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STUDIES OF ELECTROACTIVE POLYMERIC  
MATERIALS WITH PARTICULAR REFERENCE  
TO POLY (ARYL METHINE)S

A Thesis

presented for the degree of

DOCTOR OF PHILOSOPHY

in the Faculty of Science of the  
University of St. Andrews

by

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November 1988



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TO MY PARENTS AND TORIA

DECLARATION

I Linden Bruce Forsyth hereby certify that this thesis has been composed by myself, that it is a record of my own work, and that it has not been accepted in partial or complete fulfilment of any other degree or professional qualification.

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Date ..<sup>8</sup>/<sub>3</sub>/89...

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ABSTRACT

The bulk of this work is concerned with the synthesis of poly(aryl methine)s, a group of polymers which are suggested to be of interest as intrinsically, electronically conducting polymers. Direct and indirect chemical routes towards these products were attempted with mixed success.

Relevant subjects to this work have been reviewed as introductory material to the results presented. Further background material required for the understanding of data or equipment has also been included.

Monomers were synthesised which could be chemically or electrochemically polymerised to poly(aryl methine)s. Chemical polymerisation methods and detailed electrochemical studies were performed on these monomers.

Both chemical synthesis and electrochemical studies suggest that these polymers are only moderately conducting in their doped state. In addition to being of limited use as conductors, this indicates that accurate studies of these polymers can be difficult.

Some studies on metal/polymer and polymer/polymer composites were also performed. Many of these studies involved the ionically conducting polymer, poly(ethylene oxide), PEO, in which was dissolved salts to produce a polymer electrolyte.

Both the ionic and electronic conducting polymer fields were brought together in part of this work where the electrochemical synthesis of electronic conducting polymers in the solid state was studied. Here a polypyrrole/PEO bilayer was formed.

In order to perform these various studies, some items of equipment had to be designed, built and tested as part of the work undertaken.

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CHAPTER 1INTRODUCTION

Electrically conducting polymers is currently a subject of great interest and a field in which considerable research is being done by scientists from many disciplines, from organic chemists to theoretical physicists. The electrical conductivity of materials varies by more than 25 orders of magnitude, as can be seen in Figure 1.1. The classification of materials into insulators, semiconductors and metals can only be approximate because the electrical transport properties as a function of temperature need to be taken into account, as well as the room temperature conductivity of the materials. Conductivity and conduction mechanisms are discussed at some length in Chapter 2.

Organic solids (including most polymers) are generally classified as insulators. An exception to this is a group of materials called quasi-one-dimensional (Q1D) systems, which approach, but are not strictly, one-dimensional (1D) systems. The impetus for research into this field was provided by Little<sup>[1]</sup>, who suggested that the synthesis of 1D organic, room temperature, superconductors (materials that conduct an electrical current with virtually no resistance), was a possibility. The resulting research led to the discovery of many Q1D solids, ranging from charge transfer complexes, such as tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ)<sup>[2,3]</sup>, to conducting polymers.

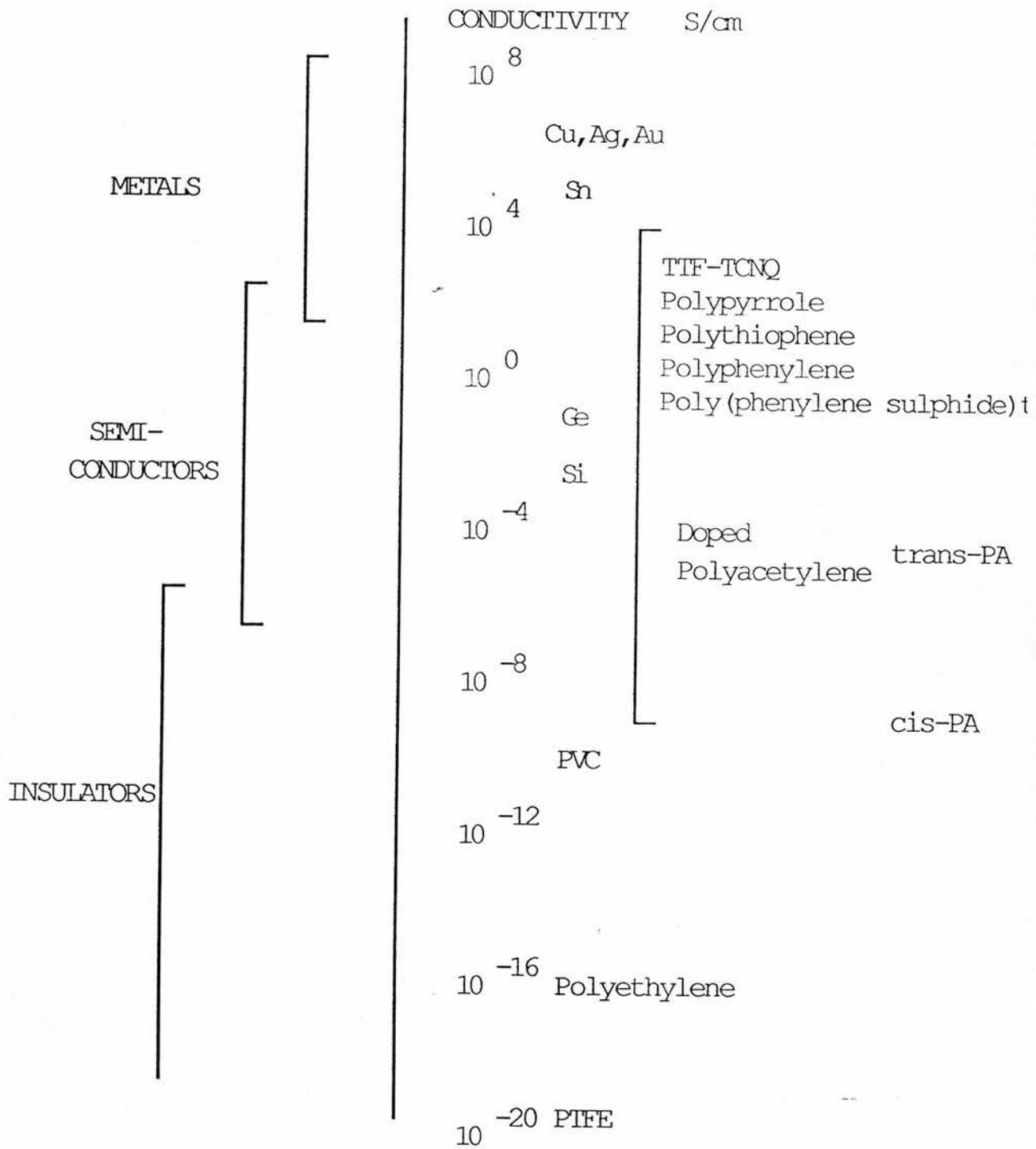


FIGURE 1.1

The latter have attracted much interest from the standpoint of both fundamental studies and perspectives of application, as can be seen in the two volumes of the "Handbook of Conducting Polymers"<sup>[4]</sup>. It is this topic of electrically conducting polymers which is the main subject of this thesis. (Hereafter these materials will simply be referred to as "conducting polymers", as is commonly the case in most of the literature).

### 1.1 Classification

Materials which conduct charge through their bulk may be broadly split into two groups: ionic conductors and electronic conductors. As these names imply, in the former, charge is transported via ions and in the latter, by electrons. Ionic conductors have mainly been investigated for use as electrolytes in batteries and materials such as sodium  $\beta$ -aluminas and lithium iodide<sup>[5,6]</sup> have been well studied. Ionically conducting polymers have recently become a topic of great interest<sup>[7]</sup> and a certain amount of work on this subject is presented in Chapter 3.

However, the bulk of work in this thesis is concerned with electronically conducting polymers. This group of materials may be divided into two sections: a) so-called "intrinsically" conducting polymers and b) composites. Composites are materials which contain a conductor such as carbon black or a metal held within a polymer

matrix. Charge is passed by the conductor, with the polymer acting as a support, which may also have the advantage of improving the mechanical properties of the electronic conductor. These materials have been known and used for many years and have been well reviewed<sup>[8,9]</sup>. Some work was done on this subject and the results may be found in Chapter 3.

A further method of obtaining conducting polymers, which has been known for some time, is to pyrolyse an insulating polymer. This generally leads to increased conjugation of the system, and it is from this that the increased conductivity results. The direct formation of Q1D conjugated polymers is however quite a recent development and it is this which will now be discussed.

## 1.2 History

Polymers generally have conductivities in the range  $10^{-10}$  -  $10^{-20}$  S/cm which makes them highly insulating materials. In 1973 the discovery of poly(sulphur nitride)  $(SN)_x$  which exhibited metallic conductivity behaviour was reported<sup>[10]</sup>. This polymer was found to be superconducting below 0.3K<sup>[11]</sup> and it was later discovered that halogens, particularly bromine, could be incorporated into the polymer to increase the room temperature conductivity by an order of magnitude without disrupting the superconducting transition<sup>[12]</sup>. This material, however, is still quite singular in both its structure and its properties.

The above work stimulated much research in the field and the first organic conducting polymer appeared in 1977 when Shirakawa and co-workers reported<sup>[13]</sup> the metallic and semiconducting properties of chemically modified polyacetylene [PA]. The following few years saw the discovery of several other conducting polymers including polypyrrole [PP]<sup>[14]</sup>, polythiophene [PT]<sup>[15]</sup>, poly(paraphenylene) [PPP]<sup>[16]</sup>, poly(phenylene sulphide) [PPS]<sup>[17]</sup> and poly(phenylene vinylene) [PPV]<sup>[18]</sup>. The structure of these and many other conducting polymers may be found in Appendix I. The field has since grown at an enormous rate and has been the subject of a large amount of review literature<sup>[3,4,19-23]</sup>

### 1.2.1 Polyacetylene

Thin films of PA with a metallic lustre were first formed by Shirakawa and Ikeda in 1971, using Ziegler catalysts<sup>[24]</sup>. Similar methods have been used for other polymers and more details about the chemical synthesis of conducting polymers may be found in Chapter 4. Exposure of PA to halogen vapours led to a large increase in conductivity<sup>[13]</sup>. It was subsequently found that both electron donors and acceptors produced increased conductivity<sup>[24]</sup> and that a wide variety of so-called dopants could be used.

This process is often referred to as 'doping', a term borrowed from inorganic semiconductors. However it is best to view this process as a redox reaction where the conducting entity is now a polymeric cation(or anion), not a neutral polymer. (Charge neutrality is maintained by incorporating the reduced form of the oxidizing agent eg  $I_3^-$ ; or oxidized form of the reducing agent.) Figure 1.2 shows how these terms relate to each other.

Figure 1.2

			<u>mole fract. dopant</u>
<u>Semiconductor</u>	n-type doping As, P Donor	p-type doping B Acceptor	$10^{-5}$ - $10^{-8}$
<u>Conducting</u>	reducing agent	oxidizing agent	0.01-0.03
<u>Polymer</u>	polymeric anion + counter ion eg $\text{Li}^+$	polymeric cation +counter ion eg $\text{I}_3^-$	

The chemical doping of PA has recently been well reviewed<sup>[25]</sup> and it has to be admitted that although PA is the most studied conducting polymer, the doping mechanism and the distribution of dopants within the materials is still to a large extent unknown. The complex morphology and the fact that PA is regarded as an ideal structure, which is doubtful, has led to difficulties in resolving this problem. Diffusion of dopants into fibres, chemical reaction with internal or surface chains and simple surface adsorption are among the explanations suggested<sup>[25]</sup>. Doping may be performed by exposing the polymer to gaseous dopant or the dopant in solution.

Conducting polymers may also be "undoped" and returned to a conductivity level similar to that of the original neutral polymer. This is often performed by exposure to oxygen or water vapour.

There are four possible structural isomers for linear PA: cis-cisoid, cis-transoid, trans-cisoid and trans-transoid. At low temperatures, the cis-transoid structure (shown in Appendix I as cis-PA) is thought to be produced. By increasing the temperature a greater degree of trans content is found<sup>[26]</sup>. Isomerisation to the trans-transoid isomer (shown in Appendix I as trans-PA) is generally performed prior to doping, although the exact mechanism of this process is still unresolved<sup>[26]</sup>. It has also been suggested that cis-trans isomerisation could take place by doping and that the transformation from the cis form to the trans form may be complete at a critical dopant concentration<sup>[27]</sup>.

The chemical synthesis, doping and undoping processes apply to all other conducting polymers with slight variations in each case. However, a major difference between PA and PPP as compared to most other conducting polymers is that they may be doped by both donors and acceptors, whereas generally only oxidation of the polymer is permitted.

In most cases electrochemical doping and undoping of the polymer is possible. This process in PA<sup>[28]</sup> and other polymers has recently been well reviewed. Oxidation or reduction of the polymer molecules leads to the incorporation of oppositely charged counterions. Nevertheless, the exact role and location of these counterions remains unknown, save that they are there to maintain charge neutrality within the system. Details of charge transport in PA and other polymers may be found in Chapter 2.

### 1.2.2 Other Polymers

Since the discovery of PA, many other conducting polymers have been found. Unlike PA however, most of them may be synthesised in two ways : chemically (as above) or electrochemically. Of these polymers PP<sup>[29,31]</sup> and PT<sup>[29,32]</sup> have been most studied. Chapter 5 discusses the electrochemistry of these and other polymers.

### 1.3 Morphology and Crystallinity

Conducting polymers vary greatly in their degree of crystallinity. For example, PPP<sup>[30]</sup> can exhibit crystallinity as high as 60% and PA<sup>[26]</sup> has been reported to be even higher (80%). In the latter case high crystallinity is often accompanied by a high disorder parameter due to low crystal perfection. However, polyheterocycles such as PP<sup>[31]</sup> and PT<sup>[32]</sup> are generally highly amorphous. The latter case has been suggested to be less than 5% crystalline. Synthesis conditions and doping levels are among the factors which can affect the crystallinity of the polymer. Although to what extent and precisely how this affects the conductivity is still unknown. Tourillon<sup>[32]</sup> has suggested that PT may have an all cis structure rather than all trans and consequently forms a coil structure within which the dopant molecules are held. Arguments for planar, linear structures in polyheterocycles have also been put forward<sup>[31]</sup>.

The final level of organisation, or morphology, of these polymers has been examined by transmission or scanning microscopy. PPP and PA have similar crystal structures and they also exhibit similar morphologies with their fibrils being orientated in either a fibrillar or a lamellar structure<sup>[30]</sup>. This is in some doubt as is the way in which the dopant is accommodated.

Monomer, dopant and film thicknesses can all affect the morphology of polyheterocycles<sup>[32]</sup>. Thin films are very homogeneous but thick films are inhomogeneous in the case of PT. Undoped PT shows a "noodle" like structure (as in PA) and has a fibrillar structure<sup>[32]</sup>. On doping the fibril, the diameter increases (also observed in PA) but some fibrils remain undoped.

#### 1.4 Properties

One of the principle properties of conducting polymers, which distinguishes them from conventional polymers, like PVC and PTFE, is their remarkably high conductivity when in the doped, conducting state. As can be seen in Figure 1.1 these polymers can have a conductivity some 20 orders of magnitude higher than an insulator like PTFE. The conductivities of the more common conducting polymers are given in Figure 1.3.

Figure 1.3

<u>Conductivity</u>				
<u>Polymer</u>	<u>Doped(S/cm)</u>	<u>Undoped(S/cm)</u>	<u>Dopant</u>	<u>Reference</u>
PA	1200	$10^{-6}$	$\text{AsF}_6^-$	33
PPP	500	$10^{-10}$	$\text{AsF}_6^-$	16
PPS	1	-	$\text{AsF}_6^-$	17
PP	100	-	$\text{ClO}_4^-$	15
PT	190	$10^{-7}$	$\text{PF}_6^-$	34,35
PPV	3	$10^{-13}$	$\text{AsF}_6^-$	18

Uniaxial stretching of the polymer film can lead to even higher conductivities : PA (2200 S/cm)<sup>[36]</sup> and PPV (2780 S/cm)<sup>[37]</sup>. The undoped polymers have conductivities of a similar magnitude to conventional polymers, but by doping an increase of 10 to 12 orders of magnitude can be achieved.

The stability of these polymers remains, in many cases, a major problem. However, some advances have recently been made. The insolubility and infusibility of these materials has also been a problem since their discovery, especially with regard to their analysis and processibility. However there have been some recent advances in these areas. These topics will be mentioned further in Chapters 4 and 5.

Doping levels can be controlled by electrochemical techniques but the maximum doping level varies. PP and PT<sup>[23]</sup> are generally 25-30% by weight dopant but PT has been doped up to 50%<sup>[32]</sup>. PA<sup>[23]</sup> however has a maximum of about 20% and at a doping level above only 1% it exhibited metallic characteristics.

### 1.5 Applications

The significance of polymeric conductors can be seen if the conductivity per unit weight is considered. For copper, mercury and PA the values are  $7.6 \times 10^4$ ,  $7.4 \times 10^2$  and  $7.0 \times 10^2$  S cm<sup>2</sup>g<sup>-1</sup> respectively<sup>[20]</sup>. If recent and unconfirmed reports on PA<sup>[38]</sup> are considered, where conductivities of  $1.47 \times 10^5$  S/cm with dramatically improved stability were measured, then a conductor has been achieved which on a weight basis is twice as good as copper. This could lead to a considerable number of applications.

These materials should be cheap, lightweight, versatile and the constituent molecules could be chemically tailored to specific needs. Practical applications such as photovoltaic devices, junction devices, rechargeable batteries, electrochromic displays and many others have been suggested.

Recent advances in stability, processibility and conductivity of these materials suggest that practical applications may soon be realised. More details of this will be given in Chapter 5.

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CHAPTER 2ELECTRICAL CONDUCTION IN POLYMERSSECTION I - INTRODUCTION

This chapter is intended to familiarise the reader with the basic physical concepts involved in the field of conducting polymers and with the electronic and conducting aspects of such one-dimensional systems. Some of these polymers, which are the subjects of considerable recent research, are shown in Appendix 1.

2.1 Introduction

The electrical conductivity of materials is a property which covers a large range of values as can be seen in Figure 1.1 (in Chapter 1). The difference between a good metal (conductor) and a good insulator (non-conductor) is greater than 20 orders of magnitude. The classifications into metals, semiconductors and insulators in terms of conductivity, can only be approximate, as other factors such as electrical transport properties as a function of temperature and structure also need to be studied. Polymers have, until recently, been thought to be exclusively insulators.

At this point a few terms which will be referred to should be introduced. The first of these is resistance, which is defined in Ohm's Law<sup>[1]</sup>Equatio 2.1:

$$V = IR \qquad \text{Eqn.2.1}$$

Where  $V$  is the electrical potential required in volts,  $I$  the current driven in amperes and  $R$ , the resistance in ohms. It is often convenient to use the reciprocal of resistance, conductance,  $G$ , the unit of which is siemens (S). In uniform conductors the following relationships apply—Equations 2.2 and 2.3:

$$R = \rho l/A \quad \text{Eqn.2.2}$$

$$G = K.A/l \quad \text{Eqn.2.3}$$

$A$  is the cross-sectional area of the conductor,  $l$  its length and  $\rho$  and  $K$  are proportionality constants which are characteristic of the nature of the material. The dependence upon shape or size has now been removed.  $\rho$  is called the resistivity and has units of ohm-meter ( $\Omega\text{-m}$ ). Resistivity is sometimes called specific resistance.  $K$  (or sometimes  $\sigma$ ) is called the conductivity and has units of siemens per meter (S/m). When dealing with conducting polymers most researchers use  $(\Omega\text{cm})^{-1}$  or more frequently S/cm as the units of conductivity.

These are direct current, DC, or time-invariant electrical relationships. A measured electrical quantity may include either (or both) a DC component or (and) an alternating current, AC, or time-variable component. Different relationships apply for AC components and will be discussed at the appropriate point.

Electrical conduction may be due to the movement of either electrons or ions and is expressed below:

$$\sigma = \sum n q \mu \quad \text{Eqn.2.4}$$

where  $\sigma$  is the conductivity,  $q$  the charge of the carrier,  $n$  the carrier density and  $\mu$  the carrier mobility<sup>[2]</sup>. In the case of most of the polymers studied here the carriers are electrons i.e. electronic conductors. The carrier mobility may be expressed by Equation 2.5:

$$\mu = \frac{V_{dr}}{E} \quad \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \quad \text{Eqn.2.5}$$

where  $V_{dr}$  is the drift velocity and  $E$  the electric field.

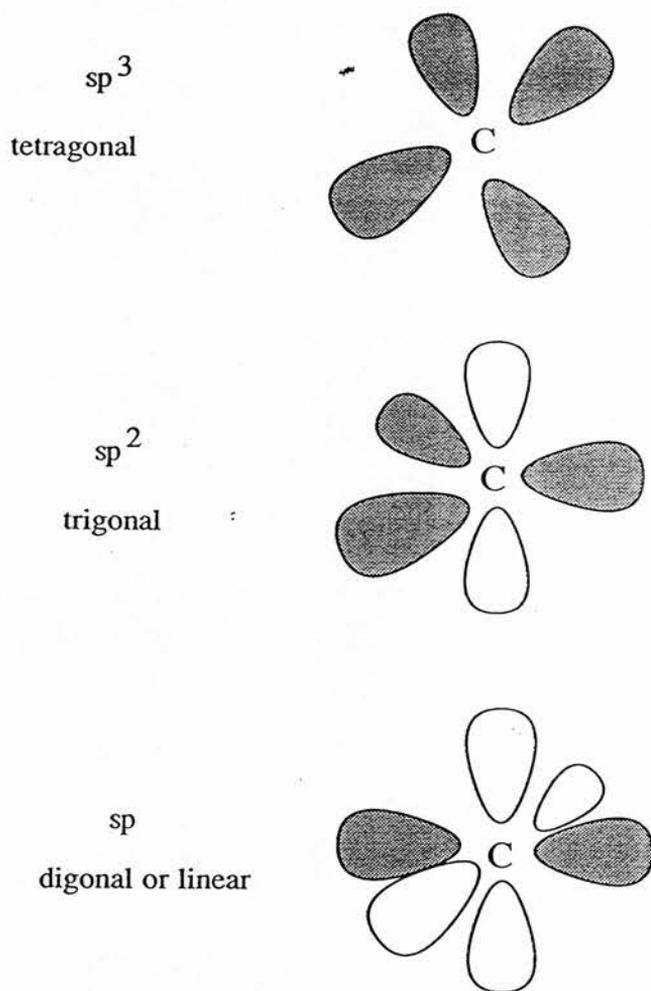
Enhancing the electronic conductivity of polymers then requires an increase in the carrier mobility and the density of charge carriers. Of particular importance is the formation of energy bands of high mobility charge carriers from delocalised  $\pi$ -electrons. This type of conjugation appears to be a necessary prerequisite for a conducting polymer.

## 2.2 Conjugated Carbon Chains

The combination of 2s and 2p orbitals in atomic carbon ( $1s^2 2s^2 2p^2$ ) into molecular orbitals is well known [3]. These highly directional hybrid bonding orbitals have different symmetries (tetragonal, trigonal and linear) which are shown in Figure 2.1. The tetragonal symmetry of  $sp^3$  hybrid orbitals is characteristic of saturated carbon compounds where all the electrons are localised in the C-C bonds. These single bonds are known as  $\sigma$ -bonds and are essentially the bonds which hold molecules together. These types of compounds are large gap insulators requiring a high energy for excitation from localised states. Trigonal  $sp^2$  and linear  $sp$  hybrid orbitals are characteristic of unsaturated carbon compounds. Here some of the p-electrons are involved in the formation of  $\pi$ -bonds normal to the plane of the molecule. These  $\pi$ -electrons tend to be much more reactive chemically than  $\sigma$ -bonds (electrons) and may give rise to extended electronic states which could provide the substructure for metallic conduction in polymers.

It should be noted here that  $\sigma$ -bonds ( $\sigma_x$ ) are axially symmetric and allow free rotation about them, whereas double bonds ( $\sigma_x, \pi_z$ ) formed with  $\pi$ -electrons allow much more limited motion. Also bond length decreases (bond strength increases) as the electron overlap increases on going from single to triple bonds.

Figure 2.1 : Hybridized States of Electrons for Carbon



shaded = sigma orbitals

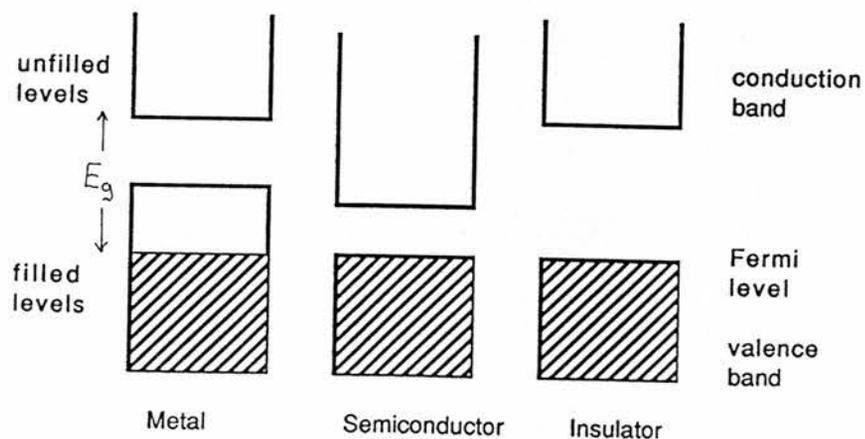
unshaded = pi orbitals

### 2.3 Band Theory

Insulation, semiconduction and metallic conduction are often expressed in terms of band theory. Therefore this subject will be briefly mentioned here, but the reader may find more complete coverage elsewhere [4,5].

Figure 2.2 shows a schematic representation of the permitted energy states for insulators, semiconductors and metals. The shaded areas represent occupied states (regions filled with electrons); unshaded areas represent unoccupied states.  $E_g$  is the energy gap between filled and empty states, often called the bandgap. The region between the valence band (VB) and conduction band (CB) represents forbidden energy levels. These bands are obtained by extending molecular orbital theory, where atoms combine to produce molecules with lower-energy bonding orbitals and higher-energy antibonding orbitals, to crystalline solids.

FIGURE 2.2



The electrical properties of a solid are determined by how these energy bands are filled and the size of the gap between them. Electrons are delocalised within each band i.e. they are spread over several atoms rather than bound to one. For electrons to move and therefore a current to flow there must be vacant orbitals for the electrons. Completely full bands have no such vacancies and empty bands have nothing to move.

The Fermi level is the highest normally occupied level in a given solid at low temperatures. When an electric field is applied to a conductor, electrons just below the Fermi level gain energy and are excited into unoccupied levels just above the Fermi level.

Insulator For an electric current to flow an electric field must be applied and electrons excited from localised states into unoccupied levels. In order for this to happen the electrons must be supplied with a finite excitation energy to cross the bandgap (energy gap) which in the case of insulators is large (7-10 eV). A typical polymer in conductivity terms, polyethylene (PE), made entirely of  $\sigma$ -bonds has an energy gap of 8.8 eV, making it an extremely good insulator<sup>[5]</sup>.

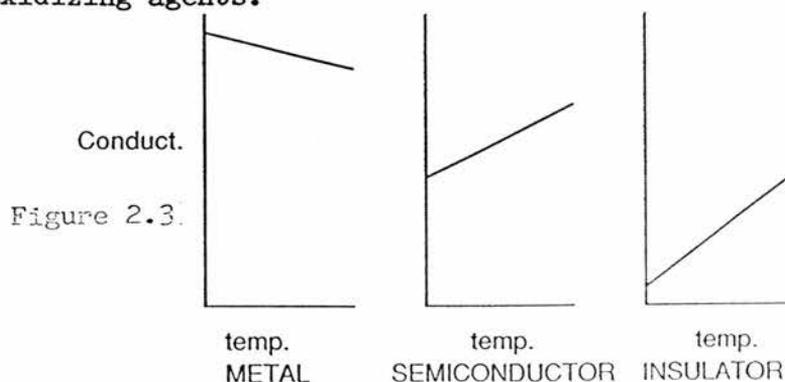
Semiconductor If the energy gap is small, at a particular temperature  $T$  there will be a small, but finite, number of electrons excited into the conduction band, leaving behind holes in the lower band which can also conduct. These electrons could easily carry an electric current giving the material a significant electrical

conductivity. This conductivity increases with increasing temperatures at higher temperatures as the density of electrons is dependant on a Boltzmann factor such as  $\exp(-E_g/kT)$ . The amount of carriers increases with temperature-Figure 2.3.

Metal Here the current-carrying states in the band are an infinitesimal distance energetically above the top occupied ground states in the system. This results in a high conductivity which is not very temperature dependant (although conductivity for most metals decreases on heating - Figure 2.3). This decrease is due to vibrating atoms interacting with electrons and scattering them.

#### 2.4 Early History of Electrical Conduction in Polymers

Interest in conjugated polymers really began more than twenty years ago when Little<sup>[6]</sup> proposed the possibility that suitable organic materials could be synthesised which could exhibit superconductivity at high temperature (eg room temperature). This led to considerable activity and in 1973 the key discovery of the inorganic conducting polymer polysulphurnitride  $(SN)_x$ <sup>[7]</sup>. This polymer remains unique as an intrinsically metallic synthetic polymer; due to each S-N unit having an unpaired electron. An important observation was that the conductivity of  $(SN)_x$  could be increased by an order of magnitude to  $10^3$  S/cm on exposure to bromine<sup>[8,9]</sup> or similar oxidizing agents.



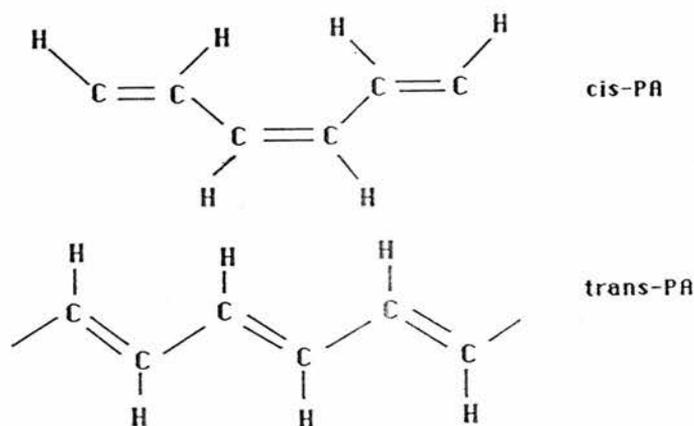
However the most significant discovery in this field came in 1977 when Shirakawa synthesised polyacetylene [PA]<sup>[10]</sup>. This material exhibits metallic and semiconducting properties on exposure to oxidizing or reducing agents with an increase in conductivity of about 10 orders of magnitude to about  $10^3$  S/cm<sup>[11]</sup>.

As the bandgap of the afore mentioned conjugated polymers is greater than 1.5eV they are intrinsically insulating. It was originally thought that their conductivity was due to a process similar to that in semiconductors. However PA<sup>[12]</sup>, PPP<sup>[13]</sup>, and PPy<sup>[14]</sup> were found to have spinless charge carriers. ESR also showed the number of free spins to be too low for the magnitude of conductivity found. Therefore a new theory was required.

## 2.5 Solitons in Polyacetylene

Polyacetylene [PA] has been the centre of substantial theoretical and experimental research directed towards the understanding of 'doping' mechanisms and the nature of transport processes and has been the subject of some extensive reviews<sup>[15-20]</sup>, within which may be found a multitude of references on the various aspects of this subject.

FIGURE 2.4



Firstly, the structure of PA should be examined, for this is a vital factor in the proposed conduction mechanism. PA may exist as either one or a combination of two isomers - cis-PA and trans-PA - Figure 2.4. The  $\sigma$  electrons are in low-lying completely filled bands, while the  $\pi$  electrons are in partially filled energy bands. Pure trans-PA (assuming equal bond lengths) would be a quasi 1D metal with a half-filled band. This system would be unstable with respect to a dimerization distortion (Peierls instability<sup>[21]</sup>) so that it becomes energetically favourable for the system to undergo a structural deformation resulting in bond alternation. Interchanging the single and double bonds in trans-PA gives two structures with the same total energy, therefore it has a degenerate ground state<sup>[22]</sup>, Figure 2.5. This degeneracy is thought to induce non-linear topological excitations or domain-walls (called "kinks" or "solitons") between these two degenerate phases - Figure 2.6. These defects are

considered to dominate the optical, electrical and magnetic properties of these materials. These defects each have an associated electronic state at the centre of the energy gap.

FIGURE 2.5

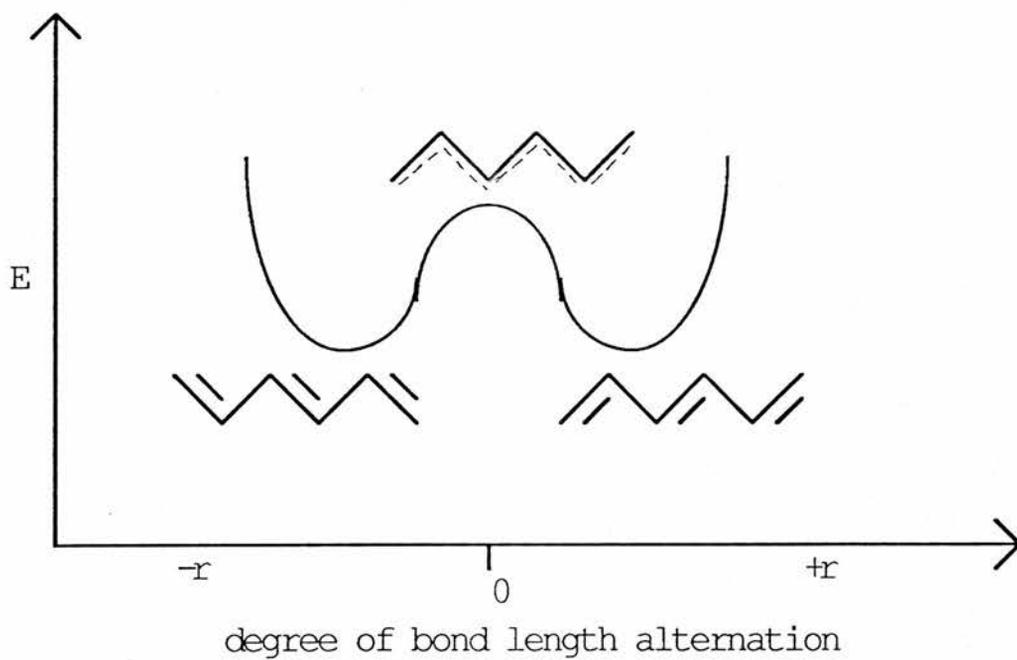
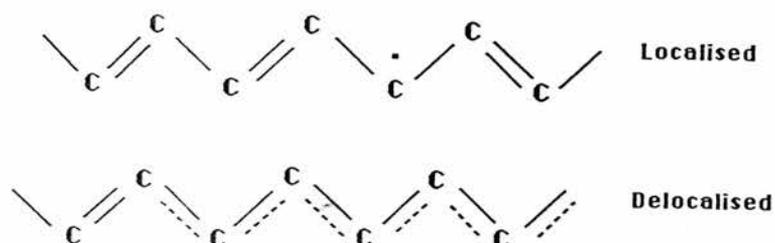
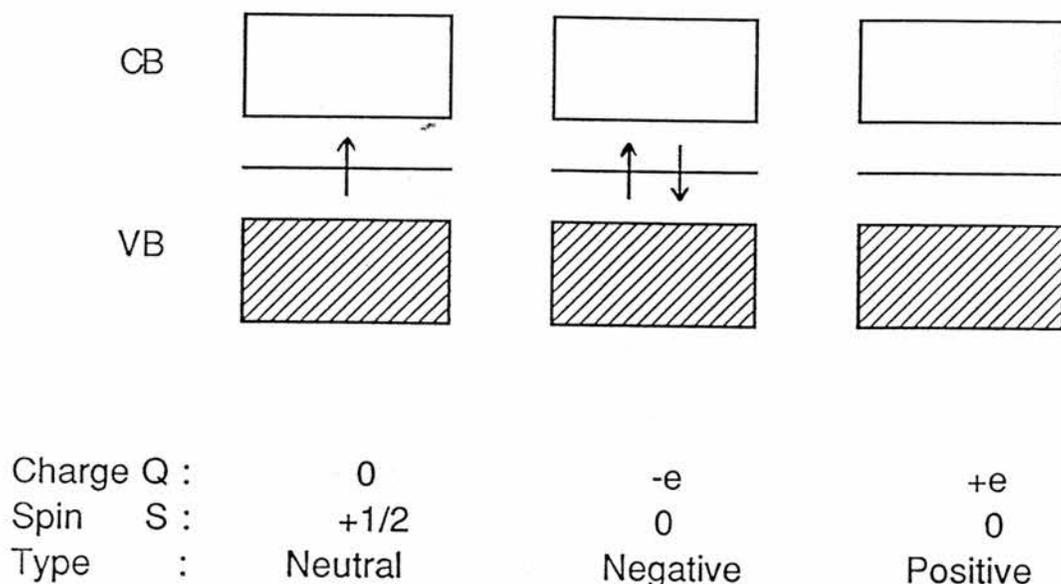


FIGURE 2.6



In pristine trans-PA, a chain with an odd number of conjugated carbons, will have an unpaired electron, a radical, which amounts to a neutral soliton - Figure 2.7. The spin (charge) density in a neutral (charged) soliton is not localised, but spread over several carbons<sup>[22,23]</sup>, giving the soliton a width. Single and double bond lengths gradually equalize on going from the extreme outside of the soliton to its centre. Going from the centre to the other side the reverse process takes place with the bond alternation reversed. The localized, mid-gap, electronic levels for neutral, positively and negatively charged solitons can be seen in Figure 2.7.

FIGURE 2.7



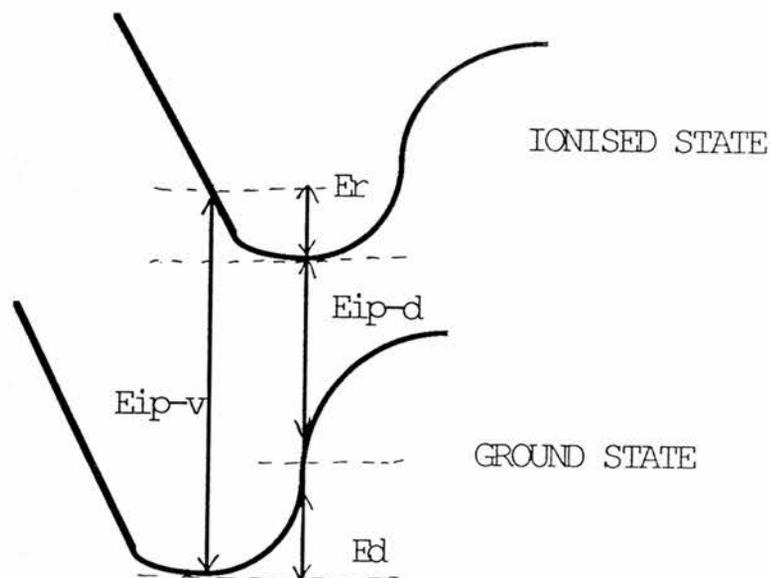
This model presents undoped PA as a semiconductor. In undoped and lightly doped (concentration of dopant  $y$  per carbon  $< 0.01$ ) trans-PA intersoliton electron hopping is the proposed conduction mechanism<sup>[24]</sup>. This is in agreement with DC and AC conductivity<sup>[25]</sup>, infrared conductivity<sup>[26]</sup>, electrochemical voltage spectroscopy<sup>[27]</sup>, pressure dependence of DC conductivity<sup>[28]</sup> and thermoelectric power<sup>[28]</sup> results. It has been shown that after charge transfer doping (both n-type and p-type) of trans-PA samples, the excess charge is stored in charged solitons and that conductivity is due to the transport of these charges<sup>[29]</sup>. At higher doping levels ( $y = 0.01 - 0.04$ ) the results agree with a variable range hopping model among states near the Fermi level  $E_F$ <sup>[30,31]</sup>. At high dopant levels ( $y > 0.05$ ) the density of states becomes metal-like and disordered metal-type

conductivity<sup>[30]</sup> has been proposed. Also not all polymers can have this doubly degenerate ground state due to their structure, in fact PA is the only polymer so far that can. This model works well for lightly doped trans-PA, but a closer look at the data has cast doubts as to its validity beyond this; particularly with regard to interchain transport, which for efficient carrier migration, must be easy<sup>[18]</sup>. Therefore a different mechanism is required for other polymers.

## 2.6 Polarons and Bipolarons

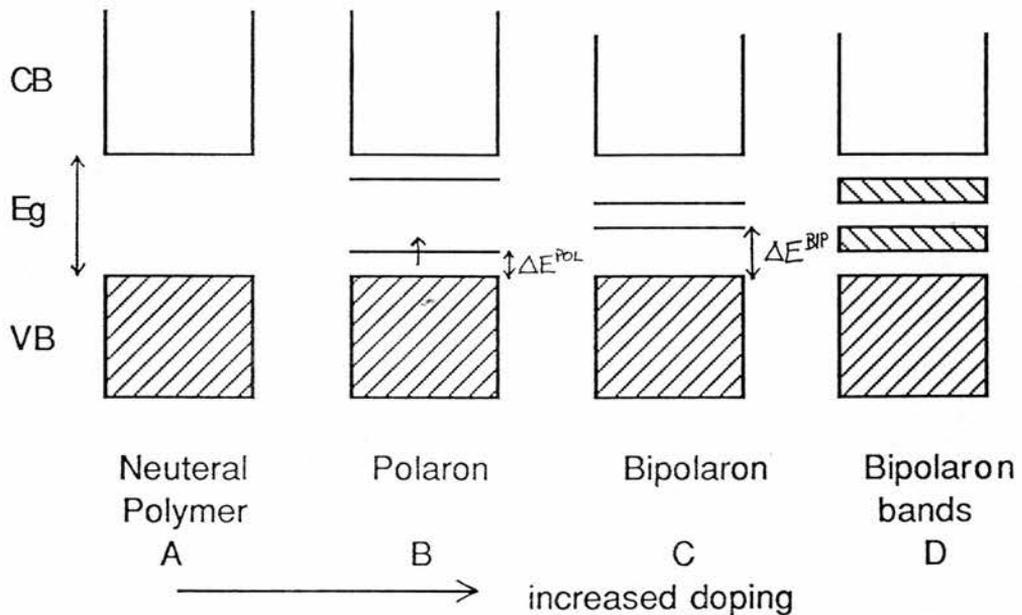
There are many polymers which have a nearly degenerate ground state such as polypyrrole (PP), polythiophene (PT) and poly(paraphenylene) (PPP). These polymers are also good conductors, but by what mechanism?

FIGURE 2.8



Before discussing polymers, a point about molecular ionisation processes should be noted - Figure 2.8. If,  $\Delta E = E_{IPV} - E_{IPd}$ , the reduction in ionisation energy upon distortion, is larger than  $E_D$ , the energy needed to make that distortion, then it is energetically favourable, to have a geometry relaxation in the ionised state. When ionisation takes place in a polymer, localisation of the charge on the chain may be energetically favourable leading to a local distortion (relaxation) of the lattice<sup>[20]</sup>. This leads to localised electronic states in the gap (see Figure 2.9) as the HOMO shifts up by  $\Delta E^{POL}$  and the LUMO shifts down. If  $\Delta E > E_D$  for the lattice locally around the charge, then this process is more favourable than the band process. Hence, what physicists call a polaron is formed. Figure 2.9 shows how this process relates to the oxidation (removing an electron lowers the ionisation energy by  $\Delta E^{POL}$ ) of PPP (although it would also apply to PP, PT and others). Removal of an electron leads to a polaron, or in chemical terms a radical-cation pair. Theoretical calculations have shown polaron formation to be energetically favourable in PA<sup>[32]</sup>, PPP<sup>[32]</sup> and PP<sup>[33]</sup>. Removal of a second electron leads to the formation of a bipolaron (or dication). Figure 2.9 shows that electronic states in the gap are further from the band edges for a bipolaron than a polaron; this is due to  $E_D$  being greater for 2 charges. Calculations have shown  $E_D$  for one bipolaron to be about equal to  $E_D$  for two polarons<sup>[32,33]</sup>, but the decrease in ionisation energy is of more consequence in the bipolaron case, hence it is more thermodynamically stable than two polarons, despite the Coulomb repulsion (which may be screened by dopant counterions)<sup>[20]</sup>.

FIGURE 2.9



### 2.7 Evolution of the Electronic and Transport Properties with Doping

The evolution of the electronic and transport properties with doping have been experimentally and theoretically investigated for several polymers : PA<sup>[34,35]</sup>, PP<sup>[14,33,36]</sup>, PT<sup>[36,37]</sup> and PPP<sup>[32,36]</sup>. Bredas and Street<sup>[20]</sup> give a good account of the process in PP.

Calculations have led to an image<sup>[33,36]</sup>, where undoped PP has a bandgap of 3.2eV (Figure 2.9A) and removal of an electron forms a polaron with allied quinoid geometry (calculated to have lower ionization potential and greater electron affinity) spread over four pyrrole rings. The polaron levels being about 0.5eV from the band edges - Figure 2.9B. These polarons of spin 1/2 have been observed by ESR measurements<sup>[14]</sup>. Removal of a second electron led to a bipolaron formation, also over four pyrrole rings, with its electronic levels

about 0.75eV from the band edges. ESR measurements<sup>[14]</sup> have shown polarons recombining into spinless bipolarons. At higher doping levels no ESR signals are observed and bipolaron states are said to overlap to form two 0.4eV wide bipolaron bands. These bipolaron states come from the VB and CB edges, therefore the bandgap increases to 3.6eV. It is suggested that applying an electric field leads to these spinless bipolarons becoming the mobile charge carriers. The evolution of optical absorption spectra of PP<sup>[33]</sup> agree very well with this whole band structure. Similar evidence has been presented for other polymers.

Highly p-doped PT has been reported<sup>[37]</sup> to exhibit metallic transport properties which is said to be due to broadening of the bipolaron states leading to the lower and upper bipolaron bands merging with the VB and CB respectively<sup>[36]</sup>. Also PT has a relatively small intrinsic bandgap (2.0eV). Recent work on PT's photoconductivity and light-induced ESR spectra has suggested that photoexcitation of polarons to carriers and the formation of spinless bipolarons<sup>[38]</sup> takes place.

At high doping levels in PA the metallic conductivity is suggested to be the result of the soliton band merging with the VB and the CB<sup>[35]</sup>. There still appears to be however some dispute<sup>[18]</sup> as to conduction mechanisms at lower doping levels in PA. The problem of interchain transport is reported to have been overcome by the interchain hopping of bipolarons<sup>[18]</sup> and by PA having a model with two charged solitons (a "bipolaron").

There is still much work to be done in this field with many of the theories related here being disputed and several problems such as the effects of dopant ions<sup>[18]</sup> and disorders<sup>[39]</sup> in the material have yet to be taken fully into account.

SECTION IICONDUCTIVITY MEASURING APPARATUS2.8 Introduction

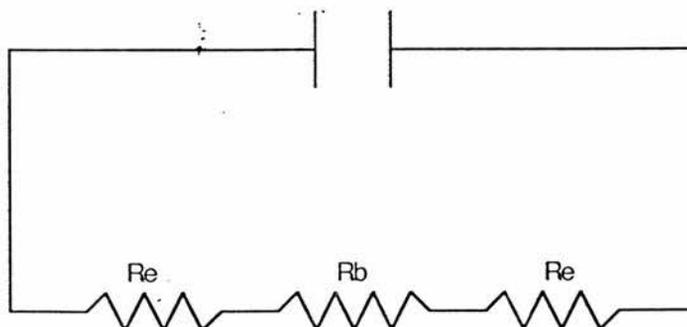
The topics of conductivity and conduction mechanisms have already been discussed previously in this chapter and most of the terms used described. The purpose here is to discuss the methods employed for conductivity measurements and to describe in some detail those methods which were used to perform the experimental work contained in this thesis.

The resistance of a sample may be measured by two methods; DC methods and AC methods. Which of these methods are used will depend on the type of conductivity to be measured and the information required. When the DC resistance is measured only the net charge which crosses the whole sample is obtained. AC measurements give the resistance as a function of an alternating electric field over a frequency range. For carriers in extended states (in metals) or excited into extended states (in ordered semiconductors), the resistance is independent of frequency up to high frequencies ( $10^{13}$  Hz). In disordered or inhomogeneous systems where the carriers are not in extended states, resistance varies with frequency. Many disordered semiconductors and insulators show a distinct frequency dependence<sup>[40,41]</sup>.

In the case of electronically conducting polymers, where the resistance of the sample is simply required, a DC method is invariably used. If more complex information is required, about charge carriers for example, AC methods may be used. The reasons for the use of AC measurements with polymer electrolytes is discussed later. An important distinction to make here concerns the mechanisms of conduction, ionic and electronic. In the former, current flow is due to the macroscopic motion of ions whereas electronic conduction involves the motion of electrons. In the case of electronically conducting polymers, any motion of the counter ions is incidental to conduction.

### 2.8.1 DC Conduction Measurement

Several books<sup>[42-45]</sup> have discussed the measurement of electronic conductivity. If we take the simplest example of resistance measurement that of two-terminal measurement with a DC source (e.g. ohmmeter). The equivalent circuit could be represented by:

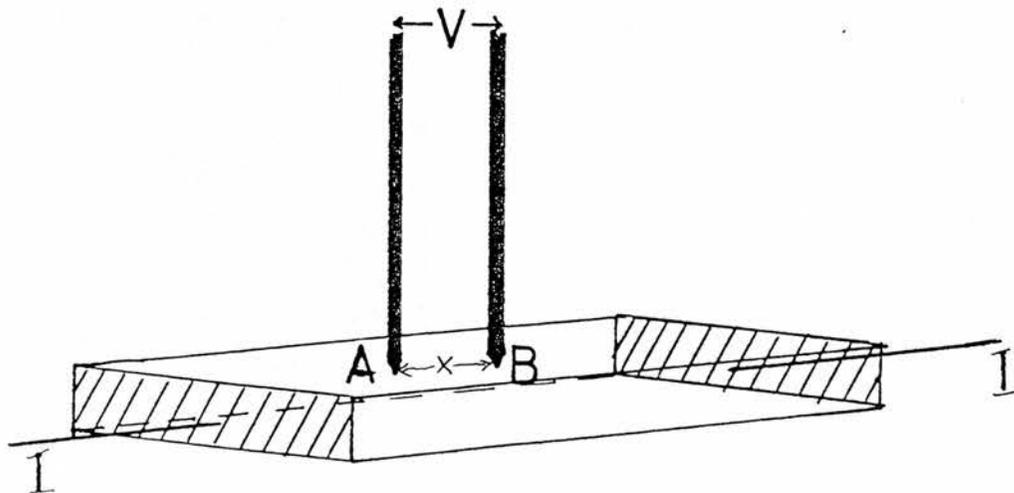


In the ideal situation the resistance of the sample to be measured,  $R_b$

could be obtained from  $R_b = V/I$ , where  $V$  is the potential difference and  $I$  the current. The definitions of resistance and conductivity may be found earlier in this chapter. The term resistance will generally be used. However resistance at the electrode interface or contact resistance,  $R_e$  would generally be far from negligible. Only if the condition  $R_e \ll R_b$  could be fulfilled would this method be valid. Contact resistances, and their elimination, tend to be one of the main problems in resistance measurements. In fact Norman<sup>[42]</sup> devoted a whole chapter to this problem and discussed the effects of resistivity of sample, type of contact, voltage applied and mechanical pressure.

A two-probe resistance method<sup>[43]</sup> is shown in Figure 2.10. Here contacts are made at either end of the sample and a constant current is passed through these contacts. The voltage is measured between A and B and therefore the conductivity of the sample may be calculated. However these methods still require 2 good ohmic contacts and there are restrictions on the size and shape of the specimen.

FIGURE 2.10



In practice the current is often passed through the same two terminals through which the voltage is measured in two-terminal methods. One of the most common ways of obtaining good contacts<sup>[42]</sup> is to attach the electrodes via silver or graphite paints (often referred to as Aquadag or Electrodag) which dries to form a good electrical contact between the sample and the electrodes.

When measuring high resistance samples one problem which can occur is that of current leakage between the ohmmeter (electrometer) terminals due to the presence of dirt or moisture on the surface of the sample providing lower resistance alternative routes. This problem may be overcome by using a guard electrode which collects currents so they are not included in the measured current.

Two-terminal methods tend to some extent still suffer from contact problems and, with some methods, restrictions in sample shape. A better way of overcoming contact resistances is to use a 4-terminal potentiometric method and in the form of the 4-point probe is one of the most commonly used and reliable methods of resistance measurement for inorganic semiconductors and electrically conducting polymers. The 4-point probe has the added advantage that measurements can quickly be made in situ and non-destructively.

2.8.2 The 4-Point Probe

In figure 2.12 the resistivity of the sample is given by equation 2.6.

$$\rho = \frac{j}{E} = \frac{I/A}{\Delta V/\Delta x} \quad \text{Eqn.2.6}$$

$j$  is the current density,  $E$  the electric field obtained by measuring the potential difference  $\Delta V$  across the inner electrodes of separation  $\Delta X$ . This method of using different probes to measure the potential difference from those which produce the constant current avoids contact resistance effects, provided the contact resistance is much smaller than the input resistance of the voltmeter. However, the use of pointed electrodes leads to non-uniform electric fields and current densities, but by a rigorous analogy of current flow and electrostatic charge equations it is possible to arrive at an equation (equation 2.7) from which the resistance may be obtained.

$$V = \frac{I \rho}{4\pi r} \quad \text{Eqn.2.7}$$

$V$  is the potential at a distance  $r$  from a point electrode which supplies a current  $I$  in a material of resistance  $\rho$ . Applying this equation to 4-point probe measurements where all four electrodes are equidistantly spaced  $S$  apart, Valdes<sup>[46]</sup> arrived at equation 2.8.

$$\rho = \frac{V}{I} \cdot 2\pi S \quad \text{Eqn.2.8}$$

If the size of the contacts  $\ll S$ , this result is independent of the electrode contact area. This is certain to be the case for point contacts. Several authors<sup>[46-48]</sup> have derived expressions for correction factors for various sample geometries. 4-point probe measurements have been given a more general treatment including sample anisotropy and different electrode arrangements.

The resistivities given here generally refer to sheet resistivities. Volume resistivities have been obtained<sup>[48]</sup> from these equations but are generally applied to thin semiconductor wafers. Some of the materials investigated in this thesis, such as polypyrrole, are reported to have large ( $10^3$ ) differences between the conductivity of the surface and perpendicular to it<sup>[49]</sup>. For this reason and the fact that most authors in the conducting polymer field give sheet (or surface) resistivities (or conductivities), these are the values to be reported here.

## 2.9 Electronic Conductivity Measuring Apparatus

Three quite different measuring systems were used for measuring conductivity depending on the magnitude of conductivity to be measured and the period of time when the work was performed. (Initially much of this equipment was unavailable, therefore what was available had to be used.) This subsection describes each of the systems used.

### 2.9.1 Wayne Kerr Bridge

In the earlier months of this research project, electronic conductivities were measured using a Wayne Kerr resistance bridge. This is a commonly used method for determining the resistance of materials, whereby the resistance and capacitance of the material being investigated are balanced with the known resistance and capacitance of the Wayne Kerr bridge. Hence the resistivity of the material can be obtained using the equation below:

$$\rho = \frac{R A}{l} \quad \text{Eqn.2.9}$$

where  $R$  is the measured resistance between the electrodes,  $A$  is the cross-sectional area of the electrodes and  $l$  the thickness of the sample. Thin samples were generally used in order to keep the value of  $R$  as small as possible.

A Wayne Kerr bridge, B221 was used in conjunction with a Brookdeal Signal Source (472) and an Ortec Brookdeal Precision Amplifier 9452. Two screws held in place by a teflon ring were used to bring two stainless steel electrodes parallel to each other into contact with the top and bottom of the sample discs. However several disadvantages were apparent. Despite every effort, this method of making electrical contact resulted in non-reproducible pressures being applied to each sample and an inability to make good ohmic contacts. It also resulted in deformation of softer samples and inaccuracies in the measurements taken.

This method is not ideal for the measurement of electronic conductivity as AC electricity is involved. One problem with AC techniques is that measurements are limited by  $1/f$  noise. This would be most significant at low frequencies where DC conductivity is approached. At high frequencies the noise is less significant, yet here the value measured may be quite different from the electronic conductivity. AC techniques have been developed to measure electrical resistivity<sup>[43]</sup> but they all require sophisticated equipment.

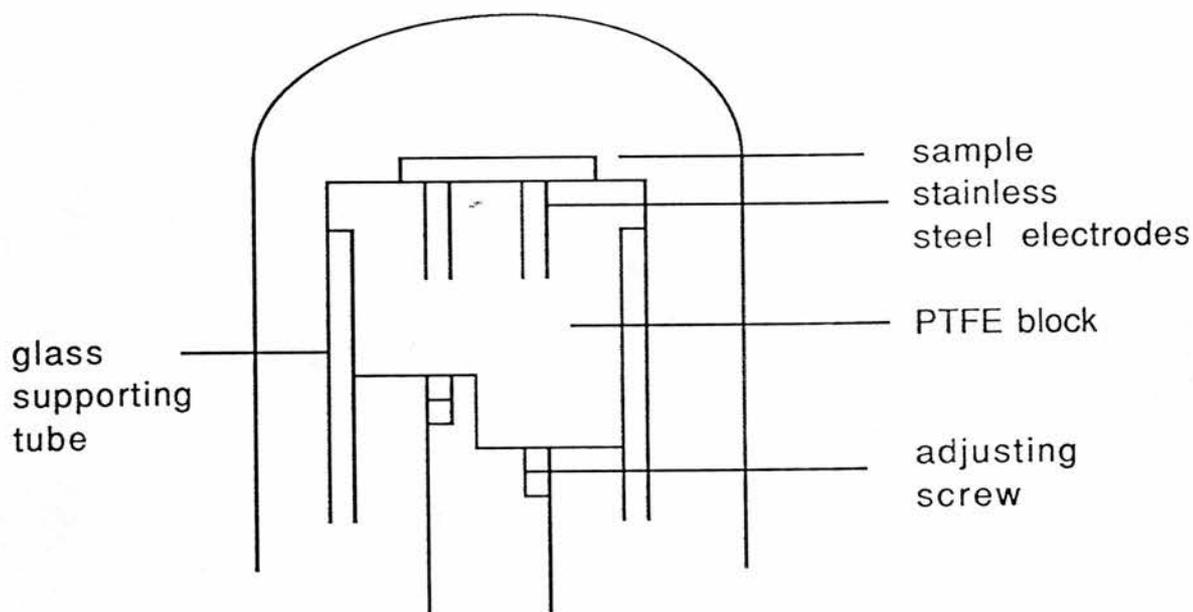
A frequency of 1kHz was generally used and it was hoped that the  $\sigma_f$  obtained would approximate quite closely to  $\sigma_{DC}$ . This method had to be used at an early stage of experimental work while the 4-point probe was being designed and built.

### 2.9.2 Two-Point DC Measurement

The probe used for two-point DC resistance measurements may be seen in Figure 2.11. The probe consisted of a PTFE block machined to fit into a glass tube. Within this block was fitted two stainless steel pins (1mm diam.) which had slight indentations in their ends and were sunk just below the surface of the PTFE by two adjusting screws. The probe was contained within a glass vessel which in turn was placed in an oven. The glass vessel was connected by both tubing, to allow gas to pass through, and electrical connections to the outside of the oven. Electrical connections from the outside of the oven to a Keithly 602 Electrometer were made via BNC connectors and shielded

cable. The oven acted as a metal box for the purposes of shielding.

FIGURE 2.11



A guard electrode was not used to ease fabrication of the probe and as samples were prepared under vacuum, stored in a dessicator and dried nitrogen gas passed over the sample both before and during measurements, it was hoped that any dirt or surface moisture would be kept to an absolute minimum.

Electrical contacts between the electrodes and the sample were made by 'dag' paint (Acheson Colloids, 915). Nitrogen, dried by a drying column (Rimer-Birlec) was passed through the glass vessel and the solvent (4-methyl-2-pentanone) allowed to evaporate for 30-60 minutes to produce a good dry contact. The resistance was then measured using the electrometer on various ranges and from equation 2.10 below<sup>[44]</sup>, the surface resistivity  $\rho$  obtained.

$$R = \frac{\rho}{\pi} \cosh^{-1} \frac{d}{2r_0} \quad \text{Eqn.2.10}$$

where  $d$  is the separation between the centres of the two terminals (5mm),  $2r_0$  the diameter of the terminals (1mm) and  $R$  the resistance value obtained by the electrometer. This method was used to measure samples with conductivities in the region  $10^{-6}$ - $10^{-12}$  S/cm.

### 2.9.3 Collinear Four-probe Resistance Method

The actual probe assembly used can be seen in Figure 2.12. In Figure 2.12 constant current is passed between the outer probes using a constant current source (Time Electronics) and the potential difference produced is measured between the inner two probes using a Solartron DMM or Keithly 602 electrometer. From this information and using various correction factors<sup>[46,48]</sup> the conductivity of the sample can be measured. Each of the four probes has a separate, identical spring attached to the assembly, which means that all the probes press uniformly on the sample. Also the same weight is placed on top of the probe so that the contact pressure on each sample will be the same.

The procedure for measurement is quite simple. The sample is placed beneath the probe assembly and the probes lowered onto it. A weight (about 100g) is placed on the probe assembly which due to internal springing should result in even, reproducible pressures for each probe. Measurements are then made using suitable ranges on the current source and the resistance calculated using Ohms Law ( $V = IR$ ). It may occasionally be necessary to check each contact using an

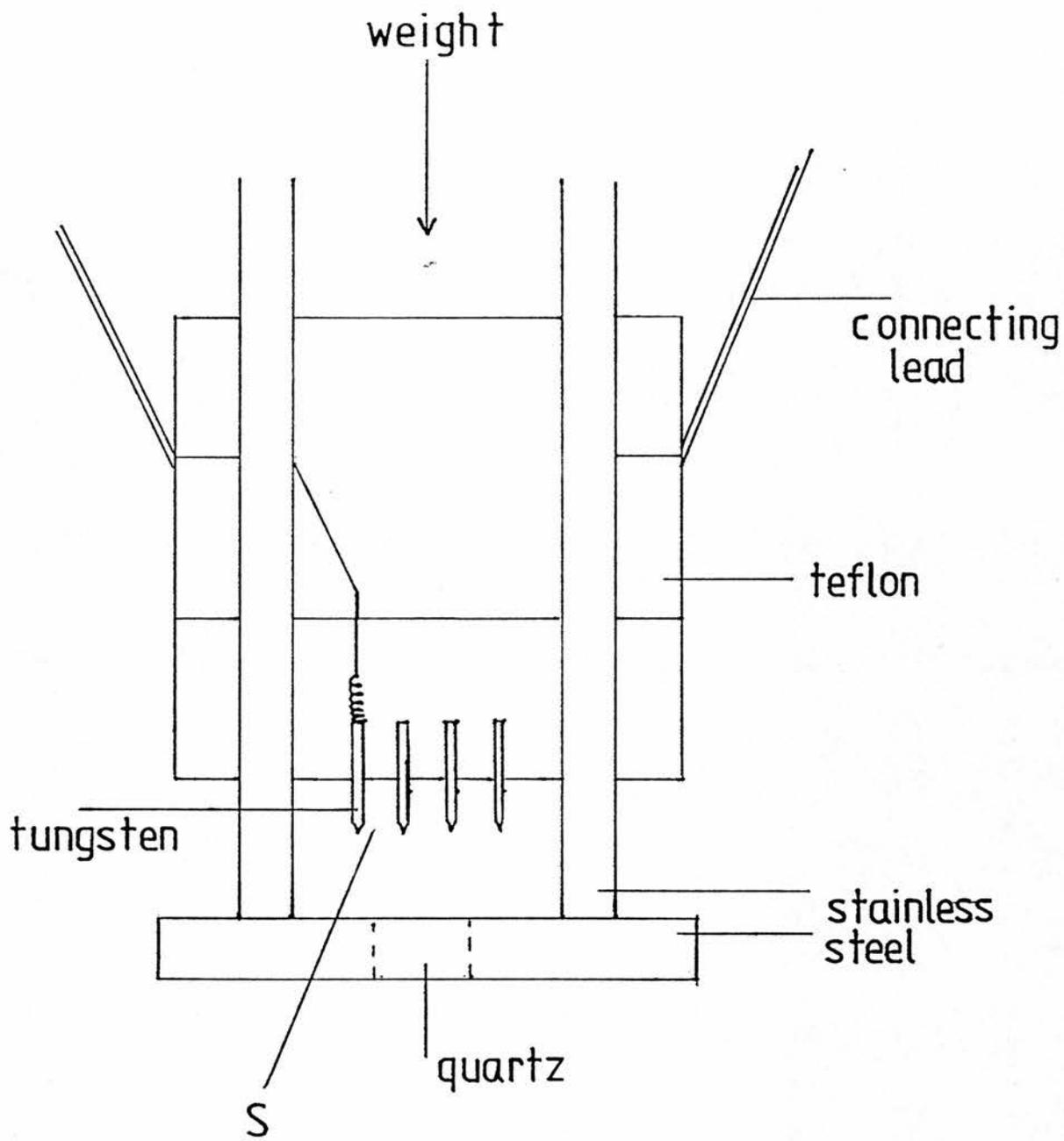


Figure 2.12.

ohmmeter.

The inter-probe space,  $S$ , is the same between any two probes ( $S=1.75\text{mm}$ ). As probes have to be sharpened to points, the diameter of the probe which can practically be used is limited. The inner probes were points, and the outer probes were rounded as was suggested by the literature<sup>[43]</sup>. Probes were made of tungsten (0.8 mm diam.) and the body of the probe assembly was made of PTFE.

Using the equation  $\rho = R.C(d/S)$  the resistance in ohm-centimeters may be obtained.  $R$  is the value obtained above and  $C(d/S)$  is a correction factor for the sample shape and size<sup>[43]</sup>. For  $d$ , diameter, of 13mm pellets  $d/S = 7.43$  and  $C(d/S) = 3.9(\text{approx.})$ . For 13mm square samples (films),  $C(d/S) = 4.0(\text{approx.})$ .

After testing and modification, the system was able to measure conductivities in the range  $10^{-6}$ - $10^3\text{S/cm}$ . The measurement of more resistive samples is limited as point contacts are inadequate for supplying currents large enough for the voltage to be easily measured. Also as the input impedance multimeter where the voltage occasionally took some time to stabilize, as opposed to when using the high impedance electrometer.

## 2.10 Ionic Conductivity Measurement

### 2.10.1 Introduction

Section 2.8 of this chapter discussed DC conductivity measurements principally with a view to obtaining electronic conductivities. In this section, the determination of ionic conductivities is of primary importance. The most common way in which these parameters are obtained, is via AC impedance measurements. Electrical measurements on polymer electrolytes<sup>[45]</sup> and more specifically AC impedance measurements<sup>[50]</sup> have been well reviewed.

In an electronic conductor the principle charge carriers are electrons and in an ionic conductor they are ions. This means that more than one charge carrier may be present making the situation more complex as the different charged species need to be identified along with their charge transport numbers.

DC methods may be used but non-blocking electrodes are required. Obtaining suitably reversible and thermally stable electrodes can be difficult. They should be used in four-terminal cells which are difficult to construct, rather than in two-terminal cells for the reasons given in section 2.1. This is a further disadvantage. However, if an AC method is used, a simple cell with inert blocking electrodes will be sufficient. The equipment and theory for interpretation of results required is unfortunately much more

complex.

By DC methods the current flowing  $I$  and the potential  $V$ , are related to each other by one parameter,  $R$ , via Ohms Law ( $V = RI$ ). However, when an alternating current is applied, there may be a phase difference between the current and the potential and therefore two parameters are required. These two parameters combine to give the impedance,  $Z$ , of the cell. This impedance is a vector quantity and has a magnitude  $|Z| = V_{\max}/I_{\max}$  and a direction, its phase angle  $\theta$ . These quantities are functions of the applied frequency and the AC method of interest here measures the impedance of a cell over a range of frequencies. The impedance may also be represented as a function of its  $x$  and  $y$  components  $|Z| \cos \theta$  and  $|Z| \sin \theta$  and on a vector diagram is analagous to a complex number in the complex plane. Hence these measurements are often referred to as complex impedance measurements and it is by this method that the electrical properties of polymer electrolytes are generally studied. AC signals also prevent electrode polarisation and avoid complications due to Faradaic processes.

### 2.10.2 A.C. Conductivity Measuring Apparatus

A Solartron 1170 frequency response analyser (FRA), controlled by a Tektronix 4052 minicomputer was used to obtain ionic conductivity measurements of polymer electrolyte films. The FRA measures the resistance of the film, held in a cell, and compares it with a standard measuring resistor, over a range of frequencies from 1MHz to 1Hz. This

process leads to complex variables a and b being obtained, and from these complex plane impedance plots using a computer program. This data together with temperature measurements leads to the Arrhenius type plots obtained over the temperature range 17-105°C. Generally samples were heated at 95°C for 12 hours and then allowed to cool to room temperature before conductivity measurements were made. This has been shown to lead to better and more reproducible results.

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CHAPTER 3POLYMER COMPOSITESSECTION I - INTRODUCTION3.1 Introduction.

Electrically conducting polymers can be categorised into two types: (a) `intrinsically` conducting polymers such as PA, PPy and PT, where the conduction of charge is via the polymer itself, and (b) polymer composites. This chapter will concentrate on materials of type (b). Polymer composites have been known and studied for some years now<sup>[1-6]</sup>. They basically consist of a conductive material, such as carbon black or metal powder, dispersed uniformly throughout, and held together by, an electrically insulating polymer matrix.

3.1.1 History and Applications

The history and applications of conductive polymer composites are closely related to the needs they were developed for; principally antistatic uses. In the 1930`s there was concern about the number of explosions due to static build-up in insulating rubbers. It was therefore desirable to develop antistatic rubbers and plastics for situations where explosive or inflammable vapours, liquids or powders were used, vehicle and aircraft tyres and hospital equipment. This was achieved in the 1940`s by adding carbon blacks (or occasionally

powdered metals) to rubbers. A current use for conductive composites, and one in which they are likely to play an increasing role, is that of electromagnetic interference shielding materials,<sup>[3]</sup> used mostly in computers and electronics devices.

Composites also have the following advantages over metals: ease of workability and processing, high corrosion resistance, low density, environmental stability, cheapness, wide range of electrical conductivity, and low thermal conductivity. They now have a variety of uses including: dissipation of electric charges, prevention of discharges from the surface of the insulant in high voltage cables, resistors and circuit connections on printed circuit boards and heating devices. However they still have the disadvantages of: lower conductivities than metals, inability to withstand such high temperatures and lower mechanical strength.

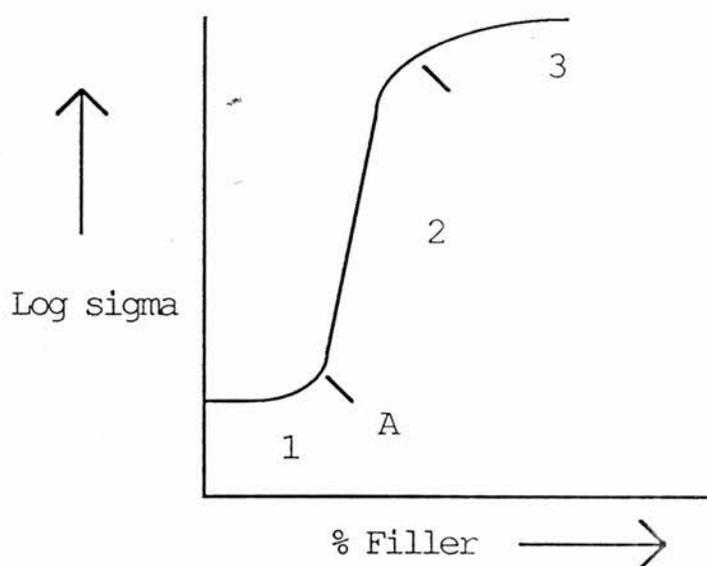
### 3.1.2 Conductivity and Conduction Mechanisms

Carbon black-polymer composites are by far the most commonly studied<sup>[6]</sup> type of composite, but metal-polymer composite studies are becoming more common<sup>[3,4]</sup>.

Conduction mechanisms in carbon black composites have recently been well reviewed by Medalia<sup>[7]</sup>. Conductivity does not vary linearly with loading (percentage of conductive filler) but typically as shown in Figure 3.1. [The amount of filler is given as percentage by volume as this is more widely used rather than percentage by weight. For

most metals there is a major difference between these values due to their high densities.]

FIGURE 3.1



Region 1 shows little change in conductivity,  $\sigma$ , which is basically that of the dielectric medium. When the percolation threshold or critical loading (point A) is reached  $\sigma$  increases sharply. This is called the percolation region (Region 2). Region 3 is the limiting high conductivity.

Each of these regions exhibits different conduction processes. In Region 1 the conduction mechanism is that of a pure polymer with no filler i.e. transport by ionic impurities and space charge. Here the gap (insulating regions of polymer) between filler particles (conductive regions) is large ( $> 10\text{nm}$ ).

In Region 2 the gap has been estimated to be 1.5-10nm. The conduction mechanisms for this region are many and varied, but have been well reviewed<sup>[7]</sup>. The conduction is nonohmic generally and the theories include tunnelling through gaps, thermal activation of electrons over the potential barrier of the gap (hopping), dielectric breakdown or capacitance (depending on the type of experiment and conditions).

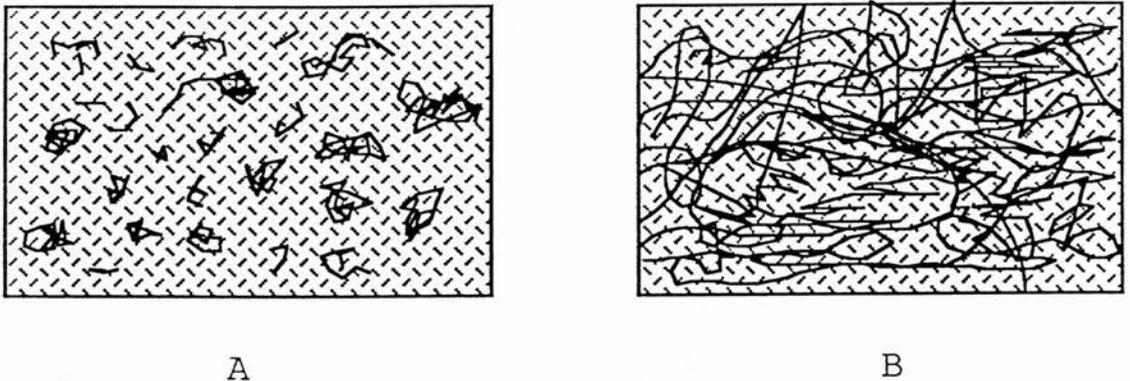
In Region 3 (high loadings) conduction is via segregated networks or `throughgoing chains` of filler. As more filler is added the aggregates come into much closer contact and are packed tighter together and eventually contact resistance becomes insignificant. The evidence for this is very little temperature or frequency dependence of conductivity. The gap is <1.5nm and conduction is ohmic.

### 3.1.3 Percolation

In considering transport of electrons by the above mechanisms from one aggregate of filler to another, a further factor is important and that is the pathways of sufficiently high conductivity through the whole specimen. Isolated aggregates do not contribute to the conductivity of the sample. The distribution of aggregates and gaps throughout a sample can be elucidated by percolation theory<sup>[7,8]</sup>.

If conducting particles are gradually added to an insulating matrix, the particles will at first be isolated from each other and will not affect the conductivity of the sample greatly (see A in Figure 3.2). However a point is reached where a through-going path along which conduction may take place (see B in Figure 3.2). This point is called the percolation threshold, where the mean number of contacts surpasses a particular level. Here conduction is possible, yet is limited by the number of through-going paths (paths of finite resistance, but which allow the passage of current, as opposed to the through-going chains mentioned earlier which have negligible resistance). Any further addition of particles leads to an increase in through-going paths and a fast increase in conductivity.

FIGURE 3.2



Kirkpatrick's<sup>[8]</sup> development of percolation theory regards a composite as conductive sites with zero resistance, joined by bonds of finite resistance and separated by a material of infinite resistance. His calculations based on insulating and conducting particles of similar shape gave the critical volume as 0.25 (25%). Above this

threshold a power law dependence of conduction on concentration is predicted (see equation below):

$$\sigma = \sigma_0 (p - p_c)^b \quad \text{Eqn. 3.1}$$

$p$  is the probability of a site or bond being present and  $p_c$  the threshold probability.

The sharp change in conductivity of metal powder filled polymers at the percolation threshold has been confirmed by Gurland<sup>[9]</sup> and Kusy and Turner<sup>[10]</sup>.

#### 3.1.4 Physical Properties and Processing

When loading polymers with conductive fillers there is a trade-off between the physical properties and conductivity. Hence the percentage of filler will affect the conductivity. The aim is to achieve the maximum conductivity at the lowest loading of filler. There are three factors which should be considered in this context.

The most obvious factor is that a material which is intrinsically highly conducting (such as Ag<sup>[9]</sup>) will produce a highly conducting composite. A second factor is that of the wettability of the filler by the polymer matrix. This has been examined recently<sup>[11]</sup> in carbon black-polymer composites. The conclusion reached was that the difference in surface tension between the polymer and the filler affected the loading at which the percolation threshold occurred. The

larger the difference, the lower the loading. This was said to be due to aggregation or 'chaining' of the filler. This is an interesting point in view of the third factor that of the particle shape of the filler. The loading at which the percolation threshold occurs can be greatly affected by the shape of the filler. Fibres, due to many more particle contacts,<sup>[4]</sup> and to a similar extent flakes, require lower loadings than spheres or irregularly shaped particles. The reduction of critical volume loading can also be influenced by the fibres aspect ratio (length/diameter)<sup>[3]</sup>. By depositing a thin conductive layer onto glass fibres<sup>[4]</sup> very low percentages of conductor are required and there is a reduction in weight. These materials should have fewer and smaller tunnelling gaps than with uniformly dispersed spherical particles.

However the method of processing and pretreatment will also have an effect. Mixing, milling and thermal treatments of carbon black and metal filled polymers and rubbers have been well reviewed by Norman<sup>[1]</sup>. The electrical and thermal properties of composites have been shown to be greatly affected by these operations at various stages of their processing.

In the work on composites (particularly PEO) presented here, the method of processing has been predetermined to optimise its AC conductivity, therefore a study of mixing or thermal treatment has been omitted. A separate study would be required to determine the result of mixing and other pretreatments on the DC conductivity. Similar studies have been well documented by Norman<sup>[1]</sup>.

### 3.1.5 Recent Developments

Research into the types of composites above is still very active, especially commercially, despite the long history of the subject. A recent development of particular interest in view of other material in this thesis shall be referred to in this subsection. In place of the more common conductive filler an 'intrinsically' conducting polymer (as described in Chapter 1) may be the conducting part of the composite. The subject has been reviewed recently<sup>[12]</sup>.

These materials have great potential due to their interesting redox properties and possible uses in batteries, displays and information storage. However poor mechanical properties and environmental stability appeared to be problems. Recent papers<sup>[13-15]</sup> have suggested that these problems may have been overcome while maintaining the good redox properties.

### 3.2 Poly(ethylene oxide) - An Introduction

Ionic conduction in polymers, where additives (salts and/or solvents) are dispersed through a polymer matrix, can be classified into 3 groups<sup>[16]</sup>: polymer electrolytes, polyelectrolytes and gel electrolytes. Poly(ethylene oxide) [PEO] is a polyether and is the most commonly studied of the 'polymer electrolytes'.

The topic of polymer electrolytes has generated a great deal of interest in recent years and has been well reviewed<sup>[16-20]</sup>. These plastic materials could have useful practical applications in high energy density batteries as they are easily processable and possibly have good power densities. It is intended to give an introduction to this subject here. However as the subject is rather large (and growing) it must be relatively brief.

Polymer electrolytes [PE] are the result of complexes formed between alkali metal salts, MX and polymers with solvating heteroatoms. An alkali metal salt-poly(ethylene oxide) [PEO], complex was first reported by Wright et al<sup>[21]</sup> and was more fully investigated by Armand and co-workers<sup>[20,22]</sup>. PEO-lithium salts are one of the most studied systems due to their relevance to high energy batteries<sup>[23,24]</sup> and is the subject of this work. Here oxygen acts as a donor for  $\text{Li}^+$  and the PEO-MX complex is stabilized by the (generally large) anion  $\text{X}^-$ .

At ambient temperatures due to PEO's high stereoregularity it is highly crystalline. However at higher temperatures an amorphous, elastomeric phase predominates. The ratio of PEO to MX, generally referred to as O/M ratio (number of oxygens per cation), is of some importance here as it affects the temperature at which a purely amorphous phase will be present. As this phase is responsible for higher conductivity (see below), knowledge of PEO/salt phase diagrams is important as for practical purposes the lowest melting temperature,  $T_m$ , should be used. For the system used in this work, PEO- $\text{LiCF}_3\text{SO}_3$ ,

$T_m = 60^\circ\text{C}$  at O/M of 30:1<sup>[16]</sup>.

### 3.2.1 Conductivity

Conductance in polymer electrolytes is due to ion motion in the amorphous phase<sup>[25]</sup> regardless of the presence of any crystalline phase. Conductivity measurements can best be made by AC impedance analysis to avoid any electrode effects. The typical variation of conductivity,  $\sigma$ , with temperature,  $T$ , (for PEO/LiCF<sub>3</sub>SO<sub>3</sub>) plotted as  $\log \sigma$  against  $10^3/T$  can be seen in Figure 3.6. The conductivity increases (Arrhenius) above the crystalline-amorphous transition temperature ( $60^\circ\text{C}$  for PEO) to  $10^{-3}$ - $10^{-4}$  Scm<sup>-1</sup> typically. There is a 'knee' at about  $60^\circ\text{C}$  and below this a region of non-Arrhenius curvature.

Free-volume theory, expressed in the form of the VTF (Vogel-Tamman-Fulcher) equation, has been used by most workers<sup>[16]</sup> to express the conductivity/temperature behaviour of these systems. Although this is only used where regions of non-Arrhenius behaviour are encountered. The VTF equation is

$$\sigma = \sigma_0 \exp\left(\frac{-E}{T-T_0}\right) \quad \text{Eqn. 3.2}$$

where  $\sigma_0$  and  $E$  are constants.  $T_0$  is a reference temperature which is often taken to be the equilibrium glass transition temperature. Polymer electrolytes exhibit different types of behaviour, some of which lead to  $E$  being a pseudo activation energy.

### 3.2.2 Mechanical Properties

A limiting factor in the case of PEO and other Polyelectrolytes, PE is that conductivities are modest ( $10^{-6}$ - $10^{-9}$  S/cm) at ambient temperatures and below. High ionic mobility can only be achieved at higher temperatures (above  $63^{\circ}\text{C}$  the  $T_m$  of PEO) where the elastomeric phase predominates. However at these temperatures PEO shows poor mechanical stability ie high flexibility, creep and even extrusion from between electrodes. Conductivity appears to be enhanced by greater backbone mobility, yet polymers with low  $T_g$ 's, which will be of most interest here, will also suffer from poor mechanical properties. It is desirable to improve these properties without reducing the conductivity of the material.

Several methods of achieving this have been attempted. Radiation-induced crosslinking<sup>[26]</sup> is one method. Here the crosslinking leads to the prevention of crystallisation, keeping the polymer in its more conductive amorphous form. This did improve mechanical properties, but at higher radiation dosage, molecular weight was altered due to chain scission. Other methods have involved mixing the conducting PEO with a second polymer which acts as a support. PEO-LiClO<sub>4</sub> supported on poly(methacrylic acid) [PMAA] has been studied by Tsuchida<sup>[27]</sup>. Although the mechanical stability had improved, conduction is impaired to a large extent.

Poly(ethylene adipate)-LiCF<sub>3</sub>SO<sub>3</sub>/poly(vinyl acetate) blends were prepared by Armstrong and Clarke<sup>[28]</sup>. This system showed good mechanical properties and conductivity at both 140 and 60°C. A further successful solution to this problem has been put forward by Gray et al<sup>[29]</sup> where polystyrene is used as a support for PEO<sub>10</sub>-LiCF<sub>3</sub>SO<sub>3</sub>. Here styrene is thermally polymerised after being mixed with the PEO complex. One further system should be mentioned here and this is the use of an inert beta-alumina filler by Weston and Steele<sup>[30]</sup>.

This work is an attempt to improve mechanical properties by adding aluminium powder and high T<sub>g</sub> polymers. The former may also produce a mixed conductor, (that is possessing good ionic and electronic conductivities).

SECTION II - EXPERIMENTAL3.3 Experimental3.3.1 Materials

Metals Aluminium[BDH, fine powder], Copper[Goodfellow Metals], zinc spheres[Hopkin and Williams] and silicon[BDH] were used as received. Aluminium and zinc flakes[Silberline] were mixed with solvent and/or lubricant which was removed by refluxing the material in a Soxhlet extractor using ethanol and then methylene chloride as solvents (3 hours each). The metal powders were then dried in a vacuum oven at 60°C for about 16 hours.

Polymers Poly(phenylene sulphide) [PPS] (Aldrich), poly(acrylamide) [PAA] (BDH mw  $7-9 \times 10^6$ ), poly(acrylonitrile) [PAN] (Courtaulds) and poly(vinyl chloride) [PVC] (BP) were used as received. Poly(methyl methacrylate) [PMMA] (BDH) and Polystyrene [PS] (BDH) were purified by dissolving the crude polymer in methylene chloride and precipitating the purified polymer by dropping the solution into a large excess of methanol. The pure polymer was then filtered and dried in a vacuum oven for at least 24 hours. Poly(ethylene oxide) [PEO] (BDH mw  $4 \times 10^6$ ) was used as received and due to its hygroscopic nature was stored in a vacuum dessicator.

Electrolyte Lithium trifluoromethylsulphonate,  $\text{LiCF}_3\text{SO}_3$  (3M, battery grade) was heated to  $100-110^\circ\text{C}$  for 6 hours under vacuum to remove water. After cooling under vacuum, the salt was then transferred to a vacuum dessicator for storage.

Solvent When films were cast from solution, the solvent used was methylene chloride. It was purified by distillation.

### 3.3.2 Grinding of Polymers

The polymer or polymer mixture was ground in a stainless steel, hemispherically-ended tube, 0.1cm thick, inner diameter 3.8cm and 11cm long. The maximum amount of polymer which could be ground was 5g, but generally 2.5-3.0g was the quantity used. Polymer and ball-bearings were added to the tube and it was firmly attached to a mechanical shaker via a specially adapted arm. The tube was then immersed in liquid nitrogen and shaking commenced. A series of trials established the optimum conditions for powdering to be 40-50 0.6cm diameter ball-bearings and a milling time of 12-15 minutes.

### 3.3.3 Mixing PEO and Electrolyte

The dried electrolyte,  $\text{LiCF}_3\text{SO}_3$ , was added to the tube containing PEO, frozen in liquid nitrogen and ground for a further 5 minutes. When the tube had reached room temperature, the mixture was transferred to a bottle and stored in a vacuum dessicator.

### 3.3.4 Cold Pressing of Pellets

Metal and polymer, in various ratios, were ground together in a pestle and mortar until a uniform mixture was achieved. Then 0.02-0.06g of the mixture was pressed in a 5mm die using a Specac 15 ton hydraulic press at 1.8-1.9 tons for approximately 60-90 seconds. The conductivity was then measured using the Wayne Kerr bridge apparatus (see section III).

### 3.3.5 Hot Pressing of Pellets (into Films)

A 5mm diameter pellet of polymer electrolyte was formed by first cold pressing the powder, releasing the pressure and heating to  $80^\circ\text{C}$ . A pressure of 0.5 tons was applied and after 15 minutes the system was allowed to cool to room temperature. The pellet was transferred to a 13mm diameter die, cold pressed at a 5 ton load and heated at  $80^\circ\text{C}$  for 15 minutes with the pressure reduced to 1.5 tons. This produced films of about 0.17-0.30mm in thickness which were stored in a vacuum dessicator.

80°C is the temperature used for PEO. At this temperature PEO is soft and can be formed into good quality, uniform pellets. Different polymers require different temperatures according to their thermal properties. PAA and PAN composites were heated to 100°C. Temperatures during hot pressing were obtained using a Comark 2001 electronic thermometer with a NiCr/NiAl thermocouple.

### 3.3.6 [PEO<sub>10</sub>-LiCF<sub>3</sub>SO<sub>3</sub>] Composites

Aluminium, PAA or PAN was thoroughly mixed in milling apparatus with PEO<sub>10</sub>-LiCF<sub>3</sub>SO<sub>3</sub> polymer electrolyte at various percentages (by weight). Films were then obtained as above and A.C.conductivity measurements made using the FRA (see Chapter 2 ). D.C.conductivity measurements were made on the Al.PEO<sub>10</sub>-LiCF<sub>3</sub>SO<sub>3</sub> composites using a 4-point or 2-point apparatus (see Chapter 2).

### 3.3.7 Thermal Expansion of PEO

Pellets of PEO and Al.PEO composites were made by pressing the powder in a 13mm die at 6 tons pressure for 2 minutes. The pellets were then heated to various temperatures, while in an evacuated die with no pressure applied, and held there for 30 minutes. The thicknesses were measured before and after using a micrometer. From this the change in volume was calculated.

The temperature was measured between the heating band and the die (Specac). Hence a calibration curve had to be obtained in order to give an accurate estimate of the temperature within the die.

### 3.3.8 Differential Scanning Calorimetry [DSC]

DSC analysis of polymer composites was performed with a Perkin Elmer DCS1 linked to a Bryans 28000 chart recorder at a heating rate of 16°C per minute. The range covered was from 20 to 90°C.

### SECTION III - RESULTS

#### 3.4 Metal/Polymer Composite Results

The electrical conductivity measurements were made using the equipment and methods detailed in Section II above.

A hot-pressing technique has been used here to produce thin films. This technique has been shown to improve conductivity<sup>[29]</sup>. The technique of casting normally used with these systems has the problem of residual solvent which is hard to remove and may lower the conductivity<sup>[31]</sup>.

Although the grinding technique and equipment used here was developed in this department specifically for PEO systems to improve the distribution of the electrolyte through the polymer by reducing the size of both, such a technique is equally important in the case of composites.

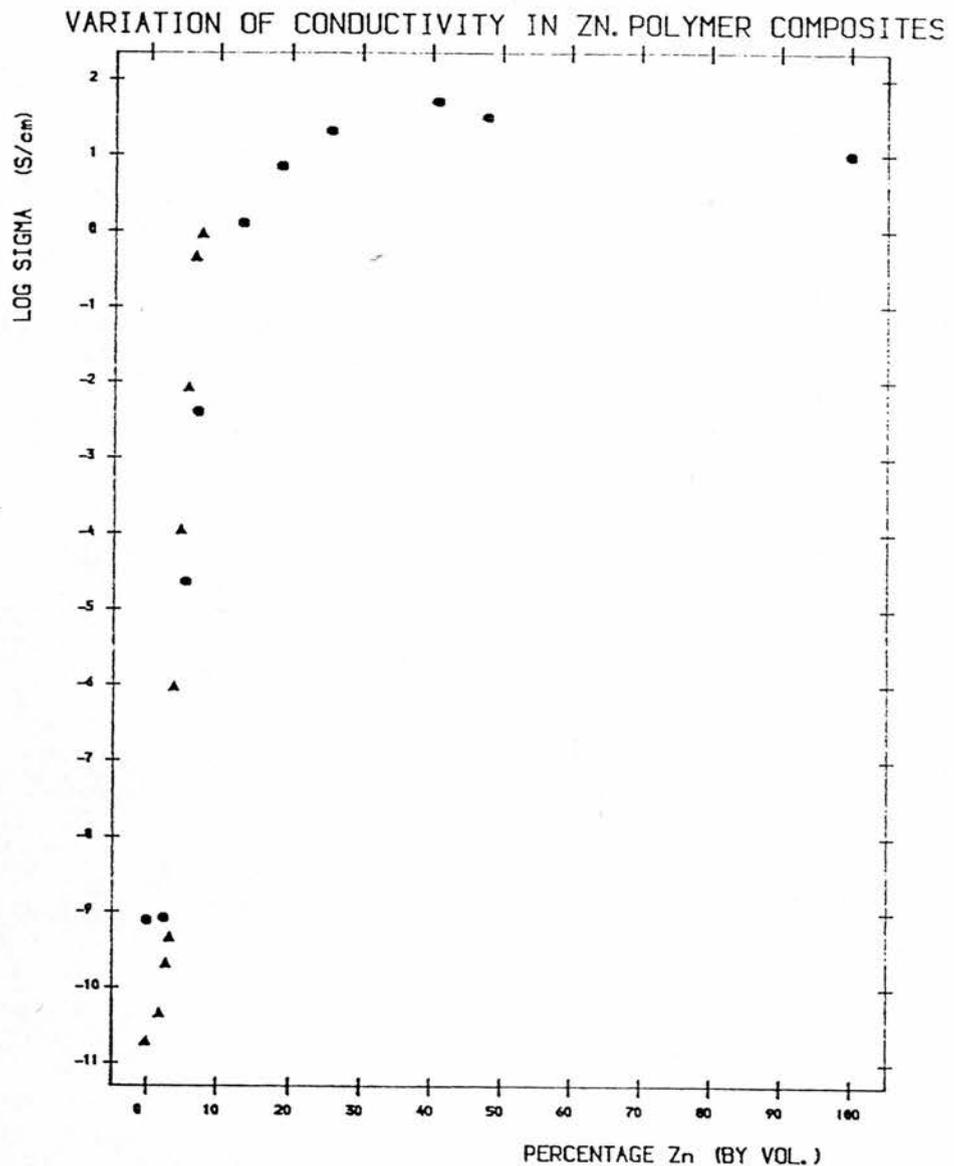
### 3.4.1 Zinc/Poly(phenylene sulphide)[PPS]

PPS is a commercially available electronic conducting polymer with a 'doped' conductivity of 1 S/cm<sup>[32]</sup>. These experiments were performed to observe the effect of mixing zinc with the polymer. It was hoped that pressed pellets or cast films of the mixture would have improved conductivities.

a) Pellets Figure 3.3 shows how the conductivity of Zn/PPS pellets varies with the percentage (by volume) of zinc added. Conductivity,  $\sigma$ , (S/cm) is plotted as  $\log \sigma$ . This result is consistent with previous reports on polymer-metal composites<sup>[1]</sup>. The percolation threshold is about 5%, a relatively small amount of metal, but the expected result for flake.

FIGURE 3.3

▲-Zn.PPS, ●-Zn.PEO



b) Films PPS films were cast by refluxing the PPS in phenyl ether at 210°C and dropping the hot solution onto heated glass slides. However poor quality films were obtained and addition of Zn to the refluxing solution produced films with conductivities little better than that of pure PPS. It is assumed from this that the zinc and PPS have reacted in some way to form a material of low conductivity. This method would not be good therefore for producing

high conductivity Zn/PPS composite films.

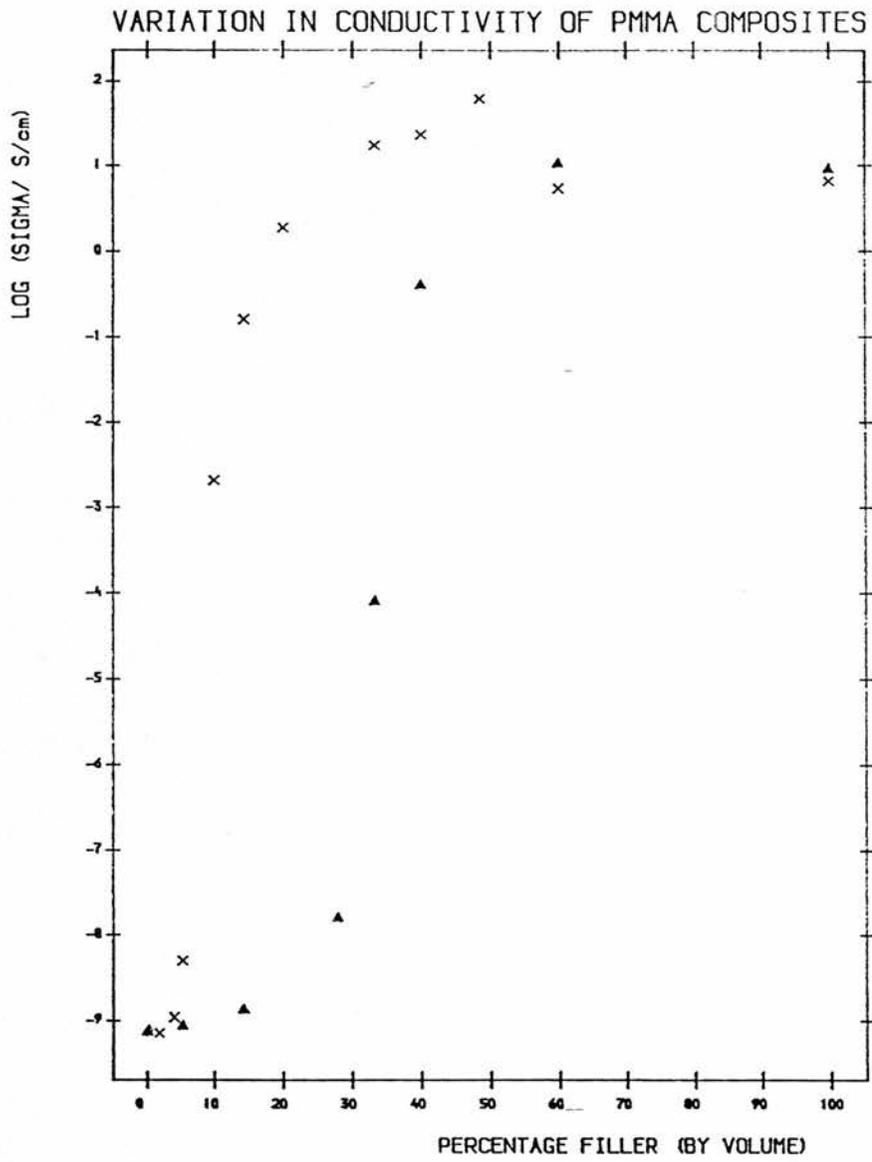
In view of these results, it was decided to investigate polymer/metal composites using polymers with better physical characteristics.

#### 3.4.2 Zinc/Poly(methylmethacrylate)[PMMA]

Figure 3.4 shows plots of  $\log \sigma$  against Zn(% by volume) for Zn/PMMA pellets. As can be seen the percolation threshold varies with particle shape. This type of behaviour has been observed previously (see section 3.1).

FIGURE 3.4

× Zn flake, ▲ Zn sphere

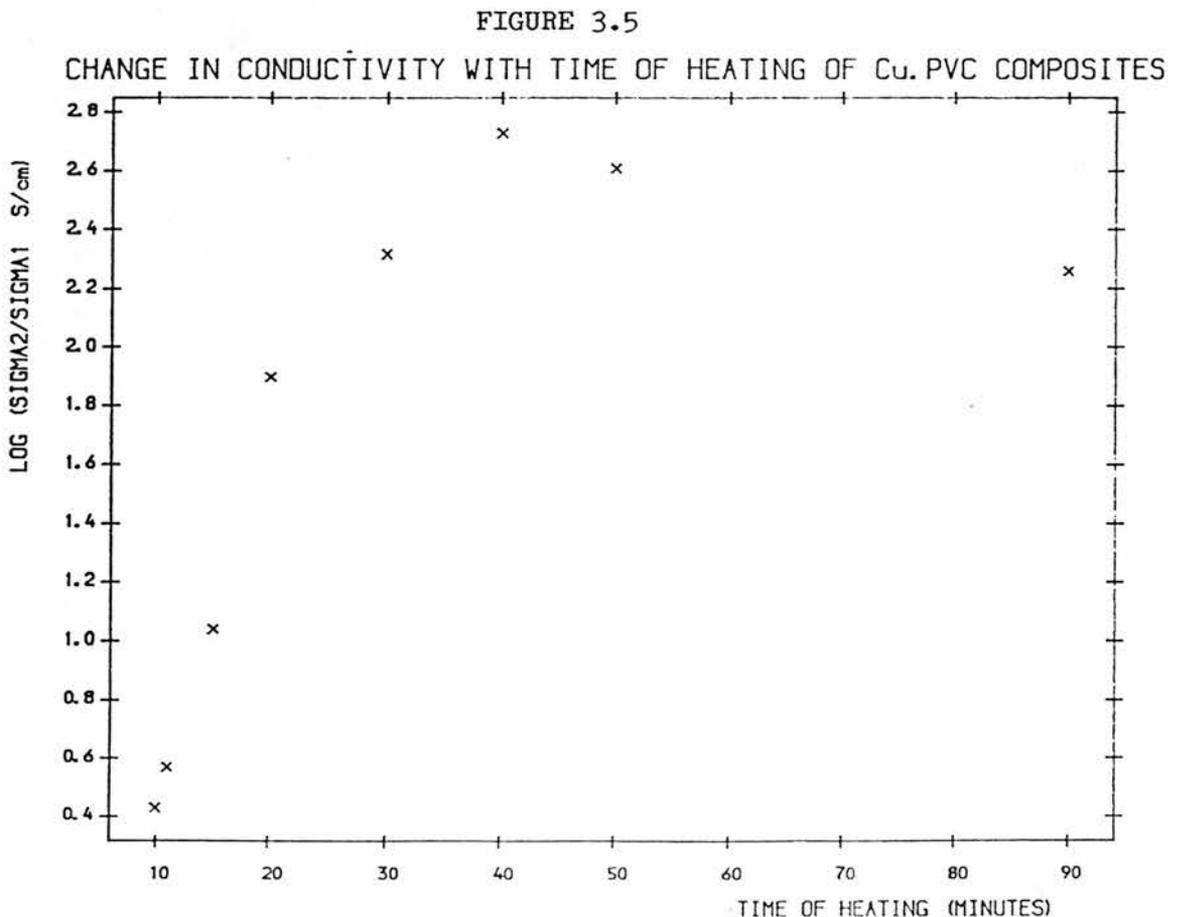


### 3.4.3 Zinc/Poly(ethylene oxide)[PEO]

Figure 3.3 shows a plot of  $\log \sigma$  against Zn (% by volume) for Zn/PEO pellets. As can be seen a good conductivity can be achieved with as little as 12% loading. The percolation threshold being about 5-7% loading.

### 3.4.4 Effect of Heat on Copper/Poly(vinyl chloride)[PVC]

A 50% by weight Cu/PVC 5mm pellet was pressed in the normal way and the conductivity measured by the Wayne Kerr bridge method before and after heating to  $140^{\circ}\text{C}$  for a set time. The variation of change in conductivity, plotted as  $\log(\sigma_2/\sigma_1)$ , against time at  $140^{\circ}\text{C}$  can be seen in Figure 3.5.

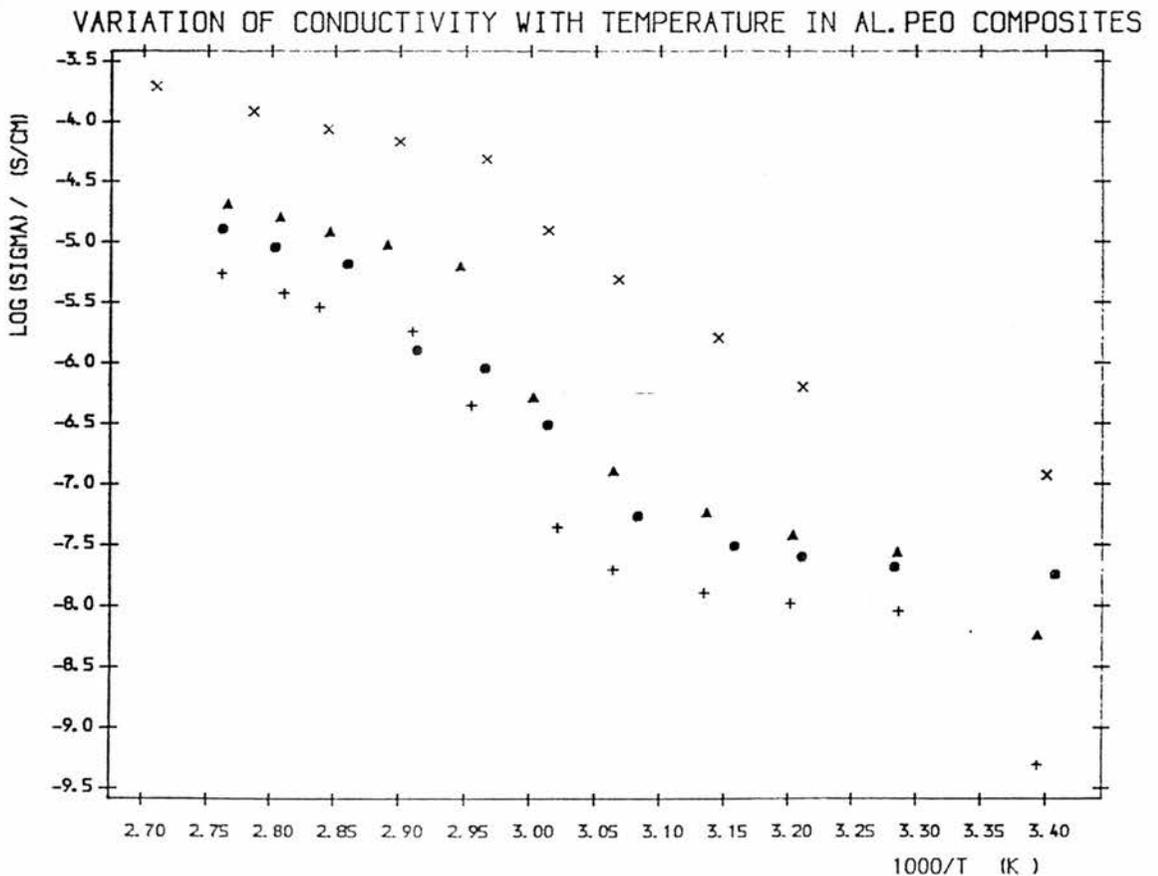


### 3.5 PEO/Metal Composite Results

#### 3.5.1 FRA Measurements

Al.PEO<sub>10</sub>-LiCF<sub>3</sub>SO<sub>3</sub> films containing 0, 11.06, 24.65 and 42.09% Aluminium by volume were made. The conductivities of these films with respect to temperature are shown in Figure 3.6. As can be seen there is a drop of 1-2 orders of magnitude over the whole range. The 'knee' appears to move to higher temperatures as more Al is added. Here ionic conductivity is being measured predominantly, which is why the conductivity decreased as the ionically active component was diluted.

FIGURE 3.6  
 x = PEO10LiCF3  
 ▲ = 11.06%VOL.  
 + = 24.65%VOL.  
 ● = 42.09%VOL.



### 3.5.2 DC Conductivity Measurements

The variation of DC conductivity with aluminium (% by volume) is shown in Figure 3.7. As can be seen, quite good electronic conductivity can be achieved, although the amount of aluminium required at the percolation threshold is quite high (30-35%). Compared to the results for zinc flake this is not an encouraging result. However as experiments had to be performed in an open atmosphere it is not surprising. The aluminium is certain to have an oxide layer, which will affect both the number and the quality of contacts between flakes, particularly at lower concentrations. At higher concentrations the aluminium particles could be forced together and the metal beneath the oxide layer break through to make contact.

FIGURE 3.7

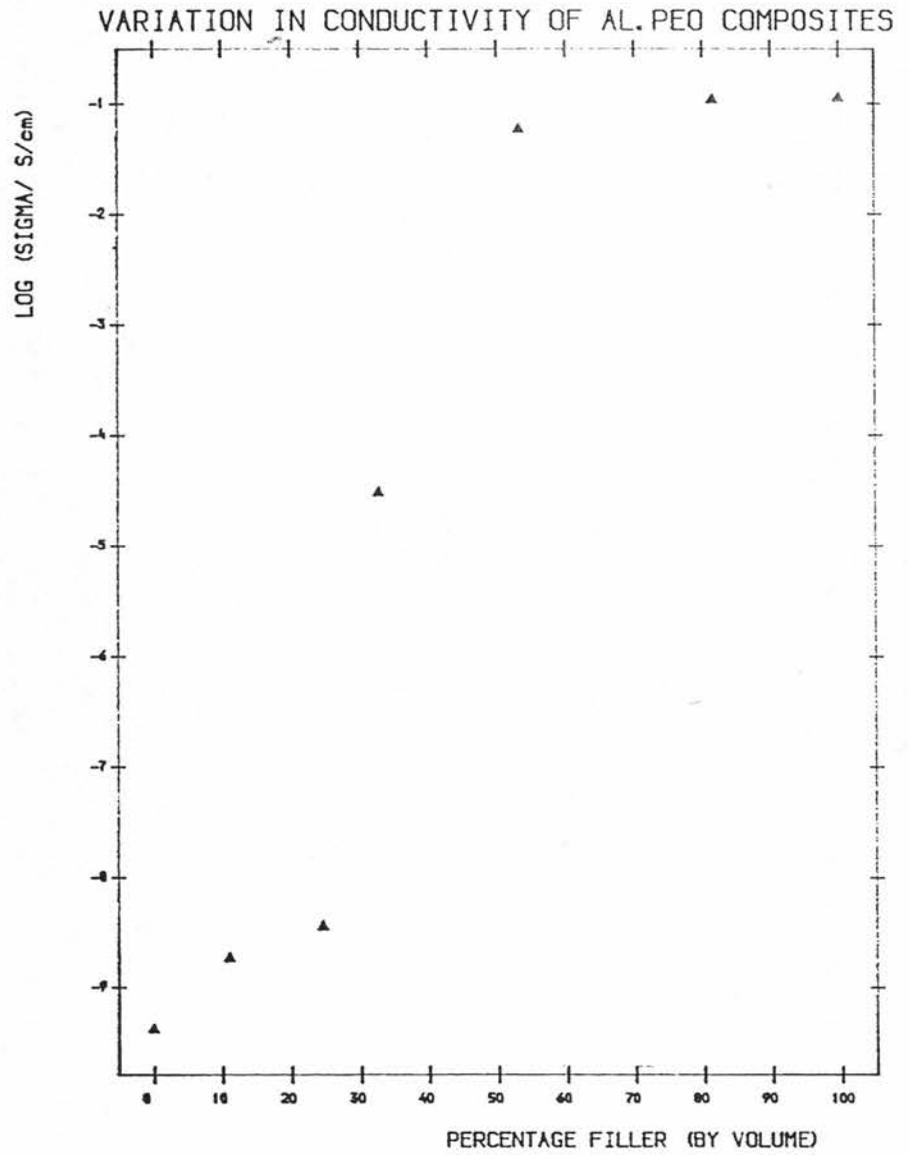


FIGURE 3.8 + = PEO  
 ▲ = 11.06%vol.  
 ▼ = 24.65%vol.

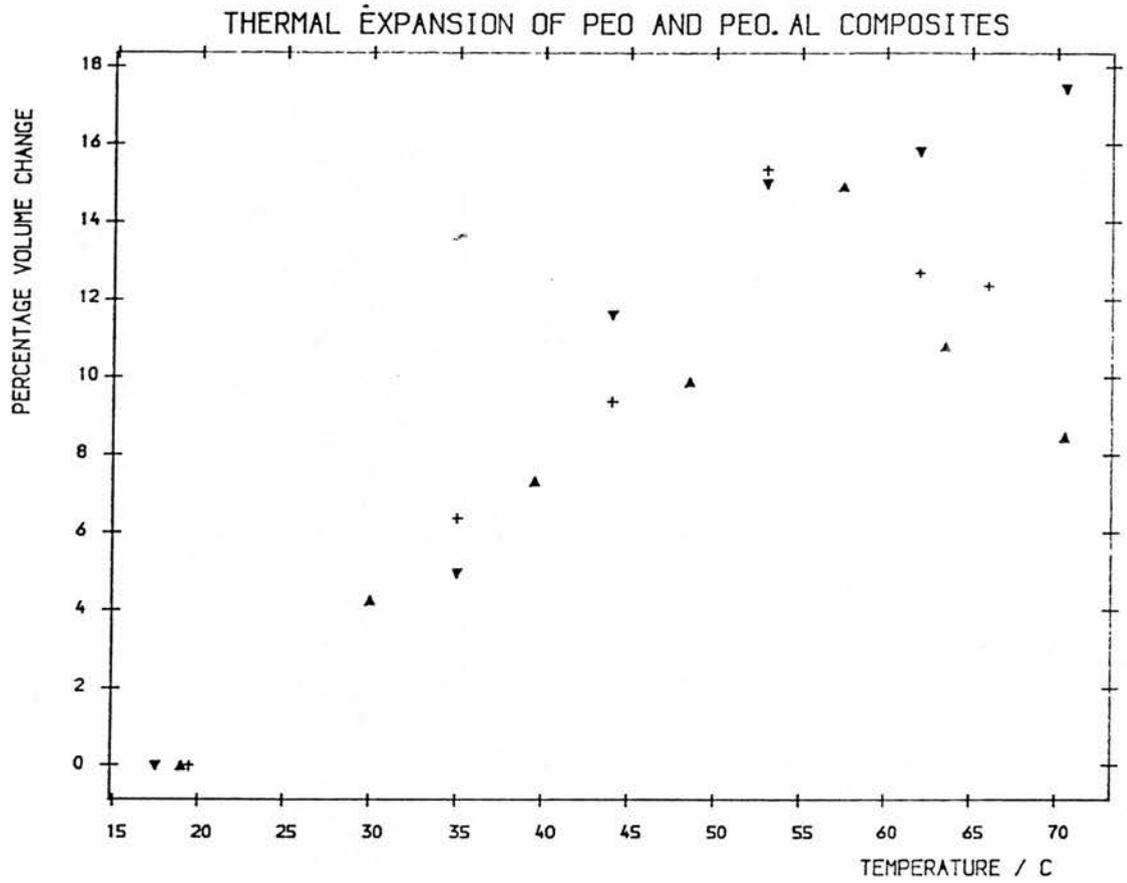
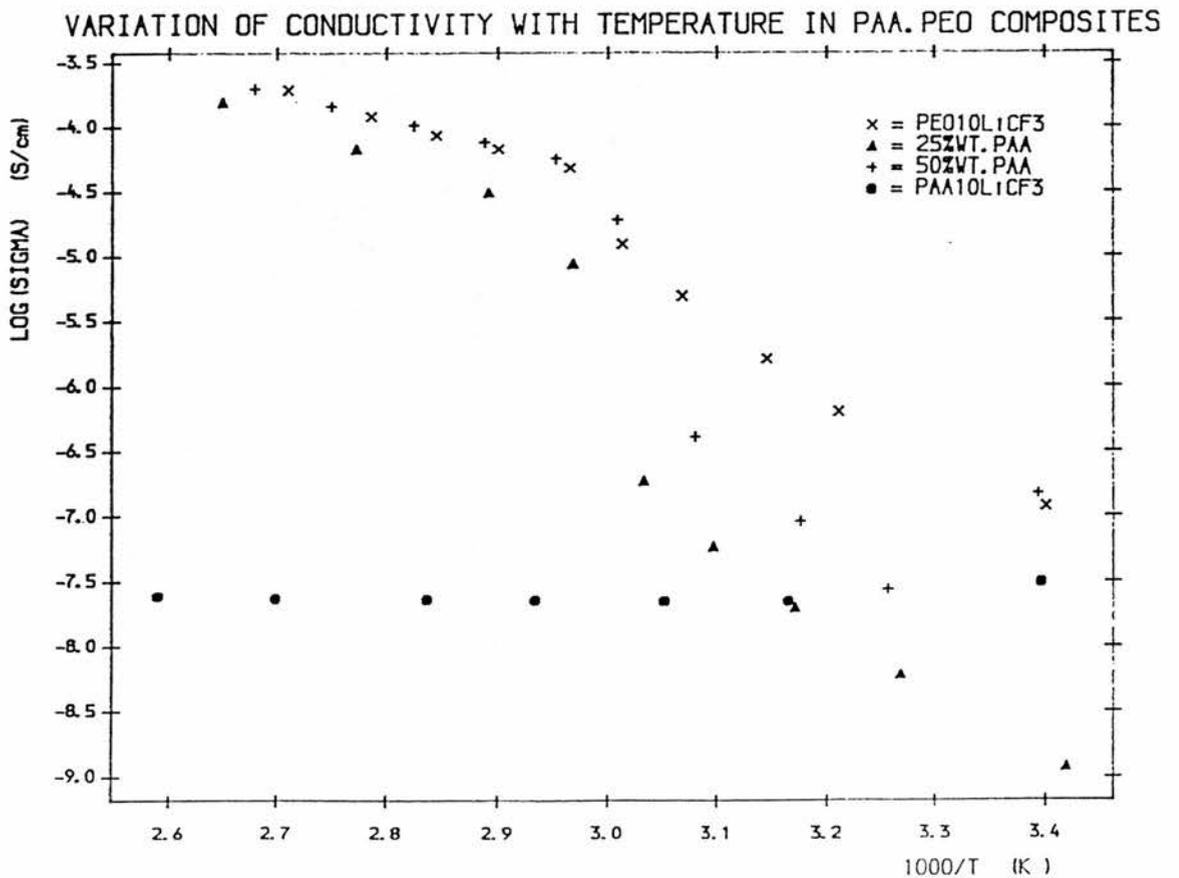


FIGURE 3.9



### 3.5.3 Thermal Expansion

It was observed, on removing the film from the conductivity apparatus, that often the thickness of the film appeared to have changed, presumably due to heating. It was decided to investigate this further.

The results of thermal expansion experiments may be seen in Figure 3.8. From ambient temperature up to the region of PEO's  $T_m$ , the composites (11.06 and 24.65% by volume) expand in the same way as PEO with perhaps different expansion coefficients. However despite the slightly crude nature of this experiment it can be seen that in the temperature region above the  $T_m$ , PEO and the 11.06% composite show a distinct contraction presumably due to the melting of the PEO, but the 24.65% composite continues to expand albeit at a slower rate. Coefficients of expansion were not calculated as they appeared to be different for each composite, which resulted in too few points per composite for an accurate calculation to be made.

An attempt was made to measure a 42.09% composite. However removal from the die to make the thickness measurement led to the pellet invariably breaking as it was too brittle. Despite these problems an interesting insight into the thermal expansion properties of PEO and Al/PEO composites was obtained.

### 3.5.4 Differential Scanning Calorimetry

The results of the DSC analysis are summarised in Table 3.1 below.

Table 3.1

<u>%Al by vol.</u>	<u>1st.Peak(°C)</u>	<u>2nd.Peak(°C)</u>
0.0	48.7	57.9
24.65	49.9	57.9
42.09	49.2	57.2

PEO shows two melting points (endotherms) in this region; one at about 50°C (associated with complexed phase), the other at about 60°C (uncomplexed PEO). As can be seen there are slight variations, but basically little change.

### 3.5.5 Summary

Aluminium was chosen for these experiments as it alloys well with lithium<sup>[33]</sup>, whose salts are commonly used in PEO. However it is not an ideal material for working in an open atmosphere and although the physical properties and electronic conductivities could be improved the levels of aluminium required resulted in too large a drop in the AC conductivity (and consequently ionic conductivity). It is possible that other methods would be better for improving the physical properties (polymer blends, copolymers etc.) or electronic conductivity (conductor coated fibres).

### 3.6 PEO/Polymer Composite Results

The work here is an attempt to improve the mechanical properties of PEO by adding polymers with much higher  $T_g$ 's.

#### 3.6.1 Poly(acrylamide)[PAA]

PAA has a  $T_g$  of  $165^\circ\text{C}$  and should improve the mechanical properties of films. PAA.PEO<sub>10</sub>-LiCF<sub>3</sub>SO<sub>3</sub> films containing 0, 25 and 50% PAA by weight were made. The conductivities of these films with respect to temperature are shown in Figure 3.9. As can be seen in the region above  $60^\circ\text{C}$  the fall in conductivity is less than half an order of magnitude at worst. This result compares quite well with most others in this field<sup>[28,29]</sup>. However below  $60^\circ\text{C}$  the fall in conductivity is much greater (up to 2 orders of magnitude).

FIGURE 3.10

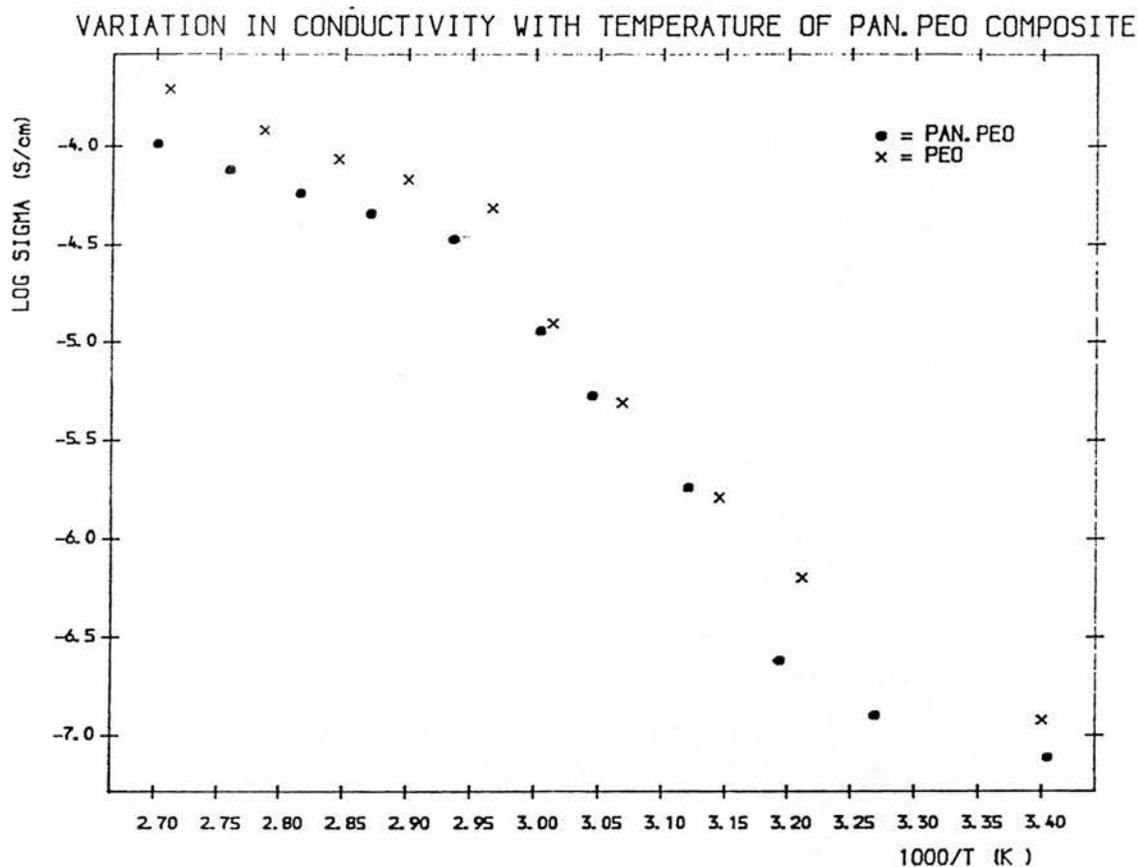
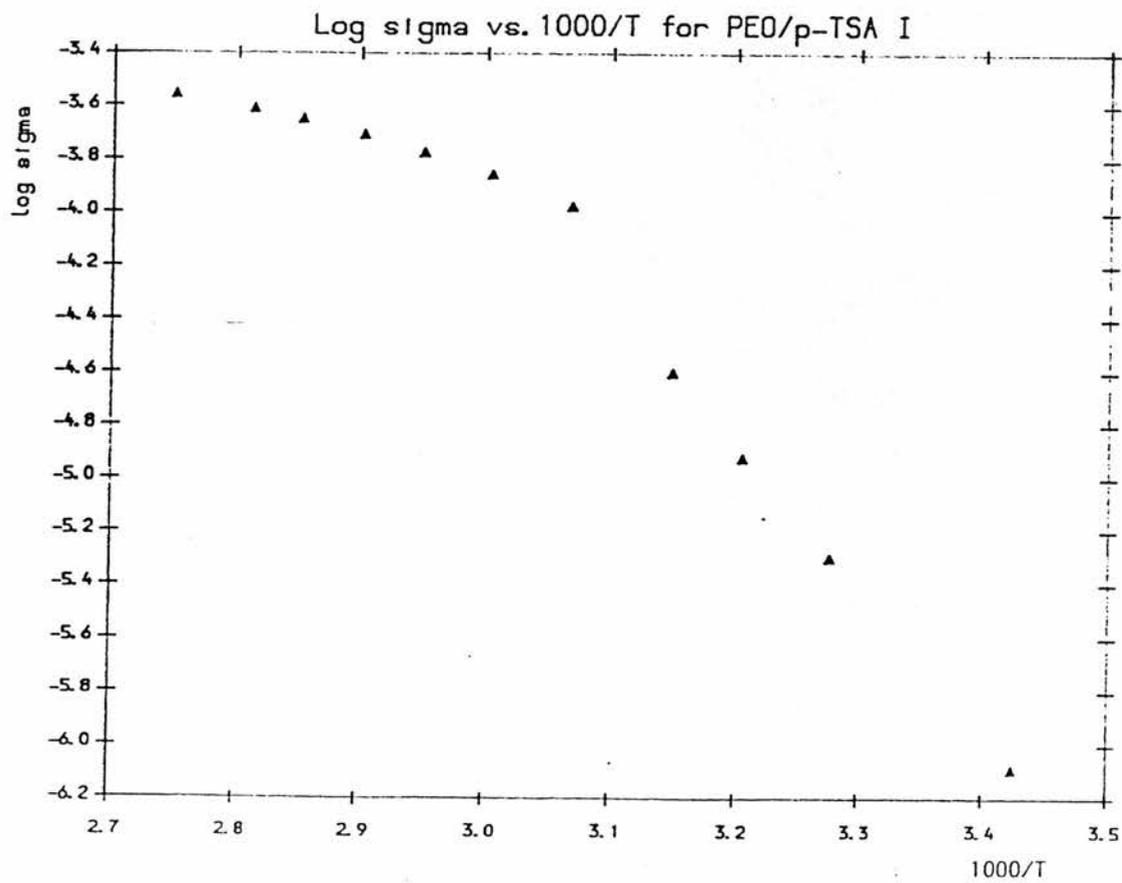


FIGURE 3.11



### 3.6.2 Poly(acrylonitrile)[PAN]

PAN has a  $T_g$  of  $85^\circ\text{C}$  which should improve mechanical properties, but it is also of interest as it has been reported<sup>[34]</sup> to produce useful conductivities in polymer/salt/plasticiser (low molecular weight polar solvent) polymer electrolytes. PAN.PEO<sub>10</sub>LiCF<sub>3</sub>SO<sub>3</sub> films containing 0 and 25% by weight PAN were made. The conductivities of these films with respect to temperature are shown in Figure 3.10. As can be seen only a very small drop in conductivity occurs over the whole temperature range.

### 3.6.3 PEO<sub>10</sub>.p-Toluene Sulphonic Acid

The conductivity of this film with respect to temperature is shown in Figure 3.11. However when the film was removed from the cell it was very gummy and it was suspected that the acid had reacted with the PEO and broken it down probably by acid hydrolysis. It is suspected that this may be due to the presence of water. Hence this approach was not pursued.

### 3.7 Conclusions

The electrical properties of various polymer/metal and polymer/polymer composites were examined and the variation of the percolation threshold with polymer, metal and metal particle shape was observed.

The system  $\text{Al.PEO}_{10}\text{LiF}_3\text{SO}_3$  was studied in some detail with a view to obtaining materials which exhibited good electronic and ionic conductivities along with good physical properties. However, the percolation threshold for DC conductivity was found to be rather high (30-35%). Therefore too much filler (aluminium) had to be added in achieving good electronic conductivities for the AC conductivity to be unaffected. Even at percentages of filler well below the percolation threshold, the AC conductivity decreased significantly (1-2 orders of magnitude). More extensive studies would be required to determine the exact physical properties of these materials. However at compositions above the percolation level, generally rather poor mechanical properties are observed.

The studies on polymer/polymer composites revealed that even at relatively high loading of polyacrylamide and polyacrylonitrile, the AC conductivity of PEO was not drastically reduced (less than one order of magnitude). Once again a full study of the physical properties of these composites would be required to determine to what extent they were affected. In principle they should have improved.

Rigorously dried p-toluene sulphonic acid and PEO may yet lead to a viable conducting polymer electrolyte, and is a system which may be worthy of further study.

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#### 4.1 Chemical Synthesis of Conducting Polymers

Chapter 1 referred briefly to the synthesis of polyacetylene, PA. It is appropriate at this point to look more closely at this and other examples of addition polymerisation.

##### 4.1.1 Addition Polymerisation

Natta et al first reported<sup>[3]</sup> the formation of PA as a red powder when acetylene gas was bubbled through a solution containing Ziegler catalyst. Later Shirakawa et al<sup>[4,5]</sup> produced PA films at the gas-liquid interface by exposing Ziegler catalyst solutions to an acetylene atmosphere. The best results were achieved using  $\text{Ti}(\text{OC}_4\text{H}_9)_4\text{-Al}(\text{C}_2\text{H}_5)_3$  (Al:Ti, 4:1) as catalyst in the concentration range 3-500 mmol/liter with a hydrocarbon solvent. The ratio of cis to trans PA is dependent on the polymerisation temperature. The cis isomer converts to the thermodynamically favoured trans isomer even at low temperatures. The conversion is much faster at elevated temperatures. Luttinger catalysts<sup>[6]</sup> (nickel and cobalt salts reduced by sodium borohydride) have also been used to produce PA which is very similar to that produced by the Shirakawa technique. Other catalysts have also been used. A fuller discussion of PA synthesis is given elsewhere<sup>[2]</sup>.

A large number of substituted acetylenes have been polymerised in similar ways<sup>[2]</sup>. The intrinsic conductivity and dopability tend to increase as the degree of deviation from polyene planarity and decreases with the size and number of substituents. The colours of the polymers give an indication of the degree of conjugation and consequently white polymers tend to be good insulators. It should also be noted that PA's tend to be highly air (oxygen) sensitive, as is the case with many conducting polymers.

Cyclopolymerisation of appropriate monomers can also lead to conjugated conducting polymers<sup>[2,7]</sup>.

#### 4.1.2 Condensation Polymerisation

Condensation Polymerisation methods have been used successfully to synthesise polyarylenes and poly(arylene vinylene)s. Conducting polymers of this type, based on phenylene<sup>[8,9]</sup>, aromatic<sup>[8,9]</sup> and heteroaromatic<sup>[9]</sup> units, have been extensively reviewed in terms of both synthesis and the properties of the polymers produced.

Many of these olefin forming reactions which involve the elimination of water result in products of fairly low molecular weight where structural characterisation is often difficult. Many alternatives to the elimination of water have been reported<sup>[2]</sup>. The problem of structural characterisation is one which afflicts a large percentage of conducting polymers due to their insolubility and

infusibility.

#### 4.1.3 Indirect Synthesis

This two-step approach is a familiar concept in polymer chemistry and two early examples are interesting with respect to organic conductors. They are 1) the pyrolytic modification of polyacrylonitrile<sup>[10]</sup> to form a conductor and 2) the pyrolytic elimination of hydrogen chloride from poly(vinyl chloride)<sup>[11]</sup>, which could provide an inexpensive, easy route to PA.

A sophisticated two-stage process has been applied recently to form poly(p-phenylene), PPP<sup>[12]</sup>. A different type of elimination process, retro-cycloaddition, has also been used recently to produce PA<sup>[13,14]</sup>. This route is particularly interesting as the prepolymer is soluble and may be purified by reprecipitation. The trans PA produced by this method is often referred to as "Durham" PA. The stability of the prepolymer was improved by increasing the size of the aromatic leaving group eliminated during the second step conversion to PA<sup>[2]</sup>.

#### 4.1.4 Doping

The chemical doping of these polymers and the effect on conductivity produced by doping is discussed in Chapters 1 and 2.

Chemical doping of PA<sup>[15]</sup>, PPP<sup>[8]</sup> and other conducting polymers<sup>[8,16]</sup> has been well reviewed. Doping generally takes two forms, either exposure of the solid pristine polymer in the form of a film, pellet, or powder to a gaseous dopant such as  $\text{AsF}_5$  or  $\text{I}_2$ , or exposing the solid polymer to a solution containing the dopant, such as  $\text{Fe Cl}_3$  or Li naphthalide.

The maximum conductivity achieved with various dopants can vary greatly; for example the range for various vapour phase dopants with PA was reported to be about six orders of magnitude, up to 560 S/cm. The saturation concentration of dopants in PA, usually expressed as  $y$ , the dopant/carbon mole ratio, also varies greatly from 0.005 to 0.25. Doping from solution is the most used method and the rate and level of doping may be controlled by the solution concentration. Gas-phase doping may be controlled by varying the vapour pressure of dopant by regulation of temperature. Doping is usually accompanied by the polymer becoming darker in colour (often nearly black) and by it having a metallic appearance. Undoping of polymers may be achieved by different means, depending on the nature of the dopant. Methods of undoping include, removal under vacuum (possibly at elevated temperature), by dissolving the dopant back into solution, or by chemical reaction, for example with  $\text{NH}_3$ . Exposure to atmospheric oxygen and/or water may achieve similar results.

A more elegant and controllable method is that of electrochemical doping. This aspect will be discussed further in Chapter 5, but it should be noted that it may be performed on chemically synthesised polymers if suitably prepared.

#### 4.1.5 Other Preparations

Recent reports have indicated that the simultaneous polymerisation and doping of pyrrole in the presence of halogens<sup>[17,18]</sup> or Fe<sup>III</sup> salts<sup>[19,21]</sup> may be possible by relatively simple methods. The polypyrrole, PP is produced either at the interface between two liquids as a film or as a powder precipitated from solution. PP produced by this method is reported to have conductivities in the range 1-30 S/cm.

In some cases<sup>[20,22]</sup>, this method has been employed to produce composite films with other polymers. These composites are also highly conducting. Further mention of conducting polymer composites is made in Chapter 5.

One further method of polymer formation should be mentioned here, namely the auto-oxidation of bromopyrroles to form conducting polymers<sup>[23]</sup>. Conductivities for these materials ranged from  $3 \times 10^{-3}$  to 5 S/cm and they are bromide ion doped.

4.2 Poly(arenemethine)s

Most of the polymers discussed so far, with the exception of PA, have contained linear chains of aromatic rings (PPP) or heterocycles (PP). However, many polymers whose backbone is composed of aromatic rings linked by heteroatoms are well known (PPS). These polymers have interrupted  $\pi$ -electron systems and can be easier to handle. They have a tendency towards slightly lower conductivities than polymers with extended conjugated  $\pi$ -electron systems.

A recent review<sup>[9]</sup> revealed the wide variety of condensed aromatic or heterocyclic, heteroatom bridged and conjugated aliphatic unit bridged polymers which have been made. The latter group of polymers contains one particularly significant member - polymeric vinylenes. Many of these exhibit quite high conductivities. The general structure is shown in Figure 4.1, where X may be an aromatic or heterocyclic group.

Figure 4.1



Conducting polymers have been well studied, both on a theoretical and an experimental basis. On the foundation of theoretical calculations, a comparison may be made between the experimental and the theoretical values for parameters which may influence the conductivity of the material such as the band gap,  $E_g$ , and good agreement is often found<sup>[24]</sup>. Consequently, using these methods it is

possible to predict, to some extent, polymers which though as yet unsynthesised are potentially good conductors<sup>[24]</sup>. Two polymers which have been synthesised after such predictions are poly(vinylene sulphide) PVS<sup>[25]</sup> and poly(thiophene vinylene) PTV<sup>[26]</sup>. Both have been shown to have good electrical properties.

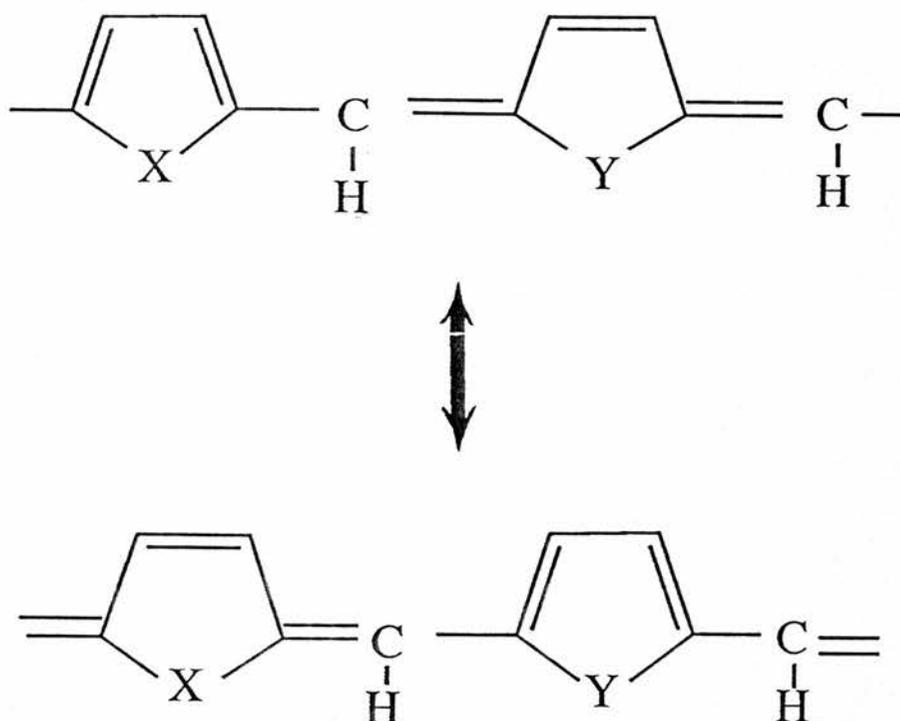
Methine bridged polymers poly(arenemethines) have been predicted<sup>[27-30]</sup> to have small band gaps and therefore are good candidates for conducting polymers. The general formula for these polymers is shown below in Figure 4.2.

Figure 4.2



X and Y may either be benzenoid or heterocyclic rings. Further they may be dimeric units such as biphenyl or bithiophene. 5-membered heterocycles are thought to be preferable to phenylene groups as steric effects causing a decrease in  $\pi$ -orbital overlap should be less important<sup>[28]</sup>. The presence of a single-carbon bridging group,  $-CH=$  leads to aromatic and quinoid groups in the polymer which, it is suggested<sup>[30]</sup>, leads to bond length alternation along the C-C backbone similar to PA. The resonance structures in these polymers is shown below in Figure 4.3. X and Y may be S or NH.

Figure 4.3

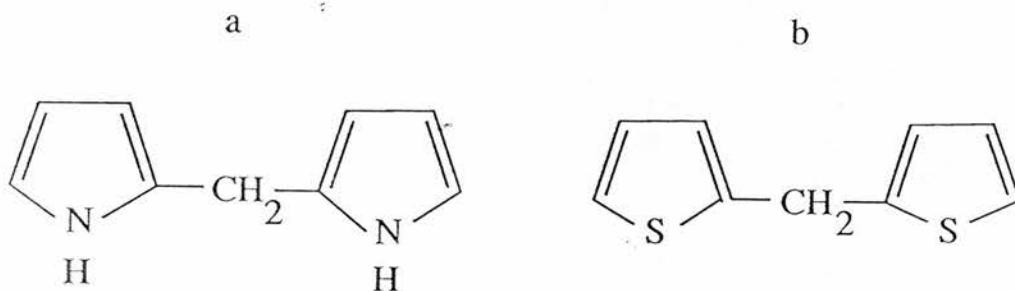


Until very recently, no literature had been published on the synthesis of these polymers. The four papers<sup>[31-34]</sup> which have emerged will be discussed in the conclusion of this chapter.

#### 4.2.1 Introduction to Experimental

Attempts were made to synthesise polymers of the above type. The two methods of synthesis used to produce conducting polymers have been employed here. The electrochemical approach is detailed in Chapter 5. The present chapter deals solely with chemical methods of synthesis. The work on chemical synthesis may be split into two areas.

Figure 4.4



1) The synthesis of the compounds di(2-pyrrolyl)methane and di(2-thienyl)methane - Figure 4.4 a) and b). These monomers may then be polymerised electrochemically (Chapter 5) or chemically to the poly(2,2' dipyrrolyl methane) which may then be oxidised to the poly(2,2' dipyrrolyl methine) for example. Alternatively, the poly(arenemethine)s may be obtained directly by polymerisation. Note that in these cases X and Y in Figure 4.2 will be either bipyrrrole or bithiophene.

2) The direct synthesis of poly(arenemethane)s which may be oxidised to poly(arenemethine) or the direct synthesis of poly(arenemethine)s. It has been stated<sup>[35]</sup> that the reaction between pyrrole and formalin gives a polymer which is poly(2-pyrrolyl methane). It should be possible to oxidise this polymer to the methine polymer as is the case with the analogous cyclic compounds porphyrinogens and porphins<sup>[36]</sup>.

A further method for obtaining methine polymers was suggested by the acid-catalysed condensation of pyrrole aldehyde with an  $\alpha$ -unsubstituted pyrrole<sup>[37]</sup> to form dipyrromethine. Consequently pyrrole-2-carboxaldehyde should react with itself to form the desired polymer. The self-polymerisation of thiophene-2-methylbromide was also investigated. This type of behaviour with the elimination of hydrogen halide gas to form a conducting polymer has been reported.

The final investigation involved the reaction between thiophene and benzaldehyde. The aim was to produce a polymer where the bridging group is C-phenyl rather than CH. It was hoped that in this case if a polymer could not be obtained then a monomer suitable for electropolymerisation could. Initially most work was done with pyrroles as at the time it was thought that they produced significantly more conducting polymers than thiophenes. However, as more research has been done on polythiophenes this has been shown to be incorrect and therefore the emphasis of the work done herein was shifted to the more stable and easier to work with thiophenes.

SECTION II - EXPERIMENTAL4.3 Monomer Synthesis

The synthesis and analysis of the compounds 2,2' dipyrrylmethane and 2,2' dithienylmethane, which are used as monomers in subsequent studies, are detailed here.

4.3.1 2,2'Dipyrryl Ketone

The method of Johnson et al<sup>[38]</sup> was followed. For this method a Grignard Reagent (ethyl magnesium bromide) was required.

To a 2 litre three-necked flask containing 600ml of dried ether was added 30g of magnesium. A few crystals of iodine were added to activate the magnesium. Ethyl bromide (144g) was added dropwise with stirring. A reaction was seen to take place (bubbles of gas evolved; colour change). The central neck of the flask contained a condenser in which the ether refluxed.

To this solution was added freshly distilled pyrrole(79.5g). The mixture was then heated under reflux for 2 hours, cooled to room temperature and then added dropwise with stirring to a solution of phosgene in toluene (500ml; 12.5%w/v) at room temperature. The mixture was stirred overnight then poured on ice(1000g). This was

left to stand for 2-3 hours. The resulting slurry was filtered and the magnesium salts were washed with ether. The organic layer was separated and the aqueous layer extracted with ether (4x100ml). The combined etherial washes and extracts were concentrated and the resulting oil/toluene mixture was then made alkaline with 5M ammonium hydroxide. Water (200ml) was added and the toluene azeotrope was vacuum distilled (30-40<sup>o</sup>C). This left a tar which was taken up in some chloroform, then steam distilled to remove unchanged pyrrole.

The resulting gum was packed on a column (95x4.2 cm) of silica gel (M60) and eluted with a light petroleum-ethyl acetate gradient. 9.97g of dipyrrol-2-yl ketone was obtained. Yield = 10.6% (c.f. 21.4%<sup>[38]</sup>).

#### Analysis

n.m.r. (CDCl<sub>3</sub>/TFA): 7.36(m), 6.48(m).

i.r. (nujol): 1560, 1400 cm<sup>-1</sup>. (only tiny band at 1700 cm<sup>-1</sup>.)

This is consistent with previous reports<sup>[38]</sup>.

#### 4.3.2 2,2'-Dipyrrylmethane

The method of Chong et al<sup>[39]</sup>, whereby the 2,2'-dipyrrylketone is reduced, was closely followed. Immediately prior to use 2,2'-dipyrrylketone was recrystallised from ethanol (99%). The method of Chong et al was followed with the following exceptions:

1.8g of 2,2'-dipyrrylketone was used.

6.5g of fresh sodium borohydride was used.

The mixture was refluxed for a further 2.75 hours (white solid formed).

Extracted with 5x30 ml ether.

The weight of 2,2'-dipyrrylmethane (white, crystalline solid) obtained was 0.750g. Yield = 40.4%.

Analysis

m.pt. : 69-71°C (72-73°C<sup>[38]</sup>)

n.m.r.(CDCl<sub>3</sub>) : 6.625(2 pyrrolic H), 6.05(4 pyrrolic H), 3.95(s, -CH<sub>2</sub>-) This is in good agreement with previous results for this product.

4.3.3 Synthesis of 2,2'-Dithienylmethane

The method of Goldfarb and Danyushevsky<sup>[40]</sup> was used here. The thiophene (Hopkin and Williams) was vacuum distilled prior to use. 41ml of hydrochloric acid (Hopkin and Williams sp.gr. 1.18) was cooled to -10°C and stirred while 54g of anhydrous zinc chloride (Hopkin and Williams) was added in portions. When the zinc chloride had dissolved, 50.4g of thiophene was added and the mixture was stirred while the temperature was in the range -8 to 0°C. 37.5g of formalin (Aldrich) was added dropwise over a period of 1.5 hours. Stirring was continued at this temperature for a further hour. After being shaken with 75ml of water, the reaction mixture was extracted extensively with ether. The brown/red solid which formed was also extracted thoroughly with ether. The combined extracts were washed with water (100ml), saturated sodium bicarbonate solution(100ml) and again with water (100ml). It was then dried over magnesium sulphate, the solvent removed under reduced pressure and the yellow residue vacuum distilled (14mm) giving a clear liquid product in the

temperature range 144-150°C. This liquid was tested for purity using TLC (in ethanol). Only one spot was observed under u.v. light indicating reasonable purity. The product was stored in a refrigerator and later examination revealed that a white, crystalline solid had formed.

#### Analysis

Yield = 8.1g (15.0%)

m.pt. = 42-43°C

microanalysis: (theory) C, 60.00; H, 4.44

(found) C, 59.86; H, 4.60

n.m.r.(CDCl<sub>3</sub>/TMS) : 4.35(2H), 6.85(4H), 7.13(2H).

The m.pt., microanalysis and n.m.r. are consistent with the expected product, MDT. The low yield is due to the temperature of the reaction mixture rising above 0°C for a few minutes. This results in the formation of the red/brown solid (possibly polymer) rather than the desired product.

#### 4.4 Chemical Polymerisation of 2,2'-Diarenemethane Monomers

Polymerisation of the monomers whose synthesis is described previously is the subject of this section. The methods mentioned earlier for the formation of conducting polymer powders<sup>[19]</sup> and films<sup>[20]</sup> were used here. These methods involved either mixing aqueous solutions of monomer and Fe<sup>III</sup> salt<sup>[19]</sup> or bringing an aqueous Fe<sup>III</sup> salt into contact with the monomer in an organic solvent<sup>[20]</sup>

such as toluene.

The powder-forming method was first tested using pyrrole as the monomer. Solutions of 0.6M pyrrole and 0.7M  $\text{FeCl}_3$  in distilled water were made. 10ml of each of these solutions were cooled to  $0^\circ\text{C}$ , mixed and stirred for 30 minutes, during which time the temperature was maintained at  $0^\circ\text{C}$ . This resulted in the rapid formation of a black precipitate. This precipitate was then filtered, washed with ethanol and dried overnight in a vacuum oven. The product was not analysed, but was almost certainly PPy of the type  $[\text{Py}, (\text{FeCl}_3)_{0.3}]_x$ . A pressed pellet of this material had a conductivity of 1.64 S/cm (4-point probe).

Interfacial contact between a 30% w/v  $\text{FeCl}_3$  aqueous solution and a 10% pyrrole solution in toluene produced a free-standing, thin, film after the solutions had been in contact for four hours. The film was black in colour and had a conductivity of 0.06 S/cm (4-point probe). After confirming the validity of this method, it was then used in an attempt to polymerise 2,2'-dipyrrylmethane.

As before a 30% w/v solution of  $\text{FeCl}_3$  was made. Now a 0.05M solution of 2,2'-dipyrrylmethane (made as previously) in toluene was prepared. After four hours a very thin film had formed. This film was removed and washed in distilled water, then acetone. The film was then pumped in a vacuum oven at room temperature for 16 hours. This metallic green/black film was treated as above. An attempt was made to obtain an i.r. spectrum of the film, but the quality of the spectrum obtained was not very good. The film was too small and thin

for conductivity measurements.

The method was next tried using 2,2'dithienylmethane,DTM as the monomer. DTM was found to be insoluble in both water and ethanol/water mixtures, therefore acetonitrile (1% water) was used as the solvent and a 0.2M solution was made. This solution was then mixed with the 0.7M  $\text{FeCl}_3$  as above. The organic phase was initially colourless, but after 15 minutes became orange. However after leaving overnight, no further colour change was observed, nor was any precipitate formed.

#### 4.5 The Reaction Between Pyrrole and Formaldehyde

The work detailed in this section and all following sections is concerned with the direct synthesis of the methane polymers or methine polymers discussed previously. Here poly(2-pyrrolylmethane) is the desired polymer.

It should be noted at this point that the reaction between pyrrole and formaldehyde can be violent if the reaction temperature is not regulated. Initial experiments involving this reaction were performed as follows.

Distilled pyrrole [Aldrich] was put in a 500ml three-necked flask with nitrogen flowing through the flask. Formalin [Hopkin and Williams or Aldrich] was added slowly with stirring. The mixture was stirred for 1-2 hours and then allowed to stand for 2-4 hours. Initial experiments were performed with a 1:1 ratio of pyrrole to

formaldehyde. These initial experiments tended to result in dark red/black, intractable masses being formed. Therefore modifications to this procedure had to be made.

Experiment A As the reaction mixture took 15 minutes to turn yellow in colour and a further 10 minutes to go red; this being an indication of how the reaction is proceeding, it was thought safe to add the formalin in one batch. The reaction mixture was stirred for two hours after the reactants were mixed, then left to stand for two hours without mixing. During all this time the reaction was cooled in ice/water. The ratio of pyrrole to formaldehyde was 1:2. The dark red product was filtered, washed with water, placed on filter paper and dried in the vacuum oven for 40 hours. On removal the product was found to be a red/brown, sticky, gum. This suggests the product may have a low molecular weight.

#### Analysis

i.r.(film): 3700-3040s, 2950s, 2890s, 1695w, 1635w, 1425m, 1390m, 1285m, 1150-900s, 770m  $\text{cm}^{-1}$ .

n.m.r.(acetone): 3.0s, 3.3d, 4.1s, 4.5-4.9m, 5.0-5.5s, 5.68s, 6.0s.

microanalysis: (theoretical) C,75.92; H,6.37; N,17.71

(found) C,51.83; H,6.52; N,6.41

The i.r. spectrum shows very little carbonyl from the formaldehyde ( $1695 \text{ cm}^{-1}$ ) and the band at  $1635 \text{ cm}^{-1}$  can be assigned to N-H(deformation). The microanalysis shows the product's composition to be quite different from that of the desired polymer as the amounts of carbon and nitrogen are much lower than expected, presumably due to the presence of oxygen.

Experiment B

Experimental details were as for A except :

- i) Stirred for 6.5 hours and left unstirred for 2.5 hours.
- ii) Temperature held between 5°C and 15°C throughout.
- iii) The product was filtered as before. However an attempt to wash with water the orange/red gum, similar to that in Experiment A, yielded up a pink solid. This solid was washed with distilled water and dried overnight on filter paper in a vacuum oven, at room temperature, containing phosphorus pentoxide.

Analysis

m.pt. > 280°C

microanalysis : (found) C, 62.30; H, 6.69; N, 10.16

i.r.(nujol) : 3600-3100m, 2700m, 1710w, 1505w, 1305m, 1280m, 1020m, 1005m, 770w, 720w  $\text{cm}^{-1}$ .

Although the microanalysis is far from the theoretical percentages and the product appeared to be very dry, there may be water present. In order to eliminate this possibility a sample was heated in a vacuum oven at 106-108°C for 23 hours. Analysis was then repeated.

microanalysis : (found) C, 65.85; H, 6.07; N, 12.57

i.r.(nujol) : identical except for the appearance of a very small band at 1610  $\text{cm}^{-1}$  and the intensities of the bands at 770 and 720  $\text{cm}^{-1}$  were reversed.

Useful n.m.r. spectra could not be obtained due to solubility problems with these products. The above results would suggest that although a small amount of water was present, an inexplicably high percentage of oxygen (presumably) was in the sample in some way.

#### 4.5.1 Long Term Polymerisation

118ml of formalin was added in one batch to 13ml of distilled pyrrole[Aldrich] in a 500ml three-necked flask with a flow of nitrogen through the flask. The contents of the flask were stirred and cooled for the first six hours. Samples were taken from the reaction mixture after the following time intervals: 2, 6 and 26 hours, 3, 7 and 22 days.

Most of these samples produced two fractions; one soluble in acetone and the other removed from water by centrifuging. The solid obtained by the latter method was dried over  $P_2O_5$  for at least 24 hours. The acetone solutions were dried with  $MgSO_4$ , filtered and the acetone removed under reduced pressure. The resulting solid was pumped in the vacuum oven at room temperature for at least 16 hours.

The sample obtained after 22 days still showed carbonyl absorption in its i.r. spectrum. This suggests that the desired polymer cannot have been formed. This may be due to pyrrole groups in the polymer which have an aldehyde group at the 2 position with the polymer chain attached at the 3 and 5 positions. Once more n.m.r.

analysis proved of little use.

Thermal analysis of these samples was performed using a Perkin Elmer DSC1, Differential Scanning Calorimeter. Exothermic peaks in the region 145-165°C were observed as was the case for samples from the initial experiments. This was suggested to be due to decomposition of the sample.

#### 4.5.2 Polymerisation under Oxygen Atmosphere

To 59ml of formalin [Aldrich] in a 100ml three-necked flask was added 6.5ml of distilled pyrrole [Aldrich]. Oxygen was bubbled through the reaction mixture for 50 minutes. The flask was cooled in ice/water and allowed to stand for 18 hours under an oxygen atmosphere.

This solution was filtered. The filtrate obtained was centrifuged and the solid obtained left in a dessicator for two days with P<sub>2</sub>O<sub>5</sub>. The filtrant was washed with acetone, the acetone decanted off and removed under reduced pressure to leave a red film. Both these solids were pumped in the vacuum oven for at least 16 hours at room temperature. DSC analysis of these samples showed consistent decomposition peaks at 146-152°C (irreversible). Carbonyl absorption was seen in the i.r. spectra.

The remaining solid in the reaction flask was left in acetone for one week. The acetone was removed under reduced pressure and the solid stored in a dessicator. This solid eventually turned black. The i.r. spectrum of this material looked more promising in that the only peak near the carbonyl region was at  $1595\text{ cm}^{-1}$  which can be assigned to N-H deformation. Therefore the conductivity of this material was tested.

#### 4.5.3 Chemical Doping

Iodine (Fisons) doping was performed by placing the sample to be doped in a small dessicator which contained some solid iodine. The dessicator was then heated to about  $40^{\circ}\text{C}$  in a large oven. The sample was removed periodically and its conductivity measured after the sample surface had been wiped carefully with a tissue to remove any iodine from the surface.

A pellet of material from 4.5.2. was pressed at 5 tons pressure for 2 minutes in a 13mm Specac die. The pressure was released and the die was heated to  $100\text{-}105^{\circ}\text{C}$  for 30 minutes (under vacuum). Two tons of pressure was applied for 2 minutes and the die was then cooled. This produced a good quality pellet, the initial conductivity of which was  $7 \times 10^{-11}\text{ S/cm}$  (using Wayne Kerr bridge method in Chapter 2). However attempting to dope the sample in an iodine atmosphere produced no significant improvement in conductivity. The conductivity of other samples from the above syntheses were tested. Initial conductivities

in the same region as above ( $10^{-10}$  -  $10^{-12}$  S/cm) were obtained, with no significant increase in conductivity on doping.

#### 4.6 Self-condensation of Pyrrole-2-carboxaldehyde

The hydrogen chloride gas used in these experiments was produced using a hydrogen chloride generator in which concentrated hydrochloric acid and concentrated sulphuric acid were dropped at a steady rate into a reaction vessel. This produced hydrogen chloride gas. The outlet for the gas is positioned in such a way that the gas is dried by the sulphuric acid on its way to the reaction vessel. The ether used was dried, distilled and then stored over sodium wire. The pyrrole-2-carboxaldehyde was used as supplied by Aldrich.

##### Experiment A

1g of pyrrole-2-carboxaldehyde was dissolved in ether (60ml). Hydrogen chloride gas was passed through the solution for 25 minutes, while the flask was cooled in ice/water. The flask was then allowed to stand in the refrigerator for 3 hours. After which time the solution was yellow and a pink crystalline solid had formed. The solution was poured into another flask and left in the refrigerator in the hope of obtaining more product. The pink crystalline solid was then washed with hexane (Fisons SLR) [2x30ml] and left overnight in the vacuum oven at room temperature. A violet-coloured solid was obtained.

wt. of product = 0.603g

m.pt. =  $41-43^{\circ}\text{C}$  (m.pt. of pyrrole-2-carboxaldehyde =  $43-46^{\circ}\text{C}$ )

An i.r. spectrum confirmed that this 'product' was in fact the

starting material. After leaving the solution for 4 days 0.121g of black solid with a slightly metallic green lustre was obtained. On this occasion the i.r. spectrum had changed from the starting material. However there were still bands in the carbonyl region. The melting point was greater than 200°C.

#### Experiment B

0.5g of pyrrole-2-carboxaldehyde was dissolved in ether(30ml). Hydrogen chloride gas was bubbled through the solution for 10 minutes with no external cooling. The flask was then allowed to stand in the refrigerator for 5 days. After which time a black solid had formed. The solvent was removed under reduced pressure. Nearly all of the resulting solid was found to be soluble in acetone. This solution was decanted off and the solvent removed under reduced pressure.

#### Analysis

m.pt. >200°C

i.r.(nujol): 3150m, 3080m, 1640s, 1400m, 1335m, 1315w, 1140w, 1090w, 1050m, 865w, 755s  $\text{cm}^{-1}$ .

n.m.r.(DTFA): 4.075(s), 6.55-6.70(m), 7.525(s), 7.65(s), 9.05(s)

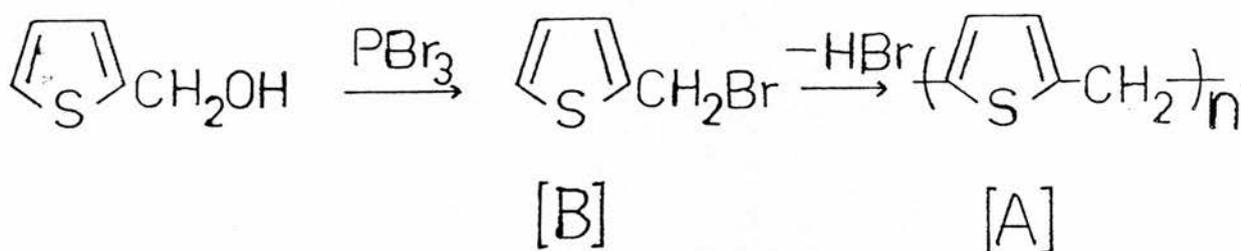
The i.r. spectrum shows only slight differences from the i.r. of pyrrole-2-carboxaldehyde. It indicated the presence of both N-H and C=O groups in the product obtained. In the n.m.r. spectrum, the peak at 9.05 can be assigned to the hydrogen of the aldehyde group. Peaks between 6.50 and 7.75 can be assigned to hydrogens on the pyrrole ring and the peak at 4.075 to a -CH= group. The ratio of the peak integrations is 4:1 for peaks at 9.05 and 4.075. This information suggested that some methine bridge groups had been formed, however

there were still many aldehyde groups present. Either the reaction proceeded via 3 or 4 and 5 positions, leaving unreacted aldehyde groups, or unreacted pyrrole-2-carboxaldehyde is present. The latter is less likely as the spectral shifts are quite different for the monomer and product. Incomplete solubility in DTFA is a further complication.

A pellet was pressed at room temperature in a 13 mm die. This pellet had a conductivity of  $8 \times 10^{-9}$  S/cm. However attempting to dope the pellet in an iodine atmosphere produced no significant improvement in its conductivity.

#### 4.7 Poly(thienylmethane)

It is suspected that poly(thienylmethane), [PTM], had been made by the following method:



The thiophene-2-methylbromide [B] (made by the method of Braun et al.<sup>[41]</sup>) was observed to darken and self-polymerise with the evolution of HBr. Some material which was thought to have undergone the above reaction was provided by Dr R.A.Aitken. This material was analysed as detailed below.

#### 4.7.1 Conductivity

The polymer was ground to a fine powder. Approximately 0.5g of this powder was transferred to a 13 mm die. The evacuated die was then pressed at 10 tons for 10 minutes, the pressure released and the die heated to 150°C for one hour. Then 5 tons of pressure was applied for 10 minutes followed by cooling of the die. The pellet produced was then doped in iodine for three days. The conductivity of the pellet was measured before and after doping, by the Wayne Kerr bridge method (Chapter 2).

Conductivity before doping =  $5.58 \times 10^{-8}$  S/cm

Conductivity after doping =  $2.52 \times 10^{-5}$  S/cm

This procedure was then repeated with a mixture of 60%(by weight) PTM and 40% polypropylene. The disc produced was then doped for three hours.

Conductivity before doping =  $1.95 \times 10^{-9}$  S/cm

Conductivity after doping =  $2.49 \times 10^{-6}$  S/cm

#### 4.7.2 Analysis

Microanalysis : (theoretical) C, 62.46; H, 4.19

(found) C, 55.90; H, 4.13

i.r.(nujol) : 3500-3300m, 2720m, 1715w, 1615w, 1300m, 1150w, 1110-1070w, 1030w, 970w, 800w, 720w.

The percentage of carbon in the sample may be slightly low due to

bromine in the polymer or hydrogen bromide being trapped within the solid.

#### 4.8 The Reaction between Thiophene and Benzaldehyde

The thiophene [Fisons] used in these experiments was distilled under vacuum and stored under dry nitrogen before use. Ether was dried by refluxing with  $P_2O_5$  [Aldrich] followed by distillation and then refluxing with  $LiAlH_4$  [Aldrich] followed by distillation. The solvent was then stored under dry nitrogen.

Experiment 1 Thiophene (8.4g, 0.1 mole) in 40 mls of dry ether was degassed with dry nitrogen and mechanically stirred. Benzaldehyde [Aldrich] (10.6g, 0.1 mole) was added over a period of 10 minutes with the temperature held between 0 and  $+3^{\circ}C$ . 1ml conc.  $H_2SO_4$  was added, the temperature was maintained for a further 10 minutes and the solution was then allowed to warm to room temperature. The solution was then refluxed at  $48^{\circ}C$  for 3 hours, after which it was dark green/brown in colour and opaque. The ether was removed under reduced pressure with slight heating (this should also have removed unreacted thiophene). The reaction solution was kept under nitrogen throughout. The residue was then dropped into about 800-1000 mls of methanol. The methanol went orange in colour and a very fine orange precipitate was formed. This solid was filtered and washed with methanol. A small amount of the residue was also precipitated in cyclohexane. The resulting product, in both cases, was found to be soluble in chloroform and gave a dark red solid on removal of the

solvent.

Total weight of product = 0.342g. If the product is the expected polymer this is a yield of 2.00%. This product will be referred to as BT1.

Experiment 2 The experiment was repeated with the following changes: 5.3g (0.05 moles) benzaldehyde was added and the reflux was at 45°C for 3 hours. This gave a yellow transparent solution. As this was not very different from the starting solution a further 0.05 moles of benzaldehyde was added and the solution refluxed for a further 2 hours at 50°C. The ether (and thiophene probably) was removed under reduced pressure with some heating. The solution darkened and became more viscous. Heating under reduced pressure was continued for a further 90 minutes and resulted in a darker, more viscous, almost black solution. This residue was then stored under nitrogen in a refrigerator for 5 days.

Approximately a quarter of the residue was purified as before in methanol. This product will be called BT2M. The remainder was dropped into a 30:70 methanol:water mixture which was stirred. A thin brown/red film formed on the surface. This film was removed periodically on filter paper, dried in a vacuum oven and the product dissolved in chloroform. The chloroform was dried over  $\text{MgSO}_4$ , filtered and the solvent removed. This product will be called BT2WM.

Some dark material stuck to the stirrer bar and beaker in which precipitation took place. This material was dissolved in chloroform and treated as above. Product called BT2Res.

Total weight of product = 0.270g

#### 4.8.1 Analysis

The products of the above reactions were analysed by various methods and the results presented below.

Melting point Determination of melting point was attempted using sample BT1. Between 70 and 90°C the product appeared to 'flow' or change shape, but it did not melt.

Infrared Spectra The infrared spectra of various products were recorded as thin films, cast from chloroform onto KBr discs, on a Perkin-Elmer 1330 Infrared Spectrophotometer. The wavenumbers for each peak are shown below:

1 (BT2Res.) 3050, 3020, 2910, 2840, 1685, 1580, 1480, 1435,  
1380-1230, 1060, 1015, 785, 740, 685 cm<sup>-1</sup>.

2 (BT1) 3040, 3000, 2900, 2830, 1680, 1590, 1480, 1440,  
740, 690, 600(w) cm<sup>-1</sup>.

3 (BT2WM) 3040, 3010, 2900, 2840, 1590, 1485, 1445, 1255,

1070, 1020, 795, 745, 690  $\text{cm}^{-1}$ .

All three spectra are very similar. The peaks in favour of the proposed structure are : 600(w) [not present in 1 or 3 as they stopped at  $625 \text{ cm}^{-1}$ ] - (C-S str) ; 690 and 740 - (mono substituted phenyl). The peaks against the proposed structure are : 1700 (C=O str) or 1200-1300 - (C-O str) and 790 - (meta disubstituted phenyl). Also rather more strong aliphatic bands in 2800-3000 region than would be expected for a -CH- group (confirmed by n.m.r. ; see below).

Nuclear Magnetic Resonance [n.m.r.] Spectra The results are shown below. Acetone was used as solvent, hence the peak at  $\delta 2.0$ .

Spectrum 4 (BT1)

peak ( $\delta$ )	0.90	1.30	2.50-3.50	7.30	7.95	10.05
integration	10	25	14	61	8	1

Spectrum 5 (BT2WM)

peak ( $\delta$ )	0.90	1.30	2.75	7.37	8.05	10.10
integration	12	27	7	40	3	0.5

Spectrum 6 (BT2Res.)

peak ( $\delta$ )	0.90	1.30	2.80	3.25	7.30	7.90	10.05
integration	18	32	14	1	86	8	2

As can be seen all three spectra are very similar. The first interesting point is that the amount of aldehyde due to benzaldehyde is very small for all samples ( $\delta 10$  region). Both thiophene and phenyl protons occur in the region  $\delta 7$ - $\delta 8$ , where the greatest amount

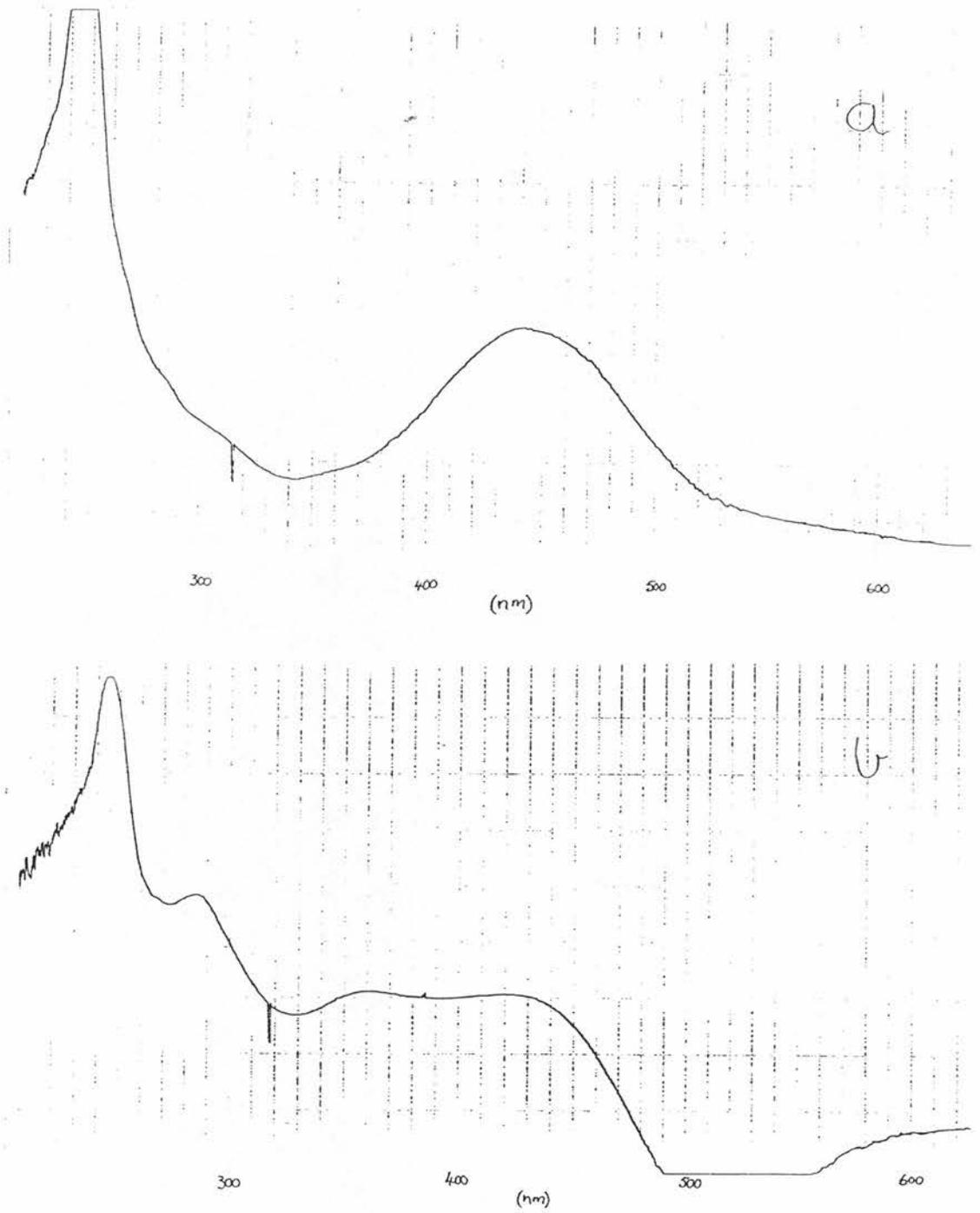
of protons in each sample are located. The peak at about  $\delta$  2.8 could be due to Ph-CHRR' [42] which corresponds to the expected product. The ratio of the integrations  $\delta$  2.8:  $\delta$  7-8 is 1:6 which is also in agreement with this product. However the peaks at  $\delta$  0.90 and  $\delta$  1.30 due to groups  $-\text{CH}_3$  and  $-\text{CH}_2-$  should not be present if the desired product has been obtained. If these were end groups then, according to the integration values, virtually no polymerisation will have taken place.

Differential Scanning Calorimetry [DSC] In view of the behaviour observed when a melting point was attempted, the thermal behaviour of the samples was further investigated using DSC.

DSC's were recorded on two different machines; a Perkin-Elmer DSC1 and a Mettler system consisting of a Mettler FP80 Processor and a Mettler FP85 TA cell. The sample BT2Res. was tested from 30 to 250°C. The system was allowed to cool to room temperature and the process repeated.

Although both scans had poor baselines, the heating cycle is not reproducible and it was strongly suspected that the sample decomposed to some extent. This was confirmed on opening the sample pan as there was a strong smell of thiophene which had not been there previously.

FIGURE 4.5



Ultraviolet/visible [uv/vis] Spectra UV/vis spectra were recorded on a Pye Unicam SP8-150 uv/vis spectrophotometer. The solvent used was chloroform [Fisons, analar] and solutions were very dilute. Chloroform was also used in the reference cell. Figure 4.5a shows a typical spectrum (BT2Res.). A broad band is seen at  $440 \pm 70$  nm which is typical of a conjugated polyene (11 or 12 double bonds in conjugation)<sup>[42]</sup>. It is also typical of spectra of polythiophene or polypyrrole<sup>[16]</sup>. A small amount of iodine[Fisons] in chloroform was added to both sample and reference. The result is shown in Figure 4.5b.

Clearly there has been a reaction between the sample and the iodine. The intensity of the band at 440nm has been reduced and bands at 285 and 360nm plus a broad band from 600-800nm emerged. (The spectrophotometer limit is about 800nm.) This type of behaviour is consistent with that of doped conducting polymers<sup>[16]</sup>. However thiophenes are also reactive to halogens particularly at the 2 position, therefore a reaction of this kind should not be discounted.

Microanalysis The results of microanalysis carried out in the department are as follows (the theoretical values refer to the predicted structure):

	<u>C</u>	<u>H</u>	<u>S</u>
BT1a	75.74	5.08	14.72
BT1b	75.65	5.75	23.92
BT2M	65.00	5.64	13.71
BT2WM	77.10	6.49	19.30
BT2Res.	79.66	6.08	12.09
<hr/>			
Theoretical	76.70	4.68	18.61

The estimation of sulphur is less accurate than the carbon and hydrogen by at least 2-3%. This can be clearly seen in BT1a and BT1b, which are the same material. Consequently it is rather difficult to draw conclusions from these results. However with one exception (BT2M) there appears to be very little oxygen present as was suggested by the nmr's.

There are several combinations of thiophene, phenyl and alkyl/allyl groups which could account for these results. The most likely explanation is a mixture of 2,3, or 4 ringed oligomers being present. Some of this material was used for further studies (Chapter 5).

Conductivity Conductivity measurements were made using the four-point probe method previously described. A 13mm pellet was pressed at 6 tons pressure for 10 minutes (under vacuum). This

produced a good quality pellet the conductivity,  $\sigma$ , of which was recorded.

The pellet was then exposed to iodine vapour in a vacuum dessicator at  $40^{\circ}\text{C}$  for 5 minutes. The conductivity was then recorded. In both cases  $\sigma < 10^{-6}\text{S/cm}$  (using 4-point method). Conductivity measurement using the resistance bridge indicated  $\sigma < 10^{-10}\text{S/cm}$ .

#### 4.9 Conclusions

The monomers 2,2' dipyrrolylmethane, DPM and 2,2'dithienylmethane, DTM were successfully synthesised and used in electrochemical studies (see later). Chemical polymerisation of these monomers proved difficult. DTM did not react and DPM could only produce very thin poor quality films.

Despite extensive experimental efforts, synthesis of poly(pyrrolemethine) by the reaction of pyrrole with formaldehyde proved difficult. The materials produced were often insoluble making them difficult to characterise. Materials which were characterised, invariably contained carbonyl groups and produced complex spectra suggesting mixtures or highly irregular polymers. Most importantly, even the products which did not contain carbonyl groups had low intrinsic conductivities which could not be improved on doping.

The acid-catalysed self-condensation of pyrrole-2-carboxaldehyde produced a poorly soluble, high melting point material which contained a high amount of carbonyl groups despite the presence of some -CH= groups. Again this material exhibited a low intrinsic conductivity on which doping had no effect.

The self-condensation of 2-bromomethylthiophene to give poly(thienylmethane) would appear to have been much more successful. The 3 orders of magnitude increase in conductivity, on doping with iodine, to a value of  $2.5 \times 10^{-5}$  S/cm, is in keeping with results published for other poly(arenemethines)<sup>[33,34]</sup>. In fact, this is almost as good as the highest value published for these materials ( $1 \times 10^{-4}$  S/cm). Many of these polymers were reported to have low initial and doped conductivities ( $10^{-11}$  -  $10^{-7}$  S/cm). The product produced here must be poly(thienylmethine) or contain a large amount of conjugated poly(thienylmethine) segments for the reported conductivity to be achieved. The initial polymer may be slightly doped with bromine, hence its rather high "undoped" conductivity (for this class of polymer). There are a great many further experiments which could be done on this system, such as : more detailed doping measurements, undoping and attempting to improve the physical properties of the polymer (such as solubility). Also several analogous polymers may be made this way.

The reaction between thiophene and benzaldehyde produced (a mixture of) oligomers. The use of a different solvent, which would allow the reaction to take place at higher temperatures, may result in polymer formation. Also a longer reaction time may be useful to this end. For the products obtained to be successfully separated and analysed, a much larger scale preparation would be necessary. Due to insufficient time this was not possible, but would be an area of future work to be considered especially in conjunction with the changes suggested above.

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CHAPTER 5ELECTROCHEMISTRYSECTION I - INTRODUCTION

This chapter is concerned with attempts to electrochemically synthesise conducting polymers and with the study of their electroactivity. Electrochemical polymerisation has in the past been associated with processes where the bulk of polymerisation takes place away from the electrode surface<sup>[1]</sup>. Electropolymerisation of pyrrole onto a platinum electrode was first reported by Dall'Olio et al<sup>[2]</sup> and investigated further by Diaz et al<sup>[3]</sup> in the late 1970's when interest in conducting polymers was beginning. Since then interest in the field has grown enormously.

Electrochemical synthesis is advantageous in that electroactive, free-standing films of variable thicknesses may be grown in their conductive form on electrodes. As many of the projected uses of these materials (see 5.7) involve films this is desirable and also facilitates electrochemical analysis. Also impurities and structural defects often found in chemically synthesised polymers tend to be absent. The electrochemistry of conducting polymers has been reviewed in several of the articles contained in "The Handbook of Conducting Polymers"<sup>[4-6]</sup>, in the publications on several conferences<sup>[7-9]</sup>, and in several reviews<sup>[10-13]</sup>.

## 5.1 Electrochemical Measuring Techniques

Electrochemical measuring techniques are fundamental tools in the study of electropolymerised conducting polymers. By these methods information may be obtained concerning : (1) the formation of polymer films and (2) the electroactivity of these films.

The theoretical and practical uses of these techniques have been well documented<sup>[14,15]</sup>. These techniques are many and varied, but with regard to conducting polymers, two are of importance : (1) potential or current step and (2) potential sweep.

### 5.1.1 Potential or Current Step

Either of these techniques may be used (and have been) to produce conducting polymers. In the current step technique, a constant current is applied through the cell, between the working and the counter electrodes and causes electroactive species in solution to react at the working electrode, WE. The technique requires relatively simple equipment and the total charge passed,  $q$ , during electrolysis may be easily obtained using Faraday's Law :

$$q = \int i \cdot dt = mnF \quad \text{Eqn 5.1}$$

where  $t$  is time of reaction,  $i$  the current,  $n$  the number of electrons/molecule involved in the electrode reaction,  $m$  the number of moles of starting material converted to product and  $F$  is Faraday's

constant. Throughout this chapter,  $i$  = current and  $I$  = current density. The voltage is generally monitored during the reaction, but a disadvantage of the technique is that the voltage may move outside the stability range of the solvent or drop to a level below which reaction proceeds.

In the potential step method a constant voltage is applied across the cell and the current monitored during the reaction. The advantage here is that the voltage is maintained at a level at which the reaction proceeds within the solvent's stability range. The current, however, may vary and must be integrated, either by the hardware involved or mathematically from the data, to obtain the charge passed. The main disadvantages are that an infinitely large current should pass through the cell initially meaning that some time may be required for accurate readings to be made. Also the potentiostat takes a finite time to reach the applied potential and the current measuring system takes time to measure the current.

The potential step method may also be used to determine various details concerning kinetics, mechanisms, adsorption and phase formation by recording the  $I-t$  (current density against time) transients. This type of experiment has only recently been applied to conducting polymers<sup>[16-18]</sup> but has produced some interesting results. In chronoamperometry the problem of charging currents due to electrochemical double-layer capacitance becomes more apparent. These double-layer charging currents are additional to the Faradaic current flowing and are revealed as a sharp spike in the current at short times which masks the Faradaic current.

### 5.1.2 Potential Sweep

Linear potential sweep chronoamperometry is similar to the potential step method except that the applied potential is varied linearly with time, (ie. a voltage ramp). This technique is useful for initial electrochemical studies of new systems and produces information on complex electrode reactions and kinetic parameters. It has been used extensively in conducting polymer studies and can provide information about both film formation and the electroactivity of film when formed. The number of electrons,  $n$ , involved in the reaction may be obtained from the Nicholson and Shain [19] treatment for a totally irreversible reaction. Details of the application of this to conducting polymers are in Section 5.3 and 5.4.

## 5.2 Synthesis Conditions and Materials

Some indication of the variety of monomers, solvents, electrolytes, electrodes used and other synthetic conditions will be given here. A single or two-compartment, three-electrode cell is generally used for electrochemical synthesis.

5.2.1 Monomers

A wide variety of organic molecules have been used to prepare conducting films electrochemically. These include both hetrocyclic and polycyclic benzenoid and nonbenzenoid hydrocarbons. Some of these molecules are listed in Table 5.1 along with some of their electrochemical data.

Table 5.1

<u>Compound</u>	<u>Monomer, Epa (V)</u>	<u>n value</u>	<u><math>\sigma</math> (S/cm)</u>	<u>Ref.</u>
Pyrrole	+1.2	2.2-2.4	200	6
Thiophene	+1.65	2.7	190	6,13,20
2,2'Bithiophene	+1.31	2.22	0.1	13,4
3-Me thiophene	+1.35	2.4	450	6,13,20
3,4-DiMe thiophene	+1.25	-	10-50	6
Carbazole	+1.30	2.5	0.001	13
Azulene	+0.96	2.1	0.01-1	13,21
Benzene	-	-	100	22
Isothianaphthene	-	-	50	23
Aniline	-	2.6-2.7	100	12,24

These are some of the compounds which have been well studied. However many others have been studied, some quite recently. They include polyindole<sup>[13]</sup>, polypyrene<sup>[13]</sup>, poly(dithienothiophene)<sup>[25]</sup> and various poly(thienothiophenes)<sup>[26,27]</sup> and poly(thienopyrroles)<sup>[27]</sup>.

An important feature of these electrochemical polymerisation reactions is that they proceed with electrochemical stoichiometry, which is more akin to the electrodeposition reactions of metals than electropolymerisation. Cyclic voltammetric studies have revealed that these molecules electrooxidise irreversibly and that  $n$  values in the range between 2.0 and 3.0 are obtained. This apparent stoichiometry includes the stoichiometry for the polymer chain, which is 2.0 (for a polymer), plus a value between 0 and 1 which is associated with the accompanying electrooxidation of the polymer film. Elemental analysis gives values in the region 0.07 to 0.45<sup>[11]</sup>. This is consistent to some extent with the  $n$  values, but as the  $n$  values represent the total reaction at the electrode surface, secondary reactions such as dimerisation to form soluble products will cause discrepancies.

Compounds used for electropolymerisation should have relatively low oxidation potentials, so as not to lead to oxidative decomposition of the solvent and electrolyte. Further the aromatic compound should sustain electrophilic substitution reactions with the aromatic structure being preserved and the cation intermediates produced should have average stability which will favour the radical coupling reaction.

The monomer, solvent and electrolyte are generally purified before electrolysis and films may be formed either potentiostatically (controlled potential) or galvanostatically (controlled current), the current or potential respectively being monitored as the electrolysis proceeds. Cyclic voltammetry was recently suggested to be a good method

for film formation<sup>[28]</sup>. The thickness of the film depends on the charge passed and is therefore dependent on current density and time. Studies on the effect of current density<sup>[29]</sup> have shown that no deposition of polypyrrole (PP) takes place at current densities  $<1 \text{ uA/cm}^2$ , only PP powder is formed which falls to the bottom of the cell. Whereas high current densities  $>0.1 \text{ A/cm}^2$  lead to insulating films. Temperature is another factor which can affect the quality of the film produced (see Section 5.4).

As can be seen from Table 5.1, there is a large variation in the conductivity of the polymers produced from different monomers. Nevertheless substituents on the monomer can also greatly affect the conductivity and other properties of polymer films, Table 5.1(thiophenes). The conductivity and oxidation potentials of PP films are greatly affected by the presence of alkyl or aryl groups in the nitrogen or 3-positions of the monomer. This is suggested to be due to steric effects adversely affecting the coplanarity of the polymer chain<sup>[4]</sup>. The more dramatic effects were from N-substituted monomers.

Recent results on PT<sup>[20]</sup> have shown poly(3-methylthiophene) P3MT (510 S/cm) to have a greater conductivity than PT (190 S/cm). It was suggested that this is due to the greater amount of 2,5 linkages produced by P3MT, a situation which does not seem to be paralleled in PP. In general both electronic and steric effects seem to be important with regard to substituents.

### 5.2.2 Electrodes

The working electrode is an important consideration as films are produced by an oxidative process, therefore the electrode should not oxidise simultaneously with the monomer. Hence platinum or gold electrodes are often used. Indium-tin oxide coated conducting glass is commonly used in experiments where spectroscopy is also involved, while many other materials have been reported to be used<sup>[4]</sup>.

### 5.2.3 Solvents and Electrolytes

As was mentioned above, solvents and electrolytes must be purified, sometimes extensively, before use in the polymerisation. The voltage limits of particular combinations of solvent and electrolyte must also be taken into account as exceeding them may cause unwanted side reactions. The choice of solvent and electrolyte will also affect the reference electrode to be used<sup>[1,30]</sup>.

As radical cations are involved in the polymerisation reaction most studies have been performed in aprotic solvents, such as acetonitrile, which are poor nucleophiles. The quality of films produced in terms of conductivity and physical properties have been shown to vary greatly with solvent and co-solvents<sup>[4]</sup>. Water has been shown to be essential for polymerisation of pyrrole in acetonitrile (otherwise soluble oxidation products are formed)<sup>[31]</sup>, but polymerisation is inhibited at higher concentration which explains why the commonly used acetonitrile with 1% water ( $0.5 \text{ mol dm}^{-3}$ ) is the

optimum solvent. Several authors<sup>[32,33]</sup> have described the properties of PP prepared in aqueous electrolytes. However, water has been shown<sup>[16]</sup> to have a strongly adverse effect on the electrodeposition of PT and that non-conducting, passivating layers may be grown on the working electrode.

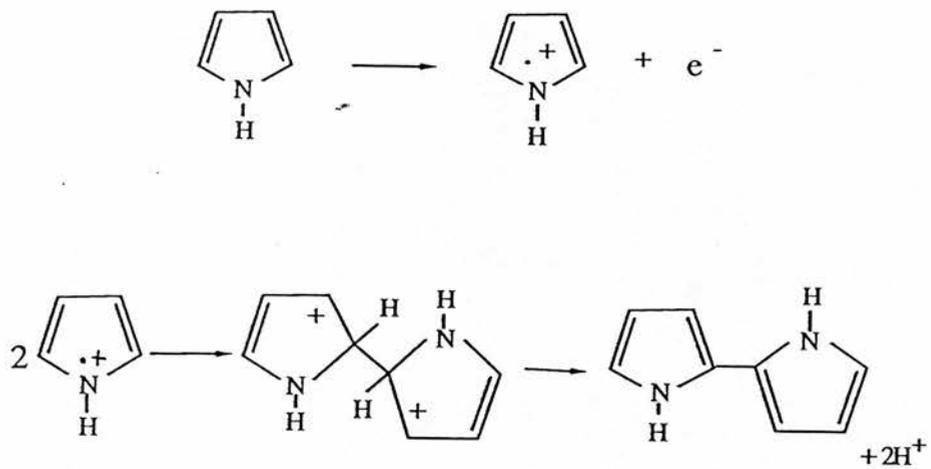
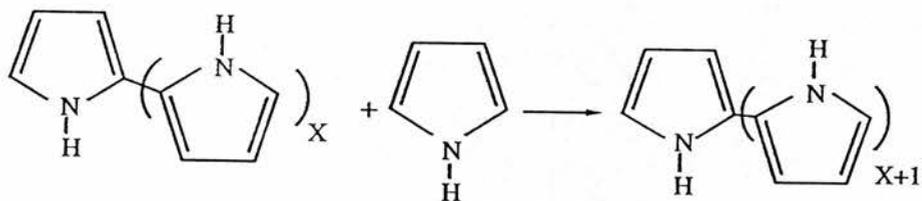
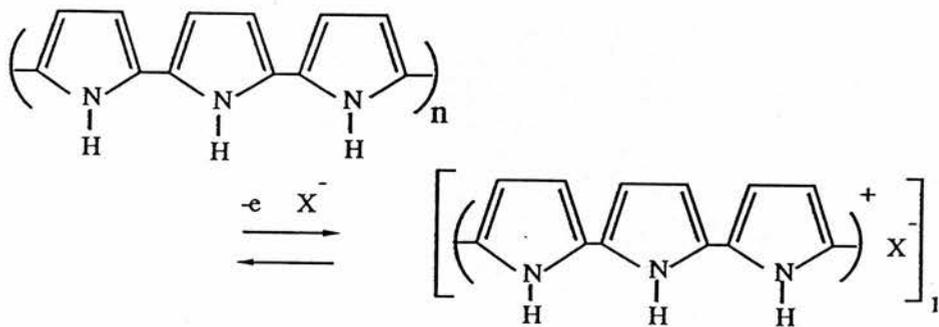
The counterion (dopant) from the electrolyte salt can also greatly affect the properties of the polymer film formed. Electropolymerised films contain about 10-35% (by weight) anion which is associated with the cationic charges on the polymer chain. The amount of anion is related to the oxidation level of the polymer and is characteristic of it<sup>[4]</sup>. A wide variety of poorly nucleophilic anions have been used to produce films with conductivities in the range  $10^{-2} - 10^{+2}$  S/cm. Although the level of oxidation is intrinsic to the polymer and independent of the anion used, the anion influences structural properties and the electroactivities of films. The electrolyte cation does not affect the produced film, although thought must be given to the reaction at the counter electrode. Tetraalkyl ammonium salts are frequently used. PP and PT, as with most other electrosynthesised conducting polymers, are anion doped.

### 5.3 Electrochemical Formation Mechanisms

Many reviews have included details of proposed film formation mechanisms and since their publication other articles on the subject have been written. Nevertheless the mechanism of film formation is still by no means certain, but a discussion reflecting current thinking will be provided here. PP and PT and their derivatives will be predominantly focussed on as most work has been done on these materials. Furthermore, their monomers are related to the materials studied in this thesis.

Taking the case of PP, the mechanism of polymer film formation was initially thought to follow the scheme in Figure 5.1. Depending on the stability of the radical cation produced, many reactions may occur, but for intermediate stability radical cations, dimerisation reactions or "electropolymerisation" of the type above is thought likely<sup>[13]</sup>. The reaction can be thought of as a cascade of ECE reactions,  $E(CE)_n$ <sup>[34]</sup>, where E is an electron transfer event and C is a chemical reaction.

Figure 5.1

PropagationRedox Reaction

The experimental evidence which supports this mechanism is as follows<sup>[13]</sup>: (1) the potential of the electrode must be sufficiently positive that pyrrole radical cations are produced for polymerisation to occur. (2) Cyclic voltammetry supports an E(CE)<sub>n</sub> process with radical cation coupling. (3) PP films grow linearly with time, implying that the radical coupling process is the rate-limiting step as opposed to diffusion of monomer from bulk. (4) Alpha-substituted pyrroles do not polymerise easily suggesting that monomer coupling takes place through the alpha positions<sup>[10]</sup>. (5) As was recently confirmed<sup>[18]</sup>, there is a zero order dependence on the initial concentration of pyrrole (as measured by chronoamperometry) at all potentials, but a first order dependence on electrolyte concentration at potentials higher than the polymerisation potential. This suggests that incorporation of the anion into the polymer film is the rate determining step. (6) The observation<sup>[5]</sup> that the pH of the solution increases during electropolymerisation suggests that protons are eliminated. Finally, (7) the number of electrons (2.25-2.33) consumed per pyrrole monomer suggests that two electrons are required for each pyrrole monomer coupling (excess being involved in oxidation of the monomer).

A problem with these conclusions is that they predict one-dimensional development, 1-D growth would lead to dendritic growth, contrary to the smooth films obtained. However, cyclic voltammograms<sup>[37]</sup> have recently shown crossovers typical of instantaneous nucleation, followed by 3D growth for PP similar to the

electrodeposition of metals. Cyclic voltammetry and potential step experiments on  $\text{PT}^{[16,17,36]}$  agree with this nucleation and 3D growth mechanism. The authors of these articles have pointed out that this implies an increase in the surface area available for electron transfer, which may be due to polymer chain-branching. It has also been suggested<sup>[36]</sup> that initially a monolayer is deposited possibly by adsorption of monomer. A similar suggestion was made in a study of bithiophene<sup>[18]</sup>.

A different hypothesis is that no monomer or radical cation is absorbed, but that the first step is a prepolymerisation in solution followed by precipitation of oligomers onto the electrode<sup>[37]</sup>. Obviously both these theories cannot be correct, therefore much work remains to be done on the subject. [Note : Polymers are obtained in their conducting state as the oxidation potentials of the polymers, oligomers and monomers generally increase in that order.]

#### 5.4 Electrochemical Properties

### 5.4.1 Conductivity

Previous sections have discussed how the conductivity of polymer films can be affected by monomer, solvent and electrolyte. The difference in conductivity between doped and undoped polymers is 8 to 10 orders of magnitude (or more). Conductivity increases with doping level, which may be limited by impurities or structural defects such as those in chemically prepared PT<sup>[38]</sup>. Different authors have reported differences in conductivity of about 100 for very similar materials, which may be attributed to differing synthesis conditions<sup>[6]</sup>. Poor interfibrillar contact may also affect conductivity adversely<sup>[6]</sup>.

The polymerisation temperature has been investigated<sup>[20,39]</sup> and found to have an important effect on conductivity. A study of the optimum conditions for electropolymerisation of P3MT suggested a polymerisation temperature range of -15 to +5°C to be best. The reason for lower conductivity at higher polymerisation temperatures in PT was suggested to be due to an increased amount of non-2,5 linkages<sup>[39]</sup>.

PP shows two<sup>[40]</sup> types of temperature dependence, a small dependence (with  $\log \sigma$  vs  $T^{-1/4}$  fairly linear) for high conductivity  $\text{BF}_4^-$ ,  $\text{BF}_6^-$  and  $\text{AsF}_6^-$  doped sample and a greater dependence for lower conductivity samples. Similar behaviour has been reported for PT<sup>[43]</sup>. Due to the rather thin films of polymer it is difficult to determine whether the conductivity is due to surface or bulk effects. In both PP<sup>[29]</sup> and PT<sup>[41]</sup> there has been reported to be a large

difference in conductivity parallel and perpendicular to the film surface; the former being at least  $10^3$  greater.

#### 5.4.2 Stability

Many conducting polymers, like polyacetylene and poly(paraphenylene) show poor stability in air or moisture<sup>[6]</sup>. Stability studies on  $\text{P3MT-SO}_3\text{CF}_3^-$ <sup>[6]</sup> (doped and undoped) have shown it to be stable in ambient air for long periods (in contrast to undoped PP). Stability in PT and derivatives would appear to be related to dopant anion, as early work using  $\text{ClO}_4^-$  and  $\text{BF}_4^-$  was reported to have produced oxidized PT that was unstable to air or protic solvents<sup>[42]</sup>. The above work on  $\text{P3MT-SO}_3\text{CF}_3^-$  and more recent studies<sup>[42]</sup> on  $\text{B}_{10}\text{Cl}_{10}^{2-}$  (from  $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ ) doped PT have shown much better stabilities. There are two factors which govern the stability : chemical reactivity and the oxidation and reduction potentials of the polymers. PP in its undoped state is close to the reduction potential of oxygen and is slowly oxidised to its stable conducting state by oxygen. Electrochemical stability is also important (see below).

### 5.4.3 Electroactivity

Electroactivity, where films can be switched between the neutral, nonconducting state and the oxidized, conducting state, is one of the most interesting and potentially useful properties of conducting polymers. These reductions and oxidations may be performed chemically, but here only electrochemical processes will be looked at. Restrictions on the solvent and electrolyte are similar to those involved in electrosynthesis, although the switching reaction is less sensitive to the nucleophilicity of the cations involved. Hence despite thiophenes' sensitivity to water in the polymerisation reaction, PT may be doped and undoped in aqueous solution<sup>[43]</sup>. Figure 5.1 shows the redox process involved. It has been shown<sup>[10]</sup> that the charge involved in this switching process corresponds to the anion concentration as determined analytically.

Switching in PP appears to be electrochemically reversible taking about 28 seconds for a complete cycle. However, repeated cycling leads to an irreversible loss of the original anion<sup>[5]</sup>. In contrast, PT has been found to be much more stable to electrochemical cycling<sup>[6]</sup>. The cycle life of PT has recently been reported<sup>[44]</sup> to have been extended to in excess of  $5 \times 10^5$  operations. Cycling of conducting polymers is invariably accompanied by electrochromic effects (reversible). The response times, lifetimes and other electrochemical data for polyheterocycles have been reviewed recently<sup>[45]</sup>.

#### 5.4.4 Other Polymers

Although PP, PT and their derivatives have been concentrated on mostly in this introduction, the electrochemistry of many other conducting polymers has been studied<sup>[12,13]</sup>. Despite the fact that polyacetylene, PA, cannot be electrosynthesised, its electrochemistry has been well studied<sup>[46]</sup> and is interesting in that it may be both p-type and n-type doped and exhibits high doped conductivities ( $10^3$  S/cm).

#### 5.5 Structure

Insolubility and poor crystallinity in conducting polymers have created problems in characterising their structure and physical properties. However, recently more information has become available by direct means rather than by inference. The 2,5 predominantly linked structure shown in Figure 5.1 was confirmed by  $^{13}\text{C}$ nmr analysis<sup>[47]</sup>. 3-substitution is reported to produce an even higher degree of regularity with regard to 2,5 linkages, as in poly(3-methyl thiophene), P3MT<sup>[48]</sup>. This is however still an idealised structure and depends to some extent on the proposed reaction mechanism being correct. Some studies have suggested<sup>[49]</sup> quite a high proportion of non-2,5 linkages.

The 2 and 5 positions of the neutral monomer have the highest  $\pi$ -electron density and are therefore the most reactive sites. Theoretical calculations agree with this<sup>[13]</sup>, however the appearance of oligomeric radical cations causes departure from this idealised situation. This is due to the unpaired electron density (reactivity) of the 2-positions being more delocalised by the presence of the unpaired electron in an oligomeric radical cation. This means a greater equalization between the reactivity of 2 and 3 sites. A significant amount of non 2,5 linkages in PT as compared to P3MT and poly (3-ethyl thiophene), P3ET is suggested to be due to the 3-position not being blocked<sup>[20]</sup>.

Experimental work on monomeric, dimeric and trimeric thiophenes<sup>[50]</sup> and on monomer concentration<sup>[51]</sup> has suggested that the conjugation length and conductivities of the resulting polymers may be profoundly affected by the structure produced from these starting materials. These authors drew attention to the effect of non-2,5 linkages on conjugation length.

## 5.6 Recent Developments

Two recent developments may have far-reaching effects with regard to the study, processability and practical uses of conducting polymers.

### 5.6.1 Soluble Conducting Polymers

The insolubility and infusibility of conducting polymers has been a problem since their discovery. However, recently it was discovered that it was possible to make soluble conducting polymers chemically<sup>[52]</sup> and electrochemically<sup>[53-55]</sup>. The polymers are generally 3-alkyl (where alkyl chain length is  $C_4-C_{20}$ ) substituted PT's. These polymers were found to be stable<sup>[52]</sup> and may be cast from common organic solvents such as chloroform generally in the reduced form but casting of the oxidized form has been reported<sup>[55]</sup>. The first water soluble conducting polymers were recently reported<sup>[56]</sup>.

### 5.6.2 Polymer Composites

The general idea here is to improve the mechanical properties of the films while maintaining their electrical properties. This has been achieved for PP/PVC<sup>[57]</sup>, PP/NBR<sup>[58]</sup>, PT/PVC<sup>[3]</sup> and others. It has been possible to produce films which are conducting on one side and insulating on the other<sup>[57]</sup>. Films are thought to be more uniform due to the host polymer controlling diffusion of the monomer and anion<sup>[59]</sup>. A PP/NBR composite has been shown to have faster ion diffusion<sup>[58]</sup> due to its structure and hence improved anion doping.

## 5.7 Applications

The applications of conducting polymers to practical devices has been discussed on several occasions<sup>[5,6,45,46,60]</sup>. As has been mentioned already, many conducting polymers show good chemical and electrochemical stability in air and moisture. The fact that some are dopable in aqueous media make them possible alternatives for practical applications.

### 5.7.1 Energy Storage

The reversible doping-undoping processes in conducting polymers make them good candidates for secondary battery electrodes. High energy capacities have been reported - 341Whr/kg for PA.ClO<sub>4</sub><sup>[60]</sup>.

### 5.7.2 Electrochromic Display Devices

Electrosynthesised polyheterocycles are good candidates for electrochromic displays. PT's and PP's exhibit a wide variety of colours at different potentials<sup>[45]</sup>. Each polymer shows at least two distinct colours, though some polymers show more. Reasonable response times (100 msec) have been obtained, but the operating life of 10<sup>4</sup>-10<sup>5</sup> cycles remains a problem. PP<sup>[60]</sup> and polyisothianaphthene<sup>[23]</sup> have been reported to produce transparent conductive films.

### 5.7.3 Photovoltaic Applications

The photoelectrochemistry of conducting polymers<sup>[61]</sup> and photovoltaic applications<sup>[62]</sup> have been well reviewed. Two main uses are envisaged for conducting polymers : (1) conversion of solar energy into electricity via undoped polymers and (2) protection against photocorrosion of small band gap semiconductors in photoelectrochemical cells by coating with conducting polymers. Many polymers have been examined; principally PT<sup>[6,61]</sup>, PP<sup>[61]</sup> and PA<sup>[61,62]</sup>, and some success has been achieved with photocorrosion. Charge carrier photogeneration remains a problem in photovoltaic energy conversion, however. Other applications suggested include erasable compact discs<sup>[60]</sup>, catalysis and photocatalysis<sup>[63]</sup> and for coating, wiring and shielding<sup>[60]</sup>.

### 5.8 Introduction to Electrochemistry Experimental

The work described in this chapter concerns the initial testing of electrochemical equipment with a known conducting polymer, PP. This work was followed by various attempts to electropolymerise the two monomers whose synthesis is described in Chapter 4 - dithienylmethane and dipyrrolylmethane.

The electrochemistry of these monomers was then studied by cyclic voltammetry and chronoamperometry in order to determine details of the electrochemical behaviour of these monomers at applied potentials. These techniques are commonly used with conducting polymers as was

previously discussed.

Attempts were also made to electropolymerise a conducting polymer film, PP directly onto a solid state polymer electrolyte, PEO. This type of experiment had been reported previously<sup>[64]</sup>, however this involved ultra high vacuum techniques and the polymerisation of pyrrole vapour. A very recent paper<sup>[65]</sup> reports on a PP/PEO bilayer composite made in an apparently similar way to that reported here. Conductivities of 10-100 S/cm are reported, but no mention was made of the polymerisation temperature.

SECTION II-EXPERIMENTAL5.9 Materials5.9.1 Monomers

Pyrrole(Aldrich) was vacuum distilled twice; the second distillation being just prior to the experiment being performed. It was stored under nitrogen. Dithienylmethane and dipyrlylmethane were synthesised as detailed in Chapter 4.

5.9.2 Electrolytes

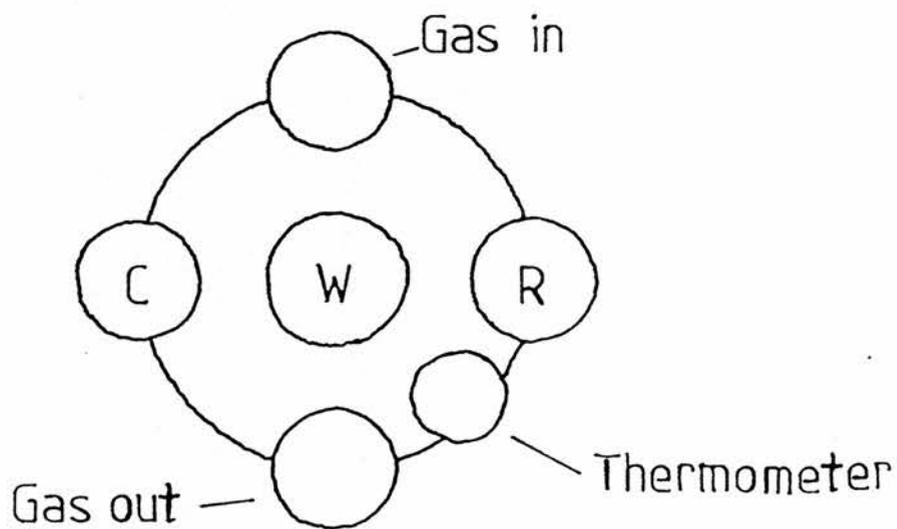
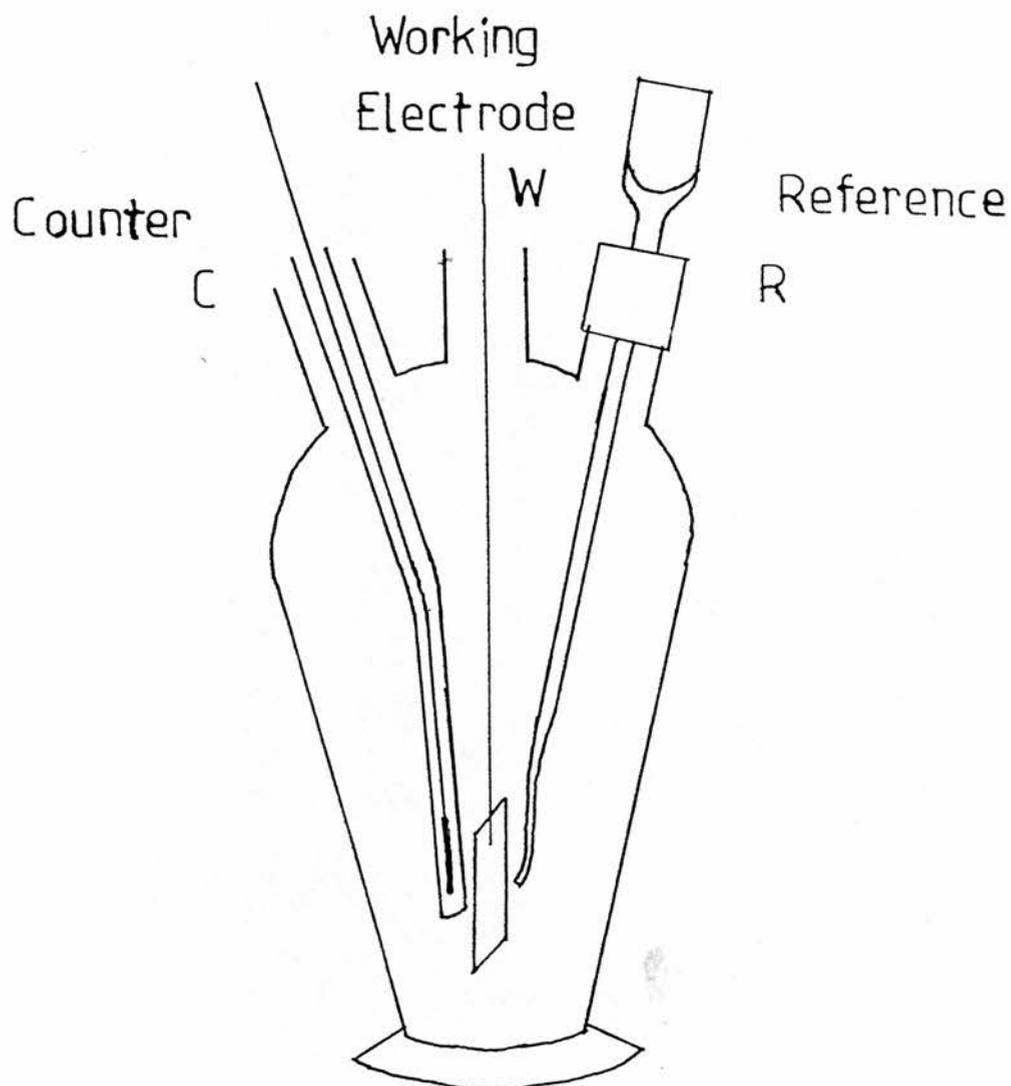
Lithium trifluoromethylsulphonate,  $\text{LiCF}_3\text{SO}_3$  (3M, battery grade) was dried in a vacuum oven at  $108^\circ\text{C}$  for 18 hours. Lithium tetrafluoroborate,  $\text{LiBF}_4$  (Aldrich) was dried in a vacuum oven at  $105^\circ\text{C}$  for 24 hours. Lithium perchlorate,  $\text{LiClO}_4$  (BDH) was dried in a vacuum tube (evacuated by oil pump) heated to  $280\text{--}284^\circ\text{C}$  and pumped for 19 hours. After cooling to room temperature the  $\text{LiClO}_4$  was carefully transferred to a container and stored in a vacuum dessicator, as were the other electrolytes.

### 5.9.3 Solvent

As the presence of water is reported to affect film formation (see Section 5.2), its removal, and the removal of other impurities, is of great importance. Cyclic voltammetry of the acetonitrile showed the presence of small, but unwanted peaks in the range +2.2 to -0.6V (vs SCE). It has been reported<sup>[66]</sup> that the method of manufacture can influence the obtainable purity of the acetonitrile. Therefore the acetonitrile to be used was initially examined by u.v. spectroscopy to determine initial purity. It was found that spectroscopic grade acetonitrile (Glenrothes Chemicals) was the best of those available. This solvent was then extensively purified by a method given by Cape and Vincent<sup>[67]</sup>. 1-litre batches of solvent were refluxed for 90 mins with 1ml of 1% aqueous KOH and fractionally distilled (10-90%). The distillate was stirred over crushed calcium hydride (5g) for over 12h. The acetonitrile was then decanted and distilled under high reflux from  $P_2O_5$  (5g) while protecting the distillate from atmospheric moisture. The fraction collected (5-80%) was then refluxed over calcium hydride (5g) for 2h and redistilled (5-90%). This last stage was done immediately before use. For some experiments distilled water was added to the purified acetonitrile.

Poly(ethylene glycol), PEG [BDH] (mw 200) was heated to 75°C in a vacuum oven and pumped for 24 hours. This is in an effort to remove any water which may be present.

FIGURE 5.2



## 5.10 Electrochemical Apparatus and Techniques

Details of the various techniques and electrochemical equipment used will be detailed here.

### 5.10.1 The Cell

Originally a simple two electrode, one compartment cell was used with one platinum and one aluminium electrode; then both platinum. The cell used for electrochemical synthesis and most other electrochemistry experiments is shown in Figure 5.2. This is a fairly standard three-electrode, two-compartment cell with the following features:

- i) A specially made saturated Calomel reference electrode, SCE (Russell CR5/B14/DRG) was used. This conversion into a three-electrode system should provide more legitimate voltage readings from the cell.
- ii) A two-compartment cell where the counter electrode is separated from the rest of the cell by a glass scinter which allows solution to reach the electrode but prevents deposits on the electrode going into the bulk solution and interfering with the reaction at the working electrode.
- iii) An opening for a thermometer to facilitate the measurement of the temperature at which the cell is operating.
- iv) The cell is shaped in such a way that only a small amount of solution (<20 ml) is needed for each polymerisation. Hence less monomer will be needed.
- v) The potential near the WE is sampled by the RE via a Luggin

capillary<sup>[14]</sup>, the tip of which is situated as close as possible to the WE to minimise iR drop, which causes errors.

### 5.10.2 Electrodes

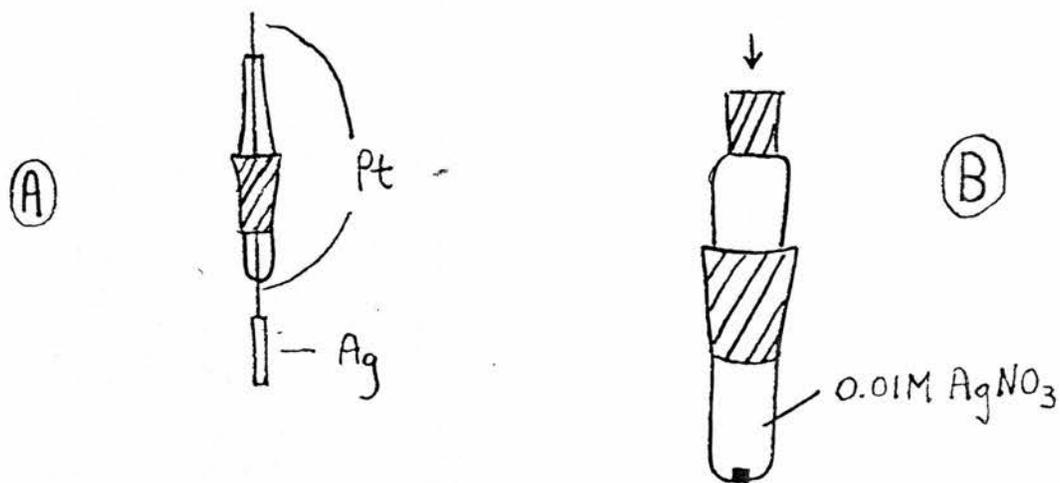
For electrochemical polymerisation reactions large working electrodes [WE] of area  $1.7 \text{ cm}^2$  approximately were used. WE's were made of platinum (attached to nickel rod by spot welding) or indium tin oxide, ITO conducting glass (attached by a stainless steel clip). Care was taken that the level of the solution in the cell was well below the nickel part of the electrode.

A platinum wire was used as counter electrode and one of two reference electrodes was used depending on the solvent. For aqueous solutions the SCE above was used. On some occasions pure, dry acetonitrile was used as the solvent, therefore the aqueous saturated calomel electrode [SCE] could no longer be used. An  $\text{Ag}/\text{Ag}^+$  RE is commonly used with acetonitrile.<sup>[68]</sup> The source of  $\text{Ag}^+$  being either silver perchlorate or silver nitrate. The nitrate was chosen as it is safer and easier to work with. It was dried in a vacuum oven at  $120^\circ\text{C}$  for 2 hours.

The electrode is shown in figure 5.3, and is very similar to the SCE used. Part B is filled with  $0.01\text{M AgNO}_3$  in acetonitrile. The silver wire on part A is cleaned by dipping into conc. nitric acid for 5-10 seconds before being placed into part B and the electrode sealed. The potential difference of this electrode (vs.SCE) was found

to be +0.215V and was stable to within 0.01V.

FIGURE 5.3

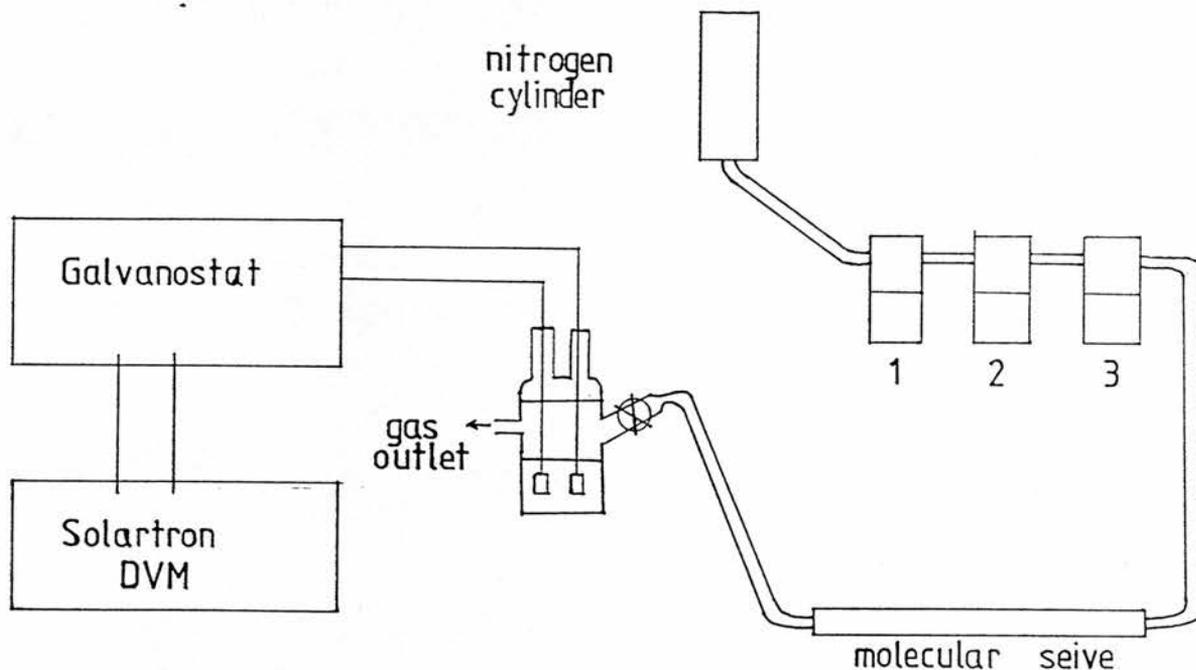


For cyclic voltametry and chronoamperometry experiments small Pt WE's were used. Initially Pt wire was used (area of 0.0648 or 0.1276 cm<sup>2</sup>), but this has limitations with regard to uniform current densities and cleaning. A Pt disc (area = 0.119 cm<sup>2</sup>) sealed with araldite into the bottom of a glass tube and contacting copper wire by mercury was used in later experiments. WEs were cleaned by repeated cycling between -0.2 and +1.2 V (vs.SCE) in 0.5M H<sub>2</sub>SO<sub>4</sub>.

### 5.10.3 Electrochemical Cell Preparation

Solutions containing the appropriate concentrations of monomer and electrolyte in the chosen solvent were prepared, transferred to the cell and the solution bubbled with dried, oxygen-free nitrogen via the system shown in Figure 5.4. Hence polymerisation can be done under nitrogen. The three Dreshel bottles and tube containing molecular sieves are used to ensure that the nitrogen is oxygen and water free. Bottle 1 contains water and bottle 3 acetonitrile (or solvent used). Bottle 2 contains an acidic solution of ammonium metavanadate with zinc amalgam<sup>[69]</sup>.

FIGURE 5.4



### 5.11 Electrical Equipment

In the early work for this project a constant current was supplied by the galvanostat (made in the department) and the voltage, during polymerisation, was measured by a digital voltmeter (Solartron A210) across the circuit. Potentiostatic electrolysis was performed using a departmentally made potentiostat in conjunction with a Solartron 7150 digital multimeter in DC current measuring mode. This system works as follows: the working electrode [WE] is held at a constant potential relative to the reference electrode. The current produced is displayed on the multimeter and transferred automatically to a microcomputer on which it is stored. A computer program, using this data as the variation of current with time, can give the area under such a curve, which will be equivalent to the amount of charge passed during polymerisation. On a few occasions the Amel equipment mentioned below was used for electrolysis.

#### 5.11.1 Cyclic Voltametry and Chronoamperometry

Amel potentiostat 553 and Amel function generator 567 were used in conjunction with a Datalab DL1200 transient recorder, BBC microcomputer, CCS IEEE interface and a purpose built interface. A cyclic voltammogram was recorded as a number of sample points of current and voltage on the DL1200. These points are then transferred to the BBC for storage on disk and from there to the VAX mainframe for manipulation. The BBC can provide timing of the run, or it may be

done manually; in these experiments the BBC was used. A similar set-up was used for chronoamperometric studies, with the Amel potentiostat set at a constant potential rather than sweeping a range. A quicker method was to use the Amel potentiostat and function generator in conjunction with a Hewlett Packard Autograph 2D-4 or Linseis LY18100 chart recorder.

### 5.12 In Situ Polymerisation on a Solid Electrolyte

The apparatus for constant voltage electrolysis was used (either potentiostat and solartron multimeter or Amel). However a different cell was employed. Here only a two electrode arrangement could be used similar to that used for Wayne Kerr bridge or FRA measurements in Chapter 2, (the reference on the potentiostat being connected to the counter electrode). A  $\text{PEO}_{10}\text{LiCF}_3\text{SO}_3$  film was placed on the lower electrode, freshly distilled pyrrole dropped onto the PEO, the conducting glass WE placed on top and connected via a clip to the top electrode. A small PTFE sheet was placed between this WE and the top stainless steel electrode. The bottom stainless steel electrode was used as the counter electrode. The whole cell is contained within an oven which is controlled by a temperature controller. A thermocouple positioned close to the two electrodes is used to monitor the temperature of the cell. The distance between the two electrodes is measured using the transducer. Hence the variation in thickness of the film during polymerisation can be recorded. It should be noted here that PEO was soluble in pyrrole and therefore the  $\text{LiCF}_3\text{SO}_3$  in the PEO mixture was available to take part in the pyrrole

polymerisation process. The oven is then heated to a predetermined temperature and allowed to reach equilibrium over a period of about 1 hour. Polymerisation then took place by applying a constant voltage. 13mm diameter films of  $\text{PEO}_{10}\text{-LiCF}_3\text{SO}_3$  mixtures were pressed by the method given in Chapter 3.

SECTION III - RESULTS5.13 Conductivity of Polypyrrole

In order to test the conductivity measuring equipment over a temperature range a polypyrrole [PP] film was prepared. For each experiment in this section the experimental conditions will be listed before the results, as below.

The working electrode [WE] used was indium tin oxide [ITO] conducting glass. The solution used for electropolymerisation was : 0.1M pyrrole, 0.1M  $\text{LiCF}_3\text{SO}_3$  in acetonitrile (1%  $\text{H}_2\text{O}$ ).

Polymerisation temperature =  $22^\circ\text{C}$ .

Area of WE =  $1.69 \text{ cm}^2$ .

Constant voltage = +1.00V (vs. SCE).

Current density =  $0.958 \text{ mA/cm}^2$ .

Total charge passed = 14.38 C.

The thick, black film produced was then washed in acetonitrile, dried in a vacuum oven overnight and then removed from the electrode and stored in a vacuum dessicator.

The DC conductivity of the film was measured by the 4-point method given in Chapter 2. Conductivity measurements were then made at various temperatures. The oven was allowed 80-100 minutes between each reading to reach equilibrium. A plot of  $\sigma / \sigma_0$  verses

temperature (see Figure 5.5) shows that conductivity is slightly dependent upon temperature as has been reported previously<sup>[12]</sup>. The plot of  $\log \sigma$  versus  $T^{-1/4}$  (see Figure 5.6) is also in agreement with previous literature<sup>[40]</sup> and indicates a hopping conduction mechanism.

#### 5.14 Cyclic Voltametry of Polypyrrole

The well-known PP system was used here in order to test all the equipment and techniques used for cyclic voltammetry. A thin PP film was deposited on the platinum WE in the same way as described in Section II. The experimental conditions were as follows.

Electropolymerisation solution : 0.1M pyrrole, 0.1M  $\text{LiClO}_4$  in acetonitrile (1%  $\text{H}_2\text{O}$ ).

Area of WE =  $0.0648 \text{ cm}^2$

Constant voltage = +0.95V (vs. SCE)

Total charge passed = 4.06 mC

The electropolymerisation solution was then replaced with a 0.1M  $\text{LiClO}_4$ /acetonitrile solution and purged with nitrogen as in Section II. The cell was connected to the cyclic voltammetry system and sweeps between -1.0 and +1.0V made at various sweep rates. The plot of  $I_{pa}$  verses sweep rate,  $\nu$  is shown in Figure 5.7. A high degree of linearity is shown which is consistent with previous papers<sup>[12]</sup>.

FIGURE 5.5

CONDUCTIVITY/INITIAL CONDUCTIVITY VS. TEMPERATURE FOR POLYPYRROLE

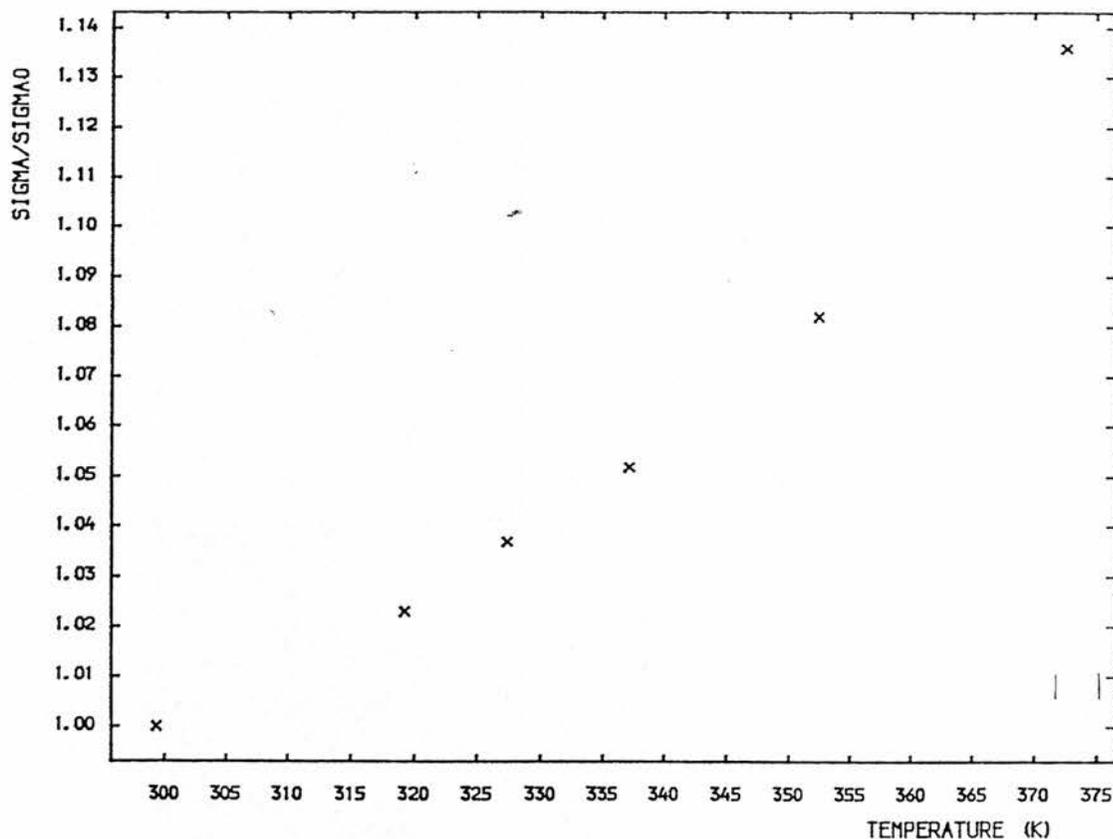


FIGURE 5.6

LOG CONDUCTIVITY VS. TEMP. TO THE -1/4 FOR POLYPYRROLE

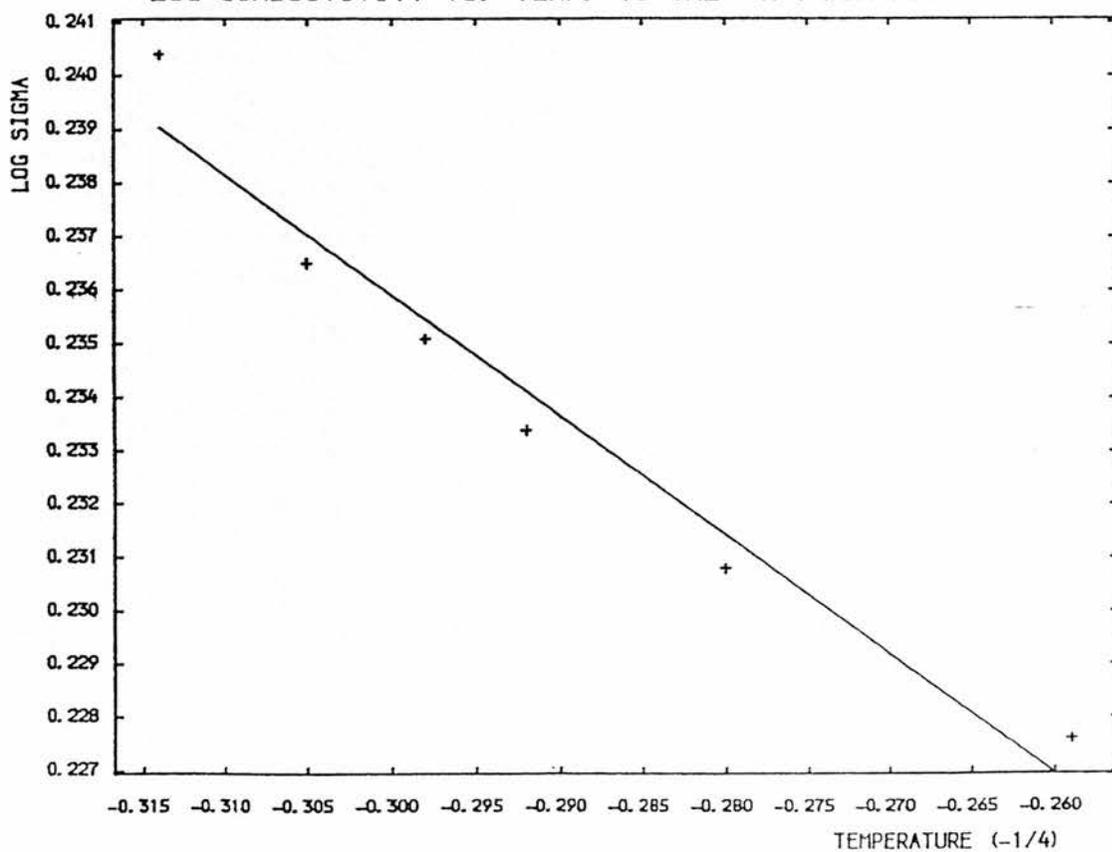
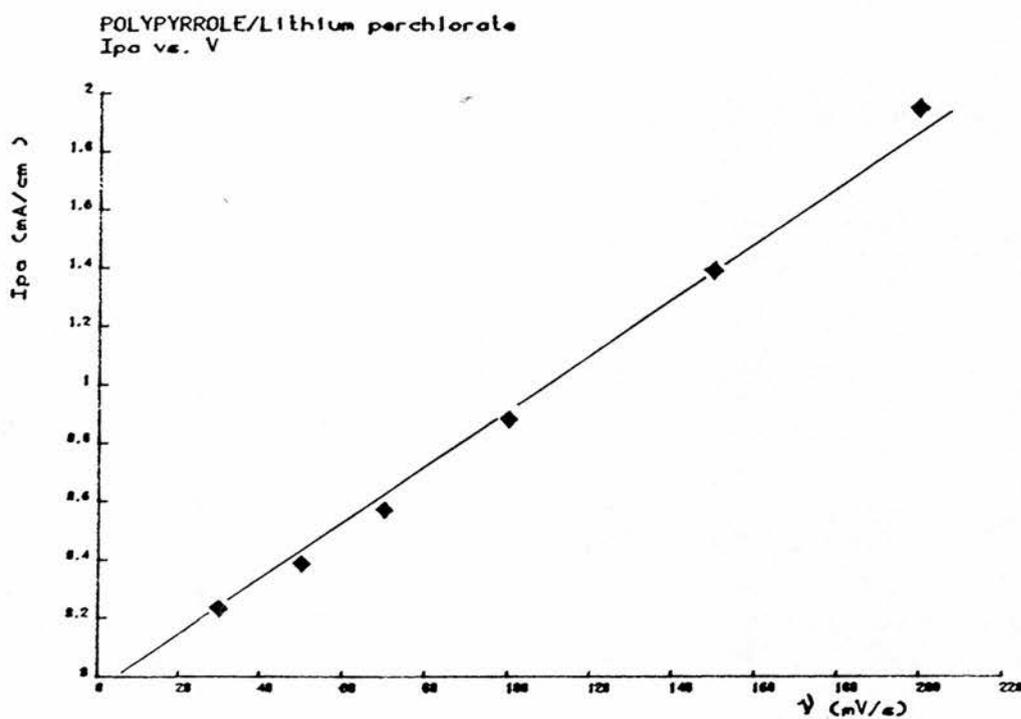


FIGURE 5.7



A further experiment was performed using  $\text{LiCF}_3\text{SO}_3$  as the electrolyte. A similar voltammogram was obtained and from it the value of  $E^0$  for the polymer was found to be about  $-0.15\text{V}$  (vs. SCE in the same electrolyte). This is comparable with a value of  $-0.2\text{V}$  in the literature.

### 5.15 Poly(ethylene glycol) as Solvent

Ethylene glycol<sup>[4]</sup> has been used as a co-solvent in the electrosynthesis of PP with only a slight loss in the resultant polymers conductivity. It was decided to try to use poly(ethylene glycol), PEG as a solvent for electrochemical polymerisation. This low molecular weight polymer may have two advantages over the usual solvents used (acetonitrile and propylene carbonate). Firstly it is a moderately viscous material and as such may inhibit diffusion of monomer molecules away from the site of reaction (the working electrode). Secondly it would not require extensive purification unlike the above mentioned solvents. PEG has however to be used at elevated temperatures as it was observed that the voltage of the cell containing PEG plus electrolyte varies greatly with temperature and at room temperature the voltage was beyond the voltage limit for the cell. It was decided to investigate this further.

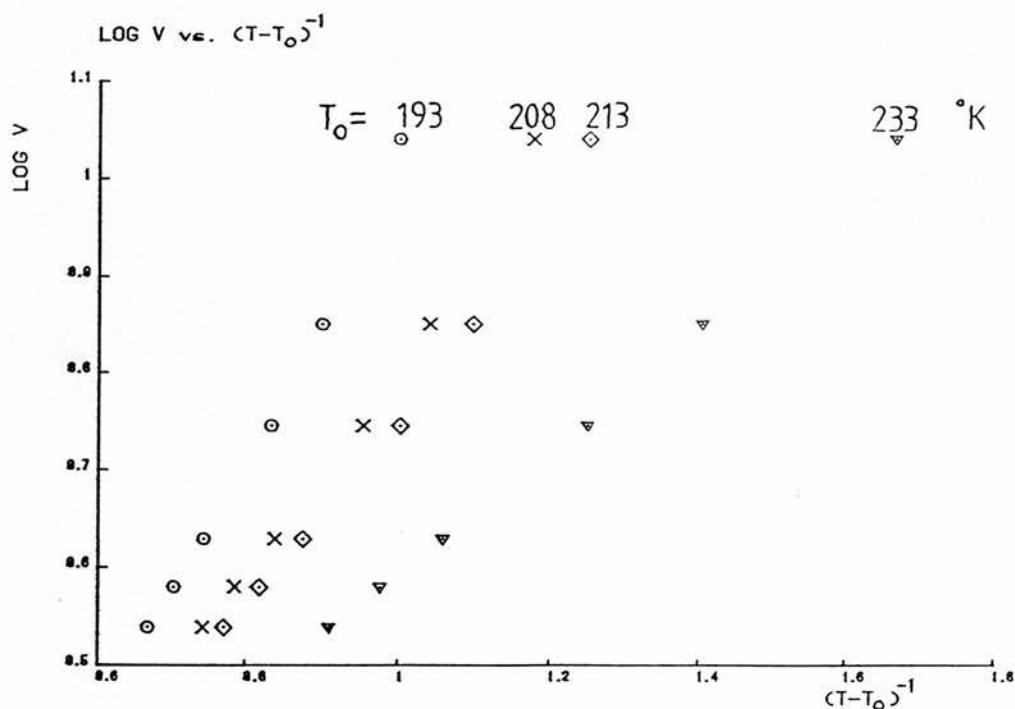
#### 5.15.1 Variation of Voltage with Temperature

A 0.1M solution of  $\text{LiCF}_3\text{SO}_3$  in PEG was used to observe the variation of voltage with temperature in the cell. This solution was made, transferred to the cell and had dry, oxygen-free nitrogen passed through it for 20 minutes. The cell was placed in a water bath (Haake) and allowed 45-60 minutes to reach equilibrium at various (increasing) temperatures. The voltage was allowed 10 minutes to steady while a current of 0.1mA was passed between the electrodes. This voltage gives an indication of the resistance of the polymer

electrolyte.

A plot of  $\log V$  against  $T^{-1}$  gave a distinct curve. Plots of  $\log V$  against  $(T-T_0)^{-1}$  with various values of  $T_0$  (generally taken to be  $T_g$ ) are shown in Figure 5.8. It was hoped that one of these plots might give a straight line. However most have only a straight line in the higher temperature region.

FIGURE 5.8

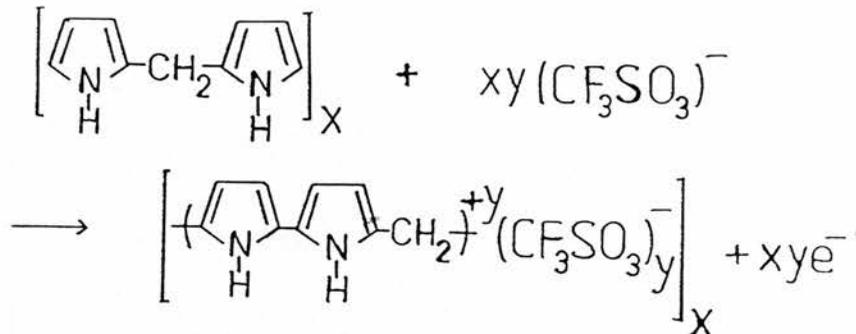


5.16 Electrochemical Polymerisation of 2,2'-Dipyrrylmethane

The PEG and  $\text{LiCF}_3\text{SO}_3$  used were dried as before and the 2,2'-dipyrrylmethane, DPM was freshly made. A solution of 0.1M  $\text{LiCF}_3\text{SO}_3$  and 0.1M DPM in PEG was made. This solution was kept in a flask under nitrogen and stirred (3 hours) until the salt and monomer had dissolved. The solution was then transferred to the cell and dry, oxygen-free nitrogen bubbled through the solution for 20-30 minutes. The cell was then heated in a water bath until the reaction solution reached a temperature of 52-53°C. A constant current of 0.1mA was then passed for 140 minutes. After an initial increase in the first few minutes the voltage remained constant at about +3.4V. After the current was switched off, the platinum working electrode was removed and it was observed that a metallic green/black film had formed on the electrode. The film was left on the electrode, washed in ethanol, pumped for 16 hours in a vacuum oven and then stored in a dessicator.

The experiment was repeated several times with the same solution and each time a film was formed. The reaction times varied from 30-240 minutes and the variation of voltage with time was found to be similar. In all of these experiments most of the polymerisation took place between +3.1V and +3.6V. However all of these films were rather thin. The following electrode reactions are suggested to have taken place:

Anode(+), working electrode :



Cathode(-), counter electrode :



### 5.16.1 Analysis of Product

a) Ultra Violet Spectrum One of the above polymerisations was performed using a conducting glass (ITO) working electrode. The reaction time was 30 minutes, and this produced a very thin, metallic-purple film which was slightly transparent. The glass electrode was then removed, washed and dried as above and placed in a Pye Unicam UV/VIS Spectrophotometer (SP8-150). The u.v. spectrum was then recorded at various time intervals with the sample exposed to the atmosphere for one hour. The spectrum did not change during this time and the only feature is a broad peak at 492 nm. (Polypyrrole gave broad bands at 450 and 860 nm.) Any bands below 300 nm cannot be observed due to the conducting glass.

b) Microanalysis

C, 55.39% ;H, 3.93% ;N, 12.95%

Assuming  $\text{CF}_3\text{SO}_3^-$  as the dopant species, the above result indicates a polymer to dopant ratio of 2.42 : 1. Therefore the film obtained has the following composition:  $[(\text{C}_9\text{H}_8\text{N}_2)_{2.42}\text{CF}_3\text{SO}_3]$

This result suggests that the film contains 29.97% dopant and 70.03% polymer, which is in good agreement with previous results for polypyrrole<sup>[4,5]</sup>.

c) Room temperature conductivity These experiments involved measuring the conductivity of the poly(2,2'-dipyrrylmethane) [PDPM], film by the 4-point method, while it was still attached to the ITO conducting glass WE. It was discovered that the films were being pierced by the probes and that on many occasions the conductivity of the ITO was being measured. As the films were too thin to be removed intact and would not amount to enough material for a 13mm pressed pellet, efforts were made to make thicker polymer films.

5.17 Further Studies on DPM

The synthesis of PDPM from DPM using PEG as a solvent was achieved, but the films which were produced were found to be too thin for the appropriate measurements to be made. Therefore it was decided to electrochemically polymerize using a more conventional solvent - acetonitrile. The polymerisation of both DPM and

2,2'-dithienylmethane MDT was attempted. Papers available at the time gave conflicting information as to whether water need be present in the acetonitrile<sup>[12]</sup>. Generally, however, it would appeared that the most commonly used solvent was acetonitrile containing 1% water. Therefore this was the solvent used.

The monomers,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiClO}_4$  and acetonitrile were prepared as in Section II. 1% distilled water (by volume) was added. The potentiostat and Solartron multimeter were used; the current versus time data being stored on the computer. An ITO conducting glass WE ( $1.7 \text{ cm}^2$ ) and SCE reference electrode were used in all these experiments.

#### 5.17.1 DPM

Experiments were performed at different potentials and with different concentrations of DPM.  $\text{LiClO}_4$  was always used at 0.1M. A potential of +2.0V and a concentration of 0.039M were the most favourable conditions. However even this could only produce a thin film. Charge passed = 636.4mC.

### 5.17.2 MDT

A solution of 0.1M MDT, 0.1M  $\text{LiClO}_4$  in acetonitrile (1% water) was used. As low potentials seemed ineffective, the potential used was +2.2V, near the solvent/electrolyte limit. Total charge passed = 4.532C. A yellow colouration was observed at the WE which diffused into the bulk. Further attempts were made using p-toluene sulphonic acid and sulphuric acid as electrolytes. However, both produced yellow coloured solutions. It was decided to investigate these reactions further using cyclic voltammetry.

## 5.18 Electrochemistry of Dithienylmethane

Here the electrochemical behaviour of MDT has been studied more fully. MDT was chosen as there was a larger supply of this monomer and it was easier to synthesise than DPM if more was needed. Also anything which was learned about its behaviour should be applicable to DPM, to some extent.

### 5.18.1 Electrolysis

It was decided to investigate this reaction further with a different WE (Pt) and longer polymerisation time. The u.v. spectra of the reaction solution were recorded on a Pye Unicam UV/VIS Spectrophotometer (SP8-150) at various intervals. The electropolymerisation solution was 0.1M MDT and 0.1M  $\text{LiClO}_4$  in

acetonitrile.

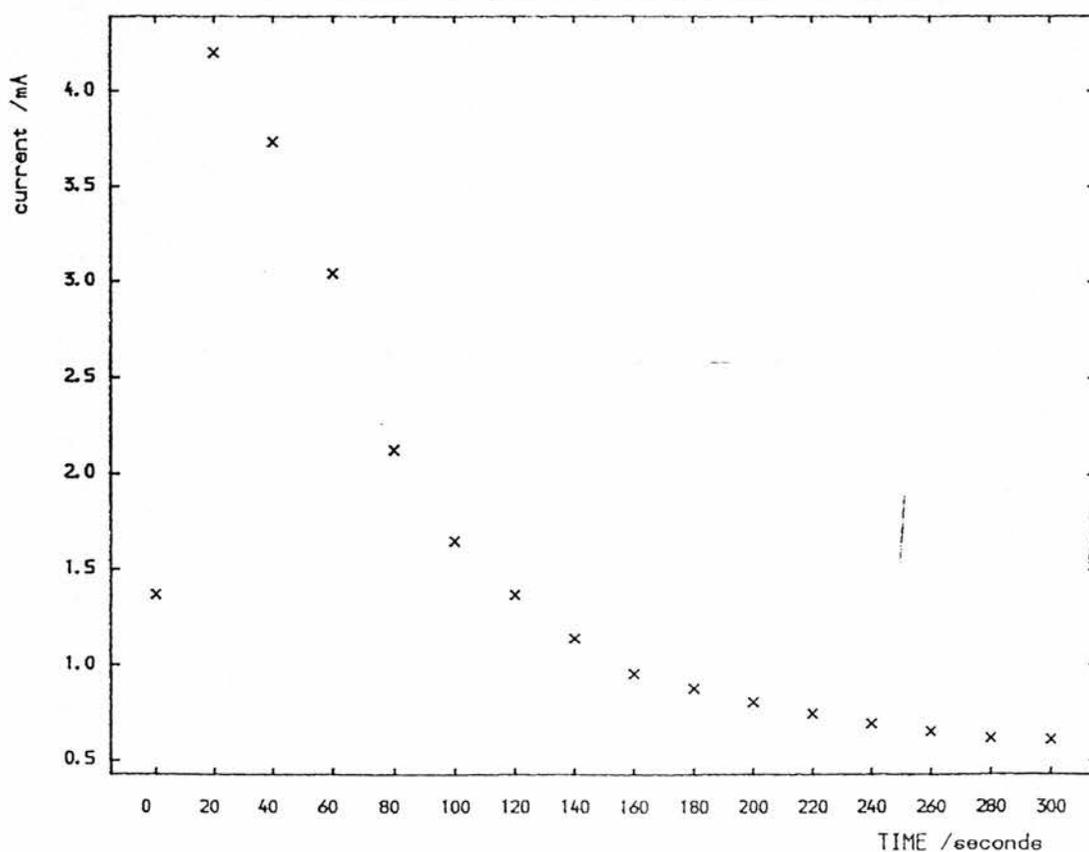
Area of WE =  $1.44 \text{ cm}^2$

Constant voltage =  $+2.0\text{V}$  (vs.  $\text{Ag}/\text{Ag}^+$ )

<u>Reaction Time</u>	<u>Total Charge Passed</u>	<u>Solution Colour</u>
0 mins.	0.0 Coulombs	colourless
5	7.0	bright yellow
105	3008.6	yellow/green

The variation of current with time during the reaction (5 min) can be seen in Figure 5.9. The current levels off at about 0.27-0.30 mA during the 100 min. reaction. A very small amount of black deposit was observed on the WE at the end of the reaction. The colouration of the solution was seen to originate in the WE region.

FIGURE 5.9  
Variation of current with time for tmt1a



The initial u.v. spectrum showed a lower wavelength limit at 280 nm. As the lower wavelength limit of acetonitrile was 210 nm, it can be assumed this is due to the MDT. There are no features between 400 and 750 nm. The u.v. spectrum recorded after 5 minutes of reaction showed a new band at 480 nm. After 105 minutes the growth of this band plus a further band at 625 nm was observed. These bands are consistent with the observed colours and may be due to the formation of a species with a greater degree of conjugation such as conjugated oligomers.

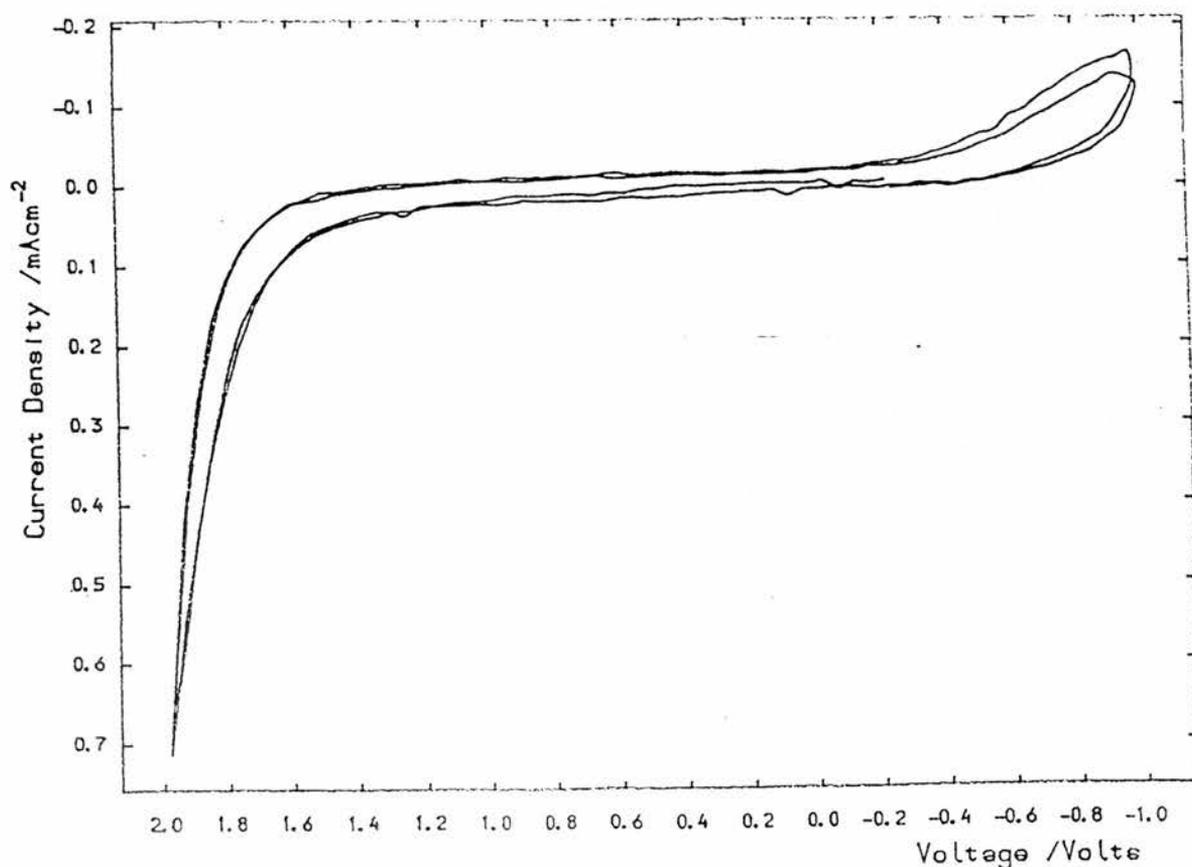
After standing (under nitrogen) for 1 week, a small amount of dark suspension was observed in the now dark green solution. Further standing produced more solid, however on filtering the amount was found to be very small. The solvent was then removed, the resulting brown oil washed with water, extracted with dry ether, the ether extracts dried over  $P_2O_5$  and the ether removed. The n.m.r. spectrum of the resulting brown/grey solid shows little difference from the original MDT. It is suspected that a small amount of oligomers may have been formed, but as they would have a similar spectrum to MDT and most of the final product would be MDT anyway, it is difficult to draw a definite conclusion.

5.18.2 Cyclic Voltammetry and Chronoamperometry

Cyclic voltammetry (CV) is very useful in the area of preliminary mechanistic investigations and can rapidly indicate the potentials at which processes occur. It was decided to continue this work therefore, with a fairly detailed study of the electrochemistry of MDT using CV. This section also contains some chronoamperometry studies.

Each of the following experiments was carried out basically, as follows : solvent was freshly distilled, a 0.1M  $\text{LiClO}_4$  solution made and degassed with dry, oxygen-free nitrogen for 15-20 mins. A cyclic voltammogram was then recorded between the anticipated voltage limits of the experiment. An example can be seen in Figure 5.10. A known amount of MDT was then introduced to the cell solution which was again degassed. The respective experiments were then performed.

FIGURE 5.10



### 5.18.2.1 Results

The first few experiments were qualitative to get a feel for the system. The first experiment involved cycling to increasingly anodic potential limits. +1.30V was the first potential at which the current was seen to increase dramatically (see Figure 5.11), indicating that some sort of reaction was taking place. The concentration of MDT was reduced to 0.01M, so that the initial currents were not too high. As the current has not yet reached its peak before the potential is reversed, it was decided to sweep to more anodic potentials.

In the following experiment the concentration of MDT was reduced to 1 mM to produce a smaller peak current,  $i_p$  and the potential limit was increased to +1.6 V. This produced a peak at +1.45 V which moved on cycling to almost +1.6 V (see Figure 5.12). This movement is probably due to using too negative a potential. Cycling between +1.75 and +0.6 V produced more regular shaped peaks which did not move,  $i_p$  however did decrease regularly (cycles 20-40) - see Figure 5.13. As can be seen a lower limit is reached (about  $0.18 \text{ mA cm}^{-2}$ ) for  $i_p$ . When the cathodic voltage limit is taken back to -1.0V and then cycled between +1.75 and -1.0V  $i_{pa}$  increases and then remains steady (see Figure 5.14). It is interesting that here the current does not fall

as before and clearly some other process is involved.

The following experiments involve chronoamperometry. The potential was increased instantaneously from +0.4 to increasingly positive potentials and held there for a certain time while recording the current and time (I-t transients). On some occasions the system was allowed to rest for a time and the process repeated. The I-t transients were recorded in the same way as detailed previously. The solution contained 5mM MDT and was stirred during the recording of the I-t transients. The results are shown in Figures 5.15 - 5.17.

The following three figures show the effect of increasingly positive potentials on the I-t transients. Figure 5.15 is typical of the behaviour observed after a potential step to +1.5V or less. The current falls quickly (80 seconds) to a low level and remains steady there. The potential step from +0.4 to +1.6V produced the result in Figure 5.16(1). Here a steady rising transient can be seen. After resting at +0.4V for 5 minutes, run number (2) produced a slight rise in the transient until 100s after which it fell very slowly. After a further minute at rest the third transient recorded (3) fell slowly. The same type of behaviour was observed when the potential step was from +0.4 to +1.65V (Figure 5.17). The rest time between each run was 0.5 and 1 minute respectively, going from run 1 to run 4. Only the first run shows a rising transient, the rest fall slowly. This type of behaviour has been recorded for other conducting polymers and has been attributed to a nucleation and growth mechanism<sup>[16,17]</sup>. These results show that this mechanism also applies to rather less conductive systems, although with more limited growth.

5 cycles between +0.6 and +1.7V were recorded under the usual nitrogen conditions. Dry oxygen was then bubbled through the solution for 15-20 mins. This caused little change in peak position or height or the trend observed on going from cycle 1 to cycle 5. The atmospheric conditions under which these reactions take place therefore seem to be of little importance.

FIGURE 5.11

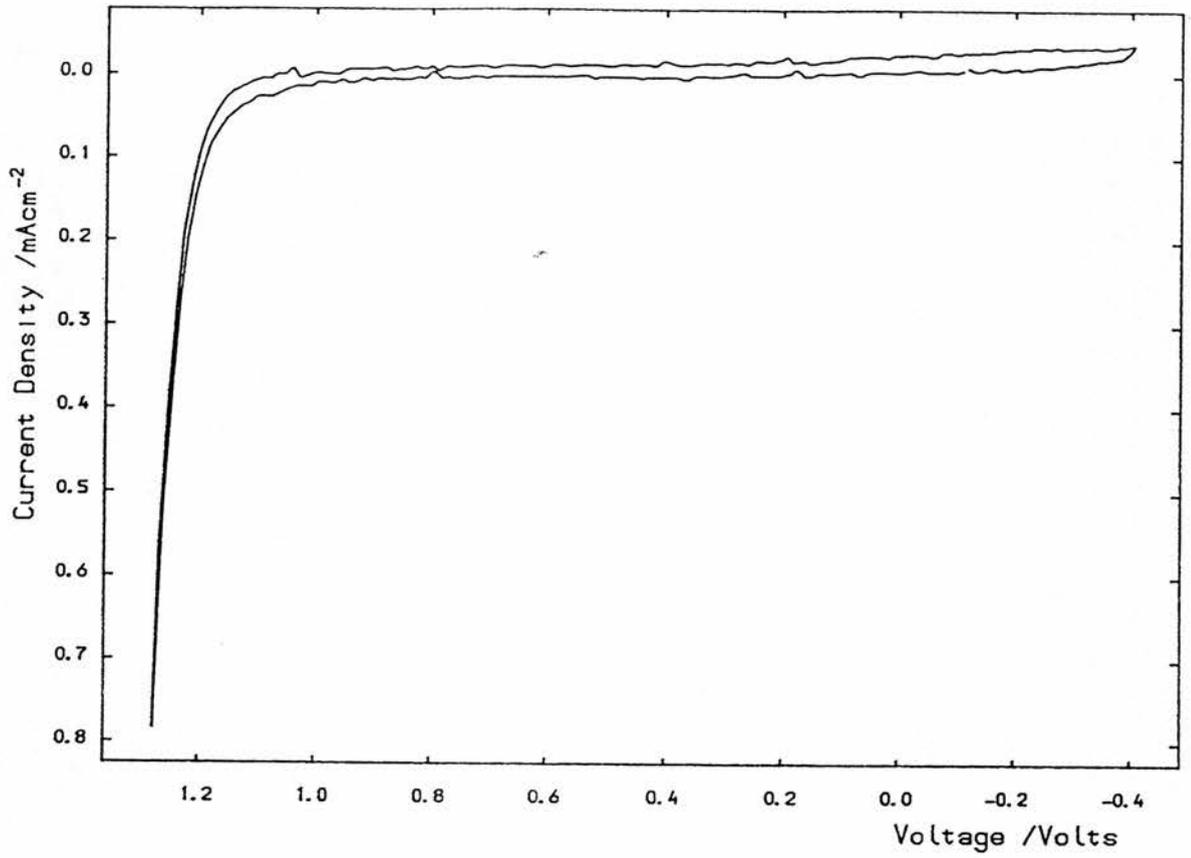


FIGURE 5.12

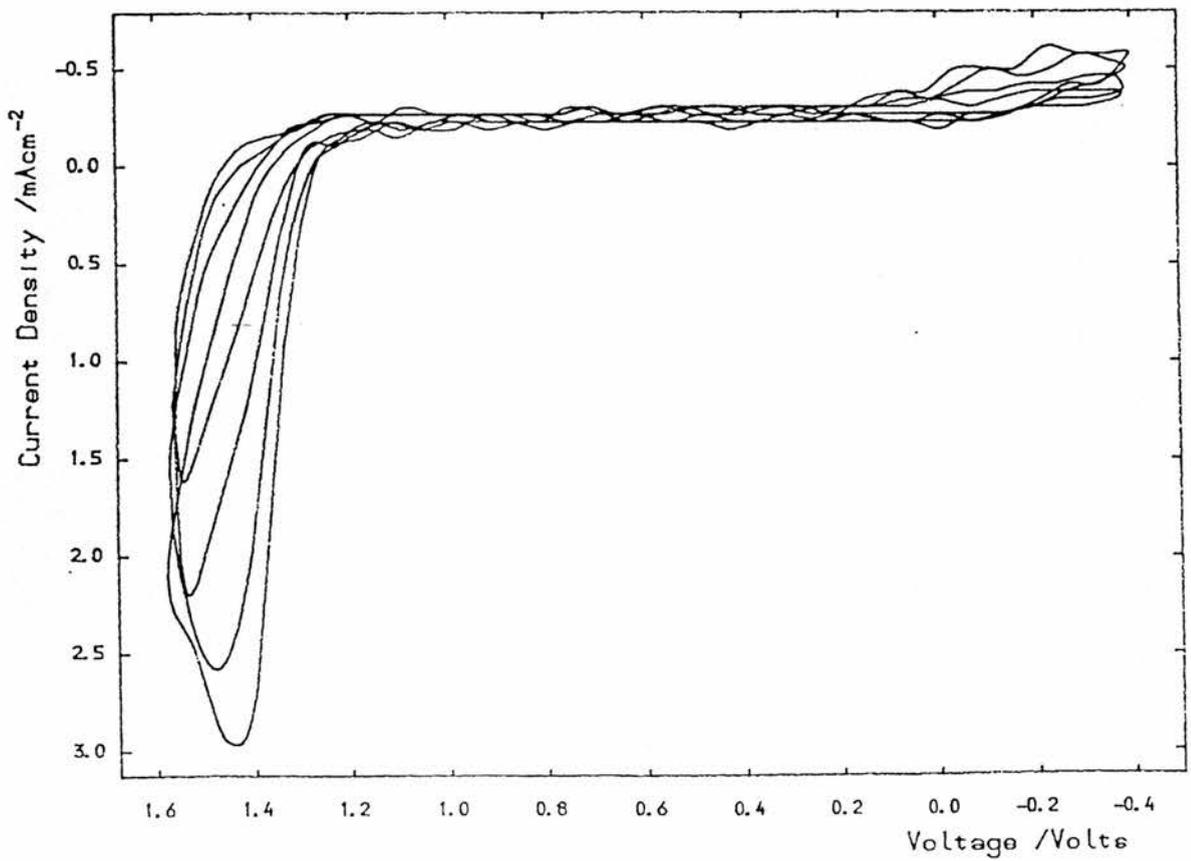


FIGURE 5.13

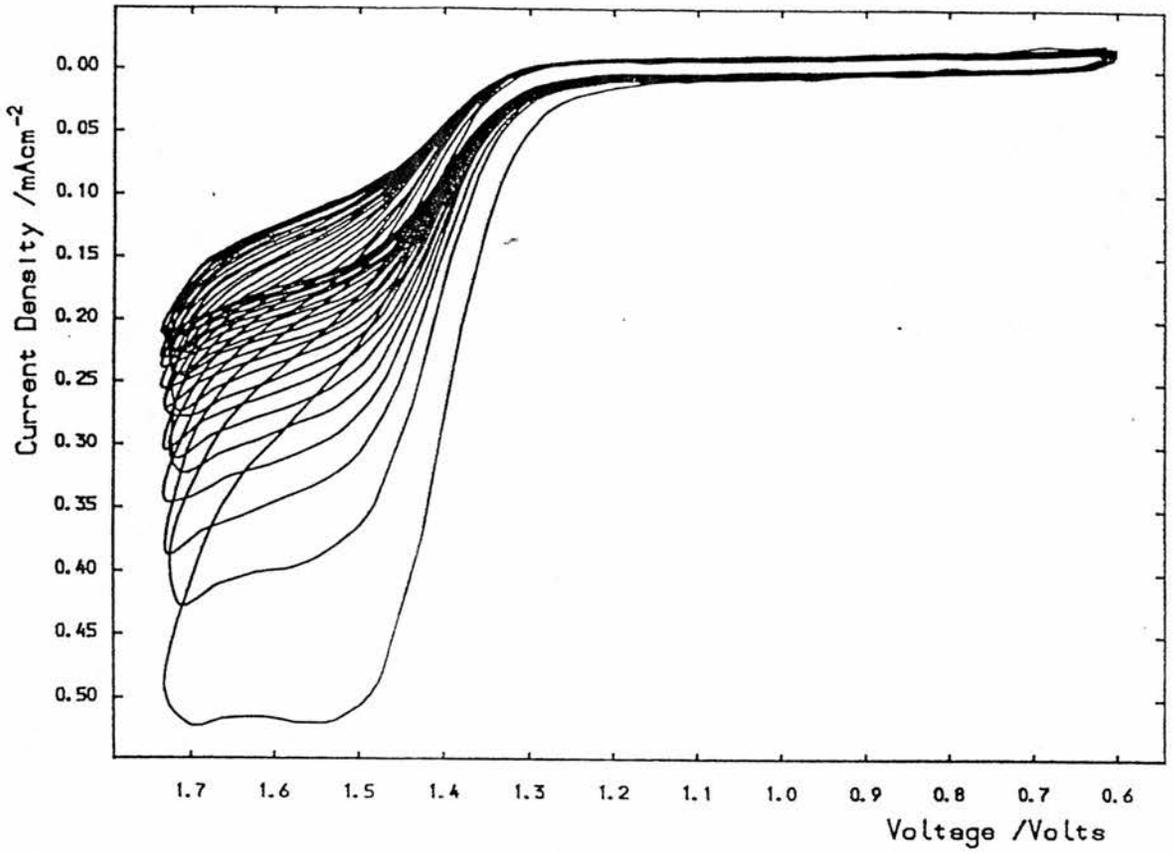


FIGURE 5.14

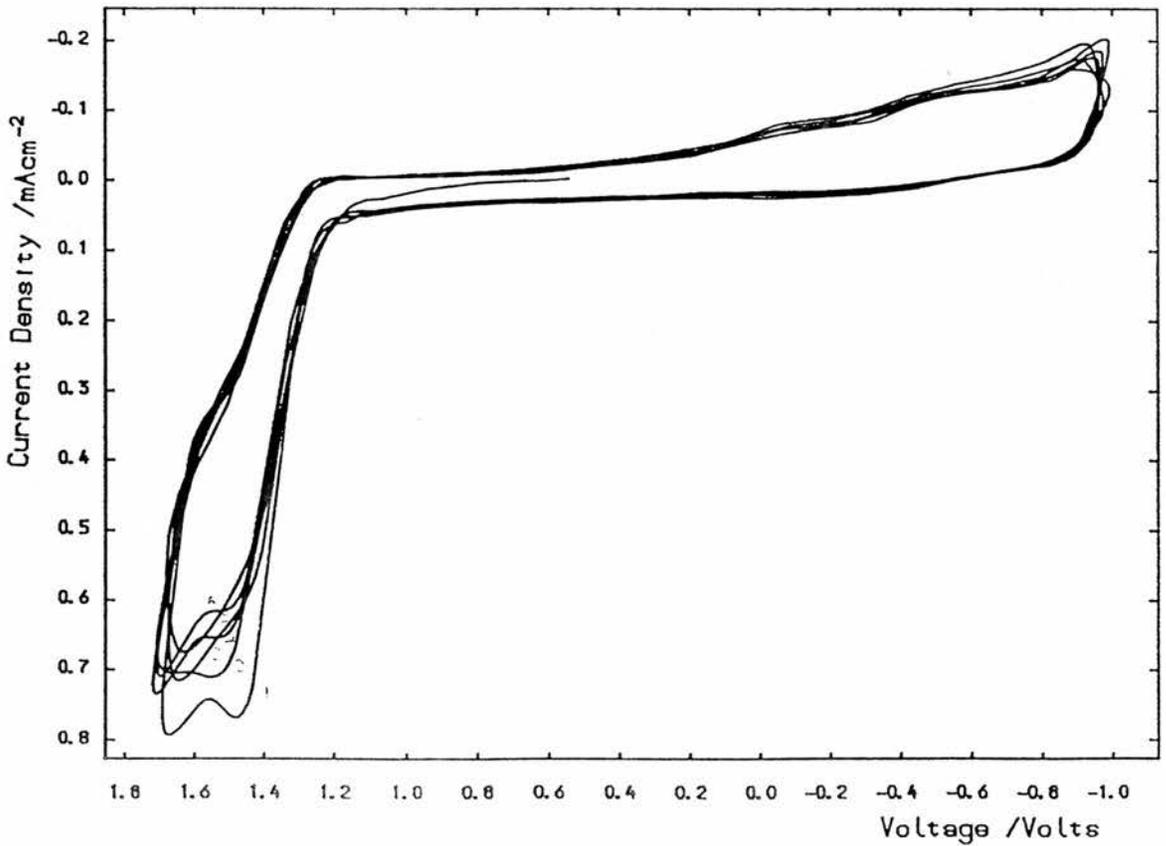


FIGURE 5.15

Variation of current with time at +1.50V

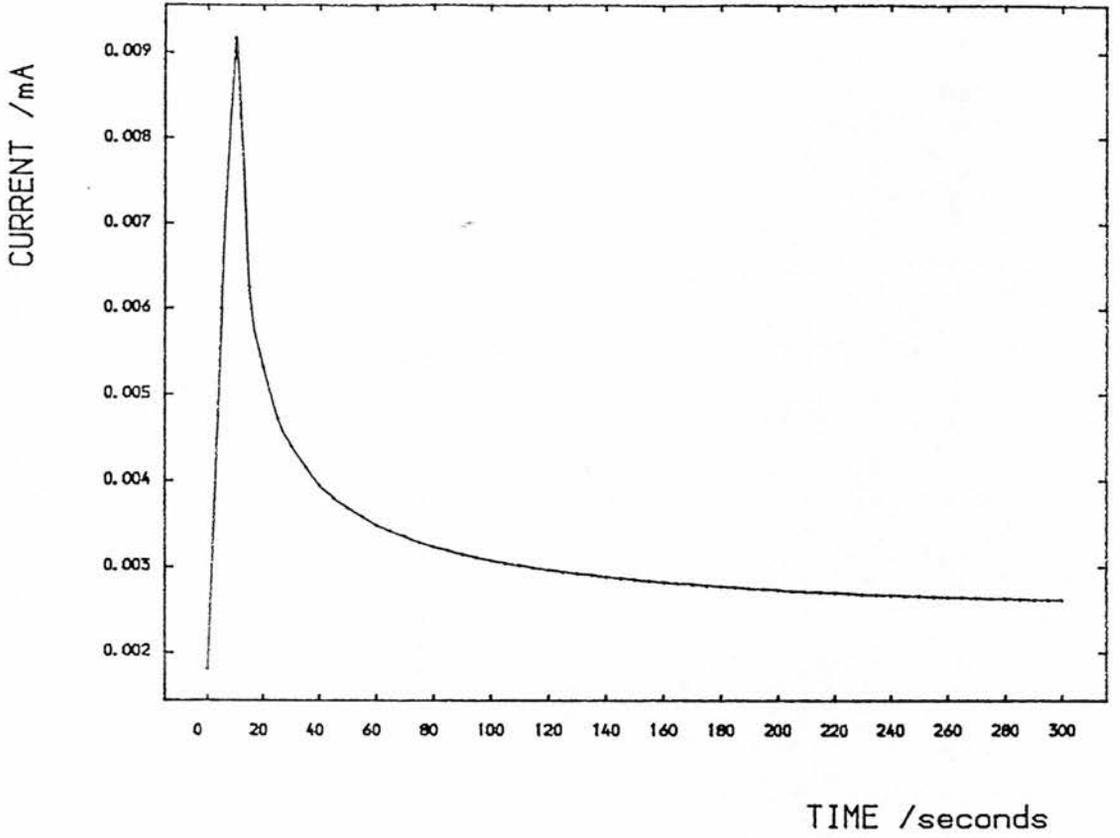


FIGURE 5.16

Variation of current with time at +1.60V (1=1st run 2=5min 3=1min)

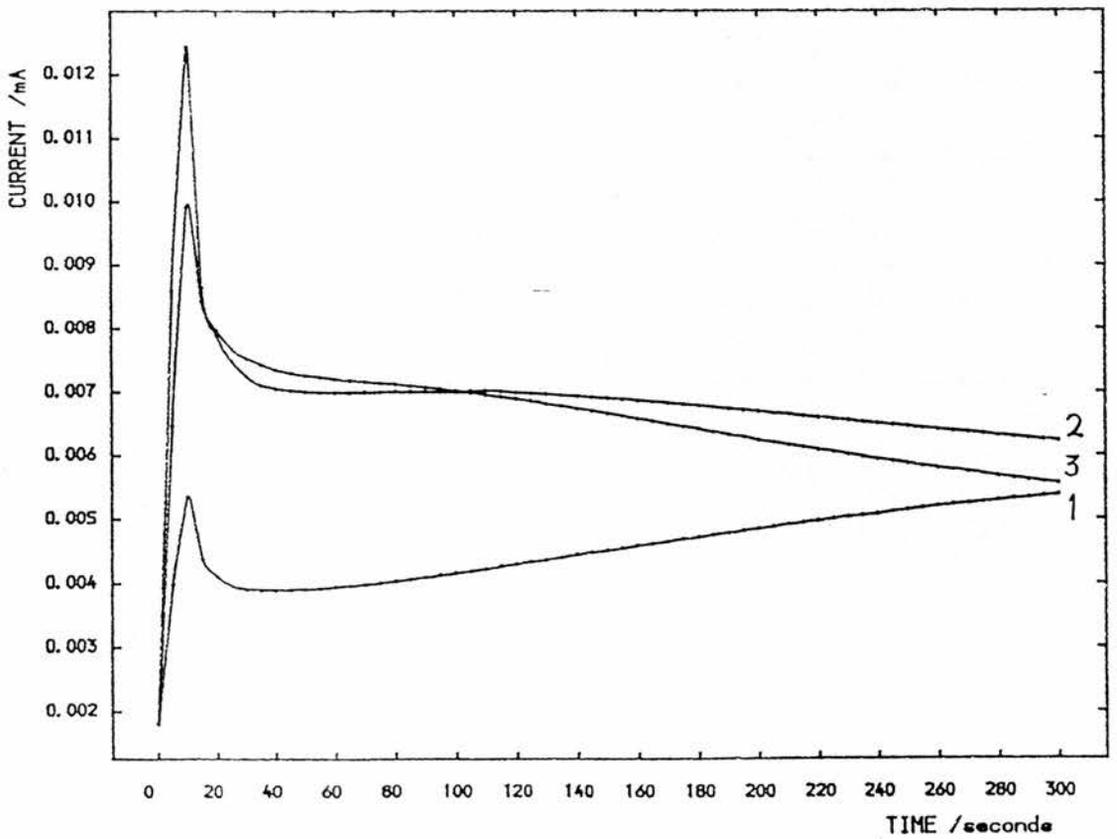
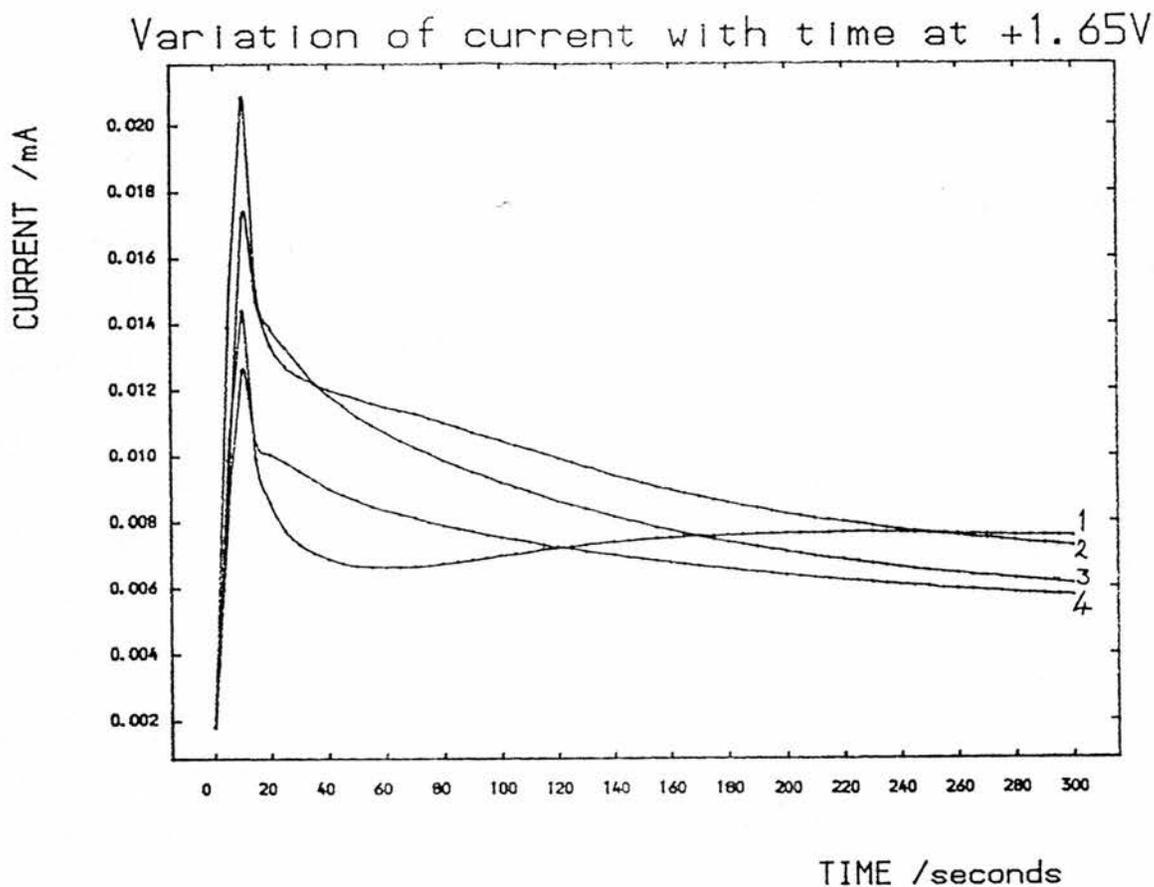
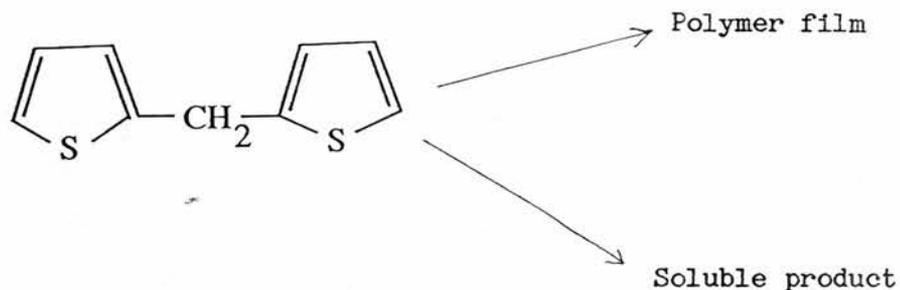


FIGURE 5.17



#### 5.18.2.2 Conclusions

A reaction starts to take place at about +1.30V. An anodic current peak,  $i_{pa}$  is observed at about +1.50 to +1.65V. Repeated cycling between +0.6 and +1.75V leads to a steady decrease of  $i_{pa}$  to a value of about  $0.18 \text{ mA cm}^{-2}$ . As thin bronze coloured films were observed on some electrodes this is a method by which films are formed. (These electrodes had been at greater than +1.6V for a reasonable period of time.) The scheme shown below is proposed.

Electropolymerisation of MDT (scheme)

Electropolymerisation of MDT resulted in the formation of poly(2,2'-dithienylmethine). Film formation was however found to be complicated by two factors : 1) Potential step experiments gave results similar to those for other conducting polymers<sup>[16]</sup>, that is a nucleation and growth process was involved. 2) Soluble products (oligomers) were also formed.

At potentials between +1.3 and +1.6V (vs Ag/Ag<sup>+</sup>) soluble products are formed. At +1.6V polymer film formation starts. When the potential is held at +1.6V or above, the current produced falls steadily until a limit is reached; this limited current is then maintained. This may be explained by assuming a moderate conductivity ( $10^{-3}$ - $10^{-7}$ S/cm) for the doped polymer film produced. This assumption is not unreasonable in view of other results shown here and elsewhere. Only a limited thickness of film may be grown due to this moderate conductivity and hence the competing reaction of soluble oligomer formation is favoured leading to the constant current which is found. DPM was not studied to the same extent as MDT and therefore is an area for future research. Nevertheless, it is reasonable to

assume that a similar scheme to that above would also apply to DPM.

There appears to be little difference between voltammograms recorded with the solution under nitrogen or oxygen.

### 5.19 Electrochemistry of Product from Section 4.8

The product from the reaction between thiophene and benzaldehyde is monomeric, or more likely oligomeric in nature, and it is hoped that electropolymerisation is possible. The following experiments were performed in order to determine this.

Studies were performed using  $\text{LiClO}_4$ , acetonitrile and the sample BT2Res. The latter was chosen due to its abundance; the samples from section 4.8 being very similar according to their analysis. The  $\text{Ag}/\text{Ag}^+$  RE was used and the results were recorded on a Linseis LY18100 chart recorder in XY mode.

#### 5.19.1 Cyclic Voltammetry

Solution preparation was as detailed previously. A cyclic voltammogram was then recorded between the anticipated voltage limits of the experiment and showed no unwanted peaks. All voltammograms were recorded at  $100\text{mV s}^{-1}$ , unless stated otherwise, with a WE of area  $0.0648\text{ cm}^2$ .

0.02g of BT2Res. was added. This gave a green coloured solution; however the solid was not 100% soluble. The initial voltammogram between +0.6 and -0.2 V showed that after the initial half cycle the following three cycles showed no change in peak current [ $i_p$ ] or peak potential [ $E_p$ ]. Figure 5.18 shows these peaks recorded at various sweep rates,  $\nu$ . The data obtained from this voltammogram is shown below:

$\nu$ (mVs <sup>-1</sup> )	$\sqrt{\nu}$	$i_a$ (uA)	$i_c$ (uA)	$i_a/i_c$
30	5.48	0.60	0.70	0.86
50	7.07	0.80	0.80	1.00
100	10.00	1.10	1.20	0.92
200	14.14	1.50	1.40	1.07

The fact that there is little variation of  $i_a/i_c$  with  $\nu$  and that a straight line plot of  $i_a$  against  $\sqrt{\nu}$  (Figure 5.19) would suggest this reaction is reversible [16,17].

Figure 5.20 shows a cycle between +1.3 and -0.4 V. It shows that there are three redox couples within this range.  $E^0$ , the electrode potentials (uncorrected), for these reactions are -0.025, +0.330 and +1.080 V respectively. The full data from this voltammogram is shown below:

$E_a$	+1.150V	+0.385V	+0.105V
$E_c$	+1.010	+0.275	-0.155
$\Delta E_p$	0.140	0.110	0.260
$E^0$	+1.080	+0.330	-0.025

Three cycles are recorded on this voltammogram without variation of  $E_p$  or  $i_p$ . This is the type of voltammogram which might be expected for a reaction in solution. No further peaks were observed up to +1.70 V.

FIGURE 5.18

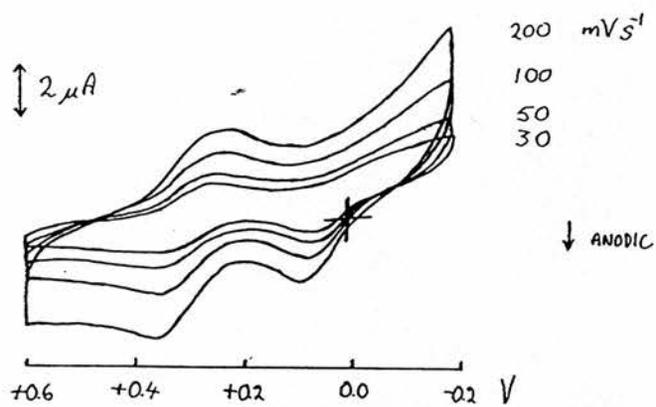


FIGURE 5.19

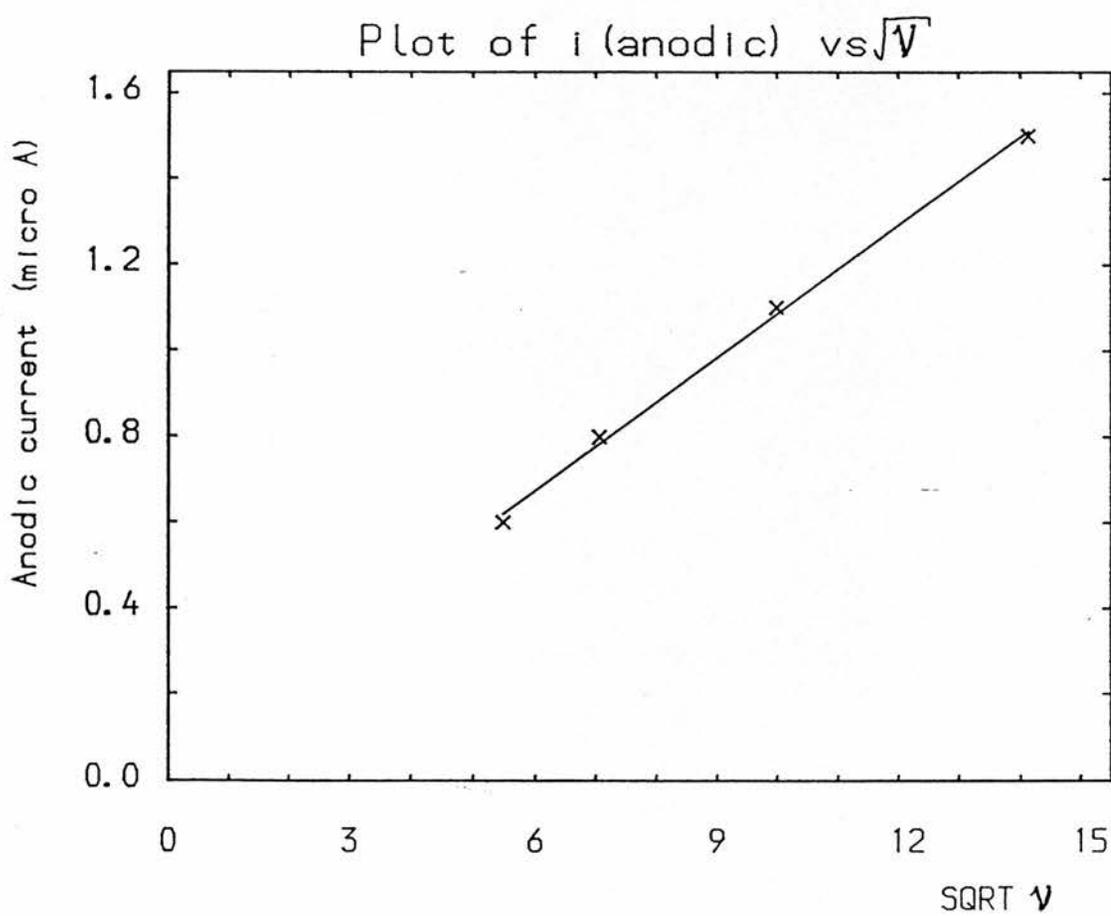
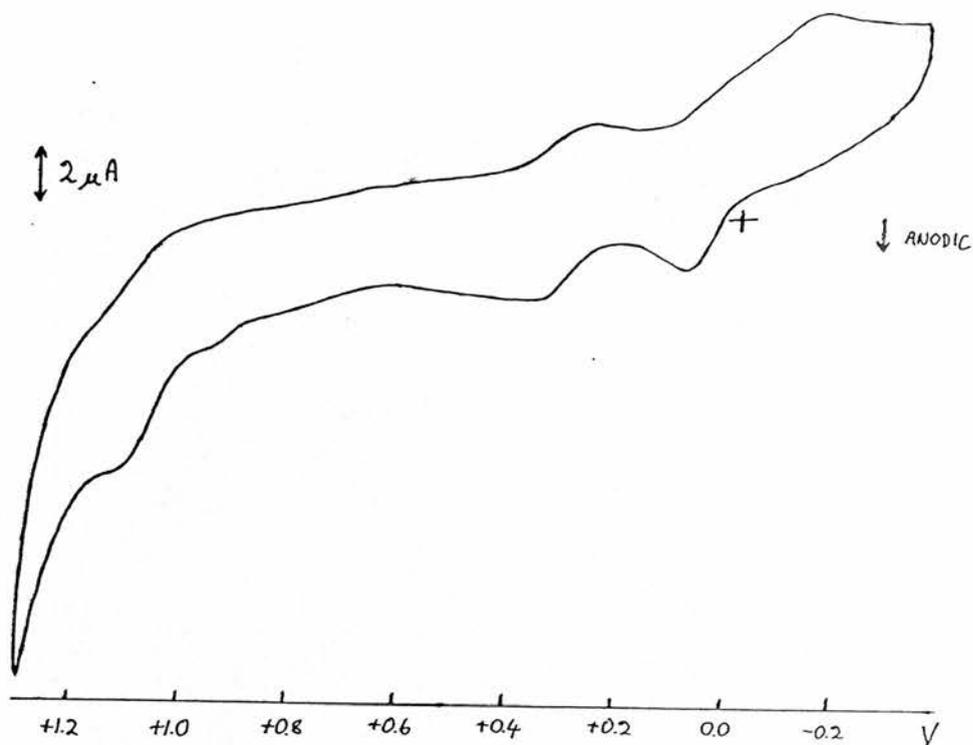


FIGURE 5.20



### 5.19.2 Electrolysis

In order to test whether a polymer film could be formed on an electrode from this solution, a constant current was passed through the solution in the following experiments.

The cell and solution used were as before, except that a larger conducting glass WE (area =  $1.69 \text{ cm}^2$ ) was substituted and the solution degassed with dry, oxygen-free nitrogen. The constant current was supplied by the Amel potentiostat used in galvanostatic mode and the

Linseis LY18100 chart recorder used in Yt mode to record the voltage with time. The Amel function generator was not used.

A constant current of 0.1 mA ( $0.0592 \text{ mAcm}^{-2}$ ) was applied and the variation of voltage with time recorded. The electrode was removed and examined but no film was observed. The experiment was repeated at three further current densities; 0.296 [a], 0.592 [b] and 3.432 [c]  $\text{mAcm}^{-2}$ . Decreases in the large voltage (3.45 V) produced in [c] was almost certainly due to solvent breakdown. However even at these relatively large current densities no polymer film was formed; only further reaction in solution.

These results all strongly suggest that whatever the product was that was synthesised, it cannot be electropolymerised to form a conducting polymer film. As analysis showed the products to be very similar, it is reasonable to assume that none of them would form films.

## 5.20 Solid State Eletropolymerisation of Conducting Polymers

The electrochemical polymerisation of electrically conducting polymers has previously been performed using PEG as a solvent. Polymerisation in these low molecular weight, viscous liquids was found to be perfectly feasible. It was therefore decided to attempt polymerisation using higher molecular weight poly(ethylene oxide) [PEO], which is a solid at room temperature. Should this approach prove successful it should result in the formation of a material

suitable as an electrode formed directly onto a solid state electrolyte. As there has already been some interest shown in completely solid state polymer batteries, this technique may prove to be a useful innovation.

During the initial experiments a weight was placed on the top electrode and the polymerisation temperature was about 125°C. However this resulted in most of the film being extruded from between the two electrodes. A temperature between 90 and 100°C was therefore selected to allow sufficient conductivity in the electrolyte and no weight was applied other than the weight of the electrode itself.

This resulted in the formation of a PP film on the PEO film. However there was one problem. The PEO could be removed quite easily from the stainless steel, but the PP adhered strongly to the stainless steel surface. To overcome this an ITO conducting glass WE was used. PP is much easier to remove from this type of surface. This resulted in a film which could easily be removed intact. The film produced was a bilayer having a shiny, black, uniform PP film on one side and PEO on the other. The details of a typical experiment were as follows.

Area of WE = 1.327 cm<sup>2</sup>

Initial thickness of PEO film = 0.330 mm

Polymerisation Temperature = 99.8 ± 0.2°C

Constant voltage = +2.00V

Total charge passed = 24.5mC

Variation of current and thickness during polymerisation - Figures 5.21 and 5.22. It should be noted that the thickness here includes the PEO, ITO glass and PTFE and is therefore only an approximate guide to the behaviour of the PEO film. However, prior to polymerisation, the thickness reading had decreased steadily as the film was heated, due to slight extrusion.

The  $\text{CF}_3\text{SO}_3^-$  doped PP film had a conductivity of  $8 \times 10^{-5} \text{ S/cm}$  (4-point probe). This is rather low compared with earlier work ( $0.5 \text{ S/cm}$ ). The conductivity of the reverse side (PEO) was beyond the range of the 4-point probe ( $10^{-7}$ - $10^{-8} \text{ S/cm}$ ) and is likely to be of a similar value to that of normal  $\text{PEO}_{10}\text{LiCF}_3\text{SO}_3$  ( $10^{-10} \text{ S/cm}$ ). The PP film showed good stability when stored under vacuum as 15 months later its conductivity was  $2.5 \times 10^{-5} \text{ S/cm}$ .

Attempts were made to perform FRA and CV studies on this system. The experiment was performed as above, except that a thin platinum disc was used as the W.E. After polymerisation the platinum disc with PEO attached was removed and a PP film could clearly be seen through the PEO. However after a lithium disc was put on the PEO side to form a cell, which could be studied, the whole cell was found to have a resistance of greater than  $10^6$  ohms at  $80^\circ$ . This made sensible FRA and CV studies impossible. Clearly despite being very thin the PP film has had a profound effect here.

The polymerisation of MDT was also attempted by this method. However, only a few unconnected small black spots were produced.

FIGURE 5.21

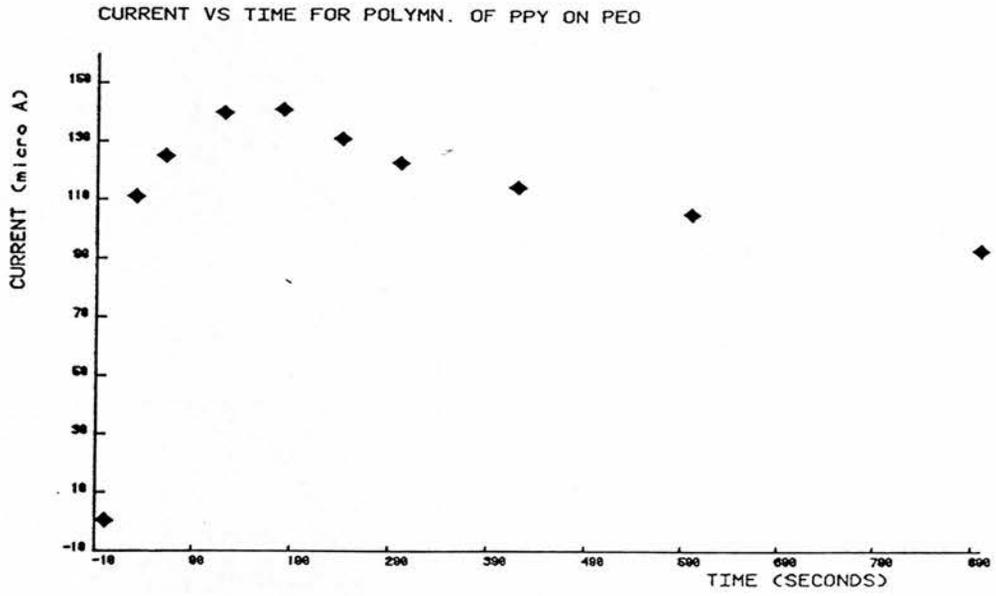
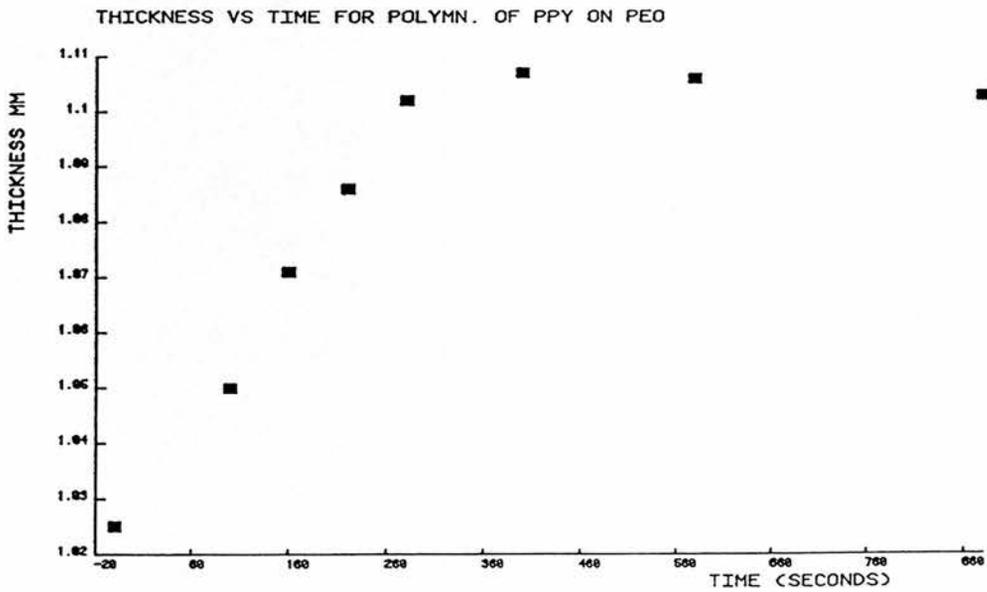


FIGURE 5.22



### 5.20.1 Conclusions

This technique would be very useful for the fabrication of solid state batteries. However, it could also be used for the polymerisation of some of the monomers already discussed in this thesis, ie. MDT and DPM. It had been shown much earlier that electrosynthesis of conducting polymers onto polymer electrolytes was possible<sup>[64]</sup>, using different techniques to those here. Recently PP/polymer electrolyte bilayers<sup>[65]</sup> were reported to have been formed by a similar method to that reported here. The reported conductivities of the PP was much higher (10-100 S/cm). There are two main differences between those experimental conditions and the conditions above: 1) the polymer electrolyte was different and 2) it is assumed that because of this, polymerisation could take place at ambient or slightly elevated temperatures. The effect of polymerisation temperature has been noted previously and one report<sup>[29]</sup> suggested that polymerisation above 80° resulted in insulating films. The drop in conductivity from the optimum value at temperatures below 80° is less than an order of magnitude, therefore polymerisation in the region 60-80°C using PEO may provide better results. The alternative is to use a polymer electrolyte which is conductive at lower temperatures. This area of work is worthy of further study.

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CHAPTER 6SUMMARY

The proliferation of interest in the electronic properties of quasi 1D conjugated polymers since Little's<sup>[1]</sup> innovative suggestion of the possibility of high temperature superconductivity and the pioneering work of Shirakawa<sup>[2]</sup>, has led to many new polymers being discovered which have interesting electrical properties. Indeed an astonishing amount of literature on this topic has surfaced since those early days, and as Feast<sup>[3]</sup> points out, the selection of data for even a large review is quite a challenge. This challenge was no less a task for the introductions to the various chapters of this thesis and it is hoped that a reasonable outline of the basic phenomena has been given.

An important part of this work concerns the measurement of electronic conductivities. The theory required, along with a description of the construction and operation of the various items of equipment used was given. These items of equipment were tested and found to be satisfactory for the tasks required of them. A prerequisite for the completion of the electrochemical experiments performed for this thesis, is to demonstrate that the equipment available may be used to measure the required parameters. This is best determined by comparison with known systems. Polypyrrole, PP was used for this purpose and the results were found to be in agreement with previously published papers.

Experiments on metal/polymer composites were performed initially to demonstrate the known theory of percolation in these materials and to test the equipment. This being successfully performed, the main issues of Al.PEO and polymer.PEO composites were tackled. Al.PEO composites, despite their potential, gave somewhat disappointing results. The presence of Al significantly inhibited the ionic conductivity of PEO and did not improve its mechanical properties to any extent. Also the percolation level with respect to electronic conductivity was quite high.

PAA.PEO gave more promising results, as although any improvements in mechanical properties could not be measured, the drop in ionic conductivity above the  $T_m$  of PEO was not significant. PAN.PEO composites gave similar results. Another interesting result was provided by the PEO.p-toluene sulphonic acid polymer electrolyte which appeared to give high ionic conductivities. However, more work would be required on this system to determine its usefulness.

There is some doubt as to the product of the reaction between pyrrole and formaldehyde. Performing this reaction under controlled conditions did not lead to the poly(pyrryl methane) suggested in the literature<sup>[4]</sup>. Red or pink solids were formed which were insoluble in common solvents and which tended to decompose at or below 150 C. Frequently carbonyl groups were found to be present, but even when absent, high oxygen contents were found. Most importantly these materials were found to be insulators both before and after exposure to dopant. Similar studies on the self-condensation of

pyrrole-2-carboxaldehyde and the reaction between thiophene and benzaldehyde also gave products with high carbonyl contents and low conductivities.

A more successful route was the self-condensation of thiophene-2-methylbromide to poly(thienylmethane), PTM. The conductivity of this polymer when doped ( $2.5 \times 10^{-5} \text{ S/cm}$ ) is similar to that reported for poly(aryl-methine)<sup>[5]</sup>, which suggests that PTM is in the methine form rather than methane. Whether the polymer is directly synthesised in the methine form, or changed to the methine from the methane as part of the doping process, is open to conjecture, but would make a good area for further study.

The monomers 2,2'-dipyrrylmethane DPM and 2,2'-dithienylmethane DTM were successfully synthesised. Chemical polymerisation of these monomers by known methods proved to be unsuccessful and consequently electrochemical techniques were employed.

DPM and, to a lesser extent, DTM both formed films on electrodes. Conducting polymers tend to present problems with regard to definitive analysis of their structure and these products proved to be no different, especially when yields were very low. Indeed, competing reactions take place with the formation of soluble biproducts (oligomers) being favoured. This problem is compounded by, or may be a direct result of, the moderate conductivity of poly(aryl methine)s; a point of some conjecture, but corroborated by recent studies<sup>[5]</sup>.

The oligomers produced by the reaction between thiophene and benzaldehyde were studied electrochemically. These oligomers did not form reactive radical cations/anions in the potential range studied and only reactions in solution took place.

The viscous, liquid, poly(ethylene glycol), PEG, was found to be a useful solvent for the electropolymerisation of heterocycles. Taking this trend of increasing viscosity to its ultimate conclusion led to PEO being used as an electrolyte. Hence the formation of conducting polymers in the solid state was investigated. Only partial success was achieved with these projects due to the high polymerisation temperatures which had to be used. Both PEG and PEO electrolytes have high resistances at ambient temperatures. A PEO-PP bilayer composite was formed, but the PP exhibited only moderate conductivity. Likewise only thin films of low/moderate conductivity were formed using PEG as a solvent. If alternatives to PEG and PEO, which exhibited low resistance at room temperature or below could be found, this field would appear to have a bright future, especially with regard to practical applications.

Many of the materials discussed herein have yet to realise their potential with regard to commercially significant applications; due to their history being very short. It is hoped that this thesis has contributed to the understanding of the diverse field of electroactive polymeric materials. When exploring new territory one often makes as many (if not more) losses as gains, but even time-consuming dead-ends can lead to a greater understanding of the topic and can provide ideas

for further, more fruitful experimentation.

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## APPENDIX I

Table I : Chemical structures of some Conducting Polymers.

<u>Polymer</u>	<u>Abbreviation</u>	<u>Structure</u>
trans-Polyacetylene	trans-PA	
cis-Polyacetylene	cis-PA	
Poly(paraphenylene)	PPP	
Poly(p-phenylene sulphide)	PPS	
Poly(phenylene vinylene)	PPV	
Polypyrrole	PP	
Polythiophene	PT	
Polyaniline	PANI	