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Effects on the Electrochemical and Electrochromic Properties of 3 Linked Polythiophene Derivative by the Introduction of Polyacrylate

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Functionalized 3-thiophene ethanol, 2-(3-thienyl)ethyl methacrylate (TE-AA) was synthesized *via* the esterification of 3-thienylethanol (TE) with acryloyl chloride. TE-PAA, precursor polymers polyacrylate (PAA) functionalized TE, was prepared by the free radical polymerization. Electrochemical polymerization of the precursor polymer TE-PAA resulted in PTE-PAA with good redox activity and excellent stability. For comparison, we have studied electrochemical and electrochromic properties of PTE and the presence of the functional groups on the polymer main chains apparently altered the optoelectronic properties. More specifically, the color was changed from blue of PTE to cyan of PTE-PAA at oxidized state, and from yellow of PTE to transparent gray of PTE-PAA at reduced state. Meanwhile, the PTE film showed a maximum optical contrast (ΔT%) of 43.1% at 1000 nm with a response time of 2.9 s and the coloration efficiency (CE) of PTE film was calculated to be 150.7 cm^2 C^{-1}. For polyacrylate functionalized PTE-PAA, the performance of electrochromic properties were reduced to a certain extent, which we have highlighted in this paper.

Keywords: PTE, PTE-PAA, free radical polymerization, electrochemical polymerization, electrochromics

1. INTRODUCTION

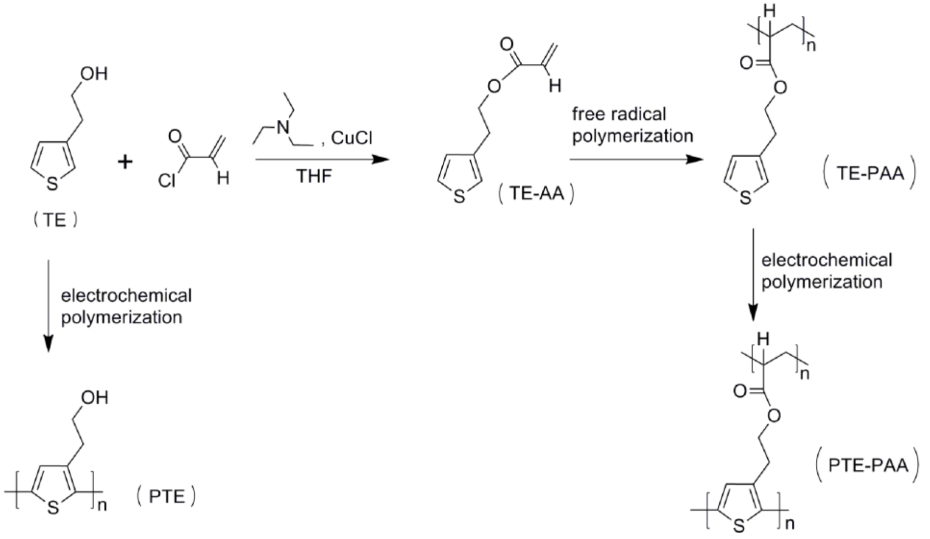
Electrochromism is defined as a reversible change in absorbance/transmittance in response to an externally applied potential on a material, which have extensive applied use for smart windows and electrochromic devices [1]. Traditionally, the electrochromic materials are mainly inorganic (such as

WO_3 and IrO_2) [2]. In recent years, as eletrochromic materials, conducting polymers (CPs) have gained a lot of attention due to their outstanding advantages over transition metal oxides, these advantages were listed as follows: long-term stability, high contrast ratio, fast response time, low switching potential, high coloration efficiency, and fine-tunability of the band gap (and the color) [3-5].

Among the large number of candidate conducting polymers that have been studied over last decades, poly(thiophene) and its derivatives (PThs) are the most extensively investigated conducting polymers in basic and applied research on account of their low oxidation potentials, high coloration efficiencies and their good stability. However, PThs have poor mechanical properties, like limited solubility and poor optical properties. In order to improve mechanical properties, one good way is to incorporate processable substitutions such as poly(styrene) [6], poly(methacrylate) [7] and poly(acrylate) [8].

3-thiophene ethanol (TE), as a popular monomer, have been used to synthesize different thiophene-based precursors bearing numerous functional groups *via* the reaction of hydroxyl group with substitutions.[9-15] These precursors or processed polymers were applied in different area, such as organic light-emitting diodes, supercapacitors, field effect transistors, and electrochromic devices, which displayed exciting performance.

In our work, we introduced the acrylate group into TE to form polymerizable precursor (TE-AA). Free radical polymerization was studied to prepared precursor polymers, TE-PAA. The responding polymer films were obtained by electropolymerization (Scheme 1). For a comparative study, the properties of PTE and PTE-PAA in electrochemical and electrochromic performance were investigated in particular by the same time.



Scheme 1 Synthesis route for monomers, precursor polymers and homo-electrochemical polymers.

2. EXPERIMENTAL

2.1 Materials

3-Thienylethanol (TE) (98%; Energy) and acryloyl chloride (98%; Energy) were used as received. Boron trifluoride diethyl etherate (BFEE) (Beijing Changyang Chemical Plant) was distilled before use. Azodiisobutyronitrile (AIBN) was purchased from Aldrich and used without further purification. Tetrahydrofuran (THF) was refluxed and distilled over sodium wire. Dichloromethane (CH_2Cl_2, analytical grade) was used after reflux distillation. Other chemicals and reagents that we used in our experiments were purchased commercially from Shanghai Vita Chemical Plant (Shanghai, China) and were used without any further treatment.

2.2 Synthesis of monomer and precursor polymer

2-(3-Thienyl)ethyl methacrylate (TE-AA)

3-thienylethanol (4 g, 31.2 mmol), dry triethylamin (4.2 g, 40.6 mmol) and a small amount of CuCl were dissolved in 30mL THF. Acryloyl chloride (3.68 g, 40.6 mmol) dissolved in 30mL THF was added slowly to the above mixture at 0^o C. Then, kept the mixture stirring for 2h fierencely. The triethylammonium chloride was treatment by the means of filtering through a silica gel column so as to obtain the usable triethylammonium chloride. The residue was stirred continued overnight in a solvent of CH_2Cl_2 and 2M NaOH (1:1 by volume) after solvent evaporation. After that, the organic layer was separated by separatory funnel, washed with water for three times, and dried over $CaCl_2$. After solvent evaporation, the remaining crude product was isolated by column chromatography with silica (ethyl acetate/petroleum ether, 1/3, by volume) to give TE-AA as a colorless liquid (yield 75 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.26 (m, 1H), 6.97-7.04 (m, 2H), 6.38-6.42 (m, 1H), 6.1 (m, 1H), 5.81 (m, 1H), 4.37 (t, 2H), 3.02 (t, 2H).

Poly[2-(3-thienyl)ethyl acrylate] (TE-PAA)

TE-PAA was prepared by free-radical polymerization with AIBN as the initiator. After polymerization, methanol was used to quench the reaction mixture. The precipitated polymer was filtered off, dried in vacuo, and purified by repeated precipitations. These TE-PAA was colorless viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.21 (s, 1H), 6.94-6.99 (b, 2H), 4.22 (b, 2H), 2.92 (b, 2H). GPC: $M_n = 5217$, $M_w = 10306$, $M_w/M_n = 1.97$.

2.3 Electropolymerization

All the electrochemical experiment was performed in a one-compartment cell with the use of Model 263A potentiostat-galvanostat (EG&G Princeton Applied Research) under computer control. The working and counter electrodes were both Pt wires with a diameter of 1 mm, respectively, while the reference electrode was Ag/AgCl. Polymer films were obtained electrochemically in the potentiodynamic regime. After polymerization, the films were washed repeatedly with anhydrous BFEE to remove the electrolyte and monomers.

2.4 Characterization

^{1}H NMR spectra was recorded on a Bruker AV 400 NMR spectrometer at ambient temperature. $CDCl_3$ was used as the solvent and chemical shifts were recorded in ppm units with tetramethylsilane (TMS) as the internal standard. Fourier Transform Infrared spectra (IR) were determined with a Bruker

Vertex 70 Fourier-transform infrared (FT-IR) spectrometer with samples in KBr pellets. Gel permeation chromatography (GPC) measurement of the sample was performed in tetrahydrofuran with a Waters Breeze GPC system. Scanning electron microscopy (SEM) measurements were made by using a VEGA II-LSU scanning electron microscope (Tescan) with the polymer films deposited on the ITO-coated glass.

2.5 Electrochromic experiments

Spectroelectrochemical and kinetic studies were carried out on a Model 263 potentiostat-galvanostat (EG&G Princeton Applied Research) and a Cary 50 UV-vis-NIR spectrophotometer under computer control. The spectroelectrochemical cell consists of a quartz cell, an Ag wire, a Pt wire, and an ITO/glass as transparent working electrode. All measurements were carried out in CH_2Cl_2-BFEE (1:1, by volume). The optical density (ΔOD) at the specific wavelength (λ_{max}) was determined by using the optical contrast values ($\Delta T\%$) of the electrochemically oxidized and reduced films, using the following equation: [16]

$$\Delta OD = \log(T_{ox}/T_{red}) \qquad (1)$$

The coloration efficiency (*CE*) is defined as the relation between the injected/ejected charge as a function of electrode area (Q_d) and the change in optical density (ΔOD) at the specific dominant wavelength (λ_{max}) as illustrated by the following equation: [17]

$$CE = \Delta OD/Q_d \qquad (2)$$

3. RESULT AND DISCUSSION

3.1 Electrochemical polymerization of TE and TE-PAA

The electropolymerization performances of TE and TE-PAA (0.01 mol L^{-1}) were examined in CH_2Cl_2-BFEE (1:1, by volume) as shown in Figure 2. To combine the facile synthesis of high-quality polymer films obtained in BFEE and the good solubility of the monomer obtained in CH_2Cl_2, a solvent electrolyte containing BFEE and CH_2Cl_2 (1:1, by volume) was chosen as the electrolyte system. In this way, the polymers became smooth, homogeneous, and continuous surfaces when electropolymerized. The first cycle of the cyclic voltammograms (CVs) test corresponds to the irreversible monomer oxidation at the platinum wire electrode. For the TE monomer, the onset of oxidation is observed at 0.94 V vs. Ag/AgCl. The oxidation potential of TE-PAA shifted to 0.91 V owing to the presence of polyacrylate group. Because the electropolymerization sites were all C(2) and C(5) positions of the thiophene ring, the onset oxidation potentials of both monomers were relatively close. Meanwhile, in contrast with TE, TE-PAA could be oxidized at relatively lower potentials, which may attribute to the increase of the conjugated length. Furthermore, the oxidation and reduction peaks were observed at 0.59 and 0.16 V for PTE, 0.52 and 0.38 V for PTE-PAA, respectively. Clearly, the presence of the polyacrylate substitution influenced the redox behavior of the electrodeposited polymer film, resulting in different redox properties. Moreover, in contrast with EDOT-PAA, whose onset oxidation potential was found at 1.05 V and the oxidation and reduction peaks were observed at 0.35 and 0.23 V [18]. As the cyclic scan continued, the current densities of the oxidation/reduction peaks increased, indicating the formation of the conducting polymers on the surface of the working electrodes [19].

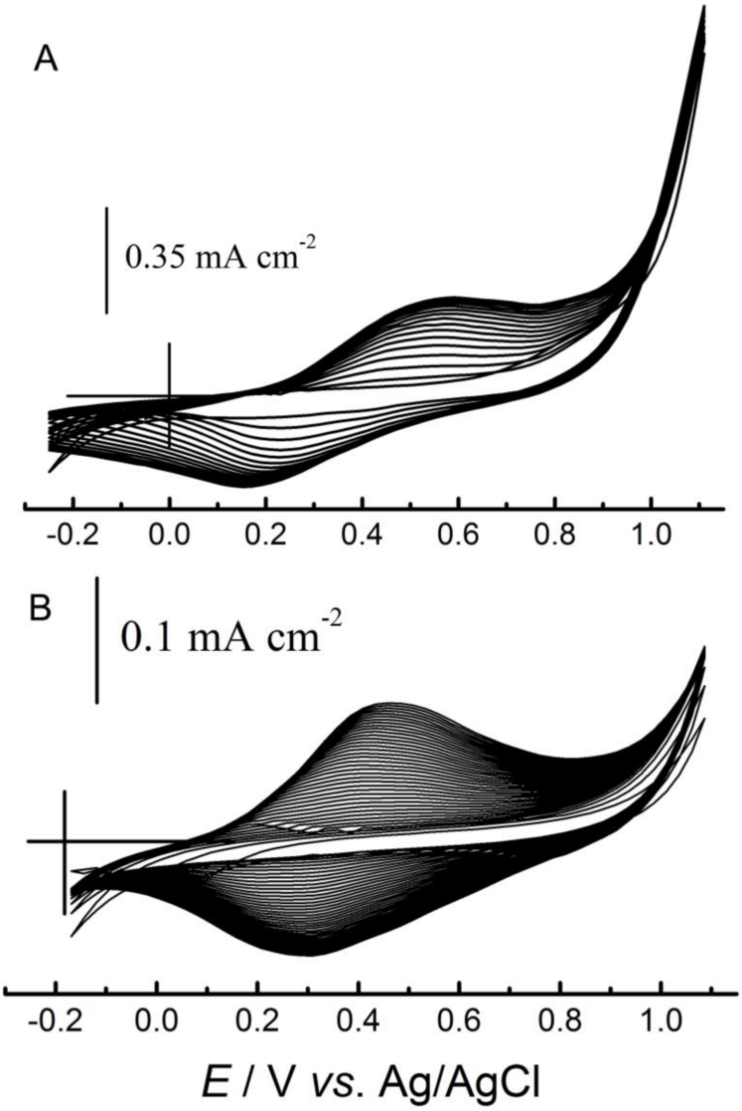


Figure 1. CVs of TE (A) and TE-PAA (B) in CH_2Cl_2-BFEE (1:1, by volume). Monomer concentration: 0.01 mol L^{-1}. Potential scan rates: 100 mV s^{-1}.

3.2 Electrochemistry of polymer films

To study on the electrochemical properties, both polymer films were prepared on Pt wire by sweeping the potentials for ten cycles. As shown in Figure 2, both the steady-state CVs of the films displayed broad anodic and cathodic peaks. The peak current densities were proportional to the potential scanning rates, indicating that the redox process is non-diffusional and the electroactive monomer is well adhered to the working electrode surface [20].

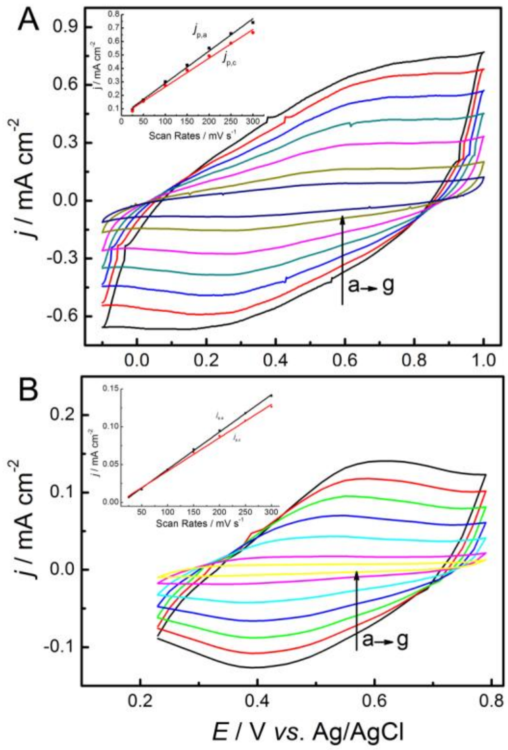


Figure 2. CVs of PTE (A) and PTE-PAA (B) in monomer-free CH_2Cl_2-BFEE (1:1, by volume). The potential scan rates were (a) 300 mV s^{-1}, (b) 250 mV s^{-1}, (c) 200 mV s^{-1}, (d) 150 mV s^{-1}, (e) 100 mV s^{-1}, (f) 50 mV s^{-1} and (g) 25 mV s^{-1}. Inset: plots of redox peak current densities *vs*. potential scan rates. j_p is the peak current density: and $j_{p,a}$ and $j_{p,c}$ denote the anodic and cathodic peak current densities, respectively.

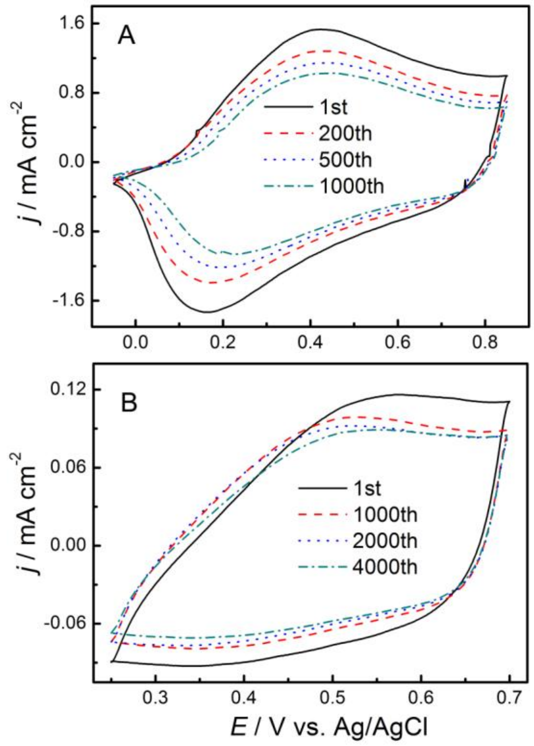


Figure 3. Long-term cyclic voltammograms of PTE (A) and PTE-PAA (B) in monomer-free CH_2Cl_2-BFEE (1:1, by volume). Potential scan rate: 150 mV s^{-1}.

We are all know that the stability and robustness of the polymer films for long-term multiple redox switching have important practical applications [21]. Hence, CVs of the polymers deposited on the Pt electrode were investigated by potential scanning between neutral and oxidized states in monomer-free CH_2Cl_2-BFEE (1:1, by volume) at a potential scan rate of 150 mV s^{-1}. Both polymer films exhibited good stability and during the above observation of the ability to switch between oxidized and reduced states of PTE, 72.1% of its electroactivity was retained after 1000 cycles. PTE-PAA displayed even better stability, with 85.8% of the exchange charge still remaining after sweeping 1000 cycles and 80.1% of its electroactivity was retained after 4000 cycles These results indicated that Both polymers have fine redox stability and their long lifetimes meant they have good effective charge compensation ability.

3.3 Structural characterization

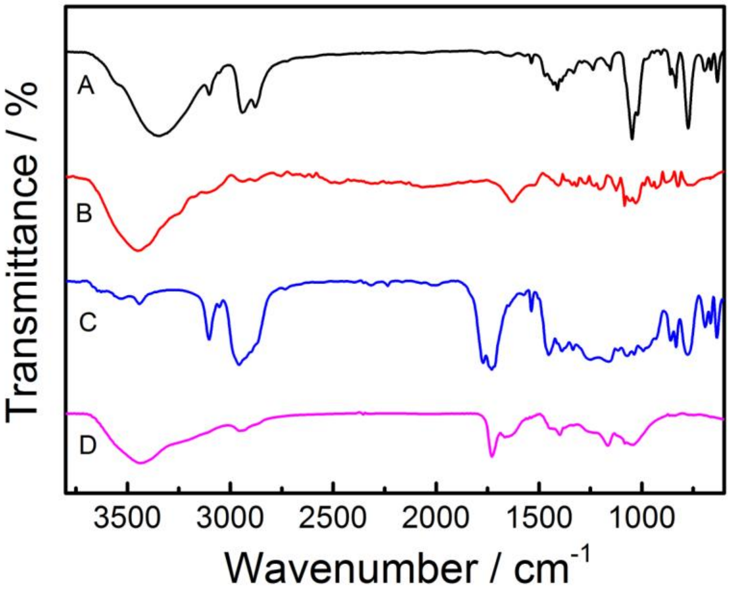


Figure 4. FT-IR spectra of TE (A), PTE (B), TE-PAA (C), and PTE-PAA (D).

A comparison of the evolution of the vibrational modes appearing in conducting polymers and monomers acting as references usually facilitates the interpretation of the experimental absorption spectra. As can be seen from Figure 4, the bands due to C–H stretching at approximately 3105 cm^{-1} in the monomer spectra were nearly absent or weak, while those in the 3000–2800 cm^{-1} region remained. This indicated the occurrence of electropolymerization were at C(2) and C(5) positions of the thiophene ring. Peaks located in the range of 2864 to 2930 cm^{-1} correspond to the CH_2 vibrations and peaks at 3105 cm^{-1} correspond to C-H vibration of the 2,5-positions in the thiophene ring were present in monomers. The peaks of 3105 cm^{-1} were retained in TE and TE-PAA but disappeared in PTE and PTE-PAA, which implied that the thiophene unit was stable during the free radical polymerization and also proved that the electropolymerization occurred at the 2,5-positions of the thiophene ring. The large peak at 1725 cm^{-1} was due to the carbonyl stretching vibrations in TE-PAA and PTE-PAA, with no detectable change in intensity or wavelength. Meanwhile, for TE and PTE, the peaks of 1725 cm^{-1}cannot find. In addition, the absorption bands of polymers were obviously broadened in comparison with the monomers, similar to those of other conducting polymers reported previously [22-23]. This mainly due to the wide chain dispersity of the resulting product composed of oligomers/polymers.

3.4 Spectroelectrochemistry

Spectroelectrochemical studies were performed to evaluate electronic structure and optical behavior of conducting polymers, consequently, to elucidate the effect of the different substitutions on the electronic properties [24]. Polymer films were eletrodeposited on ITO-coated glass slides. The cell was placed in the optical path of the sample light beam in a UV-vis-NIR spectrophotometer, which allowed us to acquire electronic absorption spectra under potential control in CH_2Cl_2-Bu_4NPF_6 (0.10 mol L^{-1}) solution. And the results of all the optical properties are summarized in Table 1.

Figure 5 showed spectra of PTE and PTE-PAA, we monitored the optical properties of polymer films with sequentially stepped between their fully oxidized and reduced states. The UV-vis absorption of both polymer films showed strong absorption peaks in the visible regime at about 400 nm, which are assignable to the creation of lower energy charge carriers at the expense of π-π* transition. Upon step increase in the applied potential, the intensity of the π-π* transition decreased, while the evolution of new absorption bands with a width from 500 nm to 800 nm was observed. This typically represented the polaron charge carrier bands along the polymer backbone. Upon further oxidation of the polymer films, appearance of absorptions at longer wavelength (>900nm) was observed, which mainly due to the formation of bipolaron charge carriers [26]. It can be seen clearly that the absorption bands with a width from 500 nm to 700 nm of PTE-PAA was showed two absorption bands in the NIR regime, which is attribute to the polymerization of acrylate, with a different phenomenon compared with PTE.

Table 1. Optical properties for polymer films

polymers	Wavelength/nm	potential step/V	ΔT/%	response time (s)		CE (cm^2/C)	λ/nm		E_g^a/eV
				oxidation	reduction		Abs. max	Abs. onset	
PTE	418	-0.5~0.5	11.1	3.0	2.2	119.7	418	541	2.29
	1000	-0.5~0.8	43.1	3.0	2.9	150.7			
PTE-PAA	400	-0.5~0.8	1.2	3.9	4.5	33.5	400	450	2.76
	910		9.3	4.5	2.7	110.7			

[a] The date were calculated by the equation: $E_g = 1241/\lambda_{onset}$ of polymer film.

E_g values of the polymer films deposited on ITO electrodes were determined from the commencement of the low energy end of π–π* transitions utilizing spectroelectrochemical data and were calculated to be 2.29 eV for PTE and 2.76 eV for PTE-PAA according to the Planck equation ($E_g = 1241/\lambda_{onset}$, Table 1). The PTE films at oxidized state showed blue and at reduced state exhibited yellow. Meanwhile, PTE-PAA film showed light cyan in oxidized state and transparent gray in reduced state. These results indicated that the pendant acrylate groups have influence on the the color of polymer films.

For a comparative study, PEDOT-PAA film exhibited two absorption bands centered at 430 and 586 nm when the state was neutral, similar to PTE-PAA. Furthermore, PEDOT-PAA film switched from the transmissive neutral state (magenta) to the highly absorbing oxidized state (blue), which is different from the color change of PTE-PAA [18].

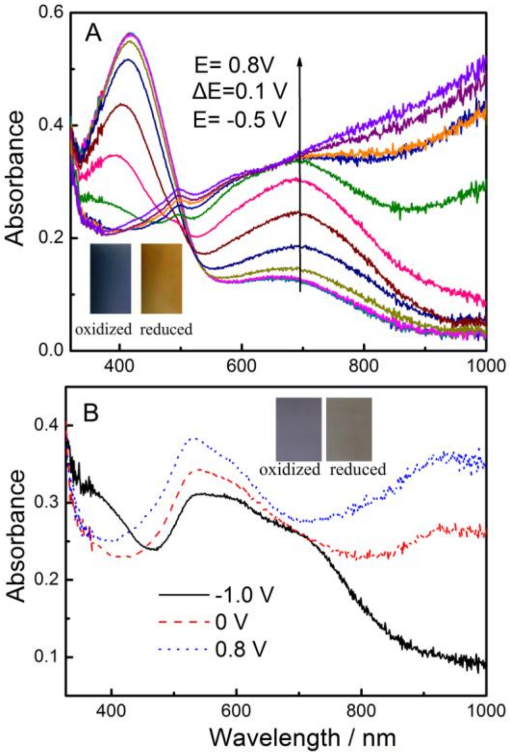


Figure 5. Spectroelectrochemistry for PTE (A) and PTE-PAA (B) on ITO coated glass in monomer-free CH_2Cl_2-BFEE (1:1, by volume).

3.5 Electrochromic switching of polymer films

A repeated potential stepping method coupled with optical spectroscopy was used to observe switching times and optical contrasts for both polymers. Electrochromic switching of the polymers was performed at regular intervals of 10 s in a monomer-free CH_2Cl_2-Bu_4NPF_6 (0.10 mol L^{-1}) solution. As seen from Figure 6, the behaviors included only slight losses in the percent transmittance contrast value after regular switching during 150 s, indicating a certain stability of both polymer films.

In this studies, the optical contrast (ΔT%) of the polymer films can be defined as the transmittance difference between the redox states was recorded at constant wavelengths. The response time, another very important characteristic of electrochromic materials, is the time necessary for 95% of the full optical switch [26]. Figure 6A showed the switching properties of PTE between -0.5 and 0.8 V at 418 nm and 1000nm. At 418 nm, the optical contrast for PTE was calculated as 11.1% and the switching time was 2.2 s. The polymer switched slowly and achieves 43.1% of its total optical change in 2.9 s at 1000 nm. PTE-PAA was switched from -0.6 V to 0.8 V at 10 s step intervals, while the change in transmittance at two different wavelengths (400 nm and 900nm) was monitored. The optical contrasts for PTE-PAA were calculated as 1.2% at 400 nm and 9.3% at 900 nm, a strong decrement in comparison with PTE. The similar phenomenon was obtained between PEDOT-AA and PEDOT-PAA, which was due to the presence of polyacrylate [18].

The coloration efficiency (CE) is also an important characteristic for electrochromic materials and obtained for a certain amount of the charge injected in the polymer as a function of the change in optical density [27]. In our study, the CE of the PTE was calculated to be 119.7 $cm^2\ C^{-1}$ at 418 nm and 150.7 $cm^2\ C^{-1}$ at 1000 nm. The PTE-PAA was calculated to have a CE of 110.7 $cm^2\ C^{-1}$ at 910 nm, lower than that of PTE and PEDOT-AA [18].

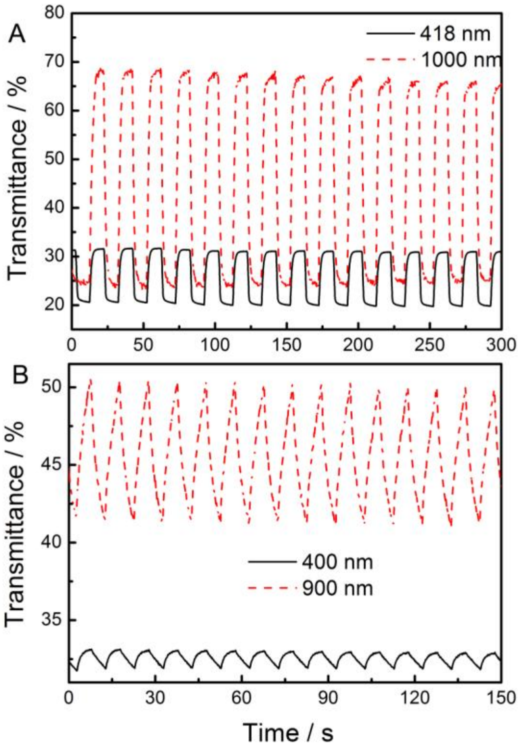


Figure 6. Electrochromic switching and optical absorbance monitored at different wavelength for PTE (A) and PTE-PAA (B) recorded during double step spectrochronoamperometry.

3.6 Morphology

Figure 7 displayed the morphology of polymer films. It is noticed that the morphological structure of PTE (Figure 8A) was porous and inhomogeneous whereas PTE-PAA showed smooth and homogeneous surface. This indicated that the incorporation of polyacrylate group can improve smoothness of the films. The polymer film with smooth and homogeneous morphology was extremely necessary to improve electrical conductivity and the performance in fabricating stable electrochromic devices [28].

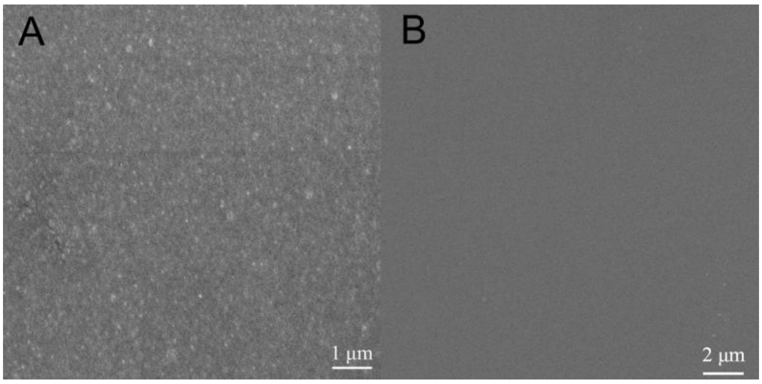


Figure 7. SEM photographs of PTE (A) and PTE-PAA (B) films deposited electrochemically on ITO electrode.

4. CONCLUSION

In summary, polyacrylate functionalized TE-PAA was synthesized, and then electrochromic polymer films was prepared by electropolymerization onto transparent ITO glass. For comparison, we have studied electrochemical and electrochromic properties of PTE. Both polymer films showed outstanding redox activity and affecting stability in monomer-free CH_2Cl_2-BFEE. Spectroelectrochemistry studies demonstrated that the introduction of polyacrylate reduced the electrochromic properties compared with PTE and resulted in low contrast ratios and slow response time. Meanwhile, the optical band gaps, defined as the onset of the π–π * transition, were calculated to be 2.29 eV for PTE and 2.76 eV for PTE-PAA according to the Planck equation ($E_g = 1241/\lambda_{onset}$).

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References

1. Y.J. Tao, Z.Y Zhang, X.Q. Xu, Y.J. Zhou, H.F. Cheng, W.W. Zheng, *Electrochim. Acta* 77 (2012) 157.
2. H. Eckert, M. Ward, *Chem. Mater.* 13 (2001) 3059.
3. Y.J. Tao, Y.J. Zhou, X.Q. Xu, Z.Y. Zhang, H.F. Cheng, W.W. Zheng, *Electrochim. Acta* 78 (2012) 353.
4. A.L. Dyer, M.R. Craig, J.E. Babiarz, K. Kiyak, J.R. Reynolds, *Macromolecules* 43 (2010) 4460.
5. C.G. Wu, M.I. Lu, S.J. Chang, C.S. Wei, *Adv. Funct. Mater.* 17 (2007) 3153.
6. B. Francois, T. Olinga, *Synth. Met.* 57 (1993) 3489.

7. S. Alkan, L. Toppare, Y. Hepuzer, Y.J. Yagci, *Polym. Sci. A: Polym. Chem.* 37 (1999) 4218.
8. N. Ranieri, G. Ruggeri, F. Ciardelli, *Polym. Int.* 48 (1999) 1091.
9. M.L. Hallensleben, F. Hollwedel, D. Stanke, *Macromol. Chem. Phys.* 196 (1995) 3535.
10. K.H. Kim, W.H. Jo, *Macromolecules* 40 (2007), 3708.
11. P. Camurlu, A. Cirpan, L. Toppare, *Synth. Met.* 146 (2004) 91.
12. P.J. Costanzo, K.K. Stokes, *Macromolecules* 35 (2002) 6804.
13. P. Waenkaew, S. Phanichphant, R.C. Advincula, *Poly. Adv. Technol.* 22 (2011) 753.
14. M.J. Im, C.H. Kim, M. Song, J.S. Park, J.W. Lee, Y.S. Gal, J.H. Lee, S.H. Jin, *Bull. Korean Chem. Soc* 32 (2011) 559.
15. L. Sacan, A. Cirpan, P. Camurlu, L. Toppare, *Synth. Met.* 156 (2006) 190.
16. C.L. Gaupp, D.M. Welsh, R.D. Rauh, J.R. Reynolds, *Chem. Mater.* 14 (2002) 3964.
17. B.D. Reeves, C.R.G. Grenier, A.A. Argun, A. Cirpan, T.D. McCarley, J.R. Reynolds, *Macromolecules* 37 (2004) 7559.
18. L.Q. Qin, J.K. Xu B.Y. Lu, Y. Lu, X.M. Duan, G.M. Nie, *J. Mater. Chem.* 22 (2012) 18345.
19. B. Lu, L. Qin, W. Chen and J. Xu, *Int. J. Electrochem. Sci.*, 9 (2014) 4535.
20. K.W. Lin, S.J. Zhen, S.L. Ming, J.K. Xu, B.Y. Lu, *New J. Chem.* 39 (2015) 2096.
21. J.S. Zhao, X.F. Cheng, Y.Z. Fu, C.S. Cui, *Int. J. Electrochem. Sci.* 8 (2013) 1002.
22. J.K. Xu, J. Hou, S.S. Zhang, G.M. Nie, S.Z. Pu, L. Shen, Q. Xiao, *J. Electroanal. Chem.* 578 (2005) 345.
23. B.Y. Lu, J. Yan, J.K. Xu, S.Y. Zhou, X.J. Hu, *Macromolecules* 43 (2010) 4599.
24. Z. Xu, M. Wang, W.Y Fan, J.S. Zhao, H.S. Wang, *Electrochimica Acta* 160 (2015) 271.
25. P. Camurlu, A. Cirpan, L. Toppare, *Mater. Chem. Phys.* 92 (2005) 413-418.
26. A. Cihaner, F. Algı, *Electrochim. Acta.* 54 (2008) 786.
27. M. Deepa, A. Awadhia, S. Bhandari, *Phys. Chem. Chem. Phys.* 11 (2009) 5674.
28. G.M. Nie, H.J. Yang, S. Wang, X.M. Li, *Crit. Rev. Solid State Mater. Sci.* 36 (2011) 209.