

Methacrylate Modified Polythiophene: Electrochemistry and Electrochromics

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A novel methacrylate modified thiophene (TE-MA) was synthesized, and the electrochemical method resulted in the formation of the polymer (PTE-MA). Structure characterization and tests of PTE-MA, including FT-IR, morphology, electrochemical, spectroelectrochemical and electrochromic properties, were systematically explored. During redox process, PTE-MA exhibited reversible color changes gray to brown. Kinetic studies demonstrated that PTE-MA exhibited good electrochromic performance, including satisfactory optical contrast ratio (20% at 420 nm; 23% at 900 nm), high coloration efficiency ($165 \text{ cm}^2 \text{ C}^{-1}$ at 420 nm; $112 \text{ cm}^2 \text{ C}^{-1}$ at 900 nm) and fast response time. In addition, as-obtained PTE-MA film showed compact morphology and favorable stability, which indicate that PTE-MA is promising material for the construction of electrochromic device.

Keywords: conducting polymer, polythiophene, methacrylate, electrochemical polymerization, electrochromics

1. INTRODUCTION

Conducting polymers used as electrochromic (EC) materials have attracted considerable attention since they found a variety of advantages including high contrast ratios, superior coloration efficiencies and numerous colors [1-7]. In this context, the design and synthesis of novel conducting polymer with excellent EC behavior has been a significant goal in electrochromic field.

Among the numerous candidate EC materials, polythiophene (PTh) and its derivatives are the most extensively explored conducting polymers due to low oxidation potential, abundant color,

superior electrochromic performance and excellent stability [1,3]. Many conducting polymers have poor mechanical properties, like limited solubility. In order to improve mechanical properties of conducting polymer, various methods can be used [1-5]. The most effective way of achieving preferable electrochromic material is the tailoring of the structure of conjugated polymer. It has clearly been demonstrated that substituents not only change the redox potential, solubility and band gap of the polymer, but modify the electrochromic performance through sterically hindering and pull-push dual-effect of substituents [5,8].

Methacrylate is regarded as a popular crosslinking and sterilizing group. Previously, methacrylate and acrylate functionalized PEDOT was obtained in Kim and Xu laboratory [9-11], and exhibited desirable EC performance. Also, methacrylate functionalized polymers revealed better solubility relative to unsubstituted PEDOT, which demonstrated that methacrylate functionalized PEDOT are solution processable material for the construction of large-area electrochromic device. Besides, 3-thiophene ethanol (TE) has been used to synthesize different thiophene-based precursors bearing various functional groups [12-17]. And these result showed that substituents of the conjugated block not only turn the oxidation potential of the precursor, but also modulate the solubility, optical property and band gap of the corresponding polymer.

Therefore, the methacrylate group was introduced into thiophene ring to obtain a precursor (TE-MA), and the corresponding polymer (PTE-MA) was electrochemically synthesized. In addition, the properties of PTE-MA, including FT-IR, morphology, electrochemical, spectroelectrochemical and electrochromic properties, were systematically explored.

2. EXPERIMENTAL SECTION

2.1 Materials

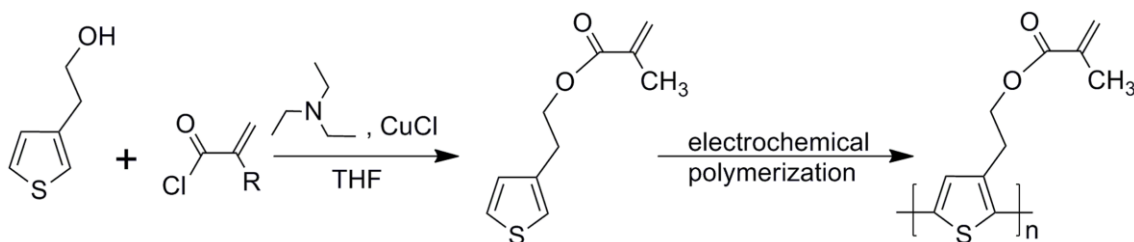
3-Thienylethanol (TE, 98%; J&K Scientific Ltd.) was used directly without further purification. Dichloromethane (CH_2Cl_2 , analytical grade; Shanghai Vita Chemical Reagent Co., Ltd.), tetrahydrofuran (THF, analytical grade; Xilong Chemical) and boron trifluoride diethyl etherate (BFEE, J&K Scientific Ltd.) were refluxed and distilled under a nitrogen atmosphere before use. Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6 , 99%; Energy Chemical) was dried under vacuum at 60 °C for 24 h before use. Other materials (analytical grade, >98%) were purchased from Shanghai Vita Chemical Reagent Co., Ltd. and were used directly without any further treatment.

2.2 Characterization

^1H NMR and ^{13}C NMR spectra were measured by a Bruker AV 400 NMR spectrometer with CDCl_3 as the solvent and tetramethylsilane as an internal standard. Infrared spectra were recorded with a Bruker Vertex 70 Fourier-transform Infrared (FT-IR) spectrometer with samples in KBr pellets. Scanning electron microscopy (SEM) image was performed on a VEGA II-LSU scanning electron microscope (Tescan).

2.3 Monomer synthesis

The monomer, 2-(3-thienyl)ethyl methacrylate (TE-MA), was synthesized according to literature procedures, as exhibited in Scheme 1 [12].



Scheme 1. Synthetic route of monomer and homo-electrochemical polymer.

2-(3-Thienyl)ethyl methacrylate (TE-MA). A small amount of CuCl was added to the solution of 3-thiophenylethanol (5 g, 39.1 mmol), methacryloyl chloride (4.15 g, 39.68 mmol), dry triethylamine (5.6g, 55.5 mmol) in THF (30 mL). The solution was refluxed at 70 °C for 8 h under a nitrogen atmosphere. The resulting solution was poured into water and extracted with CH₂Cl₂. The organic layer was washed with water, dried with MgSO₄ and removed by rotary evaporation. The crude product was purified by silica column chromatography to get 3.9 g colourless liquid. (Yield: 65%) ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.28 (m, 1H), 6.98-7.04 (m, 2H), 6.09 (t, 1H), 5.56 (t, 1H), 4.37 (t, 2H), 3.02 (t, 2H), 1.94 (s, 3H). ¹³C NMR (400 MHz, CDCl₃): δ (ppm) 167.2, 138.1, 136.2, 128.2, 125.5, 121.5, 64.5, 29.5, 18.3.

2.4 Electrosynthesis and electrochemical tests

Electrochemical tests were performed in self-assembly electrolytic cell by a Model 263A potentiostat-galvanostat (EG&G Princeton Applied Research). The electrolytic cell contains an Ag/AgCl reference electrode and two Pt wires as the working electrode and the counter electrode, respectively. To get sufficient polymer, Pt wires were replaced by Pt sheets as the work electrode and the counter electrode. During the electrochemical examinations, the two Pt sheets were placed 5 mm apart., Except for reference electrode, these electrodes were polished and cleaned carefully prior to each experiment. To remove the electrolyte, monomers, and oligomers, the polymer attached to Pt sheet was washed repeatedly with anhydrous CH₂Cl₂. Besides, the solvent-electrolyte systems were blanked by nitrogen stream before each experiment.

2.5 Electrochromic Tests.

Electrochromic performance was performed in self-assembly electrolytic cell by a Cary 50 Ultraviolet-Visible Near-Infrared spectrophotometer coupling with Model 263A potentiostat-

galvanostat (EG&G Princeton Applied Research). The electrolytic cell includes ITO-coated glass as the working electrode, a Pt wire counter electrode, an Ag/AgCl reference electrode and a transparent cuvette used as the container. All measurements were carried out in $\text{CH}_2\text{Cl}_2\text{-Bu}_4\text{NPF}_6$ (0.1 mol L^{-1}).

On the basis of the following formulas, the optical density (ΔOD) and the coloration efficiency (CE) are calculated [1,18,19]:

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

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

where T_{ox} and T_{red} are transmittance of electrochromic material at oxidized and reduced states. Q_d is injected/ejected charge of electrochromic material in per unit.

3. RESULTS AND DISCUSSION

3.1 Electrochemical polymerization of TE-MA

Cyclic voltammetry (CV) is regarded as a significant method which could monitor the electroactivity of polymer [20]. The electrochemical polymerization performances of TE-MA (1.84 g L^{-1}) were examined by CV in $\text{CH}_2\text{Cl}_2\text{-Bu}_4\text{NPF}_6$ (0.1 mol L^{-1}) and BFEE, as revealed in Figure 1.

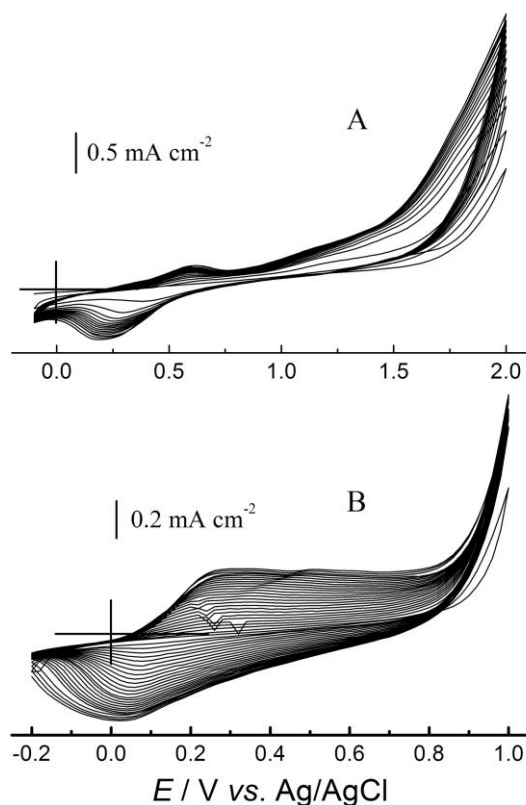


Figure 1. CVs of TE-MA in $\text{CH}_2\text{Cl}_2\text{-Bu}_4\text{NPF}_6$ (0.1 M) (A) and TE-MA in BFEE (B). Monomer concentration: 1.84 g L^{-1} . Scan rates: 100 mV s^{-1} .

The onset oxidation potential (E_{ox}) of TE-MA in $\text{CH}_2\text{Cl}_2\text{-Bu}_4\text{NPF}_6$ was approximately at 1.73 V vs. Ag/AgCl, as can be seen from the first cycle of Figure 1A. The high onset oxidation potential may lead to over oxidation during the electro-deposited progress. Furthermore, visual inspection during the CV experiments revealed that no polymer film was attached on the electrode. The behavior demonstrated that the electropolymerization of TE-MA was infeasible in $\text{CH}_2\text{Cl}_2\text{-Bu}_4\text{NPF}_6$. To choose the appropriate solvent, the electrochemical behavior of TE-MA (Figure 1B) in BFEE was also explored. BFEE was an outstanding electrolyte in which many aromatic compounds including thiophene and thiophene-based materials have been successfully electropolymerized [1,21]. Note here that BFEE was acting as both the electrolyte and the solvent (without the addition of any other electrolytes). The onset oxidation potential of TE-MA was 0.93 V vs. Ag/AgCl, greatly lowered than that in $\text{CH}_2\text{Cl}_2\text{-Bu}_4\text{NPF}_6$ (1.73 V, Figure 1A). The phenomenon for the large descent in onset oxidation potentials is mainly due to that BFEE could affect the resonance stability of the thiophene ring through the formation of π -complexes between BFEE and TE-MA, therefore making polymerization of monomer much easier.

In BFEE system, the current intensities grew steadily during the repetitive anodic potential scan, as can be seen from Figure 1B. The phenomenon clearly demonstrated that PTE-MA attached on the work electrode grew. From CV results, PTE-MA revealed broad redox peaks, which can be attributed to the formation of PTE-MA with different chain length and the transition of conductive species. Further, the peak potential change could be ascribed to the increased electrical resistance of PTE-MA [21,22].

3.2 Optimization of electropolymerization condition

The deposition potential significantly influences the structure and quality of polymers, which is in connection with various properties including stability and optical performance. In order to choose an appropriate potential, current density-time ($I-t$) curves of TE-MA at 6 different potentials in BFEE were recorded, as shown in Figure 2.

On the basis of chronoamperograms and phenomenon during the experiments, combining with the facts influence the quality of the polymer, the appropriate polymerized potential of TE-MA was 1.4 V. Also, the continuous, homogeneous and smooth polymer film was obtained under optimized potential, in agreement with the $I-t$ curves.

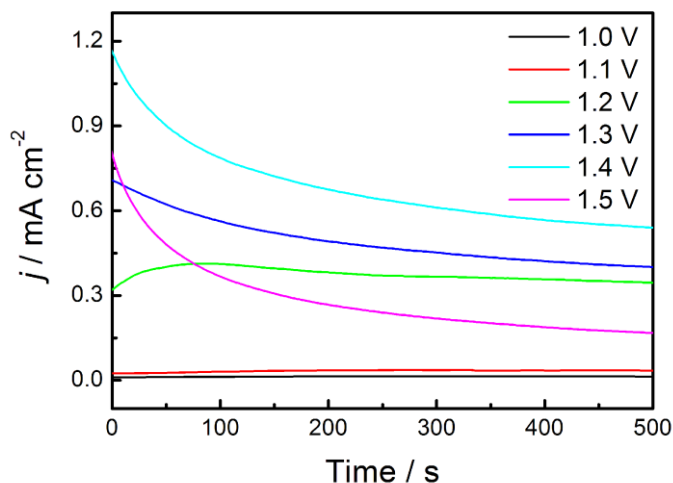


Figure 2. Chronoamperograms of TE-MA in BFEE on the Pt electrode. Monomer concentration: 1.84 g L^{-1} .

3.3 Structural characterization

For conducting polymer, FT-IR spectrum is a very useful way to investigate the polymerized mechanism. As can be seen in Figure 3, FT-IR spectra of TE-MA and PTE-MA were recorded. Also, peak assignments of TE-MA and PTE-MA were analyzed in detail. FT-IR spectral peaks of the polymer were broader relative to those of TE-MA, in agreement with other reported conducting polymers [23,24], which could be ascribed to the formation of conjugated polymer with different chain length.

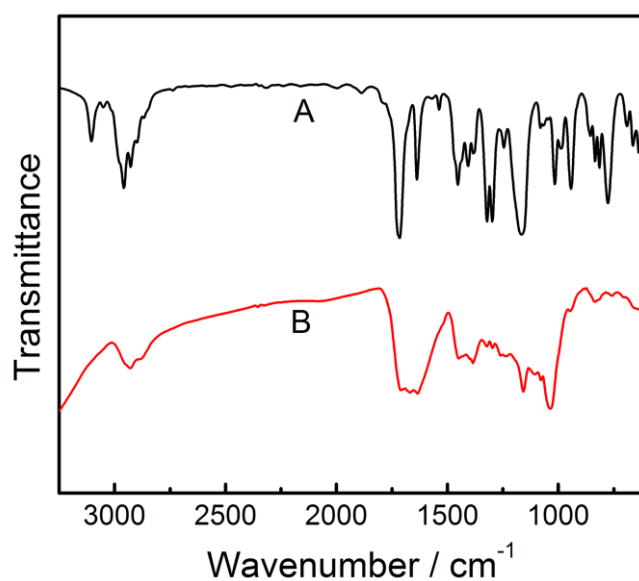


Figure 3. FT-IR spectra of TE-MA (A) and PTE-MA film (B).

The peak at 3105 cm^{-1} for TE-MA could be assigned to C–H vibration of the α -position of the thiophene unit. However, this peak disappeared in PTE-MA, demonstrating that TE-MA was polymerized to form PTE-MA through α,α' -coupling of thiophene unit. It is obvious that peaks ranged from 2960 cm^{-1} to 2925 cm^{-1} correspond to the CH_2 vibrations. A large peak at 1718 cm^{-1} was present in monomer and corresponding polymer, which could be assigned to the C=O vibration for the ester group. Furthermore, the peaks at 1640 cm^{-1} appeared in PTE-MA and TE-MA could be attributed to the C=C stretching vibration frequency of the acrylate transition. These behaviours indicated that methacrylate unit was not destroyed during the electrochemical polymerization process.

3.4 Electrochemistry of PTE-MA film

To investigate the electrochemical activity and stability of obtained polymer, the electrochemical property of PTE-MA film was performed in detail by CV in monomer-free $\text{CH}_2\text{Cl}_2\text{-Bu}_4\text{NPF}_6$ (0.1 mol L^{-1}), as can be seen from Figure 4. A true linear relation were observed between the scan rates and the peak current densities, which demonstrated that PTE-MA was well attached to the electrode and the redox process was non-diffusional. Furthermore, the calculated $j_{p,a}/j_{p,c}$ ($j_{p,a}$: the ratio between oxidized peak current densities and scan rates; $j_{p,c}$: the ratio between reduced peak current densities and scan rates.) of PTE-MA in $\text{CH}_2\text{Cl}_2\text{-Bu}_4\text{NPF}_6$ is closer to 1.0, indicating its better redox reversibility. There is a stark difference between the anodic and cathodic peak potentials in CV curves, which due to hysteresis effect during redox process. This phenomenon could be ascribed to a couple of reasons, including slow mutual transformation of various electronic species, slow heterogeneous electron transfer, rearrangement of polymer chains, and the transfer of interfacial electrons corresponding to the electrode/polymer and polymer/solution [21].

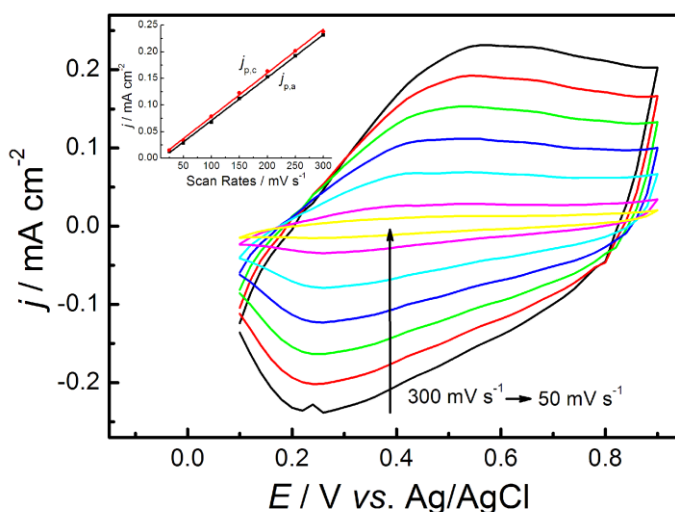


Figure 4. CVs of PTE-MA in $\text{CH}_2\text{Cl}_2\text{-Bu}_4\text{NPF}_6$. Scan rates: $300 \sim 50\text{ mV s}^{-1}$. Insert: plots of redox peak current densities vs. scan rates. $j_{p,a}$: the ratio between oxidized peak current densities and scan rates; $j_{p,c}$: the ratio between reduced peak current densities and scan rates.

3.5 Morphology

To analyze the stability, electrical conductivity and redox activity of polymer, the surface morphology of PTE-MA was investigated by scanning electron microscopy (SEM), as shown in Figure 5. PTE-MA film exhibited smooth and compact morphology at high magnifications, which was beneficial to increase the electrical conductivity of conjugated polymer. Also, the smooth and compact morphology was especially significant in fabrication of electrochromic device.

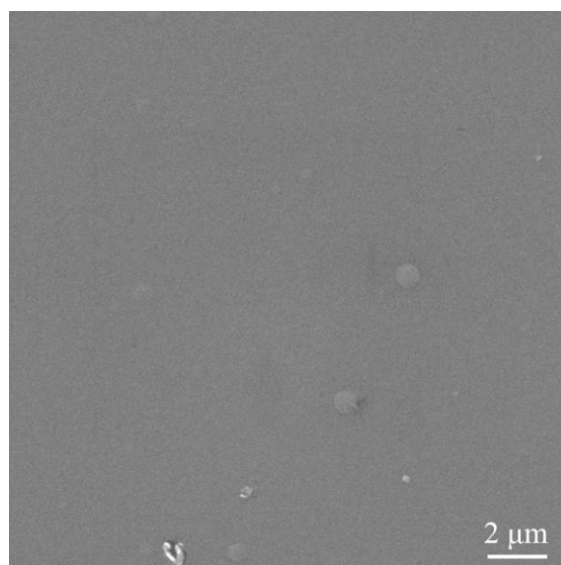


Figure 5. SEM images of PTE-MA.

3.6 Spectroelectrochemical study

Spectroelectrochemical study of PTE-MA was performed in blank $\text{CH}_2\text{Cl}_2\text{-Bu}_4\text{NPF}_6$ (0.1 mol L^{-1}) to evaluate its optical property and band gaps, as shown in Figure 6. Thin polymer film was deposited on transparent ITO-coated glass by potentiostatic method. In the reduced state, PTE-MA revealed an obvious absorption band, centered at 418 nm, which was attributed to $\pi\text{-}\pi^*$ transition of thiophene ring. Upon increase of potential applied to PTE-MA, the intensities of the absorption band at 418 nm decreased and a new polaron absorption band at 720 nm began to intensify. Further increase of potential, the polaron absorption band started to decrease, whereas a new absorption band in the near-infrared region appeared, demonstrating the transition from polaron to bipolaron. The color of PTE-MA turned from brown to gray simultaneously. In addition, the optical band gap of PTE-MA was calculated on the basis of the formula $E_g = 1240/\lambda_{\text{onset}}$, where λ_{onset} is the onset of $\pi\text{-}\pi^*$ transition. The value of the optical bandgap for PTE-MA was 2.32 eV, a little lower than that for polythiophene.

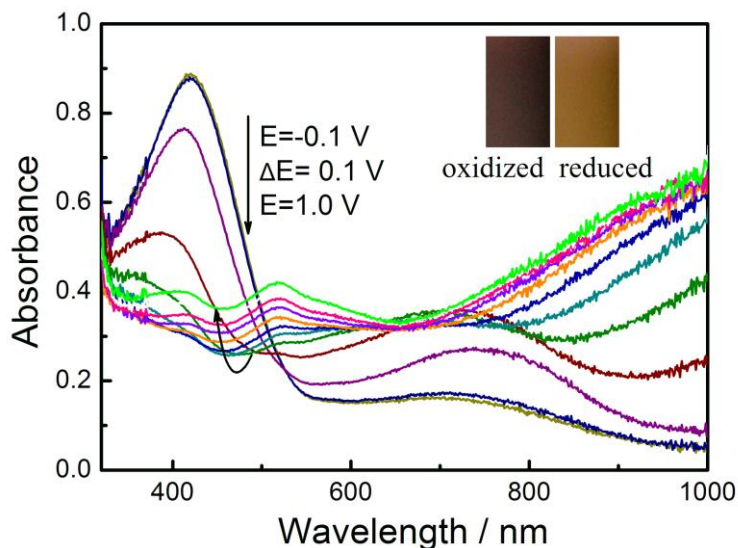


Figure 6. Spectroelectrochemistry and switching colors of PTE-MA on an ITO-coated glass in $\text{CH}_2\text{Cl}_2\text{-Bu}_4\text{NPF}_6$ (0.1 mol L^{-1}).

3.7 Electrochromic performance

The electrochromic study of PTE-MA was performed by optical spectroscopy combining with square wave potential step method in blank $\text{CH}_2\text{Cl}_2\text{-Bu}_4\text{NPF}_6$ (0.1 mol L^{-1}). The electrochromic parameters of PTE-MA, including optical contrast ratio (ΔT), response time and coloration efficiency (CE), were investigated with the changes in transmittance, as shown in Figure 7 and Table 1. The potentials applied on PTE-MA were changed alternatively between -1.0 V and 1.0 V for the switching time of 10 s .

PTE-MA showed 20% optical contrast in the visible region (420 nm) between -1.0 V and 1.0 V , which was especially significant when considering the use in window- or display-type devices. It can be seen that PTE-MA revealed 23% optical contrast at 900 nm .

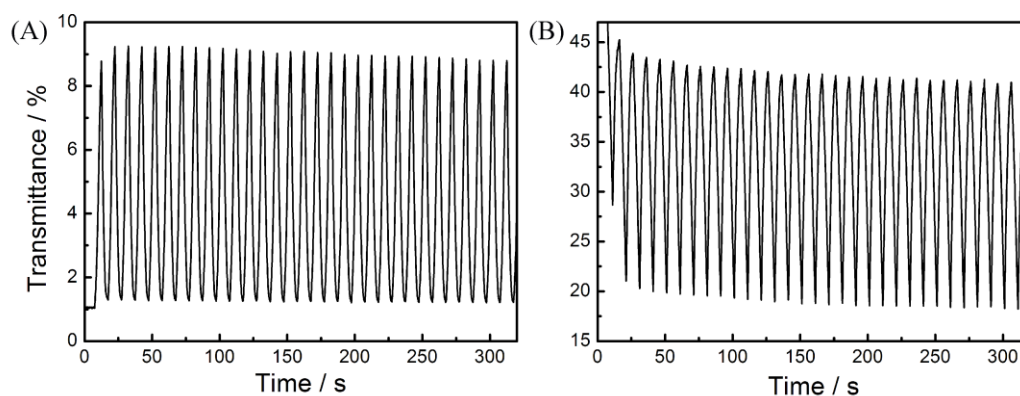


Figure 7. Transmittance monitored at 420 nm (A) and 900 nm (B) for PTE-MA between -1.0 V and 1.0 V for a switching time of 10 s .

It should be noted that PTE-MA switched rapidly and achieved 95% of its optical contrast in 1~5 s (Table 1). Especially, PTE-MA had more fast response times in reduction process relative to oxidization process (oxidation: 1.9 s at 420 nm, 4.6 s at 900 nm; reduction: 1.6 s at 420 nm, 3.8 s at 900 nm.). The behaviors demonstrated that these counterbalancing ions could pass through PTE-MA more easily during reduction process.

Coloration efficiency (CE), calculated on the basis of the following formulas $\Delta OD = \log(T_{ox}/T_{red})$ and $CE = \Delta OD/Q_d$, is also a significant criterion for identifying the performance of electrochromic material. CE of PTE-MA were calculated as $165 \text{ cm}^2 \text{ C}^{-1}$ (at 420 nm) and $112 \text{ cm}^2 \text{ C}^{-1}$ (at 900 nm), respectively (Table 1).

Table 1. Electrochromic parameters for PTE-MA

polymer	Wavelength/nm	$\Delta T/\%$	response time (s)		CE (cm^2/C)	λ/nm		E_g^a/eV
			oxidation	reduction		Abs. max	Abs. onset	
PTE-MA	420	20	1.9	1.6	165	418	535	2.32
	900	23	4.6	3.8	112			

^aThe data were calculated by the equation: $E_g = 1240/\lambda_{\text{onset}}$ of polymer film.

3.8 Stability of PTE-MA

The color persistence and stability is especially significant when considering the fabrication of electrochromic devices. The CV was used to evaluate the electrochemical stability of PTE-MA. After 1000 cycles, the electrochemical activity of PTE-MA remained 95% in $\text{CH}_2\text{Cl}_2\text{-Bu}_4\text{NPF}_6$, as shown in Figure 8A. Even after 4000 cycles, PTE-MA still had about 89% of electrochemical activity. It can be seen that the optical activity was preserved up 91% after 100 cycles (Figure 8B), consistent with electrochemical stability.

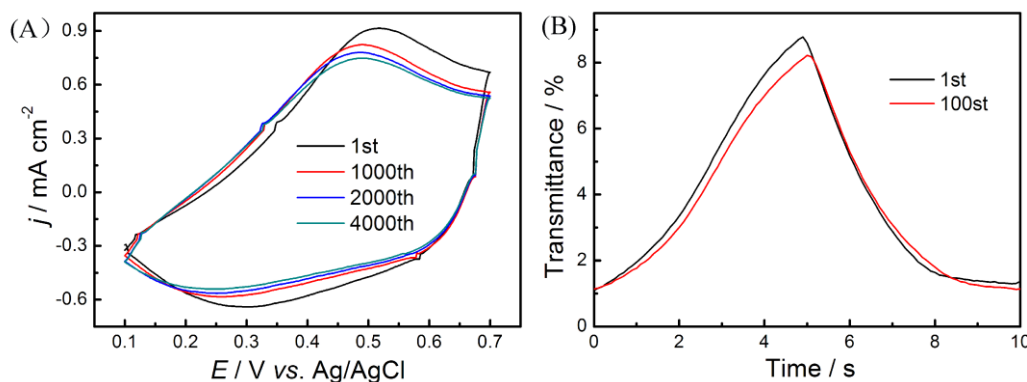


Figure 8. (A) Cyclic voltammograms of PTE-MA upon repeated cycling at the scan rate of 150 mV s^{-1} . (B) Optical activity of PTE-MA at 420 nm upon repeated cycling with the switching time of 10 s;

4. CONCLUSIONS

In conclusion, the synthesis and electrochemical polymerization of a methacrylate functionalized thiophene, TE-MA, was reported. Structure characterization and properties of the as-obtained polymer, including FT-IR, morphology, electrochemical, spectroelectrochemical and electrochromic properties, were also systematically investigated. Furthermore, PTE-MA exhibited good electrochromic performance, such as satisfactory optical contrast ratio (20% at 420 nm; 23% at 900 nm), high coloration efficiency ($165 \text{ cm}^2 \text{ C}^{-1}$ at 420 nm; $112 \text{ cm}^2 \text{ C}^{-1}$ at 900 nm) and fast response time. In addition, as-formed PTE-MA film showed compact morphology, good redox activity and stability, which indicate that PTE-MA is promising material for the fabrication and development of electrochromic device.

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