Synthesis, Characterization, and Redox and Electrochromic Behaviors of Poly(3-*n*-octyloxythiophene)

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ABSTRACT: Poly(3-*n*-octyloxythiophene), a conjugated polymer, which possessed solubility in common organic solvents, was synthesized by electrochemical polymerization in the presence of lithium perchlorate as the supporting electrolyte and sodium dodecyl sulfate as the surfactant in an aqueous medium. Characterizations of the intermediate, monomer, and polymer were performed by NMR spectroscopy, Fourier transform infrared spectroscopy, ultraviolet–visible spectroscopy, and gel permeation chromatography. The process of electrochemical polymerization and the electrochemical redox behaviors were investigated by cyclic voltammetry and the potentiostatic method. A poly(3-*n*-octyloxythiophene) film that was deposited on a platinum electrode was found to exhibit electrochromic behaviors, and it switched electrochemically between blue–green oxidized and dark red reduced states. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 120–125, 2008

Key words: conjugated polymers; electrochemistry; synthesis; UV–vis spectroscopy

INTRODUCTION

Electrochromic materials are able to sustain reversible and persistent changes of their optical properties upon the application of a voltage. Electrochromic materials have extensive applied prospects as intelligent materials and have been used for some devices.[1–3] In recent years, transition-metal oxides (e.g., WO_3[4,5]), small organic molecules (e.g., viologen[6,7]), some conducting polymers [e.g., Polypyrroles (PPys),[8] polyanilines,[9,10] and polythiophenes[11–13] have been intensively investigated for their electrochromic properties.[14] Conducting polymers as new materials have shown fine application prospects because of their advantages of light mass, extensive raw materials, and easy modification, and the research of their electrochromic properties is a hot topic in today's functional polymer studies. At present, the research on conducting polymers has mainly focused on insoluble polymers.[15] The processability of electrochromic polymers has always been a challenge because of the insolubility of conjugated polymers. Kumar and Reynolds[16] reported on organic, soluble poly(3,4-ethylene dioxythiophene), which was achieved via the polymerization of a tetradecyl-substituted 3,4-ethylene dioxythiophene with $FeCl_3$ as an initiator. A family of soluble, narrow band gap donor–acceptor conjugated polymers based on dioxy-thiophenes and cyanovinylenes was reported by Thompson et al.[17] These polymers were synthesized with Knoevenagel polycondensation or Yamamoto coupling polymerizations. Although these polymers exhibited solubility in organic solvents, their tedious multistep synthesis restricts their potential as materials of choice for organic, soluble electrochromic polymers. Recently, Mishra et al.[18] reported on a series of poly(3,4-alkylenedioxythiophene)s and the effects of substitution patterns on the electrochromic contrast. Poly(3-alkoxythiophene), which has strong electron-donating alkoxy groups as the side chain, has also been investigated,[19,20] and the electron-donating effect of the alkoxy group decreased the oxidation potential of these polymers and, consequently, stabilized the conducting states.[21] It has displayed promising electrical and optical properties. In these studies, poly(3-alkoxythiophene) was prepared from 3-alkoxy monomer by oxidative polymerization with $FeCl_3$ as a catalytic oxidizing reagent or by a Kumada cross-coupling reaction catalyzed by bis(diphenylphosphinopropane)nickel(II)dichloride. However, the electropolymerization and electrochromic properties have never been studied in detail. The electropolymerization of thiophene and its derivatives has generally been carried out in dry organic solvents.[22] The use of these solvents in industry for the realization of polythiophene thin conducting films presents serious drawbacks because of environmental and toxicological problems. It has been found that thiophene and its derivatives (e.g., 3,4-ethylene dioxythiophene and bithiophene) can also be electropolymerized in acid

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or sodium dodecyl sulfate (SDS) aqueous solutions.[23,24] In this article, we report on the synthesis and characterization of a kind of monosubstituted poly(3-alkoxythiophene) to study its electrochemical redox behaviors and electrochromic properties. Interestingly, the alkoxythiophene monomers were found to be partially soluble in aqueous solution containing electrolyte when SDS was added as a surfactant, and they could be electrochemically polymerized to yield a polymer with electrochromic properties, which possessed solubility in common organic solvents.

EXPERIMENTAL

Equipment

All electrochemical experiments were carried out with a ZF-9 potentiostat/galvanostat produced by Shanghai Zhengfang Electronic Apparatus, Ltd. (Shanghai, China) Two platinum plate electrodes (6×3 mm^2) were used as the working and auxiliary electrodes, and Ag/AgCl was used as a reference electrode. Ultraviolet–visible (UV–vis) spectra were recorded on a Purkinje General T6 spectrophotometer (Beijing, China) with a wavelength ranging from 210 to 1100 nm at a scanning rate of 1 nm/s. ^{1}H-NMR analyses were carried out on a Bruker Avance A II 400-MHz NMR spectrometer (Billerica, MA). The molecular weight analysis of the polymers was carried out on an Agilent1100 gel permeation chromatography instrument (Santa Clara, CA, USA) calibrated with linear polystyrene standards and eluted with tetrahydrofuran (THF). Infrared (IR) spectra were investigated with a Nicolet 560 Fourier transform infrared (FTIR) spectrometer (Waltham, MA, USA) from 4000 to 400 cm^{-1}.

Reagents and solutions

3-Bromothiophene (3-BrT; purity > 98%) was purchased from Zhejiang Shou and Fu Chemical (Jinyun, China). Lithium perchlorate, *p*-toluene sulfonic acid (*p*-TSA), SDS, and *n*-octanol were purchased from Kelong Chemical Reagent Co. of Chengdu (Chengdu, China). 3-BrT and *n*-octanol were used without further purification. *N*-Methyl-2-pyrrolidone (NMP), toluene, and THF were dried over sodium metal, and the last two chemicals were distilled under an inert atmosphere. All other chemicals were reagent-grade and were used without further purification.

Synthesis of the monomer

We prepared the intermediate, 3-methoxythiophene (MOT), by a nucleophilic substitution reaction following the early methods of Keegstra.[25] The substituted thiophene monomer, 3-*n*-octyloxythiophene (OOT), was synthesized by a transetherification reaction between MOT and *n*-octanol in the presence of a catalytic amount of *p*-TSA in toluene according to the literature.[26]

Preparation of MOT

In a 250-mL, three-necked, round-bottom flask equipped with a thermometer and an anhydrous calcium chloride drying tube, 16.2 g (300 mmol) of solid sodium methoxide was dissolved in 30 mL of methanol and 50 mL of NMP. The reaction mixture was heated to 110°C, and methanol was distilled off. Subsequently, 32.6 g of 3-BrT (200 mmol) and 2.9 g of Copper (I) bromide (20 mmol) were added. The addition of the catalyst resulted in a vigorous reaction, and the heating was interrupted until the temperature dropped to 110°C again. After 45 min, thin-layer chromatography indicated that the substrate was completely converted. The reaction mixture was cooled to room temperature, and 200 mL of saturated aqueous sodium chloride solution was added under vigorous stirring. The product was extracted by washing with methylene chloride (4×50 mL). The combined organic layers were dried over anhydrous magnesium sulfate, after which the solvent was distilled off at atmospheric pressure and then purified by column chromatography; the reaction afforded MOT in a 79.0% yield.

^{1}H-NMR (CDCl$_3$, ppm): 3.84 (s, 3H), 6.27–6.28 (s, 1H), 6.77–6.79 (d, 1H), 7.19–7.22 (d, 1H). IR (KBr, cm^{-1}): 3116, 2952, 1547, 1447, 1396, 1239, 1204, 1160, 1074, 1034, 935, 871, 828, 756, 659, 627. UV–vis (ethanol, nm): 223, 251.

Synthesis of OOT

MOT (1.596 g, 14 mmol) was added to dry toluene (20 mL); to this solution, *n*-octanol (2.210 g, 17 mmol) and *p*-TSA (0.241 g, 1.4 mmol) were added. The mixture was allowed to stir for 48 h at 100°C with a continuous flow of nitrogen through the reaction mixture. Excess solvent was evaporated, and the residue was purified by column chromatography with a pet ether/ethyl acetate mixture (20 : 1) to produce a colorless liquid with a 94.6% yield.

^{1}H-NMR (CDCl$_3$, ppm): 0.97 (t, $J = 7.4$ Hz, 3H), 1.31–1.36 (m, 8H), 1.43–1.50 (m, 2H), 1.75–1.82 (m, 2H), 3.96 (t, $J = 12.8$ Hz, 2H), 6.24–6.25 (s, 1H), 6.76–6.78 (d, 1H), 7.17–7.20 (d, 1H). IR (KBr, cm^{-1}): 3119, 2927, 2856, 1545, 1464, 1422, 1374, 1235, 1175, 1073, 872, 831, 752, 683, 625. UV–vis (ethanol, nm): 222, 253.

Electropolymerization

The electrochemical polymerization of OOT was carried out in a one-compartment, three-electrode cell containing 0.02M OOT, 0.07M SDS, and 0.1M lithium perchlorate (LiClO$_4$) in water. For cyclic voltamme-
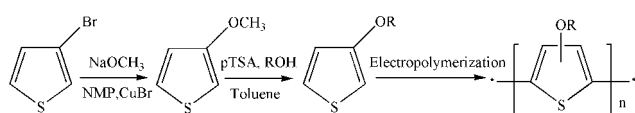
Scheme 1 Synthetic strategy for poly(3-alkoxythiophene) (R = C_8H_{17}).

try, at a scanning rate of 100 mV/s, a platinum plate was used as the working electrode. Another platinum plate counterelectrode and an Ag/AgCl reference electrode were used. After electrochemical polymerization, the thin poly(3-n-octyloxythiophene) (POOT) film on platinum electrode was washed with water several times to remove unreacted monomer and dried under nitrogen atmospheric conditions. All experiments were conducted in laboratory air at room temperature.

^{1}H-NMR (CDCl$_3$, ppm): 0.70–1.00 (m, 3H), 1.00–1.70 (m, 10H), 1.70–2.00 (m, 2H), 4.02–4.14 (m, 2H), 6.85–7.01 (m, 1H). IR (KBr, cm^{-1}): 2923, 2853, 1461, 1375, 1291, 1261, 1079, 1017, 801, 723.

RESULTS AND DISCUSSION

Synthesis and characterization of the monomer and polymer

The synthetic route is shown in Scheme 1. The intermediate MOT was prepared from 3-BrT by the nucleophilic substitution reaction, and the monomer 3-octyloxythiophene was synthesized by a transetherification reaction between the intermediate and n-octanol in the presence of a catalytic amount of p-TSA in toluene. The ^{1}H-NMR spectra of MOT and OOT are shown in Figure 1. There were three peaks in the aromatic region (δ = 6.24–7.20 ppm) for the protons of the thiophene ring. For both MOT and OOT, the peaks of protons approaching the oxygen atom appeared between 3.80 and 4.00 ppm. For OOT, the proton chemical shift (δ) values of the alkyl chain were between 0.89 and 1.80 ppm. The FTIR spectra of 3-BrT, MOT, OOT, and POOT are shown in Figure 2. The C—Br stretching vibration band was observed at 585 cm^{-1} for 3-BrT but was missing in the spectrum of MOT, whereas the CH$_3$ asymmetric and symmetric stretching bands occurred from 3000 to 2825 cm^{-1} in it. In the spectrum of MOT, the absorption bands of C—O—C coupled with C$_\alpha$—H and C$_{ring}$—O—C bending modes appeared at 1160 and 1034 cm^{-1}, respectively. All of these indicated that substituted product was synthesized. Another significant difference appeared for the thiophene ring deformation and asymmetric stretching bands. In the spectrum of 3-BrT, the ring asymmetric stretching band at 1494 cm^{-1} was very strong, but it almost disappeared in the spectrum of MOT, where a strong ring

deformation band had arisen at 1547 cm^{-1}. This occurred because the electron-withdrawing group bromine atom was substituted by methoxyl, which was a electron-donating group. Comparing the FTIR spectrum of OOT with MOT, we observed the most remarkable changes at 2927, 2856, 1464, and 1422 cm^{-1}, which were the asymmetric, symmetric, and bending absorption bands of CH$_3$ and CH$_2$.

Sakmeche[24] reported on polybithiophene and poly(3,4-ethylene dioxythiophene), which were achieved via electropolymerization in aqueous SDS solutions on a Pt electrode. In our research, we found out that 3-octyloxythiophene could also be polymerized in a similar medium because the oxidation potential of 3-octyloxythiophene is similar to that of bithiophene and 3,4-ethylene dioxythiophene. 3-Octyloxythiophene was electrochemically polymer-
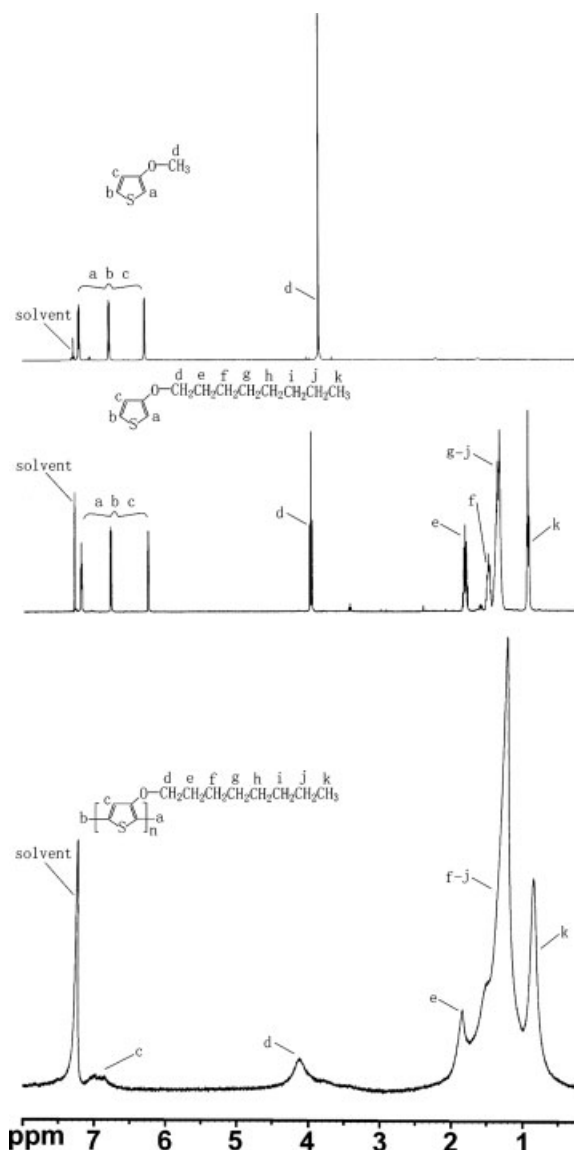

Figure 1 ^{1}H-NMR spectra of MOT, OOT, and POOT.
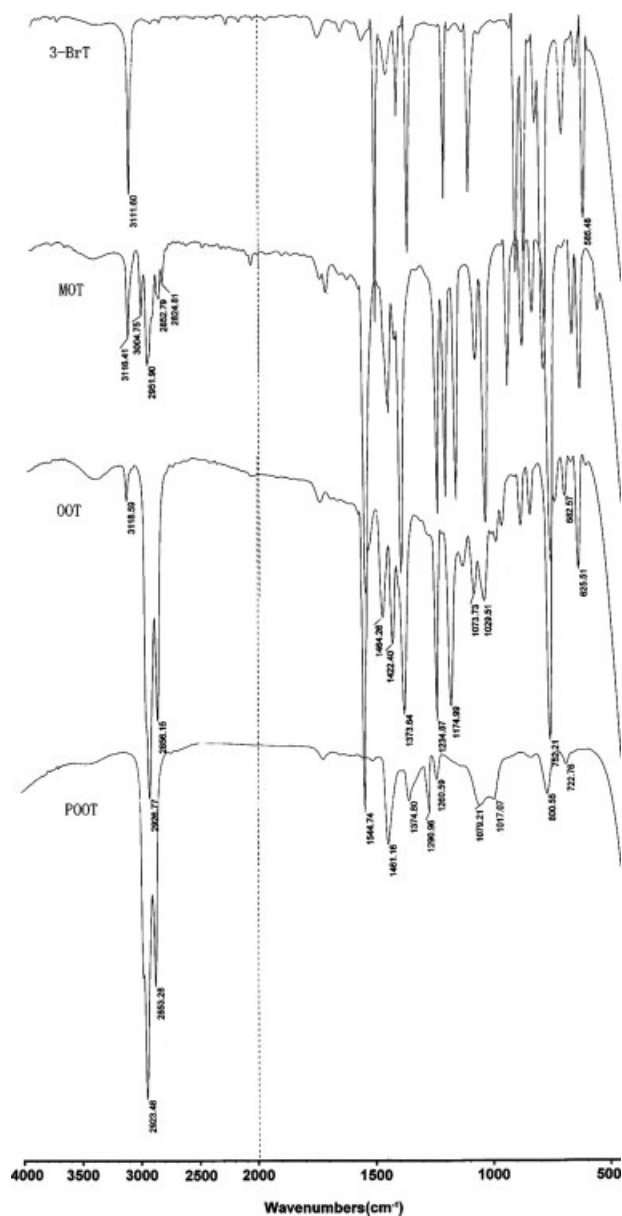
Figure 2 FTIR spectra of 3-BrT, MOT, OOT, and POOT.

ized from a solution containing 0.02*M* monomer and 0.1*M* LiClO$_4$ as a supporting electrolyte in an aqueous SDS (0.07*M*) micellar solution. The ^{1}H-NMR of POOT is shown in Figure 1, and the FTIR spectrum of POOT is shown in Figure 2. In the ^{1}H-NMR spectrum of POOT (Fig. 1), there was a small wide peak in the aromatic region (δ = 6.85–7.01 ppm) for the 4-position hydrogen of the thiophene ring. Because monoalkoxythiophene is not a symmetrical molecule, there are three relative orientations available when two thiophene rings are coupled between the 2- and 5-positions. The polymer may include three possible regiochemical couplings: head-to-tail (HT), tail-to-tail (TT), and head-to-head (HH). The wide peak of the ^{1}H-NMR spectrum was attributed to the four kinds of configuration triads: HT–HT, TT–HT, HT–HH, and

TT–HH.[27] In the FTIR spectrum of POOT (Fig. 2), the bands at 2923, 2853, 1461, and 1374 cm^{-1} were contributed by the asymmetric, symmetric stretching, and out-of-plane deformations of CH$_3$ and CH$_2$. The bands at 1261 and 723 were attributed to thiophene ring and C—S—C deformation, and the absorption bands at C$_{ring}$—O—C bending modes appeared at 1079 and 1017 cm^{-1}, respectively.[28] Electrochemically synthesized POOT could be dissolved by the dipping of the polymer-coated electrode in chloroform, THF, and methylene chloride. The weight-average molecular weight of POOT was 1700, whereas the polydispersity index was 1.36. The weight-average molecular weight was smaller, and the polydispersity index was larger than that of the soluble polythiophene derivatives synthesized by Mishra et al.[18] The adoption of different polymerization media may contribute to these differences.

The polymer, POOT, was prepared by electropolymerization in a potentiodynamic mode. The cyclic voltammograms and current–time curves were recorded during the polymerization, as shown in Figure 3. The electrode potential was swept from −800 to +1200 mV to monitor the electroactivity of OOT in the aqueous solution. The OOT monomers were electrooxidized and electropolymerized at potentials higher than 1000 mV versus Ag/AgCl. After the first cycle, there was a polymer oxidation peak at 400 mV and a reduction peak at 100 mV in the cyclic voltammogram. The currents of the redox peaks increased with the increase in scanning cycles. After 22 scanning cycles, the oxidization potential of the polymer was positively shifted to 550 mV, whereas the reduction potential was negatively shifted to 0 mV. These changes were due to the increase in polymer resistance following the increase in the film thickness and possibly to the increase of average polymerization degree along with the development of polymer. The
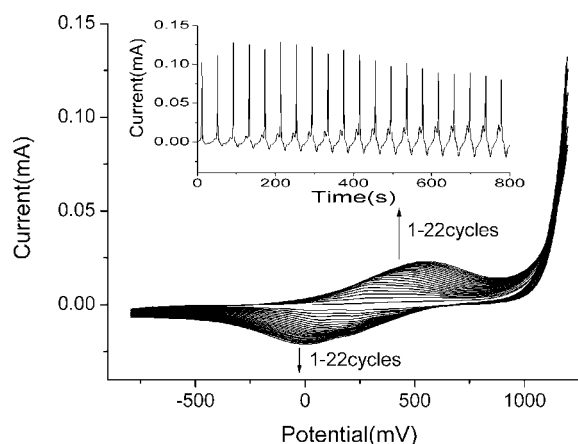

Figure 3 Cyclic voltammogram of the electropolymerization of OOT in an aqueous medium. The inset shows the current–time curve of POOT polymerization.
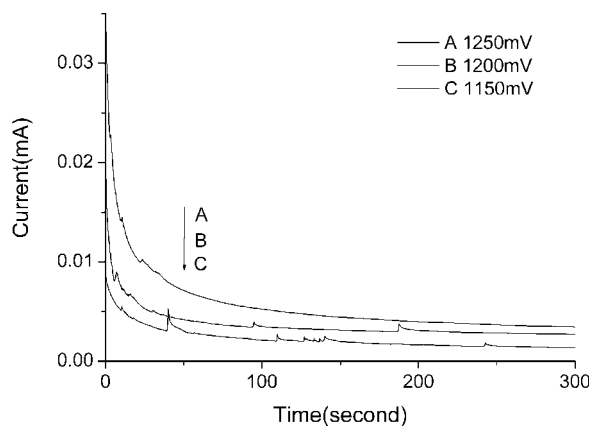
Figure 4 Potentiostatic current–time transient for the deposition of POOT in an aqueous medium.

Figure 5 Scanning rate dependence of POOT: (a) 5, (b) 10, (c) 20, (d) 50, (e) 100, and (f) 200 mV/s.

fluctuation tendency of the polymerization peak currents was shown in the current–time curve of polymerization (Fig. 3, inset). This indicated that the electrochemical nucleation and growth of POOT were proceeded through a two-dimensional (2D) layer-by-layer mechanism under cyclic voltammetric conditions in the aqueous solution. This process took place on top of the first monolayer deposited via oxidative adsorption of the OOT monomer on a bare Pt surface before polymerization, and following this, the growth rate in the parallel direction of the electrode was greater than that in the perpendicular direction.[29,30] The same conclusion was reached from the current–time curves under potentiostatic conditions (Fig. 4). As shown in Figure 4, many current peaks were found in the current–time curves, which were gained by potentiostatic polymerization at alternative potentials. The observation of several well-resolved current peaks clearly indicated the nature of a 2D layer-by-layer deposition. A subsequent visual check confirmed that the uniform polymer films had been deposited over the whole electrode surface.

Polymer electrochemistry

The redox behavior of the POOT polymer was studied through the recording of cyclic voltammograms at different scanning rates between −550 and +850 mV in 0.1M LiClO$_4$ in water (Fig. 5). The linear relationship between the peak current and the scanning rate indicated the formation of a redox-active and well-adhered polymer on the electrode, and that was indicative of a surface-confined redox process that was nondiffusion limited.[31] The Potential Difference of the Redox Peaks (ΔE_p) values of the polymer film increased with increasing scanning rate, which indicated that the redox process of the polymers was quasireversible.[18] In this study, cyclic voltammetry was exploited as a method for evaluating the stability of the polymer. For this purpose, we accom-
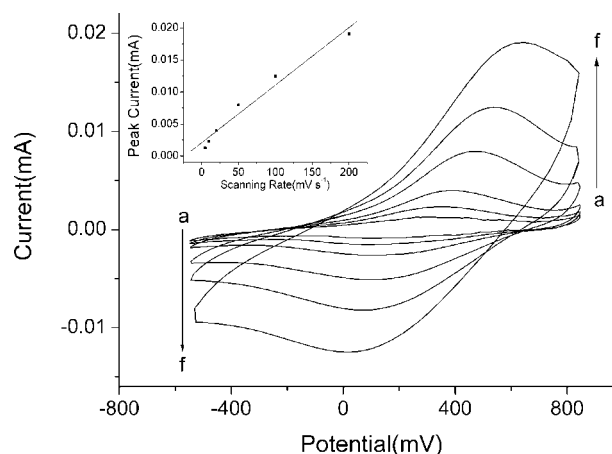
plished nonstop cycling of the applied potential between −550 and +850 mV at a scanning rate of 100 mV/s. As shown in Figure 6, even after 500 cycles, the peak currents showed only a slight decrease with a rate of 0.068% every cycle. The peak positions at +540 and +60 mV almost had no change. These results showed that POOT had a favorable and long-term redox stability in the aqueous solution, which makes it a promising material for future applications. We are trying to study the causes of the decreasing peak currents and are focusing on developing a device possessing a finer redox stability when it works in anhydrous conditions.

Electrochromism

The POOT films obtained by electropolymerization were used to perform electrochromic experiments in
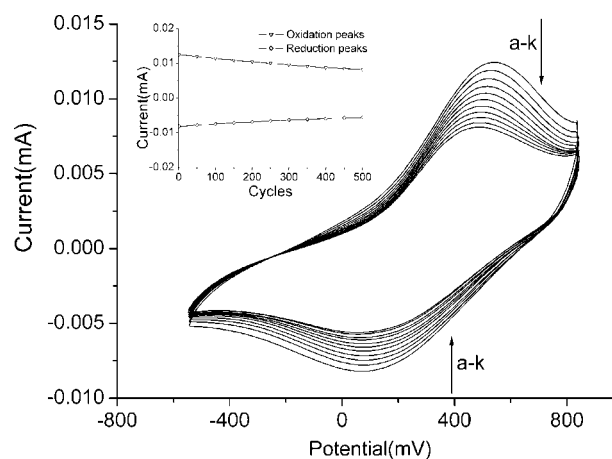

Figure 6 Cyclic voltammogram of POOT for 500 recycling cycles (scanning rate = 100 mV/s): (a) 1st, (b) 50th, (c) 100th, (d) 150th, (e) 200th, (f) 250th, (g) 300th, (h) 350th, (i) 400th, (j) 450th, and (k) 500th cycles. The inset shows the oxidation and reduction peak currents of POOT for 500 recycling cycles (scanning rate = 100 mV/s).
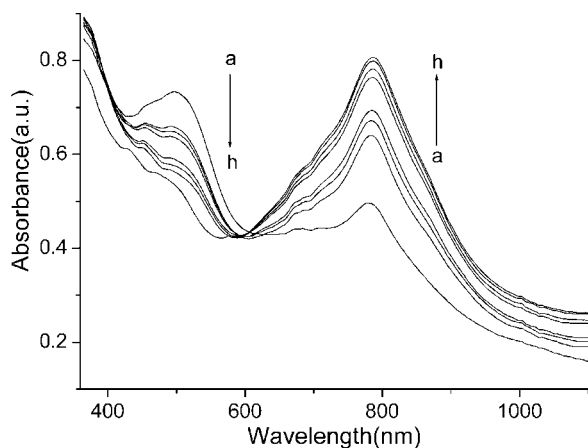
Figure 7 UV–vis absorption spectra of POOT in THF at applied potentials of (a) −550, (b) −400, (c) −200, (d) 0, (e) 200, (f) 400, (g) 600, and (h) 800 mV.

a 0.1M LiClO$_4$/water solution free of monomer. Before recording absorption spectra, we conditioned the films by applying specific potentials between −550 and +850 mV versus an Ag/AgCl electrode. After the chosen potential was exerted for 3 min to the electrode, the polymer film was dried under nitrogen atmospheric conditions and dissolved in THF to test the UV–vis spectra (Fig. 7). The color of the polymer film on the platinum electrode was blue–green when it was in its oxidation state (between +400 and +850 mV) and dark red in its reduction state (between −550 and +200 mV). Figure 7 shows the absorption spectra of the POOT films at various potentials. A peak was observed at 500 nm when the applying potential was −550 mV, at which potential the polymer was in a completely reduced state. A peak was observed at 780 nm when the applying potential was at +850 mV, at which potential the polymer was in a completely oxidized state. The wavelengths of the absorption peaks were corresponsive to the colors of electrode surface in both states. Cyclic voltammogram experiments showed that the color changes of electrode surface depended on the changes in the electrode potentials and the appearance of redox peaks. All of these experiment results show that the POOT film deposited in the aqueous solution had a good electrochromic performance.

CONCLUSIONS

In our study, soluble conjugated polymer based on 3-alkoxythiophene was synthesized by electrochemical polymerization in an aqueous medium. Cyclic voltammetric and potentiostatic study found out that the electrochemical deposition of POOT proceeded via a mechanism of 2D layer-by-layer nucleation and growth in this medium. The electrochromic properties of these polymers were studied by cyclic voltam-

metry and UV–vis spectra. The oxidation and reduction potential of POOT were observed at +540 and +60 mV (vs Ag/Ag$^+$), respectively. After 500 cycles of scanning with cyclic voltammetry between −550 and +850 mV, the peak currents decreased, whereas the peak position had almost no change. The color of the POOT film on the platinum electrode was blue–green in its oxidation state and was dark red in its reduction state, in accordance with the UV–vis spectra behaviors.

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