

The Influence of the Catalytic Amount of 1-(2-Pyrrolyl)-2-(2-Thienyl) Ethylene and 2-(2-Thienyl) Pyrrole on Electropolymerization of Pyrrole and *N*-Methylpyrrole

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Received 14 October 1998; accepted 20 January 2001

ABSTRACT

1-(2-Pyrrolyl)-2-(2-thienyl)ethylene (PTE) and 2-(2-thienyl) pyrrole (TP) were synthesized via Wittig and cyclization reactions. The electropolymerization of pyrrole (PY) and *N*-methylpyrrole (NMP) in the presence of catalytic amounts of PTE and TP have been studied by the cyclic voltammetry method. The obtained polymers showed considerable increase in the electroactivity and redoxability. The presence of PTE and TP during electropolymerization of NMP and PY lead to the increase in the rate of polymerization and decrease in the applied potentials. The electrochemical behaviour of produced polymers is described and an interpretation of the results is given.

Key Words: electropolymerization, thiophene, pyrrole, conducting polymers, cyclic voltammetry

INTRODUCTION

Electrochemical oxidative polymerization recently has been widely applied to the synthesis of conducting polymers, in particular those derived from heterocycles [1–9]. Most of the previous works in the field of polypyrrole has been devoted to the study of the physicochemical and electrical properties of the polymers and to the exploration of new monomers [10].

Polypyrrole can be prepared by either electrochemical or chemical polymerization. The chemically prepared polypyrroles have shown lower conductivities than those prepared electrochemically. The electrochemically polymerized *N*-methylpyrrole has

shown that its conductivity is lower than polypyrrole prepared in the same conditions and the redoxability and electroactivity of the prepared polymer through cyclic voltammetry also are not good.

Entezami et al. have investigated the electropolymerization of 1-(2-pyrrolyl)-2-(2-thienyl) ethylene (PTE), as a derivative of pyrrole and thiophene by cyclic voltammetry method in different conditions [11–12]. Also, 2-(2-thienyl) pyrrole (TP)[†] was prepared by Norbert et al. and electropolymerization of TP by cyclic voltammetry method have been studied [13–14].

Wei et al. have investigated the electropolymerization of 3-methylthiophene in presence of catalytic amount of 2,2'-bithiophene that exhibits its

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electroactivity and redoxability better than 3-methylthiophene in the same conditions [15].

On the basis of Wei's idea, we have prepared PTE and TP (Scheme I) and we studied the influence of their catalytic amounts on the electropolymerization of pyrrole and *N*-methylpyrrole.

EXPERIMENTAL

Solvents were purified and dried according to the common procedures in the literature [16]. Pyrrole, thiophene and *N*-methylpyrrole were purchased from Merck and Fluka Co. 2-Chloromethyl thiophene was prepared according to the literature [17].

Synthesis of 2-(2-Thienyl) Pyrrole

2-(2-Thienyl) pyrrole (TP) was prepared by the method of Engle and Steglich [18]. A mixture of 2-thienylallylcarboxamide (10 mmol), a 20% solution of phosgene in toluene (20 mL), and 2 drops of dimethylformamide is stirred for ca. 15 h at room temperature. The solution was then heated to 40–50 °C and the toluene was removed in vacuo. The residue was distilled in vacuo and stored; yield (76%), mp 65 °C IR (KBr): 3400, 3100, 1610, 1490, 1100, 1000, 785, 710 cm⁻¹ and ¹H NMR (CDCl₃, TMS): 6.2–7.7 (m, 7H).

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

2-(2-Pyrrolyl)-2-(2-thienyl) ethylene (PTE) was prepared by the Wittig reaction as follow: 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 *para*-xylene and the mixture was stirred at room temperature for 5 min. Pyrrole-2-carbaldehyde (1.9 g, 20 mmol) was then 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 was filtered. The organic layer was washed with water, dried over magnesium sulphate and evaporated under reduced pressure to leave a solid.

The obtained crude compound was purified by

chromatography from Merck kiesel gel (60) using dichloromethane-petroleum ether 50–70 (2:1 v/v) as the eluent; yield (42%) [11], mp 141–143 °C; IR (KBr): 3400, 1625, 1415, 1115 cm⁻¹; ¹H NMR (CDCl₃, TMS), δ: 6.1–7.3 (m, 9H); MS (EI, 70 eV) m/z (%): 175 (100%), 174 (51.2%), 142 (15%), 77 (15.1%), 51 (23.1%).

Electropolymerization Method

The electrochemical polymerization was carried out using digital potentiostat DP8 (home-made). A glassy carbon (GC) disk 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 P₂O₅ and lithium perchlorate was used as received (Fluka). The electrolyte concentration was 0.1 M and the mole ratio of PTE and TP to *N*-methylpyrrole (NMP) and pyrrole was 1/100.

The electropolymerization of pyrrole, *N*-methylpyrrole, 2-(2-thienyl) pyrrole and 2-(2-pyrrolyl)-2-(2-thienyl) ethylene (1 mM) in 0.1 M LiClO₄/acetonitrile electrolyte was performed in a potential range of -0.2–1.2 V vs. Ag/AgCl at the scan rate 50 mV/s. The similar conditions were used for the electropolymerization of pyrrole in the presence of TP and PTE (1/100 mol ratio), and *N*-methylpyrrole in the presence of PTE (1/100 mol ratio).

RESULTS AND DISCUSSION

The previous study of electropolymerization of 3-methylthiophene with cyclic voltammetry method in the presence of 2,2'-bithiophene has been reported by Wei [15]. In cyclic voltammograms of the electrochemical polymerization of 3-methylthiophene (0.2 M) in the presence of a small amounts of 2,2'-bithiophene (0.2 mM) showed that the anodic peak current is increased more rapidly with lesser shift of peak potential than it does in the bithiophene-free system. The resulted cyclic voltammograms showed considerable increase in the electroactivity and redoxability.

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Table 1. Anodic and cathodic peak voltages and their currents obtained from cyclic voltammograms of the resulting polymers.

Polymer	E_{p_a} (polymer) (mV)*	E_{p_c} (polymer) (mV)*	i_{p_a} (polymer) (μA)	i_{p_c} (polymer) (μA)
PPY	110	~0	+380	-350
PNMP	570	400	+480	-450
PTP	200	150	+50	-50
PPTE	360	300	+90	-100
P(PY-TP)	300	150	+380	-380
P(PY-PTE)	200	80	+450	-430
P(NMP-PTE)	550	450	+480	-460

* Versus Ag/AgCl at a scan rate of 50 mV/s.

We have investigated in similar route the influence of the catalytic amounts of the PTE and TP on the electropolymerization of *N*-methylpyrrole (NMP) and pyrrole. For this purpose, the electropolymerization of above four monomers were performed separately. Then pyrrole in the presence of catalytic amounts of TP or PTE, and NMP in the presence of PTE were electropolymerized. The obtained results from cyclic voltammograms are shown in Table 1.

Typical cyclic voltammograms of the electropolymerization of NMP with and without PTE are shown in Figure 1. The cyclic voltammograms of the

electropolymerization of NMP alone, an anodic peak due to the oxidation of PNMP in the fourth scan at ca. 500 mV vs. Ag/AgCl (Figure 1a) was observed. As the electropolymerization proceeds, the peak current was increased and a black polymer film on the electrode surface was observed.

After 5 scans, the GC electrode containing polymer film have been taken out of electrochemical cell and was washed with acetonitrile and was placed in monomer-free electrolyte solution. Cyclic voltammograms of resulted polymer in the range of -200 to 900 mV vs. Ag/AgCl at various scan rates

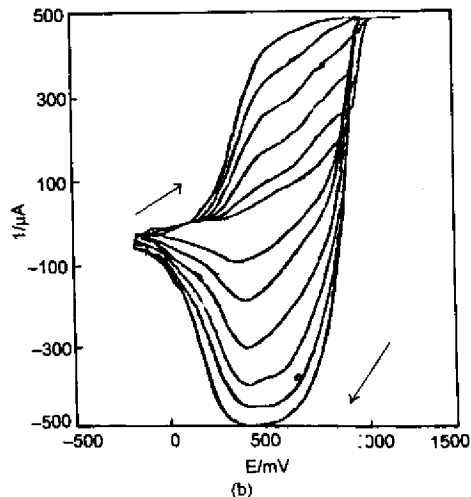
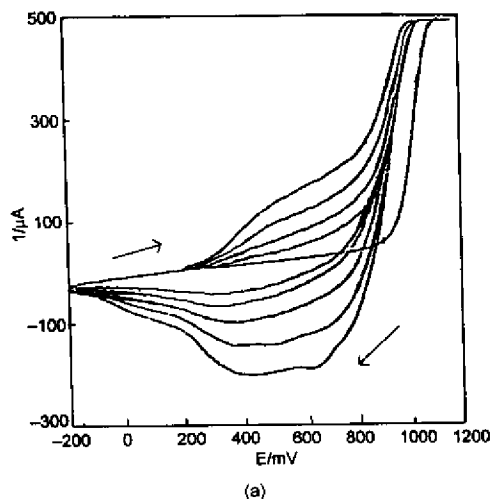


Figure 1. Cyclic voltammograms of 1 mM *N*-methylpyrrole (a) and PTE-NMP (1:100 mol ratio) (b) in 0.1 M $\text{LiClO}_4/\text{CH}_3\text{CN}$ electrolyte at scan rate 50 mV/s.

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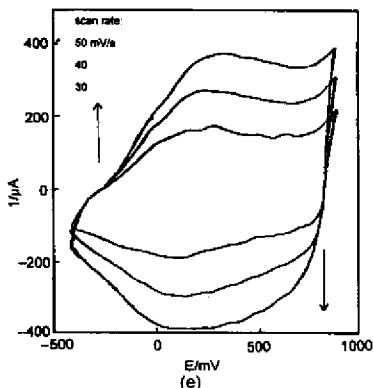
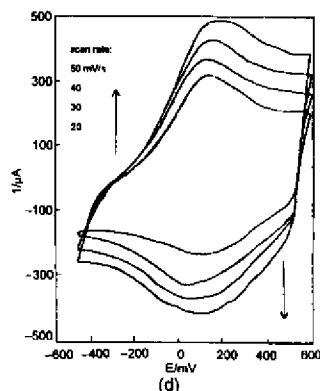
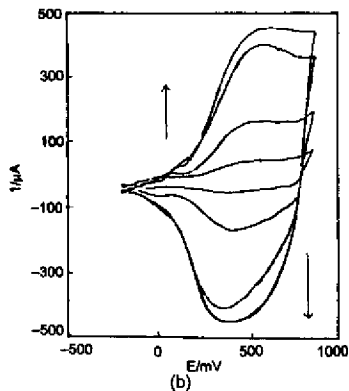
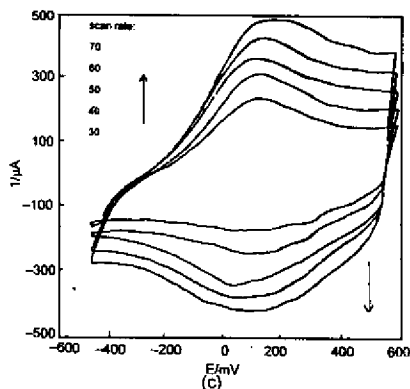
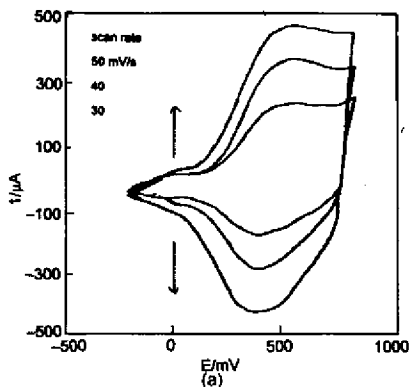


Figure 2. Cyclic voltammograms of poly(NMP) (a), poly (NMP-PTE) (b), poly(PY) (c), poly(PY-PTE) (d) and poly (PY-TP) (e) in 0.1 M LiClO₄/CH₃CN electrolyte at 50 mV/s scan rate.

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shows reversible behaviour (Figure 2a).

In the first scan of the electrochemical oxidation of *N*-methylpyrrole in the presence of the PTE (mole ratio 1/100), an anodic peak appear at ca. 750 mV vs. Ag/AgCl, this is due to the oxidation of PTE. This anodic peak was absent during electropolymerization of NMP without PTE (Figure 1b). The anodic peaks

current due to the oxidation of formed polymer (Figure 1b) increases more rapidly in comparison to the anodic peaks during the electropolymerization of *N*-methylpyrrole without PTE.

With increasing the cycle numbers the cathodic peaks were gradually broader and two near peaks were appeared.

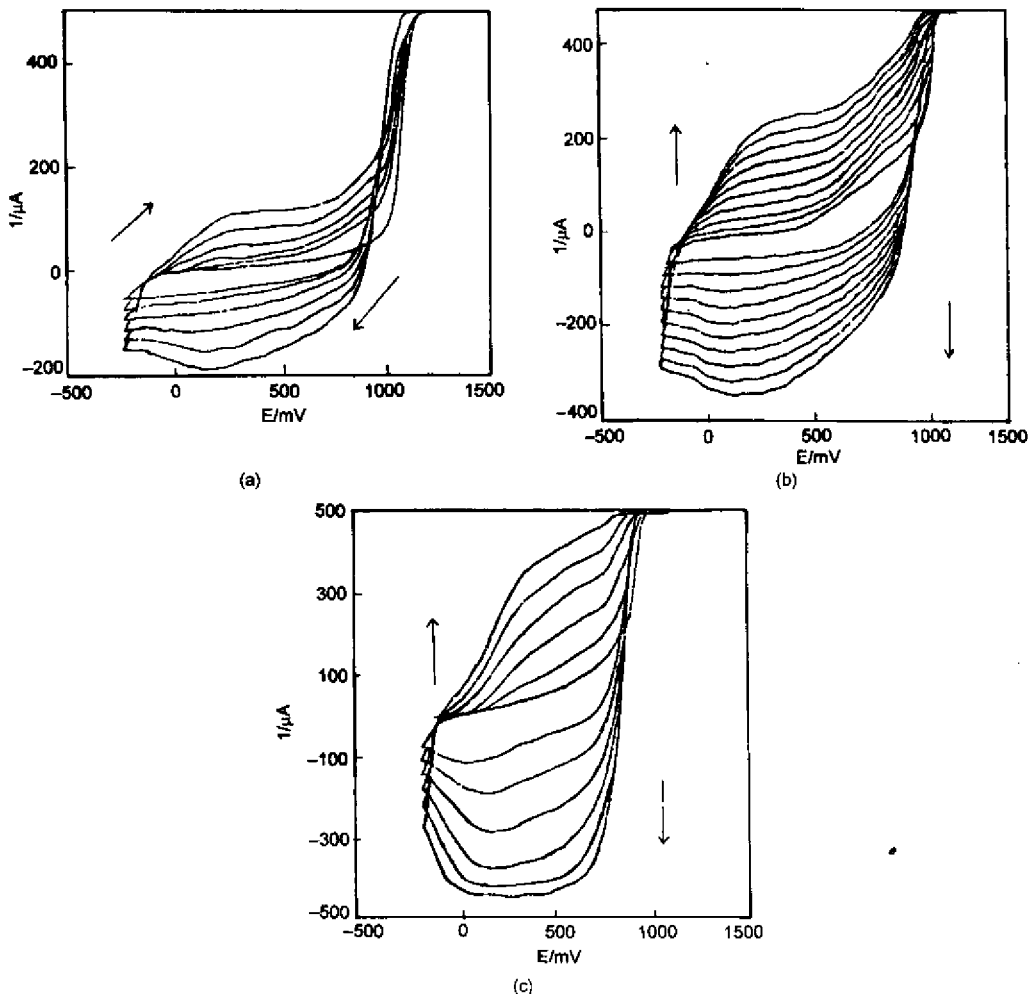


Figure 3. Cyclic voltammograms of 1 mM pyrrole (a), PTE-PY (1:100 mol ratio) (b) and TP-PY (1:100 mol ratio) (c) in 0.1 M LiClO₄/CH₃CN electrolyte at scan rate 50 mV/s.

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After 6 scans, the electrode was washed with CH_3CN and placed in monomer-free electrolyte solution. The cyclic voltammograms of resulted polymer in various scan rates showed good reversible behaviour (Figure 2b) and in comparison with Figure 1b the multiplicity of anodic and cathodic peaks was not shown. From these results we can conclude that the resulted polymer is not a simple blending of two individual polymers, so the obtained film on the electrode surface is probably a copolymer of NMP-PTE with one unit redox character.

In the other work the electrochemical oxidation of pyrrole was performed in the same manner in the absence and presence of catalytic amount of PTE and TP (Figure 3).

During to the first scan of pyrrole solution, cyclic voltammogram shows one anodic peak at 950 mV. This is due to the formation of cation radical species and the appeared weak anodic and cathodic signals in 150–0 mV indicate a reversible redox reaction of the formed polymer (Figure 3a). After 6 scans, the electrode was washed with CH_3CN and placed in monomer-free electrolyte solution. The resulted polymer is insoluble in the CH_3CN electrolyte and shows reversible behaviour at various scan rates in the range of -500–600 mV vs. Ag/AgCl (Figure 2c).

The first scan of cyclic voltammogram for electrolyte containing PTE and pyrrole (1/100 mol ratio) shows two anodic peaks at ca. 700 and 950 mV vs. Ag/AgCl due to the formation of PTE and pyrrole cation radical, respectively. After scanning with successive cycles the reversible anodic and cathodic peaks appeared. This is due to the formation of polymer film on the electrode surface (Figure 3b).

The cyclic voltammogram of prepared polymer film on the electrode surface in solution free from monomer in the potential range of -500–600 mV vs. Ag/AgCl shows reversible redox behaviour (Figure 2d). From Figure 3b it can also be concluded that the resulted polymer is not simple blending of two polymers so, the deposited film on the electrode surface is probably copolymer of PY-PTE.

Figure 3c shows electropolymerization of pyrrole in the presence of catalytic amount of TP.

During the first scan two anodic peaks at 700 and 950 mV vs. Ag/AgCl was observed due to the formation of TP cation radical and pyrrole cation radical, respectively. At the successive scans very broad anodic and cathodic peaks were appeared. After 6 scans, the electrode was washed with CH_3CN and placed in electrolyte solution free from monomer and potential range between -200–1200 mV vs. Ag/AgCl was applied. The obtained cyclic voltammograms from above scanning shows the relatively sharp anodic and cathodic peaks (Figure 2e), which indicates good redoxability. It can be concluded that the deposited polymer on the electrode surface is not a blend from two polymers and probably that is a copolymer of PY-TP.

Figure 4 shows the plots of the cathodic current peak versus of the number of cycles during the electro polymerization of NMP in presence and absence of PTE. Similarly, Figure 5 shows the plots of the cathodic current peak versus the number of cycles during the electropolymerization of pyrrole with and without addition of PTE and TP (Figure 5).

The introduction of small amount of PTE and TP to the electropolymerization systems lead to a great increases in redoxability and electroactivity of polymers and this causes the lowering of the required oxidation potentials.

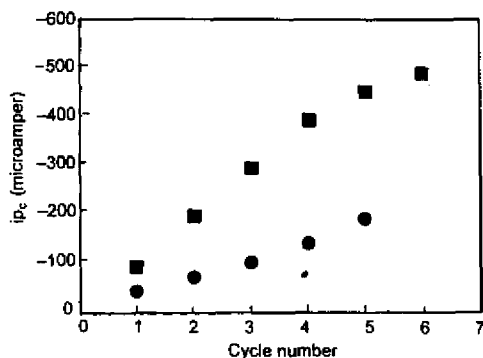


Figure 4. Plots of the cathodic current (μA) against the cycle number for the polymerization of *N*-methylpyrrole (●) without, (■) with addition of PTE (the potential cycling range: -0.2 to 1.2 V vs. Ag/AgCl; the scan rate 50 mV/s).

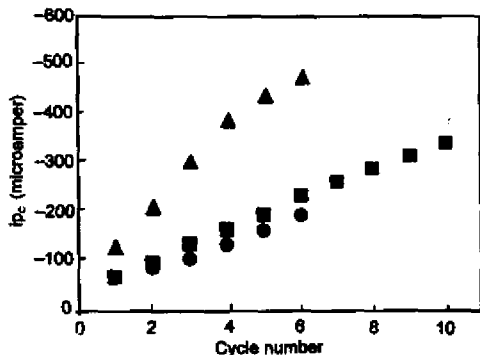


Figure 5. Plots of the cathodic current (μA) against the cycle number for the polymerization of pyrrole (●) without, (■) with addition of PTE and (▲) TP (the potential cycling range: -0.2 to 1.2 V vs. Ag/AgCl; the scan rate 50 mV/s).

For a reasonably fast polymerization of pyrrole and NMP, the up-switch potential of at least ca. 950 mV and ca. 1000 mV vs. Ag/AgCl for PY and NMP, respectively, are required in the absence of PTE and TP. At switch potentials of 950 and 1000 mV vs. Ag/AgCl, no noticeable cathodic charge at first scan could be measured. However, when a small amount of PTE or TP was added to the system, polymers were produced effectively at lower switch potential as shown in Figures 1b, 3b and 3c.

CONCLUSION

Since the oxidation potential of PTE and TP is lower than *N*-methylpyrrole and pyrrole, PTE and TP in the polymerization system should be oxidized first, leading to nucleation species in which the polymer grows. Therefore, the number of the nucleation species would increase in the polymerization system with addition of the PTE and TP, which might be responsible for the higher overall rate of polymerization.

Electropolymerization of *N*-methylpyrrole and pyrrole in presence of catalytic amounts of PTE or TP were caused by the increase in redoxability and electroactivity of polymers.

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