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Electrochemical Relaxation Studies of Bithiophene and Bromothiophene as Conducting Copolymer

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The electrosynthesis of both the polymer and copolymer were carried out from 2, 2'-bithiophene and 3-bromothiophene monomers using galvanostatic and potentiodynamic techniques. The most stable films were obtained using the galvanostatic technique in nitrobenzen solvent and $TBAPF_6$ as supporting electrolyte. A comparison relaxation study was made between the prepared copolymer and homopolymer films using the cyclic voltammetric technique in different solvents. Several studies were performed to determine the solvent effect, monomer concentration ratio, electrocopolymerization techniques and temperature which give a lower relaxation time.

Keywords: Conducting copolymer, Relaxation study, Film building, Electropolymerization,

1. INTRODUCTION

Organic conducting polymers such as polythiophene, polyaniline and polypyrrole have been the subject of increasing research efforts due to their electrochemical, optical and thermal properties, ease of preparation and processibility and wide range of applications such as electrochromic devices, organic transistors, supercapacitors and electronic noses [1, 2]. For three decades, these electrogenerated films were of growing interest in the design of chemical sensors and biosensors as well as for biomedical applications such as synthetic bones and artificial muscles [3-8]. Electropolymerization of the conducting component on an electrode previously coated with the insulating polymer is one of the most widely used methods to compensate for the certain deficiencies of conducting polymers like poor mechanical and physical properties [9-11]. Conducting graft copolymerization of random copolymers with thiophene and/or pyrrole was achieved by constant potential electrolysis [12]. The grafting process was elucidated with conductivity measurements, cyclic voltammetry, fourier transform infrared spectroscopy, differential scanning calorimetry, thermal gravimetric analysis and scanning electron microscopy studies. Design and synthesis of new films of polythiophenes by copolymerization of thiophene derivatives play an important role in the properties of the polymer film and its morphology. Several electrochemical conditions needed to be optimized in order to obtain high-quality films with good mechanical properties and longevity of their electronic response by electrochemical copolymerization. Many factors can affect these properties during the electrochemical synthesis, which include (i) The nature of the monomeric (starting) compounds and concentration ratio of the two monomers in the electrocopolymerization media. (ii)The nature and concentration of the supporting electrolytes used in the synthesis solution. (iii) The nature, purity, and dryness of the solvent. (iv) The temperature-control during film synthesis (v) The nature, pretreatment and the apparent geometry of the working electrode at which the electropolymerization is achieved (vi) The applied current density I_{app} (in the case of galvanostatically prepared films) or the number of repetitive cycles and their positive and negative potential limits (in the case of the films formed by successive cyclic voltammetric technique). The origin of the relaxation effect was explained through different studies. Heinze et al. [13] considered the relaxation from the planar to the twisted form which should accompany the quinoid- to- benzoid molecular transition upon discharging. Miller et al. [14] explained the break- in (relaxation effect) in poly (3-methoxythiophene) and stated that the film was initially hydrophobic, containing no ions and behaved as insulator. After reaching defined potential, a small amount of ions were incorporated into the film as a result of oxidation and the conductivity increased. At a sufficiently positive potential, the film is completely oxidized. On the reverse scan the film behaves as a conductor. In the second sweep (cycle), the film remains sufficiently doped with ions to allow oxidation to begin at lower oxidation potential (this is corresponding to steady state wave). Inganas et al. [15] considered the slow relaxation during holding the polymer in neutral state is attributed to mechanical process. The opened channels left after the ejection of dopant (co-ions) are gradually filled in by the adjacent polymer chains. Very recently Aoki et al. [16] investigated the potential step of absorption at conducting-to-insulating conversion of polyaniline film for demonstrating the slow relaxation. The authors found that the slope of the linearity in the charge of the conducting species left in the film (q) versus logarithmic wait time varies with the potential (E) although quantitative discussion has not yet been given to it. The observation demonstrates more directly the slow relaxation than the time dependence of the voltammetric peak potential or the charge reported previously [16]. 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 [17]. 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 [16, 18]. In earlier publications [19, 20] this phenomenon had been studied on the polythiophenes films. In this work, a trial was made to show the memory effect observed on thin films of both 2,2'-polythiophene and poly-3-bromothiophene and compare the results with those obtained by the electrosynthesised copolymer film in different conditions.

2. EXPERIMENTAL

2.1. Monomer, supporting electrolytes and solvents

2, 2'-Bithiophene (BiT) and 3-bromothiophene (BrT) were reagent grade and used as received from the commercial source (Sigma-Aldrich). Tetrabutyl ammonium hexafluorophosphate ($TBAPF_6$) (Aldrich) was used as a supporting electrolyte. The supporting electrolyte was purified through four times recrystallization from an ethanol / water mixture (9:1 v: v).The crystals were ground, dried in vacuum for 5 hours and then stored in a special tube under argon atmosphere [21]. Acetonitrile (AN) [BDH-analar], nitrobenzene (NB) [Aldrich] and 1, 2- dichloroethane (DCE) [HPLC-pure grade (Fisons Scientific Equipment Incorporating Griffin & George England)] were the solvents.

2.2. Electrosynthesis

Platinum disc electrode (1.0 mm diameter) was used for electropolymerization of the films as a working electrode, while platinum wire electrode (1.0 mm diameter) was used as auxiliary electrode in a three-electrode setup. All the potentials were cited with respect to Ag wire reference electrode (1.0 mm diameter). The solutions were degassed by argon bubbling for 10-15 min prior to polymerization. Many techniques were used to electrodepositing the films such as potentiodynamic and galvanostatic techniques. In potentiodynamic technique the potential sweep (50mV/s) started from the rest potential (i.e. potential of zero current) 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 (i.e. between the rest potential and oxidation potential of the monomers), dependent on the used monomer. In galvanostatic technique the thickness of the doped conducting film was adjusted by the electrolysis time, by applying current densities between 1-10 mA/cm^2 to the working electrode. Before each experiment the working electrode was polished with diamond past (particle size 0.25 μm) on soft leather and washed with distilled water and anhydrous solvent. After polymerization, the film was rinsed thoroughly with the same solvent used and transferred into a new degassed electrolytic medium involving solvent and supporting electrolyte. Then, the film was electrochemically reduced at a potential according to insulating state; i.e. at the rest potential; 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 imposed potential conditions, which has been discussed in detail before [19, 20].

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. The temperature in all studies was controlled by using cryostat of model RC20 CS Lauda.

3. RESULTS AND DISCUSSION

3.1. Electrosynthesis of Poly(Bithiophene-co-Bromothiophene) [Poly(BiT-co-BrT)]

Figs. 1, 2 and 3 represent the successive cyclic voltammograms during the preparation of the homopolymers (PBiT and PBrT) and the (BiT-co-BrT) copolymer which was used for comparison between the copolymer and its homopolymers at the same condition. The syntheses of these homopolymers were studied in detail in the literature [19, 20]. The electrochemical redox characteristics of 2, 2'-bithiophene, 3-bromothiophene monomers and (BiT-co-BrT) copolymer in different solvents are summarized in Table 1.

Table 1. The electrochemical characteristics of the investigated compounds.

Compounds a	**Solvents b**	**Eox monomer (mV)**	**Eox Polymer (mV)**
BiT	DCE	1219	905
	NB	1351	1099
	AN	1345	1010
BrT	DCE	2190	1385
	NB	2197	1435
	AN	2265	1379
BiT-co-BrT	DCE	1924	1221
	NB	1914	1114
	AN	2144	1209

a Peak Potential measured relative to Ag wire reference electrode.

b TBAPF6 was used as supporting electrolyte.

From Table 1 we can conclude that the electrochemical oxidation of 2, 2'-bithiophene, 3-bromothiophene and (BiT-co-BrT) copolymer yields conducting polymers which can be further oxidized at less positive potential than the corresponding monomers [23, 24].

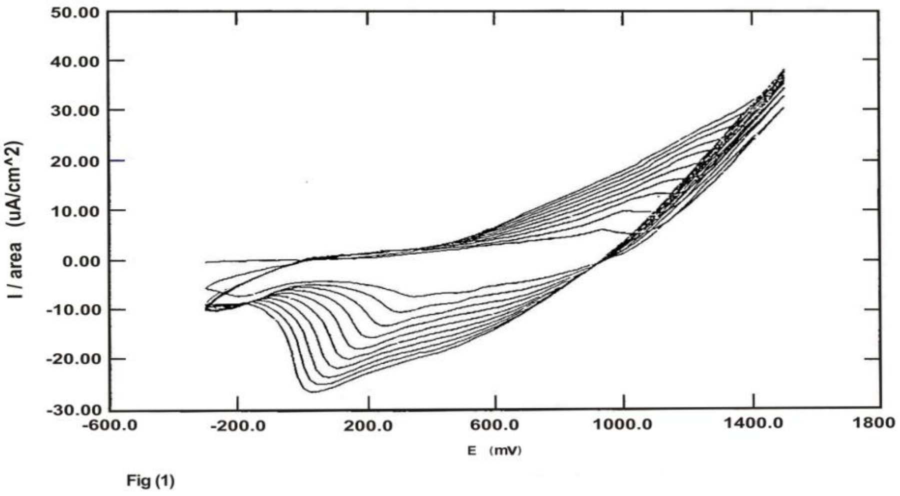

Figure 1. Successive cyclic voltammograms corresponding to the electropolymerization of 2, 2'-bithiophene at Pt-electrode from solution of 0.01M monomer and 0.05M TBAPF$_6$ in NB at scan rate 50mVs^{-1}.

These results indicate also that the (BiT-co-BrT) copolymer film formed can be oxidized at potential lies between the potential of each 2, 2'-bithiophene and 3-bromothiophene monomers. This behavior coincides with that obtained previously in case of (BrT-co-T) copolymer film [24].

The effect of different electrochemical techniques on the properties of the copolymer film formed has been studied. The current cross-over in the potentiodynamic technique during polymer deposition under swept potential control [25] is typical of deposition through a nucleation and growth mechanism [26-29]. The concentration of the monomer was varied according to the polymerization technique. In potentiodynamic method the concentration of 3-bromothiophene was 0.2M and 0.01M 2, 2'-bithiophene in nitrobenzene solvent containing 0.05M $TBAPF_6$. Figure 3 shows the potentiodynamic electrosynthesis of poly (BiT-co-BrT). The thickness of the film was controlled by the number of cycles. In the galvanostatic one; in order to obtain a stable film; the concentration was 0.2M 3-bromothiophene (BrT) and 0.04M 2, 2'-bithiophene (BiT) in nitrobenzen containing 0.05 M $TBAPF_6$. The electrolysis time was controlled until a given amount of the total anodic charge had passed to obtain a film with suitable thickness. For the films that were grafted on Pt-electrode under galvanostatic conditions, the optimum applied current density was $5mA/cm^2$ [19, 20]. The almost constant potential through the whole process using galvanostatic conditions indicated the formation of well conducting films [30, 31].

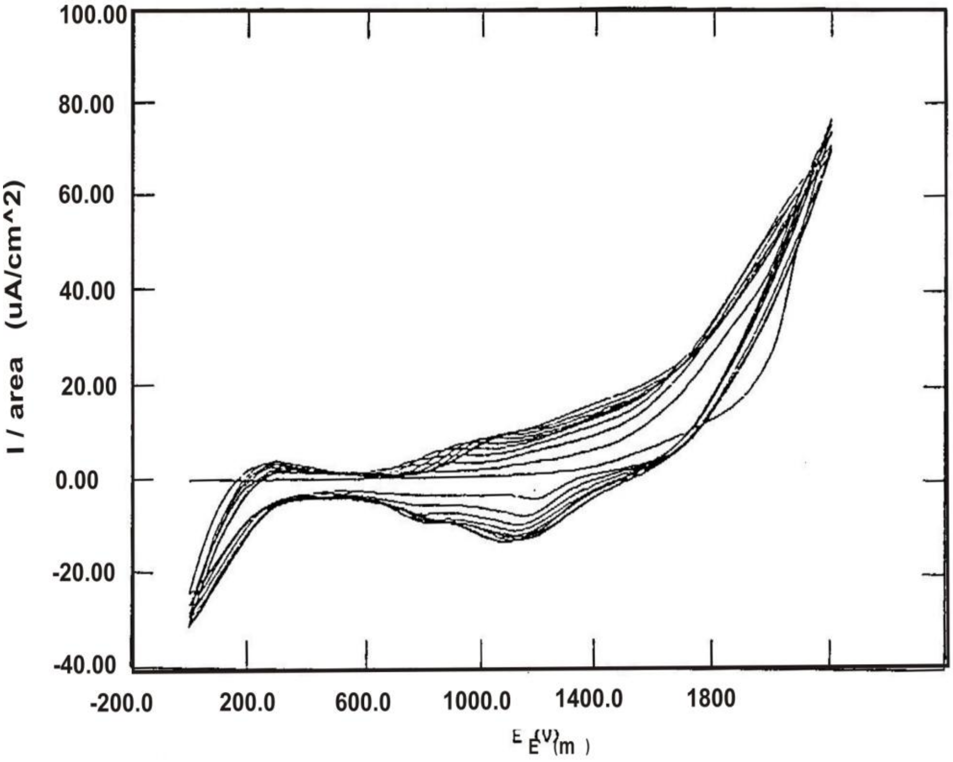

Fig. (2)

Figure 2. Successive cyclic voltammograms corresponding to the electropolymerization of 3-bromothiophene at Pt-electrode from solution of 0.2M monomer and 0.05M $TBAPF_6$ in NB at scan rate $50mVs^{-1}$.

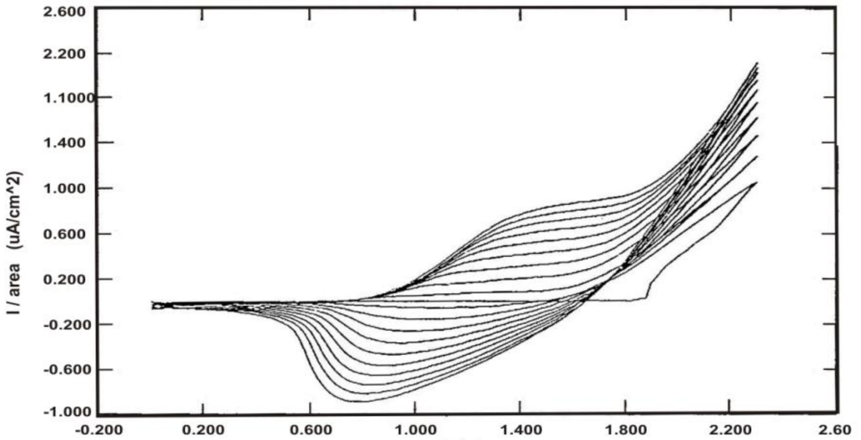

Fig (3)

Figure 3. Successive cyclic voltammograms corresponding to the electrosynthesis of the copolymer at Pt-electrode from solution of 0.2M 3-bromothiophene , 0.01M 2,2'-bithiophene and 0.05M TBAPF$_6$ in NB at scan rate 50mVs^{-1}.

The previous study [19, 20] stated that, while scanning towards more positive potential the film was conducting and 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 [32, 33]. It was found that the films obtained by successive cyclic voltammetry had lower stability than those obtained by the galvanostatic mode, where the stable film makes possible a long time of study without damage and gives reproducible results. This was achieved by subjecting the film to repetitive 10 cycles without suffering damage.

The effect of solvent on the nature and adherence of the films of copolythiophene on Pt-electrode has been extensively studied in different solvents such as acetonitrile (AN), 1, 2-dichloroethane (DCE) and nitrobenzene (NB). Using potentiodynamic and galvanostatic techniques, very stable films are obtained in NB as compared with those obtained by other solvents. Different supporting electrolytes such as tetra- butyl ammonium hexafluorophosphate TBAPF$_6$, tetraethyl ammonium perchlorate TEAClO$_4$, tetrabutytle ammoniumperchlorate TBAClO$_4$, and lithium perchlorate LiClO$_4$ are used. Generally, all the electrolytes gave a stable film but the most stable one obtained using TBAPF$_6$.

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 40°C having a shorter mean conjugation length than those prepared at 5°C [31, 34-37]. It was found that by controlling the temperature of the experiment during the film building, the most stable film was obtained at 5°C [19, 20].

3.2. Relaxation Measurements

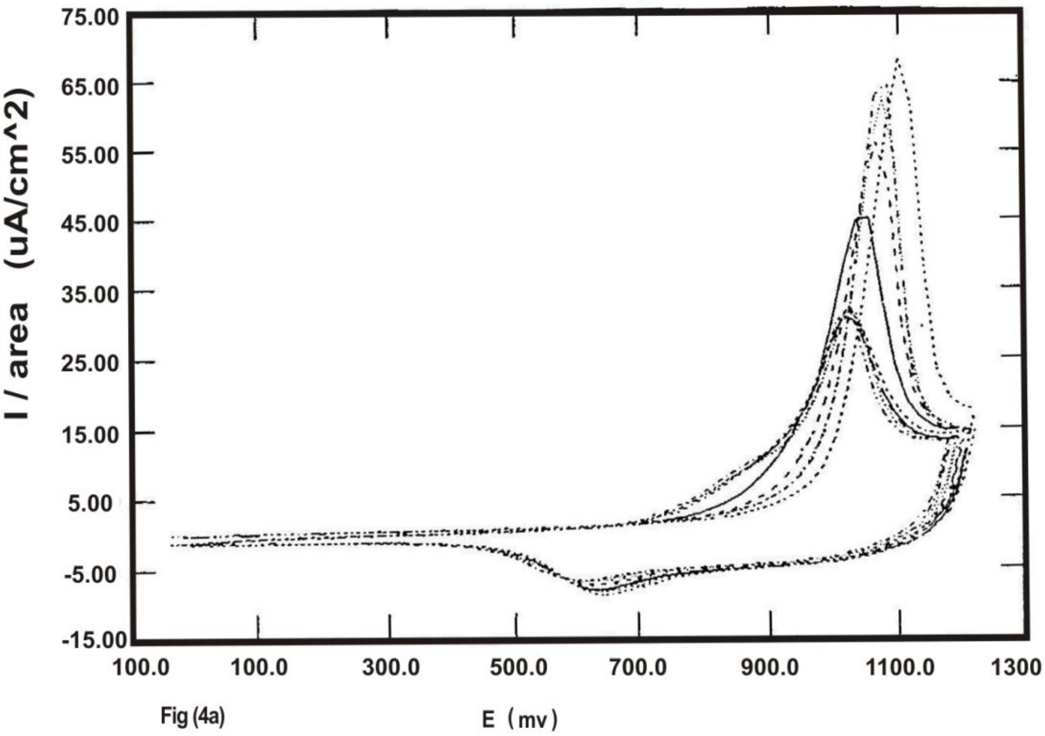

Fig (4a)

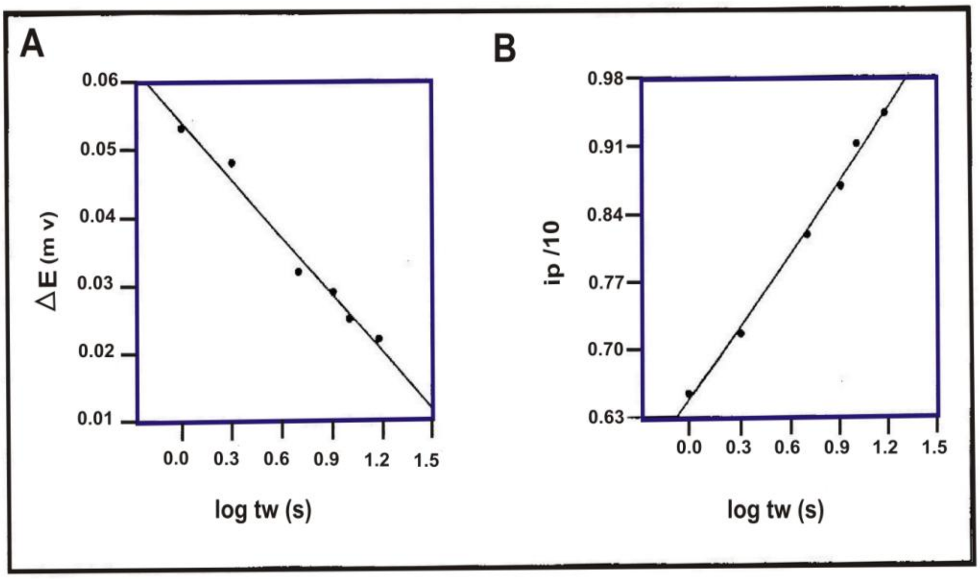

Fig (4b)

Figure 4. (a) Cyclic voltammogram of poly(BiT-co-BrT) film in 0.05M $TBAPF_6$/ AN on Pt-electrode, wait-potential V_w = 0.0V at wait-time 1, 5, 10, 20 min, 24 h; imbricated lines are steady state waves, film galvanostatically synthesized from 0.2M BrT and 0.04M BiT in 0.05M $TABPF_6$/NB at room temperature, scan rate =50 mVs^{-1}. (b) A. Difference between relaxed and full-relaxed waves; B. relative peak height of relaxed wave of (a) as a function of logarithmic wait-time.

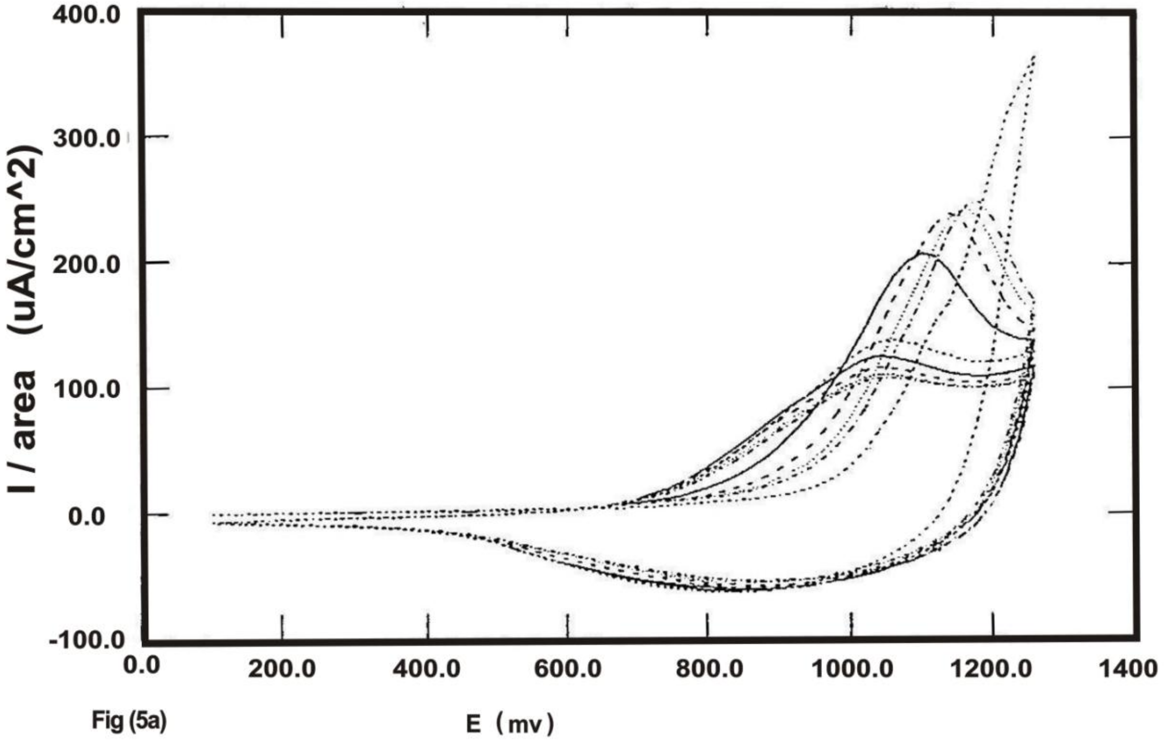

Fig (5a)

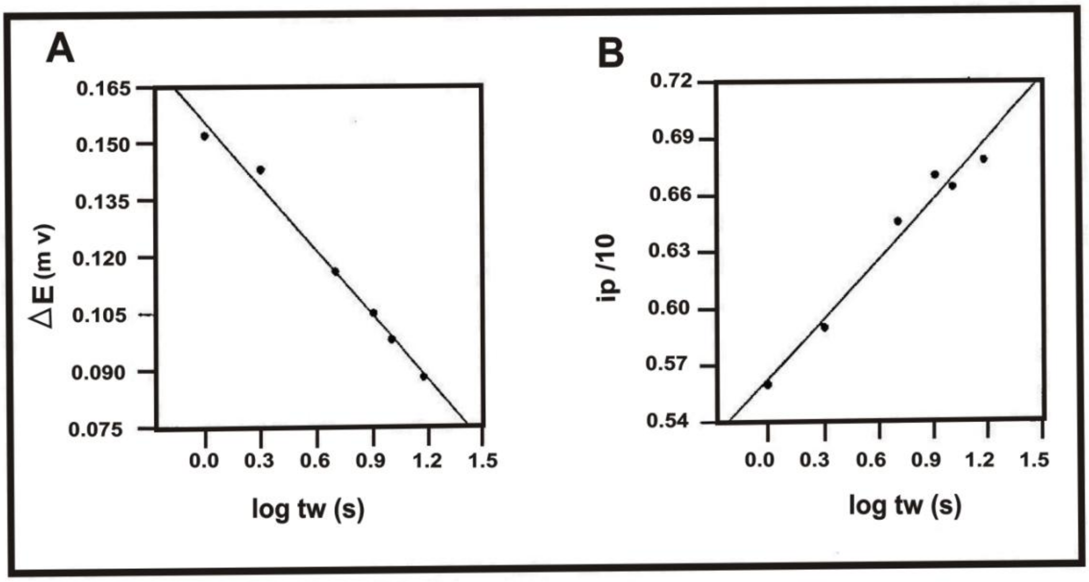

Fig (5b)

Figure 5 (a) Cyclic voltammogram of poly(BiT-co-BrT) film in 0.05M TBAPF$_6$/ AN on Pt-electrode, wait-potential V_w = 0.1V at wait-time 1, 5, 10, 15 min, 24 h; imbricated lines are steady state waves, film potentiodynamically synthesized from 0. 2M BrT and 0.02M BiT in 0.05M TABPF$_6$/NB at room temperature, scan rate =50 mVs^{-1}. (b) A. Difference between relaxed and full-relaxed waves; B. relative peak height of relaxed wave of (a) as a function of logarithmic wait-time.

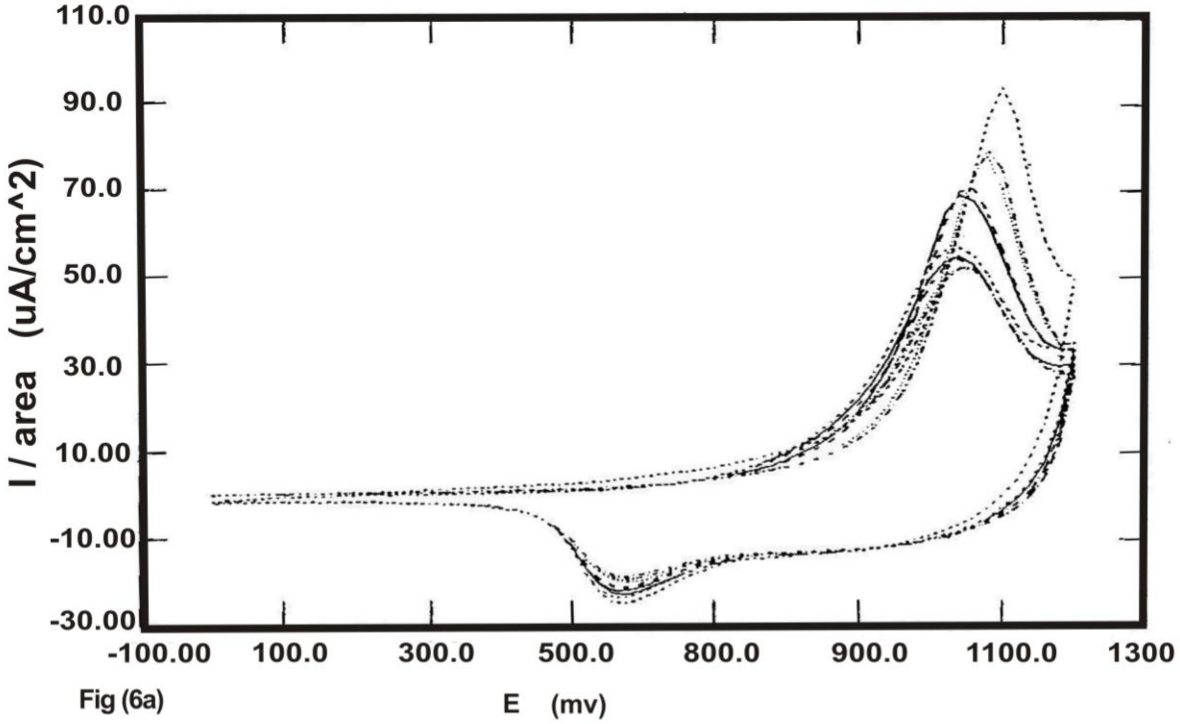

Fig (6a)

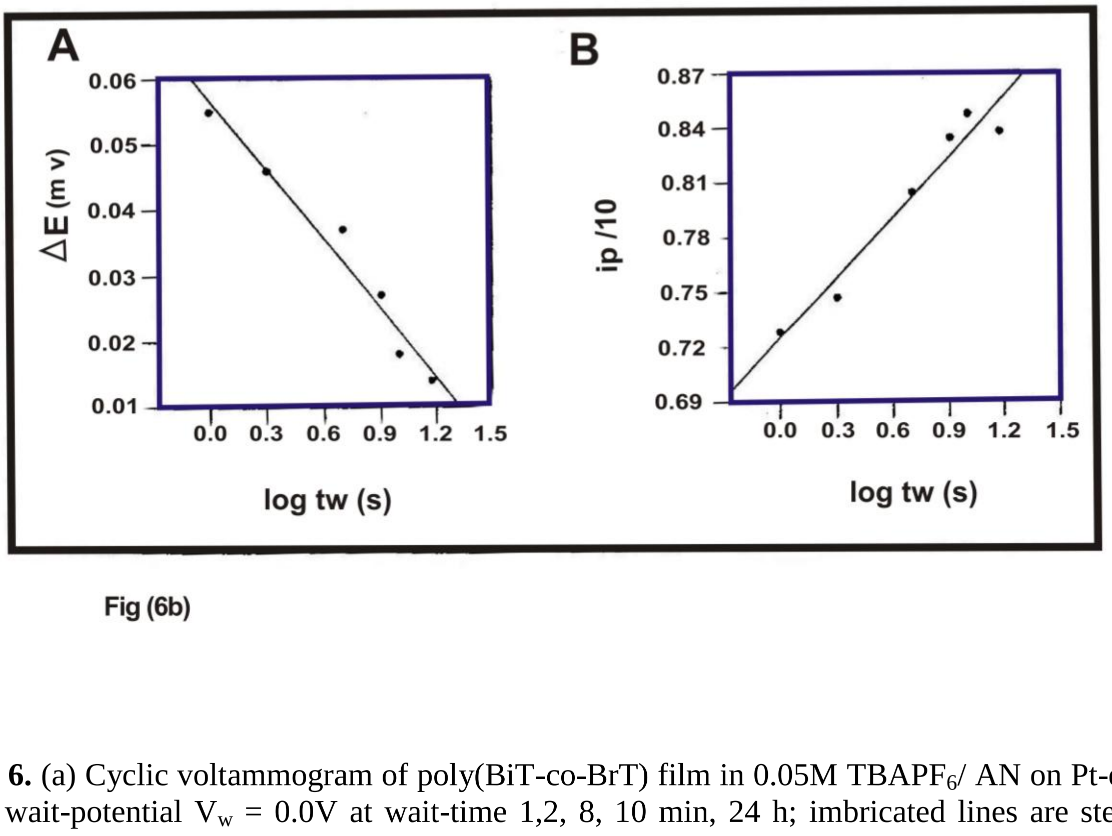

Fig (6b)

Figure 6. (a) Cyclic voltammogram of poly(BiT-co-BrT) film in 0.05M TBAPF$_6$/ AN on Pt-electrode, wait-potential V_w = 0.0V at wait-time 1,2, 8, 10 min, 24 h; imbricated lines are steady state waves, film galvanostatically synthesized from 0.2M BrT and 0.02M BiT in 0.05M TABPF$_6$/NB at room temperature, scan rate =50 mVs^{-1}. (b) A. Difference between relaxed and full-relaxed waves; B.Relative peak height of relaxed wave of (a) as a function of logarithmic wait-time.

After electropolymerization, the PBiT, PBrT and poly (BiT-co-BrT) films were rinsed with dry acetonitrile to get rid of the monomers and then immersed in dry electrolyte solution (containing only the solvent (acetonitrile) and supporting electrolyte ($TBAPF_6$)) in which the films were reduced at -0.1V for 5 min into neutral state, then subjected to 10 cycles between oxidation and reduction potentials [19, 20]. This process increases the stability of the film in solution [38]. 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 improves the properties of the polymer films [19, 20]. Both the peak potential and the peak maximum current are governed by a logarithmic law as a function of wait- time [39] with the following equations:

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

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

where E_o and 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. Aoki et al. [40] found that a very thin film would hardly show the slow relaxation, which agrees with the obtained results that for very thin films the relaxation is unclear.

After the cycling process the film was left for 24 hours as wait- time in insulating state. The relaxation of the film is followed up by recording two successive cyclic voltammograms after different wait- times (t_w) in imposed potential conditions. The first cyclic voltammogram (relaxed peak) indicates the degree of relaxation of the film while the second one represents the steady state. The relaxed peak is shifted to a more positive potential and has a higher peak current. One considers the higher relaxed peak measured after a long-time as full-relaxed peak or equilibrium state. The relaxation effect can be observed at a potential corresponding to a significant doping level of the film being conducting. Figs.4a,b and 5a,b show the corresponding results for the films prepared galvanostatically and potentiodynamically after different wait- times (t_w) in imposed potential conditions and studied in AN solvent using 0.05M TBAPF6. This indicates that the relaxation time is highly affected by this treatment, it becomes of lower values. Therefore, when the imposed potential was used, the sensitivity of the film increased leading the equilibrium state (full relaxed state) during a shorter wait-time. But when the film is subjected to the imposed potential for long time, damage began and it lost part of its sensitivity. To obtain the relaxation time of the film a plot of (log t_w) as a function of relative relaxed peak current to the full relaxed peak (i_p/i_o) was made, and also the shift in relaxed peak potential from the full relaxed peak ΔE. Figs.4a and 5a show the successive measurements at different wait-time(t_w). It is clear that the peak current increased and the peak potential shifted into more positive values with increasing the wait-time. Figs.4b and 5b show the logarithmic wait- time dependence on the i_p/i_o and ΔE values. The relaxation time can be obtained through the extrapolation of the line to intercept log t_w axis at (i_p/i_o)=1 and ΔE = zero.

Table 2. The Technique effect on the relaxation times ($Rt_E{}^a$, $Rt_I{}^b$) for PBiT, PBrT and Poly(BiT-co-BrT).

Polymer film	Galvanostatic		Potentiodynamic	
	log Rt_E	log Rt_I	log Rt_E	log Rt_I
Poly (BiT-co-BrT). Film synthesis using (0. 2M BrT+0.04M BiT in 0.05.M $TBAF_6$/NB)	1.214	2.52	2.75	4.128
PBiT. Film synthesis using (0.02M BiT in 0.05M $TBAF_6$ /NB)	2.04	4.83	3.529	10.17
PBrT. Film synthesis using (0.2M BrT in 0.05M $TBAF_6$ /NB)	10.86	14.28	2.819	5.007

a- Rt_E = relaxation times obtained from the shift in the peak potential (ΔE) calculation.

b- Rt_I = relaxation times obtained from the relative peak height (i_p/i_0) calculation.

The results obtained in Table 2 indicate that the galvanostatic synthesized copolymer film has lower relaxation time and higher sensitivity than the corresponding homopolymers and also the potentiodynamic synthesized copolymer film (Fig. 5a,b).

Table 3. The effect of concentration ratio on the relaxation times (Rt_E, Rt_I) for Poly(BiT-co-BrT) galvanostatically prepared.

Poly (BiT-co-BrT). Film synthesis using	log Rt_E	log Rt_I
(0.2M BrT+0.02M BiT in 0.05M $TBAF_6$ /NB)	5.181	6.8
(0.2M BrT+0.03M BiT in 0.05M $TBAF_6$ /NB)	2.406	4.47
(0.2M BrT+0.035M BiT in 0.05M $TBAF_6$ /NB)	1.61	4.02
(0.2M BrT+0.04 M BiT in 0.05M $TBAF_6$ /NB)	1.214	2.52

Figs 4a,b and 6a,b show as an example the effect of concentration change; for both monomers involved in the electropolymerizing solution; on the relaxation time measurements. Table 3 summarizes relaxation time measurements at different concentrations. It was found that the oxidation potential of the copolymer lies between the oxidation potentials of both homopolymers (Table 1), moreover as the concentration of bithiophene increases the oxidation potential of the copolymer shifted toward the oxidation potential of PBiT. Also, we found that poly (BiT-co-BrT) obtained from solution containing (0.2M BrT and 0.04M BiT with 0.05M $TBAPF_6$ in NB) Fig.4a has the lowest relaxation time (Rt_E) obtained from the shift in peak potential (ΔE), and also (Rt_I) obtained from the relative peak height (i_p/i_o). It is clear that the relaxation time (Rt_E) and (Rt_I) decrease as the concentration of one of the monomers increases.

Table 4. The Solvent effect on the relaxation times (Rt_E, Rt_I) for PoIy(BiT-co-BrT) galvanostatically prepared.

Copolymer	Acetonitrile DN=14.1		Nitrobenzene DN=8.1		Dichloroethane DN=0.1	
	log Rt_E	logRt_I	log Rt_E	logRt_I	log Rt_E	logRt_I
Poly(BiT-co-BrT)	1.214	2.52	2.697	3.17	3.38	4.74

The effect of solvent on the relaxation process was investigated by building up the film and studying its relaxation behavior in different solvents having large extension of donor numbers (DN). Dry acetonitrile (DN = 14.1), nitrobenzene (DN = 8.1) and 1, 2-dichloroethane (DN = 0.1) were used as solvents and $TBAPF_6$ as supporting electrolyte. The data summarized in Table 4 show that the relaxation time measurement (Rt_E, Rt_I) for poly (BiT-co-BrT) is lower in acetonitrile than that obtained in nitrobenzene or dichloroethane, i.e., as the donor number (DN) of the solvent increases the relaxation time decreases. This can be attributed to the conductivity and the charge transfer in the solvent and its effect on both the conductivity and the sensitivity of this copolymer [41, 42].

The effect of temperature on the relaxation of the film has been studied. The lowest temperature was (-15°C), because at (-30°C) the film became unstable and results were not reproducible. This indicates that inserting an anion into the film at strict conditions of low temperature became very difficult [41]. The measurements were carried out at different temperatures ranging from -15°C to + 25°C. Table 5 summarizes the obtained relaxation data at different temperatures. It is clear that the relaxation time is highly affected by temperature. Fig.7a,b give a linear relationship between relaxation time logarithm (log Rt_E, log Rt_I) with temperature.

Table 5. Temperature effect on the relaxation times (Rt_E,Rt_I) for Poly(BiT-co-BrT) in AN/0.05 M $TBAPF_6$ galvanostatically prepared.

Temperature(^oC)	log Rt_E	log Rt_I
25	1.214	2.52
15	2.32	2.742
0	2.24	4.59
-15	2.39	4.81

Generally, as the temperature increases the relaxation time decreases and the sensitivity of the film increases.

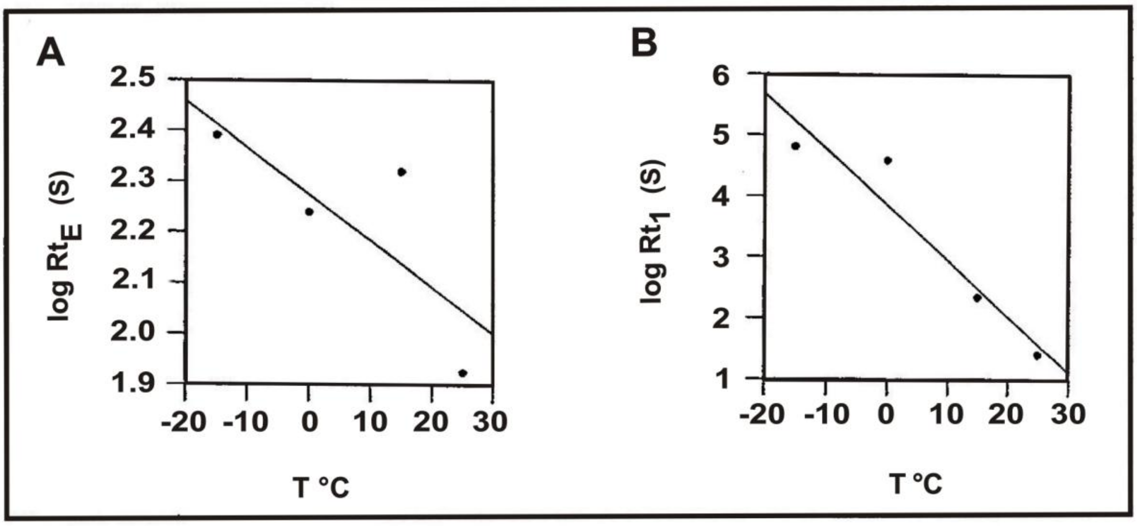

Fig (7)

Figure 7. Dependance of relaxation times A. Rt_E and B. Rt_I on temperature for poly(BiT-co-BrT); film galvanostatically synthesized from 0. 2M BrT and 0.04M BiT in 0.05M $TABPF_6$/NB.

4. CONCLUSION

The electrosynthesis of the polymer films of 2, 2'-bithiophene, 3-bromothiophene and their copolymer have been investigated using galvanostatic and potentiodynamic techniques. The most stable copolymer film was obtained galvanostatically in nitrobenzene solvent and $TBAPF_6$ as supporting electrolyte. The relaxation study was performed for the prepared copolymer and homopolymer films in different solvents. The galvanostatic synthesized copolymer film has lower relaxation time and higher sensitivity than the corresponding homopolymers and also the potentiodynamic synthesized copolymer film. The effect of concentration change reveals that the relaxation time decreases as the concentration of one of the monomers increases. The relaxation time of the film decreases as the donor number of the solvent increases. The relaxation time is highly dependant on temperature.

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