

# Electrochemical Copolymerization of Thiophene Containing Pseudo-Polyether Cages with Pyrrole

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Conducting copolymers were synthesized via the electrochemical oxidation of pyrrole (Py) in the presence of the monomer 1,12-bis(2-thienyl)-2,5,8,11-tetraoxadodecane (**I**). The presence of monomer **I** in the electrolytic solution greatly changed the CV behavior of Py during its potentiodynamic polymerization. The electroactivity of poly(**I**-co-Py) increased with the increasing amount of **I** in the comonomer mixture. Copolymer films were prepared via constant potential electrolysis in an electrolytic solution containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) dissolved in acetonitrile. The spectroelectrochemical properties of the films were investigated using UV-VIS spectroscopy.

**Key Words:** Electrochemical polymerization, spectroelectrochemistry, polymer containing pseudo-polyether cages.

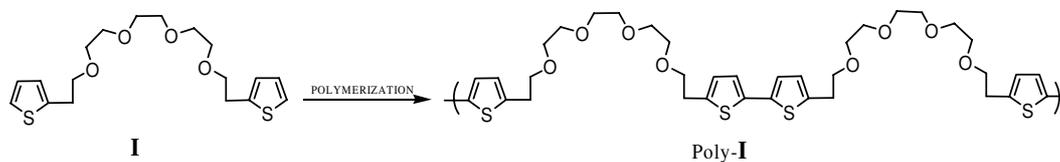
## Introduction

Copolymers and functionalized conducting polymers have been the focus of considerable attention due to their interesting electrical and optical properties in the last 3 decades because these properties are dependent not only on the nature of the polymeric backbone but also on the presence of covalently attached functional groups. It is reported that polythiophenes functionalized with 12-crown-4 and crown-5 exhibit ionochromic changes in alkali metal ion solutions.<sup>1</sup> Polybithiophenes containing crown ether moieties possess ion sensing properties.<sup>2</sup> In recent years, symmetrical monomers possessing 2 thiophene units linked together by a pseudo-polyether cages have been synthesized and their electrochemical behaviors have been investigated.<sup>3–9</sup> Simonet and co-workers<sup>6</sup> reported that polyether chains are eliminated during electrochemical polymerization, if the chains are attached to the  $\alpha$ -position of the thiophene ring. On the other hand, Marrec et al.<sup>7</sup> and Tirkeş et al.<sup>8</sup> reported that a polyether chain is retained in the polymer backbone if it is bridging the 2 thiophenes through  $\beta$ -positions. In order to clarify the polyether cleavage issue, we synthesized a new monomer containing 2-thienyl units with 2 methylene groups between the thiophene and the first oxygen of the polyether bridge<sup>9</sup> (Scheme 1). We observed that polyether chains are not cleaved

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during the electrochemical polymerization even though the polyether groups are bridging the 2 thiophenes through  $\alpha$ -positions.



**Scheme 1**

Since the product was found to have very low conductivity due to its low  $\pi$ -conjugation, we investigated the possible copolymerization of monomer **I** with thiophene via electrochemical oxidation<sup>10</sup>. The copolymer formation was confirmed using spectroelectrochemical, conductivity and electrochromic measurements.

Herein, we report the electrochemical copolymerization of **I** with Py, which has oxidation potential much lower than monomer **I**. Formation of copolymer was investigated by CV and in situ UV-VIS techniques.

## Experimental

Monomer **I** was synthesized according to a general procedure already described.<sup>5,8,9</sup> Py (Across Organics, 99%) was vacuum distilled prior to use. TBAPF<sub>6</sub> (Aldrich, 98%) was used as received. Acetonitrile was freshly distilled over CaH<sub>2</sub> under Ar atmosphere before use.

The electrochemical behaviors of monomers and copolymer films were investigated using CV. Polished platinum wire and platinum coil were used as the working (WE) and the counter electrodes (CE), respectively. A saturated calomel electrode (SCE) was used as the reference electrode (RE).

Electrochemical measurements were carried out using a HEKA IEEE-488 potentiostat/galvanostat using a 3-electrode configuration under Ar atmosphere.

### Electrochemical polymerization

Electrochemical polymerization was performed in a classical 3-electrode cell. The WE and CE were rectangular platinum sheets (1 cm<sup>2</sup>) and the RE was SCE. All polymer samples were synthesized at the oxidation potential of related monomer in 0.1 M TBAPF<sub>6</sub>-acetonitrile electrolytic solution. Samples were washed with CH<sub>2</sub>Cl<sub>2</sub> and peeled off from the surface and then kept under a vacuum at 60 °C for 12 h. For spectroelectrochemical studies, indium tin oxide coated quartz glass (ITO, Delta Tech. 8-12  $\Omega$ ) and Ag-wire were used as the WE and RE, respectively. Spectroelectrochemical measurements were carried out on a HP 8453A diode array UV-VIS spectrometer using a specially designed 3-electrode cell to allow potential application while monitoring the electronic absorption spectra.

## Results and Discussion

In our previous study<sup>9</sup> we found that both chemical and electrochemical polymerization of monomer **I** yielded a regular polymer consisting of pseudo-polyether cages (Scheme 1) with a very low conductivity (i.e.  $1.0 \times 10^{-2}$  S/cm after I<sub>2</sub> doping). In order to enhance its conductivity we studied the copolymerization of **I** with thiophene. However, we observed that the electroactivity of the film was decreased due to incorporation of

more monomer **I** in the polymer film. In the present study, we investigated the copolymerization of **I** with Py to enhance its conductivity in acetonitrile using TBAPF<sub>6</sub> as the supporting electrolyte.

## Copolymer of with Py

Since the oxidation potentials of **I** and thiophene are not very different from each other, the potential chosen for the polymerization (i.e. 1.85 V vs. SCE) results in the formation of radical cations of both monomers. This increases the possibility of incorporation of more **I** into the copolymer, which lowers the degree of  $\pi$ -conjugation. This might be the main reason for the decreasing electroactivity of copolymer film with the increasing amount of **I** in the electrolytic solution. For this reason, we have also investigated the copolymerization of **I** with a monomer having a much lower oxidation potential (i.e.  $E_{ox}(\text{Py}) = 1.3 \text{ V vs. SCE}$ ). In this case, the electron transfer to the WE will be from Py at the chosen potential and the only way of incorporation of **I** into the copolymer would be via an attack of a Py radical cation on **I**.

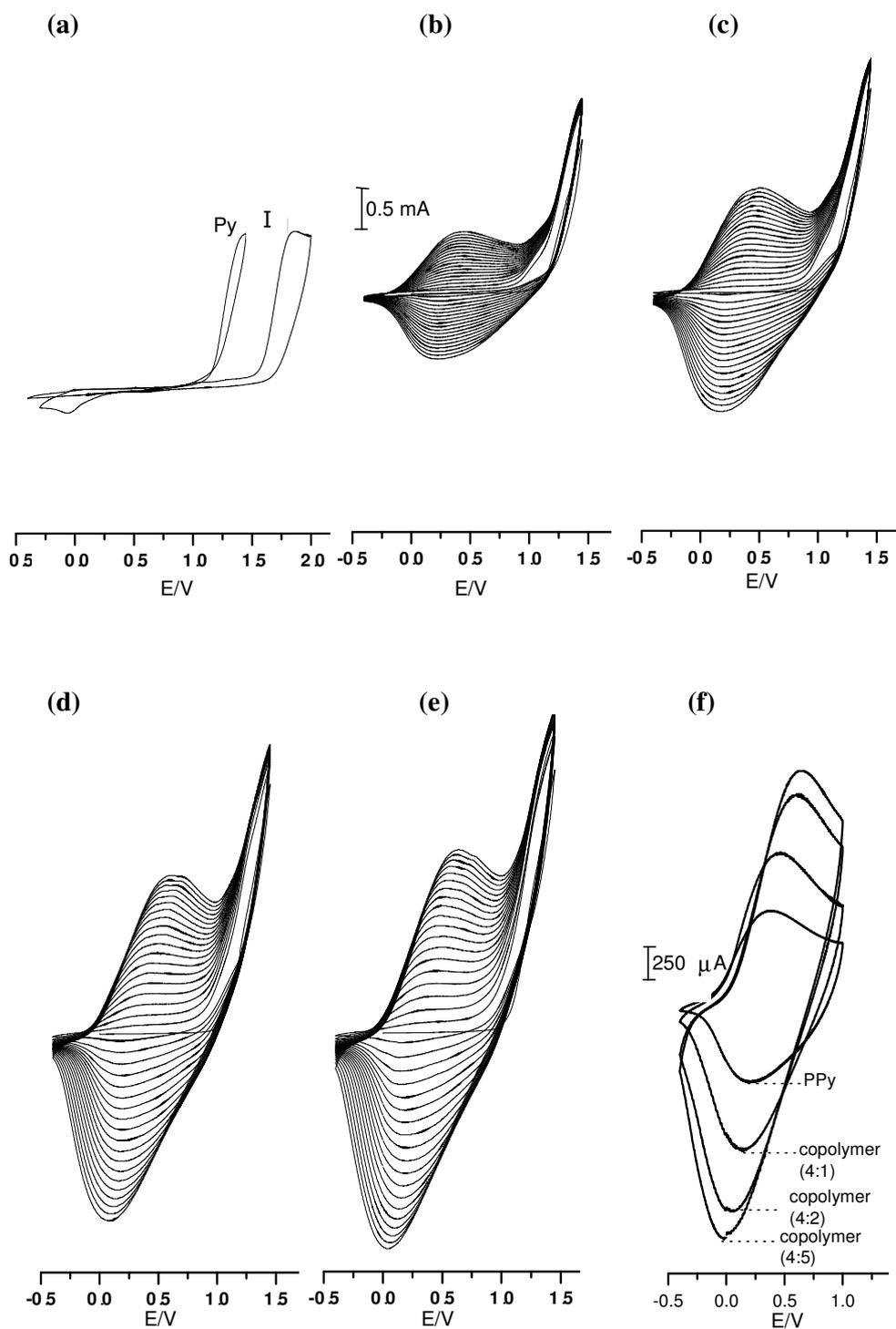
## CV studies

The CV of **I** and Py recorded in the same electrolytic medium is given in Figure 1(a). Py is more readily oxidized than **I**. Figure 1(b) depicts the CV of electrolytic solution containing  $1 \times 10^{-2} \text{ M Py}$  during repetitive cycling between  $-0.4$  and  $+1.3 \text{ V vs. SCE}$ . Formation of PPy film on the WE surface is accompanied by a continuously intensifying reversible peak at  $+0.28 \text{ V vs. SCE}$ . The height of the peak increases with the increasing ratio of **I** to Py (Figure 1(c)-(e)). In addition, electrochemical behaviors of the polymer films obtained from **I** and Py mixture were studied in the monomer free electrolytic solution and compared with that of PPy (Figure 1(f)). It is seen that redox potential values of the polymer film obtained from a mixture of Py and **I** were shifted to a higher potential value than those of the pure PPy film, indicating the formation of a copolymer.

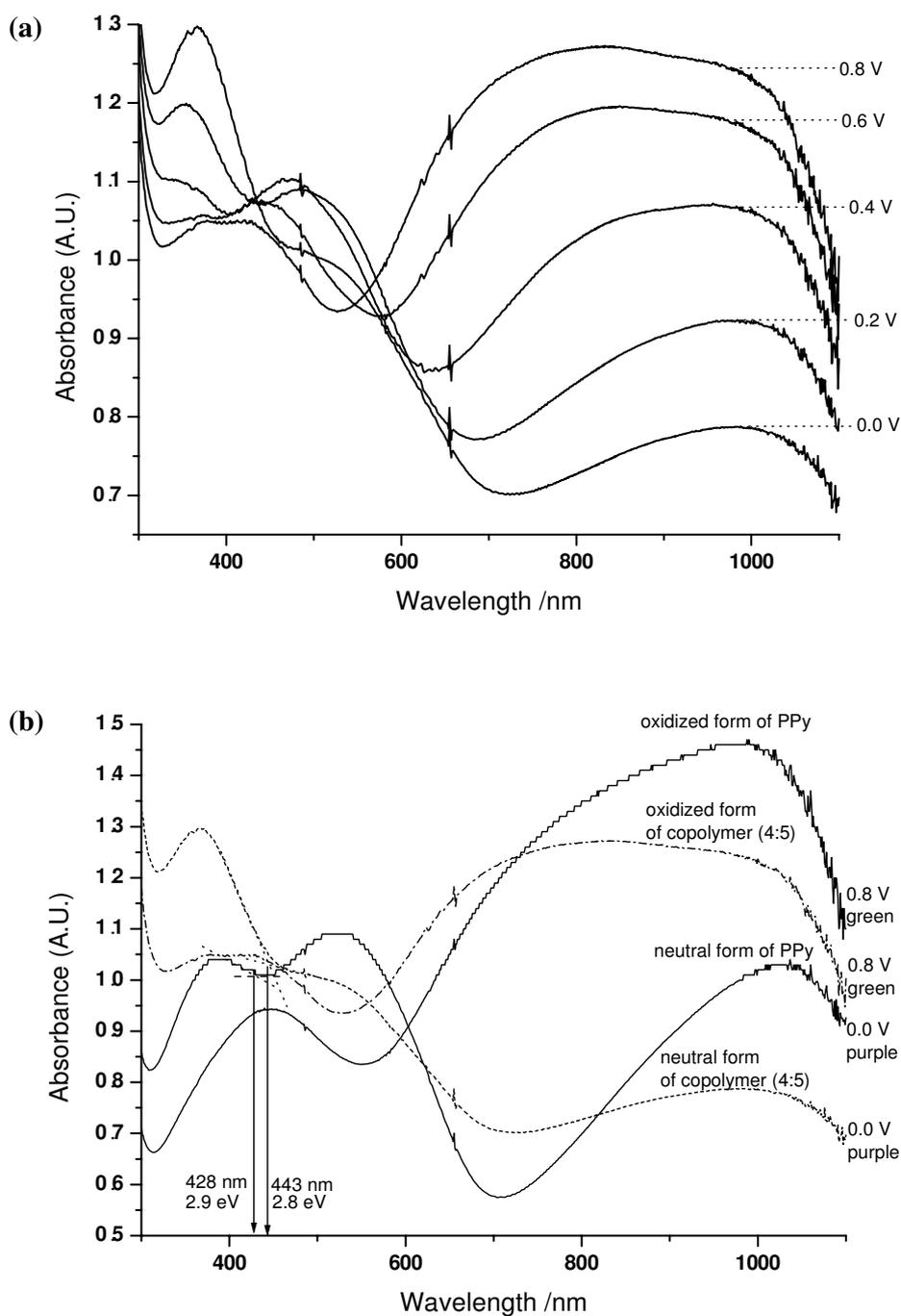
## Spectroelectrochemical behaviors

In order to get further support for the formation of copolymer from **I** and Py, the change in the electronic absorption spectrum of polymer film obtained from Py:**I** (4:5) comonomer mixture at  $+1.3 \text{ V vs. Ag wire}$  was monitored during potential scanning in  $0.1 \text{ M TBAPF}_6$  in acetonitrile. The electronic absorption spectrum of the polymer film exhibits an intense absorption band at about  $390 \text{ nm}$  due to  $\pi - \pi^*$  transition. This band loses intensity during potential scanning from  $0.0 \text{ V}$  to  $0.4 \text{ V}$  and a new band at about  $516 \text{ nm}$  starts to intensify, indicating polaron formation. This new band loses intensity with further potential scanning from  $0.4$  to  $0.8 \text{ V}$ , which is accompanied by the formation of a broad bipolaron band beyond  $700 \text{ nm}$  (Figure 2(a)).

Spectroelectrochemical studies revealed that the  $E_g$  value of the copolymer film ( $2.8 \text{ eV}$ ) obtained from **I** and Py mixture is slightly lower than that of PPy ( $2.9 \text{ eV}$ ) (in Figure 2(b)). On the other hand, the conductivity of the copolymer film ( $10^{-2} \text{ S cm}^{-1}$ ) is lower than that of PPy ( $20 \text{ S cm}^{-1}$ ).



**Figure 1.** CVs of (a)  $1.0 \times 10^{-2}$  M Py and  $1.0 \times 10^{-2}$  M I (b)  $1.0 \times 10^{-2}$  M Py, and (c) Py:I mixture (Py:I; 4:1) (d) (Py:I; 4:2) (e) (Py:I; 4:5) (f) polymer films obtained from the Py:I mixtures in monomer free electrolytic solution.



**Figure 2.** (a) Electronic absorption spectra of the copolymer obtained from Py:I (4:5) mixture in 0.1 M TBAPF<sub>6</sub> in acetonitrile and (b) comparison of electronic absorption spectra of the copolymer (4:5) and PPy in their neutral (0.0 V vs. Ag-wire) and oxidized states (at +0.8 V vs. Ag-wire) in 0.1 M TBAPF<sub>6</sub> in acetonitrile.

## Conclusion

In this paper, we report the synthesis of a new copolymer by electrochemical oxidation of Py in the presence of a polyether bridged thiophene (I) monomer. CV studies on the poly(I-co-Py) film in monomer free

electrolytic solution indicated that increasing the amount of **I** in the electrolytic solution increases the electroactivity of the film. It is also found that the band gap of the film is slightly lower than the band gap of pure PPy. In the case of poly(**I**-co-Py), the presence of **I** enhanced the electroactivity of the film. The shifts in the absorption bands, conductivity and electrochromic measurements of copolymer films in comparison to the homopolymers of Py revealed copolymer formation.

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