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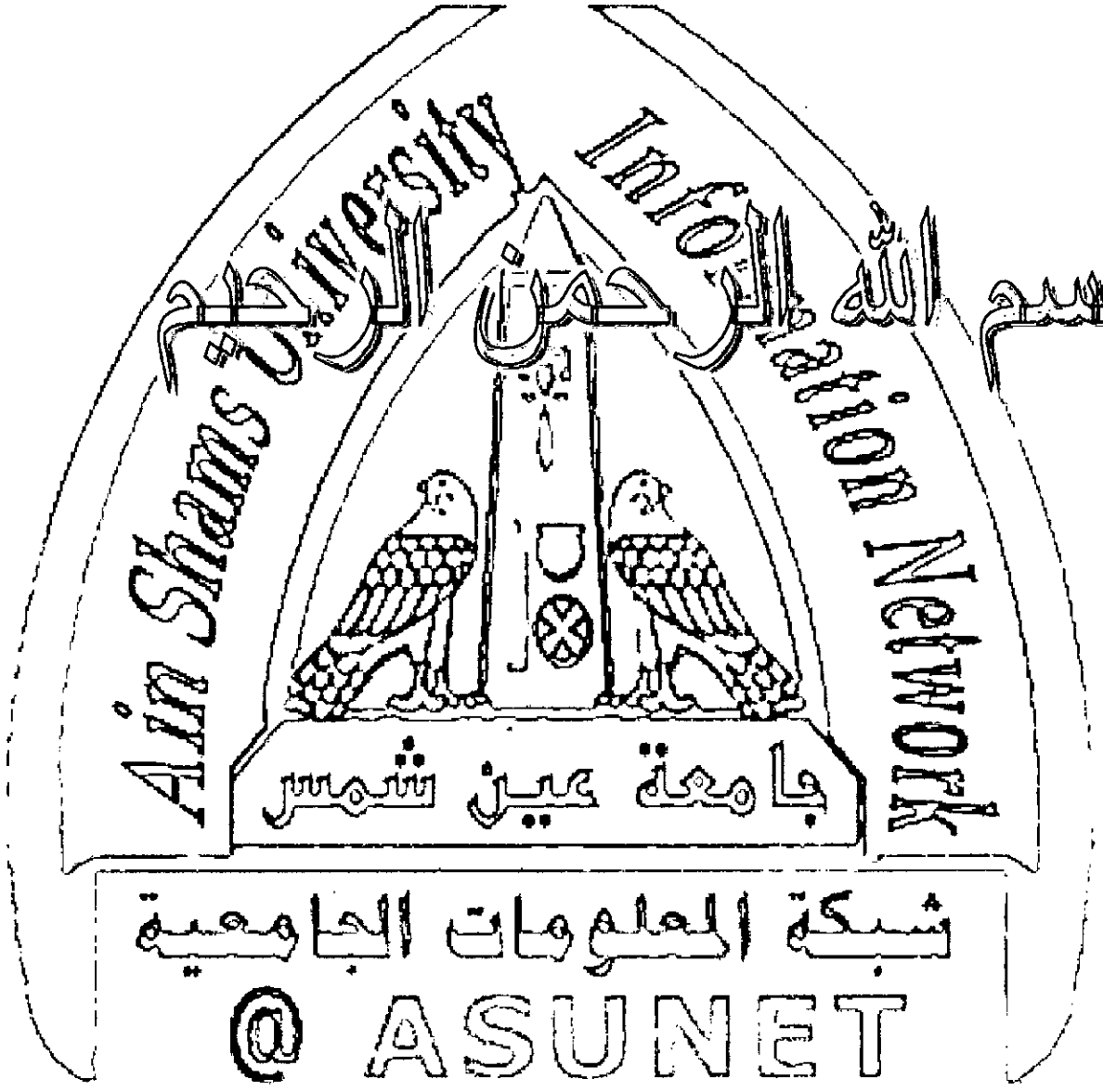

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THESIS

ENTITLED

ELECTROCHEMICAL RELAXATION STUDIES OF SOME COPOLYMERS OF THIOPHENE DERIVATIVES AS CONDUCTING POLYMERS

PRESENTED

BY

Ahmed Mohamed Kotb

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(Chemistry)

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Title of [Ph. D.] Thesis

Electrochemical Relaxation Studies of Some Copolymers of Thiophene Derivatives as Conducting Polymers

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ABSTRACT

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Title of thesis: Electrochemical Relaxation Studies of Some Copolymers of Thiophene Derivatives as Conducting Polymers

Degree: (Ph. D) Thesis, Faculty of Science, Cairo University, 2005.

This work has been carried out to investigate the electrochemical relaxation studies of some copolymers thiophene derivatives starting from the monomers: Thiophene, 2,2'-Bithiophene, 3-Methylthiophene and 3-bromothiophene. Electrocopolymerization of the mixed monomers was carried out using galvanostatic and potentiodynamic techniques in acetonitrile and nitrobenzene as solvents and $TBAPF_6$ as supporting electrolyte. The prepared films were subjected to relaxation studies using cyclic voltammetric technique. The effect of solvent, monomer concentration, electrocopolymerization techniques and temperature on the relaxation effect was investigated.

Key words: Copolythiophenes, Conducting polymers, memory effect, relaxation, cyclic voltammetry.

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Contents

1. Statement and Objectives of the Problem 1

2. Introduction 4

2.1.Heteroaromtic copolymers.

2.1.1.Copoly (3-alkylthiophene) and Copoly (3-alkoxythiophene)... 5

2.1.2. Copolymers from pyrrole and thiophene..... 6

2.1.3. Copolymers from pyrrole and Bi- or α–terthiophene 7

2.1.4. Copolymers of pyrrole and thiophene derived from α-linked ring system..... 8

2.1.5. Copolymers from indole and pyrrole 9

2.1.6. Copolymers from aniline and thiophene... 11

2.1.7. Other bithiophene copolymers..... 11

2.1.8. Copolymer nanofibrils from pyrrole and 3-methylthiophene ... 12

2.2. Electrochemomechanical Deformation of conducting polymers..... 13

2.3. Mechanism of electropolymerization of five membered heterocycles.. 15

2.4. Effect of Electrosynthesis Conditions..... 17

2.4.1. Effect of Electrolytes..... 17

2.4.2. Effect of Substituents..... 20

2.4.3. Effect of Solvents..... 22

2.4.4. Electrical Conductivity..... 24

2.4.5. Electrochemical Properties..... 26

2.4.6. Effect of Monomers Structure..... 27

2.4.7.Effect of other parameters..... 28

2.5. Stability and Degradation of Conducting Polymers..... 31

2.6. Structure of Conducting Polymers..... 33

2.7. Charge Storage Mechanism in Conducting Polymers..... 36

3. Experimental 44

3.1. Monomers and Supporting Electrolytes..... 44
3.2. Electrosynthesis..... 44
3.3 Electrochemical Techniques..... 46
3.3.1. Potential-Scan Techniques in Stationary Solution..... 46
3.3.2. Controlled-current (Galvanostatic)..... 47
3.4. Instrumentation..... 47
3.5. Building of Measurements Aparatus..... 48
3.6. Electrodes..... 49
3.6.1. Working Electrode..... 49
3.6.2. Reference Electrode..... 49
3.6.3 Auxiliary Electrode..... 50
3.7. Solvents..... 50
3.8. Argon Purification..... 51
3.9. Cleaning of the Glass Apparatus..... 51

4. Results and Discussion..... 53
4.1.Poly (Methylthiophene-co-Bithiophene) [Poly (MT- co- BiT)] 55
4.2. Poly (Methylthiophene-co-thiophene) [Poly (MT- co- T)] 63
4.3. Poly (Thiophene-co-Bromothiophene) [Poly (T- co- BrT)] 65
4.4. Poly (Methylthiophene-co-Bromothiophene) [Poly (MT- co- BrT)]... 69
4.5. Poly (Bromothiophene-co-Bithiophene) [Poly (BrT- co- BiT)] 71

5. Conclusion..... 187
6. References..... 191
7. Summary..... 211
8. Arabic Summary..... 213

Statement and Objectives of the Problem

1. Statement and Objectives of the Problem

Conjugated electroactive and electrically conducting polymers have been receiving significant attention due to their wide range of electrical, electrochemical, and optical properties. These polymers have been utilized as light emitting diodes, rechargeable batteries, membranes and electrochromic devices [1-7]. Electrochemistry has played a significant role in the preparation and characterization of electronically conducting polymer. Electrochemical techniques are particularly appropriate in controlling the synthesis of these polymers.

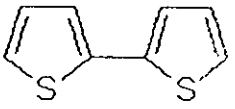
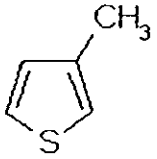
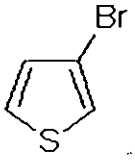
Heeger and McDiarmid [8], and Diaz et al [9], discovered that these materials would undergo chemical and electrochemical redox transitions to yield polymers with relatively high intrinsic electronic conductivities. These intrinsically conducting polymers are often named "synthetic metals". These materials are competing now with the classical surfaces such as metals and graphite in the electrochemical and electroanalytical applications [10, 11]. Many proposals for the industrial and the technological applications of these materials have been suggested. Some of the most "promising" and practical applications are ion exchange under applied electrical fields, electrocatalysis, modified electrodes for electroanalysis... etc.

The preparation, characterization and application of electrochemically active, electronically conducting polymeric systems are still in the foreground of research activity in electrochemistry [12]. 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 [13,14]. 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 [15-17]. Conducting graft copolymerization of random copolymers with thiophene and/or pyrrole was achieved by constant potential electrolysis. 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.

Polythiophenes have been often considered as a model for the study of charge transport in conducting polymers and the high environmental stability of their both doped and undoped states together with their structural versatility have led to multiple development aimed at applications [18]. In cyclic voltammetry experiments the oxidation peak of the first run after the polymer film 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 [19]. This process is reported as the slow relaxation effect or memory effect by most of researcher [19]. A complete description of this effect is yet to be developed and the mechanism is still under debate [20].

In this work, we have study that the memory effect observed on a thin-film of copolymers of thiophene derivatives in different conditions. In this dissertation the following monomers were chosen for the present study:

	Thiophene T
	2,2'-Bithiophene BiT
	3-Methylthiophene MT
	3-Bromothiophene BrT

The main objectives taken into consideration during the course of research are as follows:

1) Determination of the redox characteristics of the monomers.
2) Film building on the electrode surface using potentiodynamic (cyclic voltammetry) and galvanostatic techniques.
3) Kinetic study of the memory effect or slow relaxation, that observed in different redox polymer systems during cyclic voltammetry.
4) Study the relaxation time of the prepared films with respect to relaxed current and potential.
5) The influence of solvent, monomer concentration and temperature on the slow relaxation phenomenon.