

Improvement of the Conductivity, Electroactivity, and Redoxability of Polythiophene by Electropolymerization of Thiophene in the Presence of Catalytic Amount of 1-(2-Pyrrolyl)-2-(2-thienyl) Ethylene (PTE)

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ABSTRACT: The electropolymerization of thiophene in the presence of 1-(2-pyrrolyl)-2-(2-thienyl) ethylene (PTE) was investigated. PTE was synthesized via Wittig reaction and by the addition of catalytic amount of PTE during the electropolymerization of thiophene, the conditions of electropolymerization of thiophene were modified. The cyclic voltammograms of polythiophenes (PThs) in different conditions were obtained. The analysis of cyclic voltammograms of PThs shows a considerable increase in the electroactivity and redoxability when the electropolymerization of thiophene in the presence of catalytic amount of PTE was performed. The presence of PTE during electropolymerization of thiophene leads to an increase in the rate of polymerization too. The cyclic voltammetry (CV) measurement of electron transfer ferro/ferricyanide redox system on different modified glassy carbon (GC) electrode

has shown that the rate of charge transfer for PTh in the presence of PTE increased in comparison to pure PTh. The conductivity of obtained polymers was determined by electrochemical impedance spectroscopy (EIS) technique in 3.5% (w/v) NaCl solutions. The Zview(II) software was applied to the EIS to estimate the parameters of the proposed equivalent circuit, based on a physical model for the electrochemical behavior of coatings on GC. The R_{ct} value obtained for PTh is $7667 \Omega \text{ cm}^2$. This value decreases in the presence of PTE to $4437 \Omega \text{ cm}^2$. Thus, the new film has more conductivity. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2700–2706, 2008

Key words: electropolymerization; polythiophene; conducting polymer; cyclic voltammetry; impedance technique

INTRODUCTION

In the recent years, the field of electrically conducting polymers, such as polypyrrole (PPy), polythiophene (PTh), and polyaniline (PANI), has been studied extensively.¹ These polymers are used in many applications, such as batteries,² electrochromics,^{3,4} gas separation membranes,⁵ electromagnetic interference shielding,^{6,7} sensors,^{8,9} and metal protection against corrosion.^{10,11}

Electropolymerization is a commonly used technique for the synthesis of conducting polymers. In the past few years, the class of polyheteroaromatic compounds has been the center of great interest because of the high-electrical conductivity, chemical stability, and satisfactory processability.^{12,13} Among these polymers, polypyrrole (PPy), PTh, and their derivatives have been investigated extensively.

For the electrochemical polymerization of thiophene, relatively high potentials (e.g., ca. 1.6 V vs. SCE) are required in comparison with those for the preparation of polyaniline and polypyrrole (ca. 0.7 or 0.8 V vs. SCE). However, these polymers decompose readily at high potentials, which may result in poor quality.¹⁴

Entezami et al.^{15–18} have investigated the electropolymerization of pyrrole and *N*-methyl pyrrole in the presence of 1-(2-pyrrolyl)-2-(2-thienyl) ethylene (PTE) and 2-(2-thienyl) pyrrole (TP) as a derivative of pyrrole–thiophene by cyclic voltammetry method in different conditions.

There is little attention to the improvement of the electroactivity and conductivity of PTh. To observe the effect of PTE on the electropolymerization conditions of thiophene, the electropolymerization of thiophene and PTE performed separately, and the influence of catalytic amount of PTE on the PTh by electropolymerization of these monomers in the presence of each other were studied. For complementary experiments and confirmation of the obtained results from cyclic voltammograms of the electropolymerization,

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the conductivity measurement was performed by electrochemical impedance spectroscopy (EIS).

EXPERIMENTAL

Materials

Solvents were purified and dried according to the common procedures in the literature.¹⁹ Thiophene was purchased from Merck and purified before use. Pyrrole-2-carbaldehyde was purchased from Fluka and recrystallized in petroleum ether (50–70°C). 2-Chloromethyl thiophene was prepared according to the literature.²⁰

Synthesis of 2-(2-Pyrrolyl)-2-(2-thienyl) Ethylene

2-(2-Pyrrolyl)-2-(2-thienyl) ethylene (PTE) was prepared by the Wittig reaction as follows: 2-(thienyl) methyltriphenyl phosphonium chloride (2.92 g, 22 mmol) was added under nitrogen to a stirred suspension of sodium hydride in oil 60% (0.88 g, 22 mmol) in 150 mL toluene, and the mixture was stirred at room temperature for 5 min. Pyrrole-2-carbaldehyde (1.9 g, 20 mmol) was added to the solution of the ylide, the reaction mixture was heated at 80–85°C for 6 h, and then cooled to the room temperature and finally filtered. The organic layer was washed with water, dried over magnesium sulphate, and evaporated under reduced pressure to leave a solid.¹⁵

The obtained crude compound was purified by chromatography from Merck kiesel gel (60) using dichloromethane-petroleum ether (50–70°C) (2 : 1 v/v) as the eluent; yield (42%), m.p. 141–143°C; IR (KBr; cm^{-1}): 3400, 1625, 1415, and 1115; ¹H NMR (CDCl_3 , TMS), δ : 6.1–7.3 (m, 9H); MS (EI, 70 eV) m/z (%): 175 (100%), 174 (51.2%), 142 (15%), 77 (15.1%), and 51 (23.1%).

Electropolymerization method and conductivity measurements

The electrochemical polymerization was carried out using digital potentiostat/galvanostat (Autolab PGSTAT 30). A glassy carbon (GC) disk (2 mm ϕ diameter) was used as working electrode in cyclic voltammetry experiments. In each case, a platinum wire was used as a counter electrode, and Ag/AgCl was employed as a reference electrode. Acetonitrile was distilled over P_2O_5 , and lithium perchlorate (Fluka) was used as an electrolyte directly in 0.1M concentration. The electropolymerization of thiophene (0.01M) in 0.1M LiClO_4 /acetonitrile electrolyte was performed in 0–1.8 V potential range versus Ag/AgCl at the scan rate 50 mV/s. The electropolymerization of PTE (0.01M) was performed in a potential

range –0.3–1 V in 0.1M LiClO_4 /acetonitrile electrolyte. Similar conditions were used for the electropolymerization of thiophene in the presence of PTE (0.23M : 0.0023M). To study cyclic voltammetry experiment of electron transfer, we used 1 mM ferro/ferricyanide (Merck) in the 1M H_2SO_4 media at 50 mV/s scan rate.

The AC frequency range extended from 100 kHz to 10 mHz, a 10 mV peak-to-peak sine wave being the excitation signal. The real and imaginary components of the EIS in the complex plane were analyzed using the Zview(II) software to estimate the parameters of the equivalent electrical circuit. A computer-controlled potentiostat (PARSTATE 2263 EG&G) is used for EIS measurements.

RESULTS AND DISCUSSION

Electrochemical synthesis of polymers

Following our earlier studies in this realm,^{15–18} we have investigated the influence of the catalytic amounts of the PTE on the electropolymerization of thiophene. For this purpose, the electropolymerization of thiophene and PTE were performed separately. Then, thiophene was electropolymerized in the presence of catalytic amount of PTE. Typical cyclic voltammograms of the electropolymerization of thiophene is shown in Figure 1(a). During the electropolymerization of thiophene, an anodic peak was observed due to the oxidation of thiophene in the first scan at about 1500 mV versus Ag/AgCl. As the electropolymerization proceeds, an anodic peak current was appeared due to oxidation of PTh in the second scan at about 1000 mV versus Ag/AgCl, and also the peak current increased. A black polymer film was observed on the electrode surface.

After 15 scans, the GC electrode-containing polymer film was taken out of electrochemical cell, washed with acetonitrile, and placed in monomer-free electrolyte solution. Cyclic voltammograms of resulted polymer in the range of 0 to 1300 mV versus Ag/AgCl at various scan rates demonstrate semireversible behavior [Fig. 1(b)].

The cyclic voltammograms of the thick film reveal an increase in the separation and broadening of the peaks. In addition, the current rises as scan rate goes up gradually. As a result, the numeric value of ohmic drop is added to the oxidation and reduction potentials of the polymer. Anodic peak (i_{p_a}) and cathodic peak (i_{p_c}) currents are directly proportional to scan rate (v) in the potential scan range 0–1000 mV/s versus Ag/AgCl, and the peak forms are characteristics of an adsorption-limited process (see Fig. 2). This indicates that the deposited polymer on the working electrode during the redox cycles is stable. Large capacitive currents

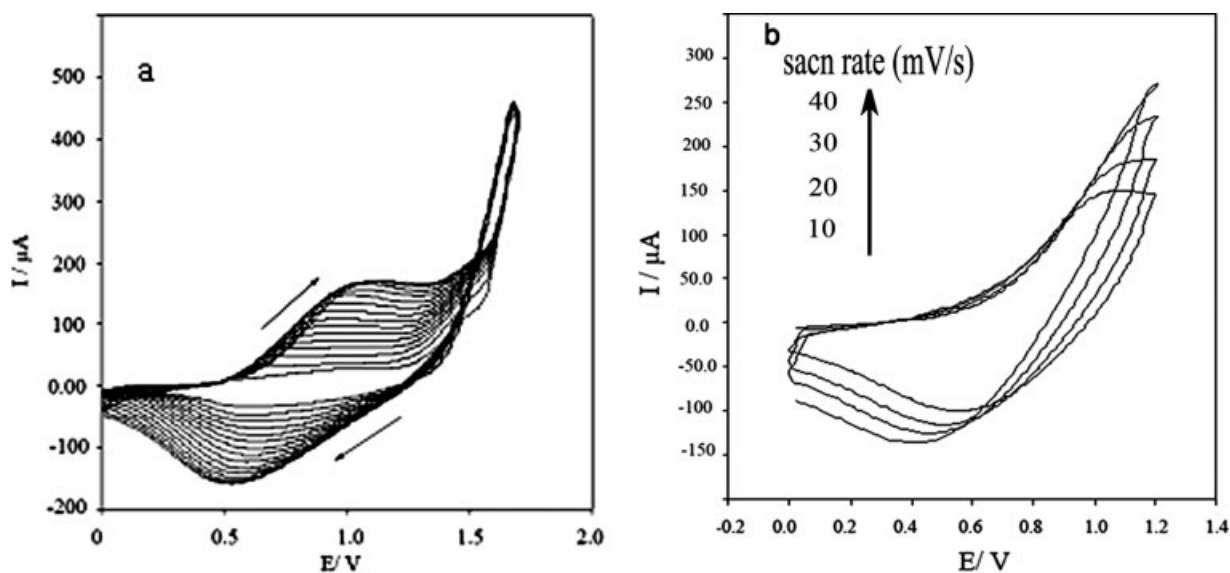


Figure 1 (a) Cyclic voltammograms of 0.01M thiophene in 0.1M LiClO₄/CH₃CN electrolyte at scan rate 50 mV/s versus Ag/AgCl; (b) cyclic voltammograms of polythiophene (PTh) in 0.1M LiClO₄/CH₃CN electrolyte at various scan rates.

were observed around the cathodic potentials and especially in anodic potentials. This was probably due to the charging and discharging of the films during the process of oxidation and reduction, but this could also be influenced by a change in the effective electrode area because of the development of microporosity when perchlorate anions are transported in and out of the films.

The electrochemical oxidation of PTE with potential scan in the range of -300 – 1000 mV versus Ag/AgCl was performed [Fig. 3(a)]. During the first scan, two maxima for E_{p_a} 570 and 700 mV versus Ag/AgCl were found as results of the oxidation of

PTE. Going down from 1000 to 400 mV versus Ag/AgCl, no maxima were found, indicating an irreversible reaction. After the first reverse scan, new cathodic and anodic peak currents were observed and increased continuously with successive potential scans, indicating the build up of the electroactive polymeric product poly-PTE and its oxidation process on the surface of the electrode poly-PTE with a salt structure. As the potential scan continued, the electrode became covered with a thin black film. The preparation of the polymer on the GC electrode surface is not clean, and it is accompanied by the bleeding of the soluble oligomers from the electrode surface. In Figure 3(b), the repetitive cyclic voltammograms of poly-PTE in the various scan rates are illustrated with no drop and increase in i_{p_a} and i_{p_c} polymer, indicating the electroactivity and stability of poly-PTE. Figure 4 shows anodic and cathodic peak currents versus scan rate of poly-PTE. Anodic peak (i_{p_a}) and cathodic peak (i_{p_c}) currents are proportioned to scan rate, and the peak forms are characteristics of an adsorption-limited process. Consequently, the dependence of peak currents on scan rate for this polymer indicates complete electroactivity.

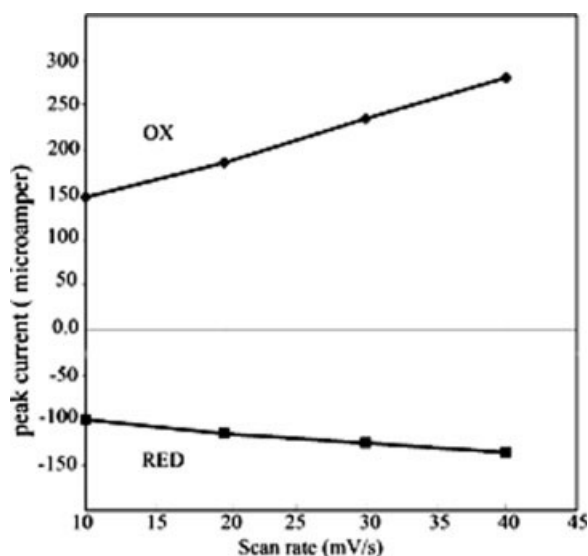


Figure 2 Plots of anodic and cathodic peak current versus scan rate of polythiophene (PTh) film.

In the first scan of the electrochemical oxidation of thiophene in the presence of the PTE (0.23M : 0.0023M), an anodic peak appeared at about 750 mV versus Ag/AgCl, which is due to the oxidation of PTE. This anodic peak was absent during the electropolymerization of thiophene without PTE [Fig. 5(a)]. Because of the oxidation of formed polymer, the anodic peak current increases more rapidly in comparison to the anodic peak during the electropolymerization of thiophene without PTE.

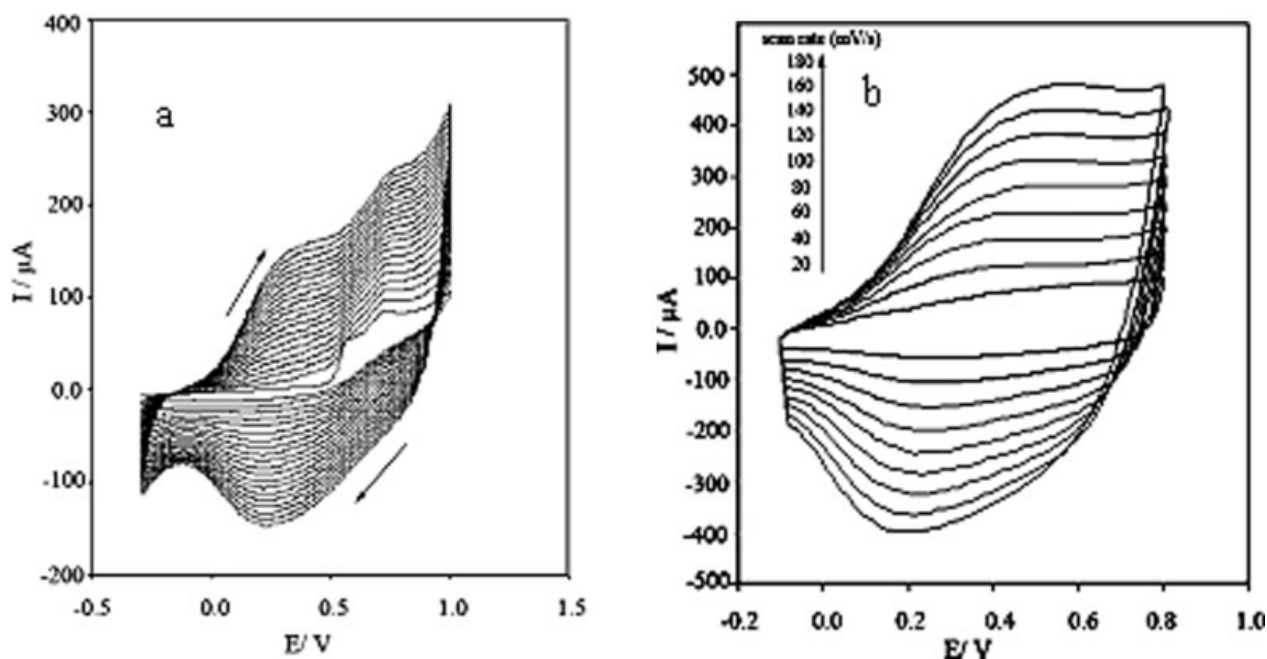


Figure 3 (a) Cyclic voltammograms of 0.01M PTE in 0.1M LiClO₄/CH₃CN electrolyte at scan rate 50 mV/S versus Ag/AgCl; (b) cyclic voltammogram of poly PTE in 0.1M LiClO₄/CH₃CN electrolyte at various scan rates.

After 15 scans, the GC electrode-containing polymer film was taken out of electrochemical cell, washed with acetonitrile, and placed in a monomer-free electrolyte solution. The cyclic voltammograms of resulted polymer in various scan rates showed good reversible behavior [Fig. 5(b)]. Based on these results, we can conclude that the obtained polymer is not a simple blending of two individual polymers, and so the obtained film on the electrode surface is prob-

ably a copolymer of thiophene-PTE (Th-PTE) with one unit redox character.

Figure 6 illustrates anodic and cathodic peak currents versus sweep rate of poly(Th-PTE). The anodic and cathodic peak currents varied linearly with the scan rate, suggesting that no diffusing species are involved, and only the polymer film was electroactive.

Also, comparison of the ΔE_p PTh with ΔE_p poly-Th-PTE shows changing from 0.68 to 0.62 V that the redoxability improvement of poly(Th-PTE) is confirmed.

Figure 7 shows the plots of the cathodic peak currents versus the number of cycles during the electropolymerization of thiophene in the presence and absence of PTE as well as for the electropolymerization of PTE. Introducing a small amount of PTE to the electropolymerization system leads to a great increase in the rate of electropolymerization.

Figure 8 presents the plots of anodic peak currents versus scan rates. These curves indicate that the rate of electropolymerization of thiophene in the presence of a catalytic amount of PTE increases considerably compared to the rate of electropolymerization of thiophene without PTE and also to the rate of electropolymerization of PTE alone.

Further cyclic voltammetry experiments were performed to assess the effect of PTE on the PTh film on the electron transfer of ferro/ferricyanide redox system. Figure 9 shows the CV of electron transfer ferro/ferricyanide redox on different modified GC electrodes with PTh, poly-PTE, and poly(Th-PTE).

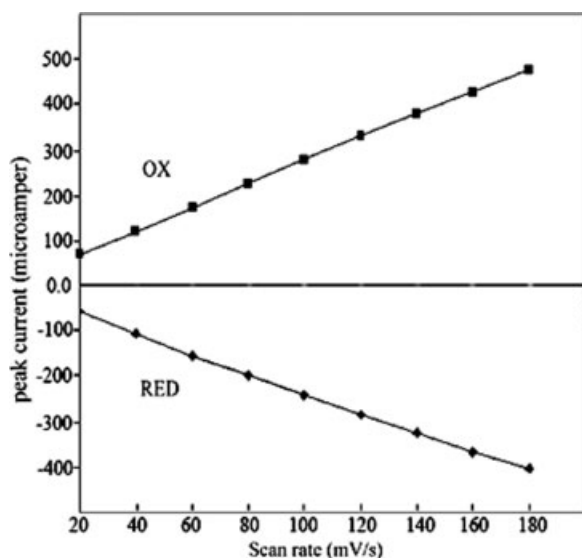


Figure 4 Plots of anodic and cathodic peak currents versus scan rate of poly PTE film.

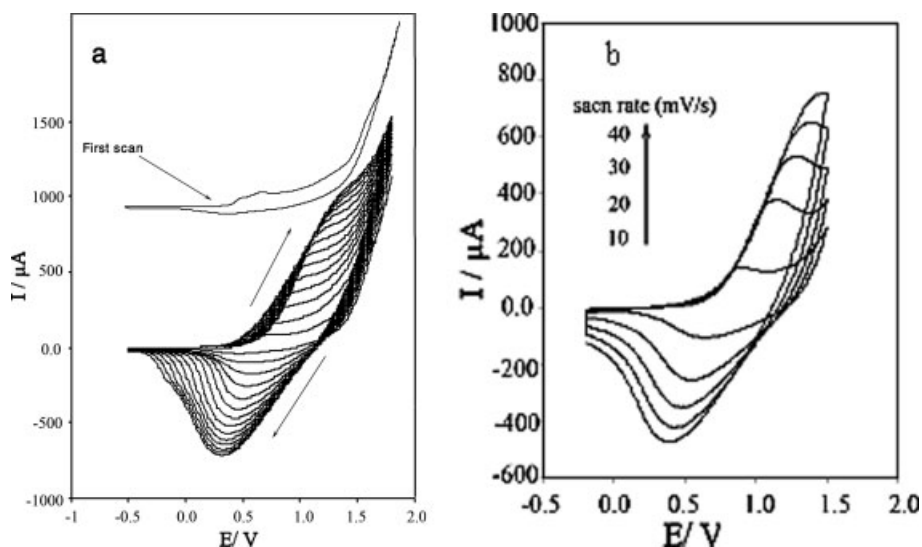


Figure 5 (a) Cyclic voltammograms of Th-PTE (0.23M : 0.0023M) in 0.1M $\text{LiClO}_4/\text{CH}_3\text{CN}$ electrolyte at scan rate 50 mV/S versus Ag/AgCl; (b) cyclic voltammogram of poly(Th-PTE) in 0.1M $\text{LiClO}_4/\text{CH}_3\text{CN}$ electrolyte at various scan rates.

This figure indicates that the electron transfer of ferro/ferricyanide for PTh in the presence of the PTE is easier than PTh alone because the conductivity of PTh significantly increases in the presence of PTE.

Evaluation of conductivity and electrochemical behavior by electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is a measurement technique that allows a wide variety of

coating evaluations. EIS is an effective method to probe the interfacial properties of surface-modified electrodes. EIS was used to characterize the electrical properties of the electropolymerized films. Nyquist plots are constructed, and appropriate equivalent circuit model is used to correlate the impedance with the capacitance and the resistance of the film. Figure 10 shows Nyquist plots (a) PTh, (b) poly(Th-PTE), and (c) poly-PTE coated on GC electrodes in 3.5% NaCl solution. These Nyquist plots are characterized by two regions: a depressed semicircle at high frequencies associated with charge transfer (R_{ct}) at the

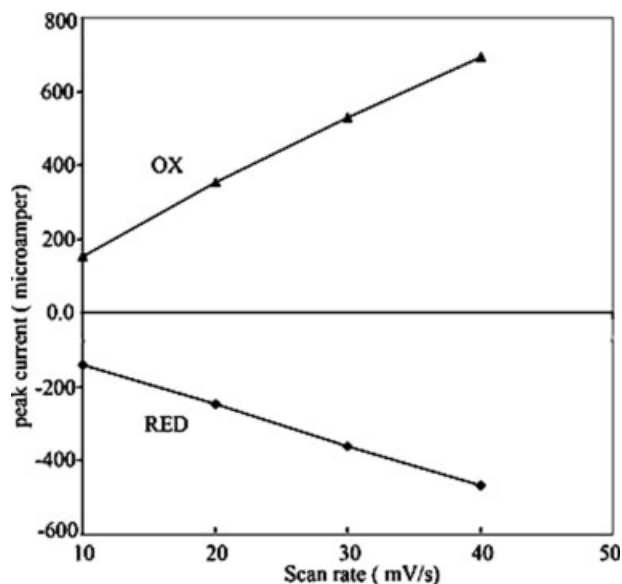


Figure 6 Plots of anodic and cathodic peak currents versus scan rate of poly(Th-PTE) film.

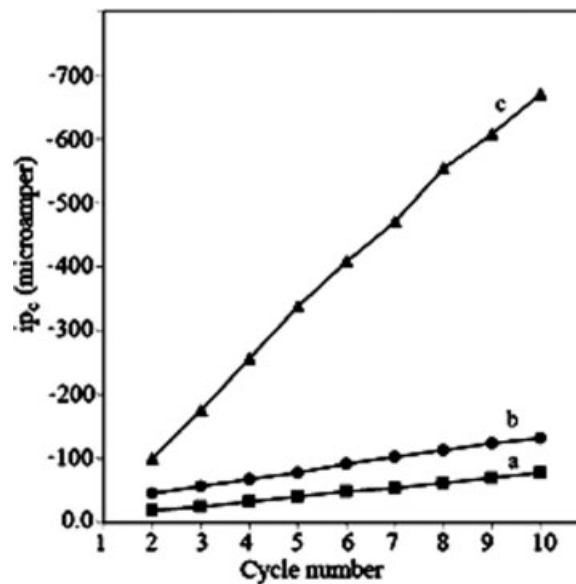


Figure 7 Plots of cathodic peak current versus the number of cycles for PTE (a), thiophene (b), and (Th-PTE) (c).

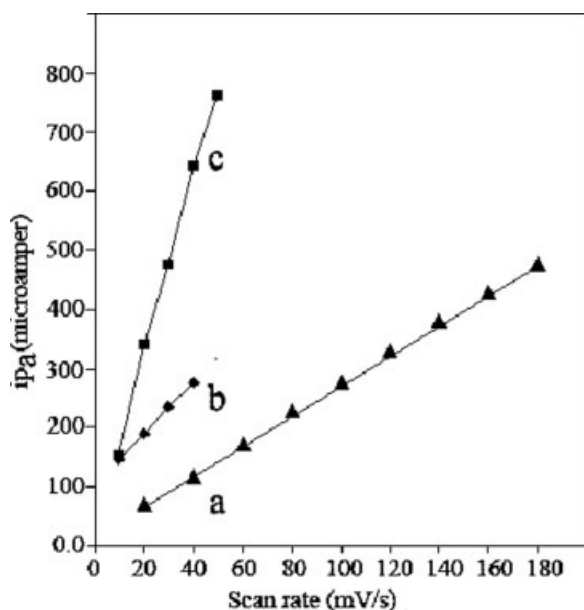


Figure 8 Plots of anodic peak current versus scan rates for poly-PTE (a), polythiophene (PTh) (b), and poly(Th-PTE) (c).

polymer/solution interface the decrease in the diameter and a second region consisting of a straight line at (Fig. 10), indicating a diffusion-controlled process at the electrode (Warburg). The electrochemical behavior of thiophene changes in the presence of PTE. Based on the Randle's equivalent circuit model with a modification, which takes into account the

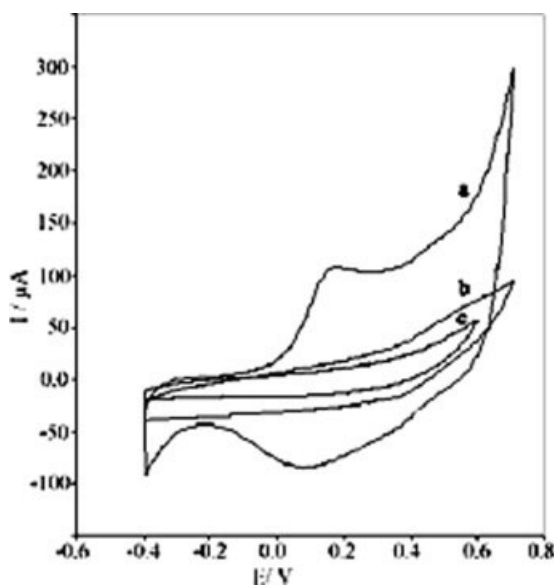


Figure 9 Cyclic voltammograms of (a) poly-PTE, (b) poly(Th-PTE), (c) polythiophene (PTh) on the GC electrode in 1M H_2SO_4 and 1 mM $\text{Fe}(\text{CN})_6^{4-/3-}$ redox system at 50 mV/s scan rate.

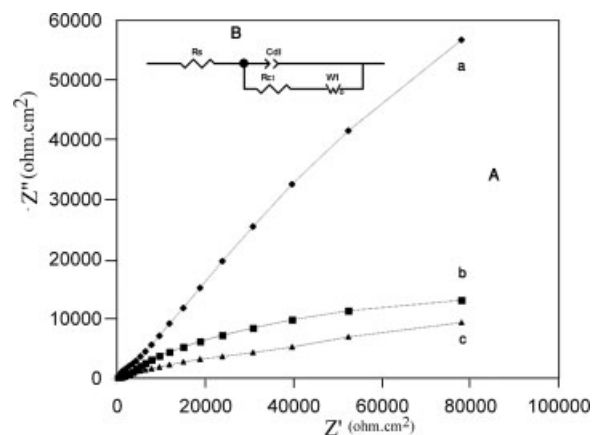


Figure 10 A: Nyquist plots for (a) poly-PTE, (b) poly(Th-PTE), and (c) polythiophene (PTh) in 3.5% (W/V) NaCl solution; (B) proposed equivalent circuit.

presence of porous interfaces on the electrodes, electrical parameters were calculated using Zview(II) software. All fitting results are presented in Table I. The electrolyte resistance in the table R_{ct} means the charge transfer resistance; C_{dl} is the double layer capacitance at the electrode/solution interface. According to these results (Table I), we can notice a decrease in the charge transfer resistance value in the case of the PTh in the presence of PTE systems when compared with pure PTh. The R_{ct} values obtained for PTh and poly-PTE are $7667 \Omega \text{ cm}^2$ and $3751 \Omega \text{ cm}^2$, respectively. This value decreases in the presence of PTE to $4437 \Omega \text{ cm}^2$. The new film seems to be more conductive. On the other hand, in the presence of PTE, value of the capacitance of the electrical double layer goes up, C_{dl} , with a probable increase in the electrode surface area. This change in the capacitance strongly supports the hypothesis of the incorporation of PTE in the PTh film. Also, these results support the results of CV in the Figure 5. In the presence of PTE, the conductivity of PTh is improved. Increasing C_{dl} for PTh in the presence of PTE compared to pure PTh confirmed the easy electron transfer of ferro/ferricyanide redox system for PTh in the presence of PTE (Fig. 9).

CONCLUSION

In the first part of this article, the electrosynthesis of PTh, poly-PTE, and poly(Th-PTE) films on GC electrode by cyclic voltammetry in acetonitrile is discussed. The results show a considerable increase in the electroactivity, redoxability, and the rate of polymerization by addition of catalytic amount of PTE during the electropolymerization.

Also, the CV measurement of electron transfer ferro/ferricyanide redox system on different modi-

TABLE I
Impedance Data Obtained by Simulation of Poly-PTE, Poly(Th-PTE), and Polythiophene
on the GC Electrode in 3.5%NaCl

Sample	C_{dl} ($\mu\text{F}/\text{cm}^2$)	ndl	R_{ct} ($\Omega \text{ cm}^2$)	W1-R ($\Omega \text{ cm}^{-2}$)	W1-T ($\Omega^{-1} \text{ cm}^{-2}$)	W1-P
Poly-PTE	153.3	0.80578	3751	0.20393	1.7267E-8	0.31395
Poly(Th-PTE)	44.96	0.51336	4437	37053	119.1	0.40033
Poly-Th	15.847	0.62511	7667	1.1991E5	159.4	0.31901

fied GC electrode has shown that the rate of charge transfer for PTh in the presence of PTE increased in comparison with pure PTh.

In the second part of this article, the conductivity of thiophene is investigated by EIS. The obtained R_{ct} value for PTh is $7667 \Omega \text{ cm}^2$, whereas this value decreases to $4437 \Omega \text{ cm}^2$ in the presence of PTE. The new film seems to be more conductive. In the presence of PTE, value of the capacitance of the electrical double layer goes up, C_{dl} , with a probable increase in the electrode surface area. There is a good correlation between the results of CV and EIS measurements.

References

1. Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R. *Handbook of Conducting Polymers*, 2nd ed.; Marcel Dekker: New York, 1998.
2. Killian, J. G.; Coffey, B. M.; Gao, F.; Pochler, T. O.; Searson, P. C. *J Electrochem Soc* 1996, 143, 936.
3. Cirpan, A.; Argun, A. A.; Grenier, C. R. G.; Reeves, B. D.; Reynolds, J. R. *J Mater Chem* 2003, 13, 2422.
4. Sonmez, G.; Sonmez, H. B.; Shen, C. K. F.; Jost, R. W.; Rubin, Y.; Wudl, F. A. *Macromolecules* 2005, 38, 669.
5. Cirpan, A.; Guner, Y.; Toppare, L. *Mater Chem Phys* 2004, 85, 222.
6. Olmedo, L.; Hourquebie, P.; Jousse, F. *Adv Mater* 1993, 3, 373.
7. Wang, Y.; Jing, X. *Polym Adv Technol* 2005, 16, 344.
8. Dai, L. M.; Soundarrajan, P.; Kim, T. *Pure Appl Chem* 2002, 74, 1753.
9. Hosseini, H.; Entezami, A. A. *J Appl Polym Sci* 2003, 90, 49.
10. Hosseini, M. G.; Sabouri, M.; Shahrabi, T. *Prog Org Coating*, 2007, 60, 178.
11. Hosseini, M. G.; Seyed Sajadi, S. A.; Bannazadeh, R.; Shahrabi, T. *Eur Corr* 2006, 25, 217.
12. Arsalani, N.; Geckeler, K. E. *J Prakt Chem* 1995, 337, 1.
13. Nalwa, H. S. *Handbook of Organic Conductive Molecules and Polymers*; Wiley: New York, 1997.
14. Wei, Y.; Tang, G. W.; Chan, C. C. *J Polym Sci Part C: Polym Lett* 1990, 28, 219.
15. Kiani, G. R.; Arsalani, N.; Entezami, A. A. *Iran Polym J* 2001, 10, 135.
16. Hosseini, S. H.; Entezami, A. A. *Eur Polym J* 1995, 31, 635.
17. Entezami, A. A.; Rahmatpour, A. *Eur Polym J* 1998, 34, 871.
18. Entezami, A. A.; Rahmatpour, A. *J Polym Mater* 1997, 14, 91.
19. Perin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: Oxford, 1988.
20. Wiberg, K. B.; McShane, H. F. *Org Synth* 1941, 3, 197.