Electrochromic properties of methylol modified poly (3, 4-propylenedioxythiophene) and its copolymer with poly (3, 4-ethylenedioxythiophene)

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Abstract. A functionalized monomer (3, 4-dihydro-2H-thieno [3, 4-b] [1, 4] dioxepin-3-yl) methanol (ProDTM) was synthesized in one step and corresponding polymer PProDTM and copolymer of ProDTM-EDOT films were obtained by electrochemical deposition. Both PProDTM and copolymer films shown light blue in the oxidized state, while in the reduced state PProDTM and copolymer films shown purple and dark blue, respectively. The optical contrast of PProDTM and copolymer films reached 43.6% and 27.7%. In addition, the coloration efficiency of PProDTM and copolymer films reached 91.3 and 107.8 cm^2C^{-1}. The results of electrochemical and electrochromic property shown that the PProDTM and copolymer films potential application in electrochromic field.

Keywords: Electrochemistry, Electrochromic, Conducting polymer, PEDOT, PProDOT.

1. Introduction

As an interesting functional materials material, conducting polymer not only has conductivity like metal, but also has the advantages of easy processing, lightweight, processability, and flexibility as polymer materials. Through conduct charge via the alternating single and double bonds, conducting polymer has excellent electrochemical performance and attracted widespread attention and has great potential applications in the fields of electrochromic, supercapacitor, electrochemical, sensor, and so on. With further widely and deeply research of conducting polymers, various monomers have been synthesized, and tremendous amount of conducting polymers with unique performance were developed.

Among various conductive polymers, poly(3, 4-ethylenedioxythiophene) (PEDOT), is one of the most attractive materials with outstanding electrochemical activity [1]. During electrochemical redox process, PEDOT shown reversible color change which also known as electrochromic property. Making use of electrochromic property of PEDOT in flexible display, antiglare rear view mirror, smart window, more comfortable and safe travel and living environment has been provided. Side chain functional groups, polymer backbone planarity, length of conjugate chain and band gap jointly determine the and electrochromic properties of conducting polymer. Therefore, chemical structure modifications of PEDOT have become a significant research branch to offset its deficiency and further improve its electrochemical application value [2].

Propylenedioxythiophene (ProDOT) have an enhanced bulkiness of annulate dioxepane ring than EDOT, and shown improved electrochromic behavior as a result of appropriate steric hindrance. Through an inner-electro polymerization method, Chunye Xu’s group directly to prepare electrochromic devices by electrochemical polymerization of the 3, 4-(2, 2-dimethylpropylenedioxy) thiophene (ProDOT-Me_2) monomer inside the ECD cell. The obtained ECDs based on poly(3, 4-(2, 2-dimethylpropylenedioxy)-thiophene) (PProDot-Me_2) obtained a maximum transmittance contrast of 49% at 580 nm and excellent cycle stability over one million cycles [3]. Xiaoming Chen et al. synthesized a novel monomer based on ProDOT derivative with diethyl malonate pendant group and a cyclobutane spacer. Corresponding conducting polymer exhibits reversible color switching between navy and transmissive, high optical contrast 44.6% at 571 nm, good coloration efficiency of 103.94 cm^2/C and response time 3.5 s [4]. Through integrated polyhedral oligomeric silsesquioxane nanocage on ProDOT unit, Salih Ertan et al. reported a conducting polymer called PProDOT-POSS.

PProDOT-POSS shown optical contrast of 55% at 555 nm, high coloration efficiency 502 cm^2/C and reversible color switching from blue to violet [5].

Herein, we carefully investigate the electro polymerization behavior of (3,4-dihydro-2H-thieno[3,4-b] [1,4] dioxepin-3-yl) methanol (ProDTM) and obtained the corresponding PProDTM and copolymer of ProDTM-EDOT films. Additionally, multiple characterization techniques including spectral, morphological, electrochemical techniques, have been used to systematically investigate the electro polymerization behavior and the optoelectronic performances of the PProDTM and copolymer of PProDTM-PEDOT films.

2. Experimental section

2.1. Materials

3,4-dimethoxythiophene (98.0%, GC) and EDOT were purchased from Aladdin Industrial Inc. 2-hydroxymethyl-1,3-propanediol (97% GC) was purchased from Shanghai Vita Chemical Reagent Co., Ltd. p-toluene sulfonic acid and toluene were purchased from J&K Scientific Co., Ltd. Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, 98%) was purchased from Energy Chemical Reagent Co., Ltd. and dried under vacuum at 60°C for 24 h before use. Dichloromethane (DCM, AR) was purchased from Shanghai Vita Chemical Reagent Co., Ltd. and purified by distillation over calcium hydride before use. Indium tin oxide coated glass (ITO glass) was purchased from Zhuhai Kaivo Optoelectronic Technology Co., Ltd. ProDTM was synthesized as Figure1. The detailed experimental procedures are illustrated as follows:

3, 4-dimethoxythiophene (2.016 g, 14 mmol), 2 - (hydroxymethyl) - 1,3-propanediol (2.021 g, 18 mmol), *p*-toluene sulfonic acid (0.254 g, 1.5 mmol) and toluene (200 ml) were added into a 250 ml three necked flask, the mixture was refluxed for 72 hours. After the reaction liquid was filtered by diatomite, most of toluene in the reaction liquid was removed by vacuum rotary evaporator, and the concentrated liquid was extracted by dichloromethane and deionized water. The organic phase was dried for 8 hours by adding anhydrous sulfuric acid, and then the organic solution was removed by vacuum rotary evaporator. The crude product was purified by silica gel column chromato-graphy (petroleum ether: ethyl acetate = 3:1 (v: v) as eluent) to obtain 0.913g white solid with a yield of 35.4%. ^1H-NMR spectra of ProDTM shown in Figure 1.

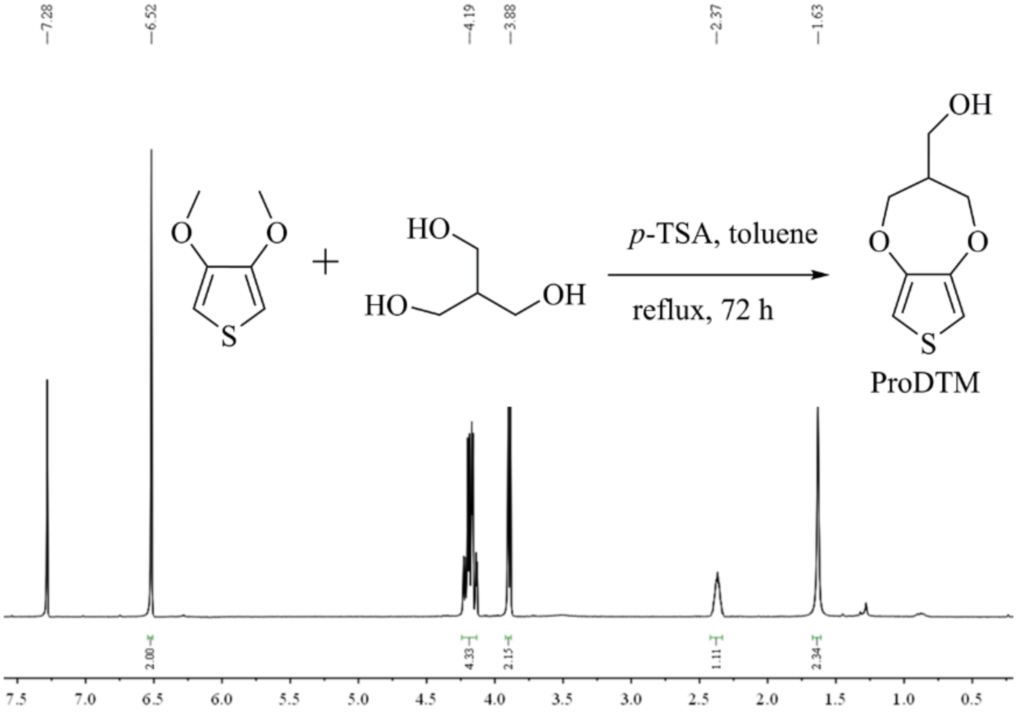

Figure 1. The synthetical route of ProDTM and ^1H-NMR spectra of ProDTM in $CDCl_3$

2.2. Characterization

^{1}H NMR spectra were recorded on a Bruker AV-400NMR spectrometer and tetramethylsilane was used as the internal standard to measure the chemical shifts. The spectral characteristics and surface morphologies of PProDTM films were further investigated by ultraviolet-visible (UV-vis, Analytik Jena) spectroscopy and scanning electron microscopy (SEM, JEOL JSM-6700F). Electrochemical studies were carried out on a CHI 660B (Shanghai Chenhua Instrumental Co., Ltd., China).

3. Results and Discussion

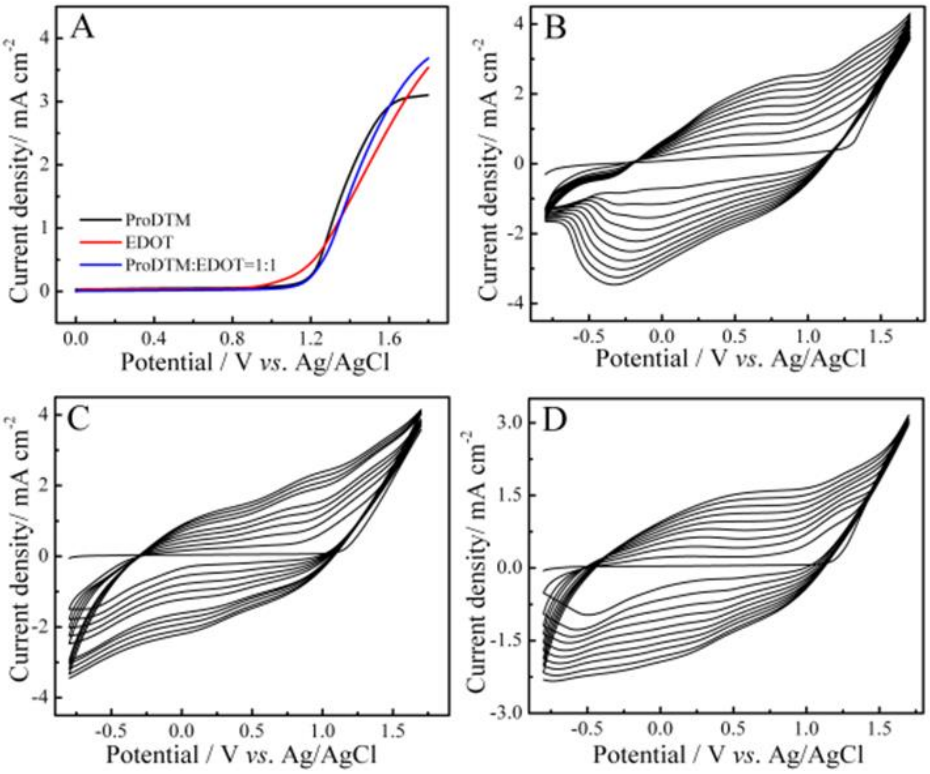

Figure 2. Anodic oxidation curve (A) and Cyclic voltammograms of ProDTM (B), EDOT (C), and copolymer (D). Supporting electolyte: 0.1 M Bu_4NPF_6; Monomer concentration: 0.01 M.

Due to the good solubility of ProDTM and EDOT in CH_2Cl_2, 0.1M CH2Cl2-Bu4NPF6 was selected as the electrolyte for electrochemical polymerization of ProDTM, EDOT and their copolymer. As shown in Figure 2A, the initial oxidation potential of ProDTM and EDOT were 1.23 V and 1.20 V, which indicated that the chemical structure modification of ProDTM didn't significantly increase the initial oxidation potential, ensure that EDOT and ProDTM could be copolymerized under similar electrodeposition conditions. As shown in Figure 2B and Figure 2C, the ProDTM and EDOT shown obvious nucleation process in the first cycle of potential scanning. Additionally, the redox peak current of ProDTM and EDOT increasing with cyclic voltammograms scanning. Meanwhile, corresponding conducting polymers were formed on the working electrode.

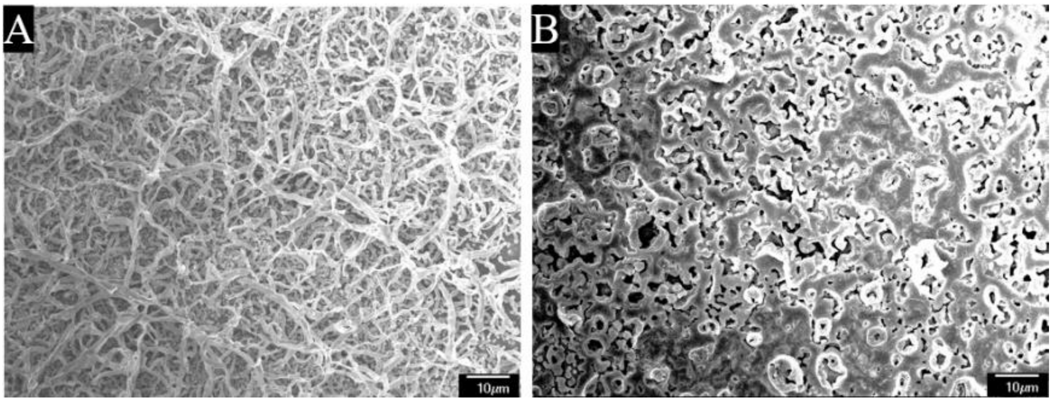

Figure 3. SEM images of PProDTM (A) and copolymer (B) on the ITO glass. Magnification: 1 000×.

As optoelectronic properties of conductive polymer materials usually attributable to their micro morphology. Therefore, scanning microscope (SEM) was used to analysed the morphology of PProDTM and copolymer films. As shown in Figure 3, the micro structure of PProDTM film was composed of polymer nanowire with different chains lengths, while the copolymer film shown porous structure. The nanowire structure of PProDTM film and porous structure of copolymer effectively increases the specific surface area and provided an effective path for the diffusion of electrolyte ions.

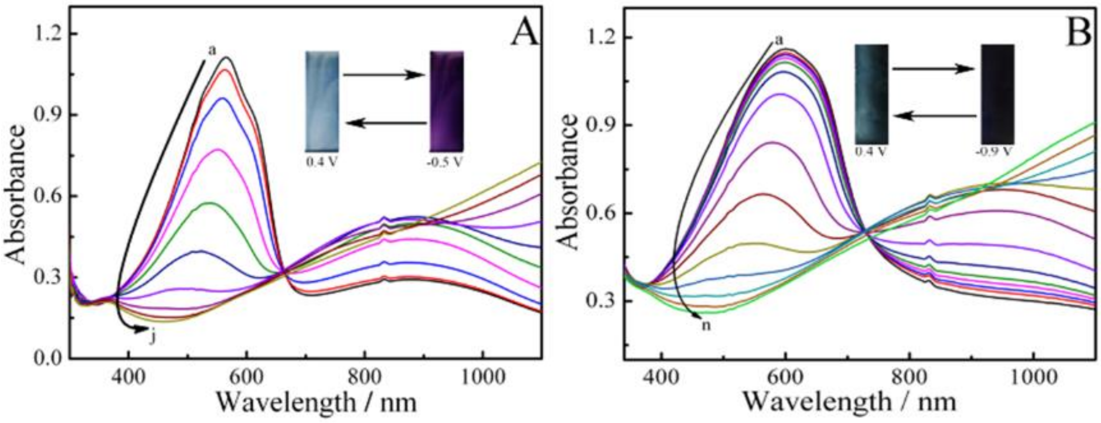

Figure 4. Spectro electrochemical spectra for PProDTM (A) and copolymer (B) on ITO glass.

The color of conducting polymer change with applied voltage, which is known as electrochromic phenomenon. To accurately describe the color changes of PProDTM and copolymer films, the Spectro electrochemical spectra of PProDTM films were recorded. As shown in Figure 4, the maximum absorption peak of the PProDTM film and copolymer films changes with the doping and de-doping reactions. The maximum absorption peak of PProDTM and copolymer films were at 850 and 900 nm under doping state. With the increasing of de-doping level, the absorption peak intensity of PProDTM and copolymer films at 850 and 900 nm decreasing, while the absorption peak of PProDTM and copolymer films at 580 and 600 nm increasing. During doping and de-doping reactions, doped PProDTM and copolymer films shown light blue, de-doped PProDTM films shown purple, de-doped copolymer films shown dark blue. As shown in Figure 4, the PProDTM and copolymer films shown obvious color change, which indicates that PProDTM and copolymer films have potential applications in the electrochromic field.

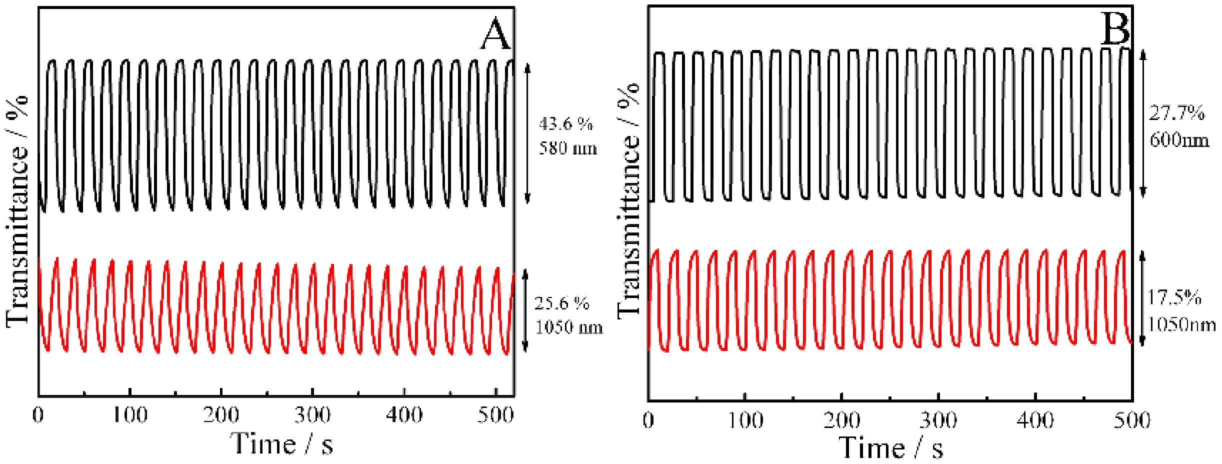

Figure 5. Transmittance-time profiles of PProDTM (A) and copolymer (B).

In order to evaluate the electrochromic ability of PProDTM and copolymer films, the transmittance time relationship of PProDTM and copolymer films were studied. As shown in Figure 5, the PProDTM and copolymer films converted between doping and de-doping state every 10 s, and the transmittance change of PProDTM and copolymer films were recorded. As shown in Figure 5, the optical contrast of PProDTM and copolymer films reached 43.6% and 27.7% at 580 nm, in addition ProDTM and copolymer films shown optical contrast 25.6% and 17.5% at 1050 nm. Response time was calculated according to the time required to reaching 95% of the maximum transmittance change between coloring or bleaching states. As shown in Table 1, PProDTM shown higher optical contrast while copolymer shown shorter response time. The coloration efficiency of ProDTM and copolymer films were also shown Table 1. to measure the relationship between the charge consumption and absorbance change of ProDTM and copolymer films. Polymers with higher coloration efficiency could switch color more effectively. As shown in Table 1, coloration efficiency of ProDTM in 580 nm and 1050 nm was 91.3 cm^2 C^{-1} and 91.3cm^2 C^{-1}, respectively. While coloration efficiency of copolymer in 600 nm and 1050 nm was 107.8 cm^2 C^{-1} and 210.2cm^2 C^{-1}, respectively.

Table 1. Electrochromic parameters for PPorDTM and copolymer

	Wavelength (nm)	T_{red} (%)	T_{ox} (%)	△T (%)	Response time (s)		CE (cm^{2}C^{-1})	Eg (eV)
					oxidation	reduction		
PProDTM	580	20.0	63.6	43.6	3.8	6.8	91.3	1.858
	1050	48.4	22.7	25.7	7.4	8.6	55.1	
Copolymer	600	37.9	66.0	28.1	1.8	3.2	107.8	1.700
	1050	28.6	9.7	18.9	3.6	7.0	210.2	

4. Conclusions

In summary, a monomer ProDTM was synthesized, corresponding polymer PProDTM and copolymer of ProDTM-EDOT films were obtained by electrochemical deposition. The similar initial oxidation potential of ProDTM and EDOT around 1.20 V ensure that EDOT and ProDTM could be copolymerized under similar electrodeposition conditions. Both PProDTM and copolymer films shown light blue in the oxidized state, while in the reduced state PProDTM and copolymer films shown purple and dark blue, respectively. The optical contrast of PProDTM and copolymer films reached 43.6% and 27.7% at their maximum absorption wavelength. In addition, the coloration efficiency of PProDTM and copolymer films reached 91.3 and 107.8 cm^{2}C^{-1} at their maximum absorption wavelength. In conclusion, the PProDTM and polymer films has good electrochemical and electrochromic properties, and has a good application prospect in electrochromic materials.

Acknowledgments

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