

Multicolor Electrochromism of Low-Bandgap Copolymers Based on Pyrrole and 3,4-Ethylenedioxythiophene: Fine-Tuning Colors Through Feed Ratio

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ABSTRACT: The copolymerization of pyrrole with 3,4-ethylenedioxythiophene (EDOT) is successfully achieved in boron trifluoride diethyl etherate via direct anodic oxidation of the monomer mixtures on indium-tin oxide working electrodes. The resultant copolymers are characterized by electrochemical methods, FT-IR, XPS, SEM, and spectroelectrochemical analysis. The copolymer films present excellent electrochromic properties especially the multicolor electrochromism which can be tuned through the feed ratio of pyrrole and EDOT. The neutral copolymer films exhibit blue-shift with the increasing feed ratio of pyrrole and EDOT, and the calculated band gaps of the copolymers are as low as that of PEDOT film. Furthermore, the electrochemical and optical stability has been improved by the incorporation of EDOT units into the polymer chains. The copolymer prepared with the changing feed ratio of pyrrole and EDOT at 1/4 retains 71% of its original electroactivity after 500 cycles and 72% of its optical contrast after 500 steps. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 1506–1512, 2013

KEYWORDS: conducting polymers; electrochemical copolymerization; electrochromism; boron trifluoride diethyl etherate

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INTRODUCTION

During the past decades, modification of structure and form of conducting polymers is one of the effect methods to tune the electrochromic properties.¹ Two main strategies are used to synthesize new conducting polymers, one is using new monomers and the other is copolymerization process of existing monomers.^{2,3} Compared to the laborious and costly synthesis approaches, copolymerization is an easy and facile method to combine the electrochromic properties of the comonomers.⁴

3,4-Ethylenedioxythiophene (EDOT) has appeared as an appropriate monomer in applications of electrochemical copolymerization because of the high conductivity, low bandgap, good electrochemical properties, and unusual thermal stability in the oxidized state of its polymer.^{5–7} Some researches have been done on the copolymerization of EDOT, the resultant copolymers exhibit excellent electrochromic properties, especially the multicolor electrochromism.^{8,9}

Polypyrrole films have received considerable attention because of its simple preparation and potential usage in nonlinear optical devices and polymer light emitting diodes.^{10,11} The electrochromic properties of polypyrrole film is difficult to exploit due

to the dissatisfactory stability. We have reported the improving stability properties through copolymerization of pyrrole with EDOT in aqueous solution.¹² However, the color change of the films prepared in acetonitrile and aqueous solution are limited and the switching rate is very slow.

Conducting polymers prepared in boron trifluoride diethyl etherate (BFEE) solution always present excellent properties, high quality polythiophene derivative films have been prepared in BFEE solution.^{13–16} However, only few copolymerization performed in BFEE has been reported. As pyrrole is difficult to polymerize in pure BFEE solution, the report about the copolymerization of pyrrole in BFEE solution is rare. In this article, copolymers based on pyrrole and EDOT are successfully prepared in BFEE solution, indicating that pyrrole can be used as a comonomer in BFEE solution. Elemental analysis indicates the low ratio of pyrrole/EDOT in the polymer chain, which is quite different from that prepared in acetonitrile and aqueous solution. The derived copolymers exhibit excellent electrochromic properties especially multicolor electrochromism. Moreover, the color change can be tuned through altering the pyrrole/EDOT feed ratio, and the absorption peaks of neutral films exhibit blue-shift with the increasing feed ratios of pyrrole and EDOT.

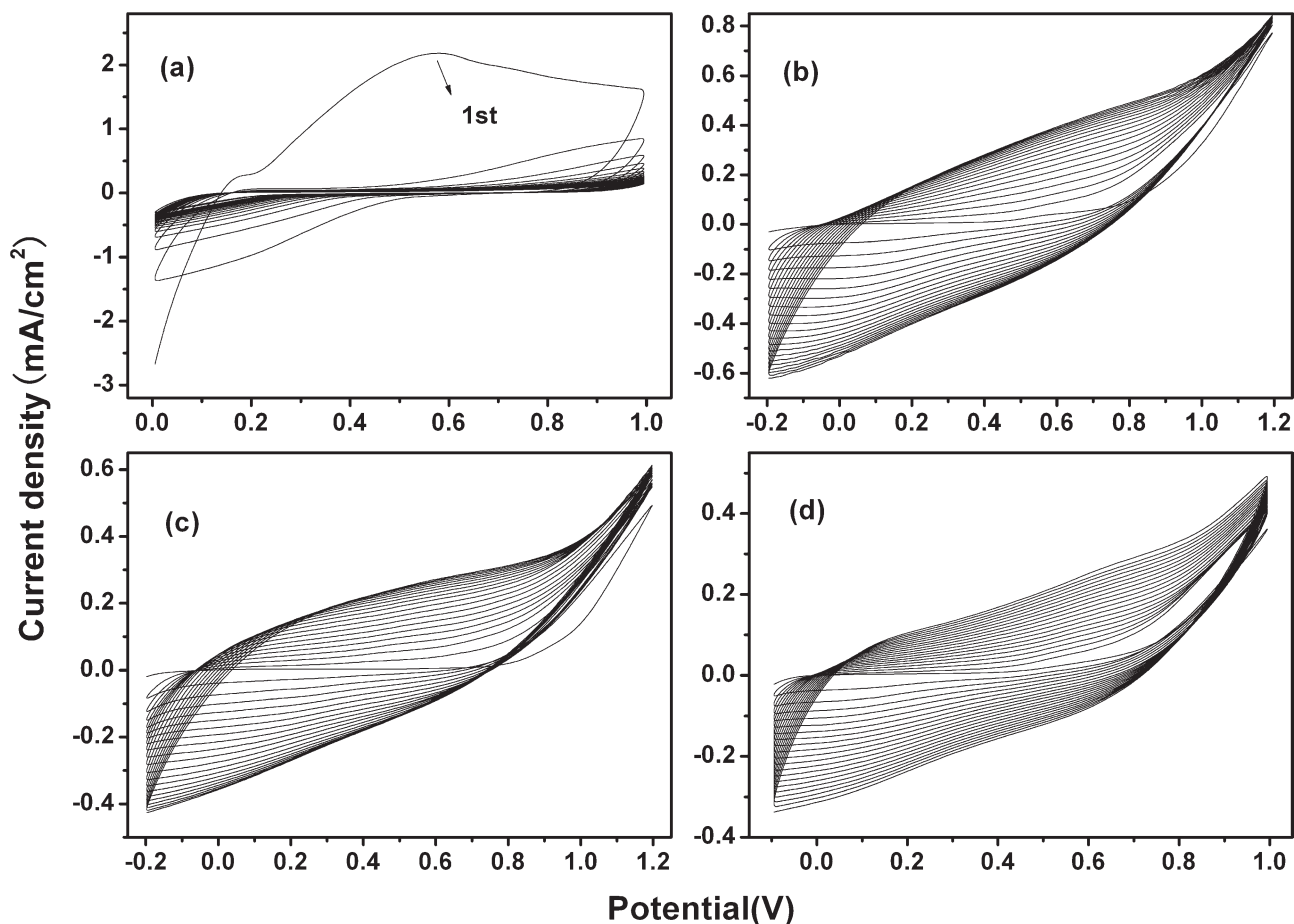


Figure 1. Successive cyclic voltammograms of (a) 20 mM pyrrole, (b) comonomer 2, (c) comonomer 3, and (d) 20 mM EDOT in BFEE at a scan rate of 100 mV/s.

The copolymers present reasonable switching rate, coloration efficiency, and stability.

EXPERIMENTAL

EDOT (Aldrich) and pyrrole (Baishun Co. Ltd. China) were used as received. BFEE, lithium perchlorate (LiClO_4), propylene carbonate (PC), ethanol, and acetone were purchased from Chemical Reagent Tianjin institute, all chemicals were of analytical grade. Deionized water (resistivity = $18.2 \text{ M}\Omega$) was obtained through Milli-Q system.

Different feed ratios of pyrrole and EDOT at 1/1, 1/2, 1/4, and 1/8 (the concentrations of EDOT in the mixtures were fixed as 20 mM) were used as the comonomer for 1, 2, 3, 4, respectively. The corresponding copolymers (marked as P1, P2, P3, and P4) were prepared by potentiostatic 1.15 V with the polymerization charge of 100 mC/cm^2 for structural and spectroelectrochemical characterizations. After polymerization, the copolymer films were rinsed with clean PC solution for several times to remove the residual BFEE and oligomers/monomers. All reactions were performed under a N_2 atmosphere, the electrochemical polymerization and measurements were performed on a CHI660D working station in $0.2 \text{ M LiClO}_4/\text{PC}$ solution. The spectra of the

copolymers were recorded on a Shimadzu UV1800 UV-vis spectrophotometer.

The film samples were dispersed in KBr for the FT-IR test that was performed on a Nicolet IS10 FTIR spectrometer. XPS spectra were recorded by using a Thermo Fisher Scientific K-Alpha1063. The morphology and thickness of the films were imaged with a Hitachi S4800 Scanning electron microscopy. The specific electrical resistance of the films on the ITO electrodes were measured by a four-point probe method using a RTS-8 probe. The images of electrochromic films were taken by a canon EOS 500D digital camera.

RESULTS AND DISCUSSIONS

Electrochemical Copolymerization

The successive cyclic voltammograms of 20 mM pyrrole, comonomer 2, comonomer 4, and 20 mM EDOT in pure BFEE solution are presented in Figure 1. Pyrrole is difficult to polymerize in pure BFEE solution because of the interaction between the N atom in pyrrole with BFEE.¹⁷ It can also be found by the cyclic voltammogram (CV) curves [Figure 1(a)]. The current density decreases with the repetitive cycles and no film can be observed on the working electrode. It is obvious that the CV curves of the comonomers are quite different from that of pyrrole as

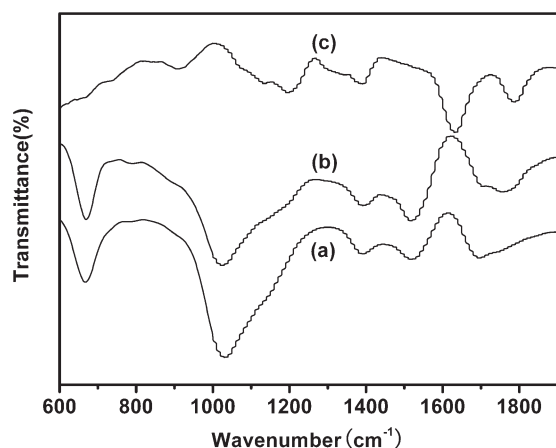


Figure 2. FTIR spectra of (a) pyrrole, (b) P3, and (c) PEDOT.

EDOT adds into the solution. The oxidation current increases with the increasing scanning cycles, and the polymer films can be observed on the working electrodes for the three systems. Furthermore, both the current increments between consecutive cycles and the redox potentials of the copolymers are different from those of homopolymers, which demonstrates the formation of copolymers.¹⁸

Structural Characterizations

The FTIR spectra of pyrrole, P3 and PEDOT are shown in Figure 2. As can be seen from the spectra of pyrrole [Figure 2(a)]. The bands at 665 and 1586 cm^{-1} originate from the stretching mode of N—H bond, the bands at 1030 cm^{-1} can be assigned to the stretching mode of C—N. The FTIR spectra of PEDOT shows that the bands at 745, 1204, 1390, and 1635 cm^{-1} can be attributed to the stretching modes of C—S, C—O, C=C, and C—C bonds, and the band at 1792 cm^{-1} originated from C=O indicates the overoxidation of PEDOT deposited under potentiostatic 1.05 V.^{19,20} Compared to the monomer and homopolymer, the copolymer presents both spectra of the pyrrole and EDOT units contained in the polymer chain. The bands at 667, 1024, and 1524 cm^{-1} indicates the existence of pyrrole units, while the absorption peaks at 772 and 1765 cm^{-1} originate from EDOT units.²¹

XPS spectra also support the formation of copolymers; the core level spectra of C1s and N1s of P3 film are shown in Figure 3. The highly asymmetric C1s photoemission has been deconvoluted into multiple components with peaks at 284.7, 287.7, and 288.6 eV, which arise from C—C, C—S, and C—O in the EDOT units.²² Furthermore, the peak at 286.9 eV, which is attributed to C—N, confirms the existence of pyrrole units. These can also be found in the spectra of N1s. All of these indicate the formation of copolymers based on pyrrole and EDOT.

The elemental analyses are used to present the ratio of pyrrole and EDOT in the copolymers, the results are shown in Table I. It is obvious that the ratio of pyrrole/EDOT in the corresponding copolymers prepared in BFEE solution are quite different from the copolymers prepared in PC or aqueous solution because of the low onset potential of EDOT in BFEE solution.^{12,23} The ratio of pyrrole/EDOT in the corresponding

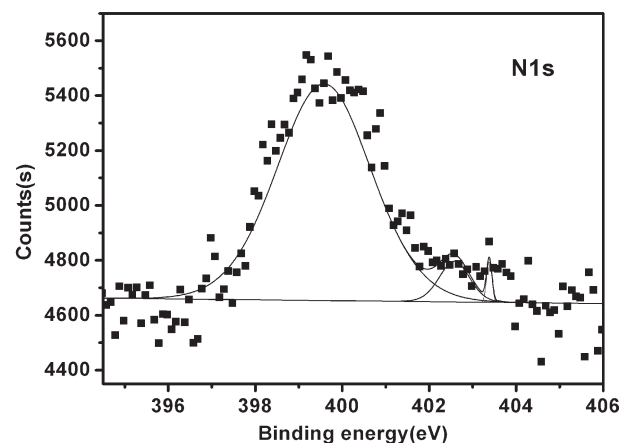
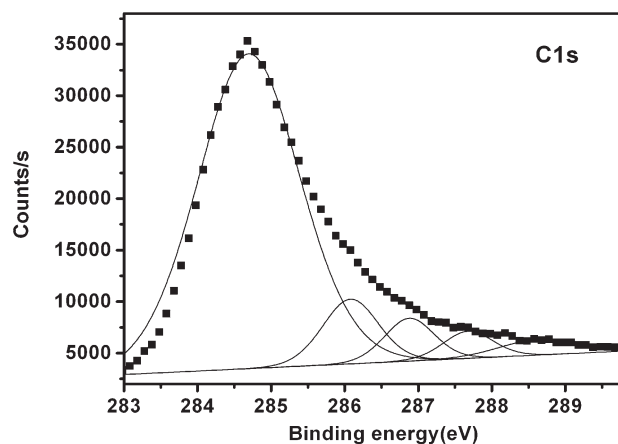


Figure 3. Core level spectra of C1s and N1s of P3 film.

copolymers decreases with the decreasing of feed ratio of pyrrole/EDOT.

Morphology and Conductivity

The properties of conducting polymers are strongly depended on the morphology and structure of the films. Figure 4 presents the SEM images of P2 and P3. The P2 and P3 films exhibit compact and homogeneous structure in globular form implying the good film forming of the comonomers, the thickness of P2 and P3 films are 205 and 159 nm.²⁴

Figure 5 presents the specific electrical resistances of the copolymer and homopolymer films. The specific electrical resistances of copolymers decrease with the decreasing feed ratio of pyrrole/EDOT, which implies the incorporation of pyrrole units

Table I. Elemental Analysis Results of the Copolymers Obtained with Various Feed Ratio of Pyrrole and EDOT

Feed ratio of pyrrole/EDOT	Elemental Analysis (%)					Pyrrole/EDOT ratio in polymer
	C	H	O	N	S	
1/1	47.43	33.08	10.14	4.27	5.08	0.84
1/2	47.06	32.27	11.86	2.80	6.01	0.48
1/4	46.56	31.59	13.59	1.46	6.80	0.23
1/8	46.50	31.12	14.14	1.16	7.08	0.16

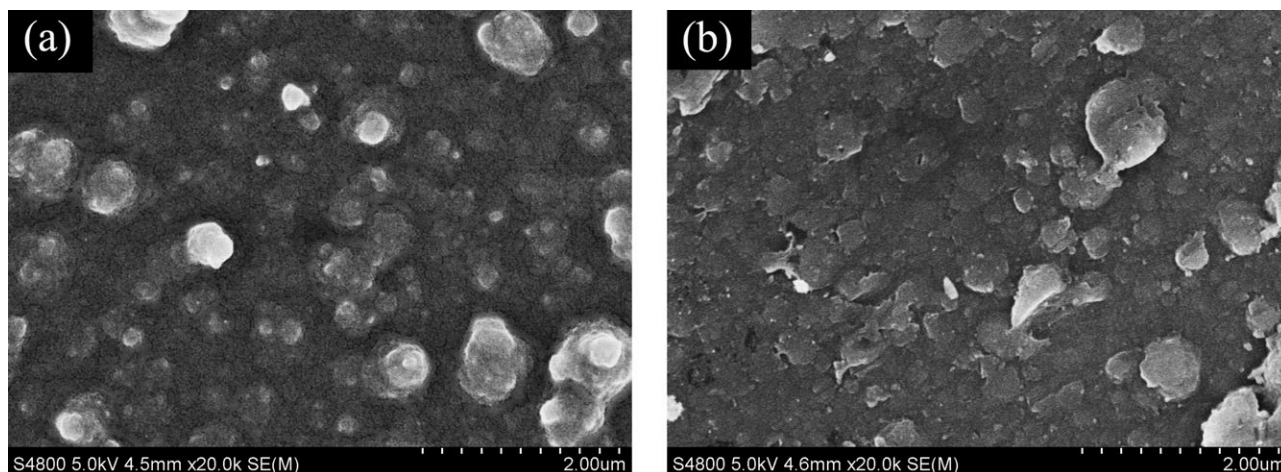


Figure 4. SEM images of (a) P2 and (b) P3 films.

into PEDOT chains increasing the conductivity.²⁵ As the feed ratios are as low as 1/4 and 1/8, the corresponding copolymer films exhibit lower specific electrical resistances than the prepared PEDOT film indicating the good conductivity of copolymer films.

Cyclic Voltammograms

The electrochemical behaviors of the copolymer films prepared under various feed ratio of pyrrole/EDOT are investigated via CVs. The CVs of P2, P3, and P4 with the scanning rate of 20 mV/s are shown in Figure 6. The copolymers present good electroactivity, and P2 shows an oxidation peak at 0.30 V and two reduction peaks at -0.2 and 0.42 V, P3 exhibits a quasi-reversible redox process between 0.38 and 0.28 V, P4 presents an oxidation peak at 0.28 V and two reduction peaks at -0.22 and 0.38 V. The redox behaviors of P3 and P4 films are quite different from the P2 film, which can be attributed to the different structure of the copolymers prepared with various feed ratio of pyrrole and EDOT.²⁶

Figure 7 shows the CV curves of P3 film at different scanning rates. Well-defined oxidation and reduction peaks confirm the conductivity of the polymer film. The anodic and cathodic

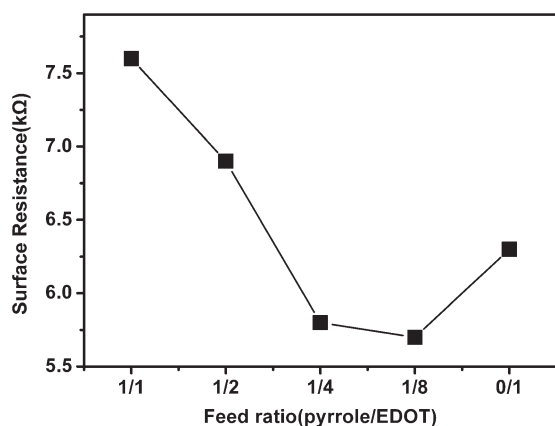


Figure 5. Surface resistance of PEDOT and the copolymer films.

peaks show linear dependence with the scanning rate, indicating that the electrochemical process is not diffusion controlled.^{18,27}

Spectroelectrochemical Properties of the Copolymer Films

The spectroelectrochemical properties of the copolymer films are investigated by applying a constant potential. Figure 8 illustrates the optoelectrochemistry of P1, P2, P3, and P4. The neutral P1 film shows absorption peak (the other peak attributes to the residual doped color, which can be seen in Figure 10(a) at 462 nm because of the $\pi-\pi^*$ transition. As the film gets oxidized, the absorption peak at 462 nm depletes while the intensity of polaron (792 nm) and bipolaron peaks (that peak in the NIR beyond the limits of the spectrophotometer) increase. The absorption assigned to $\pi-\pi^*$ transition for P2, P3 are at 483 and 501 nm, respectively. This transition is observed at 556 nm for P4. It is obviously that the absorption peaks present redshift with the decreasing feed ratio of pyrrole and EDOT.⁴

The bandgap of the copolymer films are calculated by using the wavelength value at the onset of the $\pi-\pi^*$ transition and shown in Table II. The bandgap of the copolymer films are very approachable to that of the prepared PEDOT film indicating

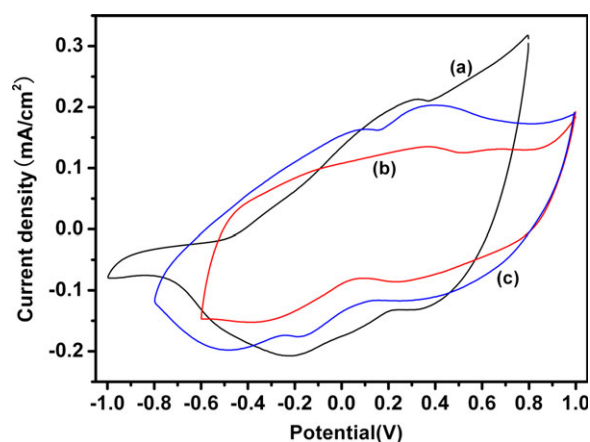


Figure 6. CV curves of (a) P2, (b) P3, and (c) P4 films. Scanning rate: 20 mV/s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

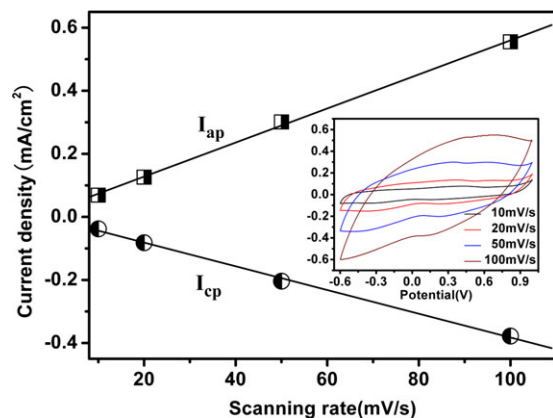


Figure 7. Anodic and cathodic peak currents of P3 film as a function of scanning rate. Inset: scan rate dependence of the copolymer film in monomer-free solution of 0.2M LiClO₄/PC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the low bandgap achieved. In addition, the decreasing bandgap of the copolymer films can be attributed to more EDOT units incorporation into the copolymer chains. And the neutral copolymer films present red to dark blue with the decreasing feed ratio of pyrrole and EDOT (Figure 9). Furthermore, it is interesting that the copolymer films exhibit different electrochromic properties and multicolor electrochromism, and the color can

be tuned through changing the pyrrole/EDOT feed ratio. Each of the copolymer film can exhibit at least four colors. The multicolor electrochromism implies the potential applications on electrochromic devices and displays.^{28–30}

Electrochromic Switching and Stability

The ability of a polymer to switch rapidly and to exhibit a striking color change is important for electrochromic application. A square-wave potential step method between -0.6 and 1.0 V with a 5 s delay at each potential coupled with optical spectroscopy is used to investigate switching time and contrast for P3 film. The percentage transmittance (%T) and response time (for 95% of the full optical contrast) at λ_{max} (501 nm) are monitored, and the results are shown in Figure 10. The optical contrast is 17.3% while the oxidized and reduced times are 1.2 and 2.8 s, respectively. The switching rate is reasonable in conducting polymers.³¹

Furthermore, nonstop steps are used to characterize the optical stability of the copolymer film. After 500 steps, the transmittance of oxidized film decreases, and it increases as the film is dedoped. The optical contrast changes from 17.3% to 12.4%. In addition, the response time especially the oxidized time increases which becomes 3.9 s after 500 steps. These indicate some electrochromic properties depleting after consecutive switching, which is normal in electrochromic conducting polymers.²³

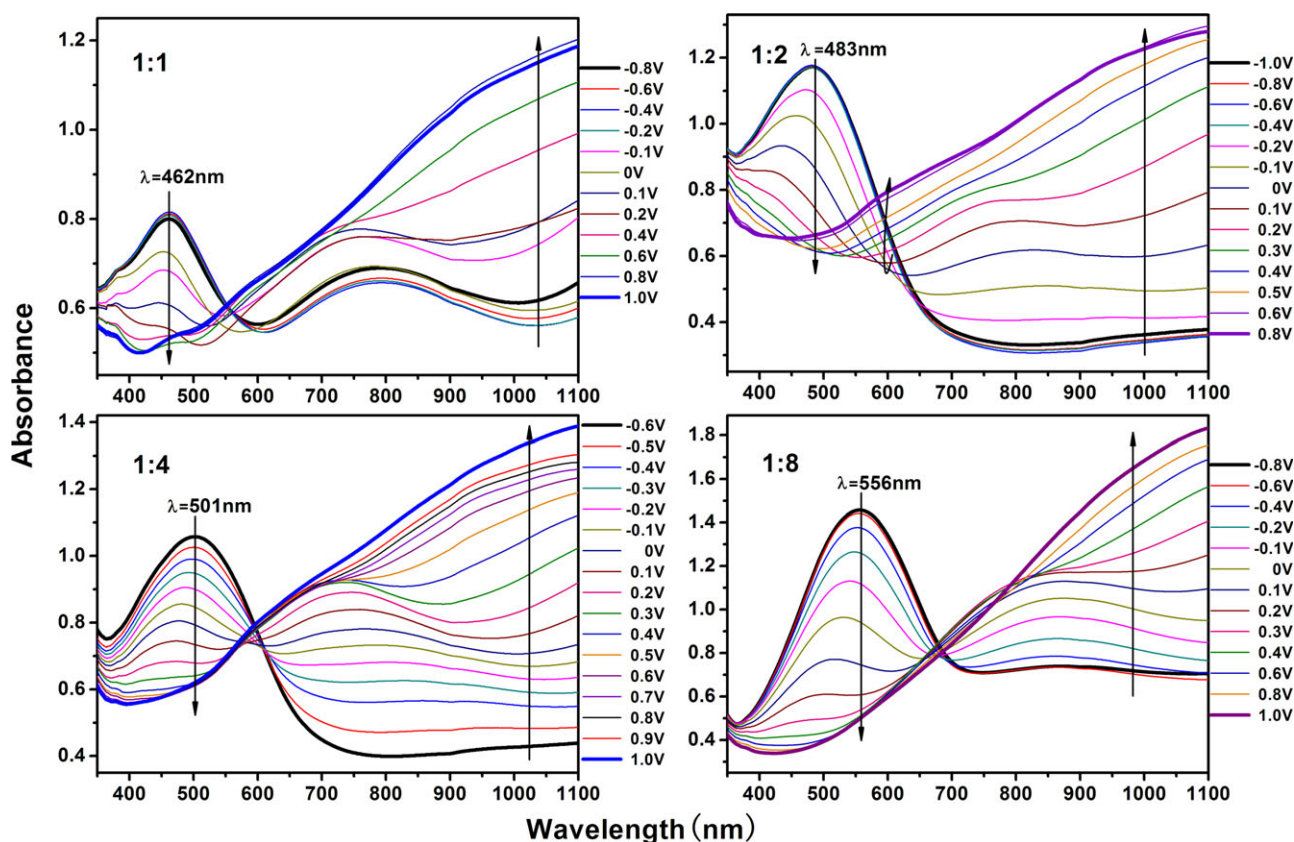


Figure 8. The Vis-NIR spectra of the copolymer films under various applied potentials. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

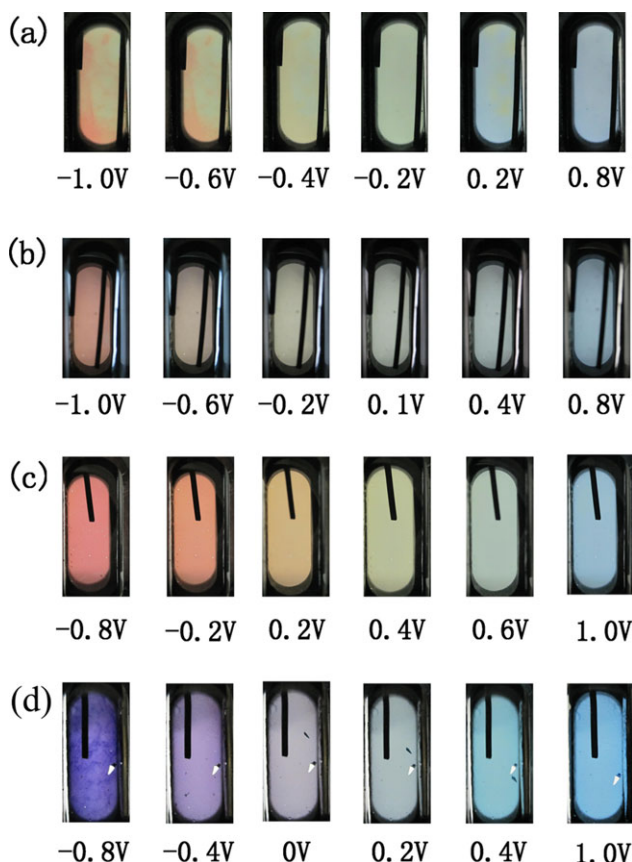


Figure 9. Optical images of (a) P1, (b) P2, (c) P3, and (d) P4 films under various applied potentials. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The electrochemical stability of P3 film is also investigated by non-stop cycling of the applied potential between -0.6 and 1.0 V with a potential scanning rate of 20 mV/s and presented in Figure 11. After 500 cycles, the film retains 71% of its original electroactivity which is reasonable in electrochromic conducting polymer.⁶ All of these imply the improving stability of polypyrrole film by copolymerization of EDOT with pyrrole.⁸

The coloration efficiency (CE) of the copolymer is calculated as another parameter to evaluate the electrochromic properties by the following equation:

$$\Delta OD = \log(T_b/T_c) \text{ and } CE = \Delta OD / \Delta Q$$

Table II. The Absorption Peaks, Onset Wavelength, and Band Gaps of PEDOT and the Copolymers

Polymer	Absorption peak (nm)	Onset wavelength (nm)	Band gap (eV)
P1	462	-	-
P2	483	724	1.72
P3	501	743	1.68
P4	556	748	1.66
PEDOT	565	756	1.64

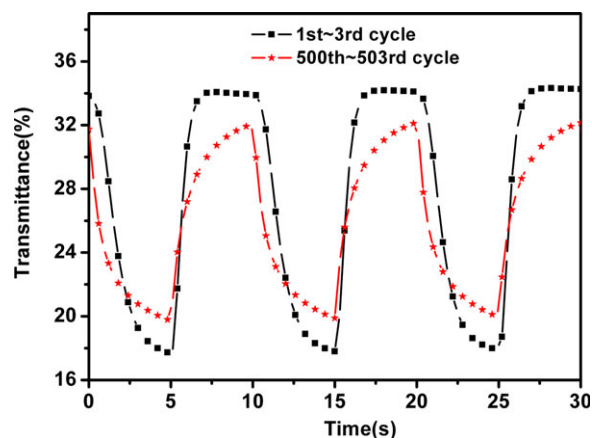


Figure 10. Switching time and optical stability of P3 film monitored at 501 nm between -0.6 and 1.0 V with residence of 5 s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

where T_b and T_c are the transmittances before and after coloration, respectively. ΔOD is the change of optical density. The CE value is calculated to be 189 cm²/C at 501 nm, which is comparable to those of PEDOT/NiO composite film (208 cm²/C) and conventional PEDOT film (183 cm²/C).^{28,32}

CONCLUSIONS

Copolymers based on pyrrole and EDOT have been successfully prepared via electrochemical copolymerization. FT-IR, XPS, and elemental analysis confirm the formation of copolymers. The copolymer films present low surface resistance and smooth morphology. Moreover, spectroelectrochemical analysis indicate the copolymers having excellent electrochromic properties, the absorption peak of neutral copolymer film shows red-shift as the feed ratio of pyrrole and EDOT decreases. Multicolor electrochromism can be observed by the copolymer films, and each of them shows at least four colors. The copolymer prepared with the pyrrole/EDOT feed ratio of $1/4$ is chosen as a representative of the copolymer films, which exhibits reasonable switching response, coloration efficiency, and stability.

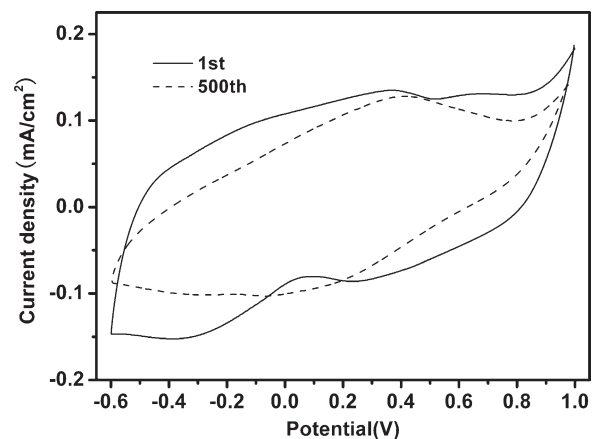


Figure 11. Electrochemical stability of P3 film.

REFERENCES

1. Cebeci, F. C.; Sezer, E.; Sarac, A. S. *Electrochim. Acta* **2007**, *52*, 2158.
2. Tarkuc, S.; Sahmetlioglu, E.; Tanyeli, C.; Akhmedov, I. M.; Toppare, L. *Sensors Actuat. B: Chem.* **2007**, *121*, 622.
3. Camurlua, P.; Tarkuc, S.; Sahmetlioglu, E.; Akhmedov, I. M.; Tanyeli, C.; Toppare, L. *Sol. Energ. Mat. Sol. C* **2008**, *92*, 155.
4. Camurlu, P.; Bicil, Z.; C. Gültekin, Karagoren, N. *Electrochim. Acta* **2012**, *63*, 245.
5. Bhandari, S.; Deepa, M.; Srivastava, A. K.; Lal, C.; Kant, R. *Macromol. Rapid Comm.* **2008**, *29*, 1959.
6. Deepa, M.; Awadhia, A.; Bhandari, S.; Agrawal, S. L. *Electrochim. Acta* **2008**, *53*, 7266.
7. Ma, L.; Li, Y.; Yang, X. Y. Q.; Noh, C.-H. *Sol. Energ. Mat. Sol. C* **2008**, *92*, 1253.
8. Zhang, C.; Hua, C.; Wang, G.; Ouyang, M.; Ma, C. *J. Electroanal. Chem.* **2010**, *64*, 54.
9. Ouyang, M.; Wang, G.; Zhang, Y.; Hua, C.; Zhang, C. *J. Electroanal. Chem.* **2011**, *653*, 21.
10. Varis, S.; Ak, M.; Tanyeli, C.; Akhmedov, I. M.; Toppare, L. *Solid State Sci.* **2006**, *8*, 1477.
11. Mortimer, R. J.; Dyer, A. L.; Reynolds, J. R. *Displays* **2006**, *27*, 11.
12. Yi-jie, T.; Hai-feng, C.; Wen-wei, Z.; Zhao-yang, Z.; Dong-qing, L. *Synth. Met.* **2012**, *162*, 728.
13. Shi, G.; Jin, S.; Xue, G.; Li, C. *Science* **1995**, *267*, 994.
14. Huang, C.; Sheng, K.; Qu, L.; Shi, G. *J. Appl. Polym. Sci.* **2012**, *124*, 4047.
15. Fu, M.; Zhu, Y.; Tan, R.; Shi, G. *Adv. Mater.* **2001**, *13*, 1874.
16. Shi, S.; Li, C.; Liang, Y. *Adv. Mater.* **1999**, *11*, 1145.
17. Xu, J.; Hou, J.; Zhang, S.; Nie, G.; Pu, S.; Shen, L.; Xiao, Q. *J. Electroanal. Chem.* **2005**, *578*, 346.
18. Zhang, C.; Xu, Y.; Wang, N.; Xu, Y.; Xiang, W.; Ouyang, M.; Ma, C. *Electrochim. Acta* **2009**, *55*, 14.
19. Krishnamoorthy, K.; Kanungo, M.; Contractor, A. Q.; Kumar, A. *Synth. Met.* **2001**, *124*, 473.
20. Akoudad, S.; Roncali, J. *Electrochem. Comumun.* **2000**, *2*, 72.
21. Kim, Y. H.; Hwang, J.; Son, J. I.; Shim, Y.-B. *Synth. Met.* **2010**, *160*, 416.
22. Deepa, M.; Bhandari, S.; Arora, M.; Kant, R. *Macromol. Chem. Phys.* **2008**, *209*, 137.
23. Sonmez, G.; Sarac, A. S. *Synth. Met.* **2003**, *135–136*, 459.
24. Du, X.; Wang, Z. *Electrochim. Acta.* **2003**, *48*, 1713.
25. Koyuncu, F. B.; Koyuncu, S.; Ozdemir, E. *Org. Electron.* **2011**, *12*, 1708.
26. Patra, A.; Wijsboom, Y. H.; Zade, S. S.; Li, M.; Sheynin, Y.; Leitus, G.; Bendikov, M. *J. Am. Chem. Soc.* **2008**, *130*, 6735.
27. Wang, B.; Zhao, J.; Cui, C.; Liu, J.; He, Q. *Sol. Energ. Mat. Sol. C* **2012**, *98*, 161.
28. Xia, X. H.; Tu, J. P.; Zhang, J.; Huang, X. H.; Wang, X. L.; Zhang, W. K.; Huang, H. *Electrochem. Comumun.* **2009**, *11*, 703.
29. Beaujuge, P. M.; Reynolds, J. R. *Chem. Rev.* **2012**, *110*, 301.
30. Ikeda, T.; Higuchi, M.; Kurth, D. G. *J. Am. Chem. Soc.* **2009**, *131*, 9158.
31. Amb, C. M.; Dyer, A. L.; Reynolds, J. R. *Chem. Mater.* **2011**, *23*, 399.
32. Gaupp, C. L.; Welsh, D. M.; Rauh, R. D.; Reynolds, J. R. *Chem. Mater.* **2002**, *14*, 3964.