.37$  s from the oxidized to the reduced state. Thus, PBTBE could be rapidly switched to the reduced state; this was attributed to the ease of charge transport in the conducting film when it was reduced.<sup>43</sup>

The EC switching of the PBTB film was reported earlier by our group,<sup>24</sup> and the PBTB film showed a  $\Delta T$  % of  $44.8\%$  at  $610$  nm in the visible region with a response times of  $1.6$  s from the reduced to the oxidized state and  $0.54$  s from the oxidized to the reduced state. CE of PBTB was also calculated to be  $162 \text{ cm}^2/\text{C}$ . Compared with the EC switching of the PBTB film, the PBTBE film presented low optical contrast and small CE in the EC experiment. However, the PBTBE film could be switched from the reduced to the oxidized state or from the oxidized to the reduced state with a shorter response time than the PBTB film because of the faster dopant ion diffusion during the redox process. This was ascribed to the introduction of EDOT units into the polymer backbone.<sup>22</sup>

## Device characterization

### Spectroelectrochemical properties of ECD

A dual-type ECD consisting of PBTBE and PEDOT was constructed, and its spectroelectrochemical behaviors were also studied. Before we composed the ECD, the cathodically coloring polymer (PEDOT)



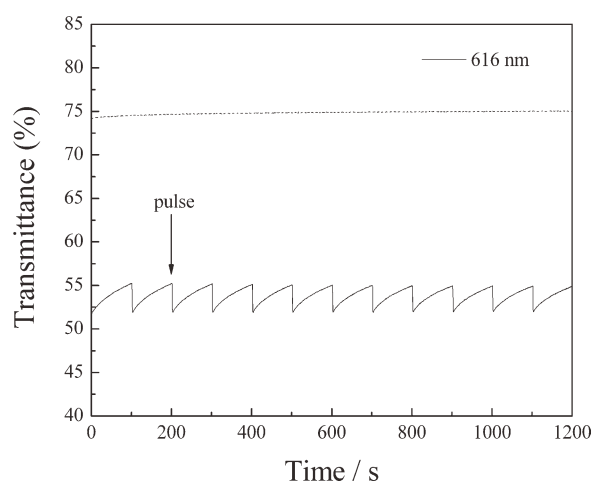
**Figure 13** Optical response (at  $616$  nm) as a function of time of the PBTBE/PEDOT device through application of square potentials between  $-0.8$  V (the neutral state) and  $1.4$  V (the oxidized state) with a residence time of  $2$  s.

was fully oxidized, and the anodically coloring polymer film (PBTBE) was fully reduced. The PBTBE/PEDOT ECD was switched between  $-0.8$  and  $1.4$  V. The spectroelectrochemical results show that the PBTBE layer was in its neutral state and PEDOT was in its oxidized state at  $-0.8$  V, and the device color was orange–yellow. As the applied potential increased, the PBTBE layer started to be oxidized, whereas the PEDOT layer was reduced. This led to a new absorption at  $616$  nm because of the reduced state of PEDOT (Fig. 12), and the dominant color of the device was blue at  $1.4$  V.

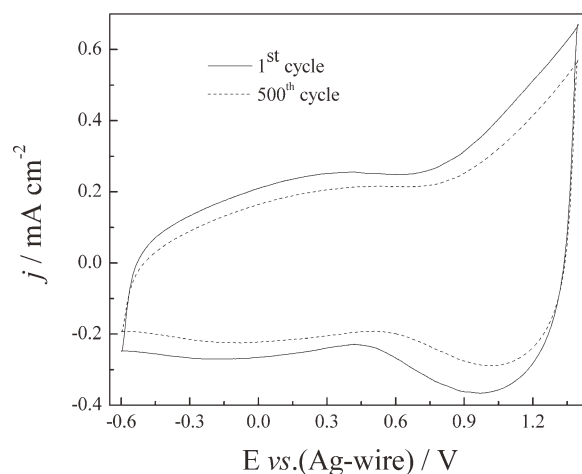
### Switching of ECD

We investigated the kinetics of the color change of the device by probing the spectral variations at a fixed wavelength while applying the potential in square wave form. During the experiment, the potential was stepped between  $-0.8$  and  $1.4$  V at a regular interval of  $2$  s, and % $T$  was monitored at  $616$  nm. The response time was found to be  $0.43$  s at 95% of the maximum transmittance from the neutral state to the oxidized state and  $0.38$  s from the oxidized state to the neutral state, and  $\Delta T$  % was calculated to be 22.2% (Fig. 13). The CE of the device (the active area was  $1.8 \times 1.8$  cm<sup>2</sup>) was calculated to be 129 cm<sup>2</sup>/C at  $616$  nm.

The spectroelectrochemical spectra and the optical response of the PBTBE/PEDOT device were also reported recently by our group,<sup>24</sup> and the ECD showed a  $\Delta T$ % of 29.5% with a response time of  $0.43$  s at  $628$  nm. Contrary to the expectation, the PBTBE/PEDOT device did not present high optical contrast (22.2%) and fast response ( $0.43$  s) compared with the PBTBE/PEDOT device, although the anodically coloring polymer film (PBTBE) included EDOT



**Figure 14** Open-circuit stability of the PBTBE/PEDOT ECD monitored at  $616$  nm.



**Figure 15** Cyclic voltammogram of the PBTBE/PEDOT device as a function of repeated scans at  $500$  mV/s.  $E$  denotes the potential.

units, which usually improve the properties of the switching of ECDs.

### Open-circuit memory of ECD

The optical memory in ECDs is an important parameter because it is directly related to its application and energy consumption during the use of ECDs.<sup>44</sup> The optical spectra for PBTBE were monitored at  $616$  nm as a function of time at  $-0.8$  and  $1.4$  V by the application of the potential for  $1$  s for  $200$ - and  $100$ -s time intervals, respectively. As shown in Figure 14, both the blue and brown–yellow states were highly stable, and the device kept its color without loss. Thus, this device showed good optical memory; this indicated that this ECD has potential applications.

### Stability of the ECD

Redox stability is another important parameter for ECDs. CV is exploited as a method to evaluate the stability of these devices. For this purpose, we performed nonstop cycling of the applied potential between  $-0.6$  and  $1.4$  V for the ECD with a  $500$  mV/s scan rate. After  $500$  cycles,  $80.2\%$  of its electroactivity was retained, and the changes in  $j_{pa}$  and  $j_{pc}$  were  $15.1$  and  $17.3\%$ , respectively (Fig. 15). These results indicate that this ECD had a reasonable redox stability.

## CONCLUSIONS

In this study, a new multielectrochromic copolymer of BTB with EDOT was successfully synthesized by the electrochemical oxidation of their monomer mixture in a  $0.2$ M NaClO<sub>4</sub>/ACN solution. According to spectroelectrochemical analyses, the copolymer

PBTBE film revealed distinctive color changes compared with that of the PBTB film and showed five different colors (brown–red, orange–yellow, yellowish green, green, and blue) under various potentials.  $\Delta T$  % and the response time of the copolymer film were measured to be 27.8% and 0.51 s at 780 nm. It was interesting that the PBTBE film could switch rapidly compared with the (PBTB) film because of the introduction of EDOT into the polymer backbone. A dual-type ECD based on PBTBE and PEDOT was also constructed and characterized in detail. This ECD showed a  $\Delta T$  % of 22.2% in the visible region with a response time of 0.43 s at 616 nm. The CE of the device was calculated to be 129 cm<sup>2</sup>/C at 616 nm. Contrary to expectation, the PBTBE/PEDOT device did not present a high optical contrast and short response time compared with the PBTB/PEDOT device, although the anodically coloring polymer film (PBTBE) included EDOT units, which usually improve the properties of the switching of an ECD. Even so, these multielectrochromic properties still make PBTBE a good candidate for potential commercial applications.

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