

Electrosynthesis and Characterizations of a Multielectrochromic Copolymer Based on Pyrrole and 3,4-Ethylenedioxythiophene

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ABSTRACT: A copolymer based on pyrrole and 3,4-ethylenedioxythiophene (EDOT) was electrochemically synthesized on an indium tin oxide ITO/glass electrode in acetonitrile containing lithium perchlorate (LiClO_4). The resultant copolymer is characterized via cyclic voltammetry, FTIR, SEM, XPS, and spectroelectrochemical analysis. The spectroelectrochemical analysis revealed the copolymer film has distinct electrochromic properties with respect to the homopolymers, and presented four colors (amaranth, brick red, dark grey, and light blue) under various applied potentials. For the copolymer in the neutral state, the calculated onset energy for the π - π^* transition (E_g) is 1.69 eV, and the absorption peak (λ_{max}) is located at 508 nm. The maximum transmittance contrast ($\Delta T\%$) is 39.2% at 946 nm between the fully oxidized and intermediate (-0.4 V) states. Successive cyclic voltammograms and electrochromic switching experiment indicate the good stability of the copolymer because of the incorporation of EDOT units into the polypyrrole. It retains 81% of the original electroactivity and 71.8% of contrast after 2000 cycles. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: electropolymerization; copolymer; EDOT; pyrrole; electrochromism

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INTRODUCTION

Researches in the area of conductive polymers have drawn more and more attention of scientists in recent years because of their potential applications in different fields such as electrochromic devices, smart windows, and antistatic coatings.^{1–4} Among a candidate of conductive polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives are superior to its parent polythiophene in many categories crucial to organic electrochromic materials such as low oxidation potentials, good stability to air exposure, electrochemical stability, and fast switching speed.^{5–8} However, as an electrochromic material, the low gap of PEDOT can only allows the polymer to be light blue in the doped state and dark blue in the dedoped state, which limits the application of PEDOT in some degree.⁹

Polypyrrole (Ppy) shows band gap (E_g) at 2.7 eV and is blue-violet ($\lambda_{\text{max}} = 670$ nm) color in doped state and yellow-green ($\lambda_{\text{max}} = 420$ nm) color in dedoped form which exhibits a rich color range.¹⁰ However, the electrochromic property of Ppy film is difficult to be exploited mainly due to the degradation of the film on repetitive color switching.¹¹ It is expected that copolymer of EDOT and pyrrole can overcome the above drawbacks.

Fine tuning of the electrochromic properties of the conducting polymers could be achieved by using three main strategies: (1) the derivatization of monomer structure of prior to polymerization, (2) copolymerization with different monomers, and (3) preparation of hybrid materials.¹² Among these, copolymerization is a promising method to obtain better electrochromic properties than the homopolymers.¹³ Recently, many works have been focused on the electrochemical copolymerization of EDOT with different monomers to improve the electrochromic properties of PEDOT.^{14–16}

To prepared a multicolor and stable conducting polymer, it is expected that copolymer of EDOT and pyrrole can overcome the above homopolymers drawbacks and realize our objective. However, some researches have been done on copolymerization of pyrrole and EDOT, Sönmez and Saraç reported that the copolymer could only be prepared when $n_{\text{EDOT}}/(n_{\text{EDOT}} + n_{\text{pyrrole}})$ is over 0.9 in propylene carbonate solution,¹⁷ and to the best of our knowledge, a high feed ratio and the electrochromic properties of the copolymer have not been reported before. In this study, a copolymer based on pyrrole and EDOT has been successfully prepared by electrochemical method at a high feed

ratio of 1 : 5 ($n_{\text{pyrrole}}/n_{\text{EDOT}}$). The resultant copolymer is characterized by cyclic voltammetry, FTIR, XPS, SEM, and spectroelectrochemistry. It presents multicolor electrochromism (amaranth, brown, dark grey, light blue) under various applied potentials, and the electrochemical stability has been improved by incorporation EDOT units into Ppy chain.

EXPERIMENTAL

Materials

3,4-Ethylenedioxythiophene (EDOT, Aldrich, Shanghai and Beijing, China) and pyrrole (Beijing Baishun Chemical Reagent) are used as received. Supporting electrolytes (lithium perchlorate, LiClO_4), acetonitrile (ACN, HPLC), and propylene carbonate (PC) are purchased from Chemical Reagent Tianjin Institute (Tianjin city, China), all chemicals are of analytical grade. Ethanol and acetone are purchased from Hunan Chemical Reagent (Changsha, China), deionized water (resistivity $\sim 18.2 \text{ M}\Omega$) is obtained through Milli-Q system. ITO ($1.5 \times 2 \text{ cm}^2$, $8 \sim 9 \Omega$) and Ag/AgCl are products of Zhuhai Kaivo Electronic Components and Shanghai Raiz (Zhuhai, China), while stainless steel sheet ($6 \times 3 \text{ cm}^2$) is self-prepared.

Electrochemical Preparation and Measurements of P(py-co-EDOT) Film

Indium tin oxide (ITO) coated glass, stainless steel sheet, and Ag/AgCl are used as working electrode, counter electrode, and reference electrode. The working and counter electrodes are sequentially rinsed 20 min in ethanol, acetone, and deionized water under ultrasonic before use.¹⁸ Electrochemical polymerization and measurements are performed on CHI660D working station. For the synthesis of P(py-co-EDOT), py (0.004 M) and EDOT (0.02 M) are used as comonomers, the copolymer film is prepared under potentiostatic 1.3 V in 0.2 M $\text{LiClO}_4/\text{ACN}$ solution with polymerization charge of 100 mC/cm^2 , while the Ppy and PEDOT films are deposited under potentiostatic 1.05 and 1.3 V, respectively. After polymerization, the resultant films are washed with clean ACN for several times to remove the supporting electrolyte and the oligomers/monomers. Electrochemical measurements are performed in 0.2 M LiClO_4/PC solution. All reactions are performed under Ar atmosphere.

Characterization

FTIR spectra of PEDOT, Ppy, and P(py-co-EDOT) are recorded on Nicolet IS10 FTIR spectrometer, where samples are dispersed in KBr. SEM measurements are taken by using a Hitachi S4800 scanning electron microscopy. XPS spectra is recorded for the copolymer film using a Thermo Fisher Scientific K-Alpha1063. The images of electrochromic film are taken by a canon EOS 500D digital camera. Electrochemical polymerization and measurements are performed on CHI660D working station. The ASD Field Spec@Fland Held Spectral device is used as a Vis-NIR spectrum test tool.

RESULTS AND DISCUSSION

Electrochemical Polymerization

It is well known that the onset oxidation potential of starting monomers are close with intention to prepare copolymer chains with alternating monomer units.¹⁹ In order to indicate the possibility of copolymerization between EDOT and pyrrole, the onset oxidation potentials are tested. The anodic polarization

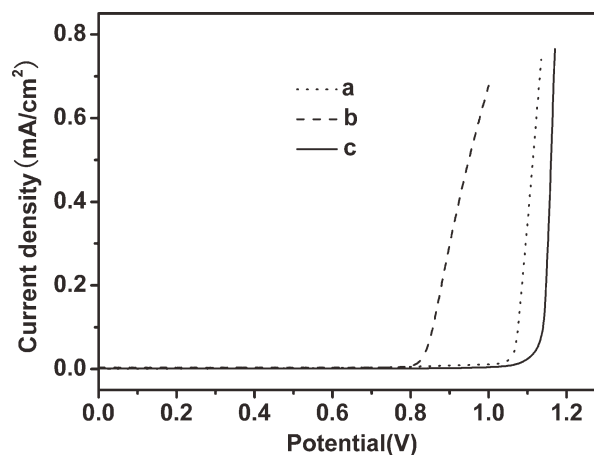


Figure 1. Anodic polarization curves of (a) 0.004 M pyrrole, (b) 0.02 M EDOT, and (c) the mixture of 0.004 M pyrrole and 0.02 M EDOT in 0.2 M $\text{LiClO}_4/\text{ACN}$ at a scanning rate of 10 mV/s.

curves of pyrrole, EDOT, and the mixture of pyrrole and EDOT in 0.2 M $\text{LiClO}_4/\text{ACN}$ are shown in Figure 1. The onset potential for anodic current ($E_{\text{pa onset}}$) of EDOT and pyrrole are 1.07 and 0.81 V [Figure 1(a,b)], respectively. The difference of $E_{\text{pa onset}}$ between the two monomers is 0.26 V. For a high difference, it seems that it is hard to achieve copolymerization of EDOT and pyrrole. In order to realize the copolymerization successfully, an appropriate feed ratio at 5 : 1 of EDOT and pyrrole has been applied.²⁰ The $E_{\text{pa onset}}$ of the EDOT and pyrrole mixture is 1.12 V, which is higher than those of EDOT and pyrrole, indicating the existence of the interaction between two monomers.²¹

Figure 2 presents the successive cyclic voltammograms of pyrrole, EDOT and the mixture of two monomers in 0.2 M $\text{LiClO}_4/\text{ACN}$ with the potential range from -0.3 to 1.3 V at a scanning rate of 100 mV/s. The increase of redox current density implies that the amount of polymer is increasing. As the cyclic voltammograms (CVs) scan continue, a film forms and can be observed on the surface of ITO electrode.

The redox behaviors and increments between consecutive cycles of the mixture of two monomers [$E_{\text{p,a}}$: 0.32 V and $E_{\text{p,c}}$: -0.14 V, Figure 2(c)] are completely different from that formation of Ppy and PEDOT. This is an indication for forming a copolymer between pyrrole and EDOT.²² Homopolymer of pyrrole presents an oxidation peak at 0.36 V and a reduction peak at -0.02 V [Figure 2(a)], and pure EDOT reveals an oxidation peak at 0.34 V and a reduction peak at -0.08 V.

Structural Characterizations

The FTIR spectra of Ppy, PEDOT, and the copolymer (P(py-co-EDOT)) are shown in Figure 3, respectively. As seen from the spectrum of Ppy [Figure 3(a)], the bands at 743 and 3402 cm^{-1} originate from the stretching of N—H, the bands at 1042, 1054, and 1227 cm^{-1} are assigned to the stretching mode of C—N, the stretching mode of C=C can be found at 1543 and 1672 cm^{-1} ,^{23,24} a very low peak at 1701 cm^{-1} originates from the stretching of C=O indicates that the overoxidation of Ppy film deposited at 1.05 V is negligible.²⁵ The FTIR spectrum of

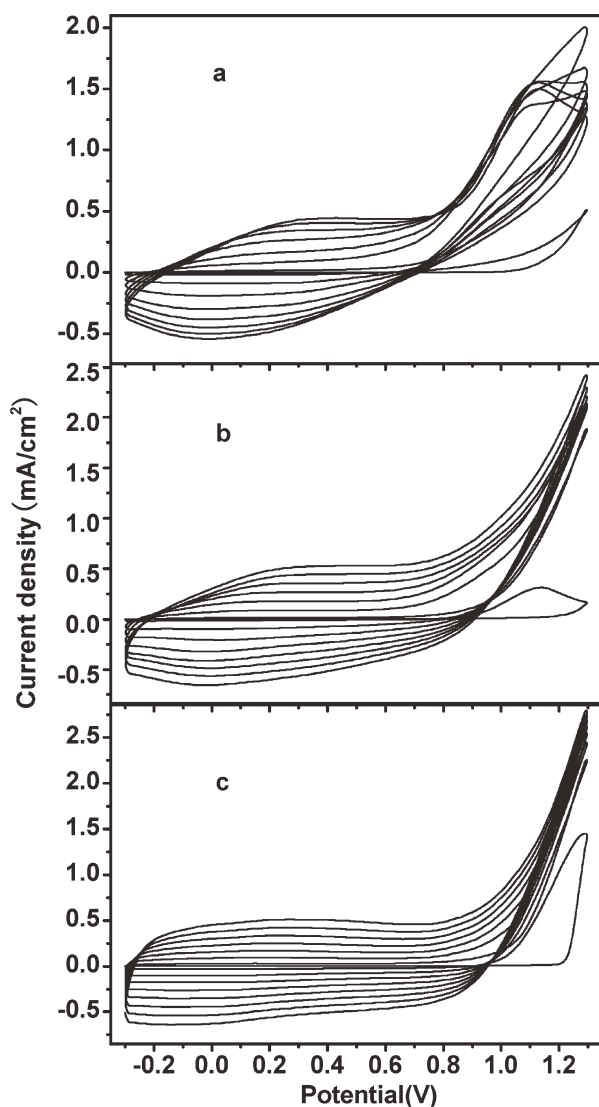


Figure 2. Cyclic voltammograms of (a) 0.004 mol/L pyrrole, (b) 0.02 mol/L EDOT, (c) 0.004 mol/L pyrrole and 0.02 mol/L EDOT in 0.2 M LiClO₄/ACN. Scanning rate: 100 mV/s.

PEDOT [Figure 3(b)] shows bands at 672, 769, and 907 cm⁻¹, which originate from the stretching mode of C–S. The bands at 1113 and 1194 cm⁻¹ are assigned to the stretching modes of the C–O–C groups. The vibration modes of the C=C and C–C bonds in thiophene rings can be found at the bands of 1609, 1389, and 1306 cm⁻¹, respectively.^{26–28} Compared with the corresponding homopolymers, P(py-co-EDOT) exhibits bands at 673, 979, 1170, and 1338 cm⁻¹, indicating the presence of EDOT rings. The bands at 1069, 1223, and 3443 cm⁻¹, originated from pyrrole units, can also be found [Figure 3(c)]. All the above features imply that P(py-co-EDOT) contain both pyrrole and EDOT units. And the very low peak at 770 cm⁻¹ indicates some β -coupling for the pyrrole units in the copolymer main chain.

To analyze the doping level and pyrrole/EDOT ratio in the copolymer, XPS spectra is used as a method to analyses the chemical composition of P(py-co-EDOT) film. The film is fully oxi-

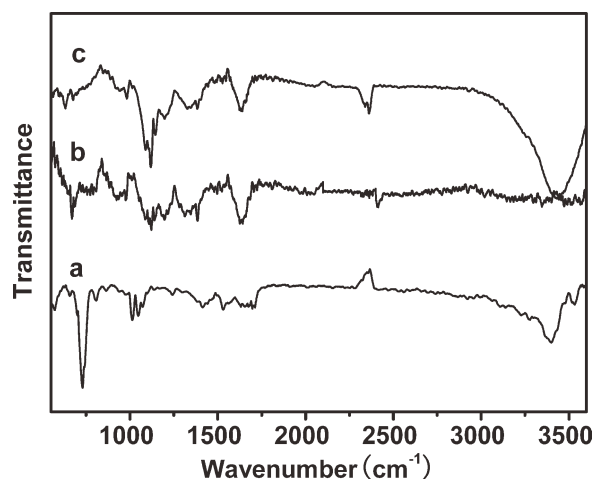


Figure 3. FTIR spectra of (a) Ppy, (b) PEDOT, (c) P(py-co-EDOT) prepared under potentiostatic 1.05, 1.3, and 1.3 V.

dized in 0.2 M LiClO₄/PC solution under an applied potential at 0.8 V before XPS test. Figure 4 presents the XPS spectra of P(py-co-EDOT). The at.% of N and S is 4.08 and 2.46, respectively. The atomic ratio I_N/I_S is about 1.66, it is obvious that this ratio of pyrrole and EDOT in the copolymer is not proportional to the pyrrole/EDOT feed ratio, the high ratio of pyrrole/EDOT can be attributed to the lower onset oxidation potential of pyrrole. As well known, the mechanism of electropolymerization involves either radical-cation/radical-cation coupling or reaction of a radical-cation with a neutral monomer.^{29,30} While the polymerization potential applies, the pyrrole is more easily to form radical/cation than EDOT, this induces a higher ratio of pyrrole units combining into the copolymer chain.

As the film gets oxidized, the doped counter ions enter into the polymer chain; the doping level can be calculated as the ratio of doped ions and the polymer units.³¹ ClO₄⁻ ions is used as doped ions here. As expected, the at.% of Cl is 2.68, the atomic ratio of Cl/(N + S) is about 0.41, which means the doping level is determined to be one ClO₄⁻ ions per 1.53 pyrrole and 0.92 EDOT units. A high doping level can be attributed to the small molecular size of the ClO₄⁻, which favors their injection into the film.

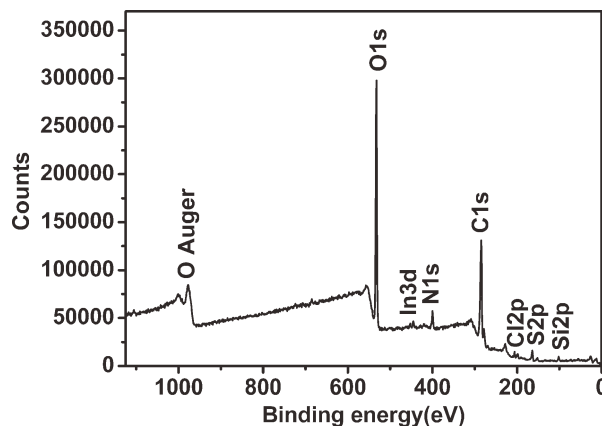


Figure 4. XPS spectra of P(py-co-EDOT) film in oxidized state.

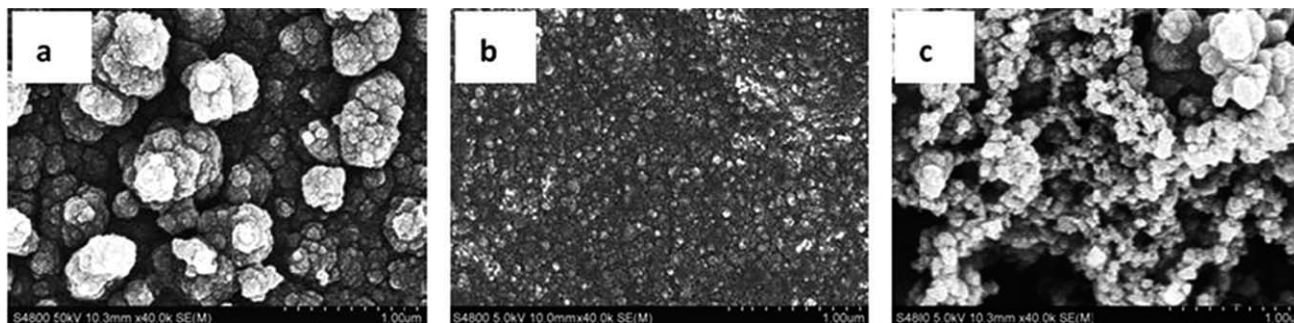


Figure 5. SEM images of (a) Ppy, (b) P(py-co-EDOT), (c) PEDOT films electrodeposited at potentiostatic 1.05, 1.3, and 1.3 V.

Morphology

The properties of conducting polymers are strongly dependent on their morphology and structure.²⁶ The obtained films are in fully dedoped state for SEM test. Figure 5 presents the morphology of Ppy, PEDOT and P(py-co-EDOT) films. Ppy film shows an accumulation state of clusters of globules, the diameters of globules range from 200 to 500 nm [Figure 5(a)]. While PEDOT film exhibits a loose globule structure [Figure 5(b)]. The surface morphology of P(py-co-EDOT) is much more compact and homogeneous than that two homopolymers, which is made of an accumulation state of weenie globules, the approximate diameters of the globules are 100 ~ 200 nm [Figure 5(c)]. The SEM image of P(py-co-EDOT) implies that the product is good in film forming.³²

Cyclic Voltammogram

CV is the most widely used technique for acquiring qualitative information about electrochemical reactions. Figure 6 gives the CV curves of Ppy, PEDOT and P(py-co-EDOT) prepared under potentiostatic 1.05, 1.3, and 1.3 V. It is obvious that PEDOT exhibits an oxidation peak at 0.31 V and a reduction peak at -0.07 V [Figure 6(a)], while Ppy shows a quasi-reversible redox process between -0.1 and 0.76 V [Figure 6(b)]. The copolymer performs an intermediate response with a reversible redox processes over a wide potential range [Figure 6(c)]. The reversible redox reaction of the copolymer between 0.06 and 0.51 V can

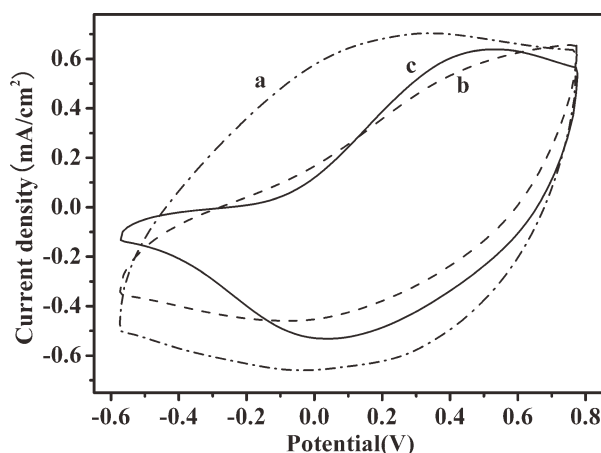


Figure 6. Cyclic voltammogram curves of (a) PEDOT, (b) Ppy, (c) P(py-co-EDOT) films in 0.2 M LiClO₄/PC at a scanning rate of 100 mV/s.

be attributed to the existence of both EDOT and pyrrole units into the polymer chain.^{21,33}

Investigation of peak current intensity with respect to scan rates will indicate the nature of electrochemical process.³⁴ The CV curves of P(py-co-EDOT) film are shown in Figure 7 in monomer free electrolyte at different scanning rates. The copolymer shows a single, well-defined redox process. The current density is proportional to the scan rates indicating that the film is electroactive and well adhesive to the electrode (Figure 7). The anodic and cathodic peak current densities show a linear proportion to scan rates as expected (Figure 7, inset), which demonstrates that the electrochemical processes are not diffusion limited.³⁵

Spectroelectrochemical Properties of P(py-co-EDOT) Films

Electrochromic material can change their color under various applied potential.³⁶ Figure 9 presents the optical images of Ppy, P(py-co-EDOT) and PEDOT films deposited potentiostatically at 1.05 , 1.3 , and 1.3 V. The Ppy film shows yellow-green color at -0.8 V and blue-violet at 0.8 V [Figure 8(a)].³⁷ The color of doped and dedoped PEDOT film are light blue (1.0 V) and dark blue (-0.8 V), respectively [Figure 8(c)].¹³ It is interesting that the electrochromic phenomena of P(py-co-EDOT) film is quite different from those of two individual homopolymers, At an applied potential of -0.6 V, the film shows a amaranth color

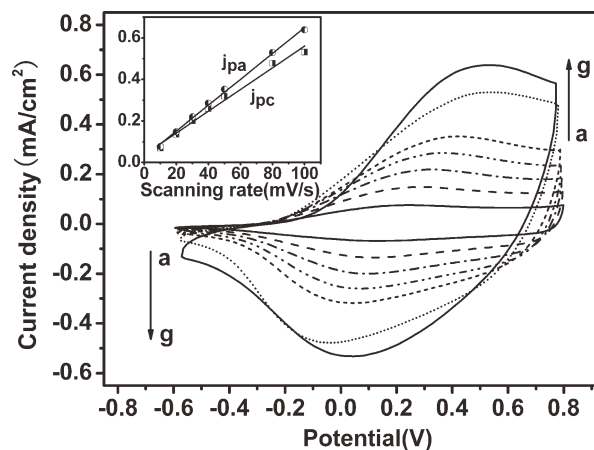


Figure 7. Cyclic voltammogram curves of the P(py-co-EDOT) in monomer free solution of 0.1 M LiClO₄/PC at different scan rates: (a) 10 mV/s, (b) 20 mV/s, (c) 30 mV/s, (d) 40 mV/s, (e) 50 mV/s, (f) 80 mV/s, and (g) 100 mV/s.

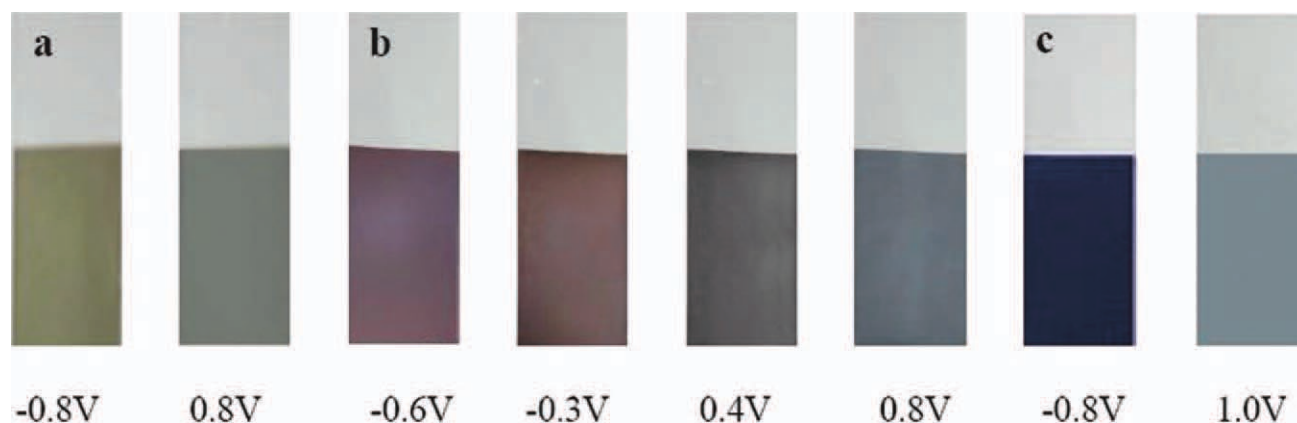


Figure 8. Stability test of P(py-co-EDOT) film deposited under potentiostatic 1.3 V via cyclic voltammogram in 0.2 M LiClO₄/PC with a scanning rate of 100 mV/s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and passes to brown at -0.3 V. With the increase of potential, P(py-co-EDOT) film turns into dark gray (0.4 V) and light blue at 0.8 V [Figure 8(b)]. This multicolor electrochromism implies potential application on ECDs.

The Commission Internationale de l'Eclairage (CIE) system is used as a quantitative scale to present and define the colors of film. According to CIE system, the color can be made up of three attributes: luminance (L), hue (a), and saturation (b).⁵ Colorimetric analysis is a useful method for investigating the electrochromic properties of conducting polymers. The values of L , a , and b are calculated by the reflectivity spectra and relative electrochromic behaviors of Ppy, P(py-co-EDOT) and PEDOT films upon various applied potential are listed in Table I.

Spectroelectrochemistry is a powerful way to investigate the optical properties of a electrochromic conducting polymer under potential change, which also provides information on the electronic structure of the conducting polymer.^{13,27} The P(py-co-EDOT) film is swept between -0.6 and 0.8 V, Figure 9 depicts the Vis-NIR absorbance spectra. The maximum absorbance wavelength (λ_{max}) in neutral state at -0.6 V for the $\pi-\pi^*$ is found to be 508 nm and the band gap (E_g) is calculated as 1.69 eV by the onset wavelength. As the film gets oxidized, the intensity of the $\pi-\pi^*$ transition decreases while the charge car-

rier bands at longer wavelengths increases in intensity, polaron bands (0.4 V) around 482 and 943 nm are observed, and the film shows minim electronic absorption at a shorter wavelength of 425 nm due to bipolaron band (1.0 V).

The transmittance spectra of P(py-co-EDOT) film under various applied potential are shown in Figure 10. The transmittance variation ($\Delta T\%$) between fully oxidized and reduced states is 31.1% at 964 nm in the wavelength range from 380 to 1050 nm. While $\Delta T\%$ between the fully oxidized and intermediate (-0.4 V) states is 39.2% at 946 nm. The higher transmittance contrast between the fully oxidized and intermediate (-0.4 V) states is ascribed to multicolor electrochromism of P(py-co-EDOT). The multielectrochromic behavior and reasonable transmittance contrast indicate that the copolymer has broad application potential in smart windows and ECDs.^{32,36}

Electrochromic Switching and Stability

Electrochromic switching studies are done to monitor the ability of a polymer to switch and observe color changes, the switching characteristic of the copolymer film is analyzed by monitoring the change in charge density. A square-wave potential step method between -0.6 and 0.8 V with a 10-s delay at

Table I. Colorimetric Properties of Ppy, P(py-co-EDOT), and PEDOT Films

Material	Color	L	a	b
Ppy	Yellow-green (-0.8 V)	53	-4	18
	Blue-violet (0.8 V)	50	-4	3
PEDOT	Dark blue (-0.8 V)	7	15	-32
	Light blue (1.0 V)	55	-5	-6
P(EDOT-co-py)	Amaranth (-0.6 V)	39	11	-6
	Brown (-0.3 V)	41	10	5
	Dark grey (0.4 V)	34	1	0
	Light blue (0.8 V)	47	-5	-7

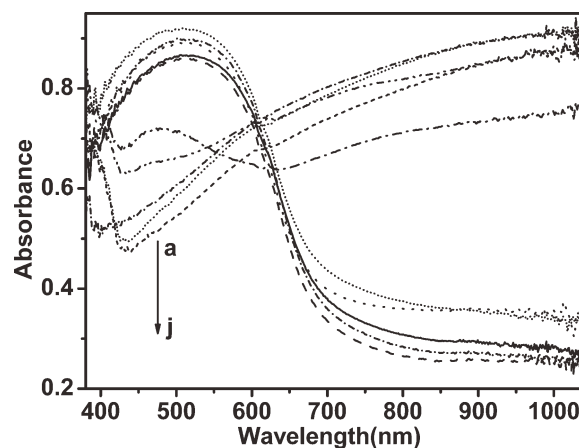


Figure 9. Optical images of (a) Ppy, (b) P(py-co-EDOT), and (c) PEDOT at various applied potentials.

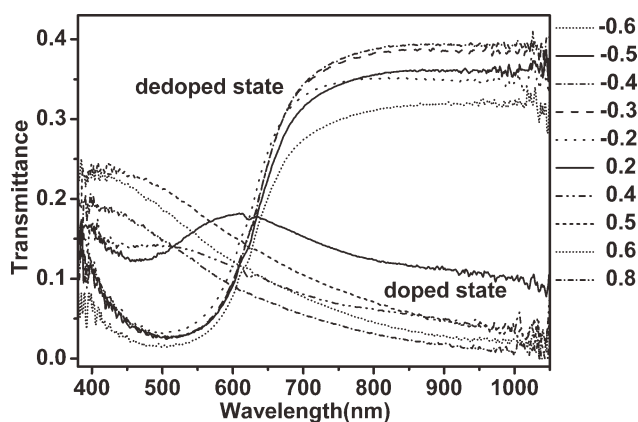


Figure 10. Absorbance spectra of P(py-co-EDOT) film under various applied potential (V): (a) -0.6 , (b) -0.5 , (c) -0.4 , (d) -0.3 , (e) -0.2 , (f) 0.2 , (g) 0.4 , (h) 0.5 , (i) 0.6 , and (j) 0.8 .

each potential is used to investigate switching time and long-term switching stability of the copolymer. Oxidation and reduction times are taken at 90% charge density.^{38,39} As seen in Figure 11, the response time for oxidation and neutralization is found to be 2.9 and 2.1 s, respectively. The switching speed is lower than those obtained in pure PEDOT. As known, switching speed of electrochromic materials can be strongly interacted by the surface morphology and electroactivity of film.⁴⁰ It is obviously that the doping ClO_4^- ions is difficult to insert or extract into the compact copolymer film, which has been confirmed by SEM, and the lower electroactivity than PEDOT is another factor contribute to the slow switching response.

The long-term switching stability studies of P(py-co-EDOT) film are shown in Figure 12. The transmittance contrast and charge capacity are monitored as a function of switching numbers. It can be seen that after 2000 double potential steps, the film retains 71.8% of maximum optical contrast and 69.6% of charge capacity which exhibits reasonable switching stability.

Cyclic voltammogram is used as a method to evaluate the electrochemical stability of the copolymer.^{5,21} Nonstop cycling of the applied potential between -0.6 and 0.8 V for P(py-co-EDOT) film with a potential scanning rate of 100 mV/s is pre-

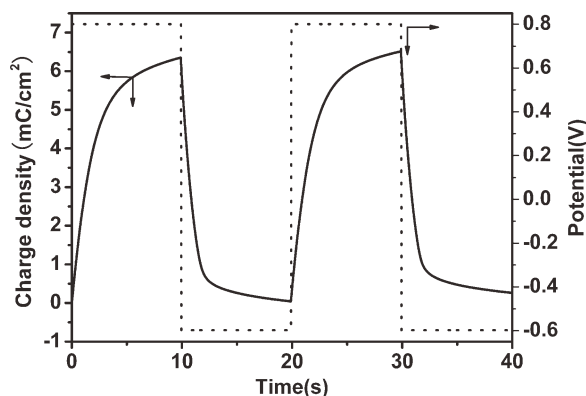


Figure 11. Transmittance spectra of P(py-co-EDOT) film under various applied potentials (V).

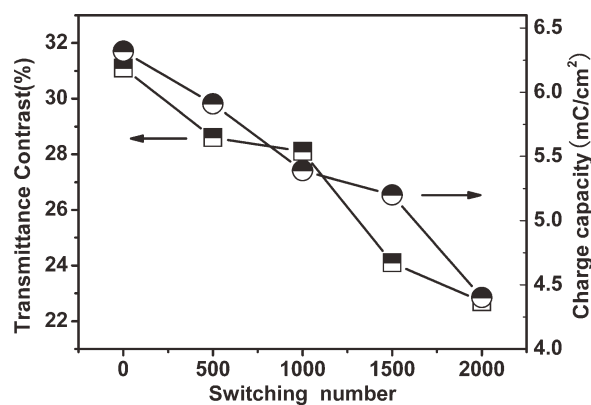


Figure 12. Chronocoulometry response between -0.6 and 0.8 V of the P(py-co-EDOT) film.

sented in Figure 13. After 2000 cycles, the P(py-co-EDOT) film retains 81% of its original electroactivity, the change in anodic current density peaks (j_{ap}) and j_{cp} are 16 and 17%, respectively. The P(py-co-EDOT) film reveals much higher stability than the homopolymer Ppy film, which loses 60% of electroactivity after 300 cycles (the figure not show here) and is comparable to PEDOT film which retains 82% electroactivity after 2000 cycles. This result indicates that the incorporation of EDOT units into the Ppy improves the electrochemical stability of P(py-co-EDOT) film. The copolymer film has reasonable environmental and redox stability which is a promising material for application in future ECD.

The copolymer shows reasonable electrochromic properties and excellent multicolor change which is comparable to other conducting polymers, and the comonomers of EDOT and pyrrole are commercially facile and inexpensive, which is very important to prepared a low-cost film for mass production; these reasons implies large potential application for electrochromic devices. Although the film is insoluble, the solubility can be solved by incorporation of long alkyl side chains in EDOT units.

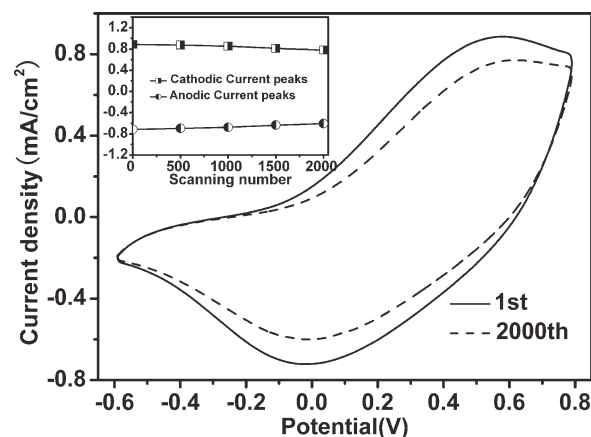


Figure 13. Long-term redox stepping results showing transmittance contrast and charge capacity during potential step between -0.6 and 0.8 V with a 10-s delay at each potential.

CONCLUSION

In this article, a multielectrochromic copolymer based on pyrrole and EDOT is successfully synthesized in 0.2 M LiClO₄/ACN solution via electrochemical method. CV, FTIR, and XPS characterizations prove that the obtained polymer contains both pyrrole and EDOT units, indicating the formation of copolymer. Successive CVs and square-wave potential step indicate that the incorporation of EDOT units into the Ppy improves the electrochemical stability of P(py-co-EDOT) film, which retains 81% of electroactivity and 71.8% of contrast after 2000 cycles. Investigation of electrochromic properties of the copolymer via spectroelectrochemistry are also achieved. P(py-co-EDOT) film exhibits excellent multicolor electrochromism (amaranth, brick red, dark grey, and light blue), the λ_{\max} of P(py-co-EDOT) in neutral state is 508 nm and the onset energy for π - π^* transition (E_g) is found to be 1.69 eV. The maximum transmittance contrast ($\Delta T\%$) is 39.2% at 946 nm between the fully oxidized and intermediate (-0.4 V) states. The multielectrochromic behavior and reasonable transmittance contrast indicate that the copolymer has a broad application potential in smart windows and ECDs.

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