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Electrochemical Synthesis of Poly (3-octylthiophene) in a Room Temperature Ionic Liquid and its Application in an Electrochromic Device

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Poly(3-octylthiophene) (POcT) was electrochemically synthesized via galvanostat method by using ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM]PF_6) as the growth medium and the supporting electrolyte. The thin film of POcT was orange yellow in its fully reduced state. After oxidization of the undoped polymer, the film underwent a reversible change to the dark blue form. Spectroelectrochemical analysis of POcT at various doping levels confirm the bipolaron band structure and a starting π-π^* interband transition around 1.94 eV. Moreover, a POcT film based electrochromic device (ECD) was constructed and its electrochromic properties were also investigated in this paper.

Keywords: Electrochemical synthesis, Ionic liquids, Electrochromic device (ECD), Poly(3-octylthiophene)

1. INTRODUCTION

Electrochromism is defined as the reversible and visible change in transmittance and/or reflectance that is associated with an electrochemically induced oxidation-reduction reaction after the application of an appropriate electrode potential [1]. Because of their low power consumption and high coloration efficiency, electrochromic devices have many potential applications such as smart windows [2], switchable mirrors [3], and information displays [4].

Ionic liquids are room temperature molten salts and have been put in a wide range of synthetic application as green solvents during the past decade for their good chemical and physical properties [5]. Rogers *et al.* predicted on 2003 Science that the next decade should see ionic liquids being used in many applications where conventional organic solvents are used today. Furthermore, ionic liquids will enable new applications that are not possible with conventional solvents [6]. Ionic liquids are also ideal electrolytes as they simultaneously satisfy the requirements of wide electrochemical windows (typically over 4 V wide), high ionic conductivity, fast ion mobility during redox events, low volatility, non-flammability and possess excellent thermal and chemical stability [7].

Conducting polymers stand for a family of important electrochromic material that have gained popularity due to their unique advantages, such as low cost, good processibility, flexibility for large-area application, and the ability to modify their structure to create multicolor electrochrome [8]. Although poly(3-methylthiophene) (PMeT) exhibits distinct electrochromism, the insolubility of this material is a disadvantage for its technological application [9]. Thus, increasing attention is currently devoted to poly(3-alkylthiophene)s bearing long and flexible alkyl side chains, which render the materials soluble and, in consequence, processable. However, it is difficult to obtain their high quality films in traditional organic solutions.

In the present study, POcT was electrochemically synthesized by galvanostat method via using air and moisture stable ionic liquid [BMIM]PF_6 as the growth medium and the supporting electrolyte. Characterizations of the POcT were performed by cyclic voltammetry (CV) and spectroelectrochemistry. In addition, a POcT film based electrochromic device (ECD) was constructed and its electrochromic properties were also observed.

2. EXPERIMENTAL PART

2.1. Materials

3-octylthiophene (OcT) was purchased from Aldrich and was not distilled before use. The ionic liquid [BMIM]PF_6 was synthesized in our lab following a procedure described in the literature [10] and thoroughly dried and degassed before use. All chemicals were of analytical grade.

2.2. Instrumentation

All electrochemical experiments were performed on CHI660C electrochemical working station (CHI, Chenhua, Shanghai, China). Spectroelectrochemical studies were carried out on a Cary 50 scan UV-Vis spectrophotometer (Varian, Australia).

2.3. Procedures

2.3.1. Electrochemical synthesis

The electropolymerization of OcT (0.1mol/L) in 5mL ionic liquid [BMIM]PF_6 was achieved by galvanostat method. All electrochemical experiments were carried out in a three-electrode one-compartment electrochemical cell in the nitrogen atmosphere. The working electrode was indium-tin-oxide (ITO) coated glass (1×5 cm^2). Platinum sheet (1×1 cm^2) and Ag/AgCl/3M KCl were employed as the counter electrode and the reference electrode, respectively. Before electropolymerization, the working electrode was carefully polished with 0.05 μm Al_2O_3 and rinsed with acetone, ethanol and water successively, then dried in a vacuum oven for 30 min.

2.3.2. Spectroelectrochemistry

POcT was electrochemically synthesized on ITO in ionic liquid [BMIM]PF_6 by galvanostat method to control charge density of 108 mC cm^{-2}. After electrochemical polymerization, the polymer film was washed with acetone for several times to remove unreacted monomer and dried under atmospheric condition. Polymer film deposited on ITO was used for spectroelectrochemistry measurements in pure ionic liquid [BMIM]PF_6 with a Ag/AgCl/3M KCl as the micro reference electrode and a Pt wire as the auxiliary electrode.

2.3.3. Fabrication of ECD

The POcT based solid ECD was constructed with a multilayer device structure consisting of glass/ ITO/ POcT/ polymer electrolyte/ ITO/ glass. The polymeric electrolyte was prepared by using $LiClO_4$: ACN: PMMA: PC in the ratio of 3: 70: 7: 20 by weight. After $LiClO_4$ was dissolved in ACN, PMMA was added into solution. To dissolve PMMA, vigorous stirring and heating was required. PC, as a plasticizer, was introduced to the reaction medium when all of the PMMA was completely dissolved. The mixture was stirred and heated until the highly conducting transparent gel was produced [11].

3. RESULTS AND DISCUSSION

3.1. Electropolymerization and electrochemical characterization

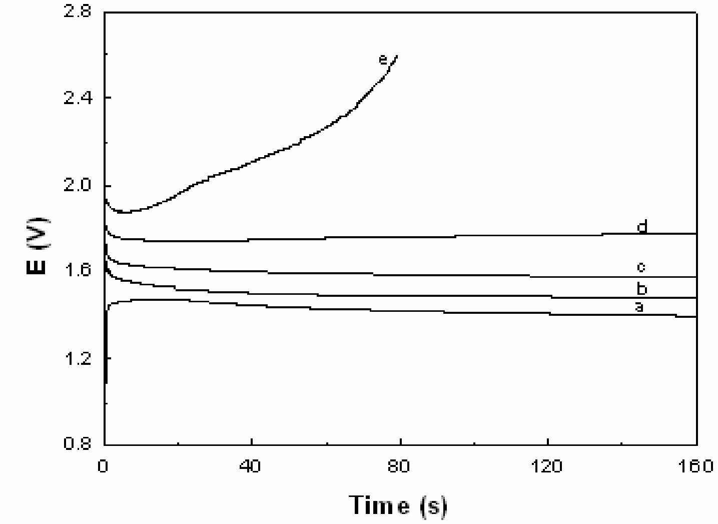


Figure 1. Chronopotentiometric curves obtained during galvanostatic polymerization of ClT in [BMIM]PF_6 at the different current densities: (a) 0.09 mA cm^{-2} (b) 0.18 mA cm^{-2} (c) 0.36 mA cm^{-2} (d) 0.72 mA cm^{-2} (e) 1.25 mA cm^{-2}

Chronopotentiometry (Figure 1) was used to determine the best condition during the galvanostatic electropolymerization of OcT in [BMIM]PF_6. Current densities between 0.09 and 0.72

mA cm^{-2} yielded a controlled growth of the polymer (Figure 1(a-d)) by the stability of the potential measured at the electrode. However, the potential changed markedly and did not achieve the stable value but increased above 2V as the current density was increased to 1.25 mA cm^{-2} (Figure 1e). Below 0.09 mA cm^{-2}, no homogeneous film was obtained. Note that during a controlled film growth although a high current density gives the fastest growth, it is usually preferable to proceed at a lower current density in order to form films with a less porous morphology [12]. Therefore, in order to combine good film quality and a reasonable rate of polymerization, a current density of 0.36 mA cm^{-2} for 300s was used for film prepared for the following experiment.

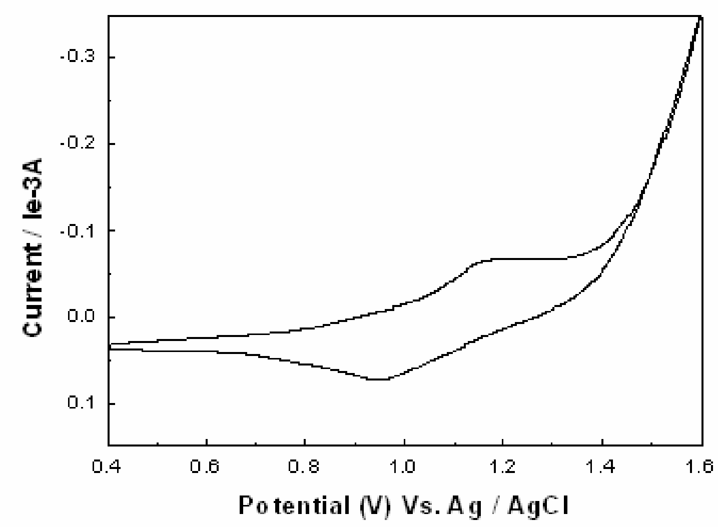


Figure 2. Electrochemical characterization of the POcT film in pure [BMIM]PF$_6$. The scan rate was 50mV s^{-1}

Typical cyclic voltammograms of POcT film in [BMIM]PF$_6$ was shown in Figure 2. As can be seen, POcT film showed one pair of well-pronounced cathodic and anodic peaks in the range of 0.9-1.2V. The electrode potentials of these peaks equal 0.94 and 1.16 V, respectively. Meanwhile the film also showed electrochromic properties: at the oxidized state the coloration of the film was orange yellow, and at the reduced state it was almost dark blue.

3.2. Spectroelectrochemical analysis

Spectroelectrochemical analyses were studied to examine the change in optical properties which is important in understanding the electronic structure of material and in examining the optical changes upon doping. Also, it gives some insight into a polymer color through the location of the absorption maxima and intensity of the peak on the main π-π* peak. Figure 3 showed a series of optoelectrochemical spectra of POcT between its reduced and oxidized forms with incremental increase in applied potential. In the reduced state at 0.4 V the λ_{max} value for the π-π* transition was at 440 nm and the film appeared an orange yellow color. Upon increase in the applied potential progressively, the color of the film easily changed to dark blue and evolution of polaron charge carriers characterized by the peak at 785 nm was observed, while the intensity of the π-π* transitions decreased. Further oxidation, it appeared absorption at longer wavelength (>1100 nm) which was due to the formation of bipolaron change carriers. The electronic band gap is defined as the onset energy for the π-π* transition and the value was 1.94 eV for POcT.

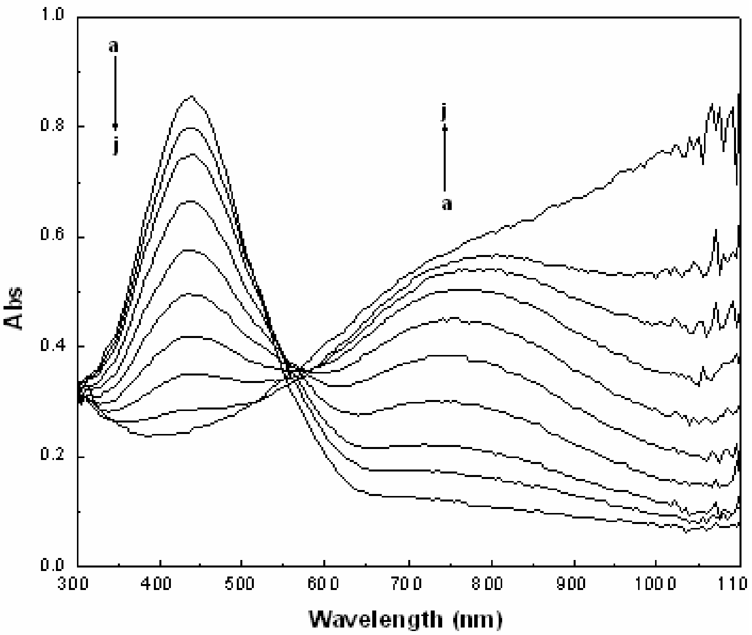
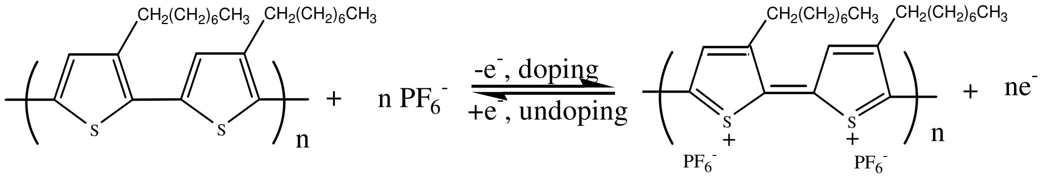


Figure 3. Spectroelectrochemistry of POcT (synthesized in [BMIM]PF_6 galvanostat on ITO) in pure ionic liquid [BMIM]PF_6. Spectra were recorded at the following potentials: a: 0.4, b: 0.8, c: 0.9, d: 1.0, e: 1.1, f: 1.2, g: 1.3, h: 1.4, i: 1.5, j: 1.6V vs Ag/AgCl.

3.3. Mechanism of electrochromism

Figure 4 can help us to understand the electrochromic phenomenon of POcT. In the oxidized state, conducting polymer was charge-balanced, doped with counter anions (PF_6^-) and had a delocalized π-electron band structure. The doping process modifies the electronic band structure of the polymer by producing new electronic state that causes the color change. The thin film was dark blue at its fully oxidized state. Reduction of doped POcT, with concurrent counter anion exit, removed the electronic conjugation to give the undoped (neutral) electrically insulating form. The thin film was orange yellow at this state.



(reduced state, orange yellow) (oxidized state, dark blue)

Figure 4. Electrochromism for POcT. The orange yellow (undoped) form undergoes reversible oxidation to the dark blue (doped) form, with insertion of charge-compensating anions (PF_6^-)

3.4. Electrochromic properties of ECD

3.4.1. Spectroelectrochrmistry of ECD

In this study, we successfully constructed a POcT based solid ECD (glass /ITO /POcT / electrolyte /ITO /glass). Spectroelectrochemical studies were carried out to examine the optical properties of the ECD upon doping or undoped form. The ECD was in its reduced (undoped) state at -2.0V with an orange yellow color. Then the ECD changed to dark blue in most oxidized state at +2.2 V. The color can be change reversibly. The corresponding spectroelectrochrmistry was showed in Figure 5.

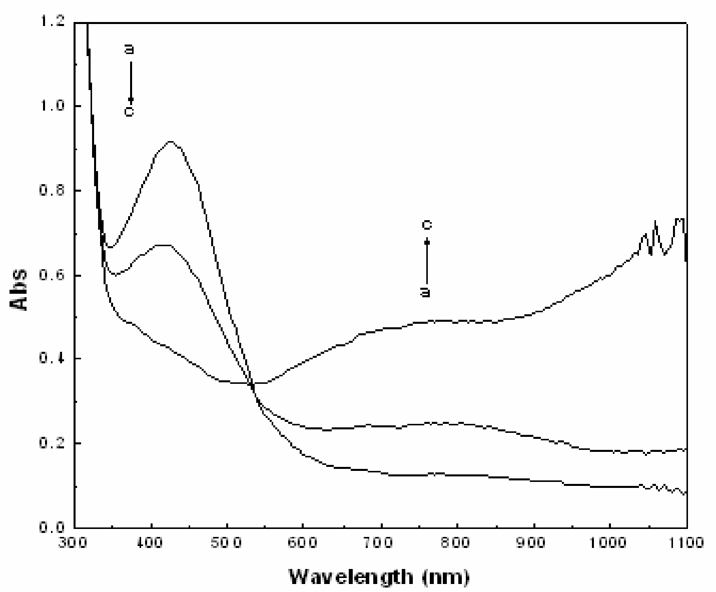


Figure 5. Spectroelectrochrmistry of POcT based solid ECD as a function of applied voltage: -2.0 V (b) 1.8 V and (c) 2.2 V

3.4.2. Stability of ECD

CV was used as the method of evaluating the stability of the device. For this purpose we accomplished non stop cycling of the applied potential between -2.5 and 2.5 V with 500 mV / s scan rate. As seen in Figure 6 even after 1000th run, device showed only a slight decrease in electroactivity accompanied by unperturbed color change. This result showed that this POcT based solid ECD has good environmental and redox stability and can be operated with an applied voltage of -2.5~2.5 V.

4. CONCLUSIONS

In this paper, it has been shown that POcT was successfully synthesized by galvanostat method in colorless, odorless and non-hazardous ionic liquid [BMIM]PF_6. The polymer film was smooth and homogeneous with good electrochemical and electrochromic properties. In its fully reduced state the thin film was orange yellow. After oxidization of the undoped polymer, the film underwent a reversible change to the dark blue form. Furthermore, an ECD made up of POcT in sandwich structure with gel polymer electrolyte was established. The device exhibited striking color changes and electrochemical stability make it become promising candidate for electrochromic layer in ECD application.

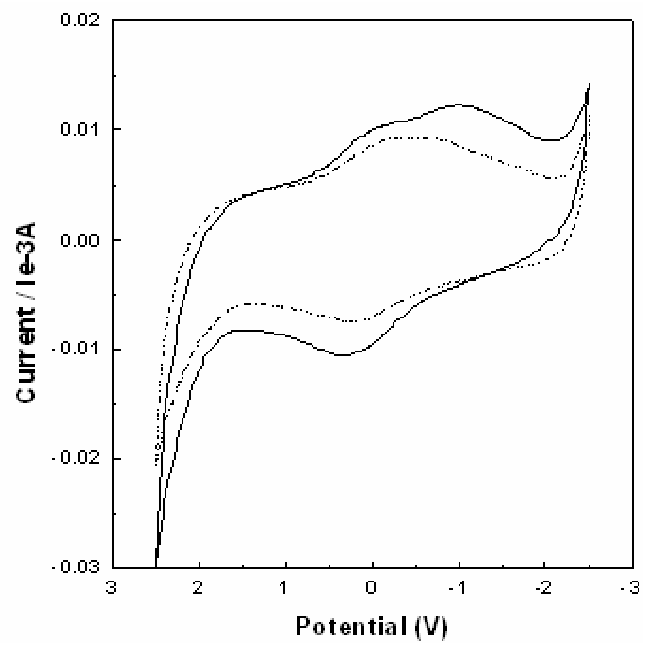


Figure 6. Cyclic voltammogram of POcT based solid ECD as a function of repeated scans at 500mV / s: (—) 1st cycle and (--) 1000th cycle

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