

## **ELECTROCHEMICAL RELAXATION STUDY OF POLYTHIOPHENE AS CONDUCTING POLYMER (II)**

G. M. ABOU-ELENIEN, A. A. EL-MAGHRABY\*, AND G. M. EL-ABDALLAH

*Chemistry Department, Faculty of Science, Cairo University. Giza,, Egypt.*

\* E-mail: [maghraby04@yahoo.com](mailto:maghraby04@yahoo.com)

### **Abstract**

The electrosynthesis of polythiophene films from thiophene, 2, 2':5, 2''-terthiophene, 3-methylthiophene and 3-bromothiophene monomers were investigated using different electrochemical techniques. The stability and electrical conductivity of the prepared films were studied. The most stable polythiophene film was obtained using galvanostatic technique in acetonitrile solvent and TBAPF<sub>6</sub> as supporting electrolyte at 5°C, except in case of electropolymerization of 3- bromothiophene the most stable film was obtained potentiodynamically. The relaxation kinetics of the films were extensively studied. It was found that a very thin film would hardly show the slow relaxation. Also by using TBAPF<sub>6</sub> as electrolyte, the most sensitive film was obtained, which has the lowest relaxation. The relaxation time is sharply affected by increasing the donor number of the solvent used and also by temperature.

**Keywords:** Electropolymerization, relaxation studies, polythiophene, conducting polymer, film building

### **Introduction**

Conducting polymers have been the subject of increasing research effort due to their electrochemical, optical and thermal properties, ease of preparation and processibility [1-6]. Among conducting polymer family, great attention has been recently devoted to polythiophene and its derivatives, which shows many advantageous properties such as high transparency in the visible range, excellent thermal stability and moderately high conductivity [7]. Since the discovery of polythiophene as an excellent conducting polymer, there have been intensive studies on its industrial applications such as electrodes of capacitors and photodiodes, antistatic coating, electrochromic windows, field effect transistors [3,7-11], sensors and biosensors as well as for biomedical applications such as synthetic bones and artificial muscles [1,11-15]. In cyclic voltammetry experiments the oxidation peak of the first run after the sample has been left for a wait-time in the neutral state, is narrower and shifted towards more positive potential than the peak observed in steady-state conditions [16]. This process is reported as the slow relaxation effect or memory effect by most of researchers. A complete description of this effect is yet to be developed and the mechanism is still under debate [17]. In earlier publication

[18] we have studied this phenomenon on polythiophene film. In this study, we are interested to use different monomers of thiophenes and compare the results with those obtained by polybithiophene. Several electrochemical and physicochemical conditions have to be optimized in order to obtain high-quality films by electrochemical polymerization. The most important properties to be satisfied by these optimization experiments are to obtain a highly conductive film with good mechanical properties and longevity of its electronic response. Many variables were found to affect these properties which include: (i) the nature of the monomeric (starting) compounds and their concentrations in these solutions, (ii) the nature of the supporting electrolytes used in the synthesis solution and their concentrations, (iii) the nature, purity, and dryness of the solvent, (iv) the temperature-control during the synthesis, (v) the means of pretreatment and the apparent geometry of the working electrode at which the electropolymerization is achieved, and (vi) the applied potential  $E_{app}$ . (in the case of potentiostatically grown films), the current density  $I_{app}$ . (in the case of galvanostatically formed films), or the number of repetitive cycles and their positive and negative potential limits (in the case of the films formed by the cyclic voltammetric technique) employed for the film synthesis.

Thiophene(T), 2, 2':5,2''-terthiophene(TT),3- methylthiophene (MT) and 3-bromothiophene (BrT) have been used as starting compounds for building up different polythiophene films.

## Experimental

### *Monomers and Supporting electrolytes*

Thiophene(T), 2, 2':5,2''-terthiophene(TT),3- methylthiophene (MT) and 3-bromothiophene (BrT), were reagent grade and used as received from commercial source (Sigma- Aldrich). Tetrabutyl ammonium hexafluorophosphate (TBAPF<sub>6</sub>) (Aldrich). Tetraethyl ammonium perchlorate (TEAP) (Fluka, Purum), Tetrabutyl ammonium perchlorate (TBAP) (Fluka, Purum) and Lithium perchlorate (Fluka, Purum) are used as a supporting electrolyte. They are purified through four times recrystallization from an ethanol/water mixtures (9:1, v:v). The crystals are grinded, dried under vacuum for 5 hours and then stored in a special tube under argon atmosphere [17].

*Electrosynthesis*

Platinum disc electrode was used for electropolymerization. Many techniques were used to electrodepositing the films such as potentiostatic, potentiodynamic, chronoamperometric and galvanostatic techniques. The thickness of the doped conducting film was adjusted by the electrolysis time. In potentiostatic and potentiodynamic electrosynthesis the potential sweep (50mV/s) started from the rest potential of the working electrode. The polymer films were grown by electrooxidation of the monomer by repetitive potential cycling between the cathodic and anodic potential limits, dependent on the used monomer. In chronoamperometric electrosynthesis the working electrode was first switched from the rest potential to value prior to the redox potential for a period of either 30 sec or 1 min. Polymerization was achieved by further step to potentials close to peak potential of the monomer. The purpose of the initial step was to allow double-layer charging of the platinum- solution interface and any oxidative monomer adsorption at the bare Pt-surface to proceed fully before the bulk monomer oxidation and nucleation and growth of the polymer initiated. In this way the distortion of the early part of the polymerization current transient by double-layer charging and monomer adsorption was minimized. The choice of polymerization potential was based on the consideration that the deposition should be controlled by the electrochemical step rather than diffusion of monomer to the electrode surface [20, 21]. In galvanostatic technique we were select the better current density value to obtain a very stable film. After polymerization, the film was rinsed thoroughly with the same solvent used and transferred into a new degassed supporting electrolytic medium involving solvent and supporting electrolyte. Then the film was electrochemically reduced at potential according to insulating state for 1 min. Such a pretreatment allows us to obtain a stable and high reproducible film [22]. The stability in electrolytic medium has also been determined after 10 cycles between oxidized and reduced state. In the relaxation study the potential sequence involved two ways: imposed potential and open circuit conditions, discussed in details in previous work [18]

The EG&G Princeton Applied Research Model 285 Potentiostat/Galvanostat Controlled from a PS-486-DX microcomputer via a National Instrument IEEE-488 through GPIB board by means of M270/250 Program was used for the electrochemical control.

However, all the potentials were cited with respect to Ag wire reference electrode. The temperature in all studies was controlled by using cryostat of model RC20 CS Lauda.

Nitrobenzene (NB) [Aldrich], 1,2- Dichloroethane (DCE) {HPLC- pure grade (Fisons Scientific Equipment Incorporating Griffin & George England)}, Dichloromethane (DCM) and Acetonitrile (AN) [HPLC- pure grade (Fisons Scientific Equipment Incorporating Griffin & George England)]. All the solvents (NB, DCE & DCM) were used as received from commercial source. Before each measurement the solvents are allowed to pass over aluminum oxide (Super I ICN) under dry argon atmosphere.

## Results and discussion

### *Electrosynthesis*

Fig.1 shows the electrochemical characteristics during the cyclic voltammogram of 2,2',5',2''-terthiophene in nitrobenzene and 0.1M TBAPF<sub>6</sub> with scan rate 50 mV/s taking as example. The electrochemical redox characteristics of the monomers in different solvents are also summarized in Table 1. From Table 1 we can conclude that the electrochemical oxidation of substituted thiophenes and thiophene oligomers yields conducting polymers which can be further oxidized at less positive potential than the corresponding monomers [23]. We start to study the effect of different electrochemical techniques on the properties of the polymer film formed. In chronoamperometric deposition, following the initial spike, the current falls to a minimum and then rises to a plateau [20]. This feature together with the current cross-over in the potentiodynamic technique during polymer deposition under swept potential control [21] is typical of deposition through a nucleation and growth mechanism [24-27]. The concentration of the monomer was varied according to the polymerization technique. For galvanostatic one the concentration of terthiophene (TT) was 0.01M while for other techniques they were  $2 \times 10^{-3}$  M in NB and  $5 \times 10^{-3}$  M in other solvents. The electrosynthesis of thiophene (T) was carried out in presence of 0.1M TBAPF<sub>6</sub> with Pt electrode under different polymerization mode. The most stable film was obtained in potentiodynamic technique at 0.05M monomer while in galvanostatic was 0.5M monomer in AN and 0.1M monomer in other solvents. A stable film of PMT in all solvents was obtained using different techniques Table 2. The solution of 0.1M MT and 0.1M TBAPF<sub>6</sub> in NB, DCE and DCM solvents while in AN was 0.2M (MT) and 0.2M (LiClO<sub>4</sub>) as supporting electrolytes. The best results for deposition of the film from 0.2M 3-bromothiophene (BrT) monomers and 0.02M TBAPF<sub>6</sub> in AN was obtained potentiodynamically while in other techniques the film was less stable. The potentiodynamic technique shows clearly that the deposition of 3-bromothiophene occurs steadily and the polymerization is much slower when

compared with thiophene. In chronoamperometric technique a sharp initial current peak is followed by very small minimum and then the current appear as a plateau. The processes involved in initial spike are considered to be mainly monomer oxidation, intermediate adsorption and polymerization deposition [20]. Better results were obtained when the electrode is polarized in the galvanostatic mode, and with optimized current density for polymerization of monomer in DCE and DCM while in the case of BN and AN the film was less stable. In galvanostatic and chronoamperometric method, the electrolysis time was controlled until a given amount of the total anodic charge had passed to obtain a film with suitable thickness. In potentiodynamic (Fig.2) method, the thickness of the film was controlled through a number of cycles. The films were obtained by potentiostatic and chronoamperometric modes having low stability as compared with those obtained using cyclicvoltammetry and galvanostatic modes. For the films that were grafted on Pt- electrode under galvanostatic conditions the optimum applied current density was  $5\text{mA}/\text{cm}^2$ . The almost constant potential through the whole process using galvanostatic condition indicated the formation of a well conducting films [28,29]. In the previous study [18] we observed that while scanning towards more positive potential the film was conducting and the response of the oxidation peak of the ferrocene was appeared in both coated film and bar electrode while in reduction state, the film was insulating and reduction peak of cobaltocene was not appeared [30, 31].

The effect of solvent on the nature and adherence of the films of polythiophene and its derivatives on Pt- electrode has been extensively studied in different solvents such as acetonitrile (AN), 1,1- dichloromethane (DCM), 1,2- dichloroethane (DCE) and nitrobenzene(NB) are used. Using potentiodynamic and galvanostatic techniques, very stable films are obtained in AN as well as in NB as compared with those obtained by other solvents, while in other techniques (potentiostatic and chronoamperometric) the films were less stable Fig.(2). Different supporting electrolytes such as tetra-butylammonium hexa flourophosphate  $\text{TBAPF}_6$ , tetraethylammonium perchlorate  $\text{TEAClO}_4$ , tetrabutyl-ammonium perchlorate  $\text{TBAClO}_4$ , and lithium perchlorate  $\text{LiClO}_4$  are used. Generally, all the electrolytes gave a stable film but the most stable one obtained using  $\text{TBAPF}_6$ , except in case of PMT 0.2M  $\text{LiClO}_4$  was used in AN solvent.

The temperature of electropolymerization affects the extent of the conjugated system and hence the optical and electrical properties of the polymer; the films produced at higher temperatures having a shorter mean conjugation length than

those prepared at lower temperatures [32-35]. By controlling the temperature of the experiment during the film building, we obtained the most stable film at 5°C.

### *Relaxation Measurements*

After electropolymerization the polythiophene films of thiophene and its derivatives were rinsed with dry solvent to get rid of the monomer and then immersed in dry electrolyte solution (contain only the solvent and supporting electrolyte) in which the films were reduced into neutral state and then subjected to 10 cycles between the oxidation and reduction potentials. This process participates in the stability of the film in solution [36]. High potentials, necessary for the polymerization of monomeric thiophene, cause an irreversible oxidation of the polymer chains. However, use of a much lower polymerization potential, which is possible in propylene carbonate electrolytes with bithiophene as the starting material, improves the properties of the polymer films. Both the peak potential and the peak maximum current are governed by a logarithmic law as a function of wait time [37] with the following equations:

$$E_r = E_o + \delta\gamma_E \log (tw)$$

$$i_r = i_o + \delta\gamma_i \log (tw)$$

Where  $E_o$  &  $i_o$  are constants for a given scan rate,  $\delta\gamma_E = \frac{dE_r}{d \log (tw)}$  is the slope of

the potential relaxation and  $\delta\gamma_i = \frac{di_r}{d \log (tw)}$  is the slope of the current relaxation.

After cycling process the film was left for at least 20 hours wait time in insulating state. The potential sequence used in the present relaxation studies is mentioned in details previously [18]. The relaxation of the film is followed up by recording two successive cyclic voltammograms after different wait times ( $tw$ ) in open circuit condition. The first cyclic voltammogram (relaxed peak) indicates the degree of relaxation of the film while the second represent the steady state. The relaxed peak is shifted to more positive potential and had a higher peak current. We considered the higher relaxed peak that measured after long-time as full relaxed peak or equilibrium state. To obtain the relaxation time of the film we plot ( $\log tw$ ) as a function of relative relaxed peak current to the full relaxed peak ( $i_p/i_o$ ) and also the shift in relaxed peak potential from the full relaxed peak  $\Delta E$ . Fig.3a shows as example for PTT the successive measurements at different ( $tw$ ). It is clear that the peak current is increased and the peak potential shifted into more positive values

with increasing the wait time. Fig. 3b shows the logarithmic wait time dependence on the  $i_p/i_0$  and  $\Delta E$  values. The relaxation time can be obtained through the extrapolation of the line to intercept  $\log tw$  axis at  $(i_p/i_0) = 1$  and  $\Delta E = \text{zero}$ .

Another trial was done by applying an imposed potential on the film during the wait- time at its neutral state (wait potential  $V_w$ ). The relaxation effect can be observed also at potential corresponding to a significant doping level of the film being conducting. Fig. 4a and 4b show the corresponding results, which are summarized in Table 3. These results indicate that the relaxation time is highly affected by this treatment, it becomes of lower values as compared with that obtained by open circuit measurement. This indicates that using the imposed potential, the sensitivity of the film increased leading to reach the equilibrium state (full relaxed) during a shorter wait time. But, when the film is subjected to the imposed potential for a long time, it began to damage and lost a part of its sensitivity.

A polythiophene film prepared on a Pt-electrode was degraded and deactivated by repeating the potential scan in electrolytic solutions. After the film formation it is subjected to 100 cycles of cyclic voltammetry in the solution free monomers before relaxation measurements. The results obtained in Fig. 5a and 5b as an example for PTT film in AN and 0.1M TBAPF<sub>6</sub> show the relaxation time ( $\log rx$ ) which indicates that the sensitivity of the film is decreased during the potentiodynamic process. The above relaxation measurements are summarized in Table 3.

By studying the effect of electrolyte on the relaxation of the film, the relaxation measurements are carried out using different supporting electrolytes. It is clear that the relaxation time is highly affected by the nature of the anion. Also Frank et al. [38] studied the effect of electrolyte on conducting polymers. It was found that the size of the dopant ion affects the oxidation kinetics and the electrical conductivity of the film. Hexafluorophosphate anion gives the most sensitive film, which has the lowest relaxation time and the higher sharpness of the peak height which is clearly proved before [18].

The effect of solvent on the relaxation process was investigated; we build the films and study its relaxation behaviour in different solvents having large extensive donor number DN (0.1-14.1) according to Guttmann acidity scale [39, 40]. Dry acetonitrile (AN), 1,2-dichloroethane (DCE), 1,1-dichloromethane (DCM), and nitrobenzene (NB) were used as solvents. TBAPF<sub>6</sub> is used as electrolyte (in all used solvents). The best solvent in which the film can be conserved for a long time

without appreciable change is DCE (DN = 0.1). The dependence of the relaxation parameters on the donor number of the solvent is illustrated in Fig. 6a and 6b which show the results of PMT-film prepared in AN and studied in various solvents; DCE, DCM, NB & AN. The calculated results are summarized in Table 4. As shown from the results, the relaxation of the film is highly affected by the nature of the solvent. As the donor number increases, the relaxation time is highly decreased. This can be attributed to the conductivity and the charge transfer in the solvent and its effect on the conductivity and also the sensitivity of the film. Table 5 summarizes the obtained relaxation data for all polythiophene derivatives that prepared in NB and studied in AN solvent. The results show that PT has the lowest relaxation time among all derivatives.

The effect of temperature on the relaxation of the film has been also studied. The measurements are carried out at different temperature ranging from  $-30^{\circ}$  to  $+15^{\circ}\text{C}$ . Table 6 summarizes the obtained relaxation data at different temperatures. As shown from these results the relaxation time is highly affected by temperature. Fig.7a and 7b as an example for PMT in AN and  $0.1\text{M LiClO}_4$  gave a linear relationship between slope relaxation  $\delta\gamma$  and relaxation time  $\log r_x$  with temperature. The results obtained using the current ratio  $i_p/i_0$  seems to be as a whole not sufficient. Other deviation that observed in the temperature effect when the film left for long time to reach equilibrium state (full relaxed) and subjecting to low temperature, the first point recorded was shown far from linearity. This deviation is checked and showed well reproducibility. This deviation reflects the higher dependence of the relaxation on the temperature and also it was found by other authors [41, 41].

## Conclusion

These studies showed that by using imposed potential at insulating state for different wait times ( $t_w$ ) the time required for reaching the equilibrium state (relaxation time) was less than that for open circuit conditions. Different factors affect the obtained relaxation time such as, the charge building density (thickness of the film), the composition of the electrolyte in which the relaxation measurements were done and the temperature of the experiments. The main purpose of this work was to define the optimum conditions at which a stable and high sensitive ( $\log t_w$ ) films can be obtained. It was found that a very thin film would hardly show the slow relaxation. PT has the lowest relaxation time among other polythiophene derivatives. TBAPF<sub>6</sub> as electrolyte, gives the most sensitive film, which has the lowest relaxation. As the donor number of the solvent increases, the relaxation time is



decreased. The relaxation time is also highly affected by temperature. The most stable polythiophene films were obtained by using galvanostatic technique in AN with TBAPF<sub>6</sub> as supporting electrolyte at a temperature of 5°C.

### List of Figures

- Fig.1. Cyclic voltammograms of  $5 \times 10^{-3}$  M terthiophene NB and 0.1 M TBAPF<sub>6</sub> at Pt-electrode with scan rate = 50 mV/s.
- Fig.2. Successive cyclic voltammograms corresponding to the electro polymerization of terthiophene at Pt- electrode from solution of  $2 \times 10^{-3}$  M monomer and 0.1 M TBAPF<sub>6</sub> in NB at scan rate 50 mV.s<sup>-1</sup>.
- Fig.3a. Cyclic voltammograms of PTT film in 0.1 M TBAPF<sub>6</sub>/AN on Pt-electrode, wait-potential  $V_w = 0V$ , open circuit ; wait-time 1min, 10min, 30min, 2h, 6h ; imbricated lines are steady-state waves. Corresponding to  $T_w = 0$  sec. at room temperature, scan rate = 100m V/S .
- Fig.3b. A. Relative peak height of relaxed wave,  
 B. difference between relaxed & full- relaxed waves of Fig(3a) as a function of logarithmic wait-time.
- Fig.4a. Cyclic voltammograms of PTT film in 0.1 M TBAPF<sub>6</sub>/AN on Pt-electrode, wait-potential  $V_w = 0.2V$  imposed potential at  $V_w$ ; wait-time 1min, 5min, 10min, 40min, 2h; imbricated lines are steady-state waves, at room temperature, scan rate = 100 m V/S.
- Fig.4b. A. Relative peak height of relaxed wave, B. difference between relaxed & full-relaxed waves of Fig(4a) as a function of logarithmic wait-time.
- Fig.5a. Cyclic voltammograms of PTT film in 0.1 M TBAPF<sub>6</sub>/AN on Pt-electrode, wait-potential  $V_w = 0.2V$ , open circuit; wait-time 10min, 1h, 2h, 14h, 25h, 48h; imbricated lines are steady-state waves, at room temperature , after stabilization for 100 cycles; scan rate = 100 mV/S.
- Fig.5b. A. Relative peak height of relaxed wave, B. difference between relaxed & full-relaxed waves of Fig(5a) as a function of logarithmic wait-time.
- Fig.6a. Dependence of slope relaxation of shift in peak potential, on donor number of PTT films prepared and studied in the same solvent DCE, DCM, NB & AN all in 0.1 M TBAPF<sub>6</sub>.
- Fig.6b. Dependence of relaxation time of shift in peak potential, on donor number of PMT films prepared and studied in the same solvent DCE, DCM, NB & AN all in 0.1 M TBAPF<sub>6</sub>.
- Fig.7a. Dependence of slope relaxation of shift in peak potential, on temperature of PMT in AN/0.1 M LiClO<sub>4</sub> the film prepared Galvanostatically in AN and 0.1 TBAPF<sub>6</sub>.
- Fig.7b. Dependence of relaxation time of shift in peak potential, on temperature of PMT in AN/0.1 M LiClO<sub>4</sub> the film prepared Galvanostatically in AN and 0.1 TBAPF<sub>6</sub>.

Table 1. The electrochemical characteristics of the investigated compounds.

Compounds <sup>a</sup>	Solvents <sup>b</sup>	E <sub>ox</sub> monomer (mV)	E <sub>ox</sub> Polymer (mV)
T	DCE	1936	1170
	DCM	1915	1095
	NB	1845	1033
	AN	1958	1130
TT	DCE	1180	1088
	DCM	1031	975
	NB	1089	930
	AN	1050	975
MT	DCE	1860	835
	DCM	1890	778
	NB	1795	765
	AN	1838	729
BrT	DCE	2190	1385
	DCM	2183	1405
	NB	2197	1435
	AN	2265	1379

<sup>a</sup> Peak Potential measured relative to Ag wire reference electrode.

<sup>b</sup> TBAPF<sub>6</sub> was used as supporting electrolyte.

Table 2. Technique effects on relative peak height and shift in peak potential for PMT films prepared in different solvents and studied in AN.

Technique	Solvent synthesis	Relative peak height ip/io		Shift in peak potential ΔE/mV	
		δv <sub>i</sub> (mA)	Log rx <sub>i</sub> (s)	δv <sub>E</sub> (mA)	Log rx <sub>E</sub> (s)
Potentiodynamically	DCE	0.145	7.36	-38.50	7.61
	DCM	0.123	5.02	-28.84	5.08
	NB	0.108	5.95	-32.00	5.33
	AN	0.029	7.27	-39.03	4.82
Chronoamperometrically	DCE	0.211	5.06	-65.33	5.24
	DCM	0.205	5.28	-47.02	5.41
	NB	0.168	5.50	-40.90	5.57
	AN	0.068	6.62	-43.21	4.78
Galvanostatically	DCE	0.19	5.38	-60.85	5.47
	DCM	0.181	5.03	-30.49	5.21
	NB	0.161	6.19	-32.00	5.41
	AN	0.164	4.93	-32.14	4.94

**Table 3. Mode effect on relative peak height and shift in peak potential for polythiophene and its derivatives films in AN / 0.1 M TBAPF<sub>6</sub>.**

Polymer	Mode	Relative peak height ip/io		Shift in peak potential ΔE/mV	
		δv <sub>i</sub> (mA)	Log rx <sub>i</sub> (s)	Δv <sub>E</sub> (mA)	Log rx <sub>E</sub> (s)
PT	Imposed Potential <sup>a</sup>	0.175	3.91	-27.39	4.14
	Open circuit <sup>b</sup>	0.266	4.33	-32.10	5.07
	After 100 Cycles	0.132	5.05	-27.10	5.05
PTT	Imposed Potential <sup>a</sup>	0.148	3.75	-21.16	4.60
	Open circuit <sup>b</sup>	0.260	5.95	-68.78	5.48
	After 100 Cycles	0.196	5.15	-20.90	5.15
PMT	Imposed Potential <sup>a</sup>	0.127	5.26	-26.40	4.83
	Open circuit <sup>b</sup>	0.164	4.96	-32.14	4.94
	After 100 Cycles	0.132	5.67	-28.70	4.65
PBrT	Imposed Potential <sup>a</sup>	0.087	3.85	-11.12	4.30
	Open circuit <sup>b</sup>	0.111	5.17	-14.25	5.21
	After 100 Cycles	0.139	6.19	-11.02	6.55

**Table 4. Donor number effect on relative peak height and shift in peak potential for all polymer films. Prepared and studied in the same solvent with 0.1 M TBAPF<sub>6</sub> electrolyte.**

Polymer	Solvent	DN	Relative peak height ip/io		Shift in peak potential ΔE/mV	
			δv <sub>i</sub> (mA)	Log rx <sub>i</sub> (s)	δv <sub>E</sub> (mA)	Log rx <sub>E</sub> (s)
PT	DCE	0.1	0.092	5.33	-50.48	5.11
	DCM	4	0.044	4.77	-9.71	4.62
	NB	8.1	0.043	5.11	-12.56	5.56
	AN	14.1	0.266	4.33	-32.00	5.07
PTT	DCE	0.1	0.211	5.53	-19.32	5.33
	DCM	4	0.076	7.37	-18.61	5.34
	NB	8.1	0.294	4.57	-28.69	4.94
	AN	14.1	0.260	5.95	-68.78	5.48
PMT	DCE	0.1	0.072	5.14	-23.87	4.92
	DCM	4	0.071	6.48	-21.54	5.83
	NB	8.1	0.049	5.93	-23.98	5.21
	AN	14.1	0.164	4.93	-32.14	4.94
PBrT	DCE	0.1	0.065	10.89	-22.04	6.08
	DCM	4	0.111	5.17	-14.26	5.21
	NB	8.1	0.296	5.31	-25.51	6.59
	AN	14.1	0.338	5.25	-74.21	4.55

**Table 5. Relaxation study of polythiophene and its derivatives that prepared in NB and studied in AN/TBABF<sub>6</sub>.**

Polymer	Relative peak height ip/io		Shift in peak potential $\Delta E/mV$	
	$\delta v_i$ (mA)	Log $rx_i$ (s)	$\delta v_E$ (mA)	Log $rx_E$ (s)
PT	0.266	4.33	-32.10	5.07
PTT	0.130	5.30	-21.61	5.42
PMT	0.161	6.19	-32.00	5.41
PBrT	0.296	5.31	-25.51	6.59

**Table 6. Temperature effect on relative peak height and shift in peak potential for all polymer films.**

polymer	T° C	Relative peak height ip/io		Shift in peak potential $\Delta E/mV$	
		$\delta v_i$ (mA)	Log $rx_i$ (s)	$\delta v_E$ (mA)	Log $rx_E$ (s)
PT	-20	0.089	9.798	-143.3	5.14
	-10	0.308	4.22	-60.00	7.07
	0	0.149	4.68	-52.40	5.24
	20	0.146	5.22	-18.40	5.24
PTT	-30	0.259	6.69	-16.97	8.29
	-15	0.132	8.86	-12.03	10.30
	0	0.107	9.89	-23.15	6.02
	15	0.247	5.38	-16.30	5.29
PMT	-20	0.059	12.90	-88.28	5.25
	-10	0.071	11.80	-30.71	4.70
	0	0.055	14.50	-26.95	3.97
	20	0.055	14.50	-26.95	3.97
PBrT	-20	0.221	5.38	-113.20	5.33
	-10	0.163	4.92	-55.27	5.26
	0	0.127	5.39	-74.50	4.23
	20	0.111	5.17	-14.26	5.21

ELECTROCHEMICAL RELAXATION STUDY OF POLYTHIOPHENE .....37

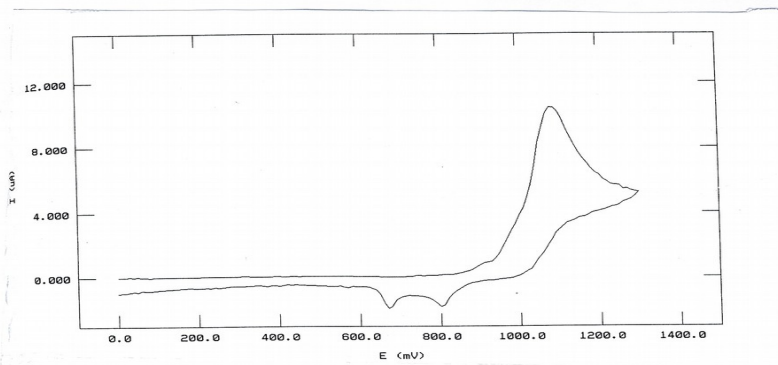


Fig. 1

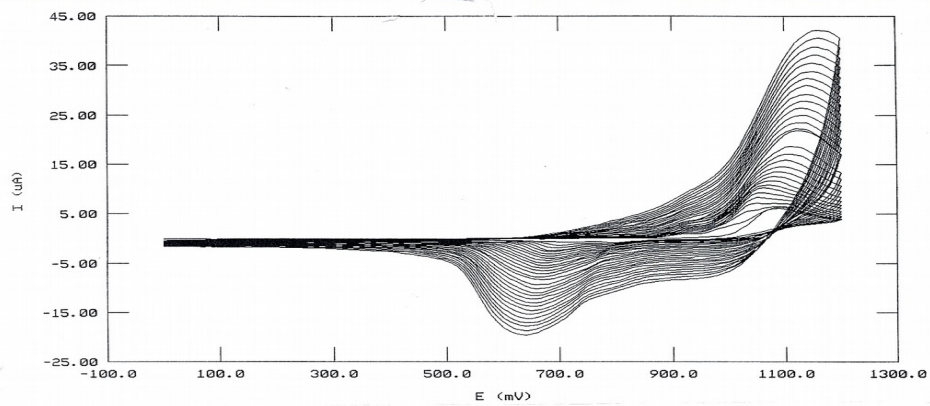


Fig. 2

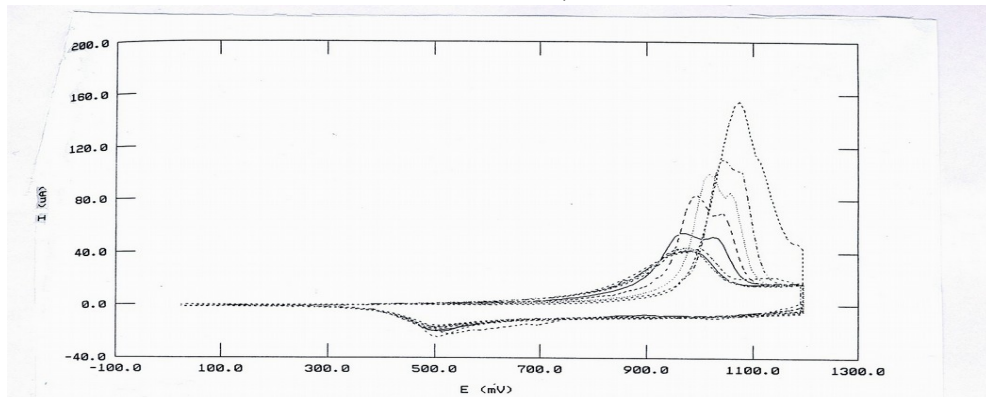


Fig. (3a)

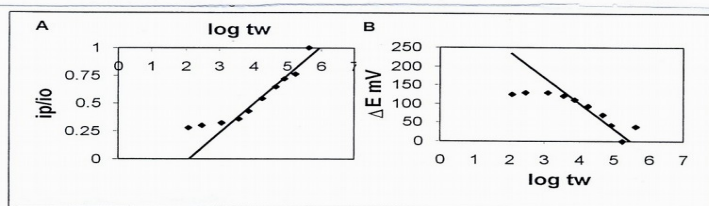


Fig. (3a)

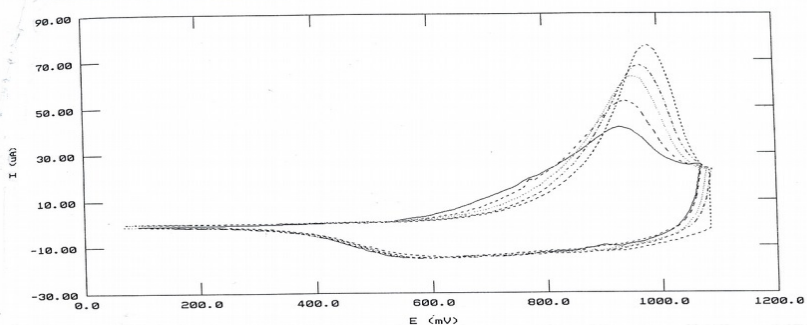


Fig. (4a)

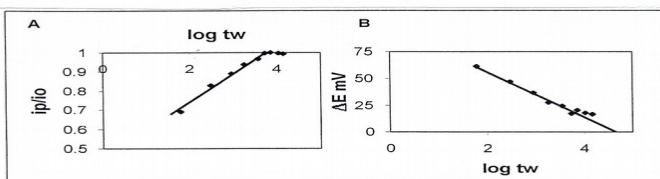


Fig. (4b)

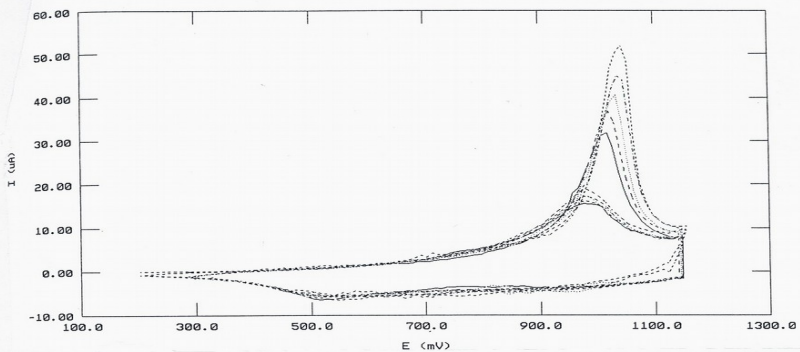


Fig. (5a)

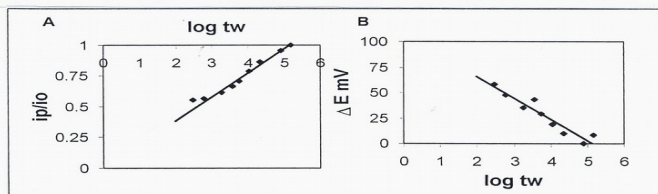


Fig. (5b)

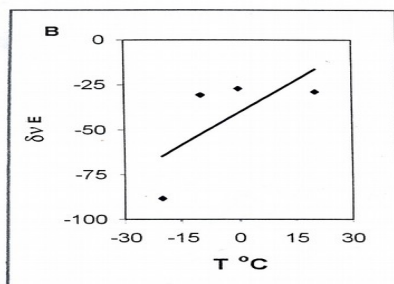


Fig. (7a)

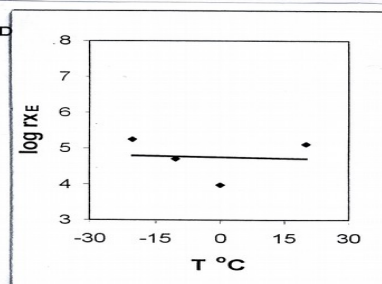


Fig. (7b)

Fig (7b)

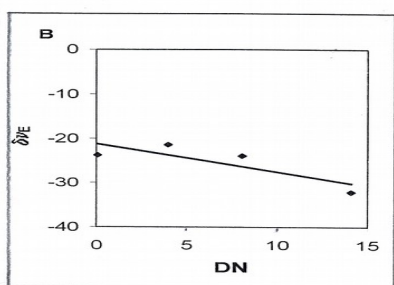


Fig. (6a)

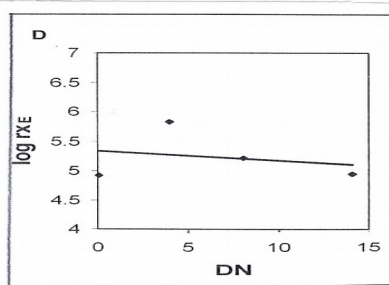


Fig. (6b)

Fig (6a)

## References

1. U.LANGE, N. V. ROZNYATOVSKAYA, V. M. MIRSKY, *Anal. Chim. Acta* 614 (2008) 1.
2. S. DING, S. COSNIER, M. HOLZINGER, X. WANG, *Electrochem. Comm.* 10 (2008) 1423.
3. R. M. WALCZAK, J. R. REYNOLDS, *Adv. Mater.* 18 (2006) 1121.
4. M. TURBIEZ, P. FRERE, P. BLANCHARD, J. Roncali, *Tetrahedron Let.* 41 (2000) 5521.
5. J. RONCALI, P. BLANCHARD, P. FRERE, *J. Mater. Chem.* 15 (2005) 1589.
6. H. J. SPENCER, P. J. SKABARA, M. GILES, I. MCCULLOCH, ET. AL., *J. Mater. Chem.* 15 (2005) 4783.
7. Y. Han, Y. Lu, *Synth. Met.* 158 (2008) 744.
8. A. A. Argun, P. H. Aubert, B. C. Thompson et. al., *Chem. Mater.* 16 (2004) 4401.



## ELECTROCHEMICAL RELAXATION STUDY OF POLYTHIOPHENE .....41

9. L. GROENENDAAL, F. JONAS, D. FREITAG, H. PIELARTZIK, J. R. RENOLDS, *Adr. Mater* 12 (2000) 481.
10. S. INAGI, T. FUNCHIGAMI, *Synth. Met.* 158 (2008) 782.
11. T. F. OTERO, I. BOYADO, *Electrochim. Acta* 49 (2004) 3719.
12. S. HARA, T. ZAMA, W. TAKASHIMA, K. KANETO, *Smart Mat. Struct.* 14 (2005) 1502.
13. S. COSNIER, *Anal. Lett.* 40 (2007) 1260.
14. T. F. OTERO IN: R. L. ELSENBAUMER AND J. R. REYNOLDS (Eds.), *Hand book of Conducting Polymers (third ed.)*, CRC Press, Boca Raton, 2007, p.591.
15. S. CONSIER IN: R. S. MARKS, D. CULLEN, C. LOWE, H. H. WEETALL AND I. KARUBE (Eds.), *Hand book of Biosensors and Biochips, vol.1*, John Wiley & Sons Ltd. Publishers, Berlin, 2007, p. 237.
16. C. ODIN, M. NECHTSHEIN, *Phys. Rev. Lett.* 67 (1991) 1114.
17. K. AOKI, T. EDO, J. Cao, *Electrochimca Acta*, 43 (1998) 285.
18. G. M. ABOU-ELENIEN, A. A. EL-MAGHRABY, G. M. EL-ABDALLAH, *Synth. Met.*, 146 (2004) 109- 119.
19. W. F. LUDER, P. B. KRAUSS, *J. Am. Chem. Soc.*, 58 (1963) 255.
20. F. LI, W. J. ALBERY, *Electrochimica. Acta.* 37 (1992) 393.
21. W. J. ALBERY, F. LI, A. R. MOUNT, *J. Electroanal. Chem.* 310 (1991) 239.
22. O. A. SEMENIKHIN, E. V. OVSYANNIKOVA. N. M. ALPATOVA, Z. A. ROTENBERG. *J. Electroanal. Chem.*, 408 (1996) 67.
23. G. INZELT, M. PINERI, J. W. SCHULTZE, M. A. VOROTYNTSEV, *Electrochim. Acta*, 45 (2000) 2403.
24. S. ASAVAPIRIYANONT, G. FC CHANDLER, G. A. GUNAWARDENA, D. PLETCHER, *J. Electroanal. Chem.*, 171 (1984) 245.
25. M. FLEISCHMANN AND H. R. THIRSK, in: P. Delahy (Ed.), *Advances in Electrochemistry and Electrochemical Engineering, Vol.3*, Wiley - Interscience, New York, 1963, p.123.
26. R. DE LEVIE, in: H. GERISHER, C. W. TOBIAS (Eds.), *advances in Electrochemistry and Electrochemical Engineering, Vol. 13*, John Wiley, New York, 1984, p.1.

27. M. S. REHBACK, J.H.WIENBERG, E. BOSCO, J. H. SLUTES, *J. electroanal. Chem.* 236 (1987) 1.
28. C. VISY. M. LAKATOS, A. SZUCS, M. NOVAK, *Electrochim. Acta*, 42 (1997) 651.
29. C. VISY, J. LUKKARI, J KANKARE, *J. Electroanal. Chem.* 401 (1996) 119.
30. R. J. WALTMAN, J. BARGON, AND A. F. DIAZ, *J. Phys. Chem.*, 87 (1983) 1459.
31. R. AUDEBERT , H. BIDAN, *J. Electroanal. Chem.* 190 (1985) 129.
32. J. PONCALI, *Chem. Rev.* 92 (1992) 711.
33. S HOTTA. T. HOSAKA, W. SHIMOTSUMA. *Synth. Met.*, 6 (1983) 317.
34. M. SATO, S. TANAKA, K. KAERIYAMA, *J. Chem. Soc. Chem.Commun.*, (1985) 713
35. K. TANAKA, T. SHICHIRI, T. Yamabe, *Synth. Met.*, 16 (1986) 207.
36. B RASCH AND W. VIELSTICH, *Electroanal Chem.* 370, (1994) 109.
37. C ODIN, M. NECHTSCHHEIN, *Synth. Met.* 44 (1991) 177.
38. F. PERN, A.J. FRANK, *J. Electrochem. Soc.* 137 (1990) 2769.
39. C. REICHARDT, *Solvents and Solvent Effects*, VCH, Weinheim, second ed., 1988.
40. S. AEIYACH, E. BAZZAOUI , P. LACAZE, *J. Electroanal. Chem.* 434. (1997) 153.
41. H. TANG, A. KITANI, M. SHIOTANI, *J. Electroanal. Chem.* 396 (1995) 377.
42. H. TANG, A. KITANI, S. MAITANI, H. MUNEMURA. AND M. SHIOTANI, *J. Electrochim. Acta* 40 (1995) 849.