1994

Design and production of novel conducting polymer colloids

Hossein Eisazadeh
University of Wollongong

Recommended Citation

Eisazadeh, Hossein, Design and production of novel conducting polymer colloids, Doctor of Philosophy thesis, Department of Materials Engineering, University of Wollongong, 1994. http://ro.uow.edu.au/theses/1489

IN THE NAME OF GOD

DESIGN AND PRODUCTION OF NOVEL CONDUCTING POLYMER COLLOIDS

A thesis submitted in fulfilment of the requirements for the award of the degree

DOCTOR OF PHILOSOPHY

from

THE UNIVERSITY OF WOLLONGONG

by

HOSSEIN EISAZADEH, M. E.

Department of Chemistry

and

Department of Materials Engineering

March, 1994

ACKNOWLEDGMENTS

I wish to express my deep gratitude to Professor Gordon G. Wallace for his help, guidance and friendship during the development of this project.

Sincere thanks are given to Dr. Geoff Spinks, my co-supervisor, for his enthusiasm and friendship throughout this work.

I greatly appreciate the help, comradeship and tolerance of all my fellow members of the electrochemistry group. Special thanks are due to Mr Trevor Lewis, Dr Norman Barisci, Dr. Anthony Hodgson and Dr Chee On Too, for their help during this work and for proof-reading this thesis.

The help and friendship of the students and staff of the department of chemistry and materials engineering is greatly appreciated specially Kerry Gilmore, Peter Pavlik and Nick Mackie.

I gratefully acknowledge the assistance of a scholarship from the Ministry of Culture and Higher Education of Iran and the University of Mazanderan during the course of this work.

Finally I would like to thank my family for their support and encouragement.

PUBLICATIONS

" Electrochemical properties of conductive electroactive polymeric colloids." H. Eisazadeh, G. Spinks, G.G. Wallace, Materials Forum, 16 (1992) 341.

" Conductive electroactive paint containing polypyrrole colloids". H. Eisazadeh, G. Spinks, G.G. Wallace, Materials Forum, 17 (1993) 241.

" Influence of steric stabilizers on the electropolymerization and properties of polypyrroles". H. Eisazadeh, G.G. Wallace, and G. Spinks, Polymer, 35 (1994) 1754.

" Electrochemical production of polypyrrole colloids." H. Eisazadeh, G. Spinks, G.G. Wallace. Polymer, In Press.

SUMMARY

One of the problems limiting the application of conducting polymers as commercial materials has been the lack of solubility in most common solvents. An alternative approach might be the preparation of sterically stabilized conducting polymer colloids via dispersion polymerization.

In general the oxidation of pyrrole and aniline is carried out in the presence of a steric stabilizer to produce a colloidal dispersion. In this work various stabilizers such as PVP, PVA, and PEO were used for colloid formation. The preparation, characterization and electrical properties of polypyrrole and polyaniline colloids have been studied. It was found that type and concentration of stabilizer affects the morphology, electroactivity, conductivity and yield of polymer. Electrocoagulation of colloids onto various substrates was considered.

The electrochemical oxidation/polymerization of pyrrole and aniline monomer in the presence of steric stabilizers (PVP, PVA, PEO) and the properties of the resultant polymers was also investigated. Various techniques such as galvanostatic oxidation (constant current), potentiostatic oxidation (constant potential), and potentiodynamic (potential ramp) oxidation were used to initiate this process. It was found that the type and concentration of stabilizer affects the rate of polymerization as well as the electroactivity and morphology of the resultant colloidal sol. It was found that the rate of polymerization and the electroactivity decreased with increased concentration of stabilizer.

The effect of rotation rate, type of stabilizer and stabilizer concentration on the rate of polymerization were studied. The results indicated that rate of polymerization/deposition decreased with increased electrode rotation rate and with stabilizer concentration. For the first time the use of electropolymerization in the presence of the steric stabilizers with various counterions in order to produce conducting polymer colloids has been investigated. The colloids produced are sterically stable and are electroactive.

Applications for conductive polymer colloids were considered. For example, the preparation of conductive electroactive paints has been investigated using polypyrrole and polyaniline colloids mixed with standard acrylic paints. The electroactivity, conductivity and adhesive strength of the resultant paints was investigated.

The use of colloids for the development of novel conductive polymer composites was studied. The electrodeposition of mixtures of polypyrrole and polyaniline colloids, polyaniline colloids and pyrrole monomer or polyaniline colloids with polystyrene sulphonate particles was investigated.

Thermal degradation of polyethylene in the presence of colloidal polypyrrole and polyaniline was investigated. The results indicated that polypyrrole and polyaniline colloids might be used as a stabilizing additive to prevent the thermal degradation of polyethylene.

This study indicated that conducting polymer colloids can be prepared both chemically and electrochemically and these colloids can be used for various applications.

ABBREVIATIONS

A	Ampere
A^-	Counterion
BAS	Bioanalytical Systems
cm	Centimetre
CPS	Cyclic potential sweep
C	Coulomb
CEPs	Conductive electroactive polymers
C	Centigrade
CV	Cyclic voltammetry
DSC	Differential scanning calorimeter
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
E_{dep}	Deposition potential
E_{app}	Applied potential
EMI	Electromagnetic interference
ESD	Electrostatic charge dissipation
E_i	Initial potential
e^-	Electron
E	Potential
g	Gram
h	Hour
i	Current
i_{dep}	Deposition Current
L	Litre
mV	Millivolt
mA	Milliampere

mL	Millilitre
mC	Millicoulomb
M_w	Molecular weight
MPa	Mega Pascal
mm	Millimetre
m	Metre
min	Minute
mol	Mole
M	Molarity
NMP	N-methylpyrrolidinone
^oC	Degrees celsius
PPy	Polypyrrole
PA_n	Polyaniline
PVP	Polyvinylpyrrolidone
PVA	Polyvinylalcohol
PEO	Polyethyleneoxide
PET	Polyethylene terephthalate
PSI	Pound/square inch
PVC	Polyvinyl chloride
PTS	Paratoluene sulphonate
r.p.m.	Revolutions per minute
r	Mole ratio
R	Resistance
RVC	Reticulated Vitreous Carbon
R_s	Surface resistivity
R_v	Volume resistivity
s	Second
S	Siemens
SEM	Scanning Electron Microscope/Micrograph

SS	Stainless steel
TEM	Transmission Electron Microscope
t	Time
T	Temperature
uA	Microampere
uS	Microsiemens
um	Micrometre
V	Volt
W	Weight
%w/w	Percentage weight by weight
Zn-Al	Zincalume
Δ	Difference
υ	Potential Scan Rate
σ	Conductivity
Ω	Ohm
ω	Rotation rate

Electrochemical convention: In cyclic voltammograms cathodic (reduction) currents are positive and anodic (oxidation) currents are negative. In linear sweep voltammograms and hydrodynamic voltammograms, all currents are displayed in the positive direction.

CONTENTS

CHAPTER ONE

GENERAL INTRODUCTION 1

1.1 Colloids - General. 2
1.2 History of Conducting Polymers. 5
1.3 Doping. 8
1.4 Factors Affecting Formation and properties of Polypyrrole. 10
1.5 Factors Affecting Formation and properties of polyaniline. 16
1.6 Conductive Polymer Colloids. 20
1.7 Improving Processability of Conducting Polymers and some Applications. 25
1.8 Stability. 28
1.9 Electrochemical Techniques for Characterization. 30
  1.9.1 Chronopotentiometry. 30
  1.9.2 Cyclic Voltammetry. 30
  1.9.3. Chronoamperometry. 30
1.10 Aims of the Project. 32

CHAPTER TWO

ELECTROCHEMICAL PROPERTIES OF CONDUCTIVE ELECTROACTIVE POLYPYRROLE AND POLYANILINE COLLOIDS. 33

2.1 Introduction. 34

2.2 Experimental. 36
    2.2.1 Reagents and Standard Solutions. 36
    2.2.2 Instrumentation. 36
2.3 Results and Discussion. 37
    2.3.1 Polypyrrole Colloid Preparation. 37
    2.3.2 Polypyrrole Colloid Morphology. 41
    2.3.3 Cyclic Voltammetry of Colloidal Dispersions. 44
    2.3.4 Electrocoagulation of Colloids on the Glassy Carbon Electrodes. 52
    2.3.5 Coating Other Substrates with Polypyrrole Colloids. 55
    2.3.6 Polyaniline Colloid Preparation. 60
    2.3.7 Polymer Colloid Morphology. 63
    2.3.8 Cyclic Voltammetry. 66
    2.3.9 Electrdeposition of Polyaniline Colloids. 67
2.4 Conclusion. 72

CHAPTER THREE

INFLUENCE OF STERIC STABILIZERS ON THE ELECTROPOLYMERIZATION AND PROPERTIES OF POLYPYRROLE AND POLYANILINE. 74
3.1 Introduction. 75
    3.1.1 Electropolymerization of Pyrrole and Aniline. 77
3.2 Experimental. 80
    3.2.1 Reagents and Standard Solutions. 80
    3.2.2 Instrumentation. 81
    3.2.3 Electropolymerization of Pyrrole and Aniline. 81
3.3 Results and Discussion. 82

3.3.1 Potentiodynamic Polymerization of Pyrrole. 82
3.3.2 Galvanostatic Polymerization of Pyrrole. 86
3.3.3 Potentiostatic Polymerization of Pyrrole. 90
3.3.4 Electron Microscopy of Polypyrrole. 103
3.3.5 Potentiodynamic Polymerization of Aniline. 107
3.3.6 Galvanostatic Polymerization Of Aniline. 112
3.3.7 Potentiostatic Polymerization of Aniline. 114
3.3.8 Electron Microscopy (SEM) of Polyaniline 116
3.4 Adhesion Characteristics of Electrically Conductive Polypyrrole and Polyaniline on Electrode Materials. 119
3.5 Conclusion 130

CHAPTER FOUR

ELECTROCHEMICAL PRODUCTION OF POLYPYRROLE AND POLYANILINE COLLOIDS. 133
4.1 Introduction 134
4.2 Experimental 135
4.2.1 Reagent and Standard Solutions. 135
4.2.2 Preparation of Polypyrrole Colloids. 136
4.2.3 Instrumentation. 136
4.3 Results and Discussion. 137
4.3.1 Preparation of Polypyrrole Colloids in a Flow Through Electrochemical Cell. 146
4.3.2 Electrodeposition of Polypyrrole Colloids. 152
4.3.3 Preparation of Polyaniline Colloids in a Flow Through Electrochemical Cell. 154

4.4 Conclusion. 158

CHAPTER FIVE

APPLICATIONS FOR CONDUCTIVE POLYMER COLLOIDS 160
5.1 Introduction. 161
5.2 Experimental 162
  5.2.1 Reagents and Standard Solutions. 162
  5.2.2 Preparation of Polypyrrole Colloids. 162
  5.2.3 Preparation of Paints. 163
  5.2.4 Instrumentation. 163
  5.2.5 Analysis of Results 164
5.3 Results and Discussion. 165
  5.3.1 Conductive Paints. 165
    5.3.1.1 Electrical Properties 165
    5.3.1.2 Adhesion. 167
    5.3.1.3 Electroactivity 170
    5.3.1.4 Preparation of Polyaniline Paint. 172
  5.3.2 Thermal Oxidation Stabilizers. 176
  5.3.3 Conductive Polymer Composites. 180
    5.3.3.1. Mixtures of Polypyrrole and Polyaniline Colloids. 180
    5.3.3.2 Mixture of Conductive and Non-conductive Colloids. 183
    5.3.3.3 Coating on Non-conductive Particles. 184
5.4 Conclusions. 188

CHAPTER SIX

GENERAL CONCLUSIONS 191

6.1 General Conclusions. 192

6.2 References. 197

CHAPTER 1

GENERAL INTRODUCTION

1.1 COLLOIDS-GENERAL

Colloid materials enter into almost every branch of chemistry. Colloid science can be applied in the following areas and the list could be developed further (1,2).

1) Agriculture (e.g. soil colloids).

2) Biology and medicine (all biological systems are colloidal).

3) Analytical chemistry (e.g. coagulation of precipitates, adsorption of impurities).

4) Organic chemistry (e.g. colloidal polymerization is an important process).

5) Industrial processes (e.g. purification of water, sugar, solvents, air).

6) Industrial products (e.g. paints, detergents, plastics, paper, ceramics, lubrication fluids).

In a true solution the size of the solute and the solvent molecules are comparable, but in a colloidal dispersions the size of the solute molecules is much larger than the molecules of the solvent. Particles whose diameters usually fall between the nanometer scale and the micrometer scale are classed as colloidal particles (1,2). Colloidal dispersions can be divided into two classes, lyophilic (solvent loving) and lyophobic (solvent hating).

Since small colloidal particles have a large surface area, it is not surprising that the physics and chemistry of the surfaces are an integral part of colloid science. The total surface area increases as the particle size decreases. The force of gravity is too weak to produce rapid settling of colloidal systems, especially when colloidal particles are small. A centrifuge or an ultracentrifuge must be used for the separation of colloids in the dispersed solution.

There are three states of matter-gas, liquid and solid. Combining two of them at a time produces possible colloidal dispersion systems, which are shown in Table 1.1.

Table 1.1: Types of colloidal dispersion (*)

Dispersed phase	Dispersion medium	Notation	Technical name	Example
gas	liquid	G/L	foam	fire-extinguisher foam
gas	solid	G/S	solid foam	charcoal
liquid	gas	L/G	aerosol	fog, mist
liquid	liquid	L/L	emulsion	milk
liquid	solid	L/S	solid emulsion	charcoal in water, ice cream
solid	gas	S/G	aerosol	smokes and dust
solid	liquid	S/L	color dispersion	most colloidal systems are of this type, eg paint
solid	solid	S/S	solid dispersion	these are usually derived from the solid in liquid type, e.g. many colored glasses and precious stones.

(*) Taken from references (1,2).

A system is colloidally unstable if collisions between particles result in the formation of aggregates. The term coagulation will be applied to aggregation which is induced by Van der Waals attraction between the colloidal particles, whereas flocculation will be reserved for polymer-induced aggregation (1,2). In general, dispersions of naked, uncharged colloidal particles undergo rapid coagulation, because the particles are constantly undergoing Brownian collisions and these collisions result in aggregation. This aggregation is a consequence of the attractive Van der Waals forces that are operative between the particles.

The most widely exploited effect of non-ionic polymers on colloid stability is called steric stabilization in which stability is imparted by polymer molecules that are adsorbed onto, or attracted to, the surface of the colloid particles. It is used industrially because it offers several distinct advantages over electrostatic stabilisation. Aqueous sterically stabilised dispersions are comparatively insensitive to the presence of electrolytes. Steric stabilization is equally effective in both aqueous and non-aqueous dispersion media, but electrostatic stabilization is ineffective in non-polar dispersion media. Sterically stabilized dispersions frequently display good freeze-thaw stability, which can be a desirable effect in some practical applications (e.g. paint systems) (1).

The most significant characteristics of many colloidal dispersions are the size and morphology of the particles, since most other properties of the system are influenced to some extent by these factors. The significant development in this area has been the transmission electron microscope (TEM) and the scanning electron microscope (SEM).

1.2 HISTORY OF CONDUCTING POLYMERS

Polymers are familiar to every one, and indeed this has been called the age of plastics (3). Their familiarity and widespread use has been due to the advantageous range of controllable mechanical and viscoelastic properties. Where electrical behaviour has been important, except for the special case of triboelectricity used in electrophotography, the main asset of polymers has been the absence of electrical activity, i.e. their high insulating capability. In recent years it has become increasingly recognized that in the vast class of existing polymers the range of electrical behaviour is surprisingly wide. Despite this, it is only very recently that detailed, systematic studies aimed at understanding these properties and their optimization have begun to be made. An important characteristic of polymers is the possibility of potential control and modification of properties by using creative chemical and synthetic concepts arising from the wide degrees of freedom in carbon-based chemistry.

In 1862 Letheby et al. (4) discovered that the final product of the anodic oxidation of aniline in aqueous sulfuric acid solution at a platinum electrode was a dark green precipitate. It was insoluble in water, alcohol, ether, or ammonia. It acquired a brilliant blue color by immersion in ammonia. Concentrated sulphuric acid dissolved it and formed a blue, a green or a violet solution according to the concentration. In 1910 Green and coworkers (5) reported aniline black and allied compounds.

Mohilner and coworkers (6) demonstrated the kinetics and the mechanism of the oxidation of aniline in aqueous sulphuric acid solution at a platinum electrode.

Peter Kovacic and coworkers (7) obtained black, insoluble organic material from the reaction of benzene with ferric chloride. Small amounts of Bronsted acids such as water, hydrogen sulfide, acetic acid and nitroethane markedly increased the formation of the black solid.

Polysulfur nitride $(SN)_x$ has been known since 1910 (8). Real interest in conducting polymers arose after the work of Walatka et al. on polysulphur nitride $(SN)_x$ (9). They investigated the effect of temperature in the range of 4.2 to 300 ^oK on the conductivity of (SN)x. Work on $(SN)_x$ was further stimulated by the observation that it behaves as a superconductor at the temperature of (0.26 ± 0.03) ^oK (10). Despite its metallic conductivity, $(SN)_x$ (known as a synthetic metal) could not find wider use due to its extreme reactivity.

The discovery of modern conducting polymers began with an accident. In the early 1970's a graduate student in Hideki Shirakawa's laboratory at the Tokyo Institute of Technology was trying to make polyacetylene from ordinary acetylene welding gas (11). Shirakawas's student produced a lustrous, silvery film that looked like aluminium foil (12). When flexible, crystalline, silvery films of the semiconducting cis-$(CH)_x$ or trans-$(CH)_x$ polymer were doped with controlled amounts of electron attracting species such as chlorine, bromine, iodine or AsF_5, the conductivity increased markedly over a wide range of 10^7 to 10^{11} S/cm, depending on the extent of doping (13-15).

Diaz et al. (16) have reported a new route to conducting polymers by electrochemical synthesis of polypyrrole. Ivory and coworkers (17) demonstrated that the conductivity of poly(p-phenylene) increases from less than 10^{-12} S/cm for the undoped polymer to over 10^2 S/cm for the doped polymer. Rabolt and coworkers (18) reported conducting polyphenylenesulphide. In 1983 Edwards et al. (19) reported on a novel colloidal form of polyacetylene which could form the basis for overcoming the problems of stability and intractability with regard to processing and insolubility in most common solvents.

Development of conducting polymers can be divided into three periods (20). The first generation of conducting polymers are made conductive by incorporating conductive fillers and/or additives. The second generation of conducting polymers conduct electric current themselves without the need for any additives. The third generation of conducting polymers are either insulators or poor conductors but on doping they become conductive. The conductivity of such doped polymers depends on the nature of the dopants and the level of doping. Organic polymers consisting of neutral conjugated chains do not exhibit high conductivity and from the point of view of their electrical properties, they resemble intrinsic semiconductors. These polymers can be, however, rendered conductive if negative or positive charges are introduced into the neutral chains by an appropriate chemical or electrochemical reaction. In chemical terms such reaction results in the transformation of the neutral polymer into a salt-like compound.

Based on their chemical properties it is convenient to divide conducting polymers into three main categories (21).

1) Amphoteric polymers, i.e. the polymers whose neutral chains can be converted either into polycarbonium cations or polycarbanions via a redox reaction. As a result, the polymers may exhibit either p-type or n-type conductivity. Polyacetylene and polyparaphenylene are typical examples of such polymers.

2) Polymers whose neutral chains can be oxidized to polycarbonium cations but cannot be partially reduced to polycarbanions, exhibit only p-type conductivity. Polypyrrole and polythiophene are typical examples of this type of conducting polymers.

3) Polymers possessing strong basic centres in their conjugated backbones. These can be converted into salt-like, conductive compounds via an acid-base reaction with a protonic acid. Subsequent treatment of this salt-like polymer with a base results in the reversion to the neutral state. Polyaniline is a typical example of this type of conducting polymers.

1.3 DOPING

To make a polymer conduct electricity, small quantities of certain chemicals are incorporated into the polymer by a process called doping. The conductivity of polyacetylene films dramatically increases on exposure to bromine, iodine, chlorine or AsF_5 vapours (22,23). This phenomenon has been termed doping by analogy to the inorganic semiconductors. But this differs from the doping of inorganic semiconductors where the incorporation of impurities (dopant) may be as high as 50 % (20). The actual mechanism of doping in inorganic semiconductors is also different (24), dopants are either strong oxidizing or strong reducing agents. On doping, therefore, positive charge carriers or negative charge carriers are created in the polymers (20).

In the case of conducting polymers, dopants are of two types, neutral dopants and ionic dopants. Neutral dopants (e.g. I_2, Br_2, AsF_5) are basically neutral molecules and change to either negatively or positively charged species during doping, with or without chemical modifications. Ionic dopants (e.g. $LiClO_4$, $FeCl_3$, NaCl, etc.) are salt systems and dissociate into ions, one of the ions participates in the doping process and the other remains as the counterion to the doped polymer (20) as shown in the following reactions:

$$\text{Polymer} + \text{Dopant (acceptor)} \xrightarrow{\text{oxidation}} \text{Polymer}^{+} + \text{Dopant}^{-}$$

$$\text{Polymer} + \text{Dopant (donor)} \xrightarrow{\text{reduction}} \text{Polymer}^{-} + \text{Dopant}^{+}$$

Doping of polymers may be achieved using gaseous doping, solution doping, electrochemical doping, self doping or radiation-induced doping. With gaseous doping, polymers are exposed directly to the vapours of the dopant (22). In the self doping process, ionizable groups covalently linked to the polymer chain serve as dopants. For example, the sulphonate group of poly-3(2-ethanesulphonate) thiophene acts as the dopant (25). High energy radiation is used to augment doping of polymers by neutral dopants. Neutron radiation, for example, was used for radiation-induced doping of thiophene by iodine (26). In electrochemical doping both polymerization and doping occur simultaneously. Dopants are used as the electrolyte in organic solvents such as nitromethane, acetonitrile or THF (20). Also insoluble colloidal particles may serve as dopants, if they are negatively charged in an electrolytic bath (27).

A consistent description of the electrical transport mechanism in conducting polymers constitutes a critical problem in the understanding of these materials. In polypyrrole polarons are formed on the chain at low oxidation levels and at higher oxidation levels, polarons combine to form spinless bipolarons (28,29,30). Spinless bipolarons are the current carriers.

1.4 FACTORS AFFECTING FORMATION AND PROPERTIES OF POLYPYRROLE

Electroactive conductive polymer films can be generated on electrode surfaces by the oxidation of aromatic compounds. These films can be prepared from benzenoid, non-benzenoid and heterocyclic aromatics, in particular, from the derivatives of pyrrole, thiophene, carbazole, azulene, pyrene, triphenylene and aniline (31). This electrochemical approach for making electroactive conductive films is very versatile and it provides a facile way to vary the properties of the film.

Polypyrrole is attractive as an electrically conducting polymer because of its relative ease of synthesis. In order to exploit this material in some potential commercial applications, it will be necessary to synthesize it at low cost.

Bulk quantities of polypyrrole can be obtained as fine powders using the oxidative polymerization of the monomer by selected transition metal ions in water or various other solvents (32,33,34). The reaction of pyrrole with aqueous ferric chloride is very rapid and the product is a black powder which is insoluble in all common solvents (35). The most efficient mole ratio of iron (III) to pyrrole is 2.38 ± 0.04 (33). Conducting polypyrrole can also be prepared by chemical oxidation of pyrrole with potassium ferricyanide [$K3Fe(CN)_6$] (36). The polymer is insoluble in all common solvents, in aqueous or in non-aqueous media.

In the chemical preparation of polypyrrole, the yield of polymer increased with the acceptor/monomer mole ratio in the reaction mixture (37). However the use of a high oxidant/monomer ratio results in non-uniform and inhomogeneous reactions.

Various factors such as solvent, oxidants, reaction temperature, reaction time and oxidizer concentration strongly affect the conductivity of chemically synthesized polypyrrole (32,34,35,38-41). These all can be explained by the change in oxidation potential of the medium. The conductivity also changes with the dopant ratio. In the chemical polymerization of pyrrole, the size and type of the dopant (anion) affect the morphology and size of the resulting polymers (42). Iron (III) salts provide a convenient means for oxidatively polymerizing pyrrole and incorporating their anions as dopant ions (35,41).

Polymerization and oxidation of pyrrole may be carried out by organic electron acceptors (43). The reaction can be carried out in bulk, in aprotic organic solvents, such as acetonitrile, and in aqueous dispersion. The conductivity of polypyrrole shows its highest values when polymerization takes place in solvents possessing an OH group such as water and alcohols which are protic solvents (32). The highest conductivity value was obtained by using methanol solution. The electrical conductivity of polypyrrole can be increased by reacting the monomer in water at low temperatures, using a short reaction time and in the presence of amides or m-substituted phenols (34). The concentration of oxidants affect the yield of the reaction.

In the electrodeposited polypyrrole films, organic sulfonate dopant anions have been shown to be the most versatile. The concentration of dopant and current density affects the morphology and conductivity of polypyrrole films (44).

Conductive polymers can be deposited onto insulating or conductive substrates using an electrodeless coating process (39, 40). In these systems a conductive monomer impregnated substrate is exposed to a solution or vapour phase of the oxidant or vice versa. The nature of the substrate seemed to have only a small effect on the film-forming process (45).

In the electrochemical preparation of polypyrrole films, increasing the anodic potential affects the homogeneity of the resultant films (46). The conductivity and tensile strength of polypyrrole films prepared electrochemically increased when mono-substituted phenols were used as additives (47).

The properties of electrochemically prepared polypyrrole are expected to depend not only on the kind of counterion, but also upon the preparation conditions, such as the type of solvent and electrodes, temperature, current density and method of polymerization (48-51). The polarity of the counterion plays an important role in the conductivity as well as in the chemical properties (52). The size and shape of counterion are expected to influence the electrical conductivity because conductivity increases which small counterions are used (52). Films prepared from spherically based counterions do not exhibit anisotropic molecular organization and display lower levels of conductivity (51).

Conductivity and mechanical properties such as tensile strength, elongation and modulus are dependent on reaction temperatures (48,49,52). Films prepared by potentiostatic methods showed higher conductivity and elongation than films prepared by galvanostatic methods (48).

In the polymerization of pyrrole the solvent and anion influence the anisotropy (53,54). Conducting polymer films have a structure that gradually changes from an ordered crystalline array at the surface to an amorphous material in the bulk (55). Transition metal salts molecularly dispersed in a true polymeric matrix may act as oxidant catalyst for the polymerization of pyrrole films (36). The electrochemical properties of the modified electrodes are strongly dependent on the nature of the polymer backbone and in particular to the polymer electrolyte interface (56).

In the polymerization of pyrrole from aqueous solution, polymer films could not be grown on some metals (e.g. Al, Ag, Fe, In) (57). The metal films were dissolved before the polymerization potential was reached. Also degradation mechanisms took place at very anodic potentials.

Electrochemical oxidation of pyrrole from an organic solvent on a platinum electrode results in the formation of flexible black polymer films, which remain unchanged under ambient storage (58). The type of substrate affects the morphology of the films, but the conductivities of the film is independent of the nature of the electrode (59). In comparison with platinum, the oxidation potential of pyrrole is increased and the current intensity reduced when Ti, Fe and Al are used (59). This is a consequence of metal-oxide film formation which impedes electron transfer during electropolymerization.

The free standing thicker films of polypyrrole are stable in air and in a wide variety of solutions (60). Polypyrrole films become insulating when they are polarized for a sufficient time at a potential sufficiently negative for the electrodeposition of certain metals. At these potentials the dopant counterions may come out of the polypyrrole matrix, causing it to become insulating (61). The conductivity and mechanical properties of films are influenced by the preparation conditions such as the electrolyte, applied potential, current density, substrate and temperature during electropolymerization (62-69). The conductivity of polypyrrole films is strongly dependent on film thickness (70). Electrically prepared films of polypyrrole in the absence of air or water are reactive to oxygen (71).

In the electropolymerization of pyrrole, as the oxidation potential is raised, the polymer changes from a compact structure to dendritic (72). The electropolymerisation starts with formation of oligomers in solution (73). These oligomers then precipitate or chemically interact with the electrode surface. Finally the growth of the polymer film proceeds by the subsequent coupling of radical ions. Stirring of the solution inhibits both nucleation and growth, suggesting the involvement of soluble species in film formation (74). This is presumably due to enhanced transport of intermediates away from the electrode surface.

Highly stable, flexible films of polypyrrole with p-type conductivities of 100 S/cm have been prepared by electrolytic oxidation of the appropriate monomer (75). Thin films of polypyrrole adhering to a platinum electrode surface can be electrochemically switched between the conducting and insulating states (76). Conducting polypyrrole is quite stable in air, but the reduced neutral polypyrrole (PP_y^0) is very easily oxidized when in contact with air or water (77). PP_y^0 changed to PP_y^+ (A^-) spontaneously when it was dipped in an acidic aqueous solution and it changed to PP_y^+ (OH^-) when dipped in an alkaline or neutral aqueous solution. The conductivity increased and mechanical properties decreased slightly for films treated with acid solution. However, both of these properties decreased dramatically after the films were exposed to sodium hydroxide solution (78).

1.5 FACTORS AFFECTING FORMATION AND PROPERTIES OF POLYANILINE

Polyaniline has a reactive NH group in a polymer chain flanked on either side by a phenylene ring, imparting a very high chemical flexibility. It undergoes protonation and deprotonation in addition to adsorption through nitrogen, which, having a lone pair of electrons, is responsible for the technologically interesting chemistry and physics (79). Protonation of polyaniline not only involves the ingress of protons, but is also accompanied by ingress of anions, to maintain charge neutrality. This suggests that the behaviour of polyaniline depends on the pH and on the counterion of the Bronsted acid used for doping. In the chemical polymerization of aniline, the redox potential of the oxidizing agent is not a dominant parameter (80). Potassium iodate (KIO_3) is the most convenient chemical oxidant because it yields good quality samples over a wide range of polymerization conditions. In the chemical synthesis of polyaniline by ammonium persulphate in aqueous solution, the chemical composition, yield and conductivity of the product depend on the initial oxidant/monomer mole ratio (r) (81). Higher values of (r) result in overoxidation of the polyaniline with a concomitant decrease in conductivity and yield. Polyaniline can be synthesized in various forms both chemically and electrochemically in aqueous media (82). Chemical polymerisation of aniline by oxidants is more facile in water than in polar organic solvents, and its oxidation is possible with HCl (HCl enhances the oxidizing power of the oxidants) (83).

The morphology of polyaniline depends strongly on the polymerization method, due to the difference in growth speeds of the films (84,85). The conductivity of polyaniline is increased by low level oxidation and then switched off by high level oxidation. Other conducting polymers can only be switched on to a conductor but no new, stable, insulating form was found upon high level doping (86).

In the chemical polymerization of polyaniline generally an aqueous solution of oxidant is added slowly to a precooled aqueous solution of aniline in acid. The base form of polyaniline can be obtained by treating the salt form with alkali (e.g. NH_4OH, NaOH). Free standing films of polyaniline can be prepared by dissolving the emeraldine base form in n-methylpyrrolidinone (85,87-89). The resistivity depends on the redox state of the film, the pH of solution and to a lesser extent on the type of anion present (90).

The conventional method of p-doping (oxidizing) an organic polymer involves removal of electrons from the pi system of the polymer by chemical or electrochemical oxidation (82):

$$\text{(polymer)} \longrightarrow \text{(polymer)}^{+y} + ye^-$$

In principle it should be possible to p-dope a conducting polymer by adding a proton, which may interact with, and hence partly depopulate, the pi system with concomitant increase in conductivity of the polymer:

$$\underset{\text{(base)}}{\text{(polymer)}} + \underset{\text{(acid)}}{(\text{y}H^{+})} \longrightarrow \underset{\text{(salt)}}{(\text{polymer } H_{y})^{+y}}$$

This is a simple acid/base interaction, in which no formal oxidation or reduction occurs.

The emeraldine oxidation state of polyaniline in its base form is soluble in several aqueous and non-aqueous solvents such as NMP, DMF, DMSO, aqueous acetic acid or formic acid (89). The best solvent for producing high quality free standing films of emeraldine base is undoubtedly NMP. The emeraldine base, which is slowly oxidized by air, can be reconverted to the emeraldine oxidative state by treatment with dilute aqueous acids.

In the electrochemical polymerization of aniline anionic species in the electrolyte are inserted into the polyaniline film during the oxidative coloration process and then eliminated from the film during the reductive decoloration process (91-93). Polyaniline films show multiple colour changes, (transparent yellow - green - black) depending on the redox reactions at different potentials. These films strongly adhere to the platinum surface and are insoluble in all the common solvents (93). The conductivity and flexibility of the doped, high performance polyaniline films are directly related to the molecular size of protonic acids (94). The films are lustrous and have good flexibility, and can only be doped by protonic acids with small molecular size, such as HCl, $HClO_4$ and H_2SO_4, to the metallic conducting regime.

Properties such as morphology, electroactivity and conductivity of films prepared by cyclic potential sweep (CPS) and potentiostatic growth are different, due to a variety of factors (e.g. cathodic scan in CPS, accumulation of unreacted oxidized species) during the growth of the polymer (95).

Potential and pH are two related factors that affect the colour of polyaniline (85,96). Polyaniline may be used as a redox indicator or as a pH indicator. Polyaniline is very stable in common solutions. The morphology of polyaniline prepared electrochemically depends on the type of acid and solvent (97). The morphology and porosity of electrochemically prepared polyaniline films can be controlled largely by the electrolyte anion, the concentration of aniline and additive (e.g. paraphenylenediamine), and by the potential or current levels (98).

It is most important to note that, whereas the conductivity of all other conducting polymers depends only on one variable, namely the extent of oxidation or reduction of the polymer, the conductivity of polyaniline depends on two variables; the extent of oxidation and the extent of protonation of the polymer (99). The anodic oxidation of aniline in aqueous sulphuric acid solution at a platinum electrode proceeds through a free radical mechanism and the final product of this electrode reaction is primarily the octamer emeraldine, or a very similar compound (100). Emeraldine base form exhibits different doping behaviour depending on the method of preparation (101). Huang and coworkers (102) showed that the emeraldine base form of polyaniline is doped by protonic acids to the metallic conducting regime by a process involving neither oxidation nor reduction of the polymer, thus introducing a new concept of doping to the conducting polymer field.

The conductivity of polyaniline and its spin concentration change in similar ways when the extent of protonation is changed (103). An optical study of polyaniline indicated that there are two systems of polaron-bipolaron (cation radical-dication) in polyaniline films when the potential is increasing (104).

1.6 CONDUCTIVE POLYMER COLLOIDS

One of the major setbacks to the development of electrically conducting polymers such as polyacetylene, polypyrrole and polyaniline as commercial materials, either in bulk form or as surface films has been their relative intractability with regard to processing, in particular their insolubility in most common solvents. Polyacetylene also suffers from its poor air stability (105). Other conducting polymers such as polythiophene, are much more stable to oxygen, particularly when doped. Unfortunately, these materials are not very resistant to moisture when in the doped state. One method of overcoming the processability problem is to attempt to prepare colloidal dispersions of the conducting polymer particles, i.e., polymer latexes (106).

Colloidal sols are normally obtained by the dispersion polymerization technique using a suitable polymeric steric stabilizer which adsorbs physically onto the growing sub-micron conducting polymer particles. Alternately the stabilizer may be grafted chemically, thus preventing the precipitation of these particles (107). These techniques result in stable colloidal dispersion with sub-micron particles, where the size of the particles depends on the nature and size of the steric stabiliser employed.

The competing interactions between solvent, oxidant, monomer, growing polymer particle and steric stabilizer are complex. They are temperature dependent phenomena that normally lead to fractal growth, resulting in aggregated nanoparticles which go on to form larger ones (108).

Polyacetylene latexes were prepared via a dispersion polymerization route in a non-aqueous solvent mixture using the cobalt-based Luttinger catalyst (109). In 1983 Edwards and coworkers reported the preparation of a colloidal form of polyacetylene (19). Since 1986 there have been numerous reports describing the preparation of sterically stabilized colloidal dispersions of conducting polymers via dispersion polymerisation techniques in both aqueous and non-aqueous media. In general the chemical oxidation of conducting polymers such as polypyrrole and polyaniline is carried out in the presence of a steric stabilizer to produce a colloidal dispersion.

Conditions for obtaining well dispersed colloids are dependent on the following factors (106) :

1) Oxidant/stabilizer compatibility.

2) An appropriate number of active sites for adsorption or grafting of the appropriate surfactant.

3) An appropriate molecular weight for the surfactant to assume sufficient coverage on the conducting core.

Chemical grafting (copolymers) of aniline onto the backbone of the polymeric surfactant is a novel way to obtain colloidal forms of this conducting polymer (107,110-112). The chemical grafting technique offers the advantage, compared to physical adsorption in the case of polypyrrole, of forming more stable materials in which desorption of the steric stabilizers does not take place. If the initial stabilizer concentration is insufficient, macroscopic precipitation is observed within two hours of the addition of monomer (113). Colloidal dispersions of polyaniline and polypyrrole could be flocculated/stabilized in a reversible manner by the addition of base/acid (114,115). If necessary the stabilizer may be subsequently removed to yield stable dispersions of bare (charged stabilised) particles (116).

Particle size, conductivity, yield, morphology and formation of stable suspensions depend on the type of stabilizer and oxidant, concentration of stabilizer and oxidant, type and volume of solvent, and the temperature employed (117-124). In the preparation of polypyrrole colloid better conductivity was obtained when ferric chloride was used as the oxidant (121). The particle size of polypyrrole colloids decreases with increasing stabilizer concentration (125).

The conductivity of polyaniline particles fell approximately linearly with pH, from a high value at pH ~ 1 (where the aqueous dispersions are green) to ~ 0 at pH ~ 10 (where the aqueous dispersions are blue) (126). Polypyrrole colloids can be prepared in a non-aqueous media such as methylacetate, methylformate, propylformate and 2-methoxy ethanol by using polyvinylacetate as a polymeric surfactant (118,124). Monodispersed particles can be obtained by decreasing the temperature, presumably due to the reduced rate of polymerization (118,122). The conductivity decreases in non-aqueous systems due to increased stabilizer adsorption, but polydispersed particles are formed as a result of an increase in the polymerization rate in the polar organic media.

Particle size and conductivity can be decreased by increasing the concentration of stabilizer (117,125). These are related to the mass of insulating steric stabilizer adsorbed. Adsorption of the stabilizer on the polypyrrole particles is primarily due to the hydrophobic component in the stabilizers, probably via a hydrogen bonding mechanism with the pyrrole N-H group (117,125).

The colloidal form of polypyrrole is less environmentally stable with respect to conductivity than bulk polypyrrole powder, probably due to the former's relatively high surface area (125). The conductivity of the doped latex pellets are lower by roughly an order of magnitude relative to those of the respective bulk electrochemically prepared materials. This is attributed to the poor microscopic inter-particle contacts in the latex pellets due to the presence of the insulating adsorbed steric stabilizer (127).

In the preparation of polypyrrole colloids, where an initiator is added to the stirred monomer stabilizer mixture, non-spherical particles of poor morphology were obtained, but in the case of injection of monomer into stirred oxidant-stabilizer mixture, spherical particles resulted (128). Polypyrrole colloids could be prepared in aqueous media by using an anionic surfactant, such as sodium dodecylbenzenesulfonate (129). Polypyrrole colloids were prepared by using a tailor-made water soluble monodispersed block copolymer as a steric stabilizer (130,131), producing particles which were spherical, slightly flocculated in the dispersed state and having high stabilizer content (54 % w/w). Colloidal dispersions of polyaniline containing uniform spherical particles have been prepared (132).

Behaviour of polymeric and monomeric emulsifiers in the emulsion polymerization of styrene with both the water soluble initiator and the oil-soluble initiator have been investigated (133). This investigation showed that the distribution of particle size depends on the type of emulsifiers and initiators.

Colloidal particles may be further processed in a variety of ways, for example polypyrrole and polyaniline particles may be incorporated into thin film polymeric films by mixing them with other film forming latex particles or coating them as dispersions in a film-forming polymer solution (134-138). Electrodeposition has evolved into a common technical method for forming protective and decorative coatings on metal surfaces. The process is based on the deposition of coating particles, dispersed as a colloid, to form a continuous film on the host surface. The mechanism of electrodeposition in colloidal systems is complex (139). The quality of deposits depends upon ion-electrode and ion-charged particle interactions. Ionic precipitation involving anode dissolution products does not appear necessary for deposition to occur, although such ions may affect adhesion and have a pronounced effect on the subsequent curing of deposited films of unsaturated polymers (139).

1.7 IMPROVING PROCESSABILITY OF CONDUCTING POLYMERS AND SOME APPLICATIONS

The insolubility in common solvents and infusibility of conducting polymers, in general, make them poorly processable either by solution technique or by melt processing methods (20). Several attempts have been made to overcome these problems, essentially by fabrication of composites, which combine the conductivity of conducting polymers with the mechanical and optical properties of a matrix polymer such as poly (vinylchloride) (140) or poly(vinylalcohol) (141). Highly transparent and conducting polypyrrole/polyvinylalcohol composite films can be obtained by exposing polyvinylalcohol films containing ferric chloride to pyrrole vapour (142). These composites are synthesised as free standing films, mainly by electropolymerization of conducting polymers into the classical polymer matrix, whether by a two step (139,143,144) or, as proposed recently, a one step (145) procedure which leads to a very homogeneous composite material. The uniformity of conductivity can be improved significantly by adding an electrolyte to the host polymer prior to the electropolymerization.

Monomer polymerization at an interface is one of the procedures for obtaining polypyrrole films and polypyrrole plastic/composites (146). Thin, flexible, transparent films or thick, sponge-like dark brown sheets were obtained according to the amount of polymer used. The chemical polymerization of the conductive polymers (e.g. polypyrrole) seem to be a general and useful tool for the preparation of conductive composites. A highly conducting polyvinyl chloride (PVC)/polypyrrole film can be prepared by electrochemical polymerization of pyrrole on a (PVC) coated electrode (147). Submicron sized latex particles (e.g. silica, polystyrene) in aqueous solution can be homogeneously coated with a thin film of conducting polypyrrole or polyaniline (134,148-152). The polyaniline/silica composites can be redispersed in media that are good solvents for the polyaniline overlayer. No solvent system is known for polypyrrole (either doped or undoped).

Conducting polymer matrices provide an interesting and useful focus for expansion of the fields of polymeric reagent research and molecular engineering (153). Particles of hematite, silica doped with hematite, and cerium oxide have reactive sites on their surfaces and can be coated with polypyrrole of controlled thickness without the use of electrochemical or soluble initiators (154). The polypyrrole composites exhibit some properties similar to carbon black-polymer composites (155). Small amounts of ammonia in air decrease the conductivity of the polypyrrole deposited on paper (155). The impregnated materials may be used as electrodes for electrochemical applications where their porous structure and larger surface area should be an advantage. An alternative approach to developing conducting polymers is to use refractory conducting inorganic particles and covalently bond them to polymeric materials (156).

Electrically conductive paints are traditionally produced by the introduction of conducting carbon or metal particles to conventional paint formulations (157-163). Conducting polymer colloids may be used to make a novel conductive electroactive paint (164).

At present the most cost-effective means of controlling electromagnetic interference (EMI) and electrostatic charge dissipation (ESD) is to use various types of conducting composites having conductive fillers such as metal fibres, metal particulates, carbon black and graphite fibre. Carbon-fibre and metal-fibre filled polyethylene composites are reported to have poor performance for EMI shielding (165) as is the case with metal fibre filled composites of polypropylene (166,167).

Paoli and coworkers (168) demonstrated that the electrochromism of polypyrrole electrodes becomes more stable and reproducible when the polymer is electrodeposited in the presence of a surfactant counter-anion such as dodecylsulfate. Electroactive polymer films (e.g. polypyrrole films) may be able to control the semiconductor-liquid interface and substantially suppress photodissolution/oxidation (169). By imbedding the material particles in polymeric films, the loss of catalytic activity or efficiency due to physical or chemical loss of the catalyst can be suppressed (170).

The influence of foreign gases (N_2, CO, CO_2, and SO_2) on O_2 reduction on the gas diffusion hybrid polymer electrode composed of polypyrrole conductive polymer, polyvinylchloride (PVC) binder and cobalt phthalocyanine crystalline powder was used as a catalyst for the electrode reaction (171). The results indicated the effectiveness of this electrode for gas sensing applications. The various possible applications of conducting polymers have been reported briefly with a focus on electrochemistry, electro-optical properties and shielding against electromagnetic interference (EMI) in the radio frequency and microwave regions (172). The morphology plays an important role in determining conductivity and mechanical properties of the materials (172).

1.8 STABILITY

The stability of polypyrrole can be improved by using acid and base treatments (173,174). The base decreases the conductivity, but acids have little effect on the conductivity, because the main feature of the base and acid treatments is the ion exchange. In the neutral form, polypyrrole films are yellow/green and are sensitive to air and oxygen while the oxidized polymer is very stable in air (28,175). The yellow/green film of neutral polypyrrole rapidly becomes black on exposure to oxygen. Polyaniline (93) and poly(N-methylpyrrole) are quite stable in air when neutral and when oxidized (175). Polythiophene and its derivatives are the first examples of conducting polymers that are stable toward oxygen and moisture both in their undoped and doped states (28,175). They can be synthesized chemically or electrochemically.

Conducting composite films containing an electropolymerizeable conducting polymer such as poly(3-methylthiophene) alloyed with poly(vinylchloride) (PVC) have been prepared in a one step process from synthesis media containing dissolved PVC (176). This procedure, based on the simultaneous electropolymerization and dip-coating processes, allows a large control of the composition, morphology, optical transmittance, conductivity and electroactivity of the composite films.

Melt processing of polyaniline is not possible, since the polymer decomposes at temperatures below softening or melting point. In addition, major difficulties have been encountered in attempts to dissolve the material. Soluble polyaniline can be prepared in concentrated sulfuric acid (177). Polyaniline which is soluble in common organic solvents has been synthesized by using organic acids of large molecular size or graft polymerization with polyaminostyrene (178). The reaction of aniline with copper(II) perchlorate as an oxidant in acetonitrile yields highly electroactive polyaniline perchlorate which is soluble in dimethylsulfoxide (DMSO) (179).

Type, concentration and size of additives can affect the mechanical and thermal stability of polymer electrolytes (180). Conductive PPy-halogens (Br_2, Cl_2, I_2) complexes are stable in air at room temperature and PPy-Br complex shows the best developmental potential for practical applications (181). The electrochemical oxidation of various heterocycles leads to the formation of new organic conducting polymers (182). These compounds are very stable in air and under vacuum, and they afford a large range of conductivities depending on the monomeric structure.

1.9 ELECTROCHEMICAL TECHNIQUES FOR CHARACTERIZATION

1.9.1 Chronopotentiometry

Chronopotentiometry involves monitoring the potential of the working electrode with respect to time during the application of a constant current. The constant current imposed at the working electrode causes the electroactive species to be oxidized or reduced at a constant rate. The electrochemical potential of the system changes accordingly to maintain the constant current. A major advantage of constant current techniques is that the amount of charge passed in an electrolysis reaction can be easily controlled by monitoring the length of time that the current is applied.

1.9.2 Cyclic voltammetry

Cyclic voltammetry involves the measurement of current at the working electrode as a function of the applied potential which is a linear ramp. The schematic time-potential curve (triangular waveform Figure 1.1 (a)) and current-potential curve or voltammogram (Figure 1.1 (b)) are shown in Figure 1.1.

1.9.3 Chronoamperometry

Chronoamperometry involves the measurement of current at the working electrode with respect to time during the application of a constant potential. When polymerization was performed at controlled potential, chronoamperometry was employed to monitor the resulting process.

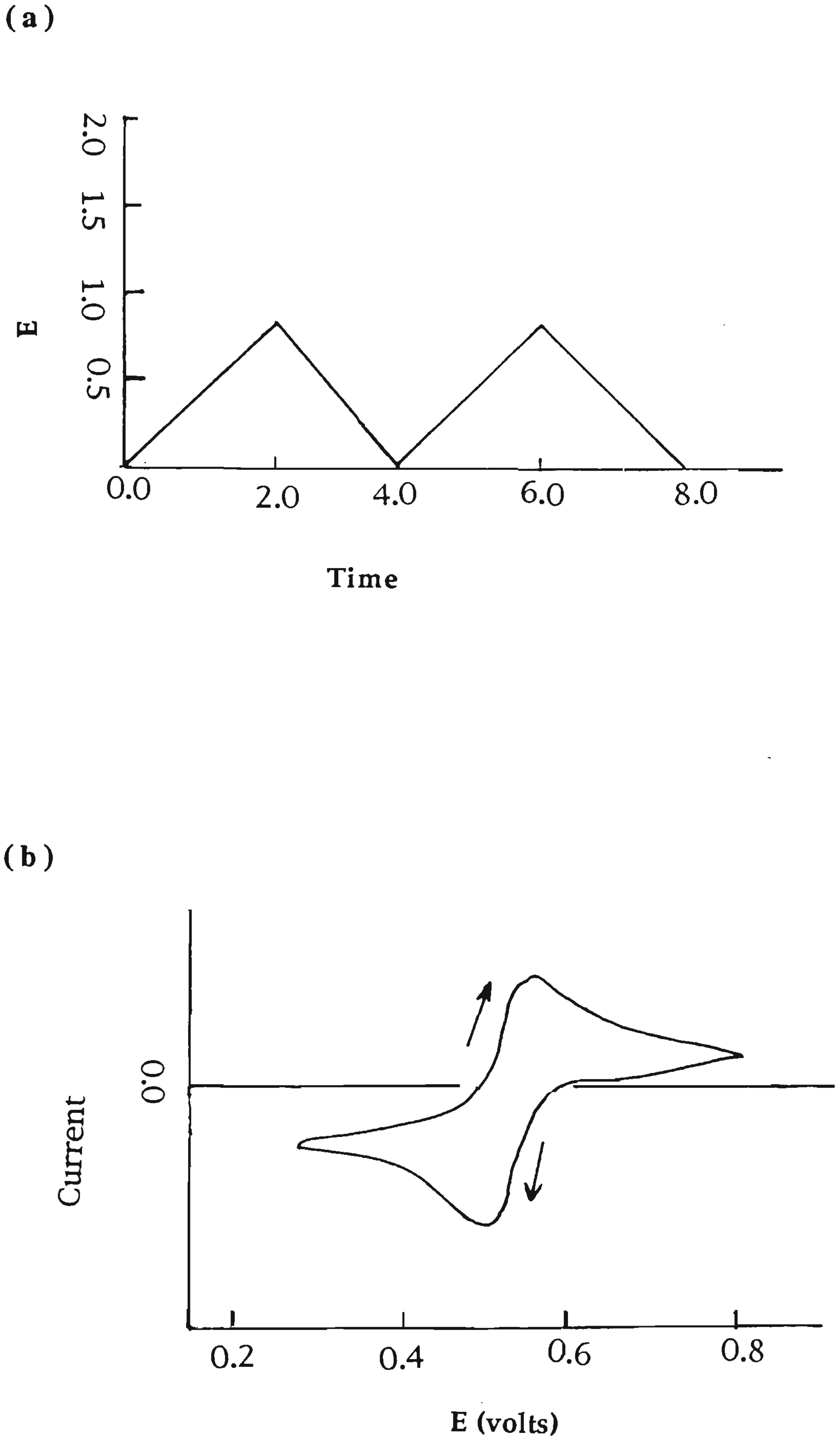


Figure 1.1: Schematic diagrams of cyclic voltammetry.

1.10 AIMS OF THE PROJECT

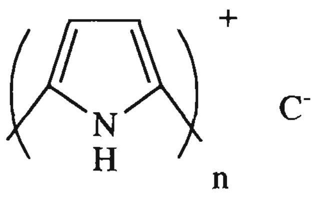
The general aim of this project was to study the preparation, characterization, development and applications of conducting polymer colloids in aqueous media. The project involved various aspects of colloids (polypyrrole and polyaniline) preparation using a range of stabilizers. Colloids were also used for the preparation of conductive electroactive paint. Electrodeposition of composites such as polypyrrole/polyaniline colloids, polyaniline colloid/sulfonate resin were investigated. Thermal stability of polyethylene was studied using carbon black, polypyrrole and polyaniline as additives. Electropolymerization of pyrrole and aniline was studied using various stabilizers and different electrochemical techniques. The major part of the work involved the design, preparation and characterization of polypyrrole and polyaniline colloids using a flow through electrochemical cell.

CHAPTER 2

ELECTROCHEMICAL PROPERTIES OF CONDUCTIVE ELECTROACTIVE POLYPYRROLE AND POLYANILINE COLLOIDS

2.1 INTRODUCTION

Conductive electroactive polymers (CEPs) such as polypyrrole (I) possess some unique chemical and electrochemical properties (183).



(I)=polypyrrole

They are electrically conductive, which makes their use as metal replacement materials of some interest. However they also possess electrochromic properties (153, 176), they can be used to produce catalytic electrodes (184, 185), sensors (68), chromatographic stationary phases (137,147,186), dynamic membranes (126, 187, 188) and controlled release devices (189, 190). The realisation of this vast technological potential depends almost entirely on the ability to produce CEPs at low cost and in appropriate forms.

It is perhaps of no surprise, therefore, that previous workers have been concerned with the preparation of conductive electroactive polymeric colloids (111, 122, 124, 136, 42, 116, 191). This drive has primarily been associated with the need to develop better processing methods for CEPs. Both polypyrrole and polyaniline colloids have been produced.

In the case of polypyrrole (both stand-alone as well as supported (111, 136, 154)) colloids have been prepared and in at least one instance polypyrrole colloids have been coated with another polymeric material (150). Numerous reports have detailed the preparation of polyaniline colloids (106,111-114,192). In general the chemical oxidation of polyaniline is carried out in the presence of a steric stabiliser to produce a colloidal dispersion. The use of the chemical oxidant potassium iodate has been studied in some detail (192) and appears to be a popular choice for formation of stable colloidal sols. Numerous stabilisers including - poly(vinyl alcohol - co-vinyl acetate) (112), polyvinyl pyridine-co-p-aminostyrene (111), or poly(vinylimidazote-(0-4-aminostyrene (113) have been used. In the case of the latter two the amino group enables the stabiliser to become grafted onto the polyaniline during polymerisation. In all cases, rice-grain like colloids are obtained. In general, conducting polymer colloids are formed by oxidation of the monomer in the presence of a steric stabiliser.

In this chapter the chemical preparation, characterisation and electrochemical properties of polypyrrole and polyaniline colloids have been studied using different stabilizers such as Polyvinylpyrrolidone (PVP_1, $M_W = 2.5 \times 10^4$ and PVP_2, $M_W = 1.2 \times 10^6$), Polyvinylalcohol (PVA, $M_W = 3 \times 10^4 - 7 \times 10^4$) and Polyethylene oxide (PEO, $M_W = 3 \times 10^5$). The electrochemical properties of these colloids have then been investigated, in order to determine those processing factors that influence the electroactivity of the colloids produced.

2.2 EXPERIMENTAL

2.2.1 Reagents and Standard Solutions

Deionised water was used throughout this work. Pyrrole (Aldrich) was distilled and stored in the fridge before use. Ammonium persulfate, sodium nitrate, sodium chloride, potassium dichromate, sodium persulphate, polyethylene oxide (PEO, molecular weight = 3×10^5), polyvinyl alcohol (PVA, molecular weight = $3 \times 10^4 - 7 \times 10^4$), were all obtained from Aldrich, polyvinylpyrrolidone (PVP_1, molecular weight = 2.5×10^4) from Merck and polyvinylpyrrolidone (PVP_2, molecular weight $=1.2 \times 10^6$) from TCI and were all used as received. Reticulated vitreous carbon (RVC) was obtained from Energy Research and Generation Inc. Anhydrous ferric chloride was filtered by using vacuum filtration through a whatman filter paper (number 542) prior to use. Aniline (BDH) monomer was freshly distilled and stored in the fridge. Hydrochloric acid (HCl), $(NH_4)_2S_2O_8$, $K_2S_2O_8$, $K_2Cr_2O_7$ and KIO_3 were obtained from (BDH).

2.2.2 Instrumentation

A Bioanalytical Systems (BAS) Model 100A Electrochemical Analyser or a BAS Model CV-27 voltammograph were used throughout this work. A glassy carbon working electrode, a platinum gauze auxiliary electrode and a Ag/AgCl (3 M NaCl) reference electrode were used throughout this work. A Sorvall OTD Ultracentrifuge was used. Transmission electron micrographs (TEMs) and Scanning Electron Micrographs (SEMs) were obtained using diluted redispersed latex dried on carbon coated copper grids and gold foil. A JEOL 2000 FX Transmission Electron

Microscope (TEM) or a Hitachi S450 Scanning Electron Microscope (SEM) were employed. An Instron 4302 tensile testing machine was used for the characterization (adhesive strength) of deposited colloids

2.3 RESULTS AND DISCUSSION

2.3.1 Polypyrrole Colloid Preparation

The key to preparing conducting polypyrrole colloids is to carry out the polymerization in the presence of soluble polymeric steric stabilizers which adsorb to the latex particles as they form, preventing gross aggregation and precipitation of the polymer (124). Iron (III) salts provide a convenient means for polymerization of pyrrole (35,41). In comparison with $Fe(ClO_4)_3$, $CuBr_2$ or $Fe(NO_3)_3$ better conductivity resulted when ferric chloride was used as the oxidant in the preparation of polypyrrole colloids (121). The order of addition of monomer to oxidant/stabilizer is an important factor in determining the morphology of the latex particles because in the case of addition of oxidant to the stirred monomer/stabilizer mixture, non-spherical particles of poor morphology were obtained (128). Solutions of oxidant/stabilizer were stirred using a magnetic stirrer for at least one hour before addition of monomer to the mixture solution. When monomer was added to the stirred aqueous solution and the reaction was carried out for nineteen hours good quality dispersions were obtained.

If the initial stabilizer concentration is not sufficient then macroscopic precipitation occurs (113). The minimum stabilizer concentration required to prevent macroscopic precipitation is shown in Table 2.1. Typical conditions used for colloid formation in this work are summarised in Table 2.2. When 0.15 M pyrrole and 53.3 g/L ferric chloride were used for the colloid preparation, any concentration of stabilizer lower than that reported in Table 2.1 produced precipitation/flocculation.

Table 2.1: Minimum stabilizer concentration for preparation of polypyrrole colloid.

Stabilizer type	Stabilizer concentration (g/L)
PVA	4.0
PEO	3.6
PVP_1	2.5
PVP_2	1.6

Conditions: 0.15 M pyrrole, 53.3 g/L ferric chloride, reaction time=19 h, room temperature.

Table 2.2: Typical conditions for colloid preparation.

Stabiliser	Synthesis Conditions
PVA	PVA = 4.0 g/L. Pyrrole = 10.0 g/L. $FeCl_3$ = 53.3 g/L. Room temperature Reaction time = 19 hours
PEO	PEO = 3.6 g/L. Pyrrole = 10.0 g/L. $FeCl_3$ = 53.3 g/L. Room temperature Reaction time = 19 hours
PVP_1	PVP_1 = 2.5 g/L. Pyrrole = 10.0 g/L. $FeCl_3$ = 53.3 g/L. Room temperature Reaction time = 19 hours
PVP_2	PVP_2 = 1.6 g/L. pyrrole = 10.0 g/L. $FeCl_3$ = 53.3 g/L. Room temperature Reaction time = 19 hours

In a typical experiment 1.0 mL of pyrrole was added to a stirred aqueous solution (100 mL) containing 5.33 g of ferric chloride and 0.10-2.50 g of one of the stabilisers (PVP, PVA or PEO). The temperature of the mixture was maintained between 4 ^{o}C and 25 ^{o}C, for nineteen hours.

The black colloidal dispersion was ultracentrifuged (50,000 rpm) for thirty minutes to produce a black sediment. The supernatant was decanted and the sediment rinsed several times with distilled water. The dispersion could be redispersed in water by ultrasonication.

The type of stabilizer used and the concentration had a slight effect on the yield of colloid obtained. This is due to the fact that the type, molecular weight and concentration of stabilizer are known to influence the rate of colloid formation (106).

Table 2.3: Influence of stabilizer type and concentration on the yield of insoluble polymer.

Stabilizer type	Stabilizer concentration (g/L)	Yield (*) from one gram of monomer (gr)
PVP_2	1.6	1.0
PVP_2	2.0	1.1
PVP_1	2.5	0.9
PVP_1	3.0	1.0
PVA	4.0	1.0
PVA	4.5	1.1
PEO	3.6	0.8
PEO	4.5	0.9

(*) The colloidal dispersions were ultracentifuged (50,000 rpm) for thirty minutes. The supernatant was decanted and the sediment rinsed several times with distilled water. The sediment was dried in the oven at 80 ^{o}C for 24 hours.

2.3.2 Polypyrrole Colloid Morphology

Transmission electron micrographs of colloids are shown in Figure 2.1.

(a)

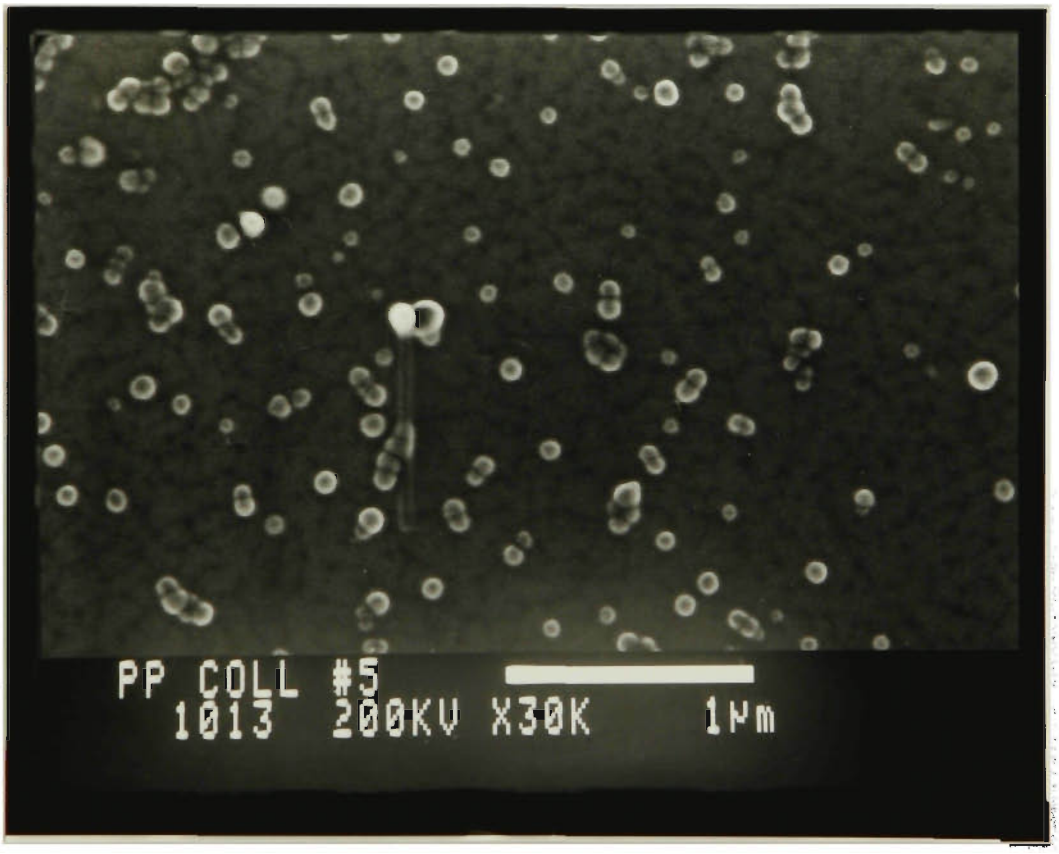
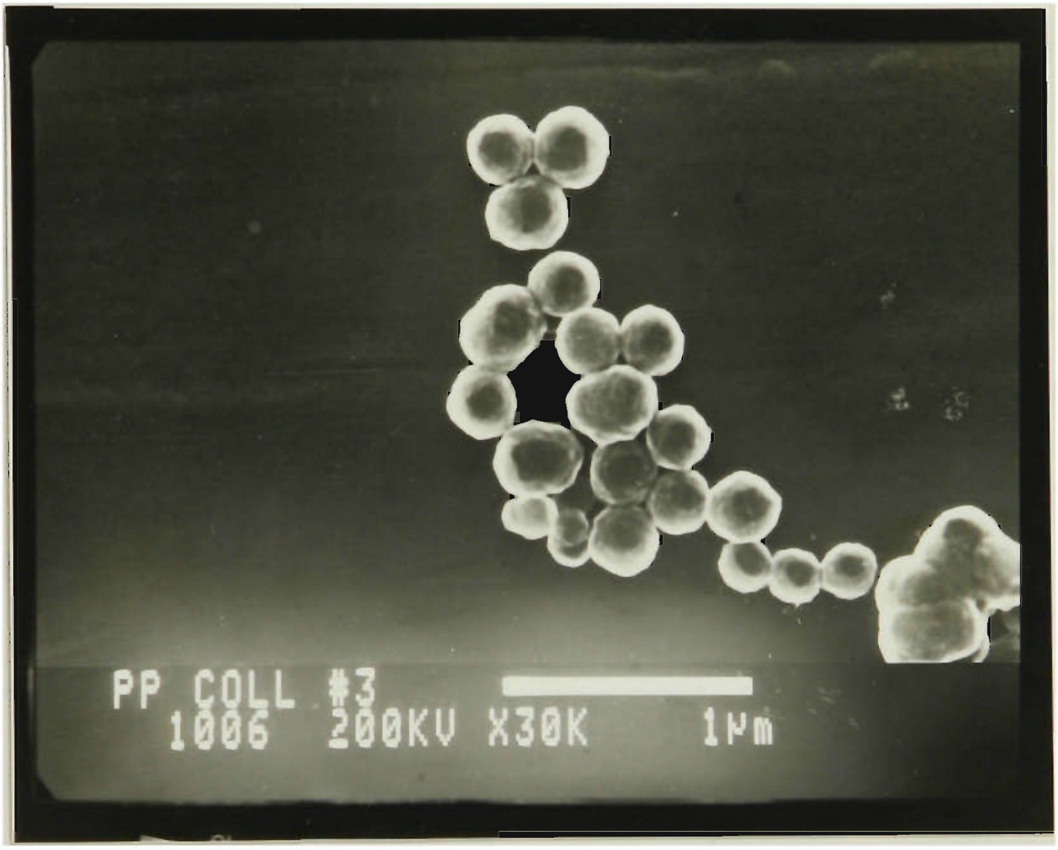


Figure 2.1: Transmission electron micrographs of polypyrrole. Latexes stabilized by: (a) PVP_2 (M_W = 1.2 x 10^6), initial concentration 3.0 g/L. (b) PEO (M_W = 3 x 10^5), initial concentration 10.0 g/L. (c) PVA (M_W = 3 x 10^4 - 7 x 10^4), initial concentration 4.0 g/L.

(b)



(c)

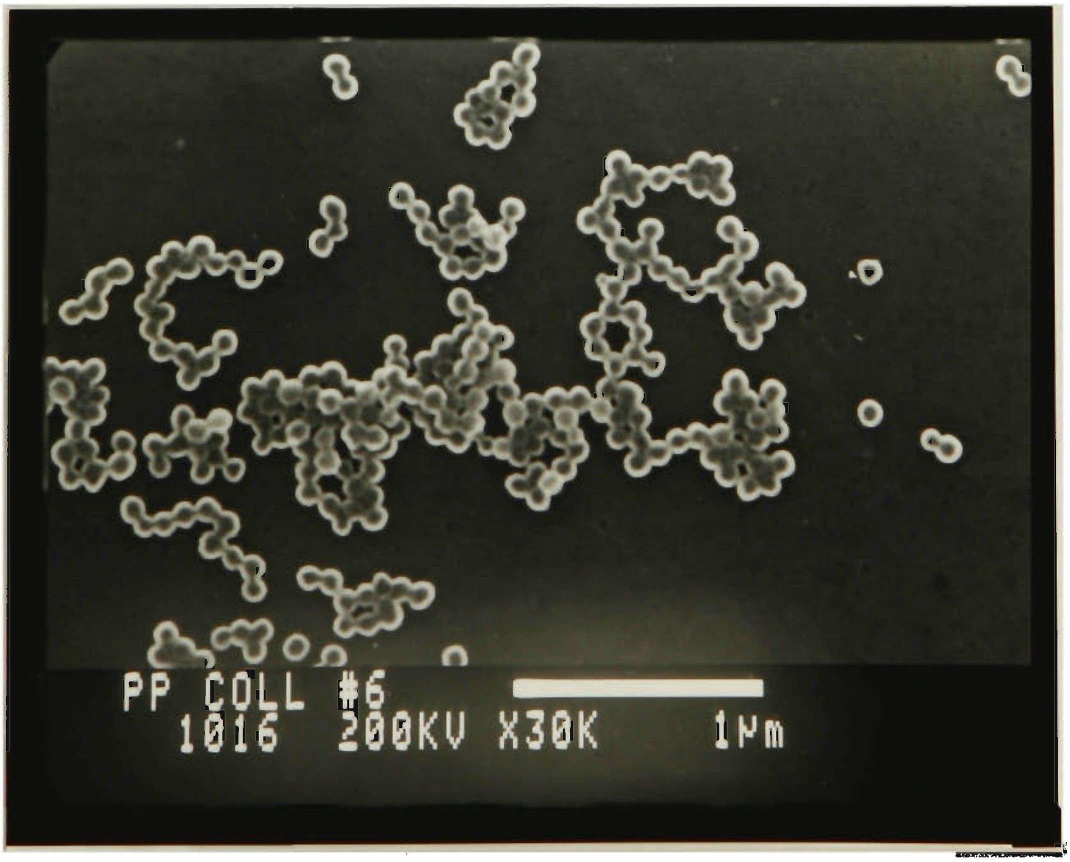


Figure 2.1 continued.

The stabilizer conditions used influenced the size and size distribution of the particles obtained (120). It is known that particle size decreases as stabilizer concentration is increased (117,125). This is presumably due to the amount of adsorbed non-ionic stabilizer on the surface of particles (107). The average particle size is shown in Table 2.4. As shown, the stabilizer type and concentration influence the size of the colloidal particles, which is in agreement with previous reports (117, 125).

Table 2.4: Average particle size of polypyrrole colloids

Stabilizer	Molecular weight of stabilizer	Stabilizer concentration (g/L.)	Particle size (nm)
PVP_2	1.2×10^6	3.0	110 ± 10
PVP_2	1.2×10^6	5.0	85 ± 10
PEO	3×10^5	10.0	265 ± 20
PVA	$3 \times 10^4 - 7 \times 10^4$	4.0	95 ± 5
PVA	$3 \times 10^4 - 7 \times 10^4$	8.0	80 ±5
PVP_1	2.5×10^4	25	50 ± 10

2.3.3 Cyclic Voltammetry of Colloidal Dispersions

Cyclic voltammetry was used to characterize the electroactivity of redispersed colloid solutions and electrodeposited colloids. Initially, the voltammetric behaviour of the stabilisers alone in 1.0 M $NaNO_3$ was studied using glassy carbon electrodes. It was found that only PVP gave small sharp non-faradaic responses at -0.50 V (A). The responses observed with PVP are shown in Figure 2.2. The peak that is observed along with the symmetric nature of the response suggests that it is due to adsorption/desorption of PVP on the surface of the electrode. The other stabilizers gave no voltammetric responses.

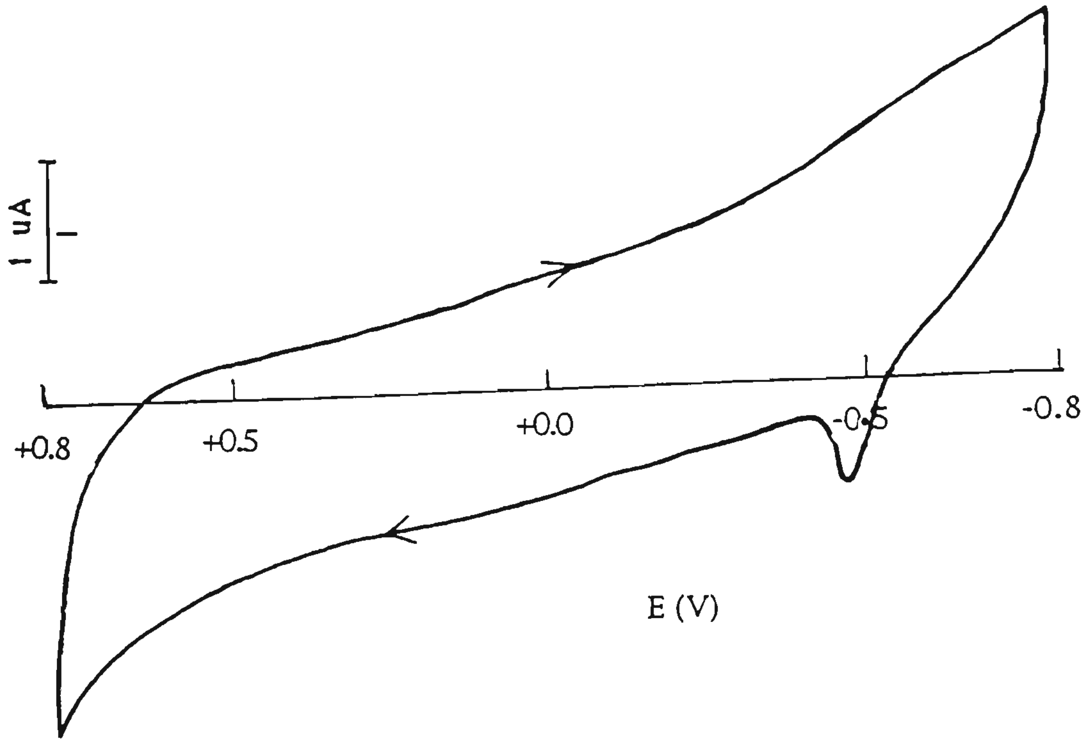
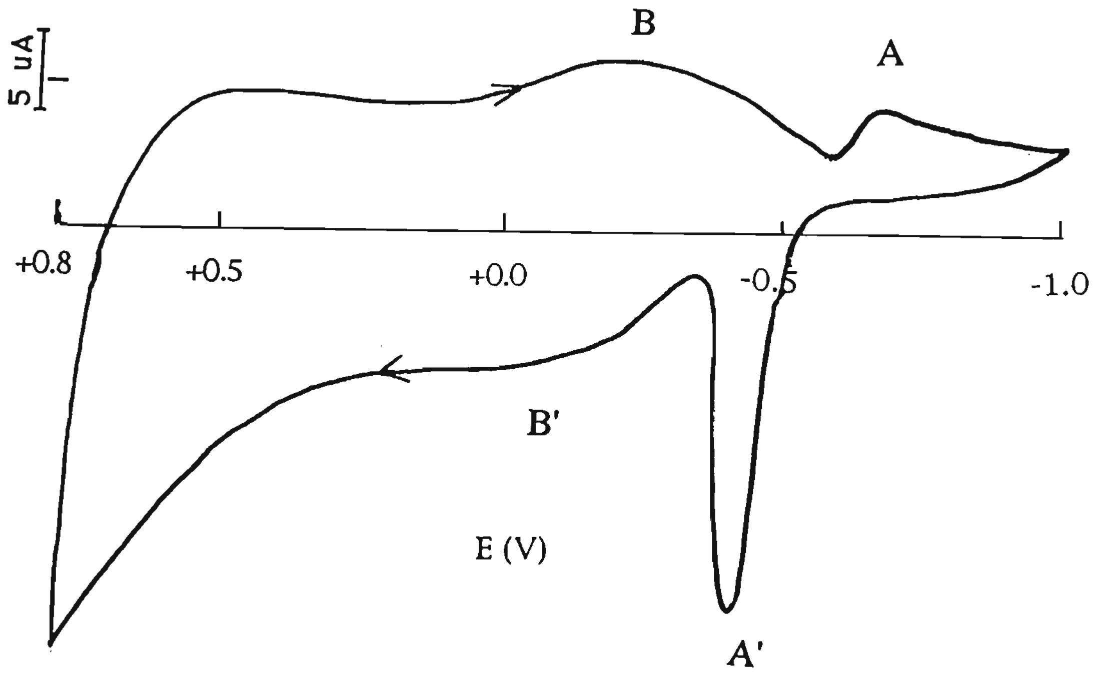


Figure 2.2: Cyclic voltammogram of PVP_2.
Conditions: Scan rate 100 mV/s; working electrode was glassy carbon; solution = 3.2 g/L PVP_2 in 1.0 M $NaNO_3$.

The electrochemistry of each of the colloidal dispersions prepared in Table 2.2 was then considered using cyclic voltammetry. It was found that when PVP was used, voltammetric responses due to the stabiliser were observed (Figure 2.3 response A/A'). These responses were not observed with other stabilisers (Figure 2.4).

The responses due to polymer oxidation/reduction (section 2.3.6, equation 2.1) were also observed (Figure 2.3 response B/B'). As shown in Figures 2.3 and 2.4 the type of stabilizer employed affected the electroactivity of the resultant colloids. This is presumably due to the fact that the amounts of adsorbed non-ionic stabilizer on the surfaces of the particles are different (107).

(a)



(b)

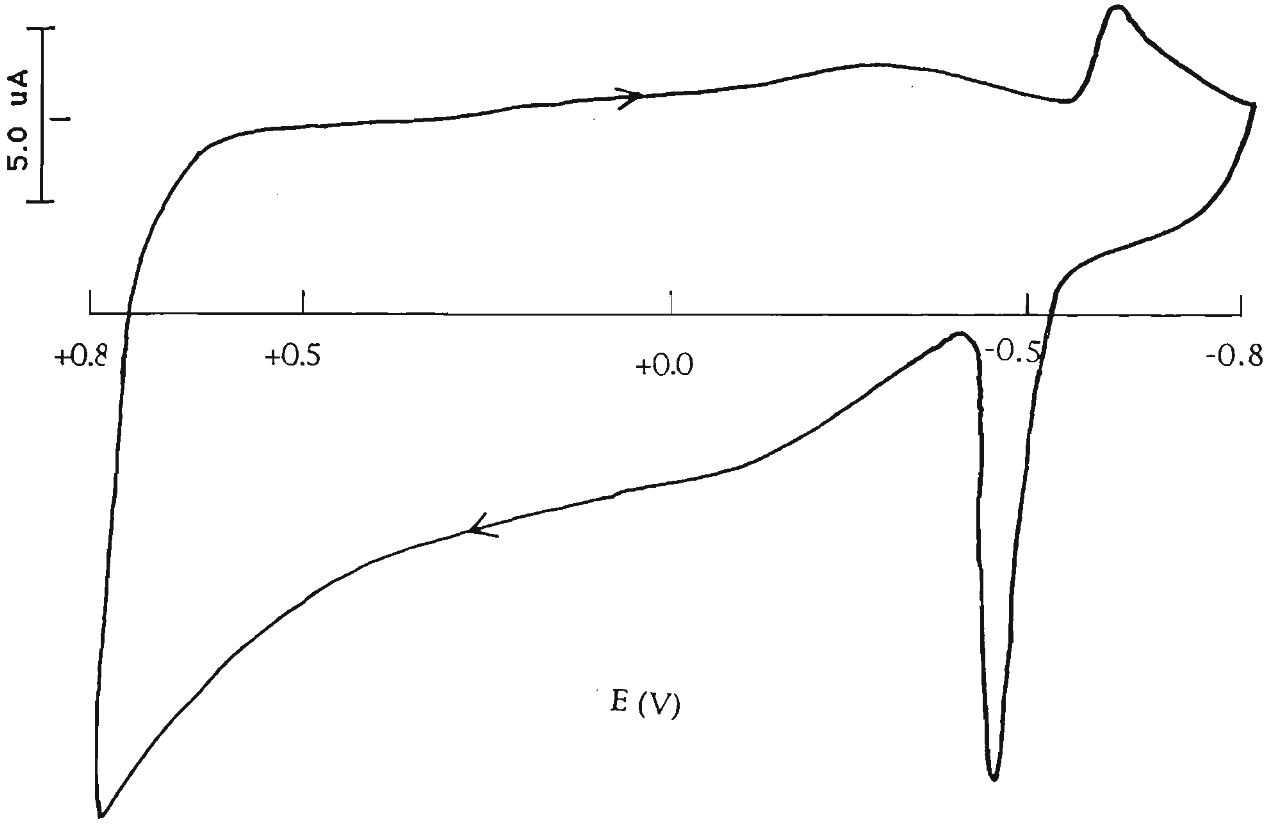


Figure 2.3: Cyclic voltammograms of a 4.0 g/L polypyrrole colloidal dispersion.

Conditions: Working electrode was glassy carbon. Scan rate 100 mV/s. Stabilizer employed during synthesis was (a) 1.6 g/L PVP_2 (b) 2.5 g/L PVP_1. Other synthesis conditions as per Table 2.2.

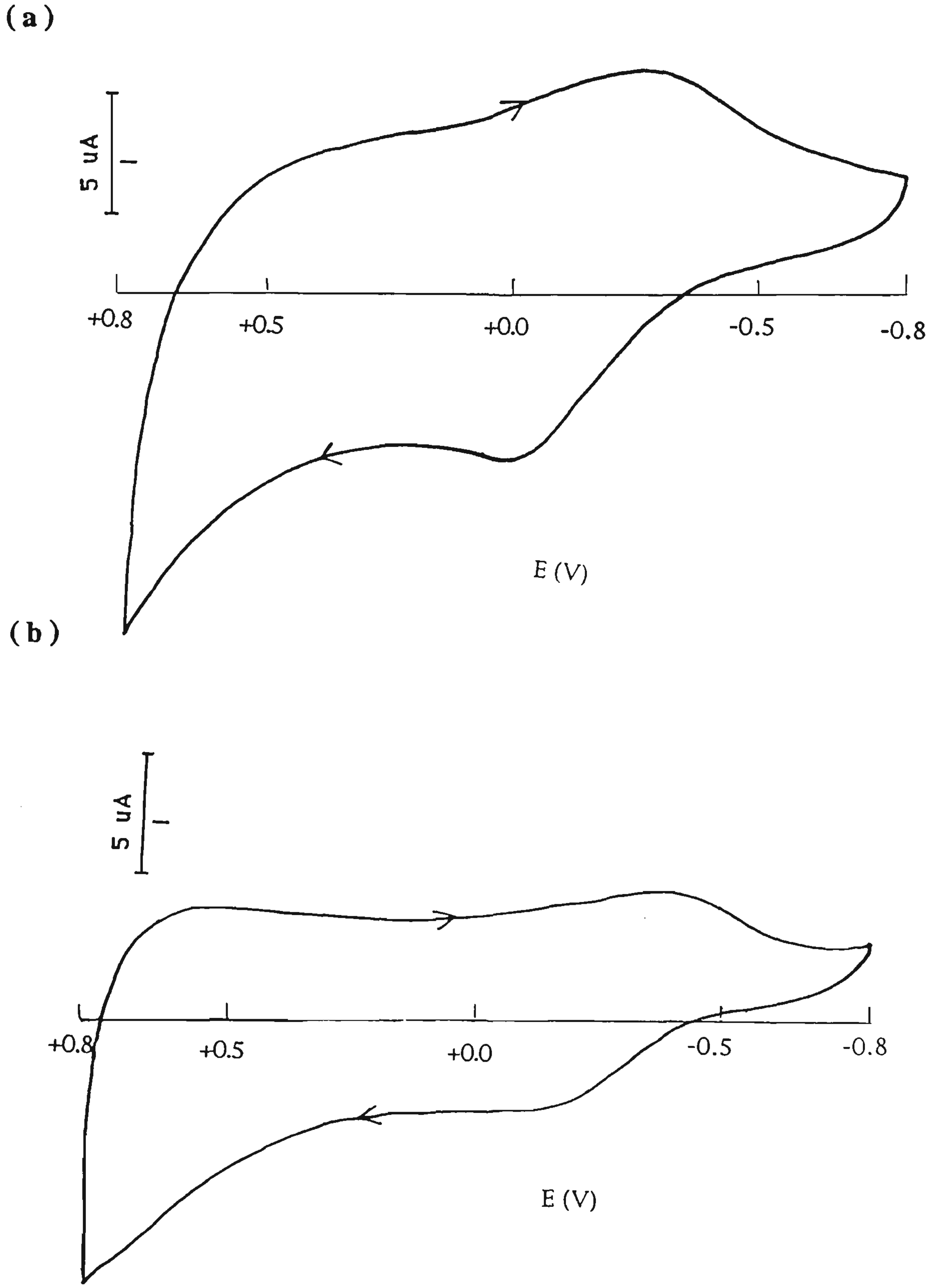


Figure 2.4: Cyclic voltammograms of a 4.0 g/L polypyrrole colloidal dispersion.

Conditions: Working electrode was glassy carbon. Scan rate 100 mV/s. Stabilizer employed during synthesis was (a) 3.6 g/L PEO; (b) 4.0 g/L PVA. Other synthesis conditions as per Table 2.2.

In all cases the limiting current increased with the concentration of colloid in the dispersion (Figure 2.5).

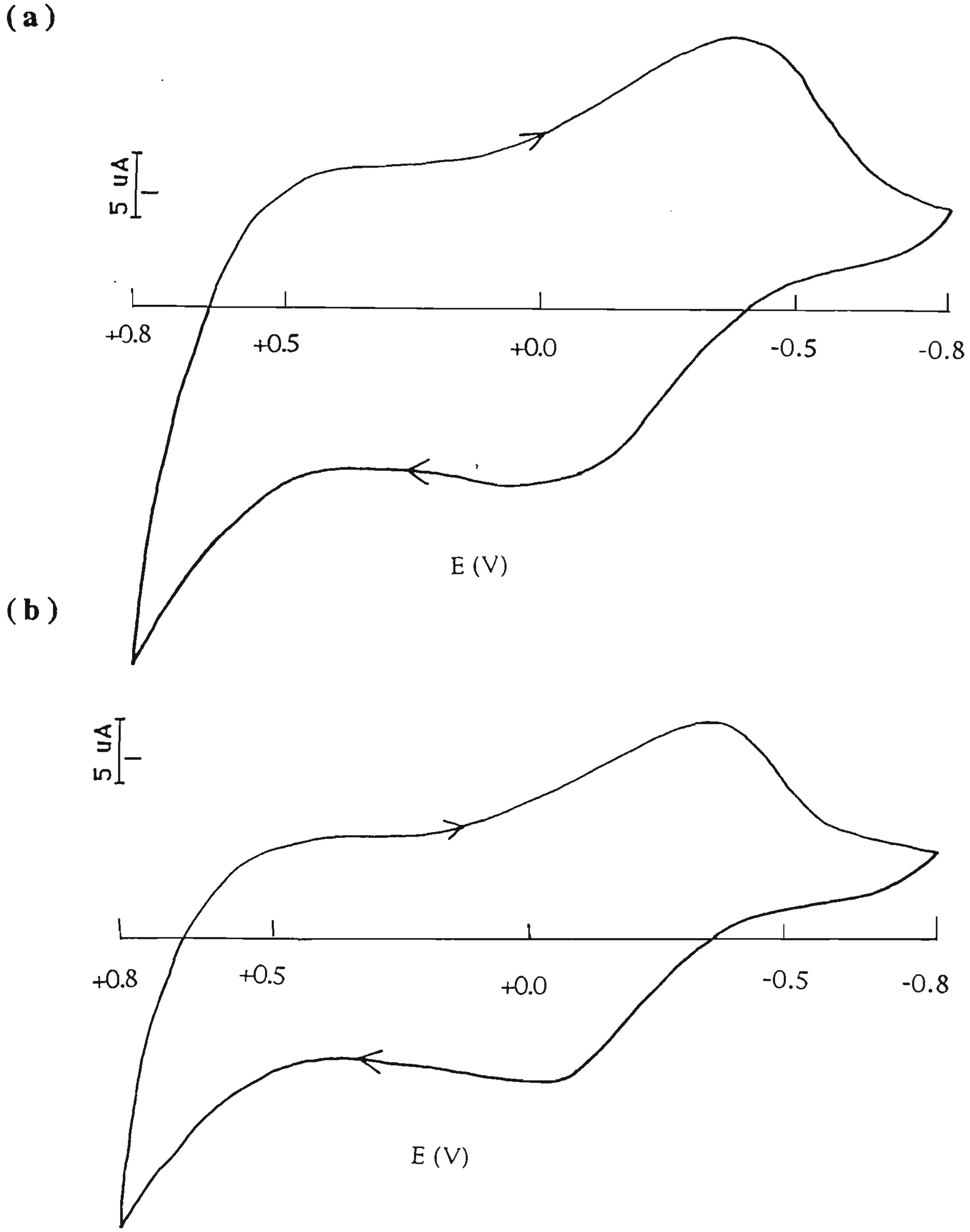


Figure 2.5: Cyclic voltammograms of polypyrrole colloidal dispersion.
Conditions: (a) 8 g/L Colloid; (b) 5 g/L colloid. Scan rate 100 mV/s; glassy carbon electrode; 3.6 g/L PEO stabilizer was used during synthesis. Other conditions as per Table 2.2.

The effect of the Stabilizer on the Electroactivity of the resultant colloids was then considered.

As shown in Figure 2.6 the electroactivity decreases with increasing stabiliser concentration used for colloid formation. This is probably due to the increased amount of insulating steric stabilizer adsorbed on the surface of the particles (106, 107). This layer may either block electron transfer or decrease the physical conductivity of the colloidal particles. It is known that the conductivity of these colloids decreases with increasing stabilizer concentration (117,125). This is possibly related to the amount of insulating steric stabilizer adsorbed onto the surface of the particles (107).

(a)

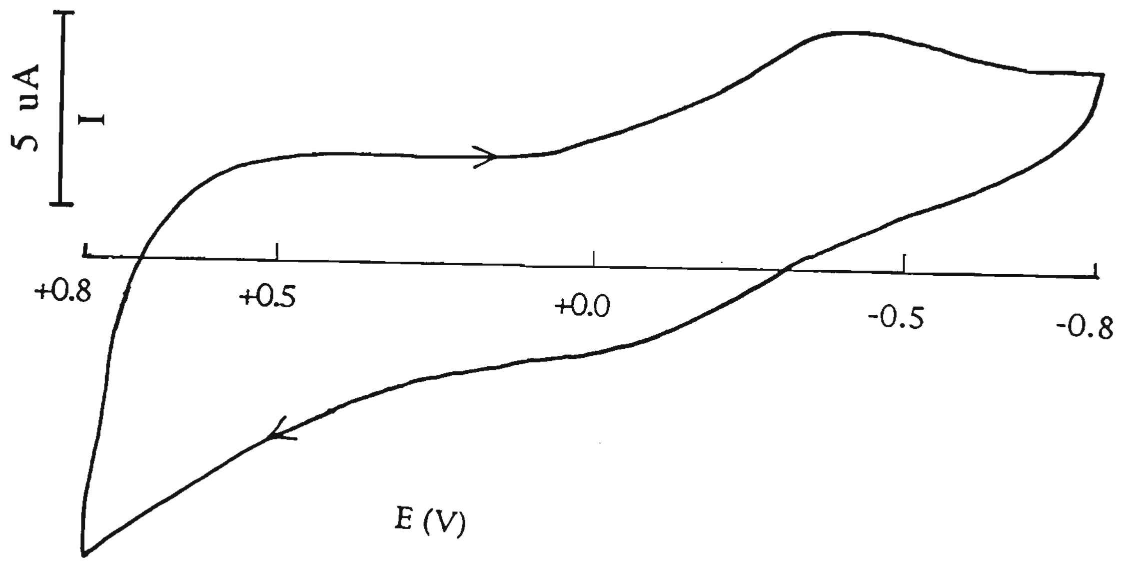


Figure 2.6: Cyclic voltammograms of a 5.0 g/L polypyrrole colloidal dispersion.
Conditions: Working electrode was glassy carbon. Scan rate 100 mV/s; (a) 5.0 g/L PVA and (b) 4.0 g/L PVA was used for the colloid preparation. Other conditions as per Table 2.2.

(b)

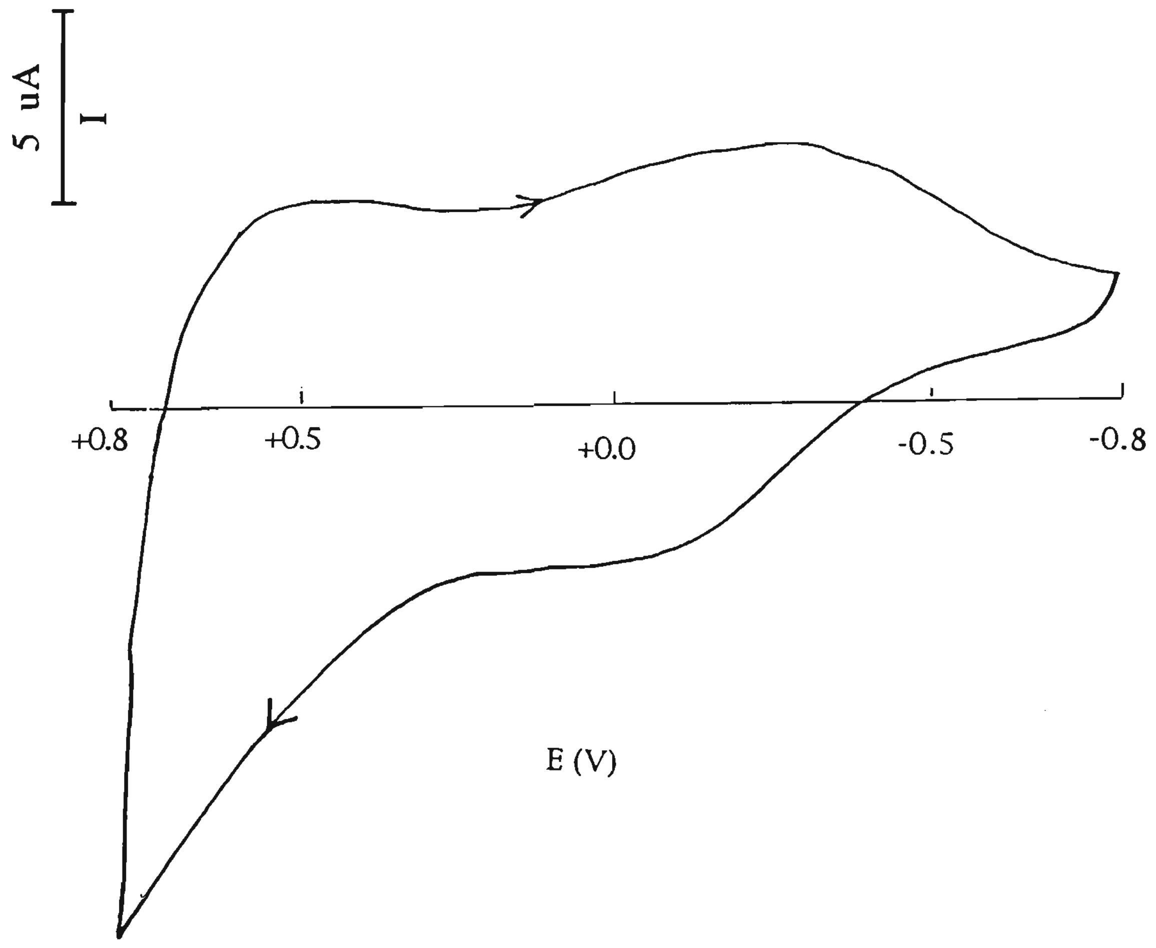


Figure 2.6 continued.

The solution conductivity of the dispersion may also vary with different colloids. In this work the conductivity of aqueous solutions containing dispersed polypyrrole colloids was measured using a conductivity meter. As shown in Table 2.5 the conductivity of the dispersion is dependent on the type, molecular weight and concentration of stabilizer. It is found that for a given colloid concentration and stabilizer type, the conductivity decreases as the concentration of stabilizer increases.

Table 2.5: Conductivity of redispersed colloid solutions

Stabilizer	Stabilizer concentration (g/L)	Colloid concentration (g/L)	Conductivity (uS/cm)
PVP_2	1.6	5.0	318
PVP_1	2.5	5.0	306
PVP_2	2.0	5.0	310
PVP_2	1.6	20.0	900
PEO	3.6	5.0	316
PEO	4.5	5.0	285
PVA	4.0	5.0	274
PVA	4.5	5.0	260

Conditions: Room temperature, conductivity meter (Philips PW 9501), conductivity cell (Philips 951201), platinum black electrode.

2.3.4 Electrocoagulation of Polypyrrole Colloids on Glassy Carbon Electrodes.

Deposition of the colloids from the redispersed solution using constant potential techniques was considered using glassy carbon electrodes. It was found that polypyrrole colloid could be deposited by imposition of a negative potential. The minimum potentials which caused electrocoagulation of colloids (5.0 g/L) on the glassy carbon electrode are summarised in Table 2.6.

Table 2.6: Electrodeposition of Colloids on the Glassy Carbon Electrode.

Stabiliser	Concentration of dispersion (g/L)	Minimum E_{dep} (V)
PVA	5.0	-1.4
PEO	5.0	-1.3
PVP_1	5.0	-1.4
PVP_2	5.0	-1.4

Chronoamperograms (Figure 2.7) showed a slow increase in current versus time. This behaviour is indicative of polymer deposition causing the surface area of the electrode to increase and consequently the current to increase.

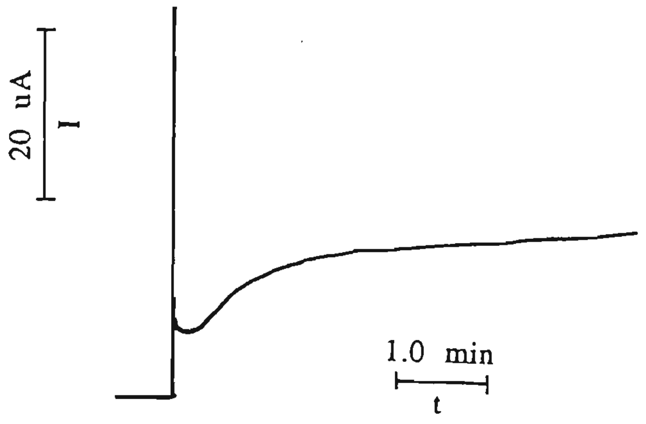
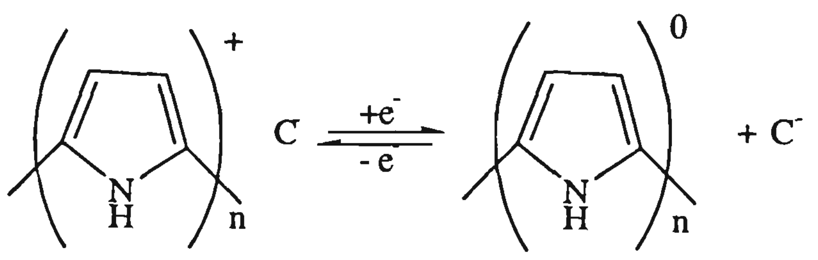


Figure 2.7: Chronoamperograms obtained during electrodeposition of 5.0 g/L colloidal dispersion onto a glassy carbon working electrode (surface area~ 0.07 cm^2).

Conditions: 1.6 g/L PVP$_2$ stabilizer was used for the colloid preparation. $E_{app.}$= -1.4 V. Other conditions as per Table 2.2.

The electrocoagulation may be due to polymer reduction. This causes the polymer to become more hydrophobic according to:



(2.1)

This may promote coagulation. However, this process would be expected to occur at approximately +0.00 volt from cyclic voltammetric data. The more negative potentials required for colloid deposition (as shown in Table 2.6) suggest that other mechanisms such as oxygen reduction which would increase the pH at the electrode surface or direct electrochemical effects on the stabiliser are also involved in producing polymer deposition. Cyclic voltammetry recorded after coagulation (e.g. Figure 2.8), indicated that in all cases conductive, electroactive polymer coatings were formed.

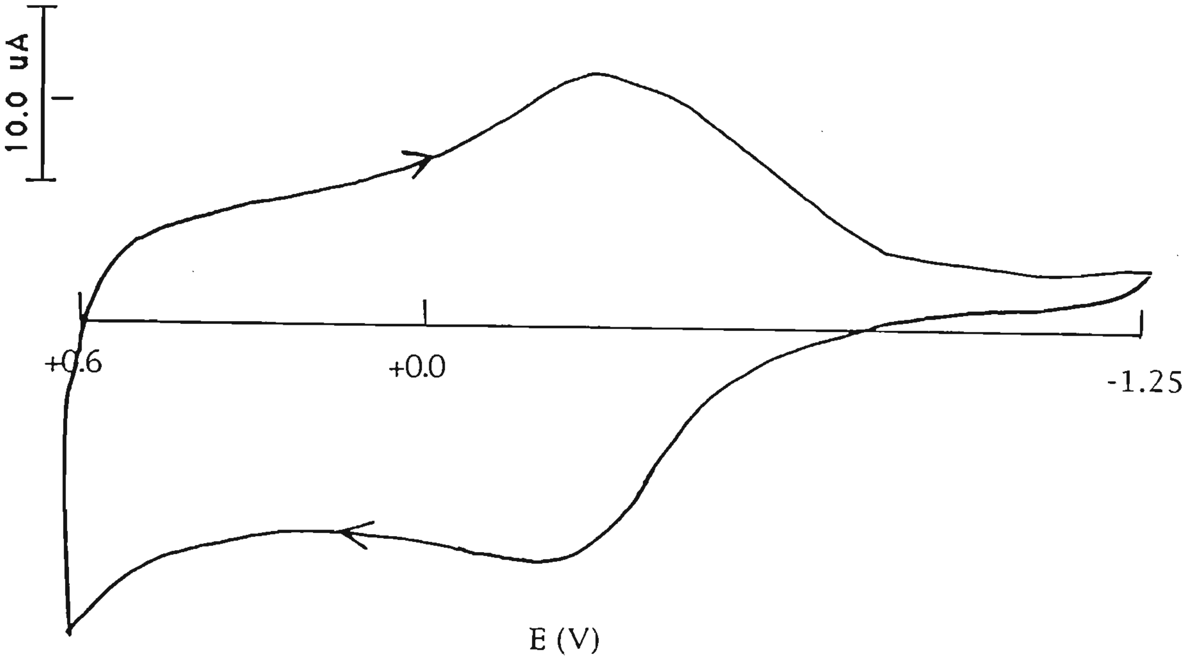


Figure 2.8: Cyclic voltammograms recorded after electrocoagulation of a 5.0 g/L colloidal dispersion onto a glassy carbon electrode.
Conditions: Electrode coated as in Figure 2.7 then removed this solution. Scan rate 100 mV/s; supporting electrolyte 1.0 M $NaNO_3$, PVP2 stabilizer.

2.3.5 Coating Other Substrates with Polypyrrole Colloids.

Polypyrrole colloids can be deposited on other substrates at negative potentials. Chronoamperograms were recorded during electrocoagulation of colloids on various substrates. Typical chronoamperogram and cyclic voltammogram of polypyrrole colloids grown on stainless steel are shown in Figures 2.9 and 2.10.

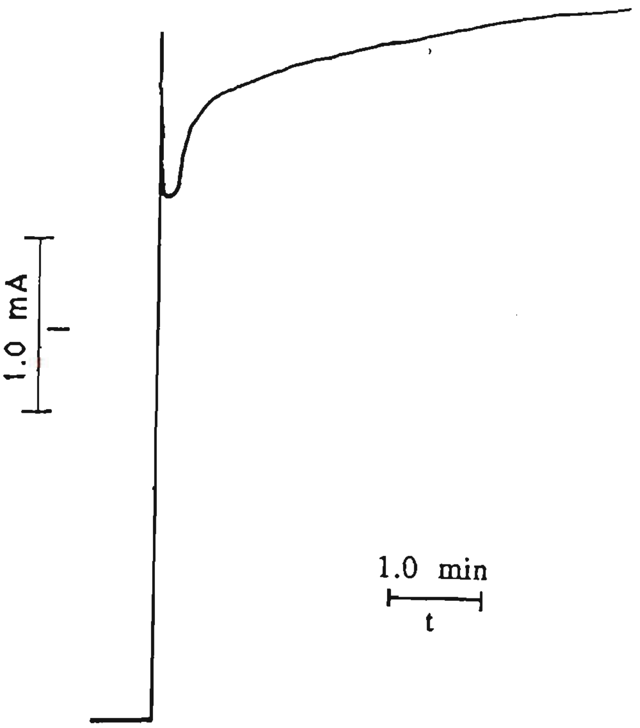


Figure 2.9: Chronoamperogram obtained during electrocoagulation of a 5.0 g/L colloidal dispersion onto a stainless steel working electrode (surface area of electrode~4.0 cm^2)

Conditions: $E_{app.}$=-2.5 V, 1.6 g/L PVP_2. Other conditions as per Table 2.2.

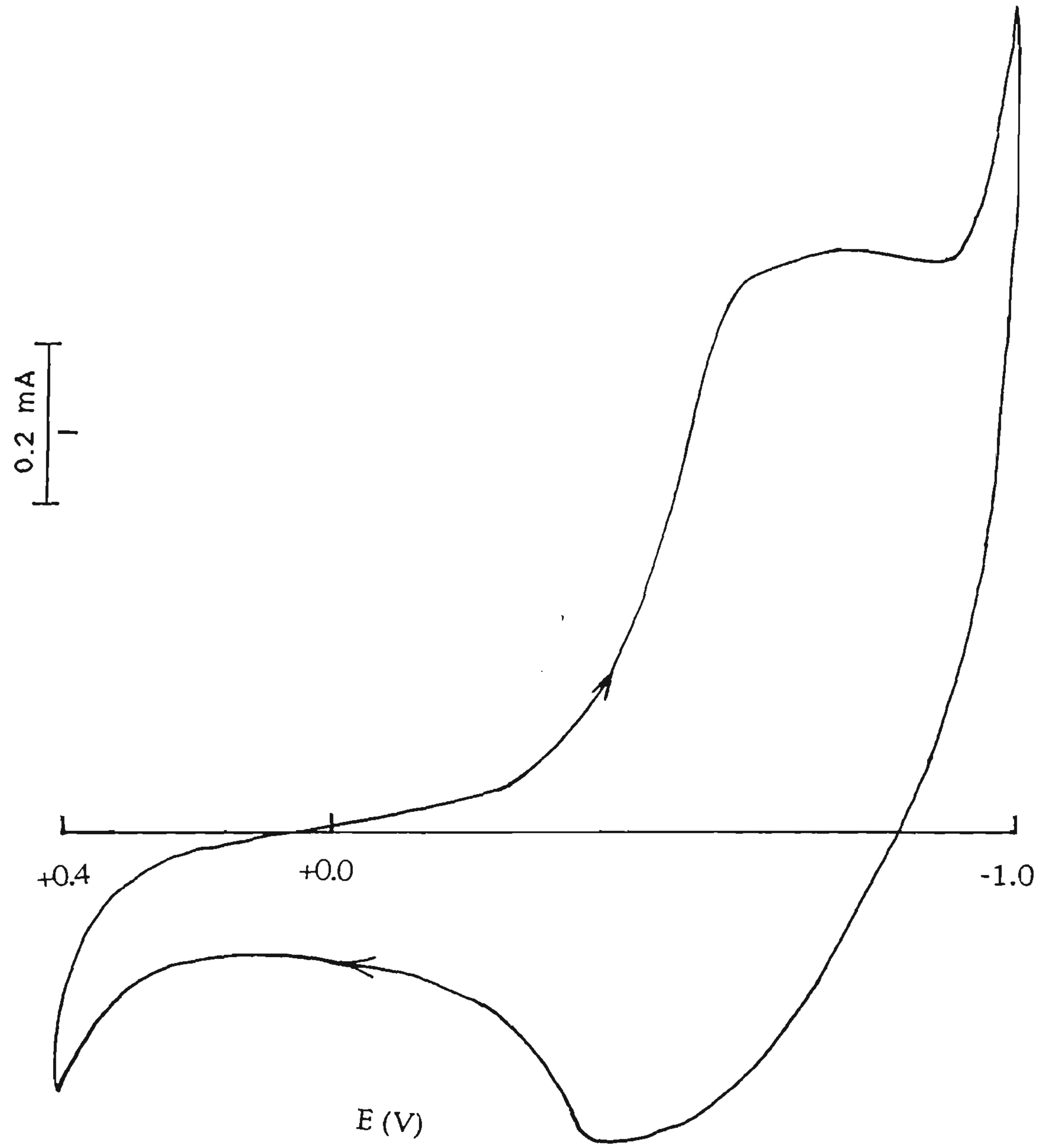


Figure 2.10: Cyclic voltammogram recorded after electrocoagulation of a 5.0 g/L colloidal dispersion onto a stainless steel electrode.
Conditions: Scan rate 100 mV/s; supporting electrolyte 1.0 M $NaNO_3$. Other conditions as in Figure 2.9.

On all substrates chronoamperograms showed a slow increase in current versus time indicating polymer deposition.

Also, cyclic voltammetry recorded after deposition indicated that in all cases conductive and electroactive polymer coatings were formed. The stabilizer type was found to have little effect on the deposition potential but the type of substrate did influence the deposition potential (Table 2.7).

Table 2.7 : Effect of Substrate on Deposition Potential

Substrate type	Deposition potential (V)
glassy carbon	-1.40
Platinum	-1.55
Stainless steel	-2.50
Zinc-alume	-1.85
Carbon foil	-2.60

Conditions: 1.6 g/L PVP_2; 5.0 g/L colloid. Other conditions as per Table 2.2.

Adhesive strength was measured using an Instron tensile testing machine. Dispersions of polypyrrole colloid (5.0 g/L) were deposited on the substrate using negative potentials. The type of stabilizer was found to have little effect on the adhesive strength. As shown in Table 2.8 the adhesive strength depends on the nature of substrate. The stability of oxide layers and their topography can affect the adhesive strength because many interactions can occur between the environment and the hydrated metal oxide layer (193, 194).

Table 2.8: Adhesive strength of coated colloids

Substrate	Adhesive strength (MPa)
Stainless steel	0.7
Platinum	0.4
Glassy carbon	0.3
Zincalume	1.1
Lead	0.9

Conditions: 1.6 g/L PVP_2 was used for the preparation of colloids. Other conditions as per Table 2.2.

The morphology of electrodeposited colloids was studied by SEM and a micrograph is shown in the Figure 2.11. Dense coatings were formed in each case.

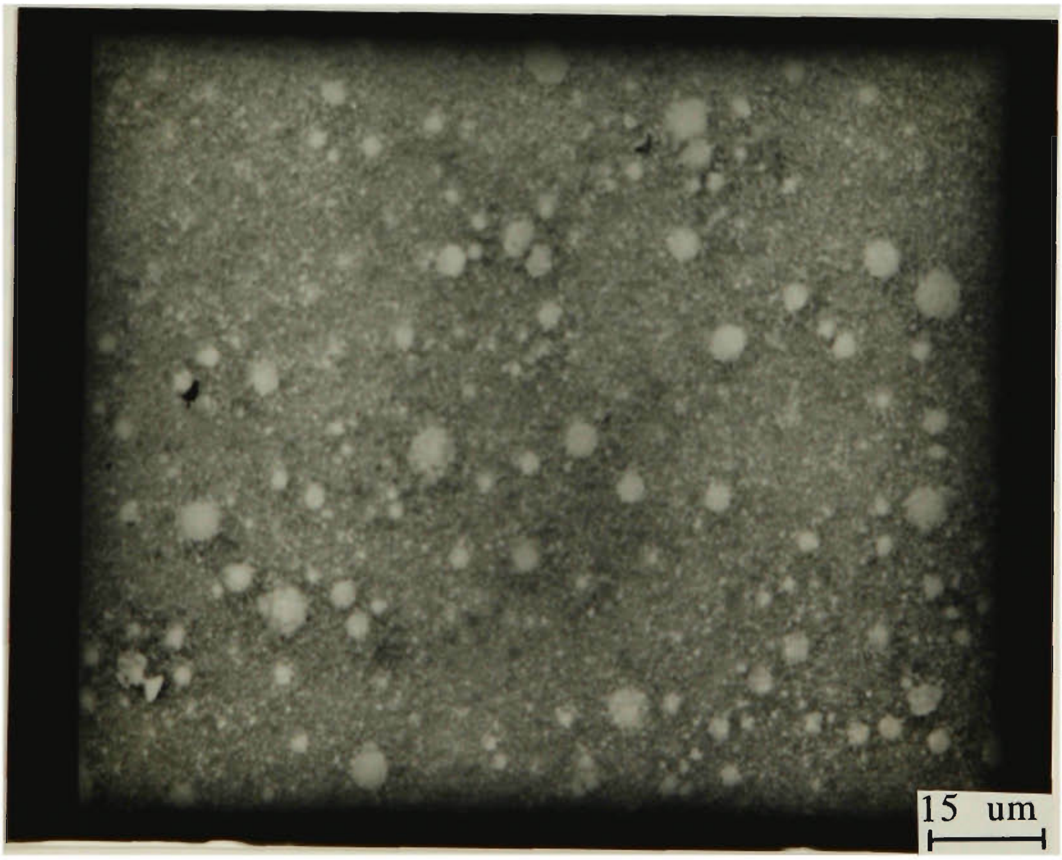


Figure 2.11: Scanning electron micrographs (SEM) of a colloid deposited onto glassy carbon electrode
Conditions: Eapp=-1.4 V, PVP_2 stabilizer.

2.3.6 Polyaniline Colloid Preparation

$(NH_4)_2S_2O_8$, $K_2S_2O_8$, $K_2Cr_2O_7$ and KIO_3 (concentration range 5.0-10.0 g/L) were used as oxidants, and PEO, PVA or PVP (concentration range 4.0-12.0 g/L) were used as the stabilisers. Typical conditions for colloidal preparation are summarised in Table 2.9. In a typical experiment 1.0 mL of aniline was added to a stirred aqueous solution (100 mL) containing 1.25 M HCl with 0.70 - 0.75 g and 0.80 - 0.90 g of one of the oxidants and stabilisers respectively. The monomer was added to a stirred aqueous solution containing a mixture of oxidant and stabilizer because the order of addition is important in the formation of uniform latex particles (128). The reaction was carried out at room temperature for 48 hours. The colloidal dispersions were ultracentrifuged at 40,000 rpm for 30 minutes to produce a dark green sediment. The supernatant was decanted and the sediment was rinsed several times with distilled deionised water. The colloid was redispersed in water using ultrasonication.

Table 2.9: Typical conditions for preparation of polyaniline colloids.

Stabilizer type	Oxidant type	Stabilizer concentration (g/L)	Oxidant concentration (g/L)	General conditions
PEO	$(NH_4)_2S_2O_8$	8.0	7.0	Reaction times=48 h Room temperature Aniline=0.1 M HCl 1.25 M=100 (mL)
"	$K_2Cr_2O_7$	"	7.0	"
"	KIO_3	"	7.5	"
"	$K_2S_2O_8$	"	7.0	"
PVA	$(NH_4)_2S_2O_8$	8.5	7.0	"
"	$K_2S_2O_8$	"	7.0	"
"	KIO_3	"	7.5	"
PVP	$(NH_4)_2S_2O_8$	9.0	7.0	"
"	$K_2S_2O_8$	"	7.0	"
"	KIO_3	"	7.5	"

The use of PEO, PVA and PVP stabilisers was investigated. It was found that with PEO stable dispersions could be obtained with all oxidants using the reaction conditions shown in Table 2.9 In all cases no sediment was detected after 48 hours.

Using PVA and PVP as stabilisers similar results were obtained using $(NH_4)_2 S_2O_8$, $K_2S_2O_8$ or KIO_3 as oxidants. It was found that PVP and $K_2Cr_2O_7$ are incompatible and causes precipitation before addition of monomer. With the use of PVA and this oxidant no colloid formation was observed.

The type of stabilizer and oxidants affected the yield of colloids. This was probably because they influenced the rate of polymerization and hence colloid formation.

Table 2.10: Influence of stabilizer type and oxidant on the yield of polymer

Stabilizer type	Oxidant type	Yield of insoluble polymer from one gram of monomer (gram)
PEO	KIO_3	0.7
"	$(NH_4)_2S_2O_8$	0.4
"	$K_2Cr_2O_7$	0.5
"	$K_2S_2O_8$	0.4
PVA	KIO_3	0.8
"	$(NH_4)_2S_2O_8$	0.4
"	$K_2S_2O_8$	0.4
PVP	KIO_3	0.7
"	$(NH_4)_2S_2O_8$	0.3
"	$K_2S_2O_8$	0.4

Conditions: The colloidal dispersions were ultracentrifuged and the resultant sediment was dried in the oven at 80 °C for 24 hours.

As shown in Table 2.10 the yield of colloid from one gram of aniline varied greatly for several oxidant types for a particular stabilizer. On the basis of the number of electrons transferred per mole of oxidant it was estimated that the 7.5 g/L concentration used for the KIO_3 oxidant would polymerise a high percentage of the aniline monomer whereas the higher molar mass $(NH_4)_2S_2O_8$ oxidant would only be expected to polymerise a low percentage of the aniline monomer.

2.3.7. Polymer Colloid Morphology

Transmission electron micrographs of colloids were obtained using diluted redispersed latex dried down on carbon coated copper grids. Transmission electron micrographs of the colloids are shown in Figure 2.12. As shown the type of stabilizer and oxidant affect the morphology of the particles obtained. " Rice-grain " or needle shaped colloids were produced with the following stabilizer/oxidant combinations: PVA/KIO_3; PEO/$(NH_4)_2S_2O_8$; PEO/$K_2S_2O_8$. The size and aspect ratio of the needles varied with the different systems which is presumably due to varying polymerization rates and different colloid formation mechanisms. The oxidant determines the former, while the stabilizer influences the latter. In the case of PVA stabilizer and $K_2S_2O_8$ oxidant more or less spherical particles were formed. Since graft copolymers can form between the polyaniline and the stabilizer, the morphology of the colloid is presumably dependent on the extent of the process. Previous worker's were shown that needle-shaped (126), rice-grains (114) or spherical (119, 132) colloidal particles can be prepared using different type of stabilizers and oxidants.

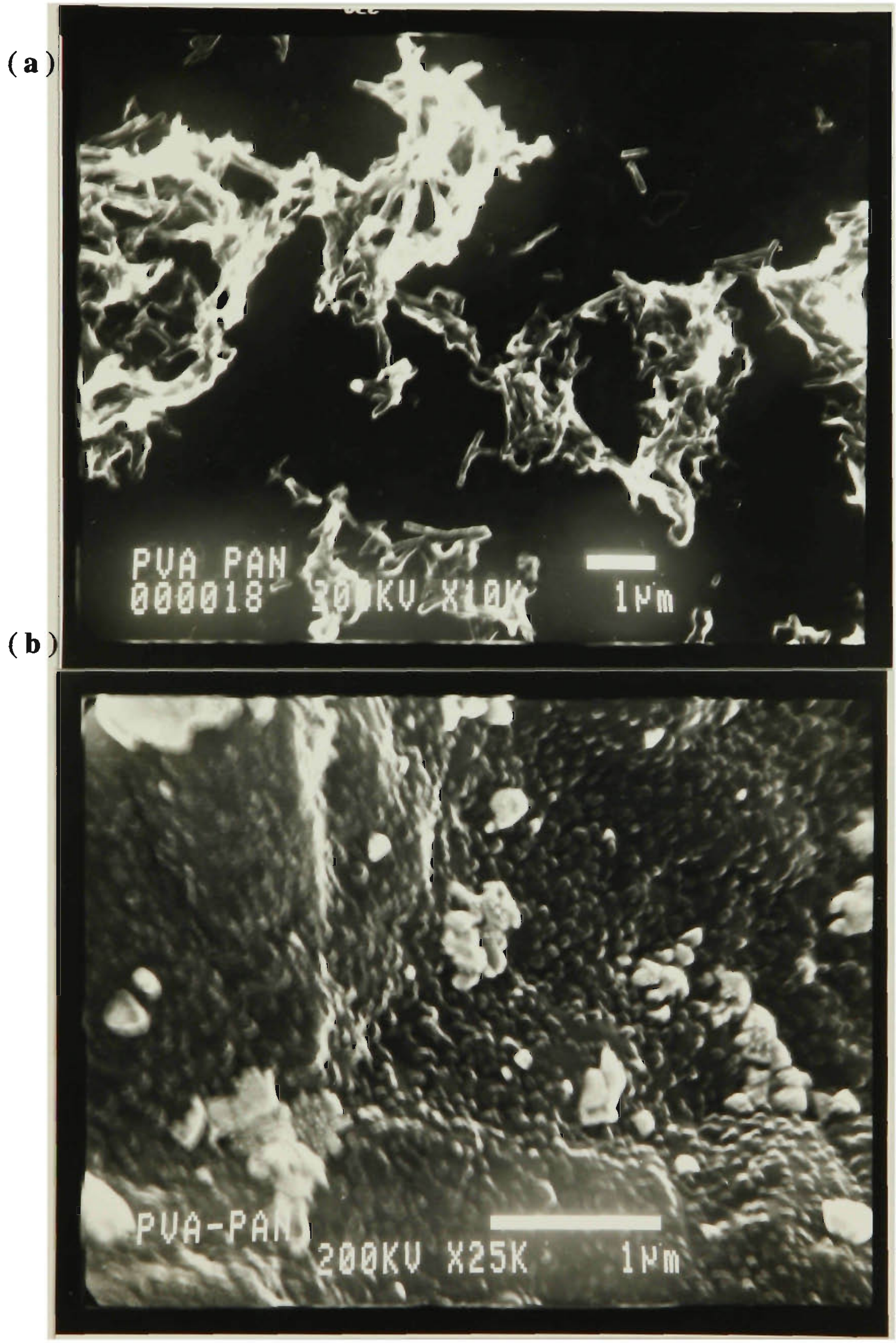


Figure 2.12: Transmission electron micrographs of polyaniline latexes stabilized by:

(a) {PVA, $M_W = (3 \times 10^4 - 7 \times 10^4)$, initial concentration = 8.5 g/L, KIO_3 oxidant}; (b) {PVA = 12 g/L, $K_2S_2O_8$ oxidant}; (c) {PEO, $M_W = 3 \times 10^5$, initial concentration = 8.0 g/L, $(NH_4)_2S_2O_8$ oxidant}; (d) {PEO = 12 g/L, $K_2S_2O_8$ oxidant}.

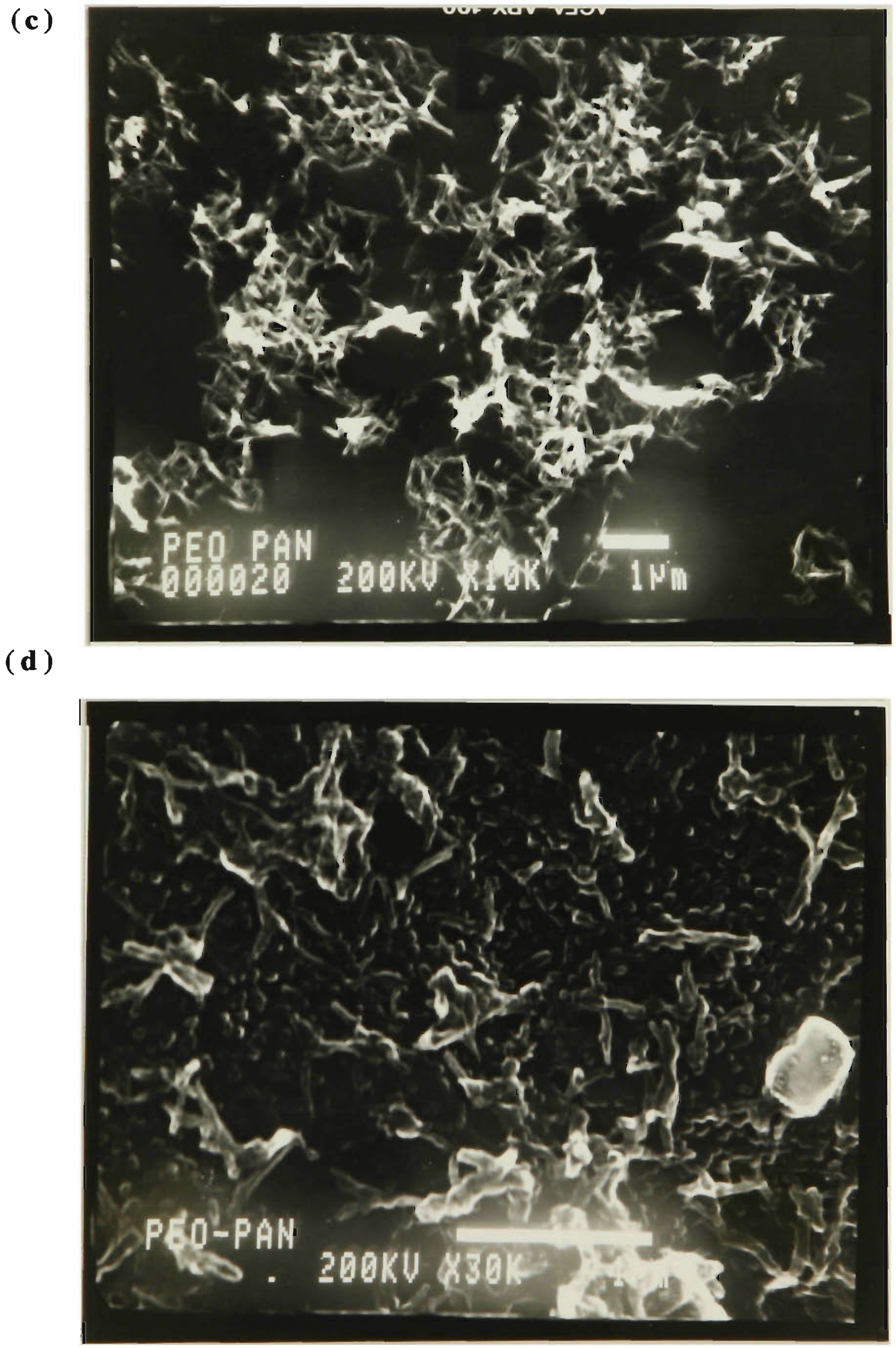


Figure 2.12 continued.

In this work similar results were obtained but a direct comparison is not possible since synthesis conditions vary markedly.

2.3.8 Cyclic Voltammetry

After centrifugation and redispersion the cyclic voltammetric behaviour of the colloidal sol was investigated using glassy carbon and platinum working electrodes. Cyclic voltammetry was used for characterizing the electroactivity of redispersed colloid solutions. Typical cyclic voltammograms are shown in Figure 2.13. The oxidation/reduction responses (A/A') indicated that this colloid is electroactive. The magnitude of the middle peak currents (B/B') is probably dependent on the potential and electrolyte concentration (195). The peaks (C/C') in the voltammograms correspond to the redox reaction of polyaniline in the diradical dicationic form (bipolaron), which take place concomitantly with a change in film conductivity (95).

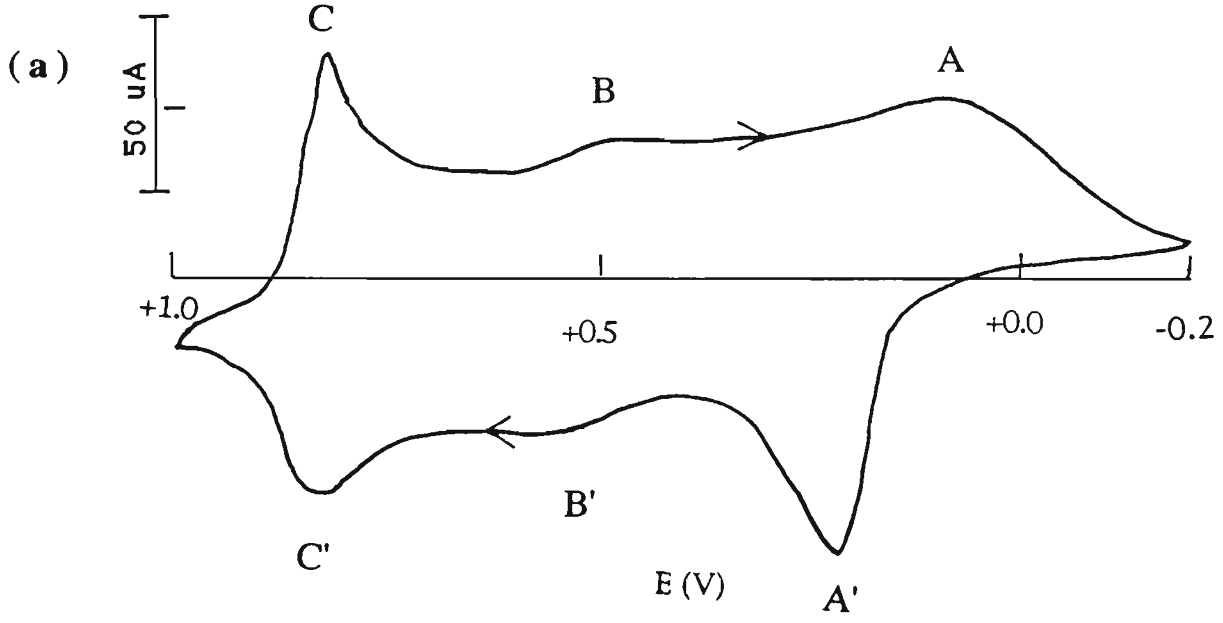


Figure 2.13: Cyclic voltammograms of a polyaniline colloidal dispersion.
Conditions: (a) PVA stabilizer, KIO_3 oxidant, colloid redispersed in 1.25 M HCl. (b) PEO stabilizer, $K_2Cr_2O_7$ oxidant, colloid redispersed in water. Scan rate 100 mV/s; glassy carbon electrode; 20 g/L colloid.

(b)

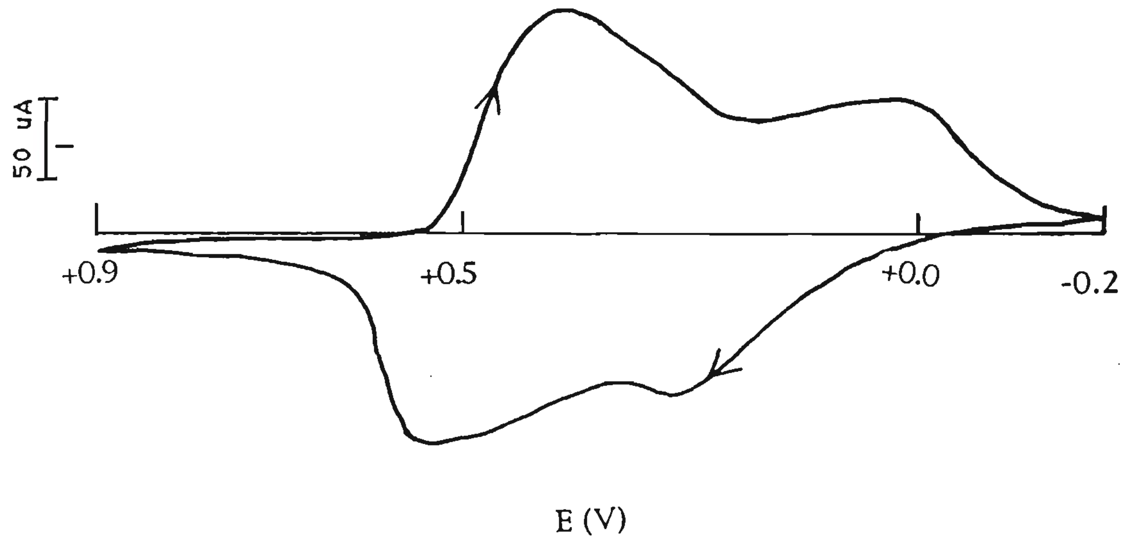


Figure 2.13 continued

2.3.9 Electrodeposition of Polyaniline Colloids

Attempts to deposit the polyaniline colloids at negative potentials from acidic media were unsuccessful due to the concomitant formation of hydrogen as protons were reduced at the glassy carbon and platinum electrode. Consequently the colloids were redispersed in water and electrodeposition was again attempted. Under these conditions all colloids prepared could be deposited on glassy carbon electrodes. Chronoamperograms were obtained during electrocoagulation of colloidal dispersion using negative potentials. A typical chronoamperogram is shown in Figure 2.14. The chronoamperogram showed a slow increase in current versus time, demonstrating that polymer deposition had occured.

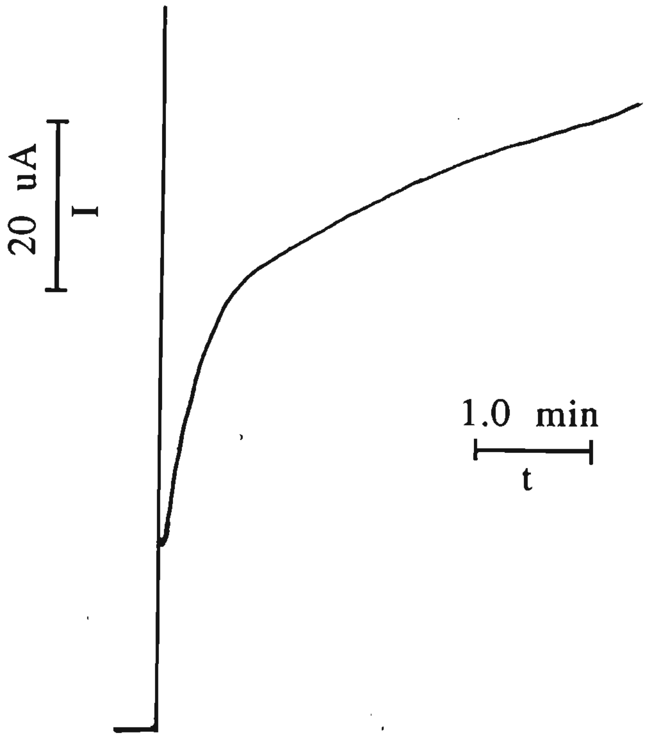


Figure 2.14: Chronoamperograms recorded during electrocoagulation of 12.0 g/L polyaniline colloidal dispersion onto a glassy carbon working electrode.
Conditions: 8.0 g/L PEO stabilizer and 7.5 g/L KIO_3 oxidant were used for the colloid preparation. E_{app}= -1.25 V. Other synthesis conditions as per Table 2.9.

It was found that the type of stabilizer and oxidants used for the preparation of colloids affected the minimum applied potential required for the electrocoagulation of colloid. The resultant charge passed during the first three minutes of electrodeposition was also influenced by the stabilizer used (Table 2.12). As discussed previously the oxidant and stabiliser used affect the yield, morphology and electroactivity of the resultant colloids. These factors would therefore be expected to influence the electrocoagulation process.

Table 2.12: Electrodeposition of polyaniline colloids onto glassy carbon electrode.

Stabilizer type	Oxidant type	Dispersion concentration (g/L)	E Dep. (V)	Charge (mC)
PEO	$(NH_4)_2S_2O_8$	12	-1.37	4.60
"	$K_2S_2O_8$	"	-1.37	6.40
"	$K_2Cr_2O_7$	"	-1.19	2.90
"	KIO_3	"	-1.25	11.20
PVA	$(NH_4)S_2O_8$	"	-1.37	7.90
"	$K_2S_2O_8$	"	-1.40	7.30
"	KIO_3	"	-1.25	10.40
PVP_2	$(NH_4)_2S_2O_8$	"	-1.37	5.40
"	$K_2S_2O_8$	"	-1.35	4.90
"	KIO_3	"	-1.30	9.70

Also cyclic voltammograms were obtained after electrodeposition of colloids onto substrates. A typical cyclic voltammogram is shown in Figure 2.15. Cyclic voltammetry recorded after deposition, indicated that in all cases conductive, electroactive polymer coatings were formed.

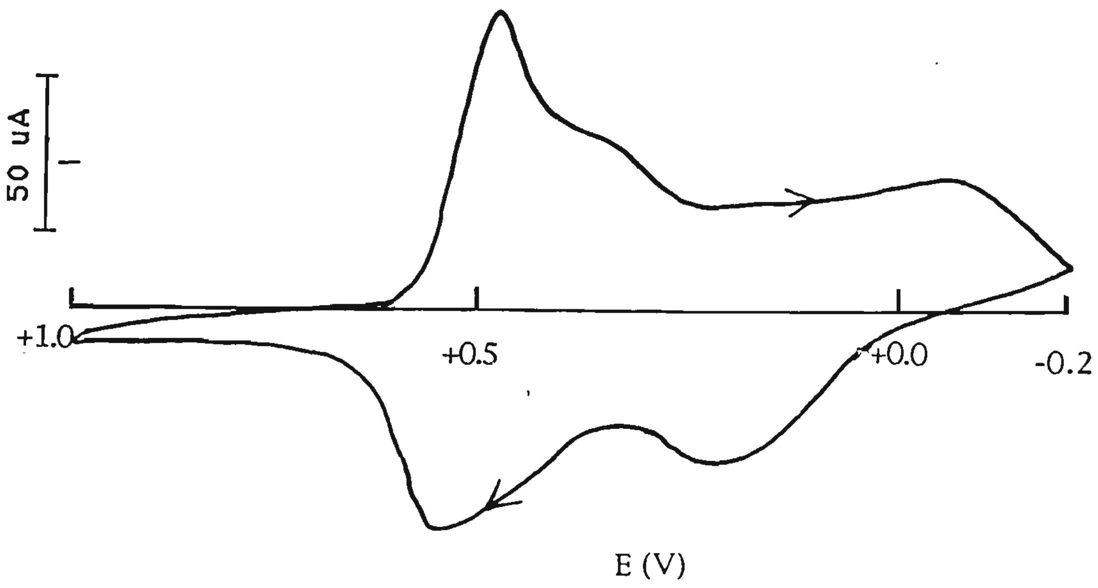


Figure 2.15: Cyclic voltammogram recorded after electrocoagulation of 12 g/L colloidal dispersion onto a glassy carbon electrode.

Conditions: Scan rate 100 mV/s; supporting electrolyte 0.01 M HCl. Other conditions as in caption Figure 2.14.

The morphology of the deposited colloidal films was studied using scanning electron microscope (SEM). A typical (SEM) is shown in Figure 2.16. These structures appeared slightly more porous than those formed by electrodeposition from monomer solutions.

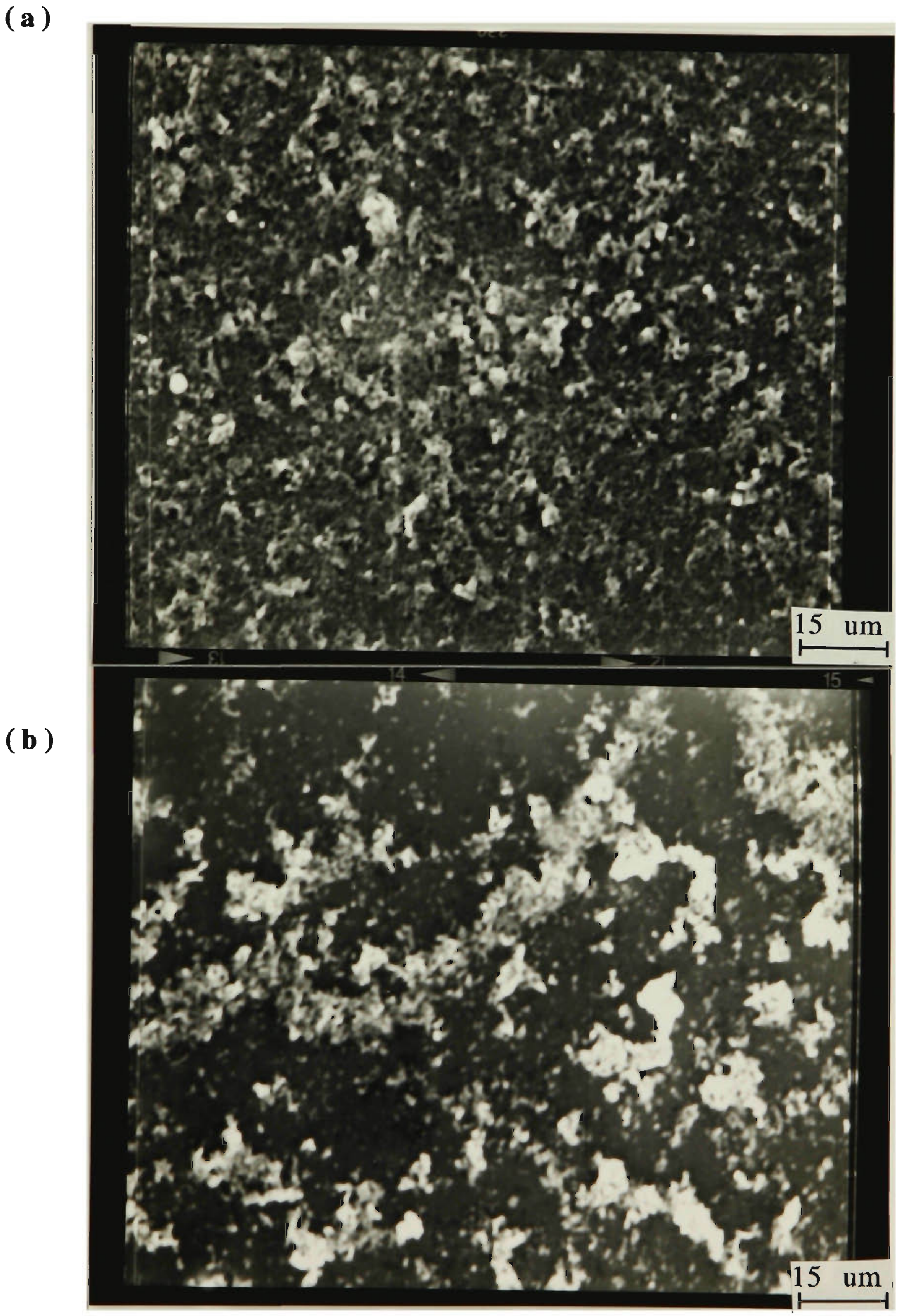


Figure 2.16: Scanning electron micrographs of colloid deposited onto glassy carbon electrode.

Conditions: (a) 8.0 g/L PEO and (b) 8.5 g/L PVA were used for the formation of colloids. Other synthesis conditions as per Table 2.9.

2.4 CONCLUSION

Polypyrrole colloids were prepared by chemical oxidation of the monomer in the presence of a steric stabilizer such as PVP, PVA and PEO. The preparation, characterization and electrochemical properties of these colloids have been studied. The type, molecular weight and concentration of stabilizer influence the colloid formation, particle size/morphology, conductivity and electroactivity. Macroscopic precipitation occurs if the concentration of stabilizer is not sufficient. Particle size, electroactivity and conductivity are decreased by increasing stabilizer concentration, because stabilizer type and concentration probably affect the amount of adsorbed non-ionic stabilizer on the surface of the particles. The type and concentration of stabilizers also influence the yield of monomer to polymer. This is presumably due to the type and concentration of stabilizer influencing the rate of colloid formation. Polypyrrole colloids can be deposited on various substrates using negative potentials. Substrate type has an effect on the applied potential required for deposition and the adhesive strength of the deposits.

The chemical oxidation of polyaniline is carried out by using different oxidant such as $(NH_4)_2S_2O_8$, $K_2S_2O_8$, KIO_3, $K_2Cr_2O_7$ and various stabilizers (PVA, PEO, PVP_2) to produce a colloidal dispersion. The characteristics of these colloids such as electroactivity, morphology and electrochemical properties with a view to developing a suitable electrodeposition procedure has been investigated. With PEO, stable dispersions of colloid could be obtained using all of the oxidants mentioned in this chapter. $K_2Cr_2O_7$ and PVP are incompatible and causes precipitation to occur before addition of monomer. PVP and PVA can be used to produce colloids with $(NH_4)_2S_2O_8$, KIO_3 and $K_2S_2O_8$. The electroactivity, morphology and yield of monomer to polymer are related to the stabiliser type and oxidant. Attempts to deposit polyaniline colloids from acidic media by using negative potentials were unsuccessful due to the concomitant formation of hydrogen as protons were reduced. Redispersed colloids in water can be deposited using negative potentials.

CHAPTER 3

INFLUENCE OF STERIC STABILIZERS ON THE ELECTROPOLYMERISATION AND PROPERTIES OF POLYPYRROLE AND POLYANILINE

3.1 INTRODUCTION

Electroactive conductive polymer films can be generated on electrode surfaces by the electrochemical oxidation of aromatic compounds. These films can be prepared from benzenoid, non-benzenoid and heterocyclic aromatics, in particular, from the derivatives of pyrrole and aniline (31). Preparation conditions such as the electrolyte employed, applied potential, current density and substrate are known to influence the mechanical properties of the film produced (48, 50, 63,64, 66).

In the electropolymerization process surfactant additives might influence the conductivity and tensile strength of polymer films (47). When cationic, anionic or non-ionic micelles are used in the electropolymerization process various types of interactions may be operative between substrates and micelles (196). The use of surfactants alters polymer growth characteristics (197). Before the potential is applied the surfactant is adsorbed onto the electrode surface possibly modifying the chemical nature of the electrode and surrounding solution. Additives may also have an effect on the order of crystallinity of the polymer obtained. Crystalline polypyrrole can be grown using poly(ethylene oxide) complexes (198). The type and/or the concentration of the additives used may influence the mechanical stability of polymer obtained (180).

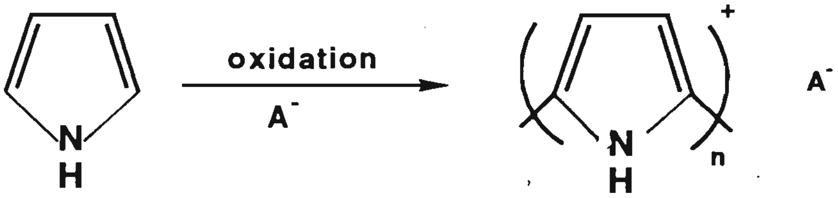
Polyaniline can be synthesized in various forms both chemically and electrochemically from aqueous media (82) and the polymerisation mode affects the morphology of the resulting films (84,85). The anodic oxidation of aniline in aqueous sulphuric acid solution was studied by Letheby (4) in 1862 and Mohilner (6) in 1962. Soluble polyaniline can be prepared in concentrated sulphuric acid (177). Polyaniline films are insoluble in all common solvents (93). The conductivity of polyaniline polymer depends on two variables- the degree of oxidation and the extent of protonation of the polymer (99).

Although the unique electrical properties of conductive, electroactive polymers such as polypyrrole and polyaniline are well recognised (16,58,93), the development of commercial products remains a challenge. In particular, the limitations on the processing routes available for the production of polypyrrole and polyaniline restrict their potential use (105). Given this limitation, the generally employed electropolymerization process is the most convenient way of preparing both membrane films and electrode coatings. However, the complexities of the electropolymerization method means that the factors that determine film quality are poorly understood and quality control is difficult to attain.

This section is specifically concerned with investigating the effect of steric stabilizers on the electropolymerization and properties of polypyrrole and polyaniline. Secondly, the use of steric stabilizers to control the adhesion of the electropolymerised films on the electrode surface is to be considered. Depending upon the application, the deposited coating is either left on the electrode, or is removed to be used as a stand-alone film. In each instance the adhesion to the substrate is critical: high adhesive strength is required in the former, and low adhesion is required for the latter. Factors such as substrate type (45,59), applied potential (57, 72, 93, 98), type and quantity of additives (47, 98, 180, 198, 199) are known to affect the electrical and mechanical properties of polypyrrole and polyaniline. These may also be important in determining adhesion, but to date there have been no reports on the factors that control the adhesion.

3.1.1 Electropolymerization of Pyrrole and Aniline

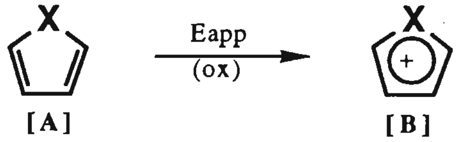
It is well known (183) that conducting polypyrrole can be formed electrochemically, according to:



(3.1)

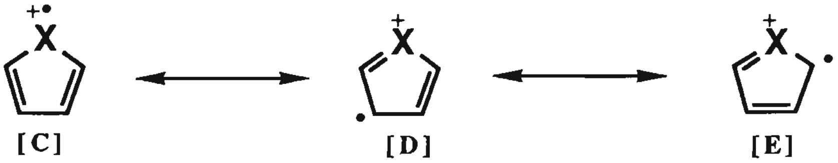
Upon application of a sufficiently positive potential this reaction is instigated and an insoluble black conducting deposit is formed on the anode. The counterion (A^-) is incorporated from the supporting electrolyte during this polymerisation. Though this simplistic description of the polymerisation of polypyrrole is often adequate, a more detailed examination (66, 200) of the process reveals that the following steps are involved.

Monomer oxidation



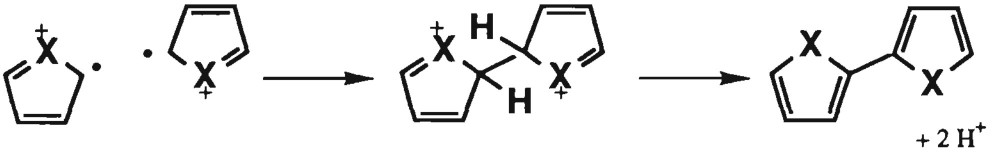
(3.2)

Resonance forms



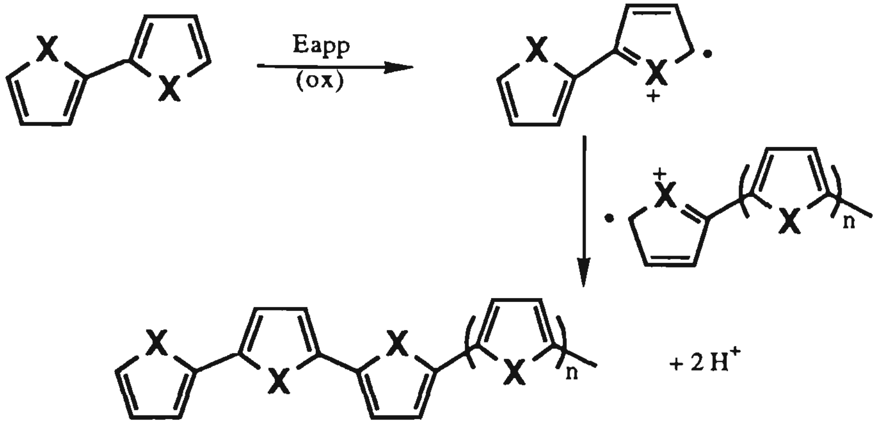
(3.3)

Radical - radical coupling



(3.4)

Chain propagation



(3.5)

(3.6)

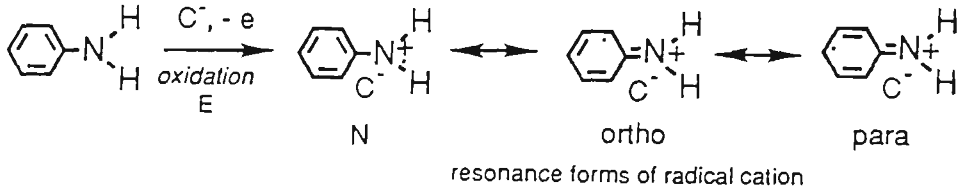
That is, upon application of a positive potential, radical cations are formed at the anode. The solvent and supporting electrolyte help to overcome the natural repulsion of such radical cations so that they combine to form dimers and higher molecular weight oligomers. These species are subsequently oxidised, at potentials even lower than the monomer oxidation. Eventually the chain length is such that an insoluble polymeric salt is formed and this deposits on the anode.

The influence of additives (such as surfactants) on the electropolymerisation process of pyrrole has been studied (201). It was revealed that such additives may also play a crucial role in the overall process. They not only act as counterions but provide a means of free radical and oligomer stabilisation during polymerisation. The additives influence the physical properties (mechanical strength, morphology, solubility) of the resultant polymer (202).

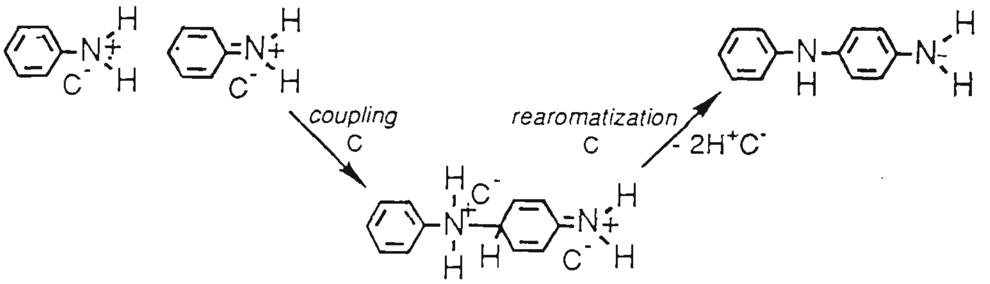
It has also been shown (106, 164, 122) that the addition of steric stabilizers has a marked effect on the chemical polymerisation of pyrrole, enabling spherical almost monodispersed colloidal sols to be prepared (chapter 2).

Polyaniline can be synthesized in various forms both chemically and electrochemically in aqueous media (82). This polymerization is known to proceed according to (203-207):

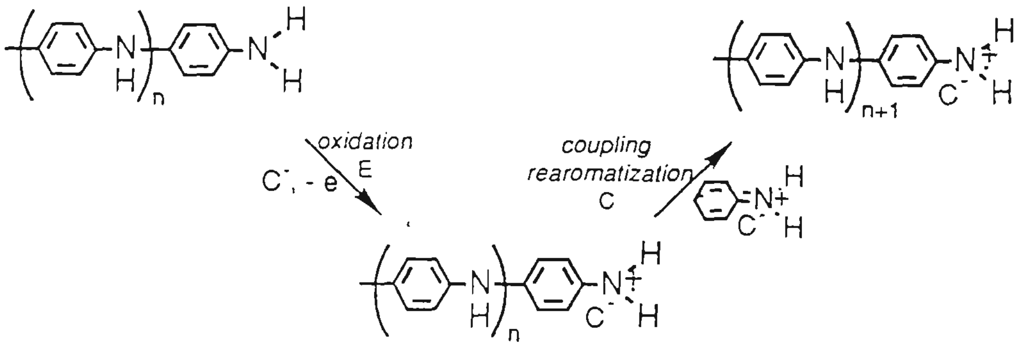
[A] Initiation



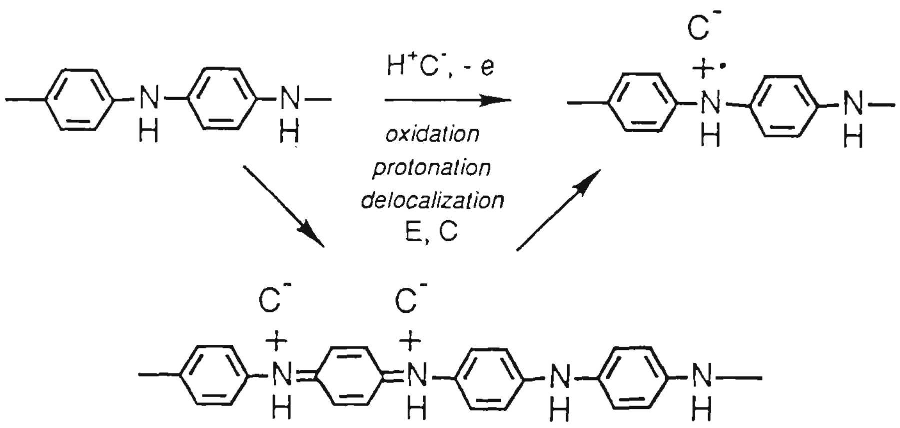
[B] Coupling



[C] Chain propagation



[D] Doping of the polymer



polyemeraldine salt intermediate

The morphology of polyaniline films depends strongly on the polymerization method which is related to differences in growth rates of the films (84,85).

In the course of this work the effect of stabilisers on the electropolymerisation process of pyrrole and aniline were considered. Of particular interest is the role of the stabiliser in the formation of the insoluble conducting deposit and the effect of the stabiliser on the physical properties of the polymer.

3.2 EXPERIMENTAL

3.2.1 Reagents and Standard Solutions

All chemicals used in this study were analytical reagent grade and were used without further purification, unless stated otherwise. Pyrrole and aniline were purified by simple distillation and storage in the fridge prior to use. The materials used in this work were pyrrole and polyvinyl alcohol (PVA, $M_W = 3 \times 10^4 - 7 \times 10^4$) obtained from Sigma, $NaNO_3$ from BDH, polyethylene oxide (PEO, $Mw = 3 \times 10^5$) from Aldrich, polyvinylpyrrolidone (PVP_2, $Mw = 1.2 \times 10^6$) from TCI, polyvinylpyrrolidone (PVP_1, $Mw = 2.50 \times 10^4$) from Merck, hydrochloric acid from BDH and potassium ferrocyanide [$K_4Fe(CN)_6$] from Ajax chemicals. Both polypyrrole and polyaniline coatings were prepared electrochemically by the the following procedure:

The solutions in the cell contained either pyrrole (0.15 M) and $NaNO_3$ (1.0 M) or aniline (0.10 M) and HCl (1.25 M) and appropriate steric stabilizer respectively. The polymerization solution was deoxygenated with nitrogen before polymerization for 10 minutes.

3.2.2 Instrumentation

Electrochemical control was achieved using either a BioAnalytical Systems (BAS) Model 100 A or a BAS Model CV-27. The adhesive strength of polypyrrole films on platinum and stainless steel substrates were measured at room temperature. An in-house built Galvanostat was used throughout this work. Electrochemical experiments were carried out in a three electrode cell employing a working electrode (glassy carbon and platinum), a reference electrode (Ag/AgCl) (3 M NaCl) and an auxiliary electrode (Pt gauze). The adhesion strength of the coatings was determined using a tensile testing technique, which is a modification of ASTM standard D 4541. A cylindrical test bar was adhered to the coating using a cyanoacrylate adhesive. The test bar was then scored around its circumference and attached to an Instron 4302 tensile testing machine. The test bar was loaded at a crosshead displacement rate of 1 mm/min and the load at which the coating became detached from the electrode was recorded.

3.2.3 Electropolymerization of Pyrrole and Aniline

Polymerisation of pyrrole was carried out using the following methods:

1) Constant potential (0.75 volt),

2) Galvanostatic growth, at a current density of 0.75 mA/cm^2,

3) Potentiodynamic growth over the potential range of -1.00 V to + 0.75 V at a scan rate of 100 mV/sec.

Polymerization of aniline was carried out using the following methods:

1) Constant potential (0.82 volt),

2) Galvanostatic growth, at a current density of 1.0 mA/cm^2,

3) Potentiodynamic growth over the potential range of -0.10 V to 1.0 V at a scan rate of 50 mV/s.

3.3 RESULTS AND DISCUSSION

3.3.1 Potentiodynamic Polymerization of Pyrrole

The effect of the stabiliser on potentiodynamic growth (i.e. cycling the potential between -1.00 V and +0.75 V at 100 mV/sec) was considered using PVA, PVP$_1$, PVP$_2$ and PEO stabilizers (concentration range=1.60-4.80 g/L). In all cases the rate of growth, as determined by the increased current flow on subsequent scans, decreased in the presence of stabiliser (e.g. Figure 3.1). The oxidation/reduction peak currents for the deposited polymer (responses A/A') gradually increased with the number of potential scans, indicating that the thickness of the conducting polymer film increased with the number of potential cycles. With higher concentration of stabilizer the rate of current increase was not so marked on subsequent scans. This may be due to the fact that the increased concentration of stabilizer blocks electron transfer at the electrode and/or that the polymeric product formed is stabilized by the presence of the stabilizer.

Cyclic voltammograms recorded after growth (Figure 3.2) indicate that the deposited material is more electroactive (i.e. oxidation/reduction responses are better defined) when less stabilizer is present.

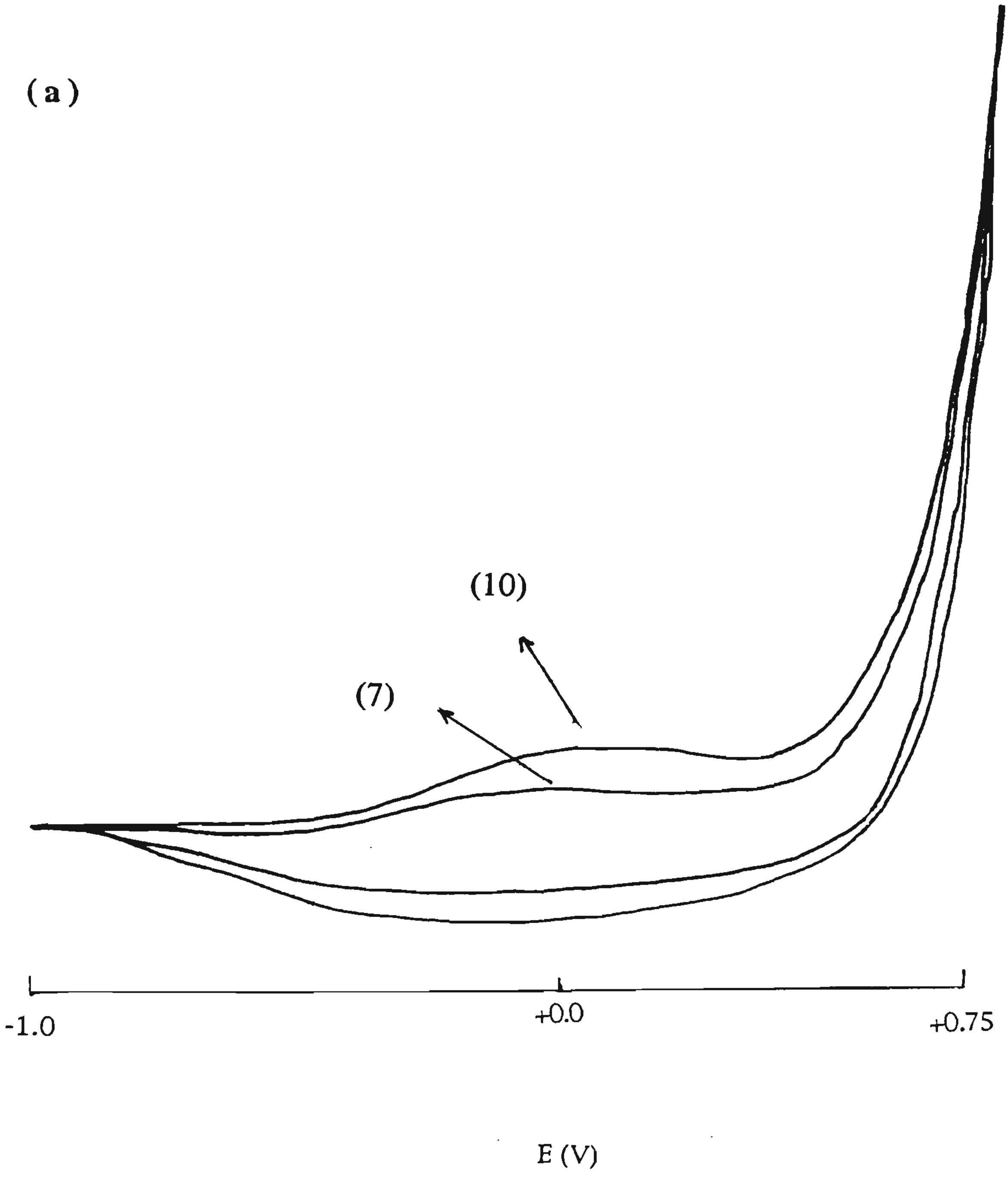


Figure 3.1: Cyclic voltammograms during growth on glassy carbon electrode.
Conditions: (a) 4.8 g/L PVA, (b) 1.6 g/L PVA. Supporting Electrolyte 1.0 M NaNO3. Scan rate 100 mV/s. (7) and (10) scan numbers.

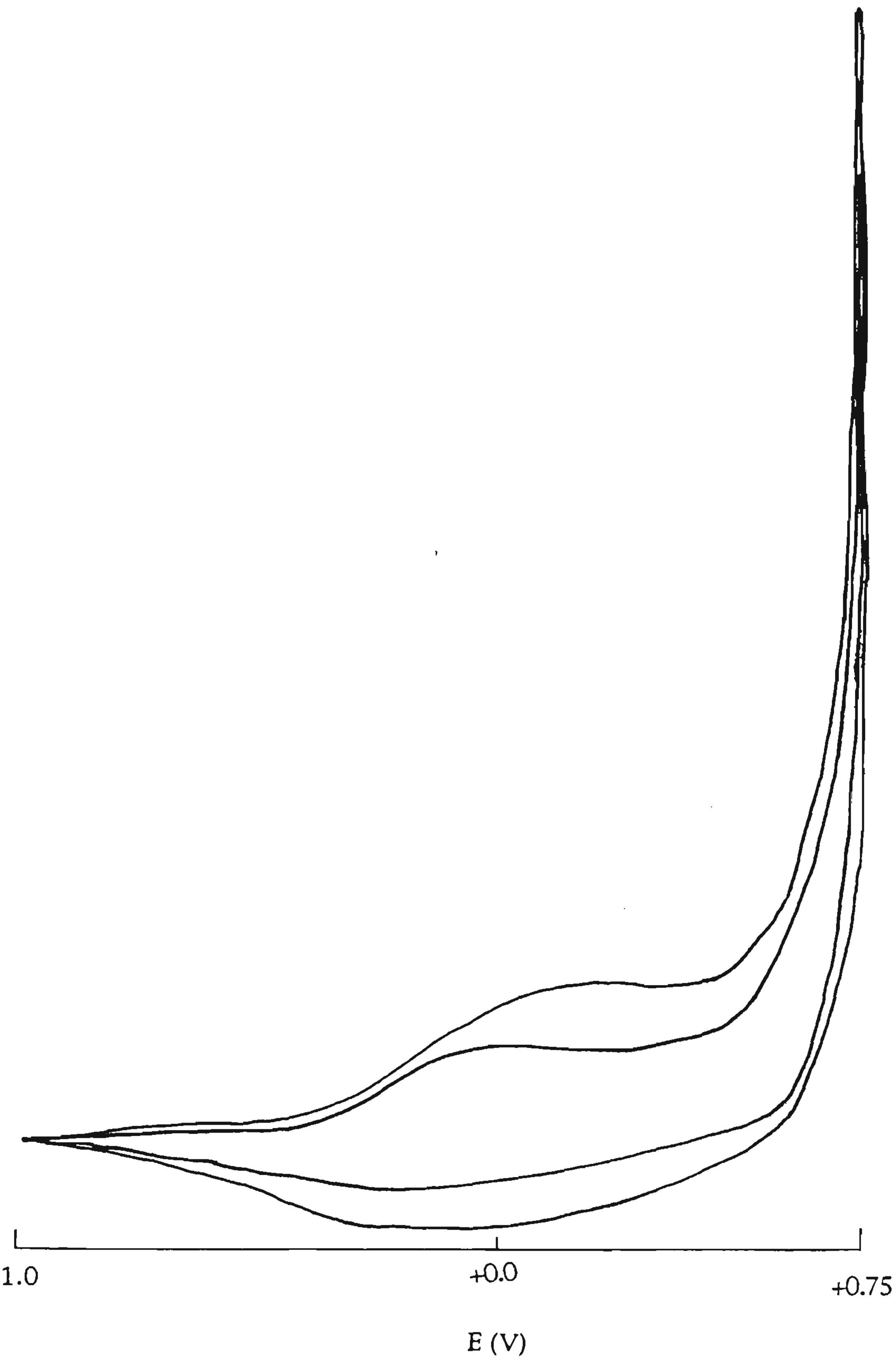


Figure 3.1 continued.

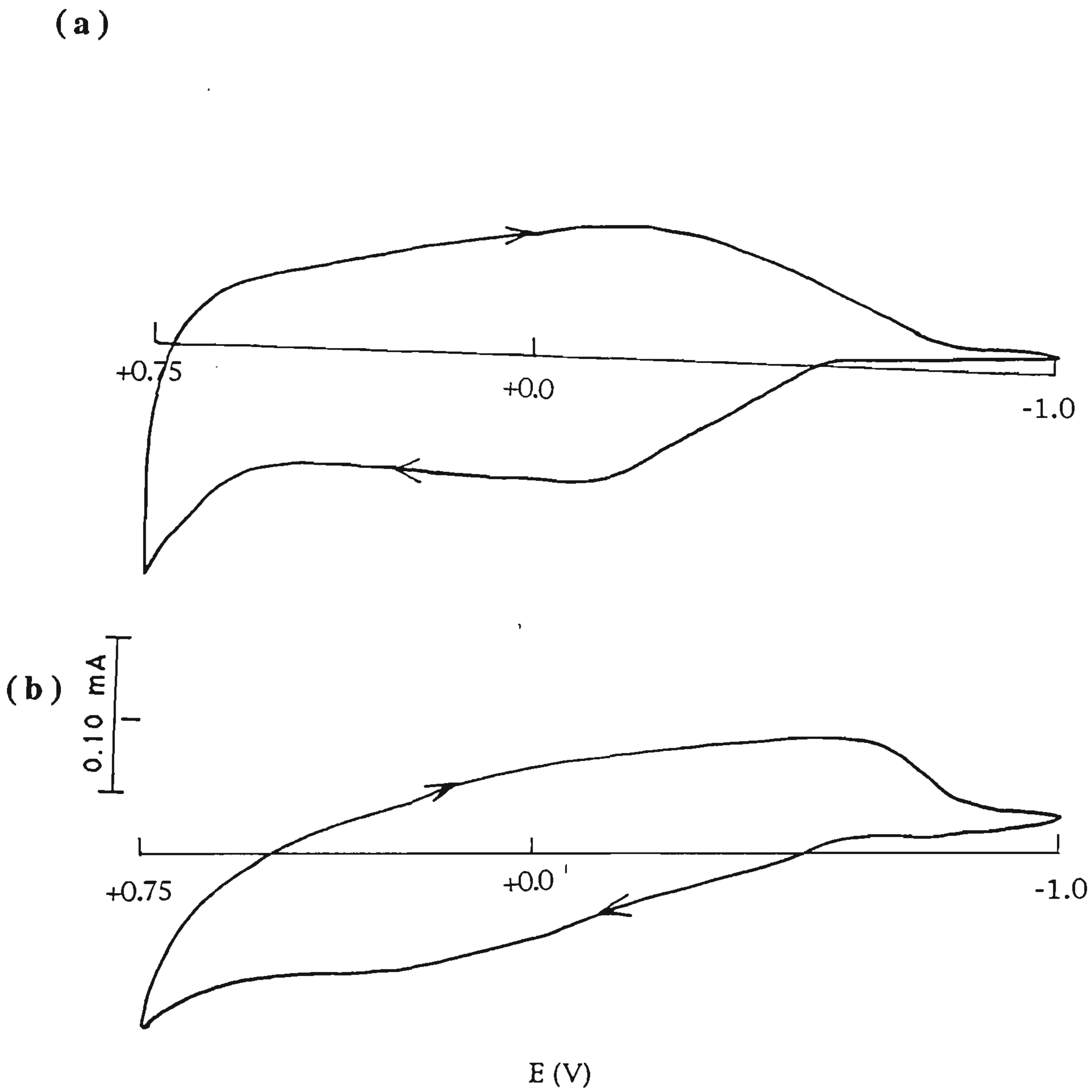


Figure 3.2: Cyclic voltammograms after growth on glassy carbon electrode.

Conditions: (a) 1.6 g/L PVA, (b) 4.8 g/L PVA. Supporting Electrolyte 1.0 M $NaNO_3$. Scan rate 100 mV/s, glassy carbon electrode.

3.3.2 Galvanostatic Polymerization of Pyrrole

Glassy carbon, platinum and stainless steel were used as substrates to consider the effect of the steric stabiliser on the electropolymerisation process. The solution in the cell contained pyrrole (0.15 M), sodium nitrate (1.0 M) and the appropriate steric stabilizer (concentration range of stabilizer 1.60 - 4.80 g/L). The stabilisers were found to have only a small effect on the potential drawn at any substrate with the application of constant current (0.75 mA/cm^2) and when a low concentration of stabilizer was used (Table 3.1).

Table 3.1: Chronopotentiometric Data for polymer growth.

Substrate	Stabiliser type	Stabiliser concentration range (g/L)	Potential of growth (V)
Glassy carbon	No stabilizer	0.00	0.63
Glassy carbon	PVP	1.60-4.80	0.80
	PEO	"	0.80
	PVA	"	0.80
Platinum	No stabilizer	0.00	0.62
Platinum	PVP	1.60-4.80	0.70
	PEO	"	0.70
	PVA	"	0.70
Stainless Steel	No stabilizer	0.00	0.73
Stainless Steel (grade 316)	PVP	1.60-4.80	0.75
	PEO	"	0.75
	PVA	"	0.75

Current density=0.75 mA/cm^2.

Chronopotentiograms were recorded to further characterize this process. Typical chronopotentiograms of polypyrrole growth on various substrates are shown in Figure 3.3. When polymer growth was started the potential gradually decreased, due to faradaic processes. The difference in peak potentials indicated that the surface properties of the electrode influences the electropolymerization processes.

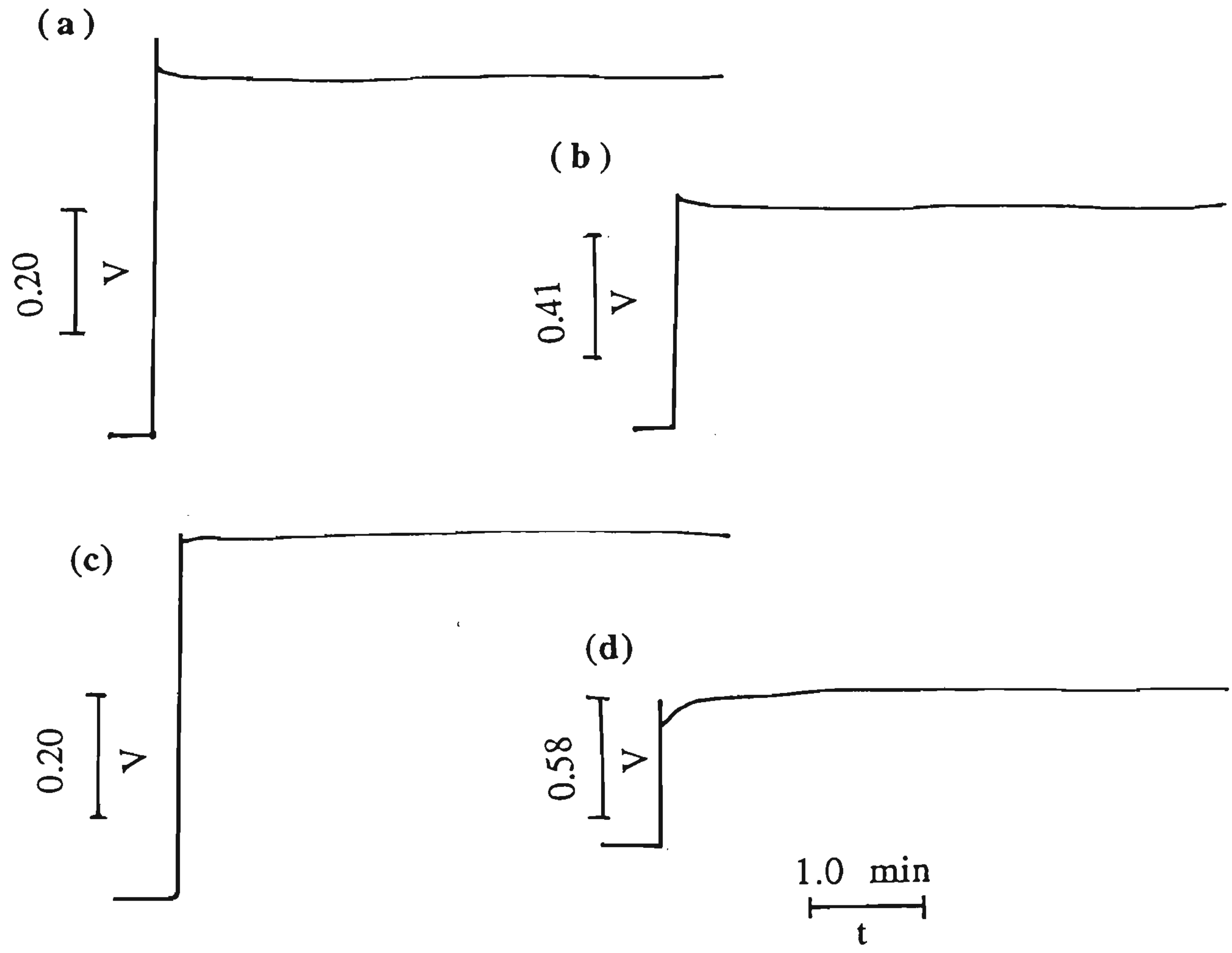


Figure 3.3: Chronopotentiograms of polypyrrole growth on various substrates:
Conditions: (a) No stabilizer present, (b) 1.6 g/L PEO stabilizer,working electrode glassy carbon, (c) No stabilizer present, (d) 1.6 g/L PVA stabilizer. Working electrode platinum.

In all cases the electroactivity of the resultant polymers was decreased by increasing the stabilizer concentration during electropolymerization (e.g. Figure 3.4). These results were similar to those obtained with potentiodynamic deposition.

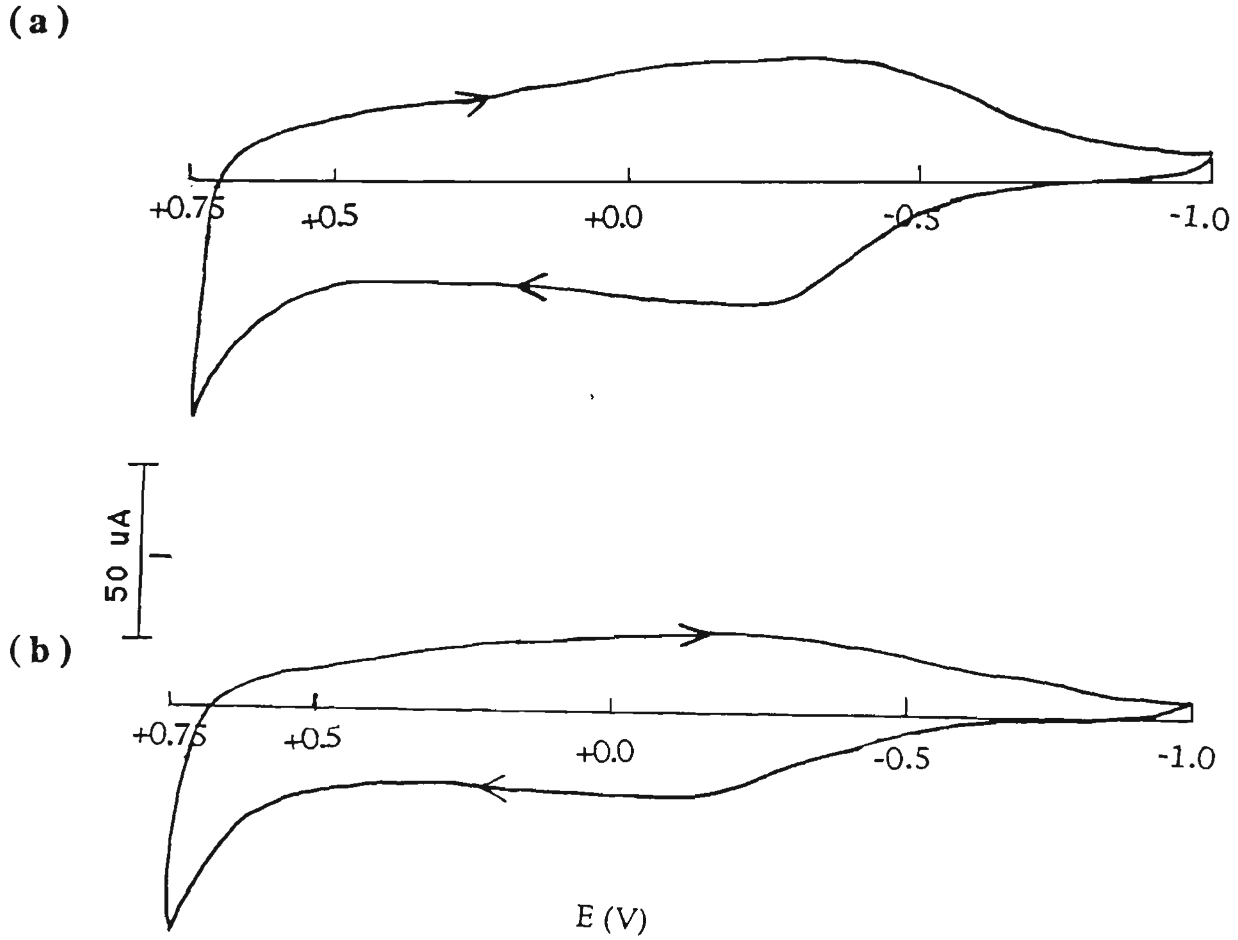


Figure 3.4: Cyclic voltammograms of polypyrrole at a platinum electrode in 1 M $NaNO_3$.
Conditions: Scan rate 100 mV/s. Polymer deposited for 5.0 minutes at a current density of 0.75 mA/cm^2. Electrolyte 0.15 M pyrrole, 1.0 M $NaNO_3$. (a) No stabilizer present, (b) 3.2 g/L PVP$_2$ stabilizer.

With stainless steel as the working electrode the presence of the stabiliser had a marked effect on the resultant electroactivity, as determined using cyclic voltammetry (Fig. 3.5). The presence of the stabiliser during growth resulted in the production of a more clearly defined electroactive response on stainless steel, presumably due to the fact that corrosion of the substrate during growth was inhibited by the stabiliser.

This result indicates that while the stabiliser had no effect on the rate of polymerization (which was controlled by the applied current), it may affect both the quantity and the properties of the deposit produced.

(a)

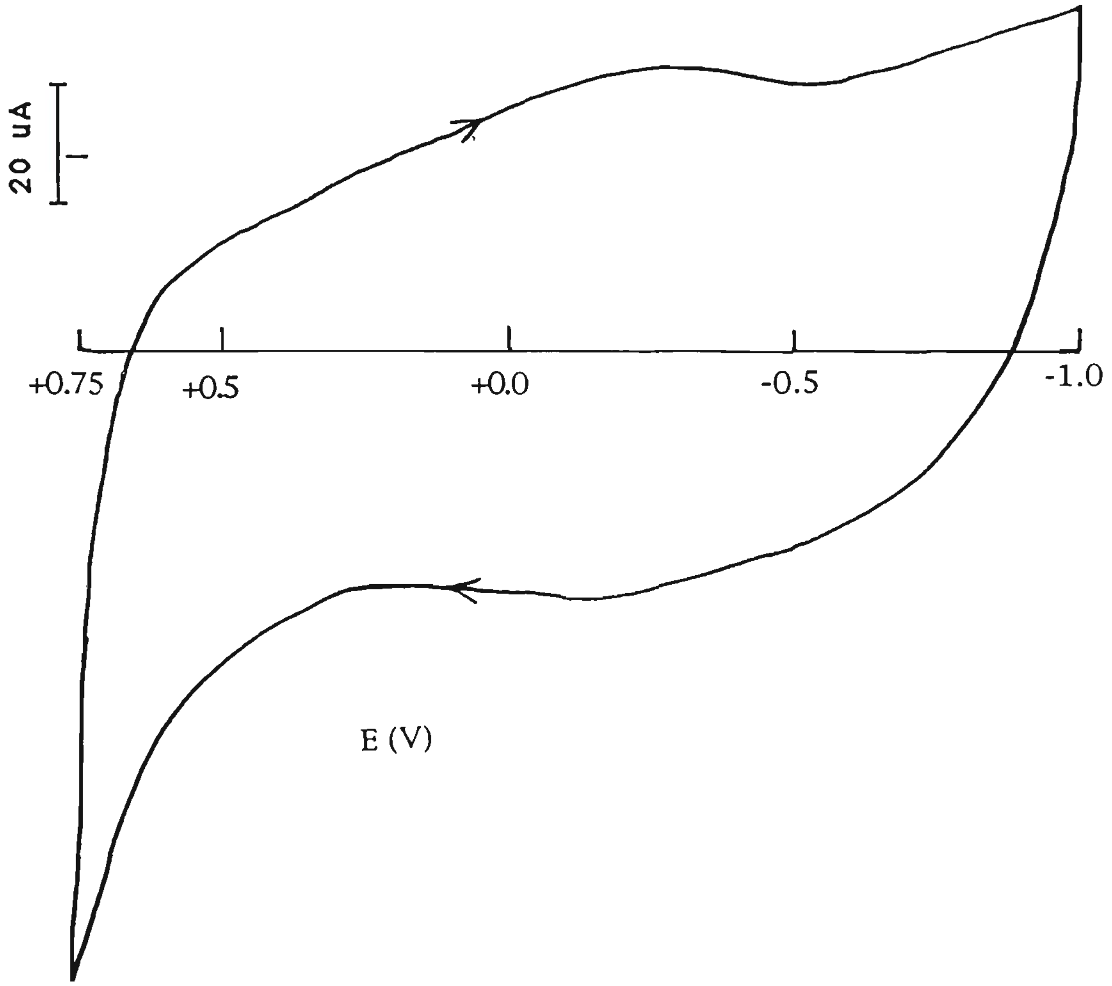


Figure 3.5: Cyclic voltammograms obtained after deposition of PPy/NO_3 on stainless steel.
Conditions: Scan rate 100 mV/s. Current density 0.75 mA/cm^2.
(a) No stabilizer present, polymerization from 0.15 M pyrrole, 1.0 M $NaNO_3$, (b) as in (a) but with 4.80 g/L PVP_2 stabilizer.

(b)

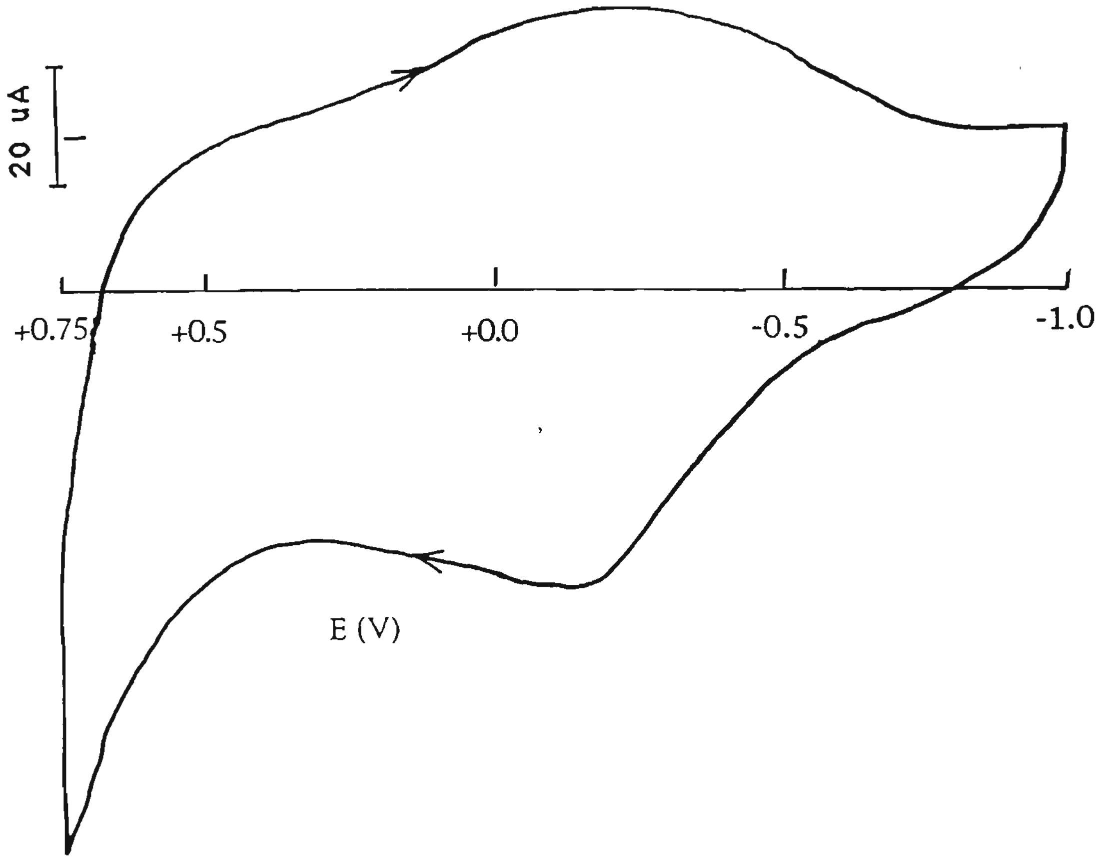


Figure 3.5 continued.

3.3.3 Potentiostatic Polymerization of Pyrrole

A constant potential (0.75 volt) was used for the electropolymerization of pyrrole onto glassy carbon, platinum and stainless steel electrodes using different stabilizers (PVP, PVA, PEO) in the concentration range of 1.60 - 4.80 g/L.

Chronoamperometry was used to characterize the influence of steric stabilizers on the electropolymerisation process. A typical chronoamperogram for oxidation of pyrrole in 1.0 M $NaNO_3$ with no stabiliser present is shown in Figure 3.6.

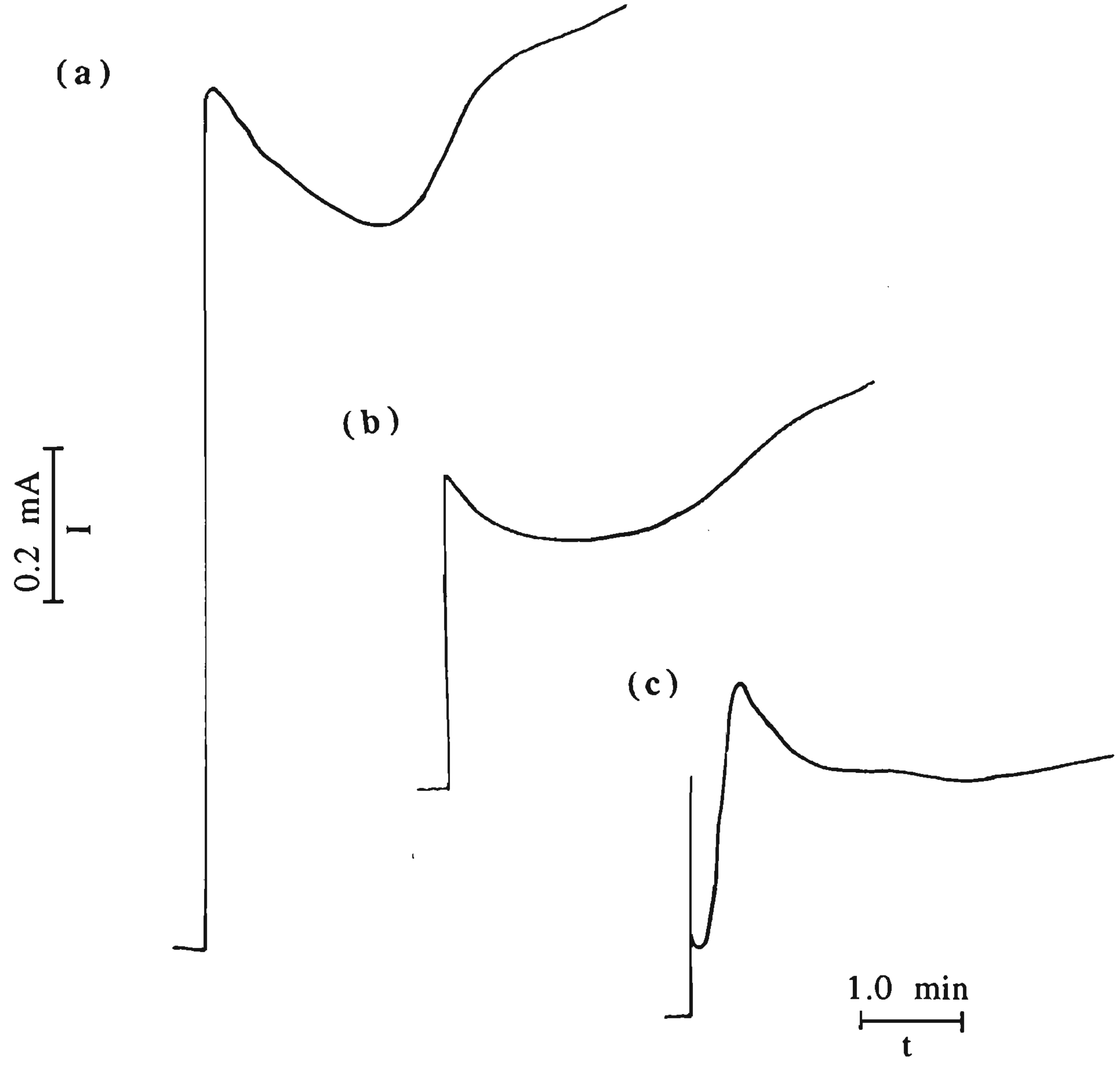


Figure 3.6: Chronoamperograms on (a) glassy carbon, (b) platinum, (c) stainless steel (316 grade) with no additives present. Conditions: $E_{app.}$=0.75 V. Polymerization was from 0.15 M pyrrole and 1.0 M $NaNO_3$.

The increasing current flow, as a function of time, is indicative of the fact that conducting polymer is deposited on the substrate. The oxidation proceeded as expected on platinum and glassy carbon. On stainless steel, polymer deposition is delayed presumably due to the polar nature of the corroding substrate (stainless steel is likely to corrode at the potential required for growth). Also the subsequent rate of deposition, as determined by the rate of increase of current, is markedly less on stainless steel. Cyclic voltammograms obtained after growth on all substrates revealed the expected polymer oxidation/reduction process. Typical cyclic voltammograms are shown in Figure 3.7.

(a)

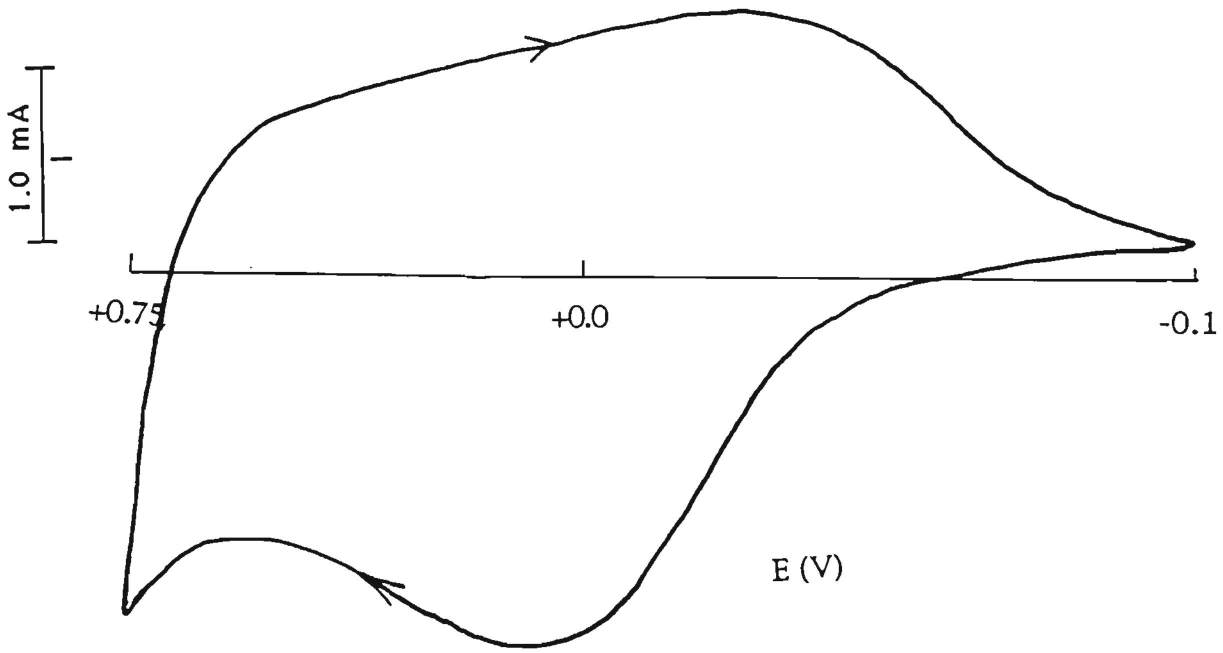


Figure 3.7: Cyclic voltammograms obtained after deposition of PPy/NO_3 onto: (a) platinum (b) stainless steel electrode.
Scan rate 100 mV/s. Supporting electrolyte 1.0 M $NaNO_3$. No stabilizer present. Polymer deposited for 5.0 minutes.

(b)

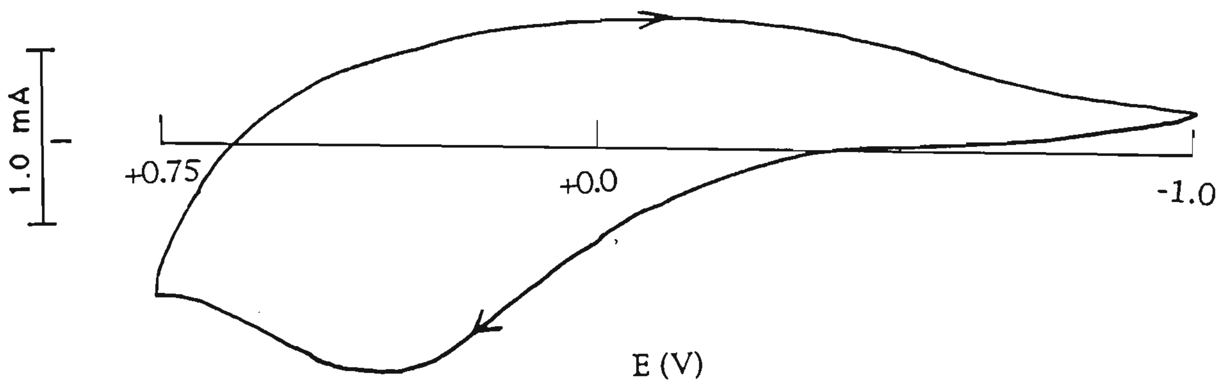


Figure 3.7 continued.

The effect of the stabilisers on potentiostatic growth at each substrate was then considered. For example, using the stainless steel substrate, each of the stabilisers under investigation (PVA, PEO, PVP_1 and PVP_2) was observed to have a significant effect on the polymerisation process. For example, chronoamperometric data for stainless steel in the presence of PVP_2 at different concentrations is shown in Figure 3.8.

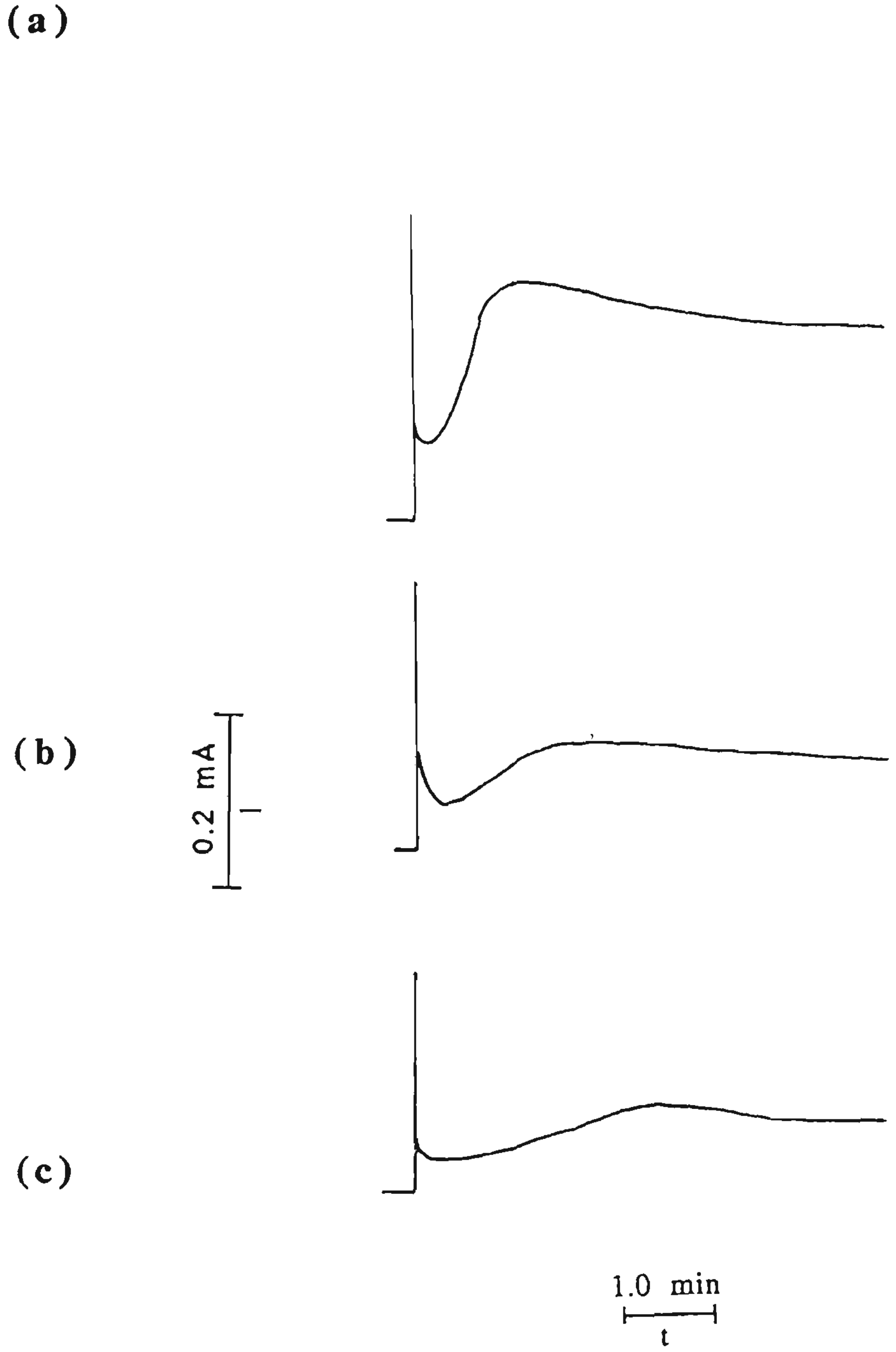


Figure 3.8: Chronoamperograms during polymerization at a stainless steel substrate with stabilizer present.
Conditions: Eapp.=0.75 V. (a) 1.60 g/L PVP_2, (b) 3.20 g/L PVP_2, (c) 6.40 g/L PVP_2.

In comparison to polymerization on stainless steel with no additives (Figure 3.6(c)) the onset of deposition of the polymer was delayed for a measurable amount of time when stabilizers were used. This, presumably, is the result of colloid formation (as observed with chemical polymerisation processes (Chapter 2) (106,164, 122) and stabilisation of the colloid in the diffusion double layer prior to polymer deposition. On all substrates the presence of the stabilisers also caused a marked decrease in the steady state current observed at longer times indicating that the presence of the stabiliser decreased the rate of monomer oxidation and/or deposition.

Cyclic voltammograms after potentiostatic growth were recorded on all substrates. The presence of the stabilisers was found to have an effect on the cyclic voltammetry after growth with the electroactivity decreasing with increasing stabilizer concentration (Figure 3.9). This may either be due to changing nature of the polymer or to decreasing amount of polymer deposited. Typical cyclic voltammograms on glassy carbon are shown in Figure 3.9.

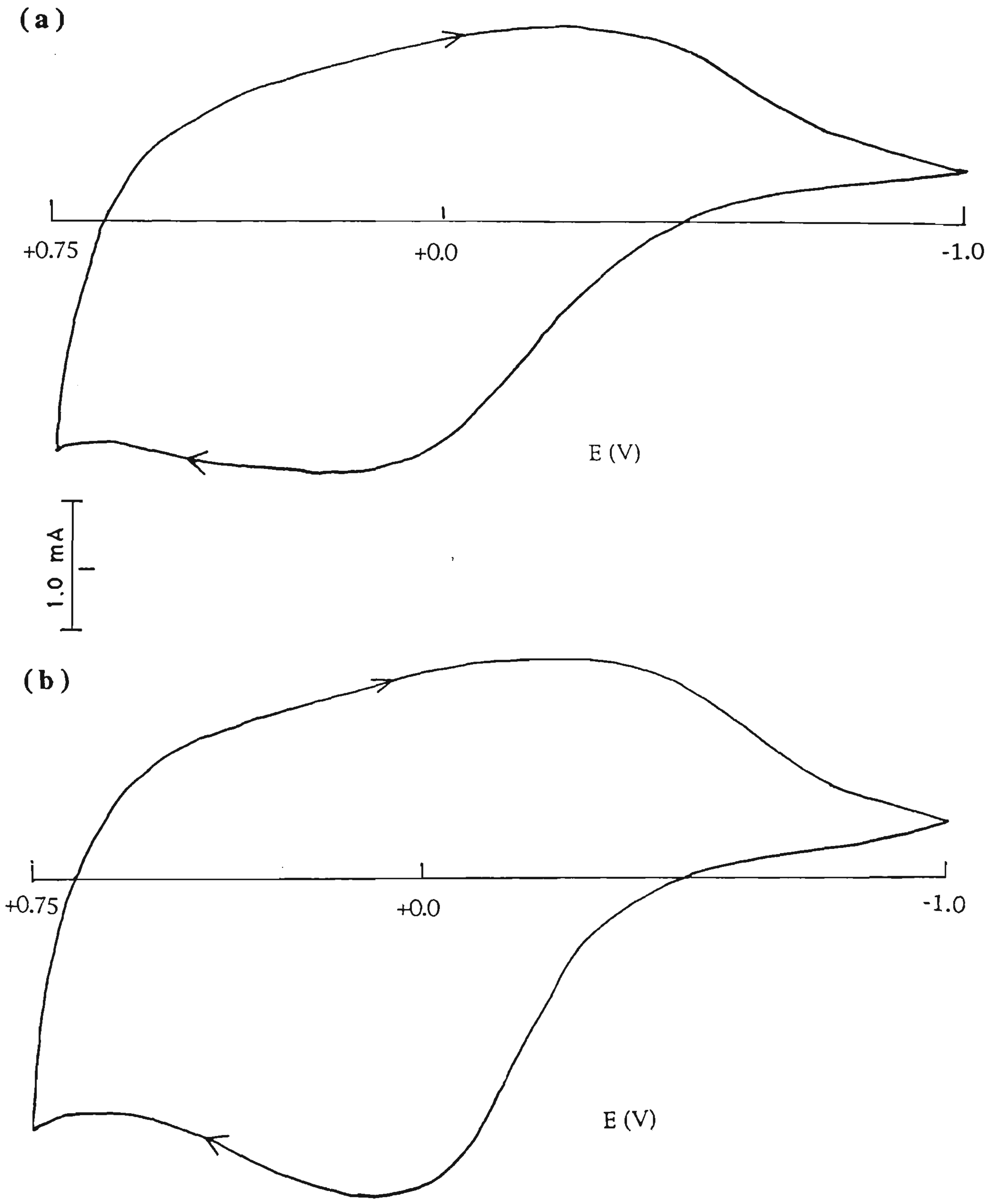


Figure 3.9: Cyclic voltammograms obtained after deposition of PPy/NO_3 on glassy carbon electrode.

Conditions: Scan rate 100 mV/s. (a) 4.80 g/L PVP_2, (b) 1.60 g/L PVP_2, (c) No stabilizer present. Supporting electrolyte 1.0 M $NaNO_3$. E Deposition=0.75 V. Deposition time = 5.0 minutes.

(c)

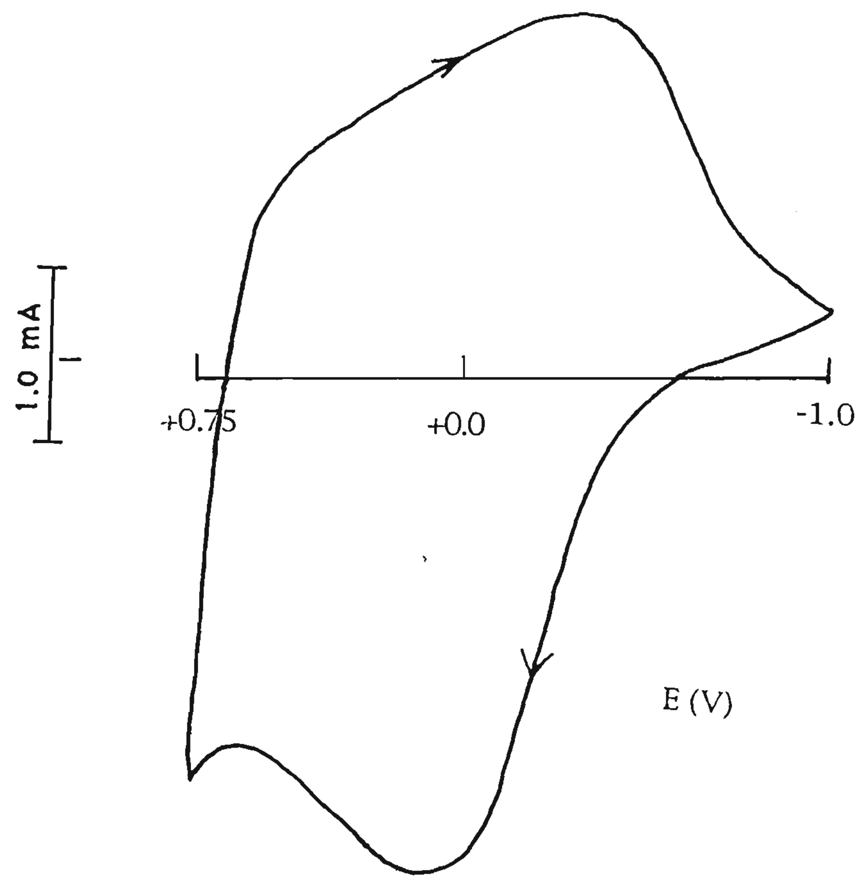


Figure 3.9 continued.

The electropolymerization of pyrrole at +0.75 V on a glassy carbon electrode was also performed to a fixed charge and with the various stabilizers (concentration range of stabilizers 0.80-11.20 g/L). Cyclic voltammograms were obtained from the resultant films in 1.0 M $NaNO_3$ (Figure 3.10). In all cases electroactivity was decreased slightly by using stabilizers. Since the same amount of polymer is assumed to have deposited in these experiments, the decrease in electroactivity observed must be due to differences in the electrical properties of the polymer.

The reaction times were also monitored in these experiments. As shown in Table 3.2, the type and concentration of stabilizers affected the rate of polymerization with a slower rate associated with higher stabilizer concentrations. This supports the stabilization of the radical species for colloid formation prior to polymer deposition.

(a)

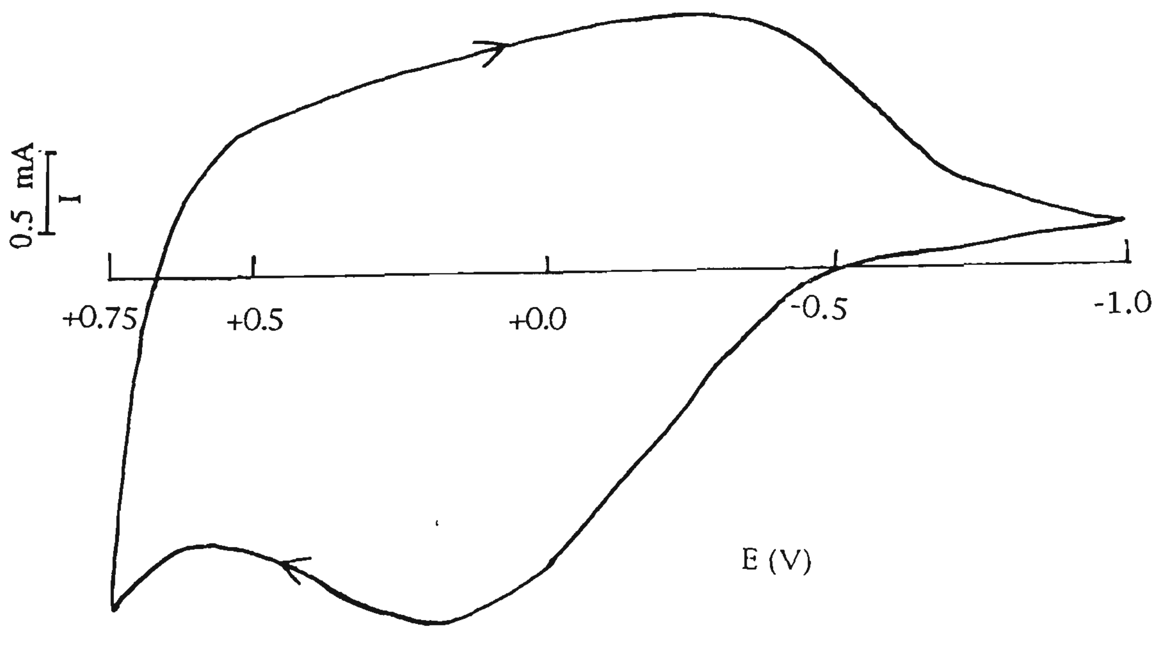


Figure 3.10: Cyclic voltammograms obtained after deposition of PPy./NO_3 on glassy carbon electrode.
Conditions: (a) No stabilizer present. Polymerization was performed from 0.15 M pyrrole, 1.0 M $NaNO_3$ for three minutes. (b) and (c) as in (a) but with, 11.20 g/L PVA and PVP_2 present respectively. Constant charge for all deposits=181 mC, scan rate 100 mV/s.

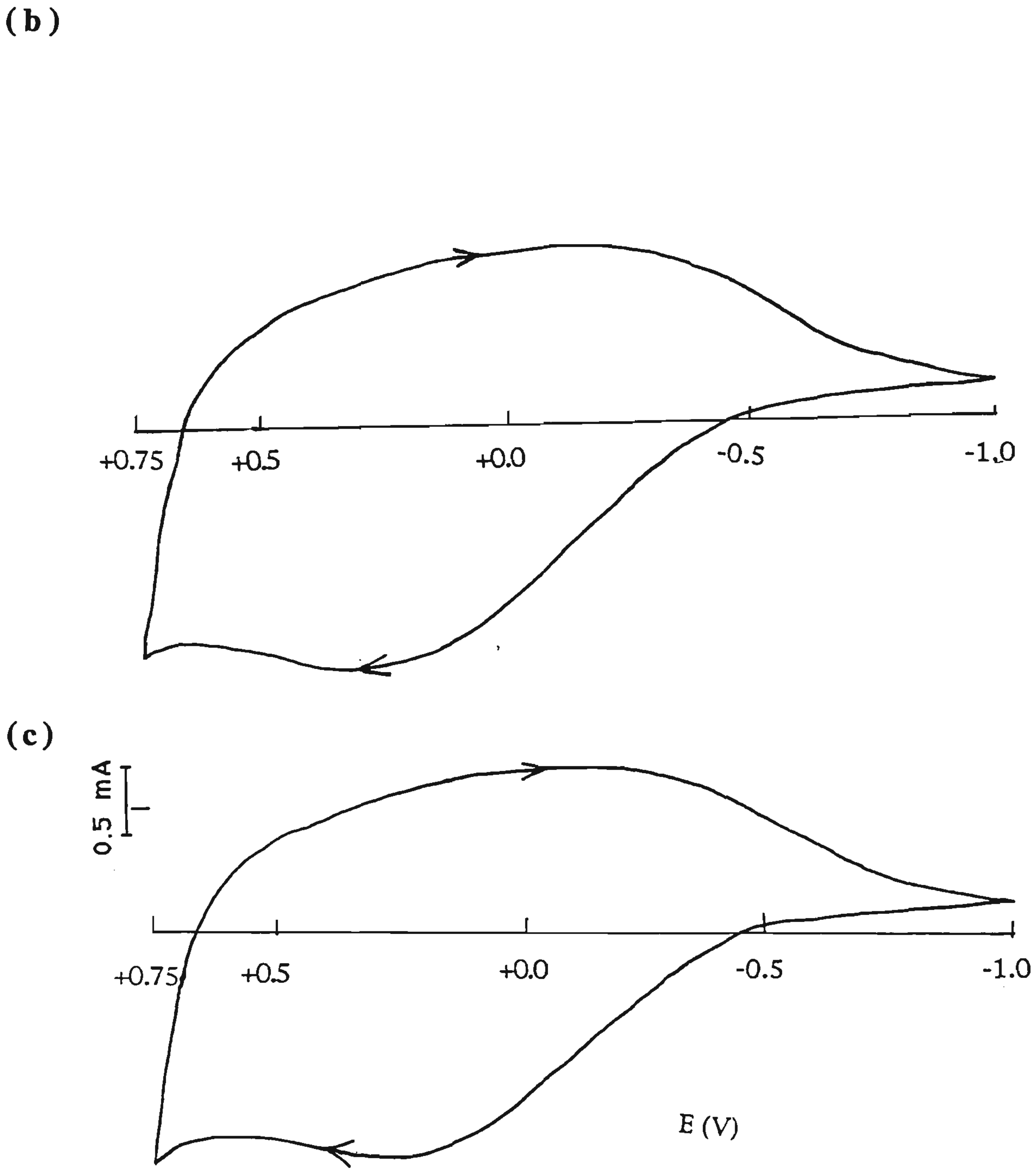


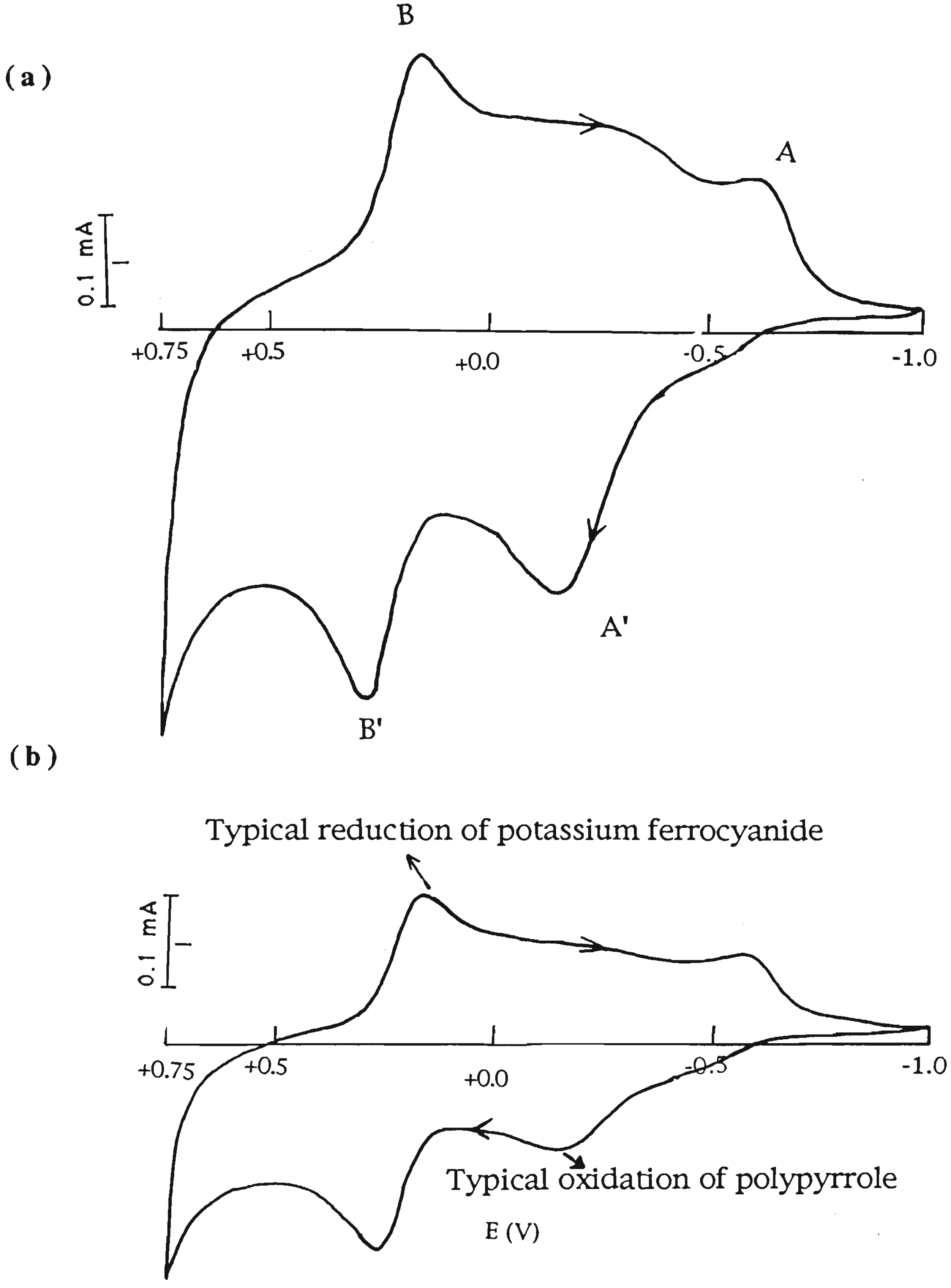
Figure 3.10 continued.

Table 3.2: Reaction time required to pass a given charge (181 mC).

Stabiliser type	Stabiliser concentration (g/L)	Reaction time (minute)
No stabilizer	0.00	3.00
PVA	0.80	3.13
	1.60	3.27
	3.20	3.49
	4.80	3.59
	6.40	4.18
	8.00	4.28
	11.20	5.10
PEO	0.80	3.16
	1.60	3.29
	3.20	3.33
	4.00	3.42
	4.80	3.59
	6.40	4.03
	8.00	4.13
	11.20	4.44
PVP_2	0.80	3.25
	1.60	3.38
	3.20	3.47
	4.00	4.02
	4.80	4.20
	6.40	4.34
	8.00	4.47
	11.20	5.08
PVP_1	0.80	3.10
	1.60	3.31
	3.20	3.35
	4.80	3.39
	6.40	3.44
	8.00	3.48
	11.20	4.32

The ability of solution species (ferrocyanide) to undergo oxidation/reduction at these modified electrodes was then considered. Using glassy carbon and platinum electrodes polypyrrole was formed at constant potential (0.75 V) in the presence of PVP, PVA or PEO steric stabilizer. Cyclic voltammograms were then obtained using the resultant modified electrodes in a solution of 0.01 M $K_4Fe(CN)_6$ plus 0.1 M $NaNO_3$. As shown in Figure 3.11 the magnitude of the responses due to ferrocyanide decreased when stabilizers were present during polymer formation. The oxidation/reduction responses of polypyrrole (A/A') and ferrocyanide (B/B') are shown in Figure 3.11. The difference in current values was presumably due to the difference of the electrode surface area which indicates that stabilizers affect the electroactive surface area. The oxidation/reduction equation of ferrocyanide is shown below:

$$Fe(CN)_6{}^{4-} \underset{e^-}{\overset{e^-}{\rightleftarrows}} Fe(CN)_6{}^{3-}$$



Figures 3.11: Cyclic voltammograms obtained after growth of PPy/NO_3 on glassy carbon electrode.

Conditions: Scan rate 100 mV/s. (a) No stabilizer present; (b) 2.80 g/L PVP_2. Supporting electrolyte 0.01 M $K_4Fe(CN)_6$ plus 0.10 M $NaNO_3$.

3.3.4 Electron Microscopy of Polypyrrole

Scanning electron micrographs of both the plate and solution side of the deposited film were obtained. The presence of stabiliser consistently increased the nodular nature of the deposit on the solution side (Figure 3.12) with smaller, more numerous nodules forming. This is consistent with the notion of colloid formation in solution prior to polymer deposition. In the chemical preparation of colloids (117,125), the particle size decreases with increasing stabilizer concentration which is probably related to the amount of adsorbed insulating stabilizer on the particle surface. A similar observation was noted in the present study with the nodule size decreasing with increasing stabilizer concentration.

(a)

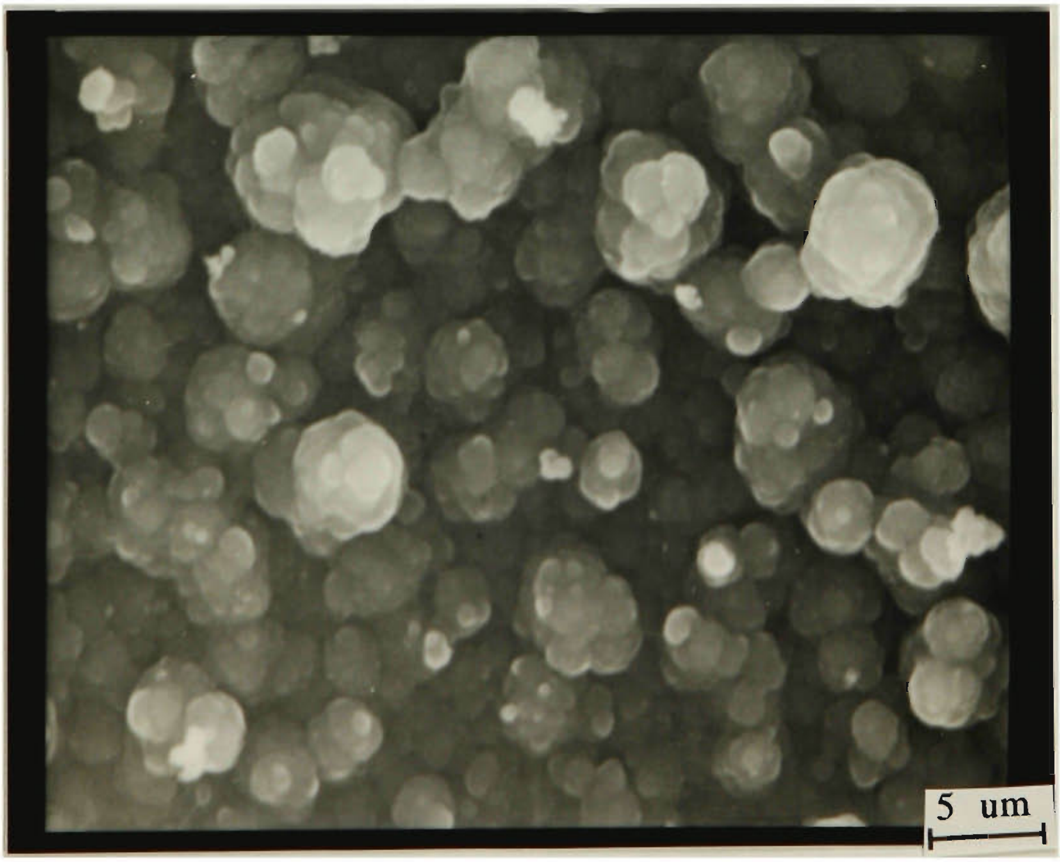


Figure 3.12: Scanning electron micrographs of solution side on glassy carbon electrode.
Conditions: Eapp.=0.75 V from 0.15 M pyrrole, 1.0 M $NaNO_3$. (a) No stabilizer present, (b) 4.80 g/L PEO, (c) 4.80 g/L PVP_2, (d) 4.80 g/L.PVA, (e) 2.40 g/L PVA.

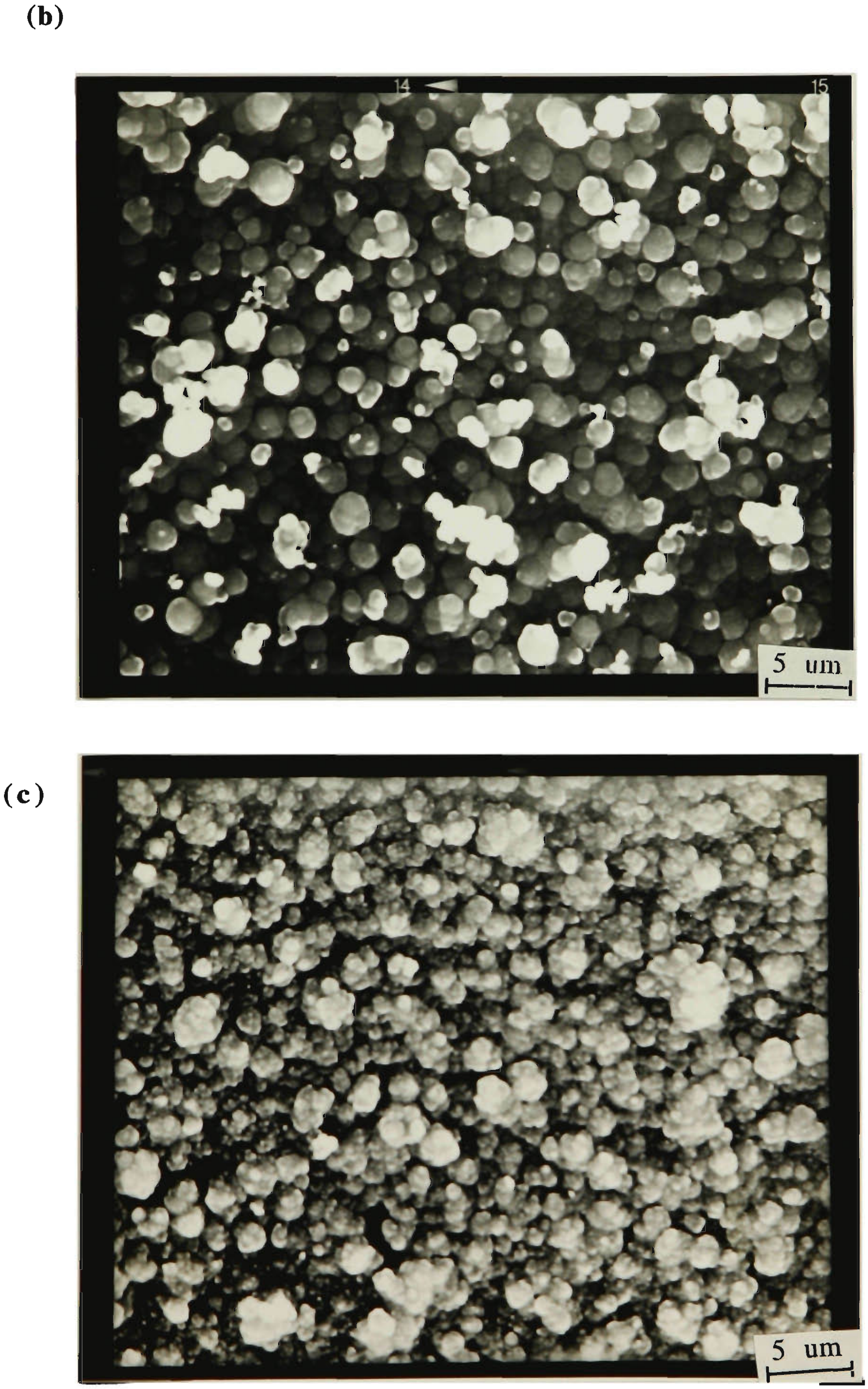
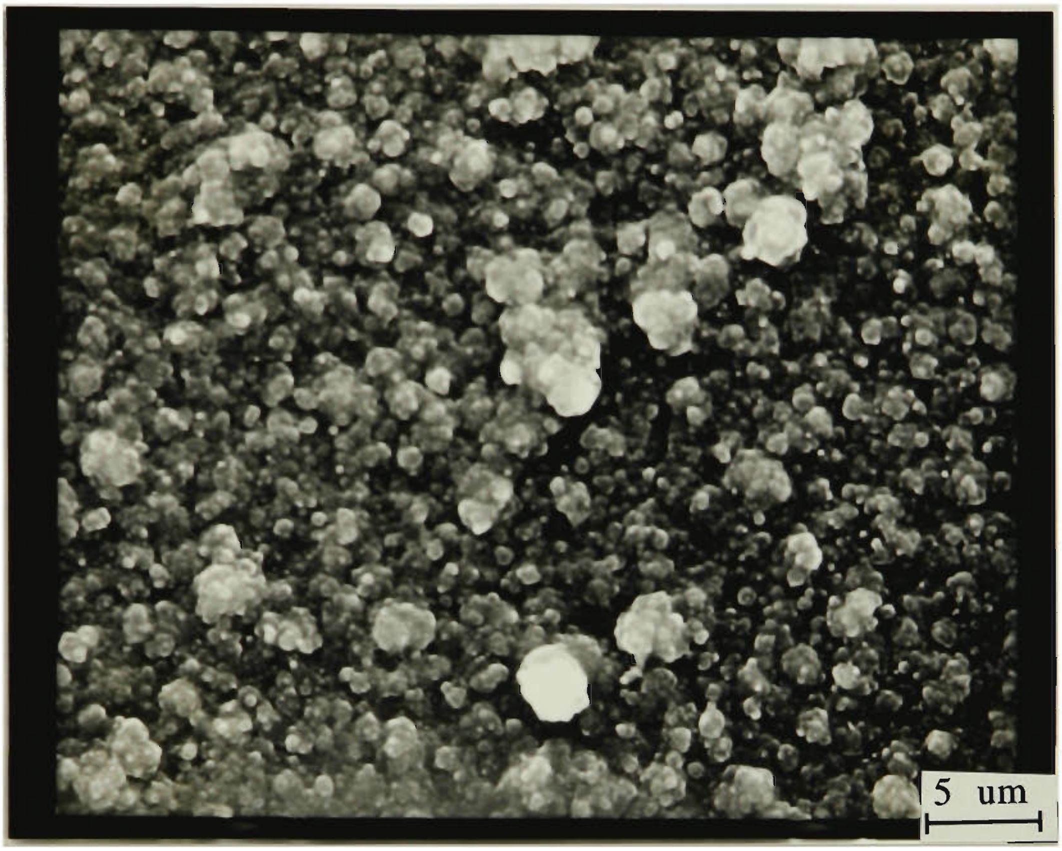


Figure 3.12 continued

(d)



(e)

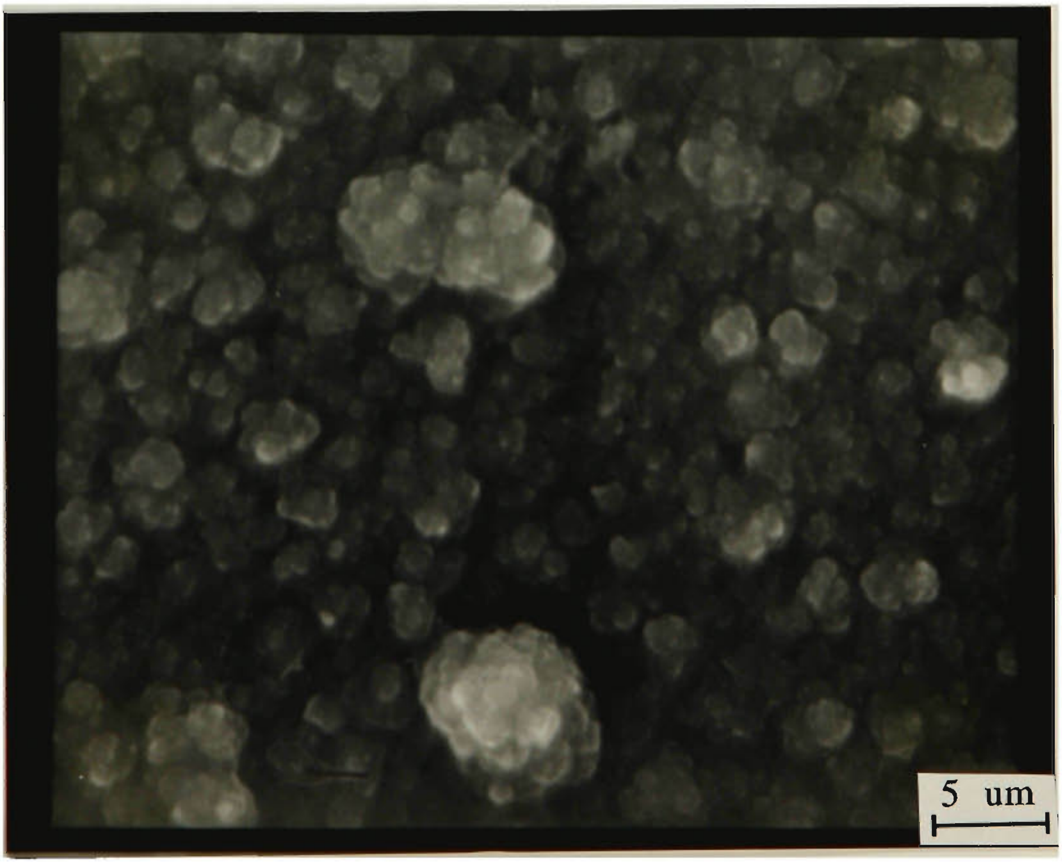
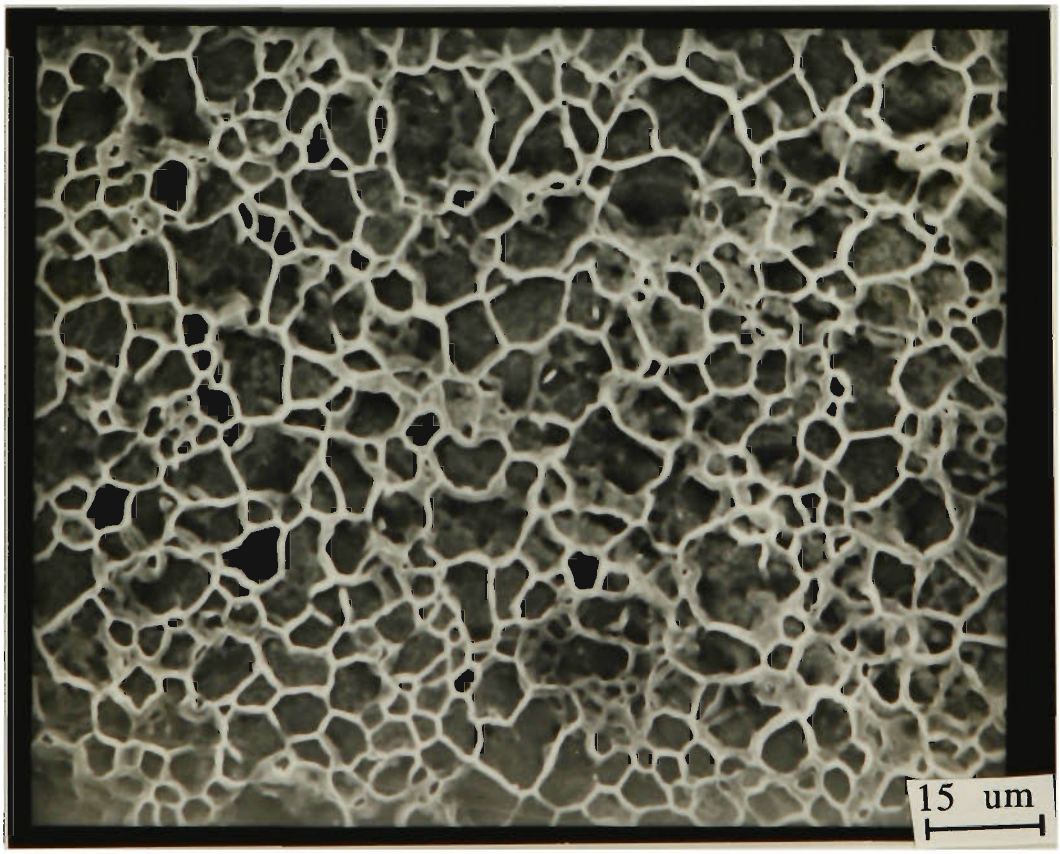


Figure 3.12 continued.

On the plate side the presence of stabiliser had a dramatic effect. For example, results obtained using a stainless steel substrate are shown in Figure 3.13. The fine network observed is presumably due to etching of the grain boundaries in the metal in the early stages of reaction which are then filled with deposited polymer. The stabiliser did not appear to affect this process. However, the stabilizers did influence the layers deposited subsequently. Close examination of these SEM's reveals a much more porous layer being deposited as the concentration of stabiliser employed during polymerisation is increased. The reasons for this are unknown, but the porosity was not evident on the solution side of the films.

(a)



Figures 3.13: Scanning electron micrographs of plate side on stainless steel:
Conditions: : $E_{app.}$=0.90 V from 0.15 M pyrrole, 1.00 M $NaNO_3$, (a) 2.40 g/L PVP_2, (b) No stabilizer present.

(b)

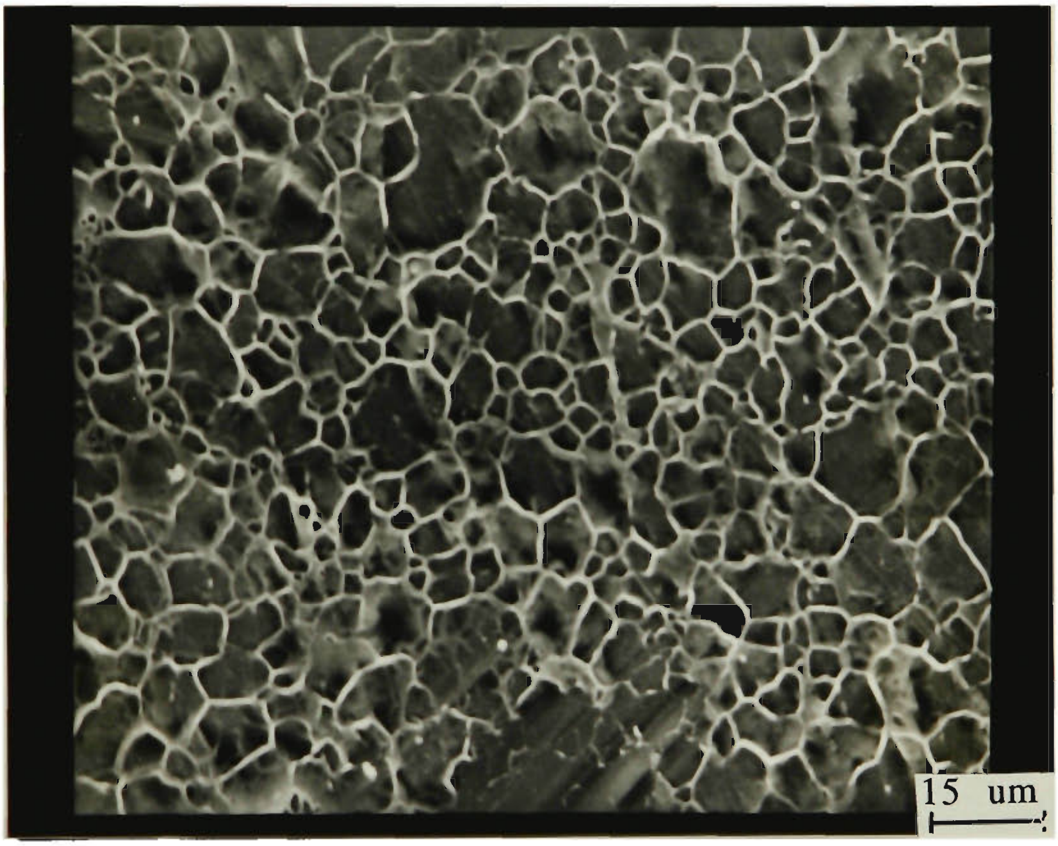
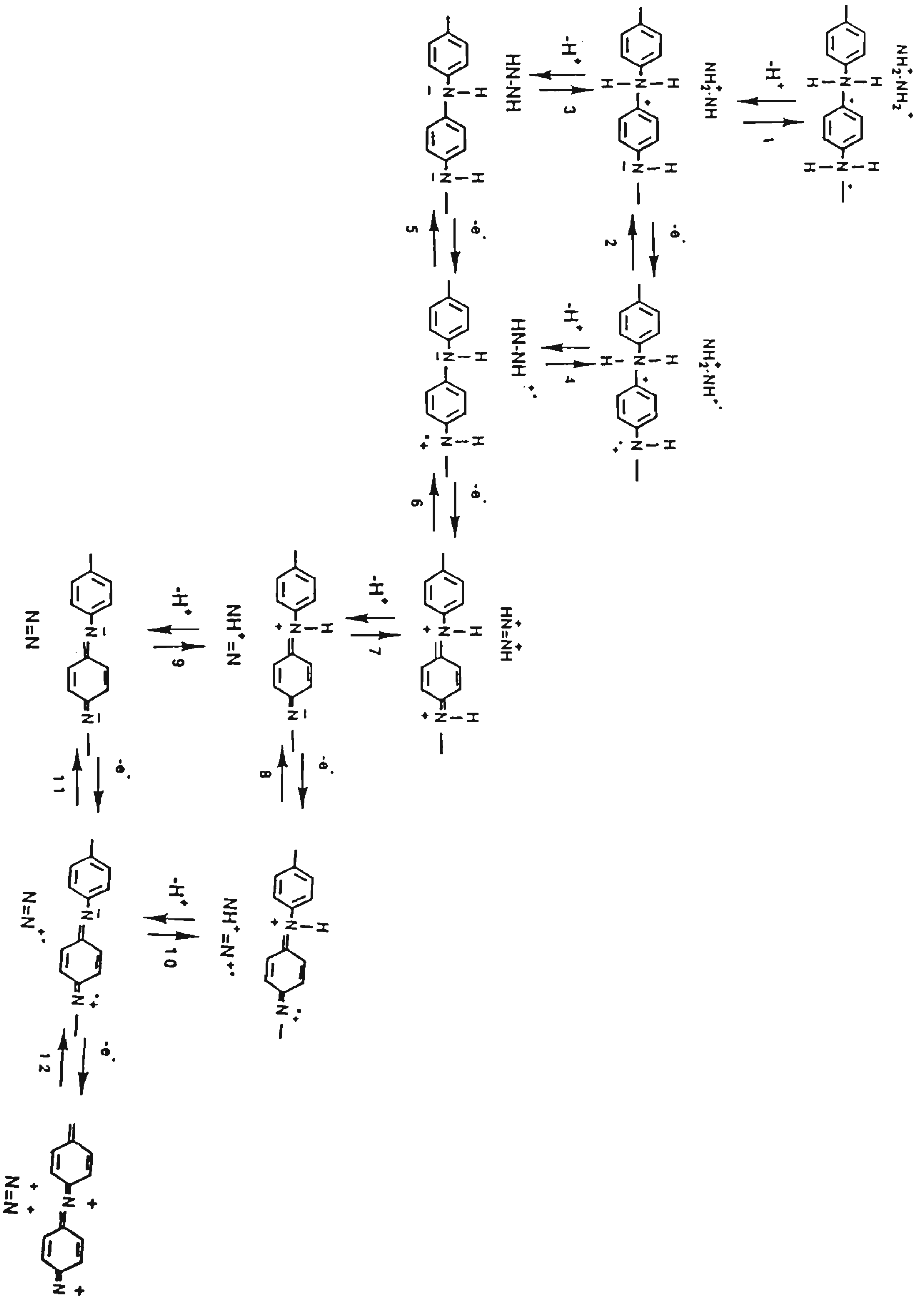


Figure 3.13 continued.

3.3.5 Potentiodynamic Polymerization of Aniline

The influence of the steric stabilizer on the potentiodynamic polymerization of aniline was considered. In all cases the rate of growth as determined by the increased current flow on subsequent voltammetric scans was observed to decrease in the presence of stabilizer. Typical cyclic voltammograms during and after growth are shown in Figure 3.14. As shown in figure the redox peak currents gradually increased with the number of potential scans, indicating that the thickness of the conducting polymer film increased. All oxidation peaks shifted positively, and reduction peaks negatively, with cycles. The middle redox peaks (B/B') did not appear when the potential scan did not exceed 0.85 volt. Therefore, the middle peak current is attributed to electroactive species formed by the partial degradation of the film as reported by other workers (195). The magnitude of the middle redox peak current decreased with decreased acid concentration in the polymerization electrolyte. Therefore, degradation of the film is dependent on the potential and electrolyte concentration (195).

The oxidation responses in particular (A) are well defined. On the other hand, the cathodic peak currents in particular (A') are smaller and broader than are the anodic peak currents, indicating the conversion of the polymer into an electrically insulating reduced state (195). The partially reversible peaks (C/C') in the voltammograms correspond to the redox reactions of polyaniline in the diradical dicationic form (bipolaron), which occur concomitantly with a change in film conductivity (95). Polyaniline at potentials more anodic than peak (C) behaves like an insulator. As the film thickens during growth, the potentials of all reduction peaks shift negatively. The shift is most pronounced for peak (C') and is indicative of the continuous decrease in conductivity of the electrode film during deposition. Figure 3.15 shows cyclic voltammograms obtained from the polyaniline films after growth. It can be seen that the stabilizer affects the electroactivity of the deposited polymer with a decrease in electroactivity occuring when stabilizers were used. A schematic complete redox mechanism of polyaniline is shown below (104):


1
2
3
4
5
6
7
8
9
10
11
12
-H⁺
-e⁻
NH₂⁺·NH₂
NH₂⁺·NH
HN-NH
NH₂⁺·NH⁺·
HN-NH⁺·
HN⁺=NH⁺
NH⁺=N
NH⁺=N⁺·
N=N
N=N⁺·
N=N⁺⁺

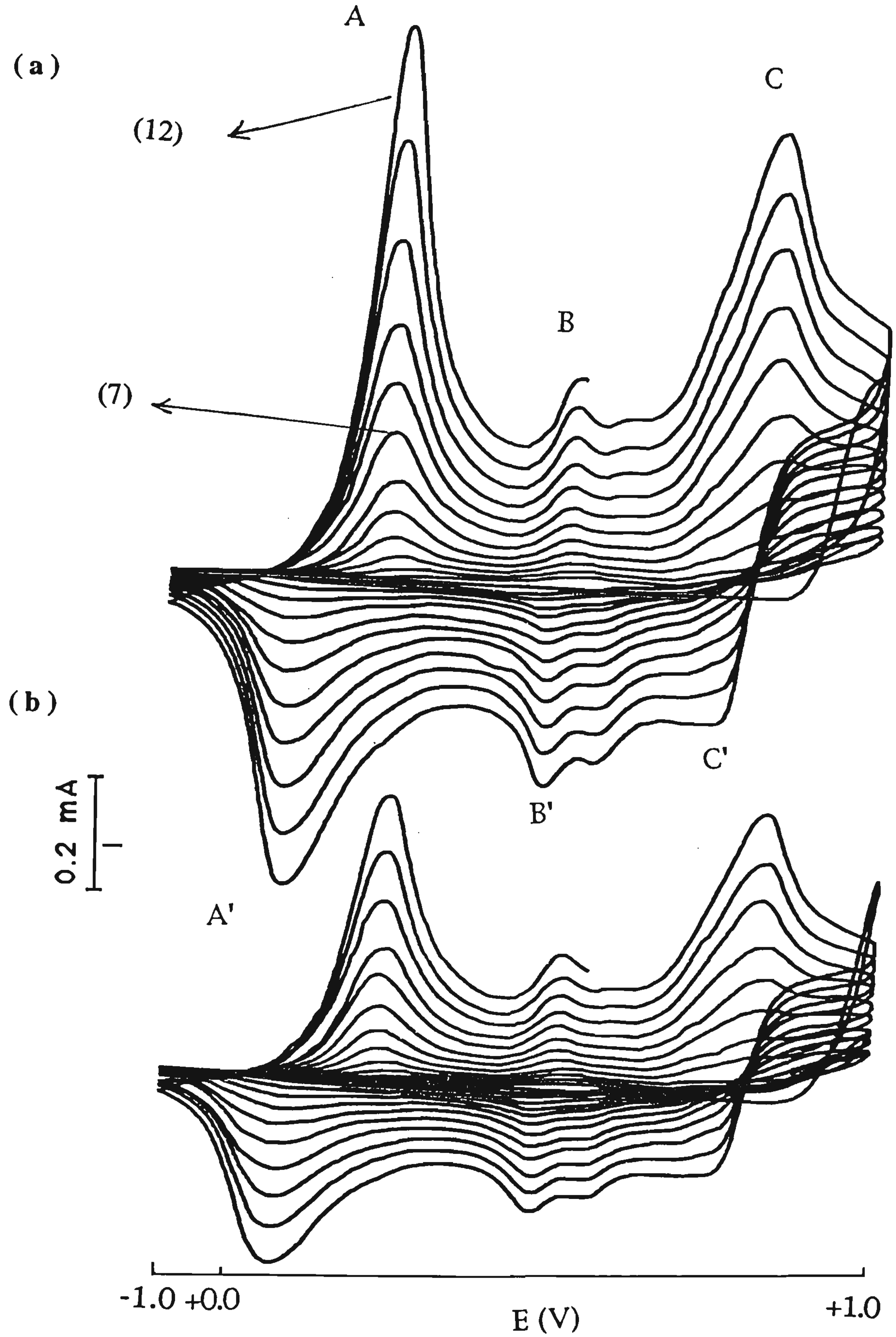


Figure 3.14: Cyclic voltammograms of polyaniline during growth at glassy carbon electrode.
Scan rate 50 mV/s.
Conditions: Polymer deposited for 9 minutes from 0.10 M aniline, 1.25 M HCl in water. (a) No stabilizer present, (b) 6.40 g/L PVA. (7) and (12) represent scan number.

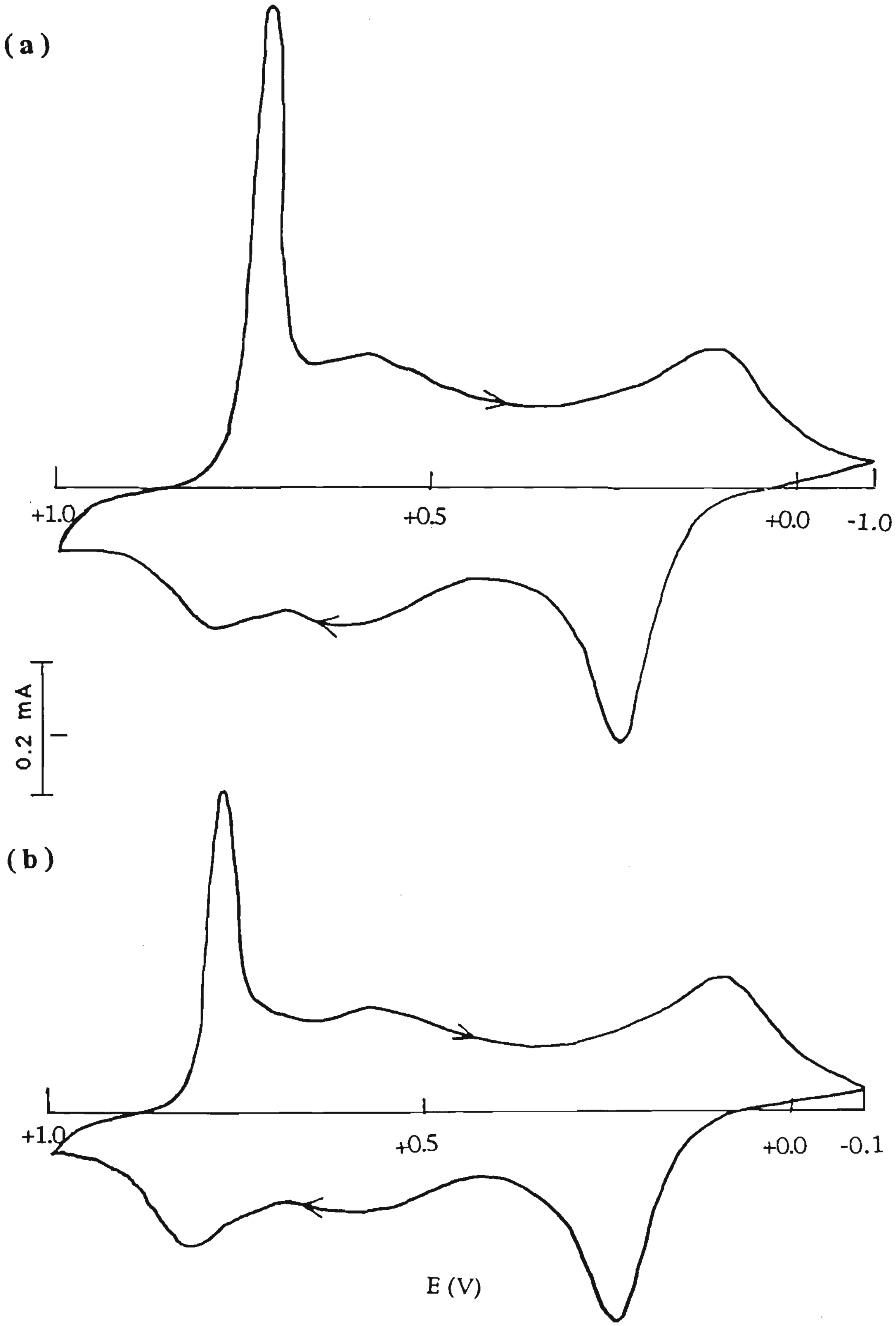


Figure 3.15: Cyclic voltammograms of polyaniline after growth at glassy carbon electrode.
Conditions: Scan rate 50 mV/s. Polymer deposited for 9 minutes from 0.10 M aniline, 1.25 M HCl in water. (a) No stabilizer present, (b) 6.40 g/L PVA.

3.3.6 Galvanostatic Polymerization of Aniline

Polymerization was carried out for five minutes onto glassy carbon and platinum electrodes. The chronopotentiograms were recorded to characterize this process. The stabilizer was found to have little effect on the potential growth on platinum however on the glassy carbon electrode the potential varied considerably with varying stabilizer type and concentration (Table 3.3). This is presumably due to the high concentration of stabilizer which blocks the surface of substrate or prevents the polymer deposition.

Table 3.3: Chronopotentiometric data for polyaniline growth.

Substrate	Stabiliser type	Stabiliser concentration (g/L)	Potential of growth (V) after two minutes
Glassy carbon	PVP$_2$	1.6-4.8	0.8
		8.0	0.9
		12.8	2.4
	PVA	1.6-8.0	0.8
		12.8	1.2
	PEO	1.6-3.2	0.8
		4.8	1.3
		12.8	2.2
Platinum	PVP2	1.6-12.8	0.8
	PVA	1.6-12.8	0.8
	PEO	1.6-12.8	0.8

In all cases electroactivity was reduced by increasing stabilizer concentrations. Typical cyclic voltammograms after growth are shown in Figure 3.16.

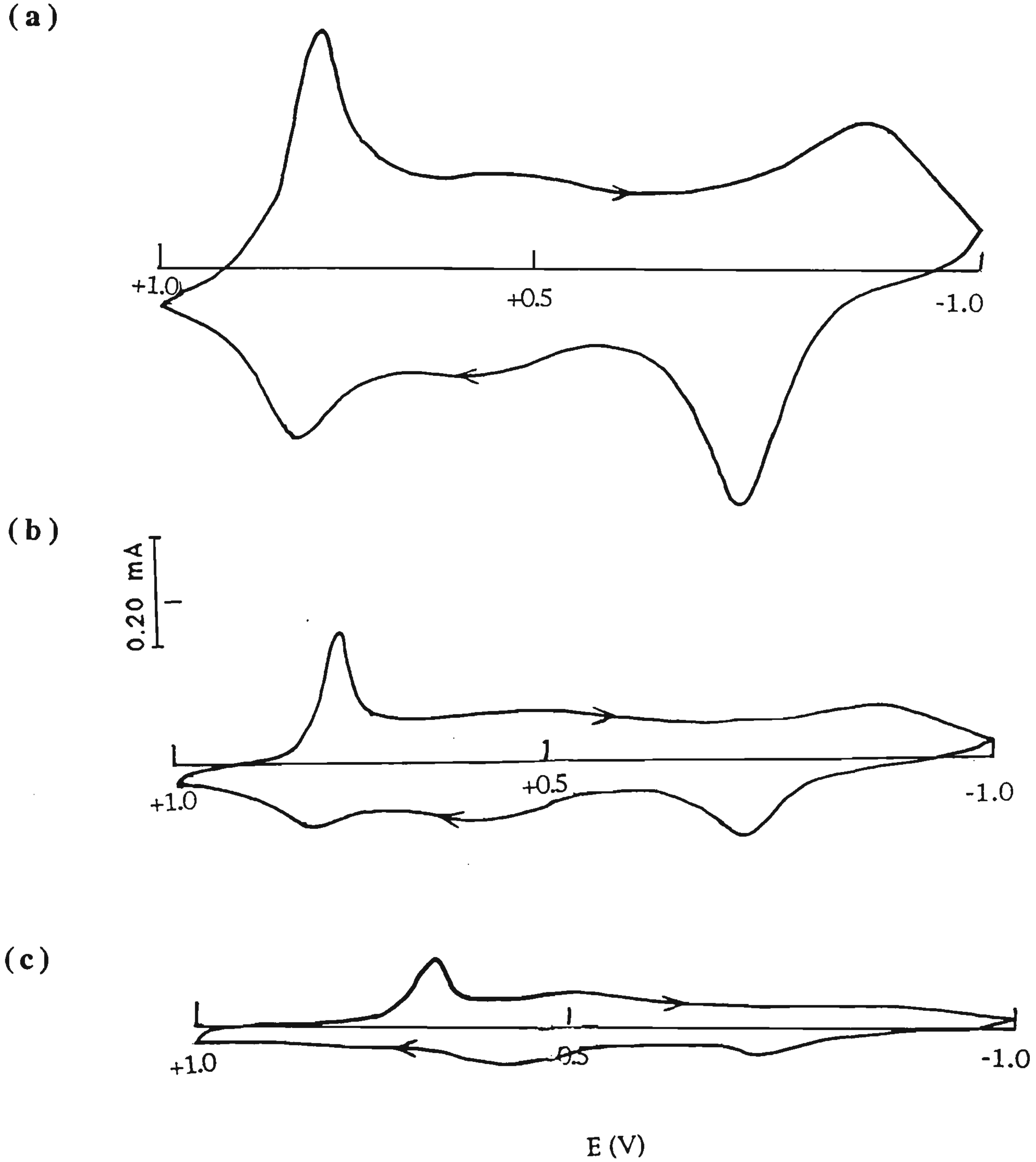


Figure 3.16: Cyclic voltammograms of polyaniline at a glassy carbon electrode in 1.25 M HCl.

Conditions: Scan rate 50 mV/s, polymer deposited for five minutes at 1.0 mA/cm^2 for 0.1 M aniline, 1.25 M HCl in water. (a) No stabilizer present, (b) 4.8 g/L PVA, c) 12.8 g/L PVA.

The decrease in electroactivity is presumably due to the insulating steric stabilizer present on the electroactive surface or to less polymer being deposited.

3.3.7 Potentiostatic Polymerization of Aniline

Constant potential (0.82 volt) was used for the electropolymerization of aniline on glassy carbon and platinum electrodes using different stabilizers in the concentration range of (1.60-12.80 g/L) in an aqueous solution of 1.25 M HCl. Chronoamperograms for the oxidation of this process were monitored. Typical chronoamperograms are shown in Figure 3.17.

On all substrates the presence of stabilizers caused a marked decrease in the steady state current observed at longer times indicating that the presence of the stabilizer decreased the rate of monomer oxidation and/or polymer deposition.

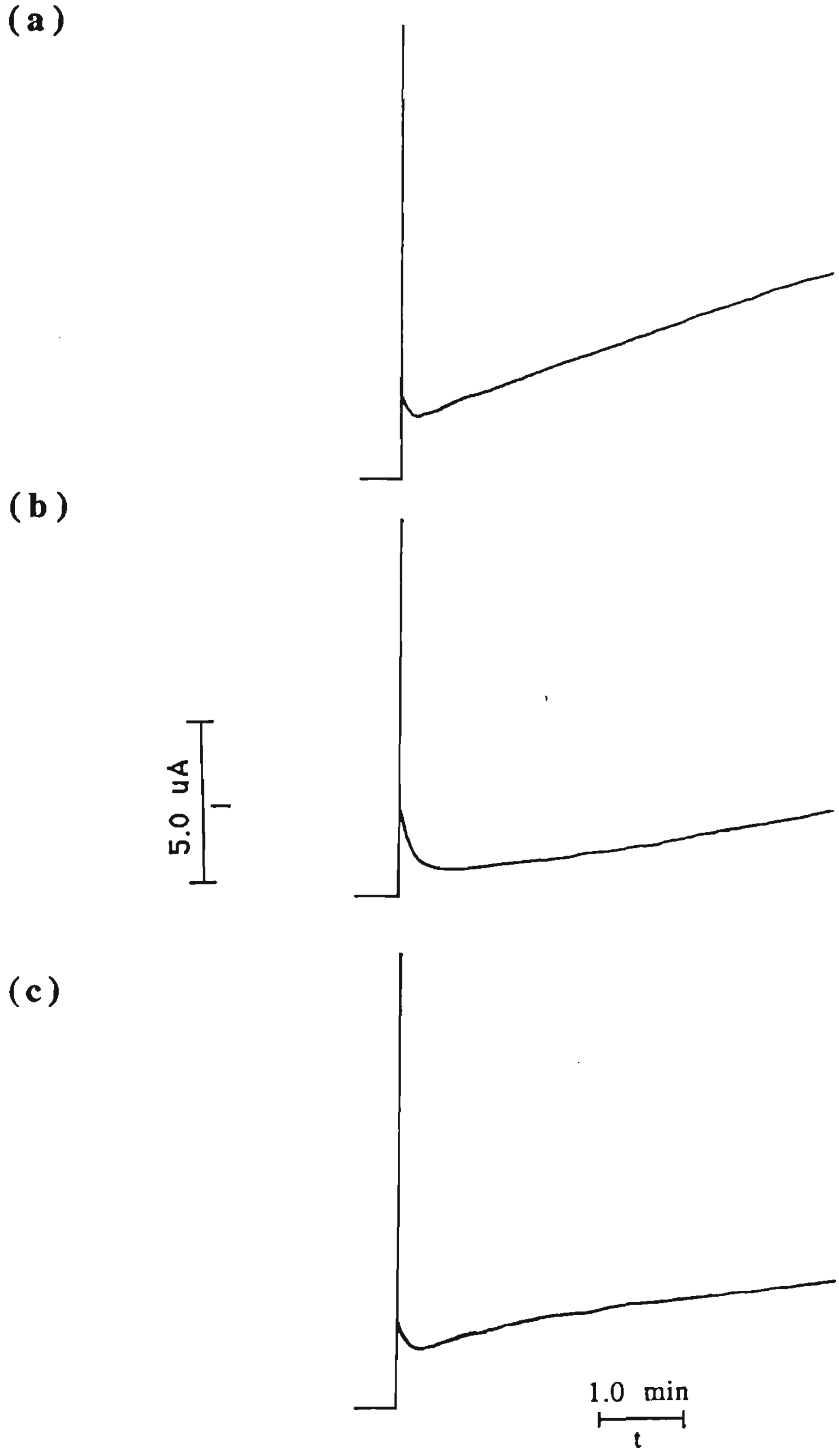


Figure 3.17: Chronoamperograms during polymerization at a glassy carbon substrate.

Conditions: Solution contained 1.25 M HCl, 0.10 M aniline; $E_{app.}$=0.82 volt.

(a) No stabilizer present, (b) 12.80 g/L PVA, (c) 12.80 g/L PVP_2.

3.3.8 Electron Microscopy (SEM) of Polyaniline

Scanning electron micrographs of the solution side of deposited films were obtained which showed that the stabilizers influenced the morphology of polymer films (Figure 3.18). Nodular surfaces were observed in all cases with the nodule size decreasing when stabilizers were used.

(a)

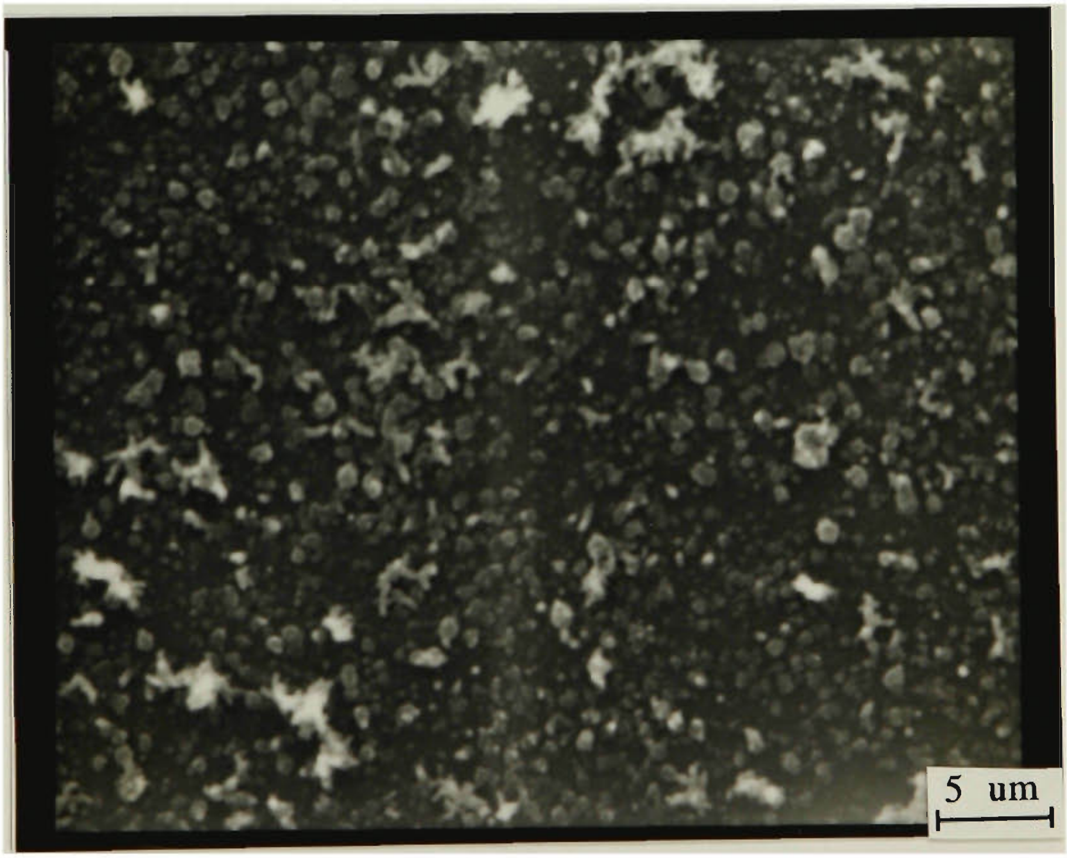
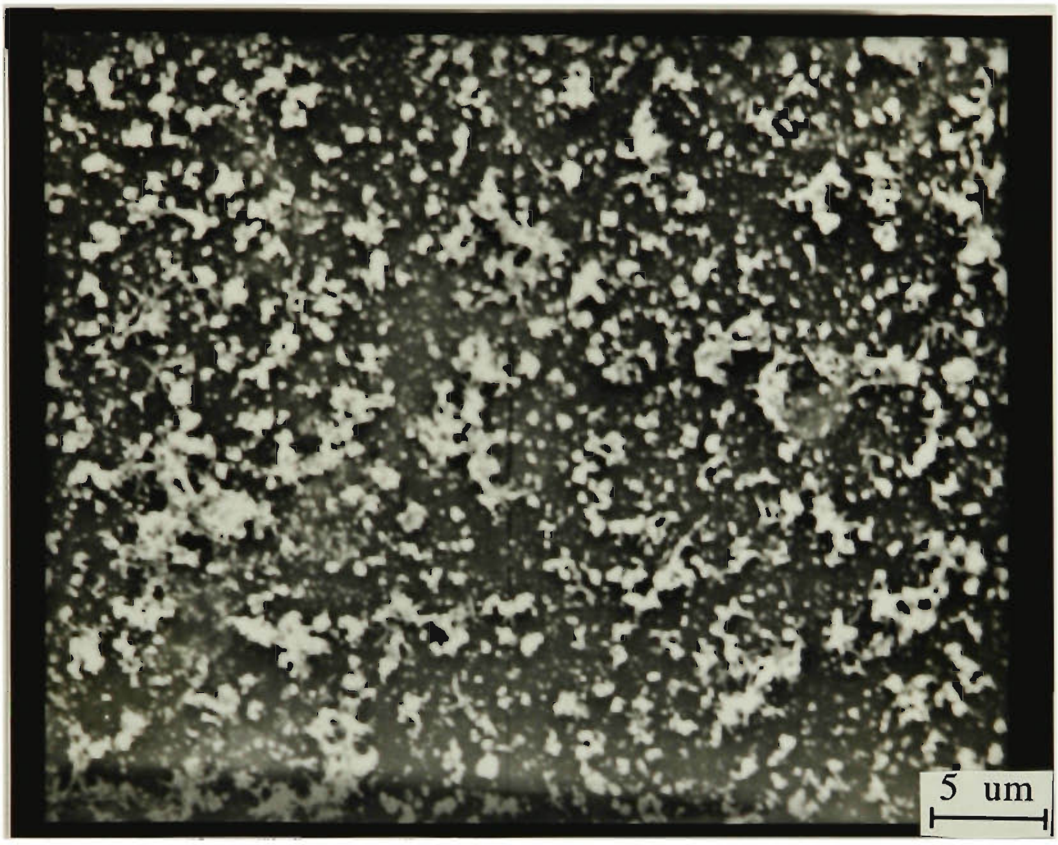


Figure 3.18: Scanning electron micrographs of solution side on glassy carbon .
Conditions: Polymer deposited at Eapp.=0.85 volt from 0.1 M aniline, 1.25 M HCl. (a) No stabilizer present, (b) 11.20 g/L PVA, (c) 11.20 g/L PEO, (d) 11.2 g/L PVP_2.

(b)



(c)

Figure 3.18 continued.

(d)

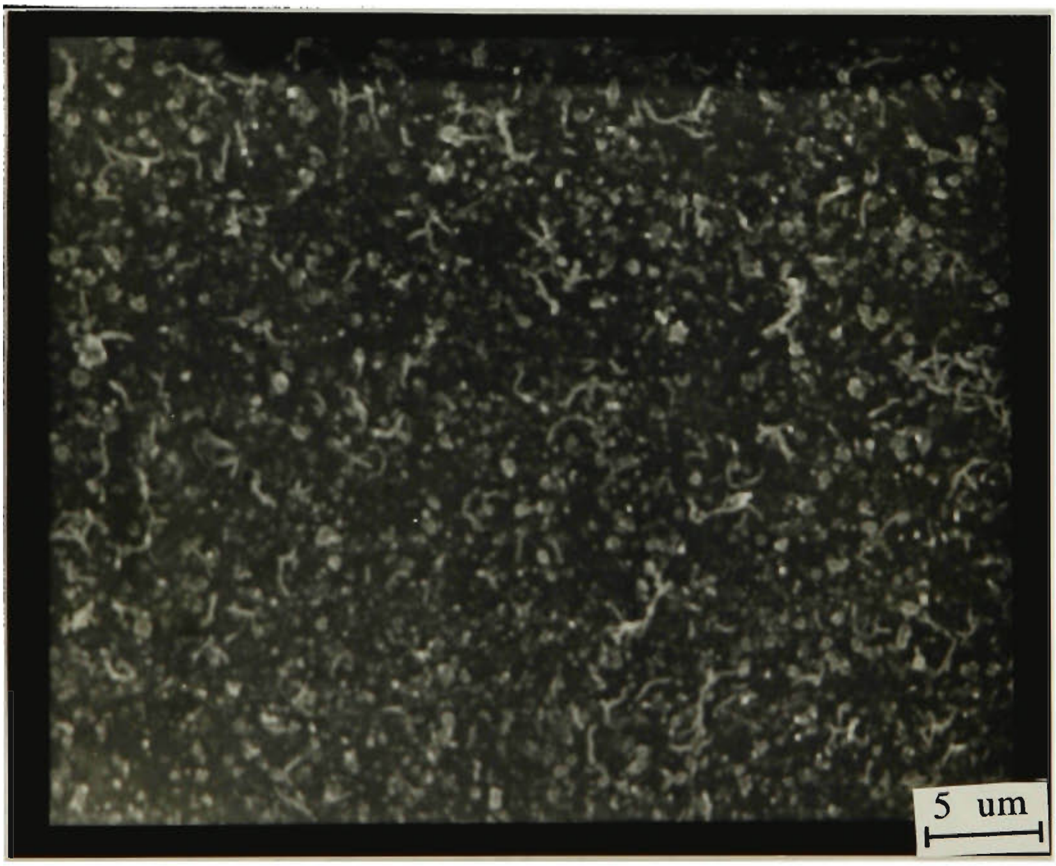


Figure 3.18 continued.

3.4 ADHESION CHARACTERISTICS OF ELECTRICALLY CONDUCTIVE POLYPYRROLE AND POLYANILINE ON ELECTRODE MATERIALS

Surface active agents or stabilizers have been used in this investigation to control the rate of deposition of polymer onto the electrode surface. The effect of type and concentration of stabilizer on the adhesive strength was also determined. A typical mechanism of separation during tensile testing is shown in Figure 3.19. Two to three repeat tests were conducted and the average value reported. For one system nine repeats were conducted and the error in this experiment was found to be ± 15 %. The results of the adhesion strength of both polypyrrole and polyaniline films on the various electrode materials are shown in Figures 3.20, 3.21, 3.22, 3.23.

In all cases the adhesive strength passes through a maximum as the concentration of stabilizer increases. Also all cases show that the type of stabilizer used has a significant effect on the adhesive strength of the coating to the substrate. Figure 3.24 summarises the maximum adhesion recorded for each system. The data in Figure 3.24 also shows that the maximum adhesion depends on the polymer type and type of electrode used. For a given electrode material (platinum) the polyaniline coating shows a higher adhesion than the polypyrrole. This is true for each type of stabilizer used. For the polypyrrole coatings, a comparison between the platinum and stainless steel electrodes show that the platinum gives higher adhesion for all stabilizer types. Similarly, polyaniline coatings on platinum electrodes show a higher adhesion than on glassy carbon for all types of stabilizer.

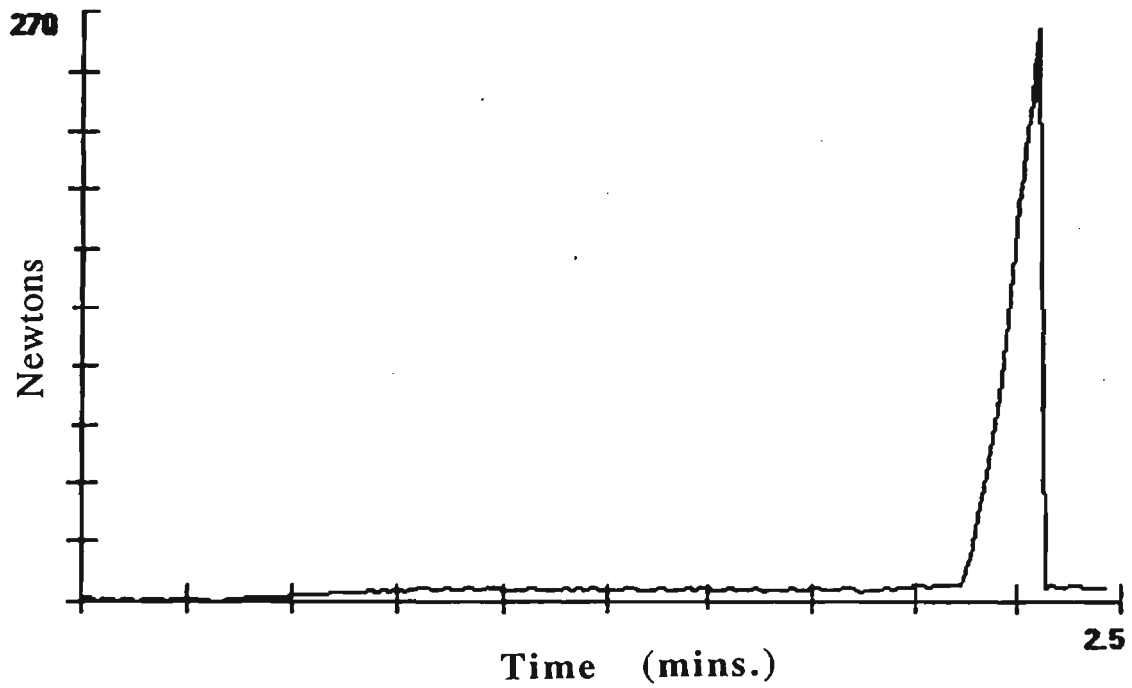


Figure 3.19: The process of detachment from the electrode surface.

Conditions: Glassy carbon substrate; Eapp.=0.82 V, PVP_2 stabilizer was used for the preparation of film; monomer solution 0.10 M aniline, 1.25 M HCl. Separation rate 1.0 mm/min.

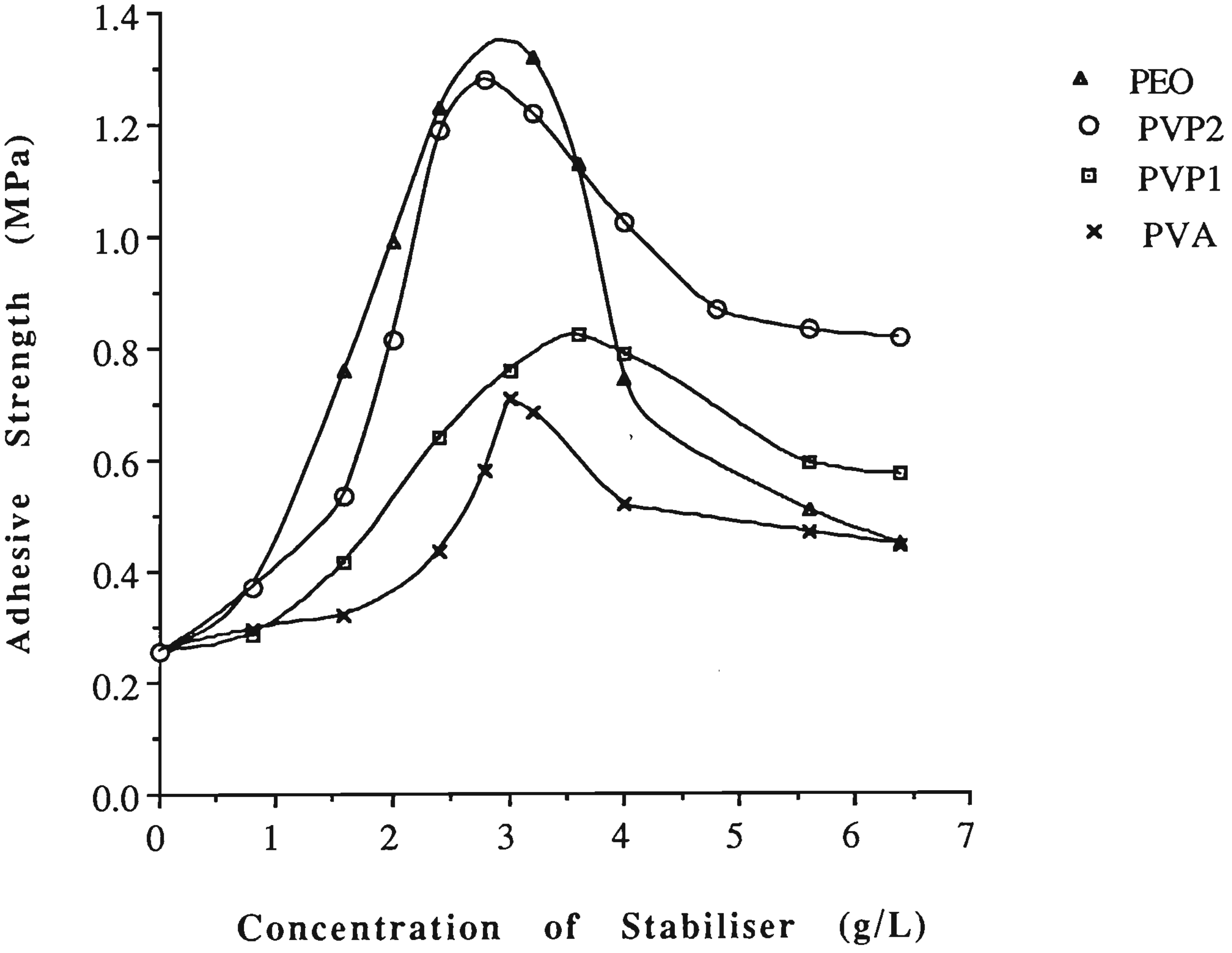


Figure 3.20: Adhesive strength of polypyrrole films coated on the stainless steel substrate.

Conditions: Deposition was carried out for five minutes; supporting electrolyte 1.0 M $NaNO_3$, 0.15 M pyrrole, Eapp.=0.90 V; stabilizer concentration range=0.80-6.40 g/L.

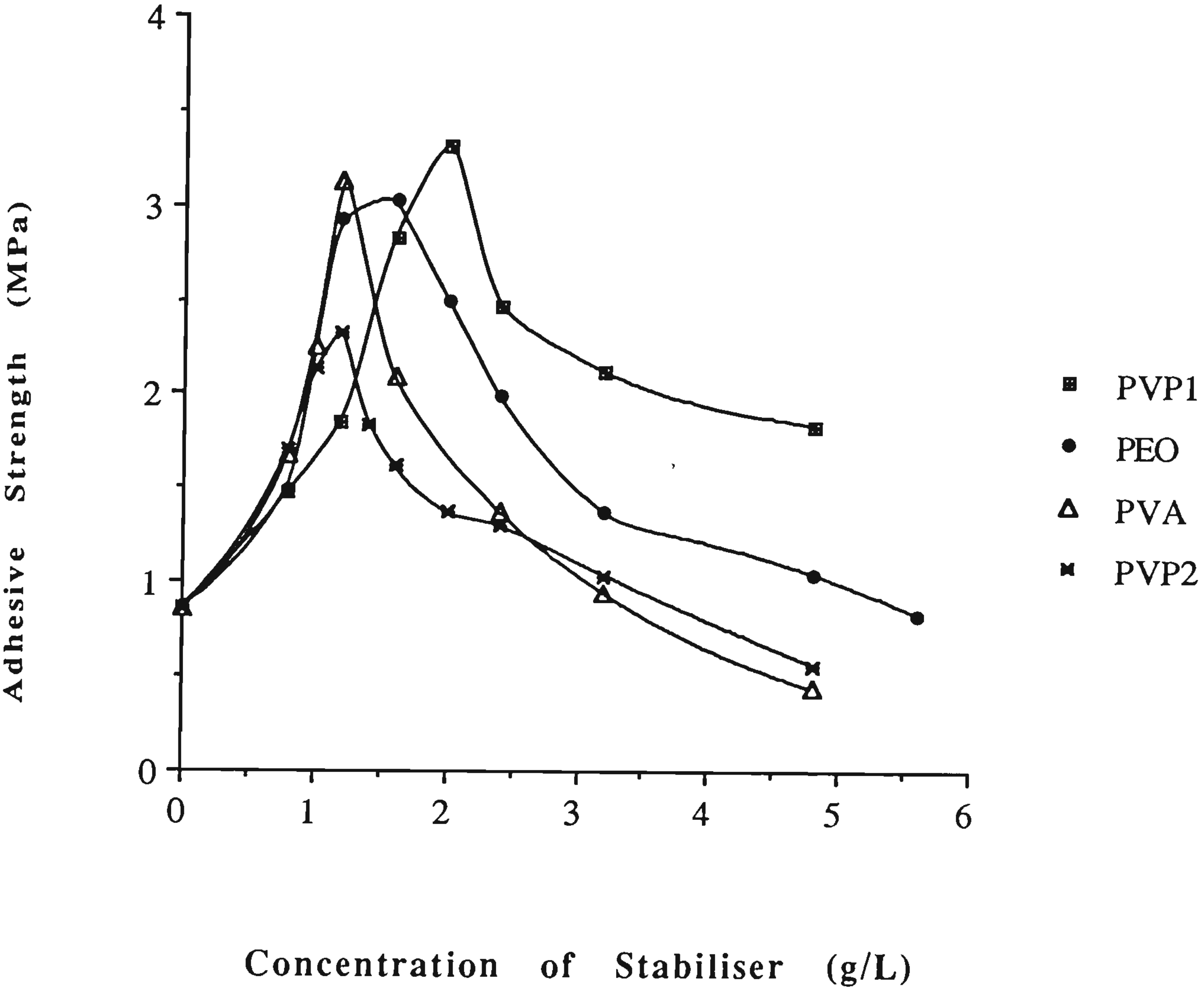


Figure 3.21: Adhesive strength of polypyrrole films coated on the platinum substrate.

Conditions: 0.15 M pyrrole, supporting electrolyte 1 M $NaNO_3$, range of stabilizer concentration 0.80-6.40 g/L. Deposition was carried out for three minutes, Eapp=0.90 V.

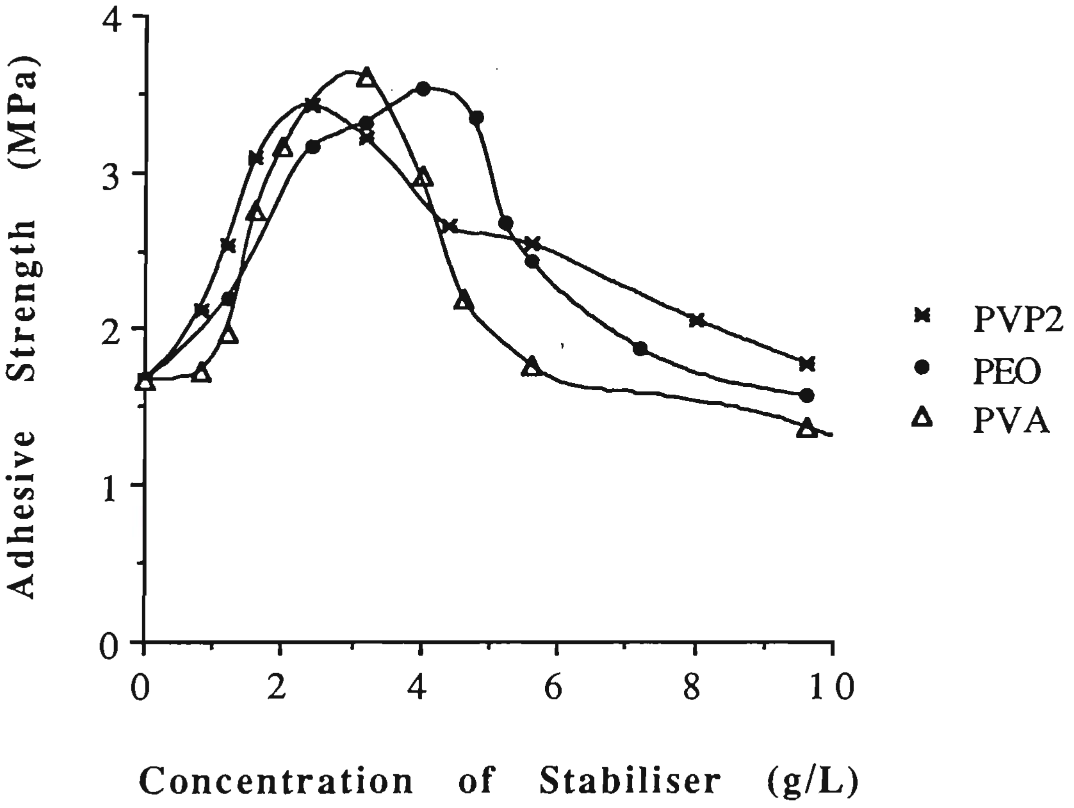


Figure 3.22: Adhesive strength of polyaniline films coated onto glassy carbon substrate.

Conditions: Deposition was carried out for 10 minutes. Supporting electrolyte 1.25 M HCl, Eapp=0.82 V, concentration range of stabilizers 0.80-12.80 g/L, 0.10 M aniline.

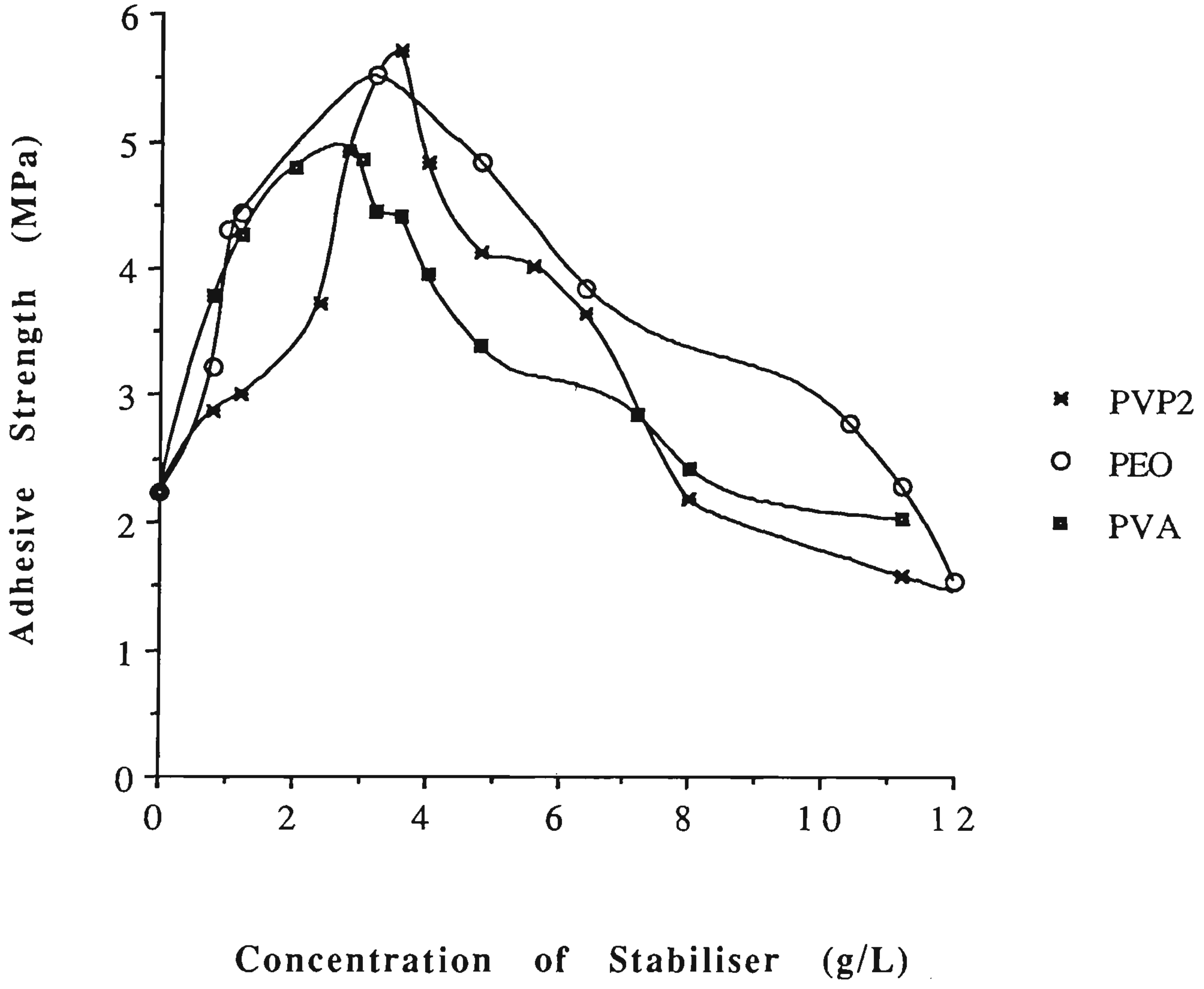


Figure 3.23: Adhesive strength of polyaniline films coated on the platinum substrate.

Conditions: Polymer was deposited for 10 minutes. Eapp= 0.82 V, supporting electrolyte 1.25 M HCl, 0.10 M aniline, range of stabilizer concentrations 0.80-12.80 g/L.

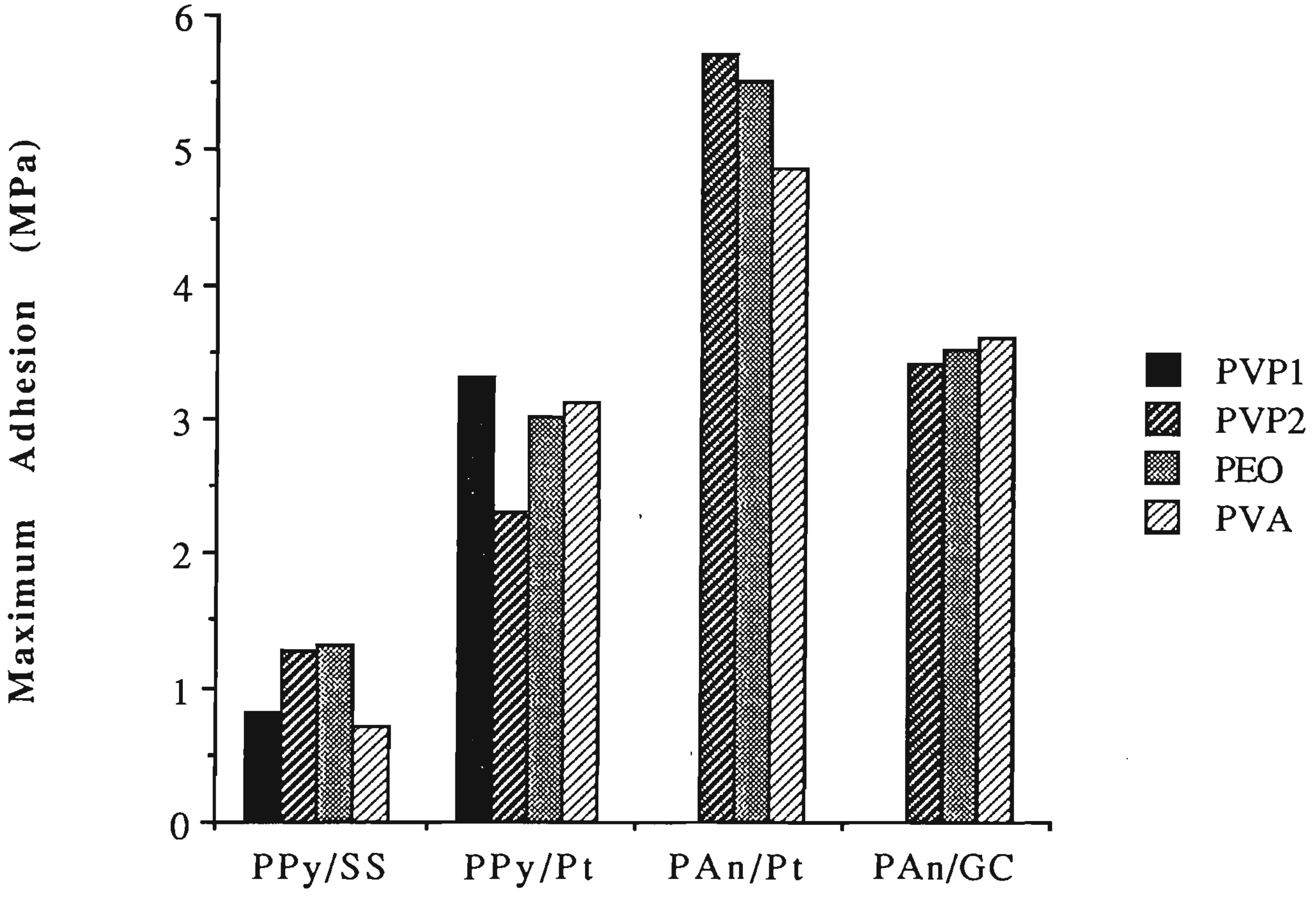


Figure 3.24: Summary of the maximum adhesion recorded for each system as follows:

[polypyrrole/stainless steel, polypyrrole/platinum, polyaniline/platinum, polyaniline/glassy carbon].

Figure 3.25 shows the result of blank experiments. In these the same processing procedure was followed except that there was no monomer in solution. Thus no polymeric coating was formed on the electrode. The adhesion strength is seen to steadily decline as the concentration of stabilizer increases. This result may also explain why the adhesion of the polymer coating decreases at high stabilizer concentrations. It is suspected that a layer of the stabilizer forms on the electrode surface at high stabilizer concentrations and this adheres poorly to the electrode. Thus, the coating can be easily removed under these conditions.

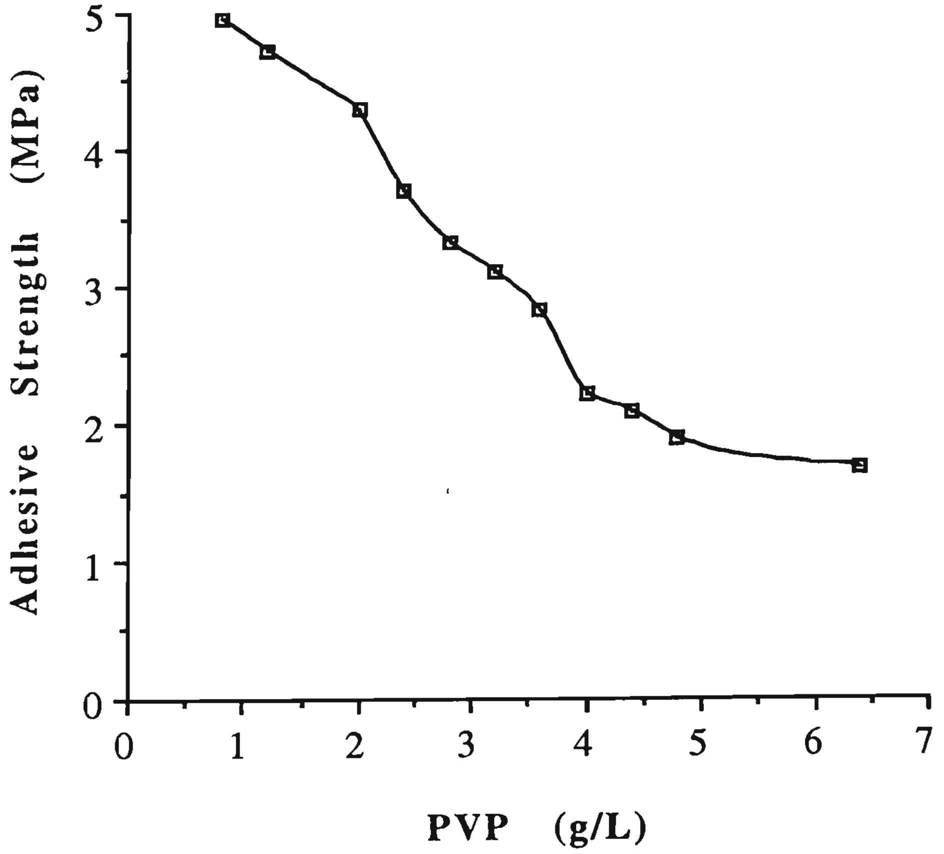


Figure 3.25: Adhesive strength with no monomer present in the solution (blank).

Conditions: PVP_2 stabilizer, Eapp=0.90 V, supporting electrolyte 1.0 M $NaNO_3$, stainless steel substrate.

Possible reasons for the initial increase in adhesion was investigated using SEM. In section 3.3.4 the morphology of the plate side of polypyrrole films deposited on stainless steel was reported. The films were observed to be porous, with porosity increasing with increasing concentration of stabilizer. From an adhesion viewpoint, the porous samples are likely to show lower adhesion strength since the degree of contact between the coating and substrate is reduced. In fact that the opposite trend was observed. The plate side of the polypyrrole films prepared on platinum electrode shows no porosity, even with higher concentrations of stabilizer (Figure 3.26). The difference in porosity may explain why the polypyrrole adheres more strongly to the platinum than to the stainless steel. However the change in porosity with increasing stabilizer content does not account for the initial increase in adhesion. The presence of stabilizer is likely to modify the surface energy of the polymer and/or its electrostatic nature. Since adhesion is influenced by these parameters, the increase in adhesion may be attributed to more favourable bonding between the polymer and substrate as the level of stabilizer increases.

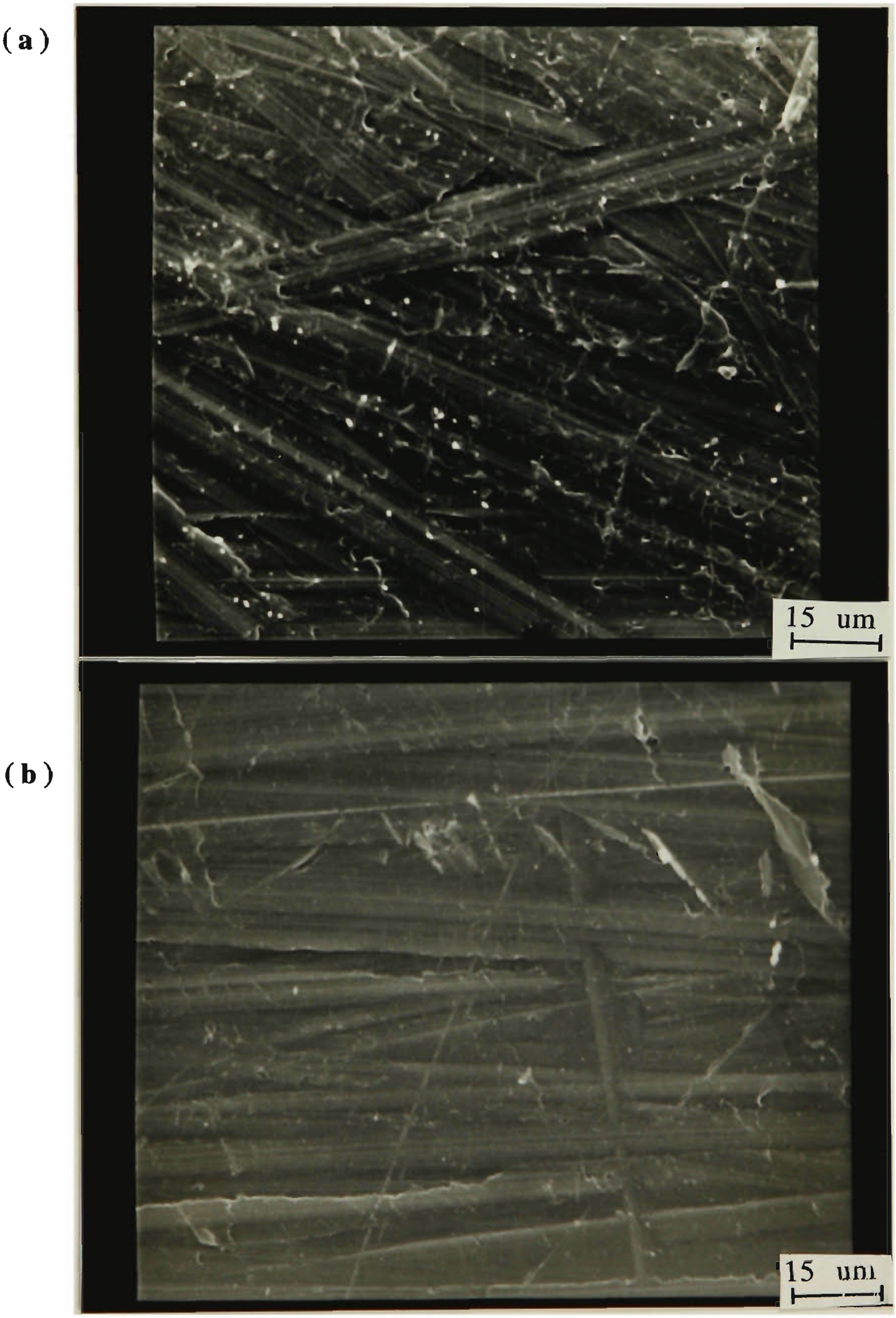


Figure 3.26: Scanning electron micrographs of plate side of polypyrrole films grown on platinum substrate.
Conditions: Polymer was deposited from 0.15 M pyrrole, 1.0 M $NaNO_3$, E_{app}= 0.90 V, (a) No stabilizer present, (b) 4.0 g/L PVP_2.

The effect of the applied potential used during electropolymerization on the adhesive strength of polypyrrole coatings on platinum and stainless steel was determined, and the results are given in Table 3.4. For the platinum substrate a lower potential resulted in a significant increase in the adhesive strength. This is probably because the applied potential affected the homogeneity of deposited films (72). However the opposite effect was observed for the stainless steel electrode. The lower potential gave a lower adhesion strength but the reason for this is unclear.

Table 3.4: Influence of applied potential on the adhesive strength (MPa)

Type of substrate	$E_{app.}$=0.90 (volt)	$E_{app.}$=0.72 (volt)
Stainless Steel	1.30 (MPa)	0.80 (MPa)
Platinum	2.30 (MPa)	3.60 (MPa)

3.5 CONCLUSION

Electropolymerisation of pyrrole and aniline in aqueous solutions of sodium nitrate ($NaNO_3$) and hydrochloric acid (HCl) with additions of different steric stabilisers (PVP, PVA, PEO) was conducted using potentiodynamic, potentiostatic and galvanostatic techniques. Different substrates (platinum, glassy carbon and stainless steel) were used. Not only were the electropolymerisation processes investigated but also the resultant polymers were characterised in terms of electroactivity, morphology and adhesion.

Thus, under galvanostatic conditions, the growth potential of the polymers was little affected by the presence of stabilisers. For potentiostatic and potentiodynamic methods, however, the presence of stabilisers reduced the rate of growth of the polymer. Furthermore, stabilisers were found to affect the morphology of the plate side and solution side of films. Adhesion to the substrate increased with increasing concentration of stabiliser until a maximum was attained, beyond which further additions of stabiliser began to reduce the adhesion. On some substrates, such as stainless steel, the presence of stabiliser improved the electroactivity of the deposited polymer.

The electropolymerisation of monomers is affected by the presence of stabilisers. Although the growth potential under galvanostatic conditions was little affected by the addition of stabilisers, the rate of growth of the polymers under potentiostatic or potentiodynamic conditions was reduced in the presence of stabilisers.

It has been clearly shown that stabilisers usually employed to affect the morphology of conducting polymers during chemical polymerisation also have a marked effect on electrodeposited material. The morphology of the electrodeposited conducting polymer can be modified by the presence of certain stabilisers. Since the morphology of electrodeposited polymers has been linked to the mechanical properties (208), the use of steric stabilizers may be a useful means of controlling the properties of conductive polymers through the control of the morphology.

This investigation has shown that the degree of adhesion of polypyrrole and polyaniline coatings to the electrode surface following electropolymerization is significantly affected by various processing variables. Especially it has been observed that:

1) Adhesion is stronger for polyaniline coatings as compared to polypyrrole coatings.

2) The adhesion strength passes through a maximum as the concentration of stabilizer increases, regardless of polymer type, stabilizer type and electrode material.

3) The effect of stabilizer type on the adhesion depends upon both the coating and electrode.

4) For a given stabilizer, the adhesion depends upon the electrode material (with platinum giving the highest adhesion) and the polymer type (with polyaniline giving higher adhesion than polypyrrole).

5) The applied potential also affects the adhesion strength.

From these results, it is apparent that the processing conditions may be manipulated so as to achieve the desired level of adhesion. In practice, the concentration of stabilizer is the most appropriate parameter to vary, since the polymer type, electrode material and applied potential are usually dictated by the need to optimise the electrical properties of the deposited polymer.

Finally it was observed that on some substrates (e.g. stainless steel) the presence of the stabiliser improves the electroactive nature of the deposited layer. This is due to the fact that corrosion of the substrate is hindered by the presence of stabiliser. Thus, the use of steric stabilisers during the electrosynthesis of conducting polymers can be useful in that it enables the deposition of more electroactive layers on easily corroded substrates and can be used to improve adhesion to substrates.

CHAPTER 4

ELECTROCHEMICAL PRODUCTION OF POLYPYRROLE AND POLYANILINE COLLOIDS

4.1 INTRODUCTION

The production of conducting polymer colloids is usually achieved via chemical oxidation of the appropriate monomer in the presence of a steric stabiliser as described in chapter 2 (106,112,114,128). This results in production of monodispersed colloidal sols in the size range 10 - 300 nm. Given the limitations imposed by the lack of solubility of conducting polymers on processing of these materials, the use of colloids to circumvent this problem has been advocated (19, 20, 35, 93,105). These colloidal sols are electroactive and indeed electrodeposition of the colloids can be initiated at negative potentials to form conductive "films" (chapter 2) (199).

However, the use of chemical oxidation to produce these colloids has some limitations. Specifically it is more difficult to control the oxidation potential during chemical oxidation and it is known that excursions to higher potentials will result in overoxidation with a subsequent deterioration in electronic conductivity and mechanical properties (209,210). In addition only a limited number of counterions can be incorporated when chemical oxidation is employed.

In chapter 3, it was demonstrated that the presence of steric stabilisers in the polymerisation solution delays the deposition of conducting polymers (211, 212). Many reports (213-215) have suggested that the first step in polymer deposition involves polymerisation in solution followed by precipitation of oligomeric chains onto the electrode surface. Lang et al (214) showed that a polymer was only deposited onto a rotating platinum disk electrode when a rotation rate of less than 2900 r.p.m. was employed. Tanaka et.al (212) and Beck (213) have also confirmed the existence of soluble, oxidized oligomeric intermediates during the electropolymerisation of pyrrole. These intermediates were detected at the outer ring of a rotating ring disk electrode. The formation of soluble intermediates during electropolymerisation has also been supported by Baker and co-worker (216). Stirring the solution also greatly inhibited polymer deposition (76). This is presumably due to enhanced transport of intermediates away from the electrode surface. The fact that stirring the solution or rotating the electrode inhibits the electropolymerization process implies the presence of soluble intermediates. These results suggest that it may be possible to prepare conductive polymer colloids using electrochemical polymerization. In order to explore this possibility, further studies were initiated into the effects of hydrodynamics on the electrochemical polymerization/deposition process by using a rotating electrode. Secondly, the effects of various steric stabilizers on these processes were also considered.

4.2 EXPERIMENTAL

4.2.1 Reagent and Standard Solutions

All reagents were used as received without further purification unless stated otherwise. Aqueous solutions were prepared using Milli-Q ^{TM} water. Pyrrole (Sigma) was freshly distilled and stored in the fridge. Materials used for preparation of colloids were polyvinylalcohol (PVA, Mw = $3 \times 10^4 - 7 \times 10^4$), sodium nitrate ($NaNO_3$), and hydrochloric acid (HCl) (AR grade) from

BDH. Polyethyleneoxide (PEO, Mw = 3 x 10^5) from Aldrich, polyvinylpyrrolidone (PVP Mw = 1.2 x 10^6) from TCI, nitric acid and sulfuric acid (AR grade) from Ajax chemicals, KI, $NaClO_4$ and NaCl (AR grade) from BDH, $C_6H_5SO_3Na$ and PTS(H) from Aldrich and PTS (Na) from Merck, reticulated vitreous carbon (RVC) was obtained from Energy Research and Generation Inc.

4.2.2 Preparation of Polypyrrole Colloids

Sodium nitrate, potassium iodide, sodium perchlorate, sodium chloride, 4-$(CH_3)C_6H_4SO_3Na$ (PTS) and $C_6H_5SO_3Na$ were used as supporting electrolytes. In addition PVP, PVA and PEO were considered for use as stabilisers. In a typical experiment 4 mL pyrrole was added to 200 mL of a stirred aqueous solution containing 1 M $NaNO_3$ and a minimum amount of the stabiliser PVP (1.80 g/L), PVA (3.0 g/L) or PEO (3.20 g/L). This solution was recirculated through the electropolymerisation cell. The polymerisation reaction was carried out at room temperature for 3.5 hours. A constant current density of ~0.58 mA/cm^2 was used for these reactions. After electropolymerisation the colloidal dispersions were ultracentrifuged (55,000 r.p.m.) for one hour to produce a sediment. The supernatant was decanted and the sediment rinsed with distilled water.

4.2.3 Instrumentation

Electrochemical experiments were carried out in a three electrode cell employing a working electrode (RVC), reference electrode (Ag/AgCl (3 M NaCl)) and an auxiliary electrode (RVC). The solution in the cell contained 0.30 M pyrrole, 0.05-3.50 M supporting electrolyte, and the appropriate stabiliser.

Electrochemical control was achieved using either a Bioanalytical Systems (BAS) model 100 A or model CV-27 potentiostat. A Sorvall OTD ultracentrifuge was used. An EG & G Princeton Applied Research potentiostat/galvanostat (Model 363) and a Master flex pump were used throughout this work. An in-house magnetic stirrer was employed. Rotating electrode model JCZ-A (7th Factory of Telecommunication Devices of Shandong, China) was employed. A JEOL 2000 **FX** transmission electron microscope (TEM) or a Hitachi S450 scanning electron microscope (SEM) were employed to examine the morphology of the dried colloid particles. Transmission electron micrographs and scanning electron micrographs were obtained using diluted re-dispersed latex dried on carbon coated copper grids and gold foil.

4.3 RESULTS AND DISCUSSION

The initial studies in this work considered the effect of the steric stabilisers (PVA, PEO and PVP) on the polymerisation/deposition process for both polypyrrole and polyaniline under static and hydrodynamic control.

Using galvanostatic polymerisation under hydrodynamic control it was found that the presence of stabiliser increased the potential required to sustain polymerisation under constant current conditions (Table 4.1) and (Table 4.2).

Table 4.1: Effect of (PVA, PVP, PEO) concentration and rotation rate on the deposition potential of pyrrole.

Rotation rate (rpm.)		0.0	500	1000	2000	3000	4000
E (V)	no stabiliser	0.68	0.71	0.73	0.77	0.84	0.84
	1.6 g/L PVA	0.71	0.73	0.76	0.83	0.84	0.83
	3.2 g/L PVA	0.71	0.78	0.82	0.83	0.84	0.84
	1.6 g/L PVP	0.71	0.73	0.75	0.82	0.84	0.83
	3.2 g/L PVP	0.71	0.73	0.77	0.82	0.84	0.84
	1.6 g/L PEO	0.70	0.73	0.76	0.78	0.79	0.82
	3.2 g/L PEO	0.75	0.75	0.76	0.80	0.82	0.83

Conditions: Current density 0.75 mA/cm^2, 0.15 M pyrrole, 1.00 M $NaNO_3$, glassy carbon disk electrode.

Table 4.2: Effect of rotation rate and stabilizer concentration on the deposition potential of aniline.

Rotation rate (rpm)		0.0	500	1000	2000	4000
E(V)	no stabilizer	0.83	0.89	0.93	0.93	1.10
	PVA 2.0 g/L	0.84	1.00	1.00	1.00	1.00
	PVA 4.0 g/L	0.88	1.00	1.00	1.00	1.00

Conditions: Current density 1.0 mA/cm^2, 1.25 M HCl, 0.10 M aniline, glassy carbon disk electrode.

The results show that in all cases the polymerization/deposition potential increased when the electrode was rotated. In most cases the potential increased as the rotation rate increased. It is also observed that the presence of a steric stabilizer further increases the polymerization/deposition potential, and that in most cases the potential increased with increasing concentration of stabilizer. These results indicate that both the presence of stabilizer and rotation of the electrode mitigated against either monomer or oligomer oxidation. The latter is more likely. This is probably due to the fact that the stabiliser blocks the electrode surface or prevents deposition. In all cases a conducting polymer was still formed on the electrode surface as confirmed by the cyclic voltammetric response of the material (Figure 4.1).

(a)

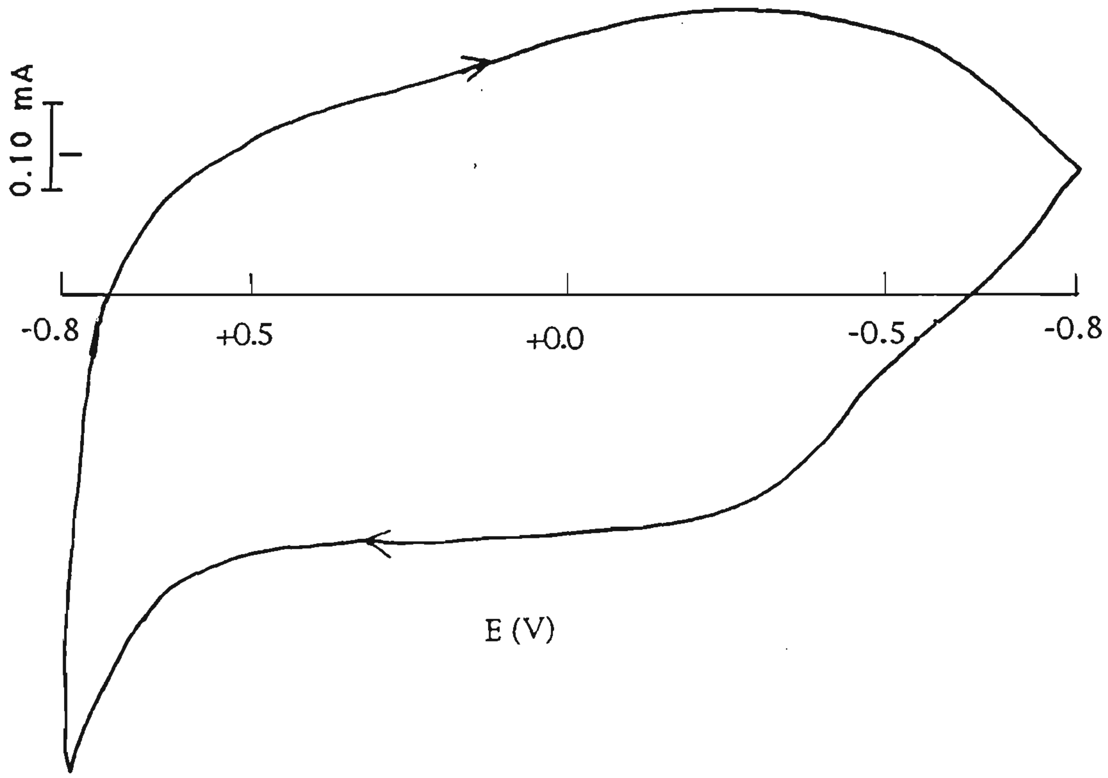


Figure 4.1: Cyclic voltammograms obtained after galvanostatic deposition of polypyrrole.

Conditions: (a) 0.15 M pyrrole and 1.00 M $NaNO_3$ no stabilizer present, ω=0.0, (b) as for (a) but ω= 2,000 r.p.m, (c) as in (b) plus PVP 2 stabilizer (3.20 g/L). Current density for electropolymerization 0.75 mA/cm^2, supporting electrolyte was 1.00 M $NaNO_3$, scan rate 100 mV/sec.

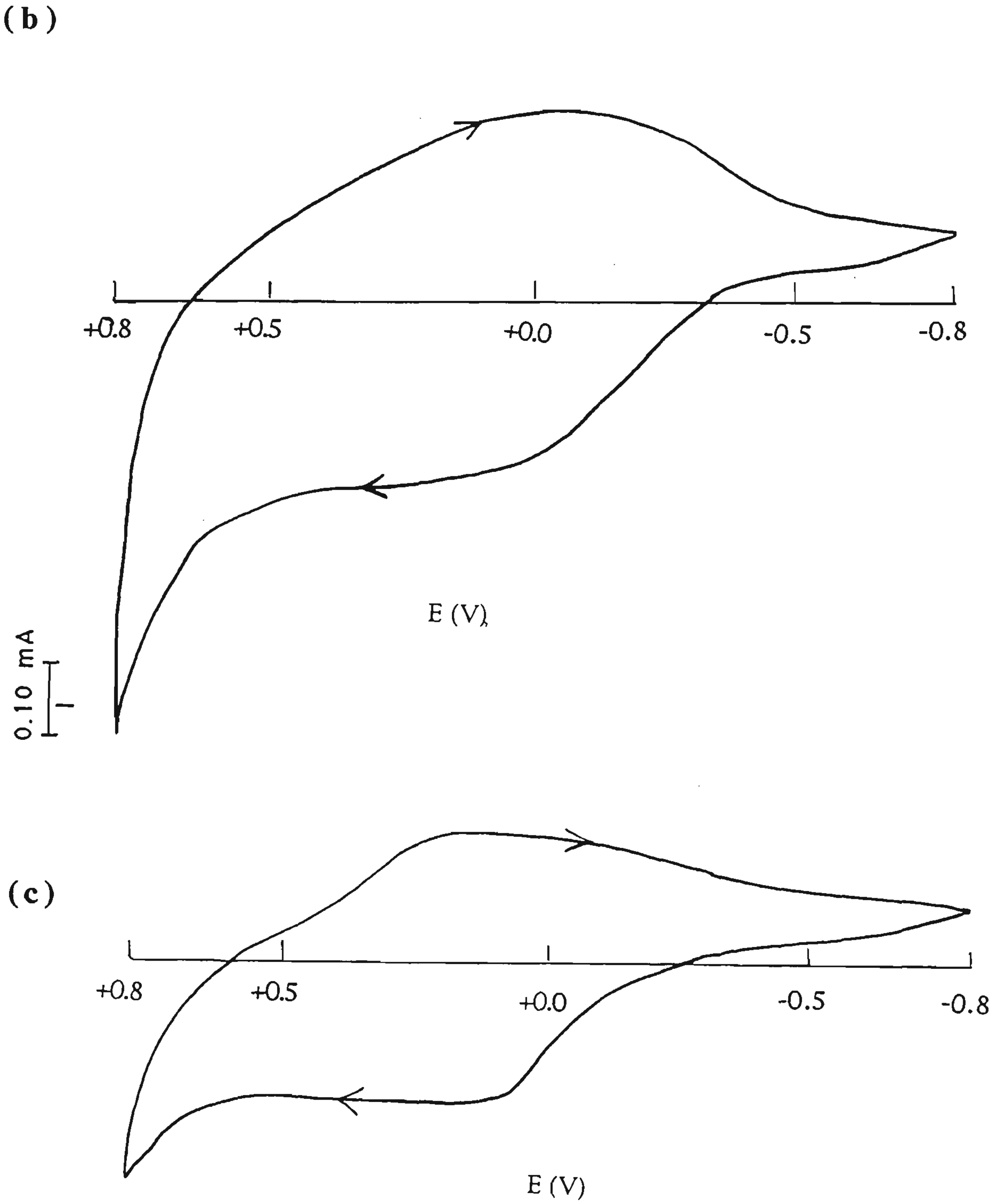


Figure 4.1 continued.

A similar series of experiments as performed using potentiostatic control.

The effect of stabilizer concentration and rotation rate on the polymerisation charge passed after five minutes is shown in Table 4.3 and 4.4 for pyrrole and aniline respectively.

Table 4.3: The effect of stabilizer concentration and rotation rate on the polymerisation charge passed during the first five minutes of polymerisation

Rotation rate (rpm.)		0.0	500	1000	2000	3000	4000
Charge (C)	no Stabiliser	0.419	0.771	0.567	0.395	0.333	0.264
	1.6 g/L PVA	0.360	0.433	0.390	0.265	0.037	0.024
	3.2 g/L PVA	0.265	0.363	0.333	0.269	0.022	0.014
	1.6 g/L PVP	0.377	0.406	0.206	0.103	0.033	0.027
	3.2 g/L PVP	0.300	0.413	0.277	0.083	0.018	0.014
	1.6 g/L PEO	0.423	0.653	0.526	0.368	0.294	0.153
	3.2 g/L PEO	0.419	0.604	0.539	0.361	0.236	0.072

Conditions: Edeposition 0.75 V, 0.15 M pyrrole, 1.00 M $NaNO_3$, glassy carbon disk electrode.

Table 4.4: The effect of PVA concentration and rotation rate on the polymerization charge passed during the first five minutes of polymerisation (aniline).

Rotation rate (rpm.)		0.0	1000	2000	4000
Charge (mC)	no Stabiliser	18.7	5.3	4.7	4.1
	2.0 g/L PVA	17.9	7.4	4.4	2.4

Conditions: $E_{deposition}$=0.82 V, 0.10 M aniline, 1.25 M HCl, glassy carbon disk electrode.

For polypyrrole production an increase in the rotation rate caused an initial increase in charge consumption as monomer is delivered more effectively to the electrode surface. However further increases in rotation decreased the charge consumed as the polymer deposition process becomes less efficient. For aniline polymerization only the latter effect was observed. This may be due to the small number of rotation rates studied and further investigation of slow rotation rates may show an increase in charge, as was observed with polypyrrole

In virtually all cases the presence of stabiliser decreased the charge consumed at all rotation rates. PEO, however, had no effect on polymerization current in the absence of rotation and the effect was markedly less than that observed with the other stabilisers at higher rotation rates. In all cases the effect was amplified with higher rotation rates (>2,000 rpm), e.g. using PVP or PVA polymerization currents at higher rotation rates (4,000 r.p.m.) were markedly decreased. The above results suggest that while PVA and PVP inhibit the normal oxidation response, the presence of PEO has minimal effect.

Cyclic voltammograms of the material deposited on the anode indicate that the rotation of the electrode and/or the presence of stabiliser decreases the amount of electroactive material deposited (Figure 4.2).

(a)

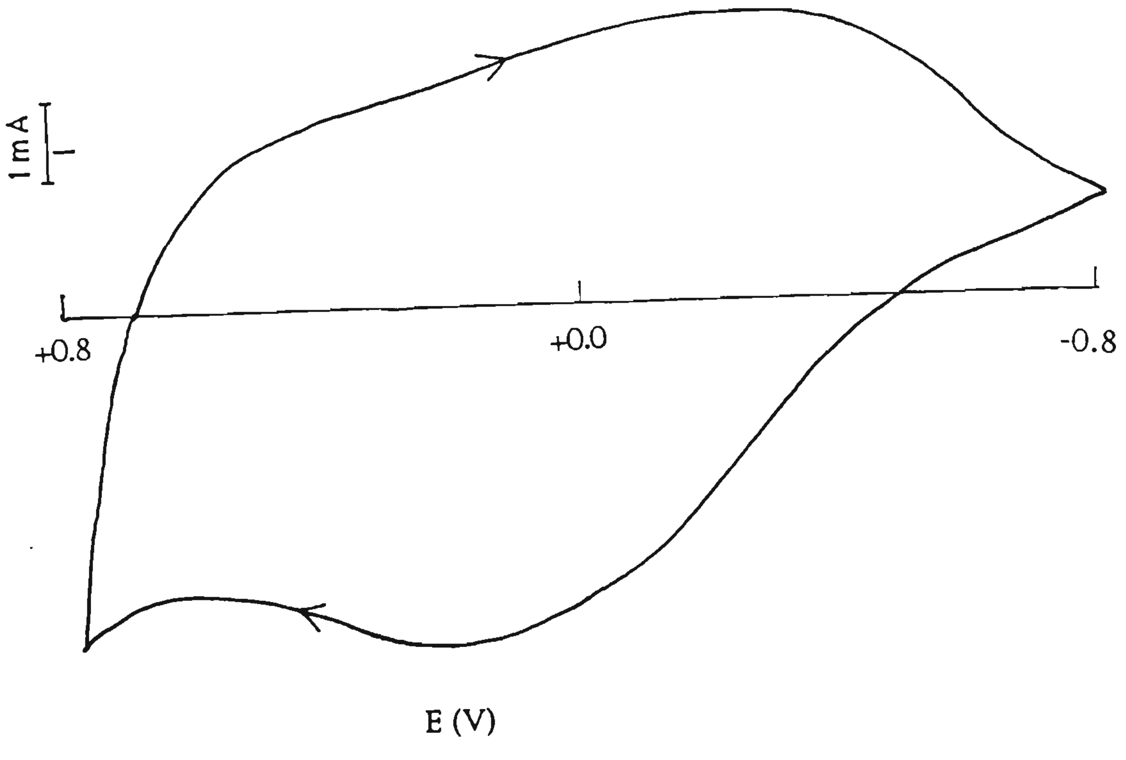


Figure 4.2: Cyclic voltammogram recorded after deposition in the presence of stabilizer under hydrodynamic conditions.

conditions. : (a) 0.15 M pyrrole and 1.0 M $NaNO_3$. ω=0.0, (b) as for (a) but ω=4,000 r.p.m. (c) as for (b) plus 3.2 g/L PEO. (d) as for (b) plus 3.20 g/L PVA. $E_{deposition}$= 0.75 volt. $T_{deposition}$ =5.0 minutes. Scan rate 100 mV/s, supporting electrolyte=1.0 M $NaNO_3$.

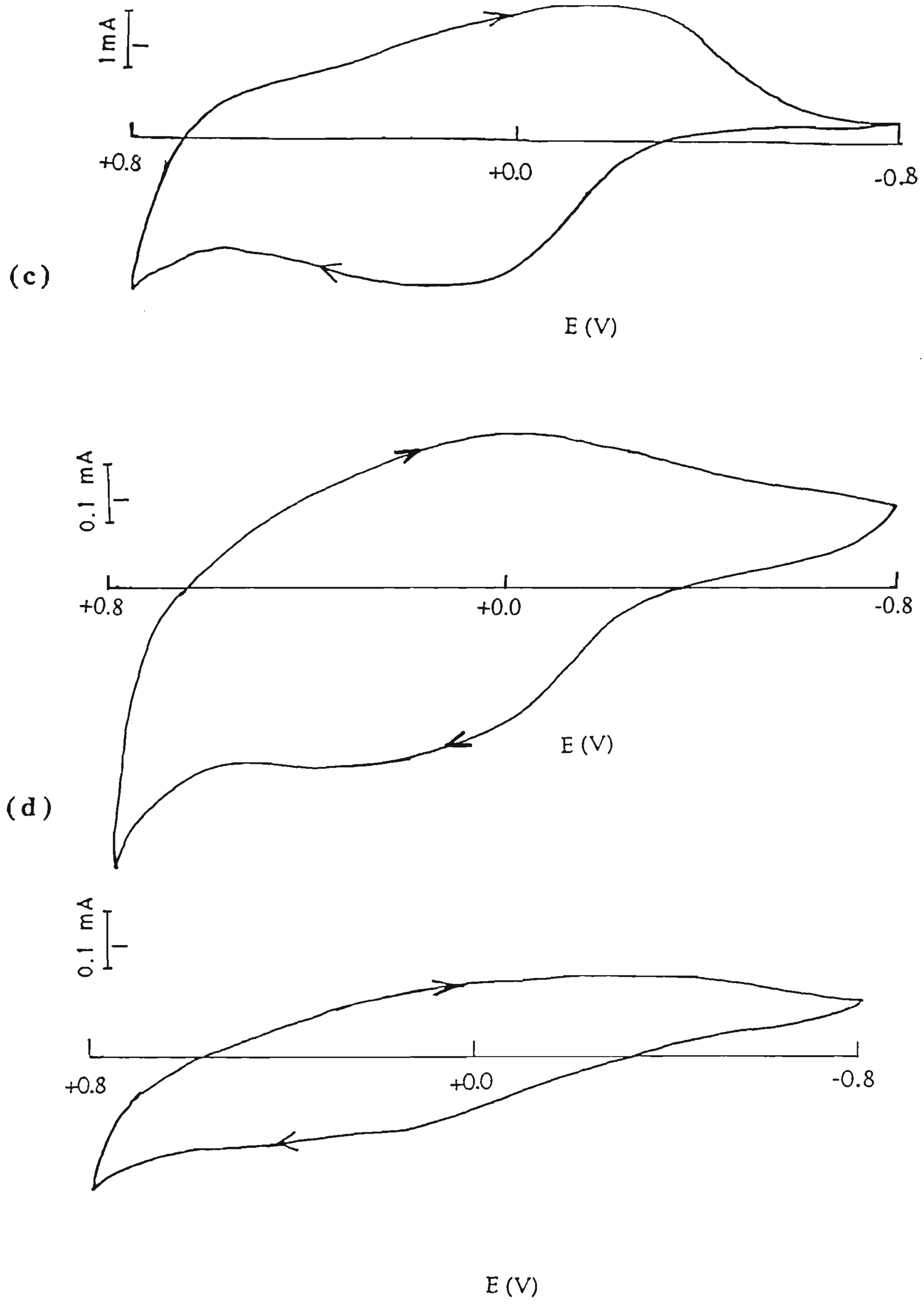


Figure 4.2 continued.

Figure 4.2 (a) and (b) show that the amount of current measured during the cyclic voltammetry scan decreases as the rotation rate employed during polymerization increases. A similar reduction was observed when higher concentration of stabilizer was used during polymerization (Figure 4.2 (c) and (d)).

This series of results as well as the results presented in chapter 3 has shown that both hydrodynamic conditions and the presence of steric stabilizers retard the polymerization/deposition process. The results suggest that the conditions may be manipulated so as to prevent deposition completely and produce colloidal polymer by the electrochemical process.

4.3.1 Preparation of Polypyrrole Colloids in a Flow Through Electrochemical Cell

In order to take advantage of the hydrodynamic effects a flow-through cell containing a porous electrode was constructed. The cell used a porous reticulated vitreous carbon working electrode and a peristaltic pump, as shown Figure 4.3.

The cell volume was 265 mL. The surface area of the working electrode was caculated to be 858 cm^2 and the auxiliary electrode was calculated at 1716 cm^2. A minimum flow rate of 25 mL/min was used throughout this work. Various counterions (NO_3^-, I^-, Cl^-, paratoluenesulfonate (PTS), benzene sulfonate (BS) and ClO_4^-) were used, in conjunction with the different stabilizers described below. A constant monomer concentration (0.30 M pyrrole) and various supporting electrolyte concentrations (0.50-1.0 M) were employed throughout.

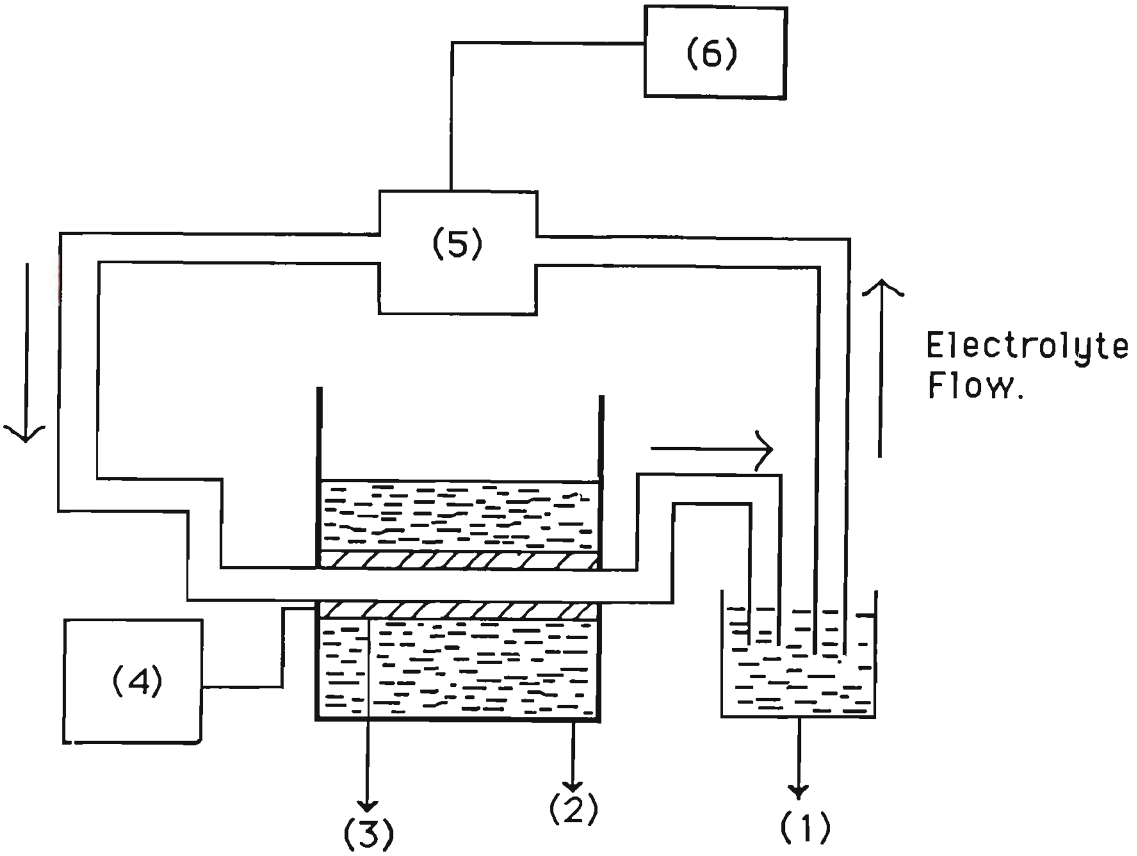


Figure 4.3: Schematic of flow through electropolymerization cell.

(1) Electrolyte solution

(2) Cell

(3) Working Electrode

(4) Galvanostat

(5) Pump

(6) Flow rate controller

Polyethylene oxide: The use of polyethylene oxide at both 3.2 and 8.0 g/L was considered. It was found that electroactive colloids could only be produced when $NaNO_3$ was employed as the electrolyte. Colloid was produced with both concentrations of stabiliser. As described previously in chapter 2 (209) these colloids could be deposited and were shown to be electroactive since the expected polymer oxidation/reduction responses were observed. With $NaNO_3$ 0.25 g of colloid was produced from ~1g of monomer after 3.5 hours (stabilizer concentration 3.2 g/L.). The transmission electron micrograph of the colloid is shown in Figure 4.4. The colloidal particles are shown to be spherical, but with a wide range of sizes. With all other counterions the solution was not discoloured after three hours of polymerisation indicating little, or no, colloid formation.

Polyvinyl alcohol: Using PVA, colloidal material was produced with both nitrate ($NO3^-$) or iodide (I^-) counterions. Colloids were produced at two different concentrations of PVA (3.0 and 8.0 g/L). A typical cyclic voltammogram of the colloidal dispersion is shown in Figure 4.5, which shows it to have considerable electroactivity.

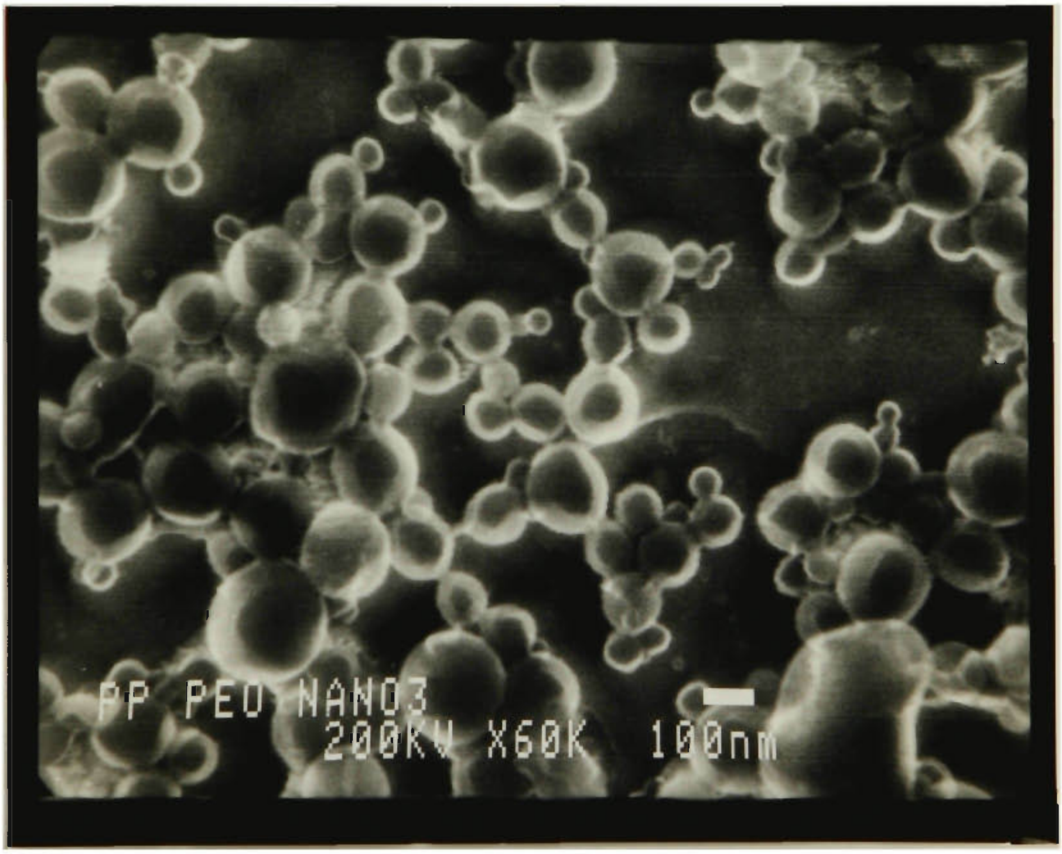


Figure 4.4: Transmission electron micrographs of polypyrrole colloid produced in the flow through cell using PEO stabilizer (6.0 g/L).

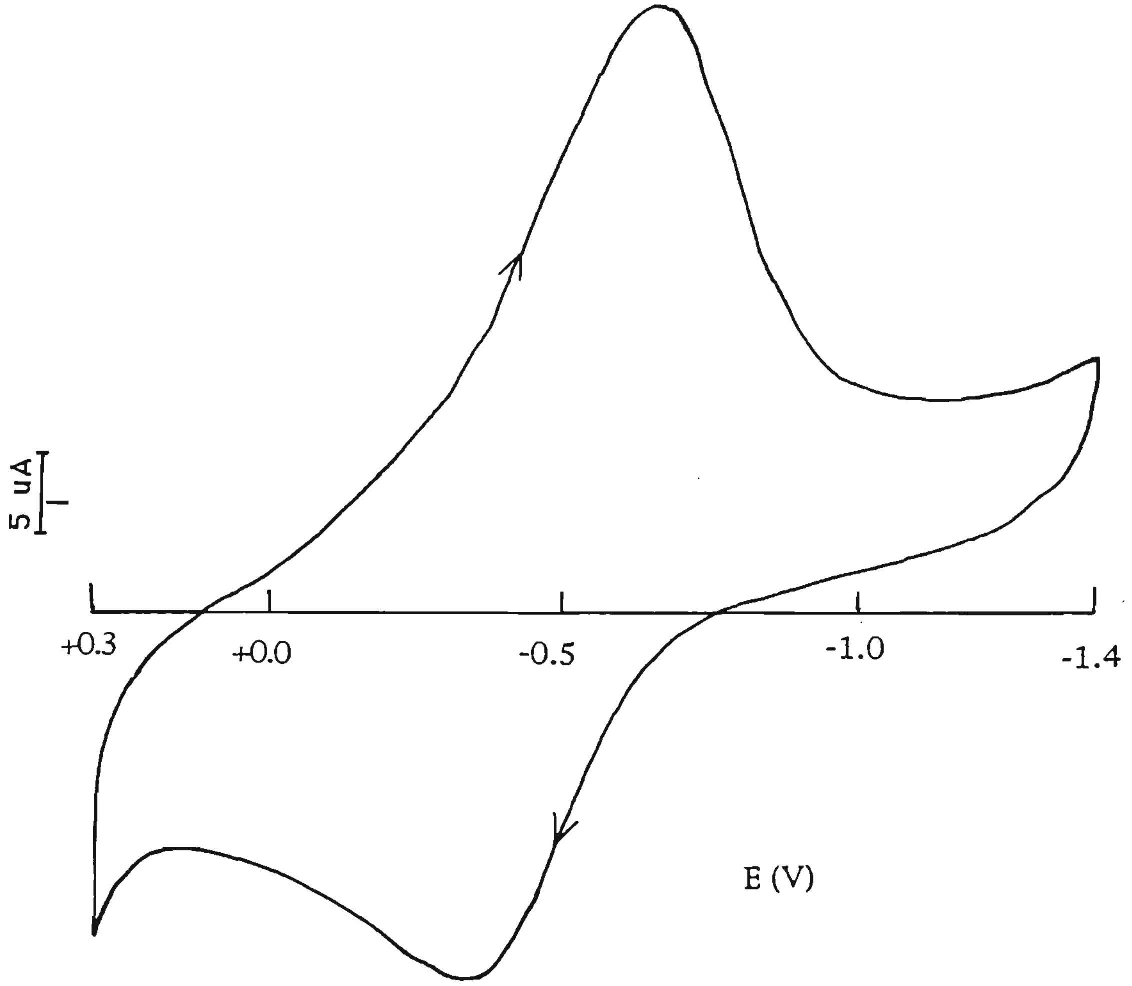


Figure 4.5: Cyclic voltammogram of a polypyrrole colloidal dispersion.
Conditions: Working electrode glassy carbon; scan rate 100 mV/s; (PVA stabilizer and supporting electrolyte KI were used for the colloid formation).

Polyvinylpyrrolidone (PVP): With PVP colloids could be produced with all of the counterions studied. The yield of colloids produced varied significantly with the type of counterion used (Table 4.5).

However the reasons for this variation are not yet clear. A typical cyclic voltammogram of a colloidal dispersion is shown in Figure 4.6, and again it was observed to be electroactive.

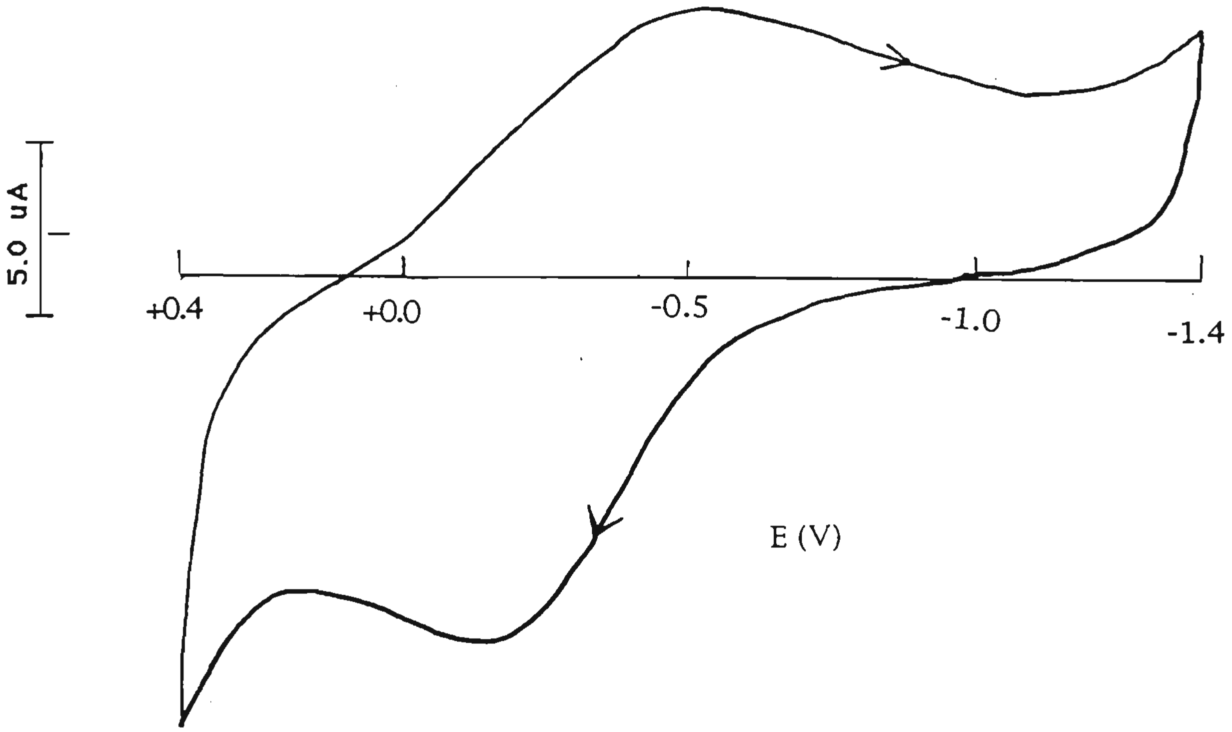


Figure 4.6: Cyclic voltammogram of a polypyrrole colloidal dispersion.

Conditions: Working electrode=glassy carbon; scan rate=100 mV/s; PVP stabilizer; supporting electrolyte=1.0 M $NaNO_3$.

Table 4.5: Yield of colloid from one gram of monomer (*).

Monomer type	Stabilizer type	Supporting electrolyte	Reaction time (h)	Yield of polymer per one gram of monomer (gram)
Pyrrole	PVA	KI	3.50	0.26
"	PEO	$NaNO_3$	3.50	0.25
"	PVP	$NaClO_4$	5.0	0.14
"	"	NaCl	5.0	0.11
"	"	PTS	5.0	0.08
"	"	BS	5.0	0.07
Aniline	PVA	HNO_3	5.0	0.18

(*) Colloid was prepared electrochemically.

4.3.2 Electrodeposition of Polypyrrole Colloids

In chapter 2 it was reported that it is possible to deposit conductive electroactive colloids onto substrates by imposition of a negative potential. It was found that all of the colloids produced electrochemically could be deposited in this way. A typical chronoamperogram for deposition is shown in Figure 4.7 with the increase in current indicating the formation of a conductive deposit. It was found that all of the colloids deposited were electroactive (e.g. Figure 4.8).

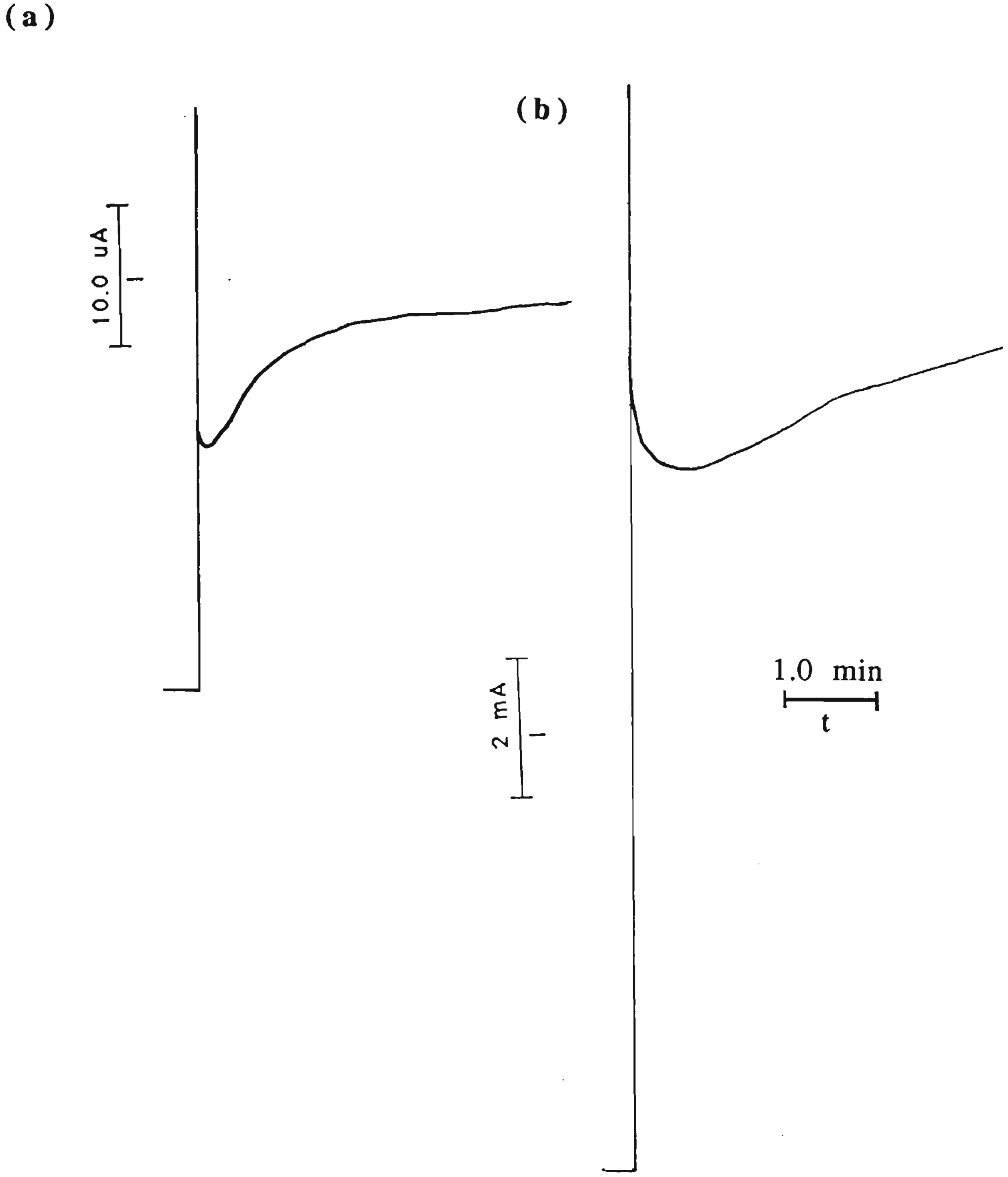


Figure 4.7: Chronoamperograms obtained during electrocoagulation of a 5.0 g/L colloidal dispersion
Conditions: (a) Glassy carbon electrode; PVA stabilizer; Eapp.-1.65 volt.
(b) RVC substrate; PVP stabilizer; Eapp.- 1.50 volt.

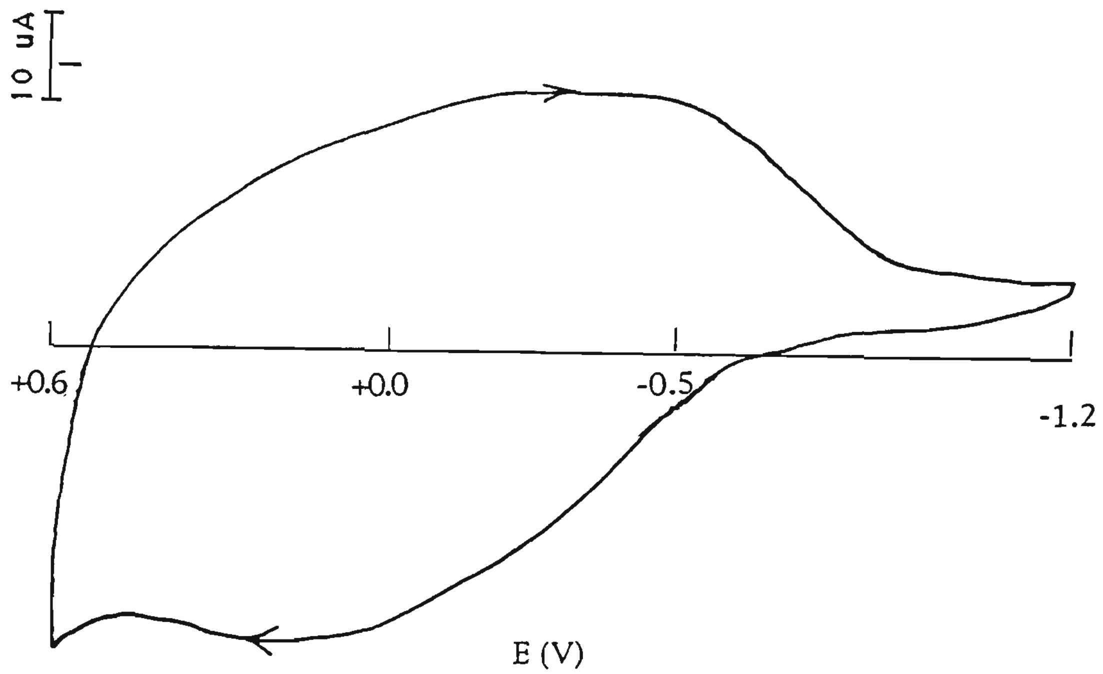


Figure 4.8: Cyclic voltammogram obtained after electrocoagulation of a 5 g/L colloidal dispersion onto a glassy carbon electrode.
Conditions: Scan rate=100 mV/s; supporting electrolyte=1.0 M $NaNO_3$.

4.3.3 Preparation of Polyaniline Colloids in a Flow Through Electrochemical Cell

The preparation of polyaniline colloids was also attempted using the flow-through cell. Nitric acid (HNO_3), hydrochloric acid (HCl), sulphuric acid (H_2SO_4) and paratoluene sulphonic acid [PTS (H)] (concentration range 0.03-3.50 M) were used as the supporting electrolyte. Again, PVA, PVP and PEO (concentration range 5-30 g/L) were considered as the stabilizers. In a typical experiment 4 mL aniline was added to a stirred aqueous solution of 200 mL 3.50 M nitric acid and 25 g/L PVA stabilizer. The reaction was carried out at room temperature for five hours. Constant current density of ~ 0.58 mA/cm^2 and a minimum flow rate of 25 mL/min. were used. The colloidal dispersion formed was ultracentrifuged for 45 minutes (50,000 r.p.m.). The supernatant was decanted and the sediment was rinsed several times with distilled water. The sediment was redispersed in water by using ultrasonication.

Colloid preparation was successful using the PVA stabilizer, giving a yield similar to that obtained for the polypyrrole colloids. However, a much higher concentration of stabilizer was required in the case of polyaniline (25 g/L) compared to polypyrrole (3.0 g/L).

The electrochemistry of colloidal dispersions was investigated using cyclic voltammetry. A typical cyclic voltammogram is shown in Figure 4.9. This colloidal dispersion showed poor electroactivity. This is probably due to the high concentration of stabilizer that was used for the colloid formation.

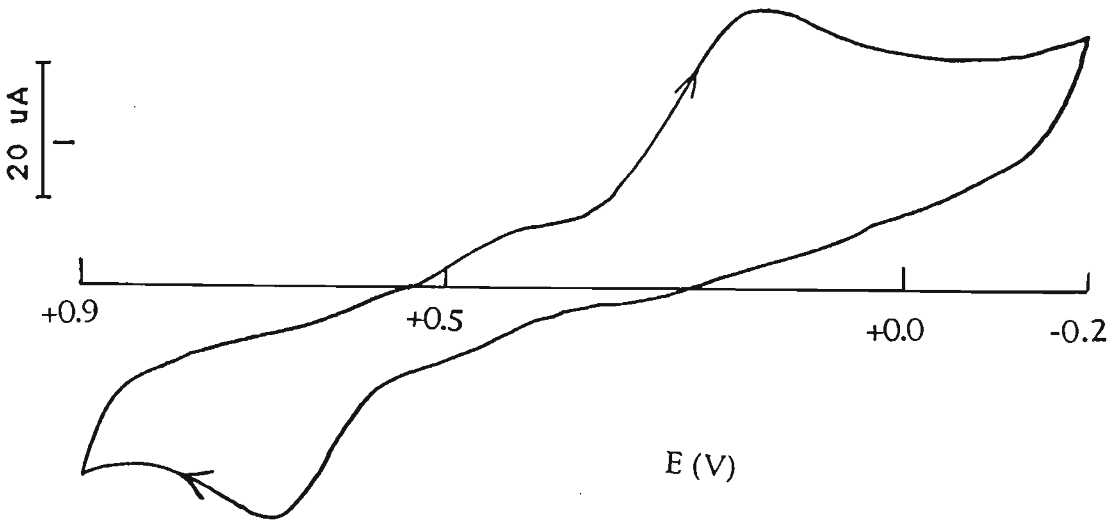


Figure 4.9: Cyclic voltammogram of a 15 g/L polyaniline colloidal dispersion.

Conditions: Working electrode glassy carbon, scan rate 100 mV/s

Transmission electron micrographs of dried polyaniline were obtained and a typical example is shown in Figure 4.10. Almost spherical particles were obtained in the flow through cell, which is probably a result of the high concentration of stabilizer (25 g/L) used for the colloid preparation. In the case of the chemical method of colloid preparation, a lower concentration of stabilizer is used and non-spherical particles are obtained (Section 2.3.7) A comparison of the chemical and electrochemical methods for preparation of polyaniline colloids suggests that the latter has a higher efficiency. After one hour of reaction 0.036 g of colloid was produced electrochemically, while only 0.016 g of polyaniline colloid was produced by the chemical method. Electrodeposition of these colloids has not yet been investigated.

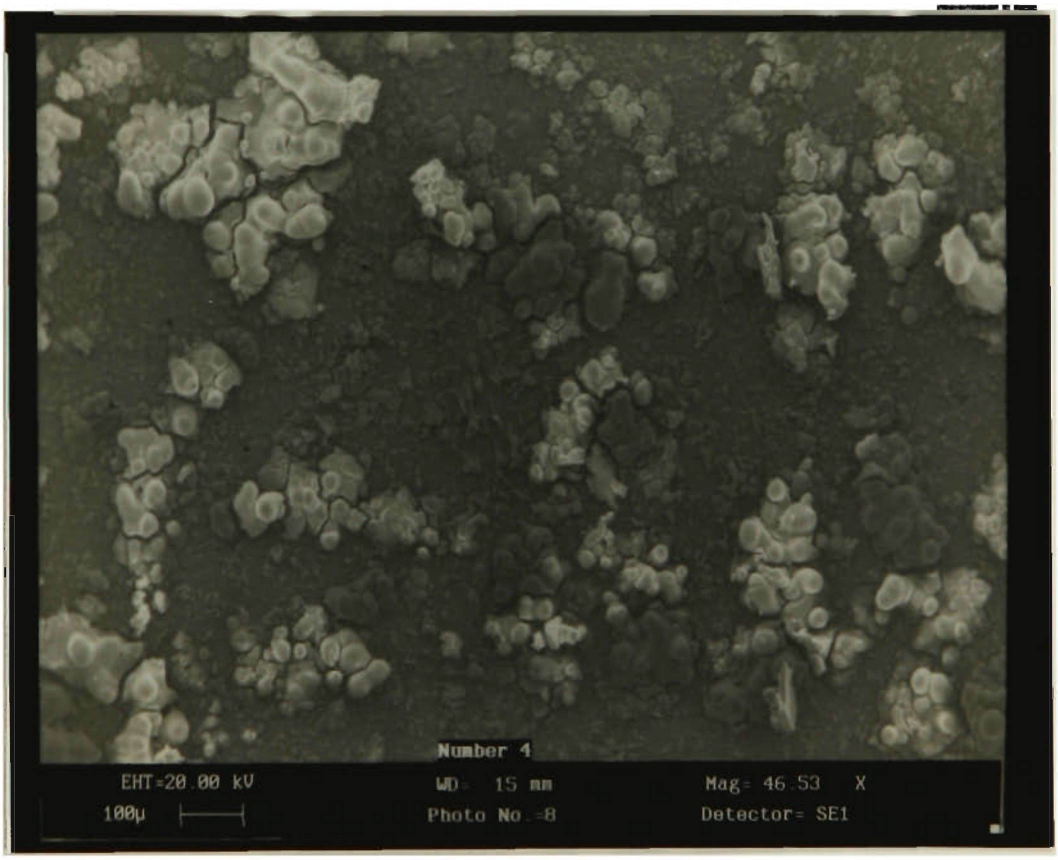


Figure 4.10: Transmission electron micrograph of polyaniline colloids stabilized by PVA stabilizer (initial concentration of PVA 25 g/L).

4.4 CONCLUSION

Conducting polymer colloids are usually prepared by the oxidation of the monomer in the presence of a steric stabilizer. Additives and steric stabilizers can be used to inhibit deposition of the polymers under electropolymerization conditions (206,207). Rotation rate, type and concentration of stabilizer all influence polymer growth. Cyclic voltammograms of the material deposited on the anode indicate that the rotation of the electrode and/or the the presence of the steric stabilizer decreases the amount of electroactive material deposited. The results indicate that the combination of appropriate hydrodynamic conditions and the use of steric stabilizers may provide a means by which colloids could be produced electrochemically.

In this work conducting polymer colloids have been produced electrochemically using different stabilizers and different supporting electrolytes in a flow through cell. The effects of the nature and concentration of stabilizers and supporting electrolytes on the colloid formation have been investigated. The electroactivity of the material produced was examined using cyclic voltammetry. Polymer formation and yield of polymer to monomer is related to type and concentration of stabilizer and type of supporting electrolyte. PVA stabilizer and nitric acid supporting electrolyte are suitable for the formation of colloidal polyaniline. The colloid can then be electrodeposited onto substrate surfaces. In comparison with the chemical method, smaller particles could be prepared by using this system.

In conclusion the ability to generate conducting polymer colloids electrochemically has been demonstrated for the first time. The colloids produced are sterically stabilised and are electroactive. The use of electropolymerisation methods to prepare the colloids means that a range of counterions can be incorporated as has been demonstrated in this study. The process also lends itself to continuous on-line production of colloids.

CHAPTER 5

APPLICATIONS FOR CONDUCTIVE POLYMER COLLOIDS

5.1 INTRODUCTION

Conventional polymers are commonly modified with conductive filler particles, such as carbon black and metal flake, for applications such as conductive additives and paints (157-161) and for electromagnetic irradiation (EMI) shelding (161). The use of inherently conductive polymer colloid particles has been considered in this study as an alternative to the conventional fillers. The effectiveness of conductive polymer colloids for making conventional polymers electrically conductive has been assessed in the case of paints.

Carbon black is also used widely as an anti-oxidant in many plastics and rubber formulations (217-219). This study also investigated whether conductive polymer colloids had any stabilizing effect on conventional polymers. The thermal oxidation of polyethylene has been assessed with different loading of conductive polymer fillers.

Finally, the use of conductive polymer colloids for the improvement of the processibility of conductive polymers has been investigated. Coating of substrates from colloidal dispersions has been evaluated, particularly for easily corroded metals that are inappropriate as electropolymerization electrodes. In addition to this, novel conductive polymer composites have been developed which are unique to the colloidal processing route.

5.2 EXPERIMENTAL

5.2.1 Reagents and Standard Solutions

All chemicals used in this study were analytical reagent grade and used without further purification, unless stated otherwise. Deionised water was used throughout this work. Pyrrole (Sigma) and aniline (BDH) were purified by simple distillation. Anhydrous ferric chloride was purified using vacuum filtration. The materials used in this section were pyrrole and polyvinylalchohol (PVA) (Molecular weight = $3 \times 10^4 - 7 \times 10^4$) obtained from Sigma, $NaNO_3$ from BDH, polyethyleneoxide (PEO) (Molecular weight = 3×10^5) from Aldrich, polyvinylpyrrolidone (PVP_2) (Molecular weight = 1.2×10^6) from TCI, polyvinylpyrrolidone (PVP_1, Molecular weight = 2.5×10^4) from Merck, anhydrous ferric chloride, $(NH_4)_2S_2O_8$ and hydrochloric acid from BDH. Poly(sodium 4-styrenesulfonate) (by weight 20% solution in water) from Aldrich. Acrylic latex paint was donated by ICI Dulux Australia Ltd.

5.2.2 Preparation of Polypyrrole Colloids

Colloids were prepared as described before (chapter 2). That is, 1.0 mL of pyrrole was added to a stirred aqueous solution (100 mL) containing 5.33 g of ferric chloride and 0.1-2.5 g of one of the stabilisers (PVP, PVA or PEO). The temperature of the mixture was maintained between 4 ^oC and 25 ^oC for 19 hours.

The black colloidal dispersion was ultracentrifuged (50,000 rpm) for thirty minutes to produce a black sediment. The supernatant was decanted and the sediment rinsed several times with distilled water. The sediment could be redispersed in water by ultrasonicating. The typical reaction conditions used to produce spherical monodisperse colloids are summarised in Table 2.2.

5.2.3 Preparation of Paints

The paints were prepared by mixing 20-80% (w/w) of the appropriate colloid dispersion in water with the acrylic latex (698-0625E) 51% (NV) supplied by ICI Dulux. The mixture was stirred vigorously for ten minutes to ensure it was homogeneous.

The paints were applied to three metallic substrates: lead (Pb), stainless steel (SS) and Zincalume® (Zn-Al: steel sheet coated with a zinc-aluminium alloy).

5.2.4 Instrumentation

Adhesive strengths were measured at room temperature using a modified version of ASTM method D 4541 with an Instron Tensile Tester Model 4302. A Sorvall OTD Ultracentrifuge was used. A JEOL 2000 FX Transmission Electron Microscope or a Hitachi S 450 Scanning Electron Microscope were employed. The four-point probe used for conductivity measurements was manufactured by the University of Technology, Sydney. The four-point probe is used to measure the volume resistivity of conducting polymer films, which is then used to calculate film conductivity. The conductivity of dry paint coated on one side of poly(ethylene terephthalate) (PET) have been measured. Sample length was 6.5 cm and width was 0.40 cm. The average thickness of the paint samples was 0.14 mm.

5.2.5 Analysis of Results

The four-point probe is used to determine the volume resistivity (R_V) of a conductive electroactive paint coated on the PET film where:

$R_V = \frac{x\ .\ y}{z}\ \frac{\Delta E}{I}$ (Ω cm); x = the thickness of paint (cm); y= width of the sample (cm); z= distance between potential electrodes (cm); ΔE= potential difference across the inner electrodes (mV); I= current passed through outer electrodes (mA).

The conductivity is calculated from:

$$\sigma = \frac{1}{R_V} \qquad \text{S/cm (or } \Omega^{-1}\ \text{cm}^{-1}\text{).}$$

$$R_S = \frac{\text{Volume Resistivity}}{\text{Average Paint Thickness}}\ (\Omega).$$

A Bioanalytical Systems (BAS) Model 100 A or a BAS Model CV-27 was used to obtain cyclic voltammetic data. The electroactivity of the coatings was investigated in a three electrode cell employing a working electrode (Glassy carbon (GC), Stainless steel (SS), Platinum (Pt), or Zincalume® (Zn-Al)), and a (Ag/AgCl) reference electrode with a Pt gauze auxiliary electrode. The supporting electrolyte used was $NaNO_3$ (1.0 M). A Kyowa Zoom Stereo-Microscope Model SDZ-TR-FLG-R was used for measuring the thickness of the electroactive paint coatings.

5.3 RESULTS AND DISCUSSION

5.3.1 Conductive Paints

5.3.1.1 Electrical Properties

The formation of conductive electroactive paints has been investigated by mixing polypyrrole and polyaniline colloids with standard acrylic paints. This approach offers a potentially more simple and versatile processing method for preparing conductive, electroactive coatings as compared with electrodeposition. In addition, the approach may produce conductive paints with advantages over conventional conductive paints. In order to explore this potential, the paints have been assessed in terms of their electrical and adhesive properties.

Using the experimental procedure described above, colloids were prepared using different stabilisers PEO, PVP and PVA. The colloids produced had a particle size range of 75-250 nm as shown in the Transmission Electron Micrograph (Figure 2.1). The acrylic formulation supplied by ICI Dulux was diluted (50/50) with water and then the colloidal dispersion (in water) was added. This was stirred until a well dispersed formulation was obtained. The as received substrates such as zincalume, stainless steel and lead were dip coated and allowed to dry. In all cases an adherent, conductive film was obtained. Conductivity data was obtained by the four point probe method on dip coated PET films. Results are summarised in Figure 5.1.

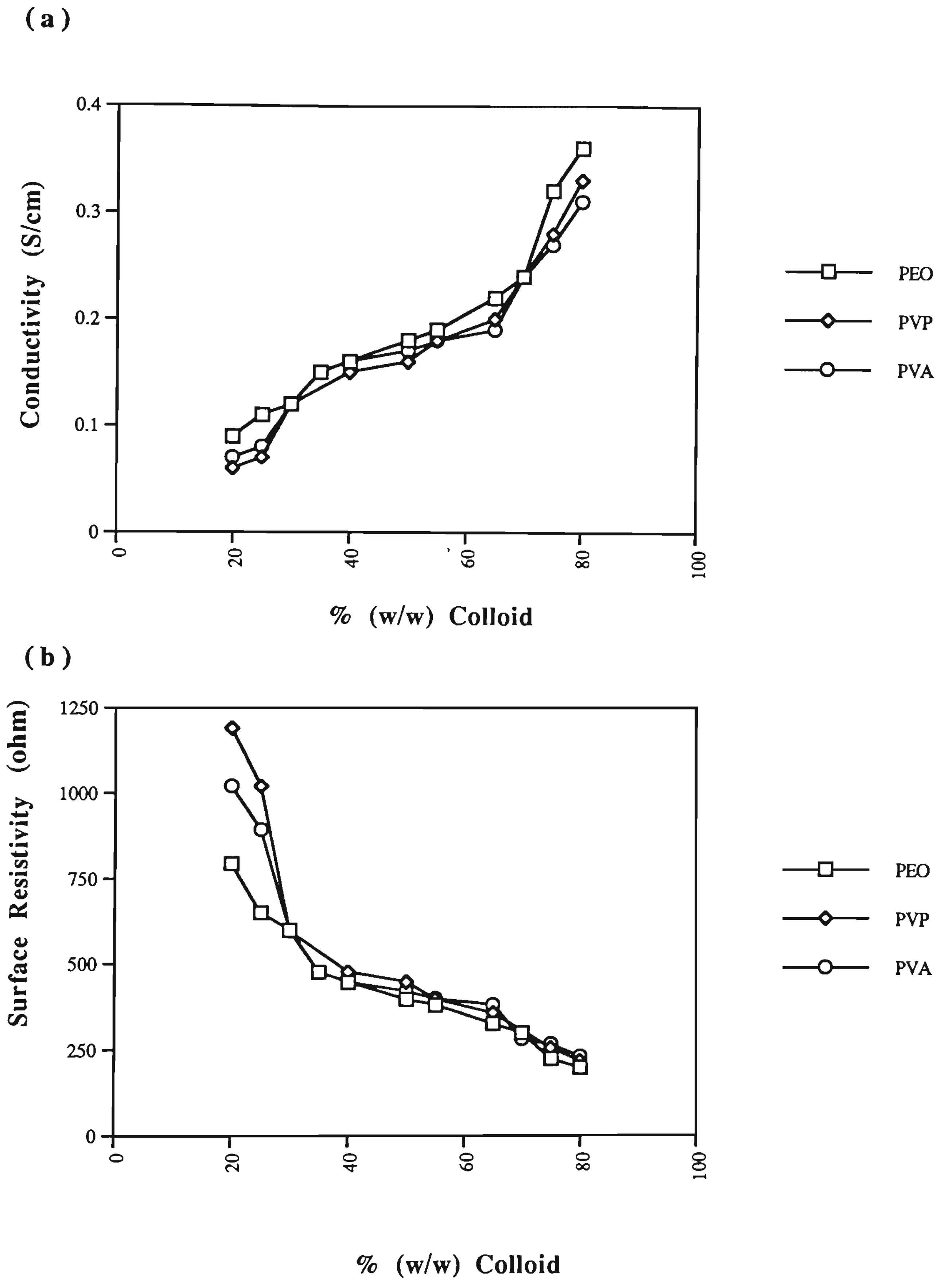


Figure 5.1: Electrical properties of paints coated on PET film as a function of colloid loading and stabilizer type:
(a) conductivity, (b) surface resistivity.

In all cases it was found that the conductivity of the paint increased as the amount of colloid added increased. The type of stabiliser used for colloid preparation had little effect on the conductivity of the paints as shown in Figure 5.1. The amount and morphology of colloid particles affect the conductivity of resultant composite films (134).

The conductivities obtained compare favourably with results quoted by other workers for conventional carbon or metal filled paints (157-163). However, the results obtained here show no percolation type behaviour. The reason for this is still unknown. Takagi (161), for example, has reviewed the electrical properties of various conductive paints and has shown that the volume resistivity varies with the type of filler: silver (1 Ωcm), copper (2 Ωcm), nickel (5 Ωcm) and carbon (20 Ωcm). The polypyrrole colloid modified acrylic paints investigated in the present study showed volume resistivities over the range 3-17 Ωcm depending upon the concentration of colloid. Thus, these paints have similar electrical conductivities to other paints filled with conductive particles.

5.3.1.2 Adhesion

It is known that the adhesion of electrodeposited layers on easily corroded substrates is poor due to the fact that the potentials required to initiate polymerisation causes concomitant substrate oxidation (220). Hence, the adhesion of the paint coatings on Pb, SS, and Zn-Al was considered. In all cases it was found that the adhesion of the paint was very good, and actually increased as the amount of colloid added increased, at least up to approximately 50% (w/w) (Figure 5.2). The type, quantity and size of the conductive filler influence the adhesive strength (221). Many interactions can take place between the environment and the hydrated metal oxide layer which can affect the adhesive bond strength (e.g. electrostatic/electromagnetic attractions and/or the formation of chemical bonds) (193, 194). The presence of the conductive colloids within the paint may promote this additional bonding which would explain the 0bserved increase in adhesive strength. For example, the electroactivity of the colloids may induce redox reactions that cause oxidation of the metal and/or polymer which enhances the chemical interactions between the two. Alternatively, the increase in adhesive strength may due to the reinforcing effect of the colloid particles. The adhesion of conventional paints is known to increase with increasing filler content (e.g. silica) at least up to a maximum value. The fact that the different stabilizers and substrates show different relationships indicates that the adhesion is not determined by the reinforcing effect alone. Differences in chemical interactions must account for the different behaviour observed for the PEO/Lead and PEO/Zn-Al system for example.

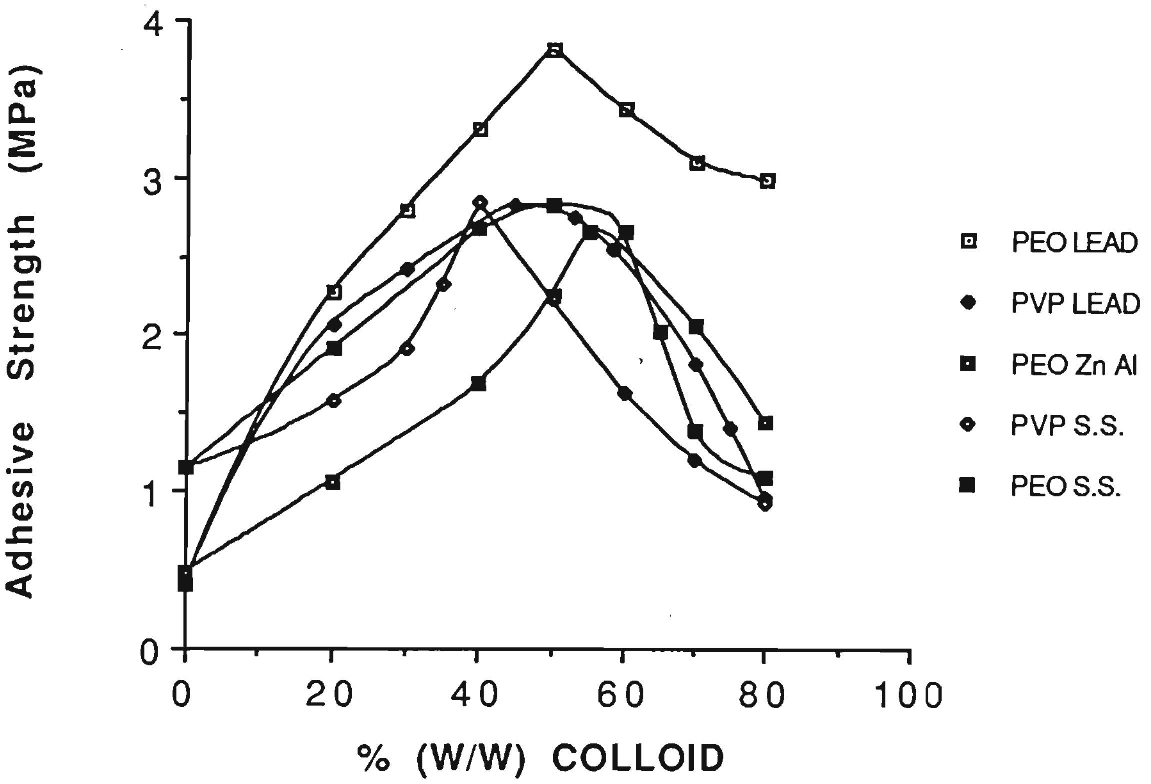


Figure 5.2: Adhesive strength as a function of colloid loading for stainless steel, lead, and Zincalum substrates and PEO and PVP stabilizers.

The results show that these paints have higher adhesion than the unmodified acrylic paint (i.e. 0% colloid), and should therefore be satisfactory for commercial use. The decrease in adhesion at higher colloid contents is presumably due to the decreasing concentration of acrylic binder.

Little quantitative data is available concerning the adherence of conventional conductive paints to different substrates. Birnbaum et al (159) and Park and Clatterbuck (158) have noted good adhesion of carbon-filled paints, but have not indicated quantitatively the degree of adhesion, nor the influence of carbon content on adhesion.

5.3.1.3 Electroactivity

The electroactivity of these coatings was subsequently investigated on lead, glassy carbon and stainless steel substrates. Well defined responses were observed in all cases. For example results for glassy carbon are shown in Figure 5.3.

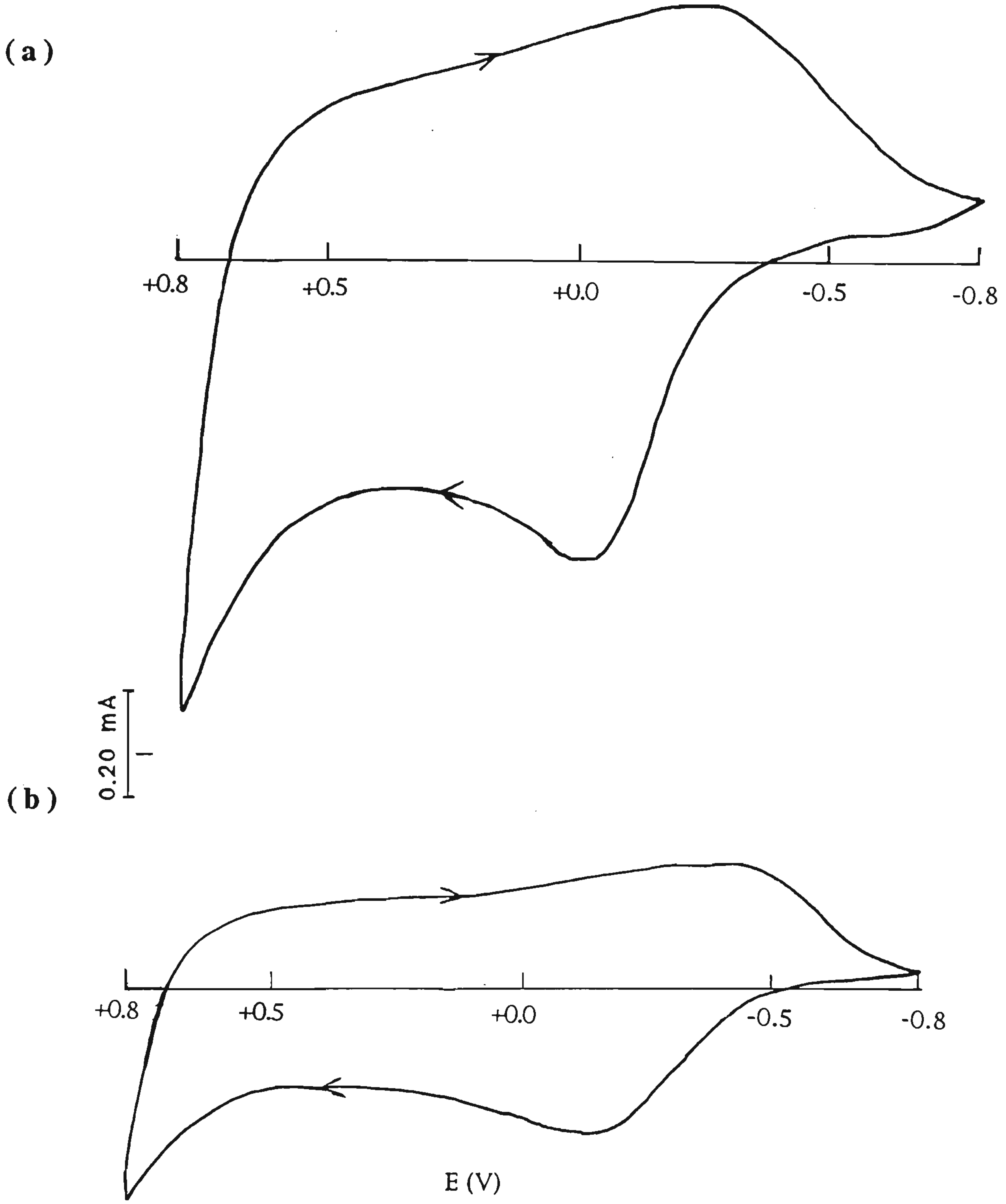


Figure 5.3: Cyclic voltammograms obtained for painted glassy carbon.

Conditions: Paint contained 50 %w/w colloid. Colloid stabilized using PEO, and PVA. Supporting electrolyte 1.0 M $NaNO_3$. Scan rate 100 mV/s.

In all cases the electroactivity increased with the percentage of colloid added. With all of the stabilisers used for colloid formation well defined electrochemical responses were observed.

5.3.1.4 Preparation of Polyaniline Paint

Colloids were prepared as described in chapter 2 (Table 2.8). That is, 1.0 mL of aniline was added to a stirred aqueous solution of 1.25 M HCl (100 mL) containing 0.70 g of ammonium persulphate and 0.80-0.90 g of one of the stabilizers (PVA, PEO and PVP_2) at room temperature for 48 hours. The ultracentrifuge was used for the separation of colloids from redispersed solution.

Paints were prepared using the same procedure was described for polypyrrole previously. The electroactivity, conductivity and adhesive strength of this paint was studied and are summarised in Figures 5.4, 5.5, 5.6. Figure 5.4 shows a cyclic voltammogram obtained from the polyaniline paint coated on a glassy carbon substrate. The result shows that the paint is electroactive and shows the responses typical of polyaniline. Figure 5.5 shows the conductivity of the polyaniline paints and it is seen that the conductivity increases as the concentration of colloid increases. The conductivity values are similar to those obtained for the polypyrrole paints. The adhesion strength (Figure 5.6) shows similar behaviour to the polypyrrole paints with a maximum observed at approximately 50% (w/w). The adhesion is, in general, lower than that observed for the polypyrrole paints, which may be due to differences in the morphology or electroactivity of the colloids.

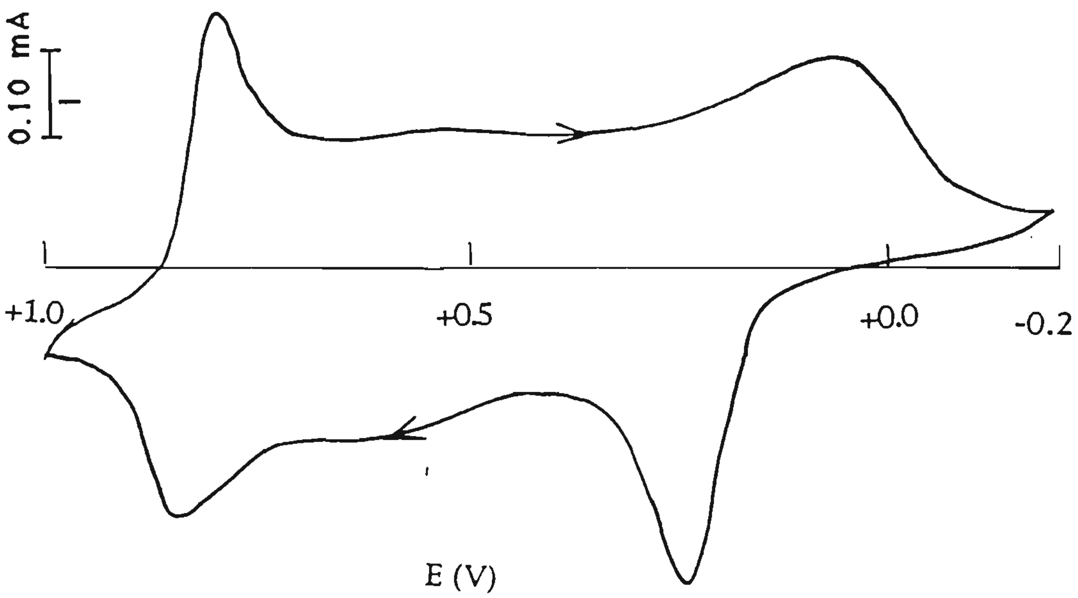


Figure 5.4: Cyclic voltammograms obtained for painted glassy carbon.

Conditions: Paint contained 50 %w/w colloid. Colloid stabilized using PEO. Supporting electrolyte 1.25 M HCl, scan rate 100 mV/s.

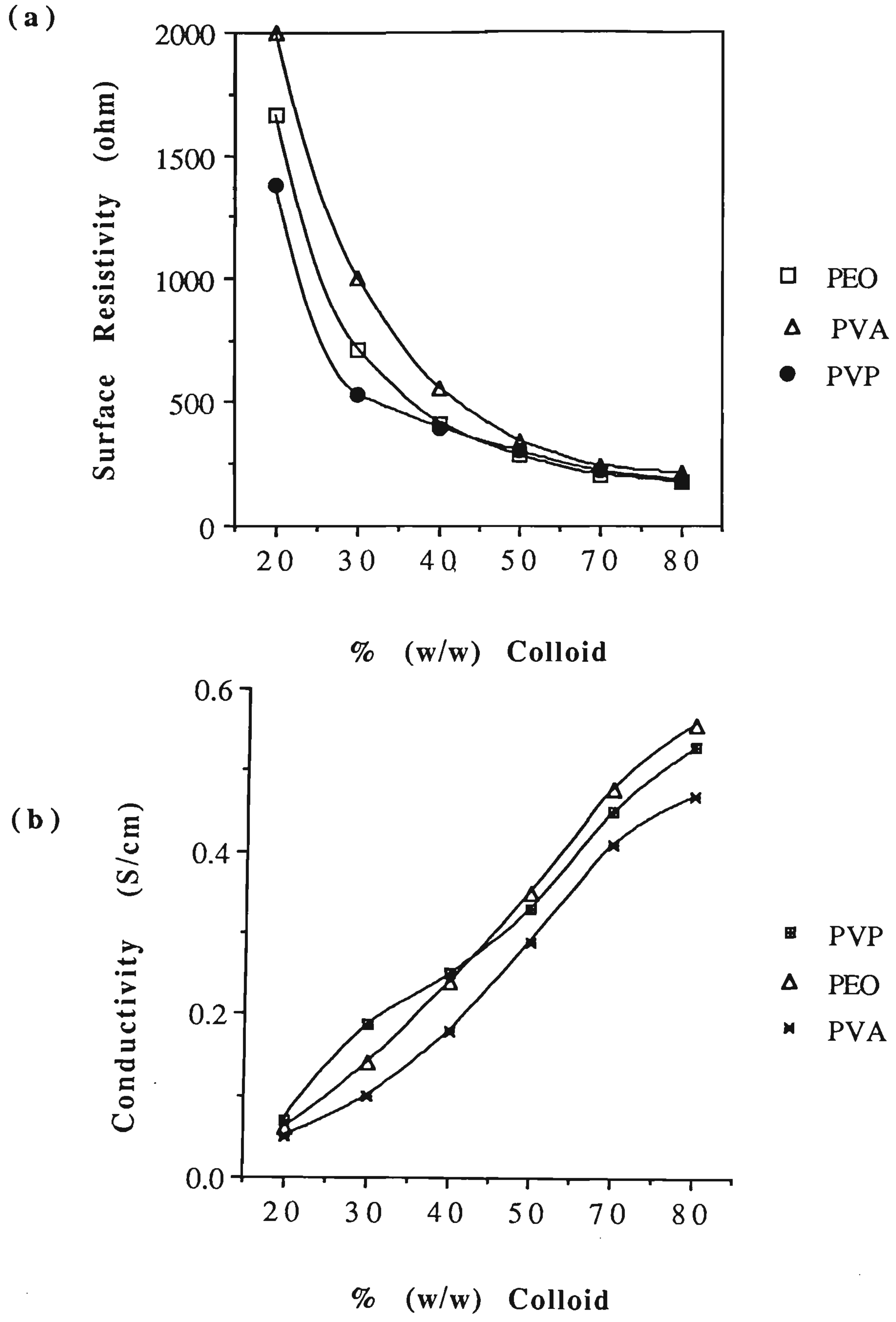


Figure 5.5: Electrical properties of paints coated on PET film as a function of colloid loading and stabilizer type:
(a) conductivity, (b) surface resistivity

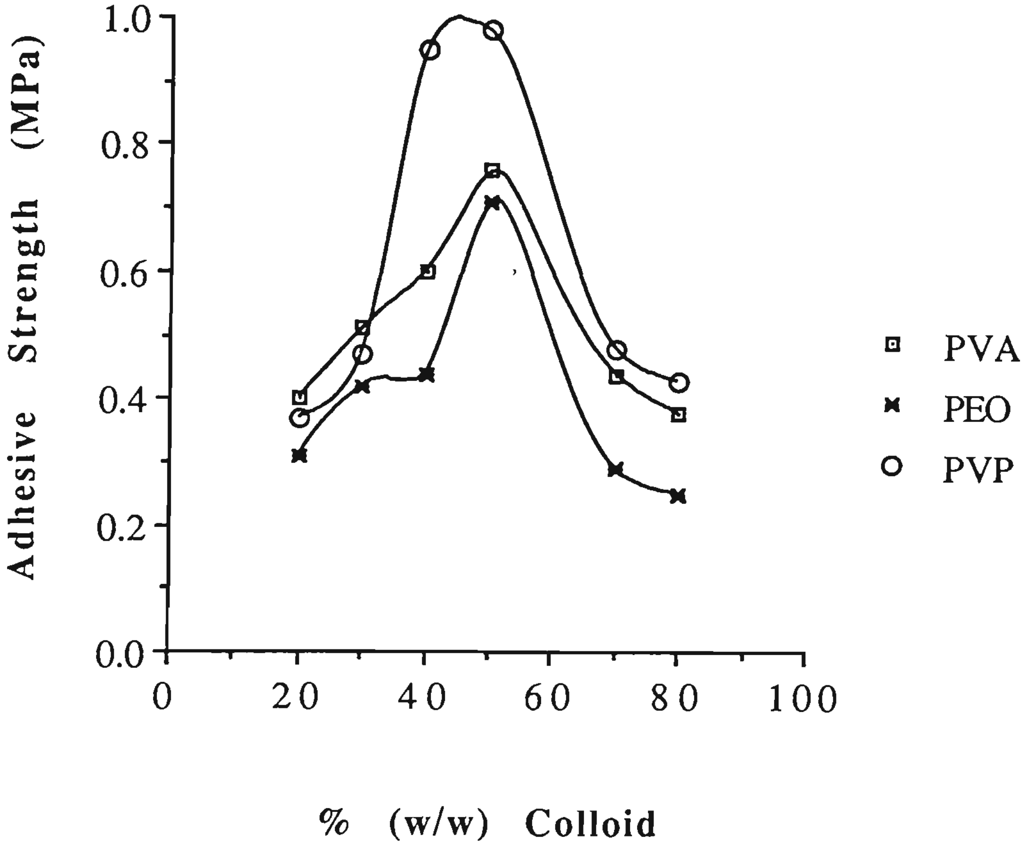


Figure 5.6: Adhesive strength as a function of colloid (polyaniline) loading for stainless steel substrate and PEO, PVA PVP stabilizers.

This study has shown that conductive, electroactive paints can be prepared by physically mixing colloidal dispersions with commercial water-based paints. These conductive paints have been shown to have conductivities similar to carbon -filled and metal flake filled paints. The adhesion of the paints to various metal substrates was found to be excellent and superior to the unmodified acrylic paint. The paints were also found to be electroactive, which is unique to these types of paints. This method provides a versatile technique for appling conductive, electroactive coatings to substrates that are unsuitable for electropolymerisation, e.g. easily corroded or non-conductive. The technique combines the simplicity of painting with the unique properties of electropolymerised conductive coatings.

5.3.2 Thermal Oxidation Stabilizers

The thermal degradation of various polymers, polyethylene, PVC, nylon 6/6 with different fillers such as carbon black, copper, aluminium, brass, nickel have been previously investigated (222,223). Oxidation of polyethylene, which results eventually in physical or dielectric failure of the polymer, is caused by heat and/or ultraviolet radiation. Carbon black has been shown to function as a mild thermal anti-oxidant for polyethylene at 140 ^{o}C (224). The amount of protection increases with concentration of carbon black and is dependent on the chemical nature of the carbon surface. The effect of carbon black on anti-oxidant behaviour is observed over a wide pH range, the effect decreases and finally disappears as the particle size of carbon black is increased. Ultimate failure of stabilized polyethylene on exposure is probably hastened in many instances by the removal of the oxidant by aqueous extraction and/or evaporation. This loss can be overcome by using those compounds that are most resistant to these influences, such as polymeric-type anti-oxidants and carbon blacks (225).

In this section the thermal degradation of polyethylene filled with carbon black, polypyrrole or polyaniline particles was investigated.

Composites of carbon black, polypyrrole and polyaniline colloids were prepared in the range of 1.5-10 % (w/w) by compression moulding of the dry-blended powders at 180 ^{o}C and 4200 PSI pressure for five minutes. Thermal degradation of composites (9.80 mg sample) was measured within the measuring cell of the Mettler differential scanning calorimeter at a flow rate of 50 mL/minute oxygen and a constant temperature of 170 ^{o}C. The oxidation onset time was determined when an exotheromic signal was detected (Figure 5.7). The results are given in Table 5.1 and shows that increasing the percent of colloid and carbon black decreases the rate of degradation. Thus the conductive polymers show an anti-oxidant effect, which is comparable to carbon black. At equivalent filler contents the order of effectiveness increases as PPy<carbon black<PAn. The polyaniline colloids, therefore, show considerable promise as oxidation stabilizers. The oxidative mechanism of polyethylene involves free radical reactions with oxygen in which peroxides are formed. These then decompose to produce new radical products that ultimately lead to the reduction in molecular weight of the polymers. Conventional thermal stabilisers for polymers operate either as free radical scavengers or as peroxide decomposers. It is assumed that the conductive

polymer colloids act in a similar manners , however, the exact stabilisation mechanism has not been determined and is beyond the scope of the present work.

Table 5.1: Onset of thermal degradation of polyethylene at 170 °C in oxygen.

Type of additive	Percent of additive (% w/w)	Onset time (minutes)
No additive	0.0	0.0
Carbon black	3.0	11.7
"	4.5	17.7
"	7.0	24.8
"	10.0	33.7
Polypyrrole colloid	1.5	8.0
"	3.0	11.0
"	4.5	14.7
"	7.0	18.8
"	10.0	19.8
Polyaniline colloid	1.5	16.3
"	3.0	21.5

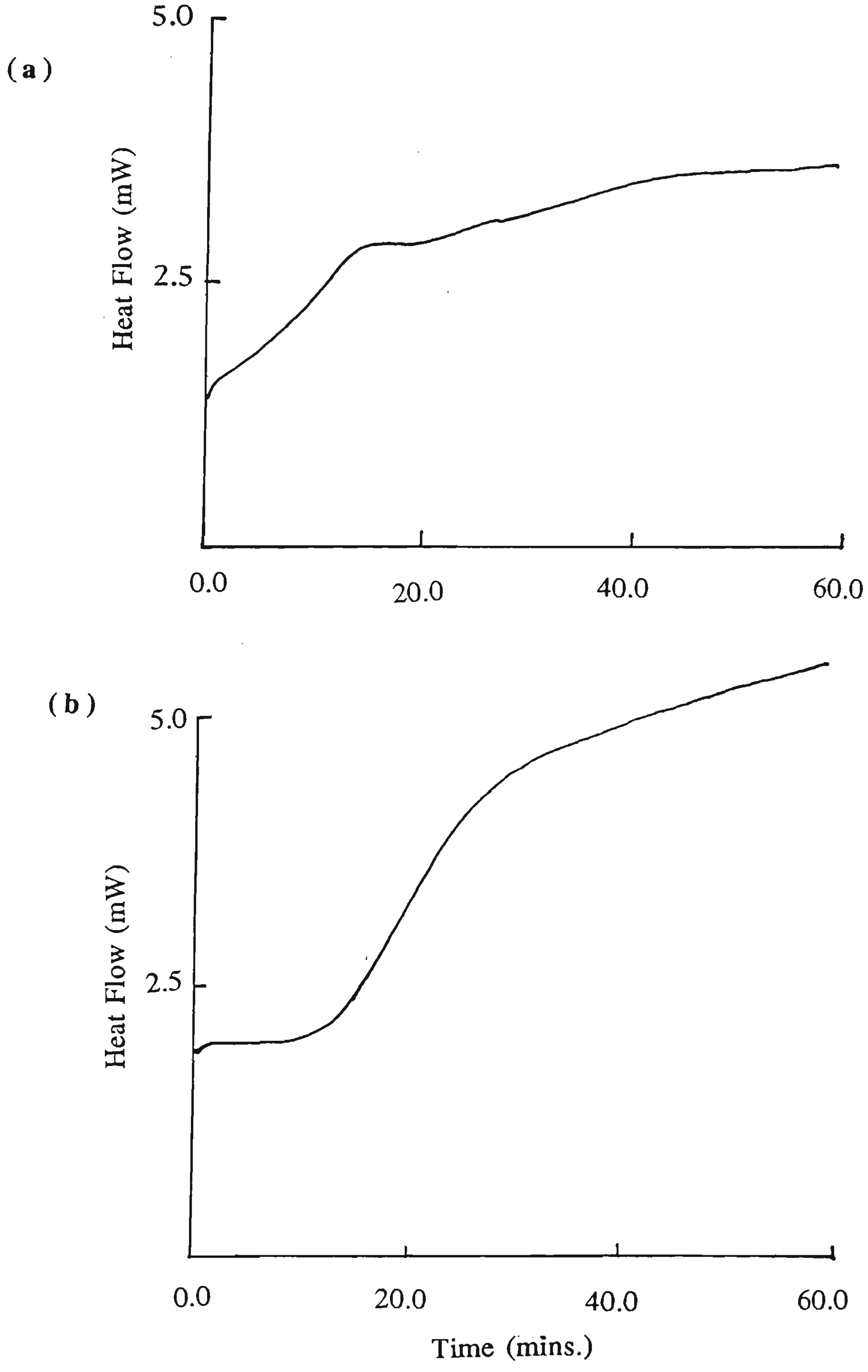


Figure 5.7: DSC trace of stabilized polyethylene samples (a) no additive present, (b) polypyrrole colloid 4.50 %.

5.3.3 Conductive Polymer Composites

The use of colloidal polymers was also investigated for the production of novel composites. For example, the possibility of depositing composite materials from mixtures of conducting polymers was investigated.

5.3.3.1 Mixtures of Polypyrrole and Polyaniline Colloids.

It was found that a conducting film could be deposited at negative potentials from mixtures of polyaniline and polypyrrole colloids. A chronoamperogram was obtained during electrocoagulation of the composite onto a glassy carbon electrode as shown in Figure 5.8. A slow increase in current versus time was observed which is indicative of polymer deposition causing the surface area to increase and consequently, the current to increase.

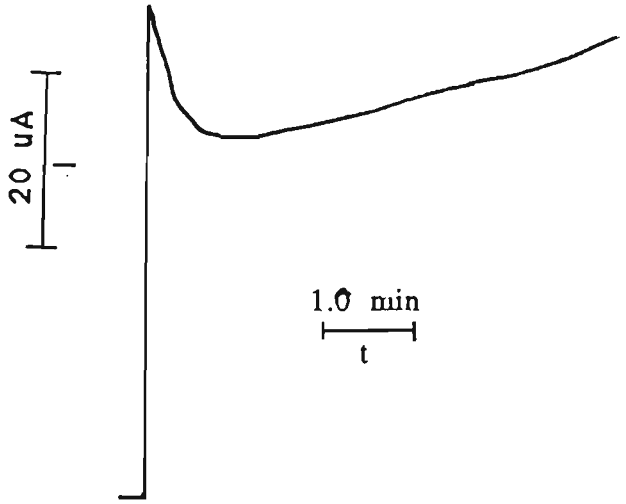


Figure 5.8: Chronoamperogram recorded during electrocoagulation of a (50/50 % w/w) PPy/PAn colloid onto a glassy carbon working electrode, E_{app}= -1.35 V.

A cyclic voltammogram was obtained after electrodeposition of the composite onto a glassy carbon electrode, as shown in Figure 5.9.

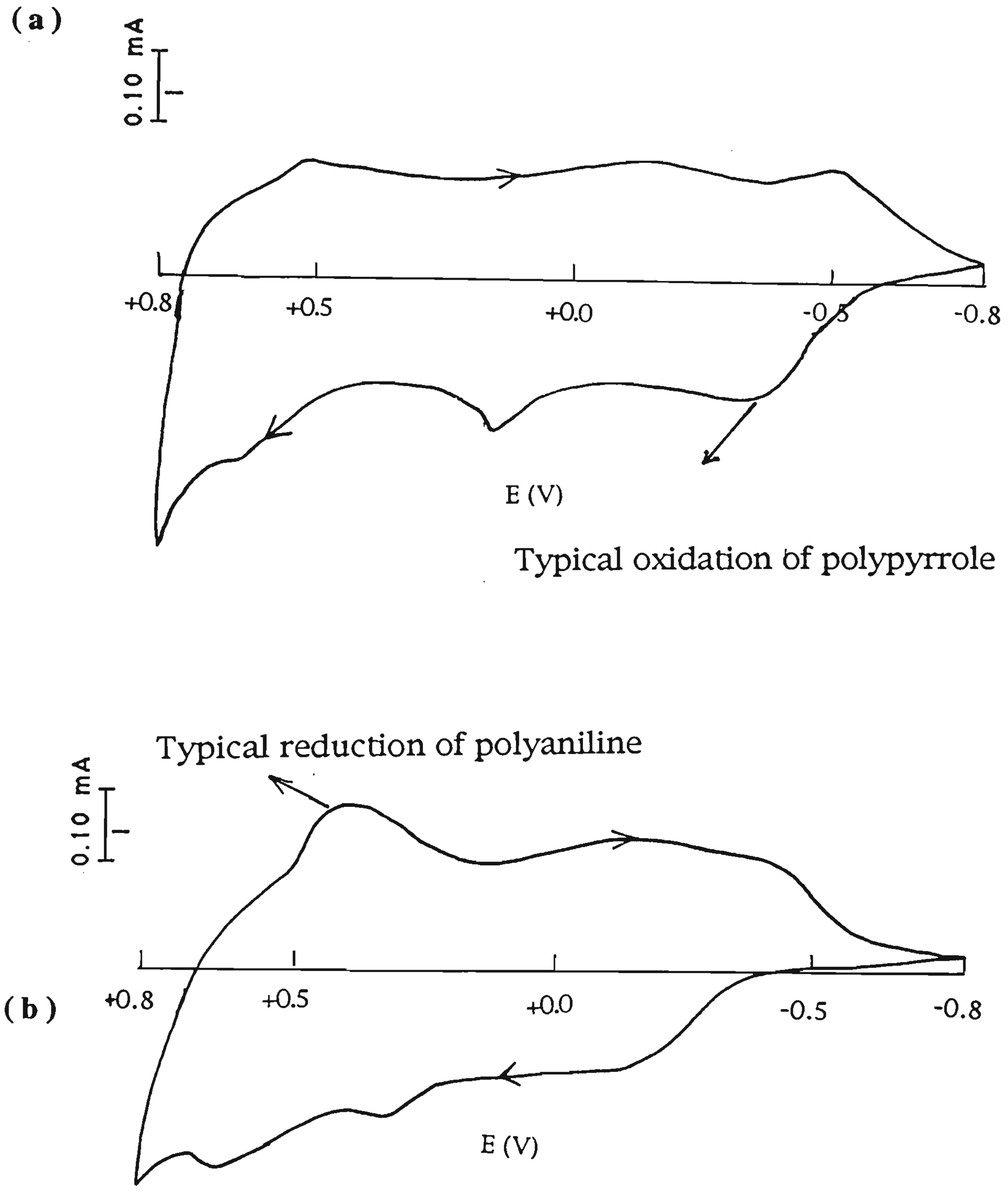


Figure 5.9: Cyclic voltammograms recorded after electrocoagulation of (50/50 % w/w) polypyrrole and polyaniline colloidal composite onto glassy carbon electrode.
Conditions: Scan rate 100 mV/s, (a) supporting electrolyte 1.00 M $NaNO_3$, (b) supporting electrolyte 0.02 M HCl

Responses from both polypyrrole and polyaniline are observed in the cyclic voltammograms of composite film. This indicates that both polypyrrole and polyaniline deposits are present in the composite. SEM micrographs of the codeposit were obtained and a typical example is shown in Figure 5.10. The micrographs show that dense deposits were obtained.

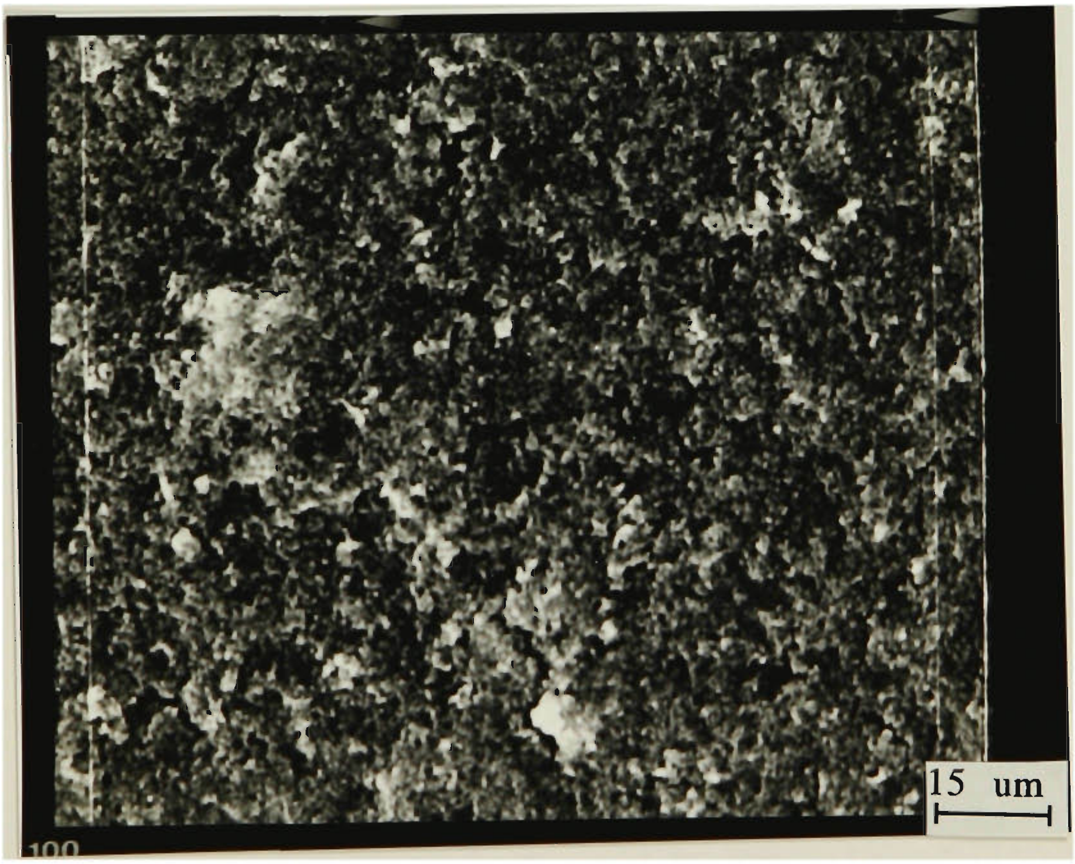


Figure 5.10: Scanning electron micrograph of PAn/PPy composite deposited onto glassy carbon electrode.

5.3.3.2 Mixtures of Conductive and Non-conductive Colloids

The codeposition of polystyrene sulfonate colloids and polyaniline was considered. This composite could only be deposited at positive potentials. A typical chronoamperogram is shown in Figure 5.11, which shows an increase in current with time.

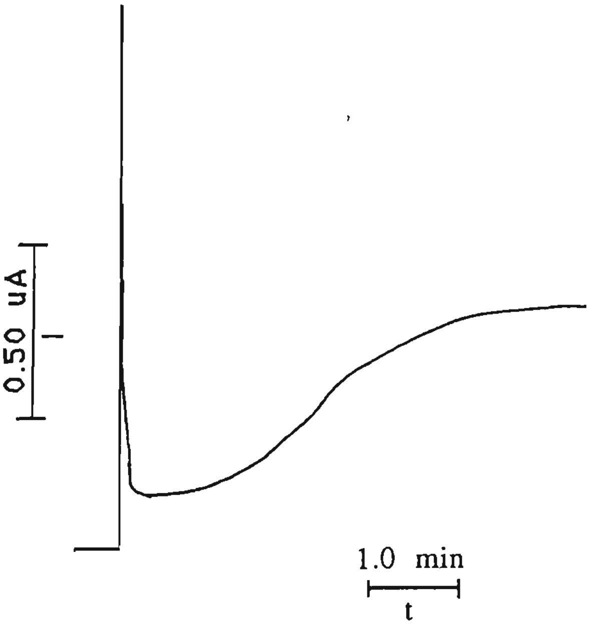


Figure 5.11: Chronoamperogram recorded after deposition of polyaniline and polystyrene sulfonate (50/50 % w/w).
Conditions: Eapp= 2.15 V, glassy carbon electrode.

A typical cyclic voltammogram of the deposit on glassy carbon is shown in Figure 5.12. This indicated that electroactive polymer coatings were formed.

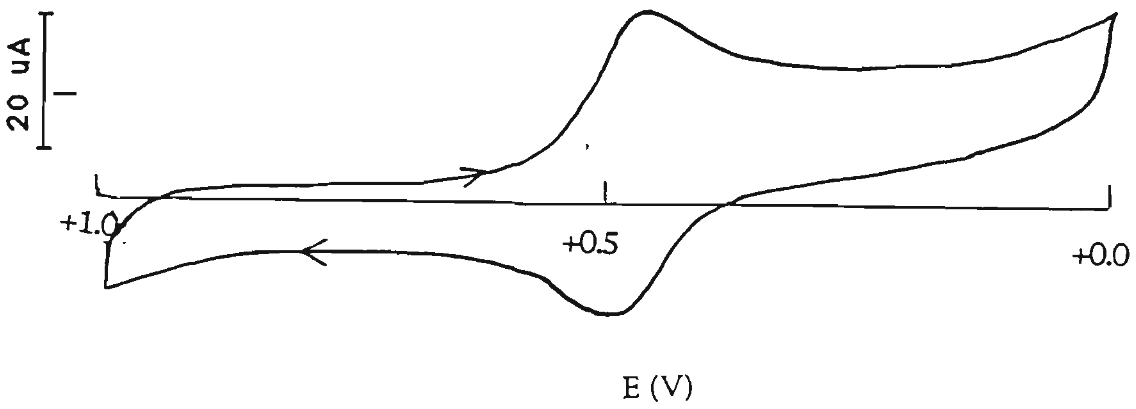


Figure 5.12: Cyclic voltammogram after electrocoagulation of polyaniline and polystyrene sulfonate composites.
Scan rate 100 mV/s, supporting electrolyte 0.02 M HCl, glassy carbon electrode. Details mentioned in caption for Figure 5.11.

5.3.3.3 Coating on Non-conductive Particles.

Codeposits were also prepared on non-conductive particles (polystyrene sulfonate). These are of interest for chromatography purposes. The deposits were prepared by first dispersing the polypyrrole and polyaniline colloids in water and then adding to a stirred aqueous dispersion of sulfonate resin particles. After two hours of mixing the particles were collected and examined by SEM (Figure 5.13). In each case a coating formed because of the electrostatic attraction (e.g coulombic attractions) between the negatively charged particles (sulfonate resin) and the positively charged colloids. The thickness of the coating depends on the type of steric stabilizer used for the chemical polymerization of the colloid particles because as described in chapter two the stabilizer type affect the electroactivity and conductivity of the colloids (PEO> PVP>PVA for polypyrrole and PVA>PEO>PVP for polyaniline).

(a_1)

Figure 5.13: Scanning electron micrographs of sulfonate resin coated polypyrrole and polyaniline colloids.
Conditions: (a_1) and (a_2) PVA, (b_1) and (b_2) PVP, (c_1) and (c_2) PEO stabilizer were used for the colloid preparation of polypyrrole and polyaniline respectively.

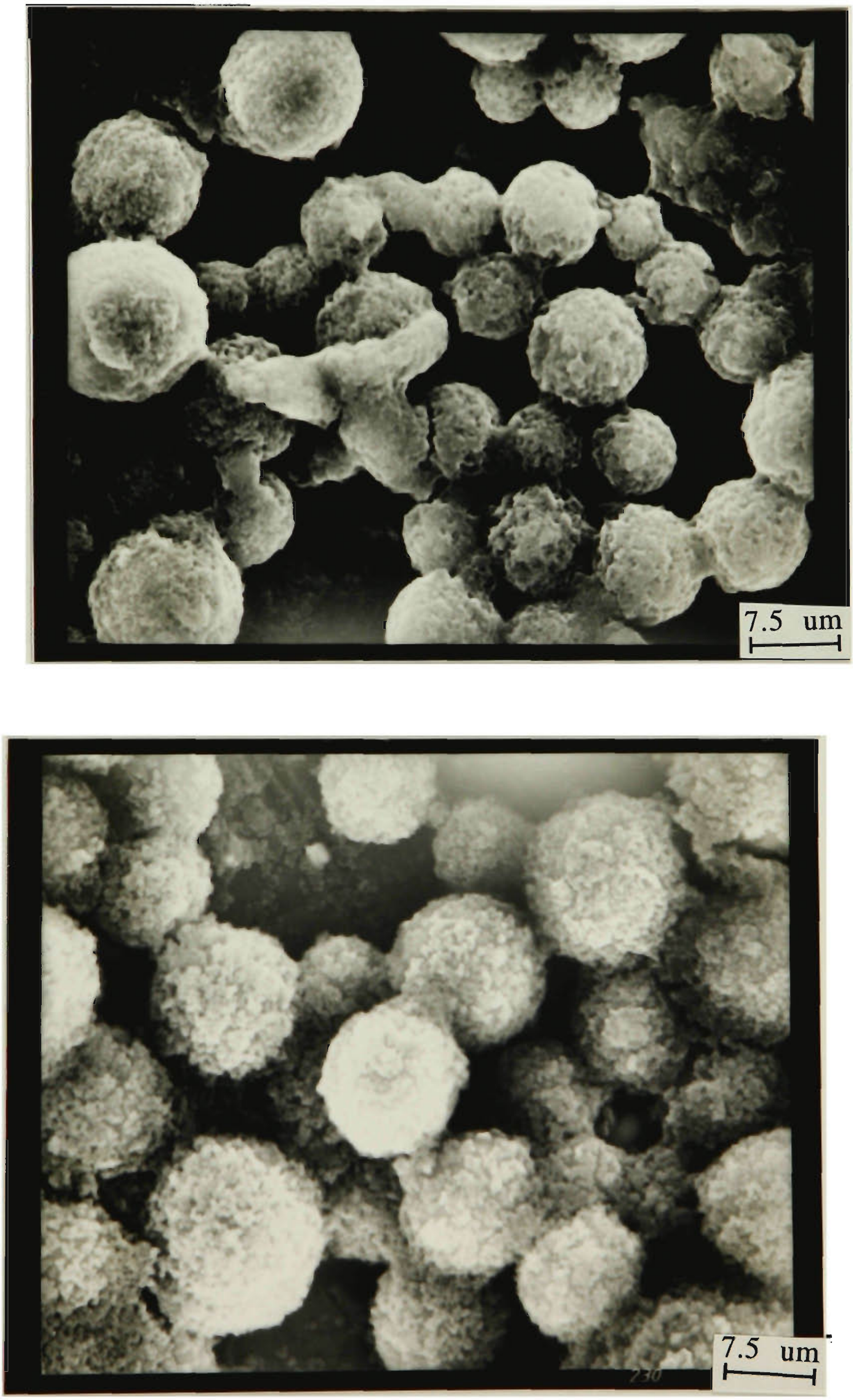


Figure 5.13 continued.

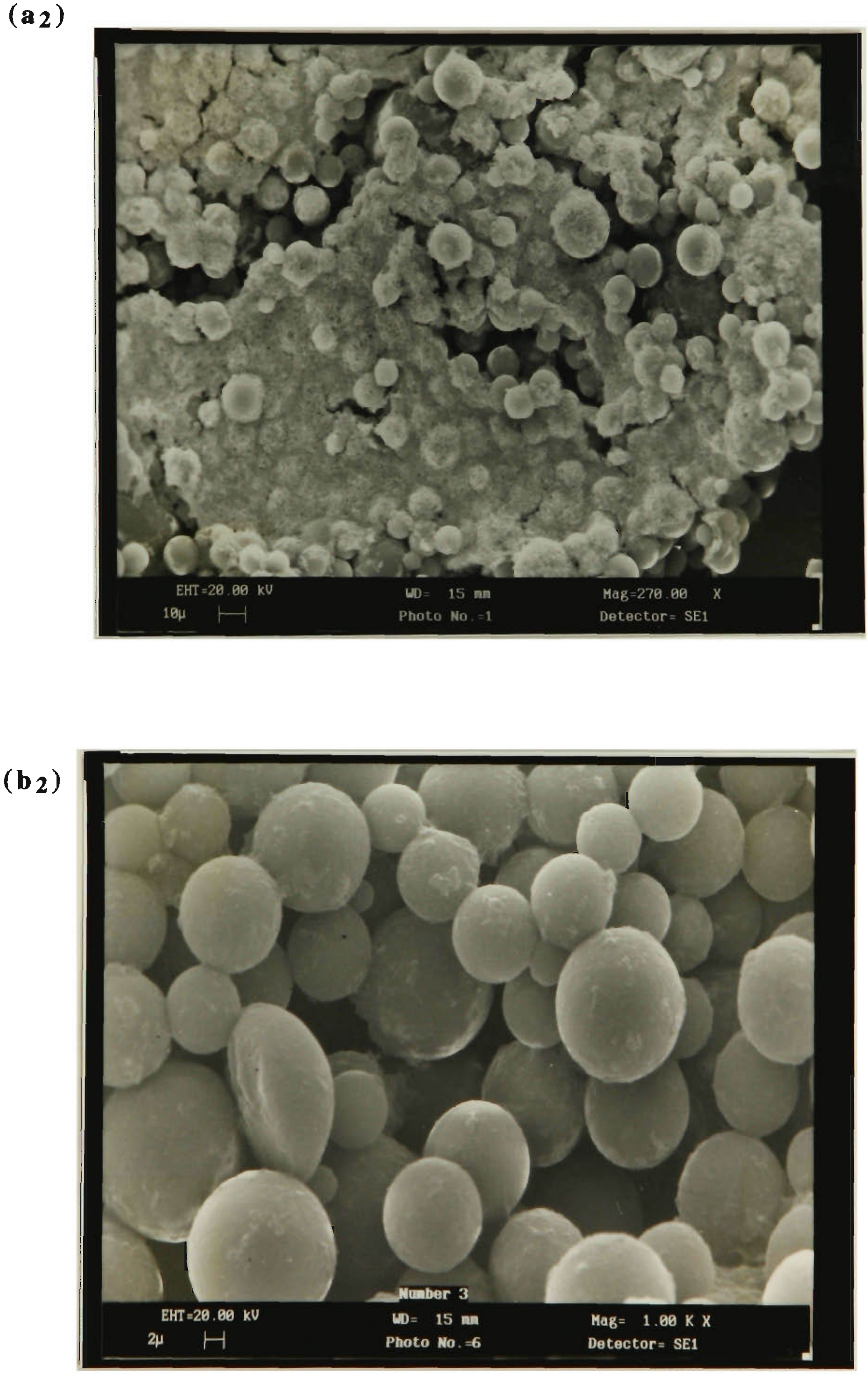


Figure 5.13 continued.

(c$_2$)

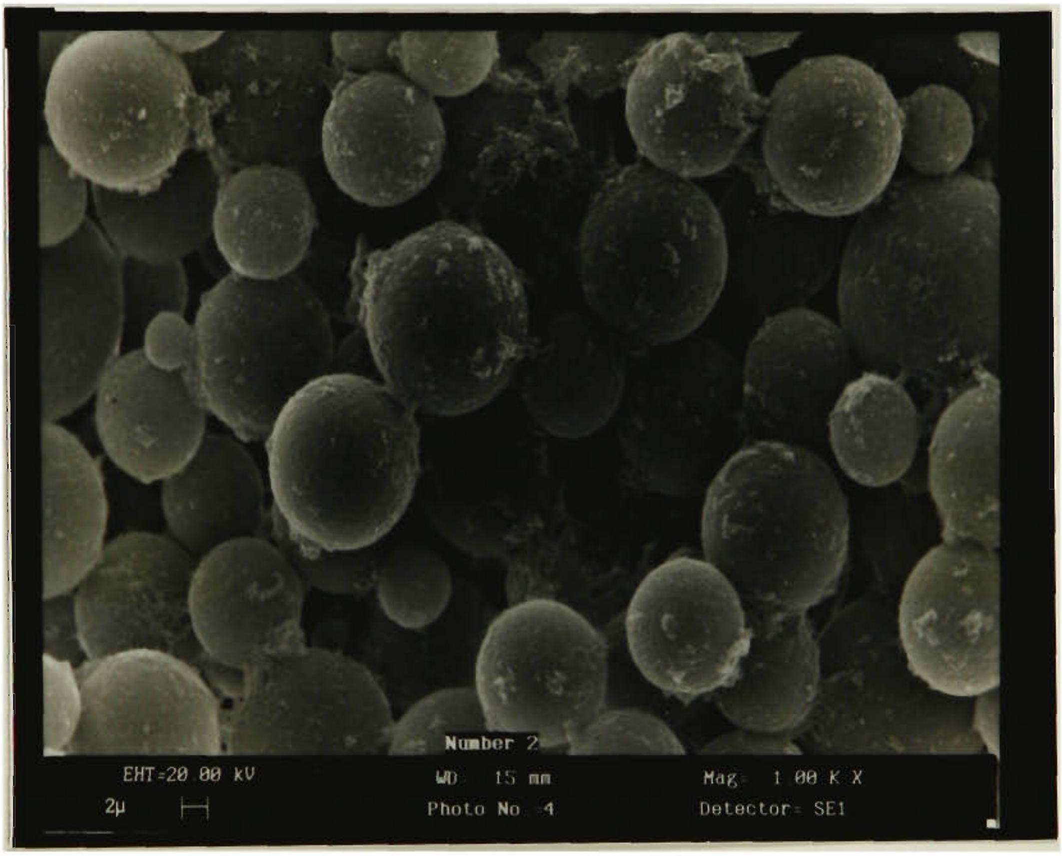


Figure 5.13 continued

5.4 CONCLUSIONS

Conductive electroactive paints have been prepared by mixing polypyrrole and polyaniline colloids and an acrylic latex formulation in water. A range of colloid concentrations [20-80% (w/w)] were considered. Different substrates (lead, stainless steel, zincalume®) were dipped in the solution of paint and after drying the adhesive strength, conductivity and electroactivity of the paint coating were investigated. The films were found to be strongly adherent to all substrates, showed electrical conductivities similar to carbon filled paints and were electroactive. The results demonstrate that conductive electroactive coatings can be applied in a versatile manner by using acrylic paints containing polypyrrole and polyaniline colloids as filler.

In conclusion, the addition of conductive electroactive polypyrrole and polyaniline colloids to an aqueous solution of acrylic latex results in the production of an electrically conductive paint. The conductivity and electroactivity of the coatings increased as the percentage of colloid was increased. Adhesion to the substrates considered also increased as the percentage (w/w) of colloid was increased up to a maximum, then the adhesion decreased with further additions. In all cases the adhesion to the substrates was greater than that of the unmodified acrylic paint.

These results demonstrate that conductive, electroactive coatings may be applied by painting onto substrate surfaces, using commercial acrylic paints containing PPy and PAn colloids as fillers. It has been demonstrated that these paints can be applied to easily oxidised metals, which are difficult to coat by the electrodeposition method. The paints also showed similar electrical conductivities to conventional conductive paints, but also had the added ability of demonstrating electroactivity. Thus, these coatings combine the unique properties of electrodeposited conductive, electroactive polymers with the simplicity and versatility of conventional paint technology.

Composites of polypyrrole and polyaniline colloids can be deposited by using negative potentials. Blends of polystyrene sulfonate/polyaniline colloid could be deposited by using positive potentials. It was found that a polymer could be grown from a solution containing pyrrole monomer and polyaniline colloid. Also polypyrrole and polyaniline colloid were coated onto the surface of sulfonate resin.

These examples demonstrate the enhanced processability of the colloidal process for preparing conductive polymers, as compared with the chemical and electrochemical methods. The thermal degradation of polyethylene in the presence of carbon black, polypyrrole and polyaniline colloids was investigated. The results indicate that polyaniline and polypyrrole colloids could be used as a filler to prevent the thermal degradation of polyethylene.

CHAPTER 6

GENERAL CONCLUSIONS

6.1 GENERAL CONCLUSIONS

One of the major setbacks to the development of electrically conducting polymers as commercial materials has been intractability in the processing, in particular the lack of solubility in most common solvents. An alternative approach might be the preparation of sterically stabilized conducting polymer colloids via dispersion polymerization. Efforts toward improving the processability of conducting polymers using the colloidal approach started with the preparation of polyacetylene colloids (19).

Two methods have been used to produce stable dispersions. The first utilizes a dispersion polymerisation route in which macroscopic precipitation is prevented by a thin, physically adsorbed outer layer of suitable polymeric surfactant which acts as a steric stabilizer. The second consists of a graft polymer (copolymer) in which one of the components is a steric stabilizer (107).

This thesis has considered the preparation, characterization and some applications of conducting polymer colloids e.g. conductive electroactive paints. In chapter two the chemical oxidation of pyrrole and aniline monomer was carried out using different stabilizers. The electroactivity, morphology and electrochemical properties of the resultant colloids were determined. The results indicate that the nature of the stabilizer employed during synthesis had an influence on the colloid formation, morphology, and electroactivity. Electroactivity, particle size and conductivity decreased when stabilizer concentration was increased. This was presumably due to the amount of adsorbed insulating stabilizer on the surface of the colloidal particles. The nature of the stabilizer and its concentration also have an influence on the yield of polymer obtained from a given amount of monomer. This is probably due to the fact that the type and concentration of stabilizer have an affect on the rate of polymerization. Macroscopic precipitation/flocculation takes place if the concentration of stabilizer is not sufficient.

Under certain conditions, polypyrrole colloid can be directly deposited on various substrates using negative potentials. Deposition of polyaniline colloids from acid media was unsuccessful due to the concomitant formation of hydrogen as protons were reduced at the glassy carbon and platinum electrode at negative potentials. Polyaniline colloids could be deposited from water (at neutral pH) onto various substrates at negative potentials.

In chapter three the influence of several steric stabilizers on the electropolymerization and properties of polypyrrole and polyaniline were investigated. Electropolymerization of pyrrole and aniline were studied using different techniques and different stabilizers. The resultant polymers were characterized in terms of morphology, adhesion and electroactivity. The electropolymerization of monomers was influenced by the presence of steric stabilizers. The growth potential under galvanostatic conditions was not significally affected by the addition of stabilizers. However, the rate of growth of polymers under potentiostatic or potentiodynamic conditions was reduced in the presence of stabilizers. Stabilizers were found to affect the morphology of the plate and solution side of the films. On stainless steel the presence of the stabilizer improves the electroactive nature of the deposited layer. This is due to the fact that the corrosion of the substrate is hindered by the presence of stabilizer.

The adhesion and morphology of electrodeposited polymers on the various substrates were investigated. The stabilizer type, its concentration, the electrode material, the polymer and the applied potential all had an effect on adhesive strength. It was found that adhesion was stronger for polyaniline coatings as compared to polypyrrole coatings. Adhesion to the substrates increased as the concentration of stabilizer increased. Then the adhesion decreased with further stabilizer addition. This is probably due to the formation and deposition of colloidal particles increasing the surface area of contact and hence adhesion. However the presence of excess stabilizer may cause preliminary coating of the electrode with the stabilizer and subsequently a reduction in adhesion. These results may be used to manipulate the degree of adhesion, as required.

In chapter four the electrochemical production of polypyrrole and polyaniline colloids was investigated for the first time. It was found that rotation rate, type and concentration of stabilizer all affected the polymer growth. The potential increased further under hydrodynamic conditions indicating that both the presence of stabilizer and rotation of the electrode mitigated against either monomer or oligomer oxidation. The stabilizer probably blocks the electrode surface or prevents deposition. Cyclic voltammograms of the material deposited on the anode indicate that the rotation of the electrode and/or the presence of the steric stabilizer decreases the amount of electroactive material deposited.

It was found that conducting colloids can be prepared electrochemically by using a flow-through cell. The effect of supporting electrolyte, flow rate, type and concentration of stabilizers on the colloid formation were considered. This colloid can be deposited using negative potentials. The electroactivity and morphology of these colloids were studied. The colloids produced are sterically stabilised and are electroactive. The reaction times appear shorter than with the chemical process. With the electrochemical system various counterions can be used for the preparation of conducting polymer colloids.

In chapter five the preparation and characterization of conductive electroactive paints and their adhesion to electrode materials was studied. Conductive electroactive paints have been made by mixing colloids of polypyrrole and polyaniline with acrylic latex in water. The adhesive strength, conductivity and electroactivity of the paint coating were investigated. The electroactivity and conductivity of the coatings increased as the percentage of colloid was increased. Adhesion to the substrate was studied and results indicate that adhesion increased as the percentage of colloid increased up to a maximum, then adhesion decreased with further addition. These results indicate that conductive electroactive coatings may be applied by painting on substrate surfaces, using commercial acrylic paints containing polypyrrole or polyaniline colloids as a filler.

Composites of polypyrrole and polyaniline colloids can be deposited on conducting substrates at negative potentials. Composites of polyaniline and polystyrene sulfonate can also be deposited but using positive potentials. The thermal degradation of polyethylene mixed with carbon black, polyaniline and polypyrrole colloids was considered. This investigation indicates that polypyrrole and polyaniline colloids can be used to improve the thermal degradation of polyethylene when used as a filler.

The observations and conclusions made from this study have added to the general understanding of conducting polymer colloids. In particular the unique electrochemical properties that allows the colloids to be electrocoagulated at negative potentials and the investigation into the electrochemical material of products for these colloids have proven to be valuable findings. Some prelimary studies into applications of these colloids have also been considered. This knowledge might be practically used in this or other laboratories and industries in the future.

6.2 REFERENCES

1. R.J. Hunter, Foundations of Colloid Science, Volume 1, Oxford University Press, New York (1989).

2. R.B. Dean, Modern Colloids, D. Van Nostrand Company, New York (1949).

3. J. Mort and G. Pfister, Poly. Plast. Tech. Eng, **12** (1970) 89.

4. H. Letheby, J. Chem. Soc, **15** (1862) 161.

5. A.G. Green and A.E. Woodhead, J. Chem. Soc, (1910) 2388.

6. D.M. Mohilner, R.N. Adams and W. J. Argersinger, Amrican Chemical Society Journal, **84** (1962) 3618.

7. P. Kovacic and C. Wu, Journal of Polymer Scince, **47** (1960) 45.

8. F.P. Burt, Chemical Society Journal, (1910) 1171.

9. V.V. Walatka, Jr., M.M. Labes and J.H. Perlstein, Physical Review Letters, **31** (1973) 1139.

10. R.L. Greene, G.B. Street and L. J. Suter, Physical Review Letters, **34** (1975) 577.

11. R.B. Kaner and A.G. MacDiarmid, Scientific American, **258**, (1988) 60.

12. H. Shirakawa and S. Ikeda, Polymer Journal, **2** (1971) 231.

13. H. Shirakawa, E. J. Louis, A.G. MacDiarmid, C. K. Chiang, and A. J. Heeger, J. Chem. Soc. Chem. Commun, (1977) 578.

14. C.K. Chiang, C.R. Fincher, Jr, Y.W. Park, A. J. Heeger, H. Shirakawa, E.J. Louis, S.C. Gau, and A.G. MacDiarmid, Physical Review Letters, **39** (1977) 1098.

15. C.K. Chiang, M.A. Druy, S.C. Gau, A.J. Heeger, E.J. Louis, A.G. MacDiarmid, Y.W. Park, H. Shirakawa, Journal of the American Chemical Society, **100:3** (1978) 1013.

16. A.F. Diaz , K.K. Kanazawa and G.P. Gardini, J.Chem.Soc. Chem. Commun, (1979) 635.

17. D.M. Ivory, G.G. Miller, J.M. Sowa, L.W. Shacklette, R.R. Chance, and R.H. Baughman, J. Chem. Phys, **71** (1979) 1506.

18. J.F. Rabolt, T.C. Clarke, K. K. Kanazawa, J. R. Reynolds, and G. B. Street, J. Chem. Soc. Chem. Commun, (1980) 347.

19. J. Edwards, R. Fisher, B. Vincent, Makromol. Chem., Rapid Commun, **4** (1983) 393.

20. S. Maiti, Journal of Scientific and Industrial Research, **48** (1989) 577.

21. A. Pron, Materials Science Forum, **21** (1987) 13.

22. C.K. Chiang, Y.W. Park, A.J. Heeger, H. Shirakawa, E.J. Louis, and A. G. MacDiarmid, J. Chem. Phys, **69** (1978) 5098.

23. Y.W. Park, A.J. Heeger, M.A. Druy and A.G. MacDiarmid, J. Chem. Phys, **73** (1980) 946.

24. A.G. MacDiarmid, R.J. Mammone, J.R. Krawczyk and S.J. Porter, Mol. Cryst. Liq. Cryst., **105** (1984) 89.

25. A.O. Patil, Y. Ikenoue, N. Basescu, N. Colaneri, J. Chen, F. Wudl and A.J. Heeger, Synthetic Metals, **20** (1987) 151.

26. S. Hayashi, S. Takeda, K. Kaneto, K. Yoshino and T. Matsuyama, Synthetic Metals, **18** (1987) 591.

27. O. Ikeda and H. Yoneyama, J. Electroanal Chem, **265** (1989) 323.

28. A.O. Patil, A.J. Heeger and F. Wudl, Chem. Rev. **88** (1988) 183.

29. J.C. Scott, P. Pfluger, M.T. Krounbi and G.B. Street, Physical Review B, **28** (1983) 2140.

30. J.L. Bredas, J.C. Scott, K. Yakushi and G.B. Street, Physical Review B, **30** (1984) 1023.

31. A.F. Diaz and J.C. Lacroix, New Journal of Chemistry, **12** (1988) 171.

32. S. Machida, S. Miyata, A. Techagumpuch, Synthetic Metals, **31** (1989) 311.

33. S.P. Armes, Synthetic, Metals, **20** (1987) 365.

34. S. Rapi, V. Bocchi and G.P. Gardini, Synthetic Metals, **24** (1988) 217.

35. T.H. Chao and J. March, Journal of Polymer Science: Part A: Polymer Chemistry, **26** (1988) 743.

36. A. Pron, J. Suwalski, S. Lefrant, Synthetic Metals, **18** (1987) 25.

37. E.T. Kang, K.G. Neoh, K.L. Tan, Mol. Cryst. Liq. Cryst,**173** (1989) 141.

38. A. Pron, Z. Kucharski, C. Budrowski, M. Zagorska, S. Krichene, J. Suwalski, G. Dehe, S. Lefrant, J. Chem. Phys., **83** (1985) 5923.

39. M.M. Castillo-Ortega, M.B. Inoue and M. Inoue, Synthetic Metals, **28** (1989) C65.

40. R.E. Myers, Journal of Electronic Materials, **15** (1986) 61.

41. J.A. Walker, L.F. Warren and E.F. Witucki, Polymer Preprints, **28** (1987) 256.

42. A. Ohtani and T. Shimidzu, Bull. Chem. Soc. Jpn, **62** (1989) 234.

43. E.T. Kang, K.G. Neoh, T.C. Tan and Y.K. Ong, Journal of Polymer Science: Part A: Polymer Chemistry, **25** (1987) 2143

44. D.S. Maddison and J. Unsworth, Synthetic Metals, **30** (1989)47.

45. A. Mohammadi, I. Lundstrom, W.R. Salaneck and O. Inganas, Synthetic Metals, **21** (1987) 169.

46. G.R. Mitchell and A. Geri, J. Phys. D: Appl. Phys, **20** (1987) 1346.

47. M. Fukuyama, N. Nanai, T. Kojima, Y. Kudoh and S. Yoshimura, Synthetic Metals, **58** (1993) 367.

48. T. Hagiwara, M. Hirasaka, K. Sato and M. Yamaura, Synthetic Metals, **36** (1990) 241.

49. M. Ogasawara, K. Funahashi, T. Demura, T. Hagiwara and K. Iwata, Synthetic Metals, **14** (1986) 61.

50. M.S. Kiani and G.R. Mitchell, Synthetic Metals, **48** (1992) 203.

51. G.R. Mitchell, F.J. Davis and C.H. Legge, Synthetic Metals, **26** (1988) 247.

52. M. Yamaura, T. Hagiwara and K. Iwata, Synthetic Metals, **26** (1988) 209.

53. G.R. Mitchell, F.J. Davis, R. Cywinski and A. C. Hannon, Polymer Communications, **30** (1989) 98.

54. A. Kassim, H. Block, F.J. Davis and G. R. Mitchell, J. Mater. Chem., **2(9)** (1992) 987.

55. R. Yang, D. F. Evans, L.Christensen, and W.A. Hendrickson, J. Phys. Chem, **94** (1990) 6117.

56. S.M. Geraty and J.G. Vos, J. Chem. Soc. Dalton Trans, (1987) 3073.

57. J. Prejza, I. Lundstrom, and T. Skotheim, J. Electrochem. Soc.: Electrochemical Science and Technology, **129** (1982) 1685.

58. K. K. Kanazawa, A.F. Diaz, W.D. Gill, P.M. Grant, G.B. Street, G. P. Gardini, J.F. Kwak, Synthetic Metals, **1** (1979/80) 329.

59. K.M. Cheung, D. Bloor, G.C. Stevens, Polymer, **29** (1988) 1709.

60. A. Diaz, Chemica Scripta, **17** (1981) 145.

61. N.S. Chong, M.L. Norton, and J.L. Anderson, J. Electrochem. Soc, **138** (1991) 1263.

62. M. Satoh, K. Kaneto and K. Yoshino, Synthetic Metals, **14** (1986) 289.

63. M. Takakubo, Synthetic Metals, **16** (1986) 167.

64. A.F. Diaz, and B. Hall, IBM J. Res. Develop, **27** (1983) 342.

65. B.F. Cvetko, M.P. Brungs, R.P. Burford, M. Skyllas-Kazacos, Journal of Applied Electrochemistry, **17** (1987) 1198.

66. R. John and G.G. Wallace, Polymer International, **27** (1992) 255.

67. T. F. Otero, R. Tejada and A.S. Elola, Polymer, **28** (1987) 651.

68 M.D. Imisides, R. John, P.J. Riley and G.G. Wallace, Electroanalysis, **3** (1991) 879.

69. K. Tanaka, T. Shichiri, S. Wang and T. Yamabe, Synthetic Metals, **24** (1988) 203.

70. P. Shair, A. Zemel and B. Zinger, Synthetic Metals, **41-43** (1991) 443.

71. G.B. Street, T.C. Clarke, M. Krounbi, K. Kanazawa, V. Lee, P. Pfluger, J.C. Scott, and G. Weiser, Mol. Cryst. Liq. Cryst, **83** (1982) 253.

72. J.H. Kaufman, O.R. Melroy, F.F. Abraham, A.I. Nazzal, A. Kapitulnik, Synthetic Metals, **18** (1987) 19.

73. P. Lang, F. Chao, M. Costa and F. Garnier, Polymer, **28** (1987) 668.

74. L.L. Miller, B. Zinger, and Q.X. Zhou, J. Am. Chem. Soc, **109** (1987) 2267.

75. K.K. Kanazawa, A.F. Diaz, R.H. Geiss, W.D. Gill, J.F. Kwak, J. A. Logan, J.F. Rabolt, and G.B. Street, J. Chem. Soc. Chem. Commun, (1979) 854.

76. A.F. Diaz and J.I. Castillo, J. Chem. Soc. Chem. Commun, (1980) 397.

77. Y. Li and R. Qian, Synthetic Metals, **53** (1993) 149.

78. B. Sun, J.J. Jones, R.P. Burford, M. Skyllas-Kazacos, Journal of Materials Science, **24** (1989) 4024.

79. D.C. Trivedi and S.K. Dhawan, J. Mater. Chem, **2** (1992) 1091.

80. A. Pron, F. Genoud, C. Menardo and M. Nechtschein, Synthetic Metals, **24** (1988) 193.

81. S.P. Armes and J. F. Miller, Synthetic Metals, **22** (1988) 385.

82. A.G. MacDiarmid, J.C. Chiang, M. Halpern, W.S. Huang, S.L. Mu, N.L.D. Somasiri, W. Wu and S.I. Yaniger, Mol. Cryst. Liq. Cryst, **121** (1985) 173.

83. S.K. Manohar and A.G. MacDiarmid, Synthetic Metals, **29** (1989) 1349.

84. M. Wan, Synthetic Metals, **31** (1989) 51.

85. W.S. Huang, B.D. Humphrey and A.G. MacDiarmid, J. Chem. Soc, Faraday Trans, **82** (1986) 2385.

86. R.J. Cushman, P.M. McManus and S.C. Yang, J. Electroanal Chem., **291** (1986) 335.

87. Y. Wei, G.W. Jang, K.F. Hsueh, E.M. Scherr, A.G. MacDiamid, A.J. Epstein, Polymer, **33** (1992) 314.

88. K.R. Cromack, M.E. Jozefowicz, J.M. Ginder, A.J. Epstein, R.P. McCall, G. Du, J.M. Leng, K. Kim, C. Li, Z. H. Wang, M.A. Druy, P.J. Glatkowski, E.M. Scherr, A. G. MacDiarmid, Macromolecules, **24** (1991) 4157.

89. M. Angelopoulos, G.E. Asturias, S.P. Ermer, A. Ray, E.M. Scherr, A.G. MacDiarmid, M. Akhtar, Z. Kiss, A.J. Epstein, Mol. Cryst. Liq. Cryst., **160** (1988) 151.

90. W.W. Focke, G.E. Wnek, and Y. Wei, J. Phys. Chem. **91** (1987) 5813

91. T. Kobayashi, H. Yoneyama and H. Tamura, J. Electroanal Chem, **161** (1984) 419.

92. T. Kobayashi, H. Yoneyama and H. Tamura, J. Electroanal Chem, **177** (1984) 281.

93. A.F. Diaz and J.A. Logan, J. Electroanal Chem, 111 (1980) 111.

94. W. Lixiang, J. Xiabin and W. Fosong, Synthetic Metals, **41-43** (1991) 683.

95. C.Q. Cui, L.H. Ong, T.C. Tan and J.Y. Lee, Synthetic Metals, **58** (1993) 147.

96. C.D. Batich, H.A. Laitinen, and H.C. Zhou, J. Electrochem. Soc, **137** (1990) 883.

97. S.A. Chen and T.S. Lee, Journal of Polymer Science: Polymer Letters, **25** (1987) 455.

98. J. Desilvestro and W. Scheifele, J. Mater. Chem, **3** (1993) 263.

99. J.C. Chiang and A.G. MacDiarmid, Synthetic Metals, **13** (1986) 193.

100. D.M. Mohilner, R.N. Adams and W.J. Argersinger, Journal of the American Chemical Society, **84** (1962) 3618.

101. M.E. Jozefowicz, A.J. Epstein, X. Tang, Synthetic Metals, **46** (1992) 337.

102. W.S. Huang, A.G. MacDiarmid, and A.J. Epstein, J. Chem. Soc. Chem. Commun, (1987) 1784.

103. V.M. Geskin, Y.A. Letuchy, B.Z. Lubentsov, L.M. Grundel, S. M. Tikhomirov and M.L. Khidekel, Journal of Molecular Electronics, **5** (1989) 207.

104. E.M. Genies and M. Lapkowski, J. Electroanal Chem, **220** (1987) 67.

105. P.J.S. Foot, F. Mohammed, P.D. Calvert and N.C. Billingham, J. Phys. D: Appl. Phys, **20** (1987) 1354.

106. M. Aldissi and S.P. Armes, Progress in Organic Coatings, **19** (1991) 21.

107. M. Aldissi, Adv. Mater, **5** (1993) 60.

108. S.P. Armes, M. Aldissi, M. Hawley, J.G. Beery, S. Gottesfeld, Langmuir, **7** (1991) 1447.

109. L.B. Luttinger, J. Org. Chem, **27** (1962) 1591.

110. S.P. Armes and M. Aldissi, Am. Chem. Soc. Div. Polym. Mater. Sci. Eng. Proc, **60** (1989) 751.

111. S.P. Armes, M. Aldissi, S. Agnew, and S. Gottesfeld, Langmuir, **6** (1990) 1745.

112. S.P. Armes, M. Aldissi, S, Agnew and S. Gottesfeld, Mol. Cryst, Liq. Cryst, **190** (1990) 63.

113. R.F.C. Bay, S.P. Armes, C.J. Pickett and K.S. Ryder, Polymer, **32** (1991) 2456.

114. S.P. Armes and M. Aldissi, J. Chem. Soc. Chem. Commun, (1989) 88.

115. S.P. Armes, M. Aldissi, and S.F. Agnew, Synthetic Metals, **28** (1989) C 837.

116. N. Cawdery, T.M. Obey, and B. Vincent, J. Chem. Soc. Chem. Commun, (1988) 1189.

117. S.P. Armes, J.F. Miller, and B. Vincent, Journal of Colloid and Interface Science, **118** (1987) 410.

118. M. Beaman and S.P. Armes, Colloid and Polymer Science, **271** (1993) 70.

119. C. DeArmitt and S.P. Armes, Journal of Colloid and Interface Science, **150** (1992) 134.

120. S.P. Armes, M. Aldissi, G.C. Idzorek, P.W. Keaton, L.J. Rowton, G.L. Stradling, M.T. Collopy and D.B. McColl, Journal of Colloid and Interface Science, **141** (1991) 119.

121. F. Epron, F. Henry, O. Sagnes, Makromol Chem, Macromol Symp, **35/36** (1990) 527.

122. G. Markham, T.M. Obey and B. Vincent, Colloids and Surfaces, **51** (1990) 239.

123. H. Hirai, H. Wakabayashi, and M. Komiyama, Bull. Chem. Soc. Jpn, **59** (1986) 367.

124. S.P. Armes and M. Aldissi, Synthetic Metals, **37** (1990) 137.

125. S.P. Armes and M. Aldissi, Polymer, **31** (1990) 569.

126. B. Vincent and J. Waterson, J. Chem. Soc. Chem. Commun, (1990) 683.

127. S.P. Armes and B. Vincent, Synthetic Metals, **25** (1988) 171.

128. S.P. Armes and B. Vincent, J. Chem. Soc. Chem. Commun, (1987) 288.

129. C. DeArmitt and S.P. Armes, Langmuir, **9** (1993) 652.

130. P.M. Beadle and S.P. Armes, Synthetic Metals, **55-57** (1993) 1114.

131. P.M. Beadle, L. Rowan, J. Mykytiuk, N.C. Billingham and S.P. Armes, Polymer, **34** (1993) 1561.

132. N. Gospodinova, P. Mokreva and L. Terlemezyan, J. Chem. Soc. Chem. Commun, (1992) 923.

133. P.L. Kuo and C.J. Chen, Jounal of Polymer Science: Part A: Polymer Chemistry, **31** (1993) 99.

134. E.C. Cooper and B. Vincent, J. Phys. D: Appl. Phys, **22** (1989) 1580.

135. D.N. Furlong, P.A. Freeman, and A.C.M. Lau, Journal of Colloid and Interface Science, **80** (1981) 20.

136. R.B. Bjorklund and B. Liedberg, J. Chem. Soc. Chem. Commun, (1986) 1293.

137. H. Ge and G.G. Wallace, Analytical Chemistry, **61** (1989) 198.

138. H. Ge and G.G. Wallace, Journal of Liquid Chromatoghraphy, **13** (16) (1990) 3245.

139. J.F. Belliveau, E.G. Bobalek, and G.L. Simard, J. of Paint Technology, **42** (1970) 377

140. M.A.D. Paoli, R.J. Waltman, A.F. Diaz and J. Bargon, J. Chem. Soc. Chem. Commun, (1984) 1015.

141. S.E. Lindsey and G.B. Street, Synthetic Metals, **10** (1984/85) 67.

142. T. Ojio and S. Miyata, Polymer Journal, **18** (1986) 95.

143. O. Niwa and T. Tamamura, J. Chem. Soc. Chem. Commun, (1984) 817.

144. T.T. Wang, S. Tasaka, R.S. Hutton, and P.Y. Lu, J. Chem. Soc. Chem. Commun, (1985) 1343.

145. J. Roncali and F. Garnier, J. Chem. Soc. Chem. Commun, (1986) 783.

146. V. Bocchi and G.P. Gardini, J. Chem. Soc. Chem. Commun, (1986) 148.

147. O. Niwa, M. Hikita and T. Tamamura, Synthetic Metals, **18** (1987) 677.

148. H. Ge and G.G. Wallace, Journal of Chromatography, **588** (1991) 25.

149. S.P. Armes, S. Gottesfeld, J.G. Beery, F. Garzon and S.F. Agnew, Polymer, **32** (1991) 2325.

150. A. Yassar, J. Roncali and F. Garnier, Polymer Communications, **28** (1987) 103.

151. E.C. Cooper and B. Vincent, Journal of Colloid and Interface Science, **132** (1989) 592.

152. E. Kokufuta and K. Takahashi, Macromolecules, **19** (1986) 351.

153. T. Shimidzu, R. Polymers, **6** (1987) 221.

154. R. Partch, S.G. Gangolli, E. Matijevic, W. Cai, and S. Arajs, Journal of Colloid and Interface Science, **144** (1991) 27.

155. R.B. Bjorklund and I. Lundstrom, Journal of Electronic Materials, **13** (1984) 211.

156. J.S. Miller, Inorg. Chem, **22** (1983) 3681.

157. A. Calahorra, Journal of Coatings Technology, **60** (1988) 25.

158. J.J. Park and C.H. Clatterbuck, 11th National SAMPE Technical Conference November, 13-15 , (1979) 125.

159. M.M. Birnbaum, E.C. Metzler, E.L. Cleland, Scattering in Optical Materials, Bellinsham, WA, SPIE, **362** (1983) 60.

160. M. Alonso, M. Satoh, K. Miyanami, K. Higashi, T. Ito, Powder Technology, **67** (1991) 11.

161. S. Takagi, Japan Plastics Age, (1984) 17.

162. A.C. Hart, JOCCA, **3** (1989) 95.

163. M. Yoshizumi and K. Wakabayashi, 17th National SAMPE Technical Conference October, **22-24** (1985) 410.

164. H. Eisazadeh, G. Spinks, and G.G. Wallace, Materials Forum, **17** (1993) 241.

165. J.M. Chiou, Q. Zheng and D.D.L. Chung, Composites, **20** (1989) 379.

166. M.S. Ahmad, M.K. Abdelazeez, A.M. Zihlif, Journal of Materials Scince, **24** (1989) 1795.

167. Z. Osawa, K. Kobayashi, Journal of Materials Scince, **22** (1987) 4381.

168. M.A.D. Paoli, S. Panero, P. Prosper and B. Scrosat, Electrochimica Acta, **35** (1990) 1145.

169. T. Skotheim, I. Lundstrom, and J. Prejza, J. Electrochem. Soc, (1981) 1625.

170. W.H. Kao and T. Kuwana, J. Am. Chem. Soc. **106** (1984) 473.

171. M. Sakaguchi, M. sato, M. Kawashima and Y. Sato, Polymer Journal, **23** (1991) 247

172. M. Aldissi, Makromol. Chem, Macromol. Symp, 24 (1989) 1.

173 S. Kuwabata, J. Nakamura, and H. Yoneyama, J. Chem. Soc. Chem. Commun, (1988) 779.

174. H. Munstedt, Polymer, **27** (1986) 899.

175. A.F. Diaz, J. Crowley, J. Bargon, G.P. Gardini and J.B. Torrance, J. Electroanal Chem, **121** (1981) 355.

176. J. Roncali and F. Garnier, J. Phys. Chem, **92** (1988) 833.

177. A. Andreatta, Y. Cao, J.C. Chiang, A.J. Heeger, and P. Smith, Synthetic Metals, **26** (1988) 383.

178. S. Li, Y. Cao, and Z. Xue, Synthetic Metals, **20** (1987) 141.

179. M. Inoue, R.E. Navarro and M.B. Inoue, Synthetic Metals, **30** (1989) 199.

180. J. Przyluski, K. Such, H. Wycislik, W. Wieczorek, Z. Florianczyk, Synthetic Metals, **35** (1990) 241.

181. K.G. Neoh, E.T. Kang and T.C. Tan, Polymer degradation and Stability, **21** (1988) 93.

182. G. Tourillon and F. Garnier, J. Electroanal. Chem, **135** (1982) 173.

183. T.A. Skotheim (Ed.), Handbook of Conducting Polymers,Vols.1 and 2, Marcel Dekker, New York, 1986.

184. R.A. Bull, F.R. Fan and A.J. Bard, J. Electrochem. Soc, **130** (1983) 1636.

185. A. Elzing, A.V. Patten, W. Visscher and E. Barendrecht, J. Electroanal Chem, **233** (1987) 113.

186. H. Ge and G.G. Wallace J. Liq. Chromatography, **13** (1990) 3261.

187. P. Burgmayer and R. W. Murray, J. Phys. Chem, **88** (1984) 2515.

188. E. Wang, Y. Liu, J. Dong and J. Ding, J. Chem. Soc. Faraday Trans, **86** (1990) 2243.

189. H. Zhao, W.E. Price and G.G. Wallace, J. Electroanal. Chem, **334** (1992) 111.

190. L.L. Miller, B. Zinger and Q.X. Zhou., J. Am. Chem. Soc, **109** (1987) 2267.

191. Y. Lin and G.G. Wallace, Anal. Lett, **22** (1989) 669.

192. S.P. Armes, M. Aldissi, Polymer, **32** (1991) 2043.

193. D.M. Brewis, Materials science and Technology, **2** (1986) 761

194. R.G. Schmidt and J.P. Bell, Advances in Polymer science, **75** (1986) 33

195. S.N. Bhadani, M.K. Gupta, and S.K. Sen Gupta, **49** (1993) 397.

196. G.L. McIntire, D.M. Chiappardi, R.L. Casselberry, and H.N. Blount, J. Phys. Chem, **86** (1982) 2632.

197. R. John, M.J. John, G.G. Wallace, and H. Zhao, R.A. Mackay (Ed.) and J. Texter (Ed.) Electrochemistry in Colloids and Dispersions, VCh, New York (1992) 225.

198. S. Radhakrishnan and D.R. Saini, Synthetic Metals, **58** (1993) 243.

199. H. Eisazadeh, G. Spinks, G.G. Wallace, Materials Forum, **16** (1992) 341

200. R. John and G.G. Wallace, J. Electroanal. Chem, **319** (1991) 365.

201. A. Hodgson, M. John, G. G. Wallace, React. Polymers, **18** (1992) 17.

202. H. Zhao, W.E. Price, G.G. Wallace, J. Memb. Sci., **87** (1994) 47.

203. J. Przyluski, Conducting Polymers-Electrochemistry, Sci-Tech Publications, Vaduz (1991).

204. A.A. Syed and M.K. Dinesan, Talanta, **38** (1991) 815.

205. Y. Wei, Y. Sun, S. Patel and X. Tang, Polymer Preprints, **30** (1989) 228.

206. E.M. Genies and C. Tsintavis, J. Electroanal Chem, **195** (1985) 109.

207. G. Zotti, S. Cattarin and N. Lomisso, J. Electroanal Chem, **239** (1988) 387.

208. M. Gandhi, R. Burford, G. Spinks, G.G.Wallce, 3rd Pacific Polymer Conference, Gold Coast, Dec, (1993).

209. F. Beck, P. Braun, M. Oberst, Der. Bunsenges, **91** (1987) 967.

210. J. B. Schlenoff, H. Xu, J. Electrochem. Soc, **139** (1992) 2397.

211. H. Eisazadeh, G.G. Wallace and G. Spinks, Polymer, **35** (1994) 1754.

212. P. Carden, A.J. Hodgson, R. John, M.J. Spencer, G.G. Wallace, R.A. Mackay (Ed.) and J. Texter (Ed.) "Electrochemistry in Colloids and Dispersions" VCH New York, ACS Symp. Ser, (1992) 235.

213. K. Tanaka, T. Shichiri, S. Wang and T. Yamabe, Synthetic Metals, **24** (1988) 203.

214. P. Lang, F. Chao, M. Costa and F. Garnier, Polymer, **28** (1987) 668.

215. F. Beck, Electrochimica Acta, **33** (1988) 839.

216. C.K. Baker and J.R. Reynolds, J. Electroanal Chem, **320** (1988) 307.

217. V.A. Garten, D.R. Nat, and D.E. Weiss, Reviews of Pure and Applied Chemistry, **7** (1957) 69.

218. A.S. Kuzminskii, L.I. Lyubchanskaya, N.G. Khitrova, and S.I. Bass, Rubber Chemistry and Technology, **26** (1953) 858.

219. H.R. Anderson, Journal of Applied Polymer Science, **3** (1960) 316.

220. H. Ge, PhD Thesis, University of Wollongong, (1990).

221. K.G. Chorbadjiev and D.L. Kotzev, Int. J. Adhesion and Adhesives, **8** (1988) 143

222. Z. Osawa, K. Kobayashi, Journal of Materials Science, **22** (1987) 4381.

223. D.M. Bigg, Polymer Composites, **7** (1986) 69.

224. W.L. Hawkins, R.H. Hansen, W. Matreyek and F.H. Winslow, Journal of Applied Polymer Science, **1** (1959) 37.

225. W.L. Hawkins, M.A. Worthington, and W. Matreyek, Journal of Applied Polymer Science, **3** (1960) 277.