

THE ELECTROPOLYMERIZATION OF BITHIOPHENE AND 3-METHYLTHIOPHENE COPOLYMER AND THEIR ELECTROCHEMICAL RELAXATION STUDIES

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Abstract

The electrosynthesis of the copolymer of bithiophene and 3-methylthiophene has been investigated using galvanostatic and potentiodynamic techniques. The most stable films were obtained using galvanostatic technique in acetonitrile solvent and TBAPF₆ as supporting electrolyte. A comparison study was performed for the prepared copolymer and homopolymer films whose were subjected to a relaxation studies using cyclic voltammetric technique in different solvents. The effect of solvent, monomer concentration ratio, electrocopolymerization techniques and temperature on the relaxation time were investigated.

Introduction

Organic conducting polymers such as polythiophene, polyaniline and polypyrrole have been the subject of increasing research effort 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]. For three decades, these electrogenerated films are used a growing interest in the design of chemical sensors and biosensors as well as for biomedical applications such as synthetic bones and artificial muscles [2-7]. The preparation, characterization and application of electrochemically active, electronically conducting polymeric systems are still in the foreground of research activity in electrochemistry [8]. Many unsubstituted conducting polymers have limited solubility and are intractable and infusible. This is due to the rigid rod nature of conducting polymers (CPs) arising from their extended-delocalization. In order to make the polymer soluble, fusible and processable, polythiophene substitution at positions 3 and/ or 4 was achieved by various groups [9,10]. Synthesis of conducting polymer composites, graft and block copolymers is proved to be effective ways to compensate for the certain deficiencies of conducting polymers like poor mechanical and physical properties. Electropolymerization of the conducting component on an electrode previously coated with the insulating polymer is one of the most widely used methods for that purpose [11-13]. Conducting graft copolymerization of random copolymers with thiophene and/or pyrrole was achieved by constant potential electrolysis [14]. 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). 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 [15]. 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, 17]. In this work, we show the memory effect observed on a thin films of both polythiophene and copolythiophene in different conditions.

Experimental:

Monomer, supporting electrolytes and solvents:

Bithiophene (BT) and 3-methyl-thiophene (MT) were reagent grade and used as received from commercial source (Sigma-Aldrich). Tetrabutyl ammonium hexafluorophosphate (TBAPF₆) (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 grinded, dried in vacuum for 5 hours and then stored in a special tube under argon atmosphere [18]. Acetonitrile (AN) [BDH-Analar], Nitrobenzene (NB) [Aldrich] and 1,2- Dichloroethane (DCE) [HPLC-pure grad (Fisons Scientific Equipment Incorporating Griffin & George England)] were the solvents.

Electrosynthesis

Platinum disc electrode was used for electropolymerization of the films in a three-electrode setup. The solutions were degassed by argon bubbling for 10-15 min prior to polymerization. In potentiodynamic technique the potential sweep (50 mV/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 galvanostatic technique the thickness of the doped conducting film was adjusted by the electrolysis time, by applying current densities between 1-10 mA/cm² 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 potential according to insulating state for 1 min. Such a pretreatment allows us to obtain a stable and high reproducible film [19]. The stability in electrolytic medium has also been determined after 10 cycles between oxidized and reduced state. Scanning electron microscopy (SEM) experiments were performed on the electrochemically as-grown films. The polymer films were formed on a platinum sheet (4mm × 8mm). The obtained sample was rinsed thoroughly with the same solvent used in electrosynthesis then rinsed with acetone and dried in oven at 45°C. In the relaxation study the potential sequence was involved imposed potential conditions, which have been discussed in details before [20].

The EG&G Princeton Applied Research Model 283 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. JEOL JEM-100s Electron Microscope instruments with typically 40kV, the sample at 45°C, was used to obtain the scanning electron micrographs of the polymer films. 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.

Results and Discussion

Electrosynthesis of Poly(Bithiophene-co-Methylthiophene) [Poly(BiT-co-MT)]

We start to study the effect of different electrochemical techniques on the properties of the polymer film formed. 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 [22-25]. The concentration of the monomer was varied according to the polymerization technique. In

potentiodynamic method the concentration of bithiophene was 0.01M and 0.05M methylthiophene. The successive cyclic voltammograms during the preparation of the homopolymers (PBiT and PMT) which used as comparison between the copolymer and its homopolymers at the same condition are made, where the synthesis of these homopolymers are studied in detail in the literature [20]. The thickness of the film was controlled by the number of cycles. In galvanostatic one; in order to obtain a stable film; the concentration are raised to 0.02M bithiophene (BiT) and 0.1M methylthiophene (MT) in acetonitrile containing 0.05 M TBAPF₆. Figure 1 shows the potentiodynamic electropolymerization of poly (BiT-co-MT). The electrolysis time is controlled until a given amount of the total anodic charge 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/cm². The almost constant potential through the whole process using galvanostatic conditions indicated that the formation of a well conducting films [26, 27]. We found that the films obtained by successive cyclic voltammetry had lower stability than those obtained by the galvanostatic mode, where, the stable film has a long time of study without damage and gives reproducible results. In agreement with Abou-Elenien et al [20], using tetra- butyl ammonium hexafluorophosphate TBAPF₆ as supporting electrolyte, the most stable polymer film has been obtained.

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 [27, 30]. 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 PBiT, PMT and poly (BiT-co-MT) films were rinsed with dry acetonitrile to get rid of the monomers and then immersed in dry electrolyte solution (contain only the solvent (acetonitrile) and supporting electrolyte (TBAPF₆)) 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 [20]. This process increases the stability of the film in solution [33]. 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 [20]. Both the peak potential and the peak maximum current are governed by a logarithmic law as a function of wait time [34] 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, $\delta \gamma_E = \frac{dE_r}{d \log(tw)} \sim 30$

mV/decade 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. [35] found that a very thin film would hardly show the slow relaxation, which in agreement with our results that for very thin films the relaxation is unclear. After 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 (tw) 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 more positive potential and has a higher peak current. We considered the higher relaxed peak that measured after long-time as full-relaxed peak or equilibrium state. The relaxation effect can be observed at potential corresponding to a significant doping level of the film being conducting. Figs.2a,b and 3a,b show the corresponding results for the films have been prepared galvanostatically and potentiodynamically, which indicate that the relaxation time is highly affected by this treatment, it becomes of lower values. This indicates that by using the imposed potential, the sensitivity of the film increased leading to reach the equilibrium state (full relaxed state) during a shorter wait-time. But, when the film is subjected to the imposed potential for long time, it is began to damage and lost a part of its sensitivity. 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 ΔE . Fig.3a shows 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_o and ΔE values. The relaxation time can be obtained through the extrapolation of the line to intercept $\log tw$ axis at $(i_p/i_o) = 1$ and $\Delta E = \text{zero}$.

A polythiophene and copolythiophene films prepared on a Pt- electrode was degraded and deactivated by repeating the potential scan in electrolytic solutions. After the film formation, it subjected to 100 cycles of cyclic voltammetry in the solution free monomers before relaxation measurements. The results obtained in

Figs.2a,b and 3a,b show the relaxation time ($\log rx$), in case of galvanostatic and potentiodynamic, which indicate that the copolymer has lower relaxation time and higher sensitivity than corresponding homopolymers, when the copolymer film prepared galvanostatically (especially relaxation time (Rt_E) obtained from the difference in oxidation peak potential between the relaxed and full relaxed waves (ΔE) curve). The above relaxation measurements are summarized in Table 1.

Figures 4a,b to 6a,b show the effect of concentration change; for both monomer involved in the electropolymerizing solution; on the relaxation time measurements. It is found that the oxidation potential of the copolymer lies between the oxidation potentials of both homopolymers, moreover as the concentration of methylthiophene increases the oxidation potential of the copolymer shifted toward the oxidation potential of PMT.

Also, we found that poly (MT-co-BiT) obtained from solution containing (0.02M BiT and 0.1M MT with 0.05M TBAPF₆ in AN) Fig.2a has the lowest relaxation time (Rt_E) obtained from the shift in peak potential (ΔE) curve . While, poly (MT-co-BiT) obtained from solution containing (0.02M BiT and 0.25M MT in 0.05M TBAPF₆ /AN) has the lowest relaxation (Rt_i) obtained from the relative peak height (i_p/i_o) curve Fig. 4a. The results obtained from current measurements (i_p/i_o), as said before, is not consistent and we will concern with that obtained from potential difference measurements (ΔE). Table 2 summarizes relaxation time measurements at different concentrations.

The effect of solvent on the relaxation process 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 = 4.4) and 1, 2-dichloroethane (DN = 0.1) were used as solvents and TBAPF₆ as supporting electrolyte. The data summarized in Table 3 show that relaxation time measurement (Rt_E , Rt_i) for poly (BiT-co-MT) in nitrobenzene is lower than that obtained in acetonitrile or dichloroethane, i.e., the relaxation of the film is highly affected by the nature of the solvent.

The effect of temperature on the relaxation of the film has been studied. The lowest temperature was (-15°C) while at (-30°C) the film became unstable and results is not reproducible. This indicates that the insert of anion into the film at strict conditions of low temperature became very difficult. The measurements are carried out at different temperature ranging from -15°C to + 25°C. Table 4 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 logarithm relaxation time ($\log R_{tE}$, $\log R_{tI}$) with temperature. Generally as a temperature increases the relaxation time decreases and the sensitivity of the film increases.

Table (1): The Technique effect on the relaxation times (R_{tE} , R_{tI})^a for PBiT, PMT and Poly(MT-co-BiT).

Polymer film	Galvanostatic		Potentiodynamic	
	$\log R_{tE}$	$\log R_{tI}$	$\log R_{tE}$	$\log R_{tI}$
Poly (MT-co-BiT). Film synthesis using (0.02M BiT+0.1M MT in 0.05M TBAF ₆ /AN)	2.67	10.6	4.86	6.73
PBiT. Film synthesis using (0.02M BiT in 0.05M TBAF ₆ /AN)	5.64	4.83	6.307	10.6
PMT. Film synthesis using (0.1M MT in 0.05M TBAF ₆ /AN)	3.38	3.1	2.92	3.93

a- R_{tE} = relaxation times obtained from the shift in the peak potential (AE) calculation .

R_{tI} = relaxation times obtained from the relative peak height (i_p/i_0) calculation.

Table (2): The effect of concentration ratio on the relaxation times (R_{tE} , R_{tI}) for Poly(MT-co-BiT) galvanostatically prepared.

Poly (MT-co-BiT). Film synthesis using	$\log R_{tE}$	$\log R_{tI}$
(0.02M BiT+0.1M MT in 0.05M TBAF ₆ /AN)	2.67	10.6
(0.02M BiT+0.14M MT in 0.05M TBAF ₆ /AN)	3.46	13.11
(0.02M BiT+0.2M MT in 0.05M TBAF ₆ /AN)	2.88	3.53
(0.02M BiT+0.25M MT in 0.05M TBAF ₆ /AN)	3.7	3.29

Table (3): The Solvent effect on the relaxation times (R_{tE} , R_{tI}) for Poly(MT-co-BrT)

Gopolymer	Acetonitrile	Nitrobenzene	Dichloroethane

	log R_{tE}	log R_{tI}	log R_{tE}	log R_{tI}	log R_{tE}	log R_{tI}
Poly(BiT-co-MT)	2.67	10.6	2.16	2.12	2.2	2.219

Table (4): The Temperature effect on the relaxation times (R_{tE} , R_{tI}) for Poly(BiT-co-MT) galvanostatically prepared.

Temperature(°C)	log R_{tE}	log R_{tI}
25	2.165	2.39
15	2.79	2.183
0	3.23	2.218
-15	2.94	3.54

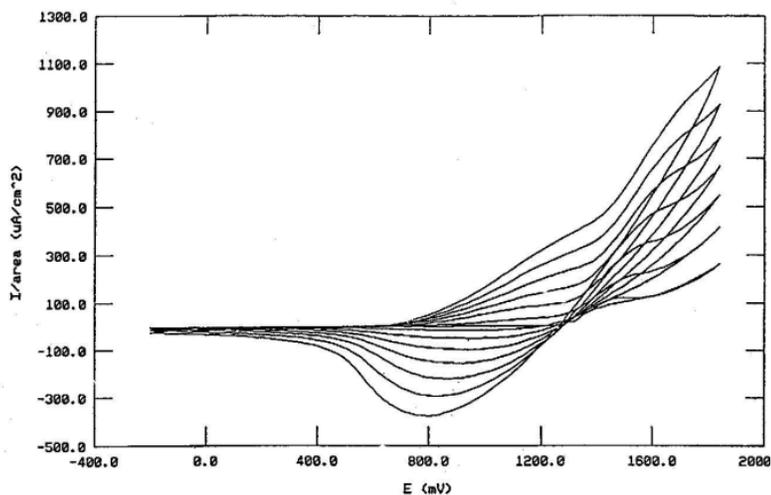


Fig.1 Successive cyclic voltammograms corresponding to the electropolymerization of copolymer at Pt-electrode from solution of 0.05M methylthiophene , 0.01M bithiophene and 0.05M TBAPF₆ in AN at scan rate 50mVs⁻¹.

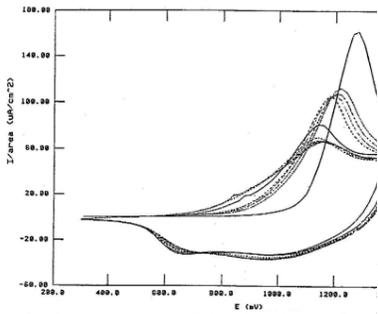
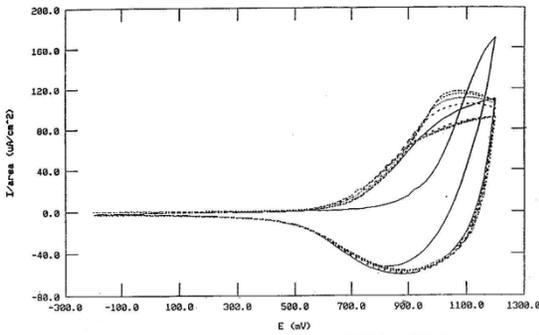
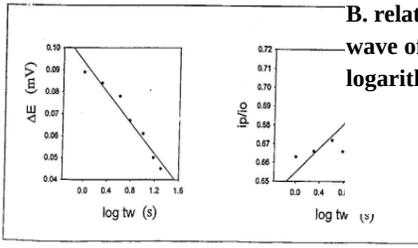
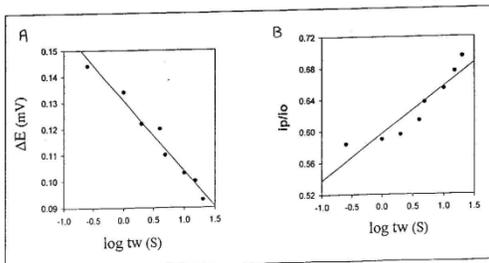


Fig. 2 (a) Cyclic voltammogram of poly(BiT-co-MT) film in 0.05M TBAPF₆/AN on Pt-electrode, wait-potential V_w = 0.3V at wait-time 2, 6, 10, 15 min, 24 h; imbricated lines are steady state waves, film galvanostatically synthesized from 0.02M BiT and 0.1M MT at room temperature, scan rate = 50 mVs⁻¹. (b) A. Difference between relaxed and full-relaxed waves; B. relative peak height of relaxed wave of (a) as a function of logarithmic wait-time.



mmogram of film in 0.05M t-electrode, = -0.2V at , 20 min, 24 h; re steady state iodynamically 0.02M BiT and temperature, s⁻¹. (b) A.



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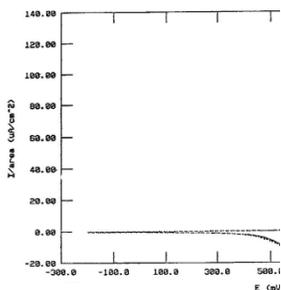


Fig. 4(a) Cyclic voltammogram of poly(BiT-co-MT) film in 0.05M TBAPF₆/ AN on Pt-electrode, wait-potential $V_w = 0.3V$ at wait-time 2, 6, 10, 15 min, 24 h; imbricated lines are steady state waves, film galvanostatically synthesized from 0.02M BiT and 0.25M MT at room temperature, scan rate = 50 mVs^{-1} . (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.

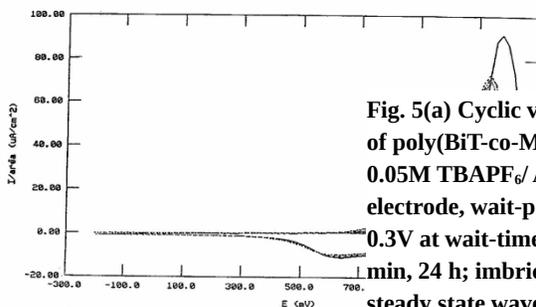
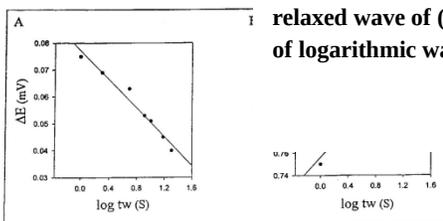
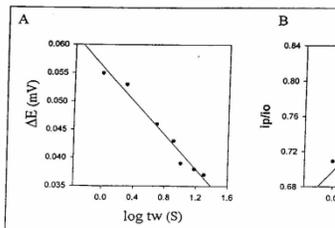


Fig. 5(a) Cyclic voltammogram of poly(BiT-co-MT) film in 0.05M TBAPF₆/ AN on Pt-electrode, wait-potential $V_w = 0.3V$ at wait-time 2, 6, 10, 15 min, 24 h; imbricated lines are steady state waves, film galvanostatically synthesized from 0.02M BiT and 0.2M MT at room temperature, scan rate = 50 mVs^{-1} . (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.



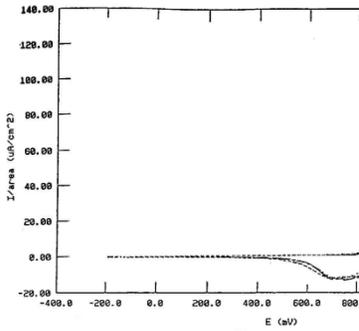


Fig. 6 (a) Cyclic voltammogram of poly(BiT-co-MT) film in 0.05M TBAPF₆/AN on Pt-electrode, wait-potential V_w = 0.3V at wait-time 2, 5, 12, 15 min, 24 h; imbricated lines are steady state waves, film galvanostatically synthesized from 0.02M BiT and 0.14M MT at room temperature, scan rate =50 mVs⁻¹. (b) A. Difference between relaxed and full-relaxed waves; B. relative peak height of relaxed wave of (a) as a function of logarithmic wait-time.

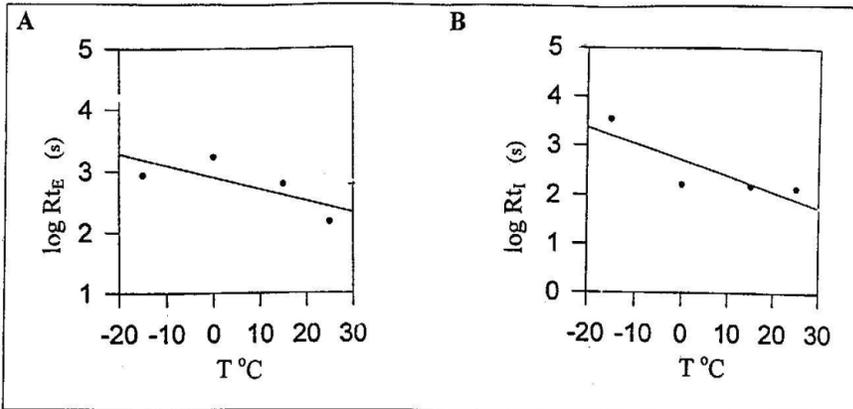
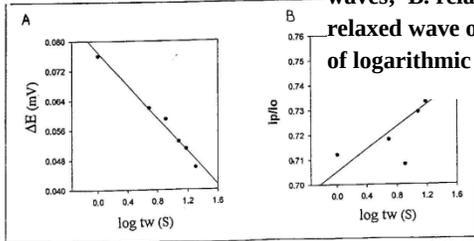


Fig. 7 Dependence of relaxation times A. Rt_E and B. Rt_I on temperature for Poly(BiT-co-MT); film galvanostatically synthesized from 0.02M BiT and 0.1M MT AN and 0.05M TBAPF₆.

Fig. 7 Dependence of relaxation times A. Rt_E and B. Rt_I on temperature for Poly(BiT-co-MT); film galvanostatically synthesized from 0.02M BiT and 0.1M MT AN and 0.05M TBAPF₆.

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