Electroactive polymers from -substituted thiophenes

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How to cite:

Chissel, André Duncan (1989) Electroactive polymers from -substituted thiophenes. Doctoral thesis, Durham University.

ELECTROACTIVE POLYMERS FROM β-SUBSTITUTED THIOPHENES

by

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A Thesis submitted for the degree of
Doctor of Philosophy at the University of Durham.

August 1989

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DECLARATION

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Pour ma mère.

Schaffa, schaffa, Häusle baua
und net nach de Mädle schaua.

ABSTRACT

ELECTROACTIVE POLYMERS FROM β-SUBSTITUTED THIOPHENES

The work reported in this thesis can be broken down into three main areas. The first describes the synthesis of a series of β-substituted thiophenes bearing long, lipophilic chains (either ether, polyether or amido in nature). Cyclic voltammetry studies on the monomers revealed their oxidation potential but did not prove to be a successful method of electropolymerisation. This was achieved using constant current electrolysis and further studies involving FTIR, ESCA and SEM were carried out on the most highly conducting polymer. This polymer was also solution processible in its conducting form.

The second area also describes the synthesis of a series of β-substituted thiophenes, but this time the pendant side group consists of bulky phenoxy moieties (liquid crystals, phenol ethers and aminophenol ethers). In this case the cyclic voltammetry studies carried out did appear to provide a successful means of generating polymers.

Finally, the synthesis of a series of β-substituted thiophenes bearing pendant macrocyclic substituents (an N-0-5 cycle, an oxo-cyclam and a 14-0-4 cycle) are described. Their cyclic voltammetry behaviour is reported in detail and the results of experiments to determine metal ion selectivity is also described, in the case of the 14-0-4 cycle.

A.D. Chissel (August 1989)

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to my supervisors, Dr. D. Parker and Dr. M.R. Bryce, for their guidance, good humour and friendship throughout the course of this work.

I also wish to thank my colleagues from Labs. 29 and 27 for providing me with many happy memories, their companionship is sorely missed.

A debt of thanks is also due to all the technical staff at the University of Durham, especially those responsible for providing me with analytical data and equipment.

I am grateful to Professor G.W. Gray (University of Hull) for a useful discussion on the properties and uses of liquid crystalline materials, thereby aiding the progress of Chapter 3. In the same breath, I am also grateful to Mr. P.E. Nicholson (University of Durham) for providing me with a sample of 4,7-dioxa-1,10-dichlorodecane, enabling much of the work of Chapter 4 to be carried out.

I also wish to take this opportunity to thank Dr. P.J. Parsons (University of Southampton) for first, suggesting that I should consider a postgraduate course and second, for being instrumental in my obtaining a place here at Durham. Thanks Phil.

For the excellent typing of this script, thanks are due to my colleague and friend Dr. N.R.M. Smith.

In order to thank my mother for all that she has done would take more pages than there are in this thesis, I would, however, like to take this opportunity just to say "thanks" and "Tiens on dirait pas à le voir eh ?!"

At this point, a debt of gratitude should also be given to Dagmar Sigurdardottir for her love, companionship and continued friendship. Good luck with *your* Ph.D, Dagmar!

There are obviously many other people, too numerous to mention, that by rights also deserve my sincerest thanks for making my stay at Durham a very happy one. I would now like to take this opportunity to thank them all.

Finally, I wish to thank Cookson Group PLC, for financial support.

ABBREVIATIONS

A. POLYMERS

EAP	Electroactive Polymer
$(SN)_x$	Poly (Sulphur-Nitride)
$(CH)_x$	Poly (Acetylene)
PPP	Poly (Para-Phenylene)
PPPS	Poly (Para-Phenylene-Sulphide)
PMPS	Poly (Meta-Phenylene-Sulphide)
PMP	Poly (Meta-Phenylene)
PBT	Poly (Benzo-Thiophene)
PDTS	Poly (2,8-Dibenzo-Thiophene-Sulphide)
PP	Poly (Pyrrole)
PT	Poly (Thiophene)
PVDF	Poly (Vinylidene-Fluoride)
PVC	Poly (Vinyl-Chloride)

B. TECHNIQUES

SEM	Scanning Electron Microscopy
FTIR	Fourier Transform Infrared
ESCA	Electron Spectroscopy for Chemical Analysis
XPS	X-Ray Photoelectron Spectroscopy
IR	Infrared
NMR	Nuclear Magnetic Resonance
DSC	Differential Scanning Calorimetry
UV/Vis	Ultraviolet/Visible Spectroscopy
CV	Cyclic Voltammetry
FAB	Fast Atom Bombardment
EI	Electron Impact
DCI	Desorption Chemical Ionisation
MS	Mass Spectroscopy

C. CHEMICALS AND SOLVENTS

AIBN	Azo-bis-Isobutyro-Nitrile
TsCl	Para-Toluene Sulphonyl Chloride
KOH	Potassium Hydroxide

HCl	Hydrogen Chloride
Na_2CO_3	Sodium carbonate
RCOCl	Appropriate Acid Chloride
$MgSO_4$	Magnesium Sulphate
DEM	Diethyl Malonate
TATD	1,4,7,10-Tetra-Aza-Tridecane
N_2H_4	Hydrazine
TBAHFP	Tetrabutylammonium Hexafluorophosphate
Et_3N	Triethylamine
CuO	Copper Oxide
KI	Potassium Iodide
Li	Lithium
Na	Sodium
Cs	Caesium
K	Potassium
LiBr	Lithium Bromide
H_2	Hydrogen gas
N_2	Nitrogen gas
Pd	Palladium
C	Activated Carbon
Hg	Mercury
CCl_4	Tetrachloromethane
CH_3CN	Acetonitrile
THF	Tetrahydrofuran
DMF	Dimethyl Formamide
CH_2Cl_2	Dichloromethane
EtOH	Ethanol
H_2O	Water

D. ELECTROCHEMICAL

E	Measured Electrode Potential
E^0	Standard Electrode Potential
n	Number of Electrons
F	Faraday constant
R	Molar Gas constant
T	Temperature
mV	Millivolts
mA	Milliamps

s	Seconds
C.L.R	Coefficient of Linear Regression
ν	Scan Rate
E_{pa}	Peak Anodic Potential
E_{pc}	Peak Cathodic Potential
I_{pa}	Peak Anodic Current
I_{pc}	Peak Cathodic Current
$\|i_o\|$	Modulus of the Peak Current

E. EXPERIMENTAL

M.Pt	Melting Point
B.Pt	Boiling Point
mm	Millimetres
^oC	Degrees Centigrade
d	Days
h	Hours
min	Minutes
mmol	Millimoles
g	grams
M	Molar
mL	Millilitres
m/e	Mass/charge Ratio
%	Percent

F. OTHER

μ	Microns
Å	Angström
ISE	Ion Selective Electrode
HOMO	Highest Occupied Molecular Orbital
MO	Molecular Orbital
BASF	Badische Anilin & Soda Fabrik
RSC	Royal Society of Chemistry
OD	Outer Diameter
VPO	Vapour Pressure Osmometry
ONPOE	Ortho-Nitrophenyl Octyl Ether
KTpClPB	Potassium Tetrakis(4-Chlorophenyl Borate)
T_g	Glass Transition Temperature

SEAS	School of Engineering and Applied Sciences
PVD	Photo Voltaic Device
WRT	With respect to
K	Degrees Kelvin

CHAPTER TWO - β-LONG CHAINS 45

CHAPTER ONE

INTRODUCTION

1.1 INTRODUCTION

The majority of known organic materials are electrical insulators. Over the past decade, new organic materials with remarkable electrical properties have been synthesised. These new materials fall into three distinct categories:

I) Charge-transfer complexes

II) Metallo-organic assemblies

III) Conducting polymeric systems

and together they encompass the field of research known as "Organic Metals". All these categories have been the subject of books[1] and comprehensive reviews[2,3,4], but what follows will, in the main, only be concerned with the last category.

1.2 CONDUCTING POLYMERIC SYSTEMS[4]

Organic polymers, with conjugated π-electron backbones, display unusual electronic properties, such as low ionisation potentials and high electron affinities. The result is a class of polymers which can be reversibly oxidised or reduced more easily than conventional polymers. Charge transfer agents effect this oxidation or reduction and in so doing convert an insulating polymer into a conducting polymer. The emergence of conducting polymers as a new class of electronic materials has attracted considerable attention as they have led to the postulation of entirely new scientific concepts as well as offering scope for new technology. As polymers, these materials possess a quasi one-dimensional structure, making their ability to conduct electricity in one direction (parallel) far greater than the other (perpendicular). It is this anisotropy that makes these systems so fundamentally different from conventional electrical conductors or semi-conductors.

1.2.1 Poly (Sulphur Nitride) - An Intrinsically Conducting Polymer[5]

A key development in the evolution of organic conducting polymers, was the discovery that the inorganic polymer, poly (sulphur nitride) otherwise known as poly(thiazyl) or $(SN)_x$ was a metal[6]. That is, its electrical conductivity decreased with increasing temperature. The discovery that it was superconducting at low temperatures provided the impetus for the enormous amount of work necessary to synthesise other polymeric conductors[7]. The intrinsic conductivity arose from the presence of one unpaired electron associated with each sulphur-nitrogen unit (Figure 1.1).

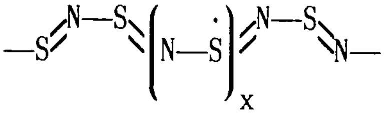

Figure 1.1 $(SN)_x$

This electron was free to move under an externally applied electric field. Although interesting, other physical properties did not lend to the polymer's commercial exploitation. $(SN)_x$ is itself unstable and was initially synthesised from explosive intermediates. However, further insight, which was to prove *highly* significant in the development of organic conducting polymeric materials, was the observation that the conductivity of $(SN)_x$ could be increased by reacting it with bromine or with other oxidising agents.[8]† The resultant polymer was no longer a

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†The use of the term "oxidising agent" or "reducing agent" when employed in the context of conducting polymers is generally referred to as "P-doping" or "N-doping" respectively. Although strictly not correct (see section 1.6.1) the term "dopant" is now accepted locution in the literature and will be used in this thesis.

neutral system but a polymeric cation (neutrality being maintained by the incorporation into the polymer of the reduced oxidant).

$$(SN)_x + 3/2y\ Br_2 \longrightarrow (SN)_x^{y+} + y\ Br_3^-$$

Figure 1.2 *$(SN)_x$ Doping.*

1.2.2 Poly(Acetylene) and Non-Intrinsically Conducting Polymers[9]

Poly(acetylene) (PA) or $(CH)_x$, first synthesised by Natta *et al* in 1958[10], provided the first example of a chemically synthesised *organic* polymer that could be reversibly doped (p or n) to form an electrically conducting polymer when exposed to dopants.

$$\text{OXIDATION (p-doped): } (CH)_x + 3/2y\ Br_2 \longrightarrow (CH)_x^{y+} + y\ Br_3^-$$

$$\text{REDUCTION (n-doped): } (CH)_x + y\ Li \longrightarrow (CH)_x^{y-} + y\ Li^+$$

Figure 1.3 *(CH_x) Doping.*

Two landmarks in its development came firstly, with the discovery of a synthetic route to mechanically strong, free-standing films of the polymer[11] and secondly, with the discovery that these films could be chemically doped (either p or n, see above)[12,13] to give highly conducting systems [$\sigma(273K) = 4.4 \times 10^{-5}$ to 38 S cm^{-1}].[12]‡

The undoped polymer itself could be prepared as either the *cis*[11] or *trans*[11] isomer, however, total isomerisation to the *trans* form could be achieved on heating (Figure 1.4)[14].

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‡Conductivity (σ) can be expressed as either reciprical Ohm centimetres (Ω^{-1} cm^{-1}) or Siemens per centimetre (S cm^{-1}). The latter term will be used throughout this thesis.

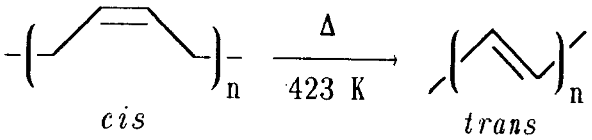


Figure 1.4 *$(CH)_x$ Isomerisation.*

The *trans* isomer is frequently viewed as the electronically active isomer of $(CH)_x$ for two reasons:

(1) The chemically doped conducting polymer is in the *trans* configuration, independent of whether the neutral starting polymer was *cis* or *trans*[15].

(2) In the pure form the undoped *trans* polymer is significantly more conducting [σ(rt) = 4.4×10^{-5} S cm^{-1}] than the *cis* [σ(273K) = 1.7×10^{-9} S cm^{-1}][12].

Neither of these observations [(1) and (2)], however, establishes unequivocally whether the *trans* configuration is required for conductivity, as the first is a consequence of a dopant induced isomerisation and the second is due to defects generated in the thermal isomerisation process.

The revelation that $(CH)_x$ could be electrochemically doped to provide an electroactive polymer (henceforth abbreviated to EAP in this thesis) of the same conductivity as chemically doped $(CH)_x$ was another significant landmark in the development of these new materials[16]. The material, $(CH)_x$ not only provided the first demonstration of an organic polymer that could be doped in this way, it also yielded the possibility of other systems being doped in a similar fashion. The efforts to understand the chemistry and physics of conducting $(CH)_x$ have, however, been hampered by its insolubility and low crystallinity and by impurities trapped in the polymer during the polymerisation process. All this has made traditional methods of polymer characterisation difficult. Progress in this direction was however made with the advent of a new route to $(CH)_x$ (Durham route) *via* a soluble precursor polymer (Figure 1.5).[17]

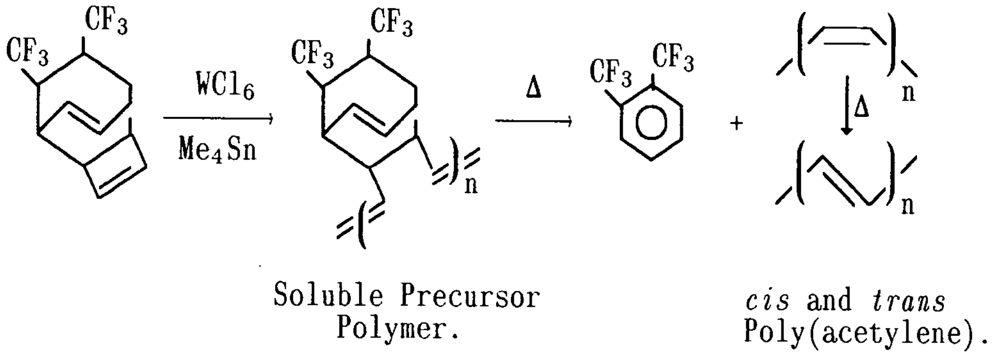


Figure 1.5 *"Durham Route" to Poly(acetylene).*

The soluble precursor polymer can be purified, paving the way for high yields of pure $(CH)_x$ and the commencement of characterisation studies. Although $(CH)_x$ is the most extensively studied[18] and to date the most highly conducting (σ_{rt} = 800,000 S cm^{-1}) of the organic polymers, $(CH)_x$[19] like $(SN)_x$ is an inconvenient material for commercialisation: it cannot be melt processed below degradation temperatures, it is insoluble in organic solvents and until recently has been unstable to air.

1.2.3 Poly (p-Phenylene)[20]

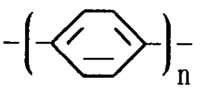


Figure 1.6 *Neutral Form of Poly(p-phenylene).*

The flurry of research into organic EAPs that was initiated by $(CH)_x$ led to the discovery that the chemically synthesised polymer, poly-(p-phenylene), (PPP) could also be reversibly chemically doped (p or n) to give the first example of an electroactive, non-acetylenic, hydrocarbon polymer[21]. When P-doped with AsF_5, the conductivity rose dramatically (from $\sigma_{rt} = 10^{-12}$ to 10^4 S cm^{-1}) and a colour change in the polymer from brown to metallic green was observed. Electrochemical doping of the chemically prepared polymer soon followed[22], but the drawbacks of its insolubility and non melt processibility again led to little progress in its commercial exploitation.

1.2.4 Poly-(p-Phenylene Sulphide)[23]

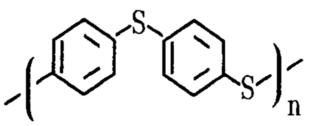


Figure 1.7 *Neutral Form of Poly(p-Phenylene Sulphide).*

Poly-(p-phenylene sulphide) (PPPS) is a commercially available melt and solution processible polymer which possesses a variety of uses as a thermoplastic[24]. Unlike $(CH)_x$ or PPP it is a non-rigid polymer that does not possess a continuous system of overlapping carbon π-orbitals. However PPPS provided the first illustration of such a system that could also be chemically (p) doped (reversibly) to form a highly conducting polymeric complex[25] (also with a concomitant colour change from tan to blue-black). The AsF_5 doped PPPS also provided the first example of a new *class* of conducting polymer. $(CH)_x$, PPP and poly(pyrrole) (*vide infra*) fell into the first class, *ie.* those that had undergone simple electron transfer upon doping to produce the conducting complex, whilst PPPS, and later poly-(m-phenylene sulphide) (PMPS) and poly-(m-phenylene) (PMP), were to fall into the second class, *ie.* those that exhibited *chemical modification* (carbon-carbon bond formation) when doped (Figure 1.8)[23].

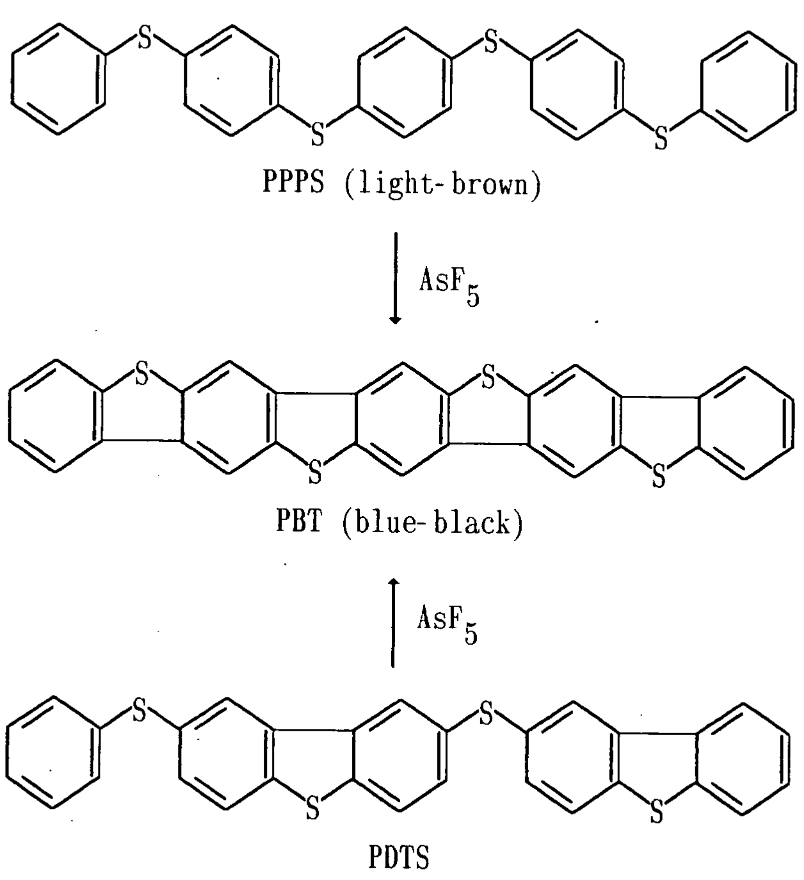


Figure 1.8 *Alternative Routes to the Electroactive Polymer Poly(benzothiophene).*

Both PPPS and poly-(2,8-dibenzothiophene sulphide) (PDTS) tended to form the fully bridged material poly-(benzothiophene) (PBT). PPPS was not only the first processible polymer to be made conducting but it was also the first system discovered to be *processible* in its conducting form (see section 1.9.4). Although this latter class of conducting polymer is now the subject of considerable research, what follows will only be concerned with the former class of conducting materials.

1.2.5 Poly(Pyrrole) and Other Poly Heteroaromatics[26]

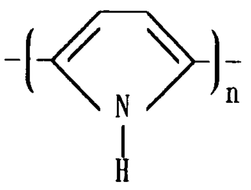


Figure 1.9 *Neutral Form of Poly(pyrrole).*

The non conducting chemically synthesised form of poly(pyrrole) (PP) or pyrrole black has been known since 1916[27]. Although first electrochemically synthesised in 1968[28], it was the improved electrochemical preparation by Diaz *et al.* in 1979[29] that afforded highly conducting (σ_{rt} = 100 S cm^{-1}), mechanically robust, free-standing films of the material. The extremely facile, one step method of entry into this new type of EAP, (incorporating simultaneous polymerisation with oxidative doping), starting directly from the monomer, meant that PP automatically became an attractive system for further study. Although electroactive forms of PP could also be generated by the use of chemical oxidants[30] (again starting from the pyrrole monomer) it was the electrochemically generated form that was more desirable. PP grown electrochemically also offered several advantages over the existing EAPs:

(1) PP was thermally and chemically more stable than $(SN)_x$ or $(CH)_x$, although stability was only conferred on the material in its p-doped state [no n-doped PP is ever likely *cf.* poly(Thiophene)][31].

(2) The possibility existed to modify the polymer backbone by the use of N and C_3 substituted pyrrole monomers.

(3) The electrochemical doping process allowed for the incorporation of various dopant anions to alter the physical and mechanical properties of the polymer[32].

(4) The level of doping could, in principle, be controlled electrochemically providing materials which spanned the entire range from insulator to conductor.

The colour change invoked by electrochemical switching of the polymer from its oxidised to neutral form attracted most interest in the form of optical switching devices (see section 1.8.3). The rapid progress that followed with PP led to the attempted electrochemical polymerisation of many other benzenoid and non-benzenoid molecules[33]. The results, were the systematic electrochemical polymerisation of a wide variety of monomer systems to give films which typically possessed good adhesion and electrical contact with the electrode surface. Arguably the EAP that offered the most promise for development in devices was another polyheterocyclic material, poly(thiophene) (PT)[3b].

1.2.6 Poly(Thiophene)[34]

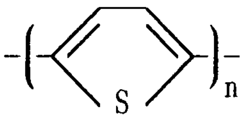


Figure 1.10 *Neutral Form of Poly(thiophene).*

Although electrogenerated PT was a relative late-comer to enter the conducting polymer field[35], it probably attracted the most attention as it was rapidly shown to offer advantages beyond those already established by PP:

(1) The synthesis of β-substituted thiophene monomers is far more facile than its PP analogue (see Chapter 2,3 and 4 of this work).

(2) The extent of oxidative doping could be made far higher than in the case of PP[36].

(3) As well as p-doped PT, n-doped PT was obtainable[37].

(4) PT was stable in its doped and neutral forms and was generally far more stable than PP[38].

Emphasis will now be directed towards the PT system and its derivatives with the mention of other systems where appropriate.

1.3 MECHANISM OF ELECTROPOLYMERISATION[39]

When the monomer M (M = thiophene, pyrrole *etc*) is electrooxidised to its radical cation ($M^{+\cdot}$) at the electrode surface, the electron transfer reaction that it undergoes is much faster than the diffusion of M from the bulk solution to the electrode surface. This means that only monomer molecules close to the electrode surface will be oxidised leading to a very high concentration of ($M^{+\cdot}$) at the electrode surface. This concentration is maintained by the steady state diffusion of M from the bulk. These monomeric radical cations can undergo a series of "follow up" reactions depending on their intrinsic stability[40].

$$M \longrightarrow M^{+\cdot} \longrightarrow \left\{\begin{array}{l}\text{Polymer}\\ \text{Radical cation diffuses away from electrode surface}\\ \text{Nucleophilic substitution product}\end{array}\right.$$

When ($M^{+\cdot}$) is relatively stable, it can diffuse away from the electrode surface and undergo reactions to form soluble low molecular weight oligomers. This type of reaction can be seen occurring at the electrode surface, and is attributed to the "streaming" of coloured material away from the electrode surface.

If ($M^{+\cdot}$) is very unstable it can rapidly undergo indiscriminate side reactions involving solvent molecules or the electrolyte itself, again to form soluble low molecular weight products. If the reactivity of ($M^{+\cdot}$) lies somewhere in between these two extremes, radical cation coupling and subsequent electropolymerisation can occur[33]. With electrochemically prepared poly(heterocycles), the polymerisation pathway seems to proceed *via* a "step growth" type process which appears to be general and can be depicted as follows (Figure 1.11).

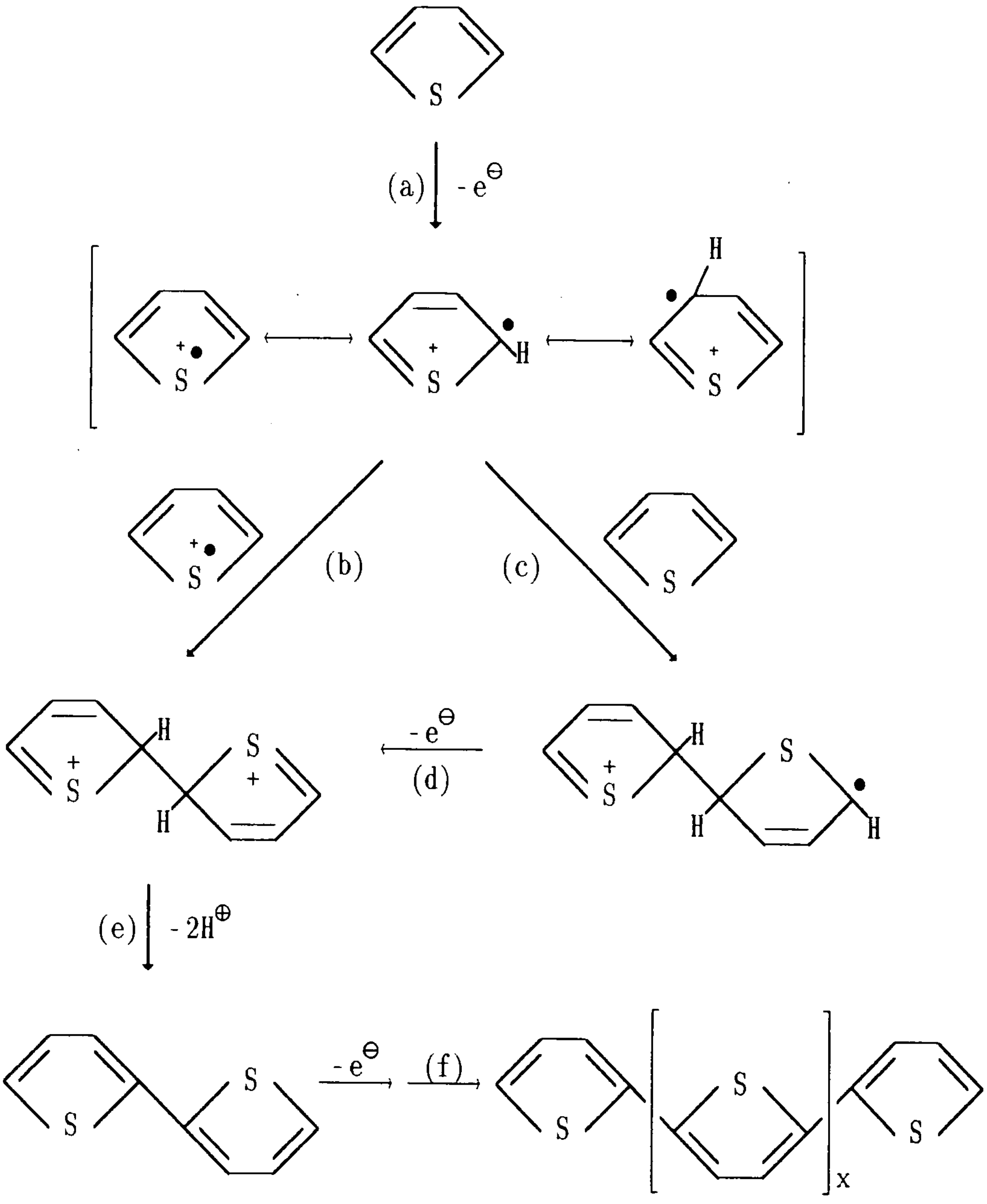


Figure 1.11 *Mechanism Proposed for the Electrochemical Polymerisation of Thiophene.*

After the initial oxidation step it could be argued that the radical cation could react like an electrophile and add to a neutral monomer (step c). This cannot happen for two reasons.

(1) It would lead to another radical cation (propagation) and imply continued polymer growth even after the curtailment of further electrogenerated radical cations.

(2) The concentration of un-oxidised monomer at and around the electrode surface is essentially zero so the coupling reaction must proceed *via* the coupling of two radical cations.

The electropolymerisation reaction therefore proceeds *via* an intermediate dihydro-oligomer dication (step b), which then loses two protons to form the neutral oligomer (step e). The observation that the pH of the solution becomes increasingly acidic supports this mechanism[26a]. As the oxidation potential of the oligomer is lower than that of the monomer, the former immediately electro-oxidises and undergoes further reaction with other monomeric radical cations (step f). Electropolymerisation is sustained because reactive monomer radicals are continuously produced. The chain growth is terminated either when the radical cation of the growing chain becomes too unreactive or, more likely when the reactive end of the chain becomes sterically blocked from further reaction. As indicated above, the electropolymerisation reaction proceeds with electrochemical stoichiometry *ie.* 2 electrons per monomer with 2n (where n = number of electrons) electrons being involved in the polymerisation process[39c]. The n values can be measured in several ways: one of the most convenient is from cyclic voltammograms utilising the Nicholson and Shane treatment for a totally irreversible reaction[41].

1.4 POLYMER STRUCTURE

The ideal structure of the five-membered heterocyclic polymers is depicted as being *α-α* linked when electropolymerised. The initial work to establish the coupling sites and to confirm that the monomer unit remained intact on electropolymerisation was performed with PP.

All of the measurements were indirect due to the poor crystalline nature of the polymer. However the following studies and conclusions were drawn: *α,α*-disubstituted pyrrole monomers failed to electropolymerise[42] but *β,β*-[43] or N-substituted monomers did[39c]. The oxidative degradation of these polymers led to α,α-disubstituted derivatives[44]. The tritiating of the α-α sites of pyrrole and subsequent electropolymerisation led to a polymer with a much reduced radioactivity, and also led to the first molecular weight determination of the polymer[45]. ^{13}C NMR analysis of the reduced forms of PP and PT were both consistent with the retention of the monomer moiety, as was IR data[46].

Having established the idealised structure of these systems as being α-α linked with preservation of the heterocyclic moiety[47], two conformations for these polymers existed (a) all *trans* and (b) all *cis* arrangements (Figure 1.12).

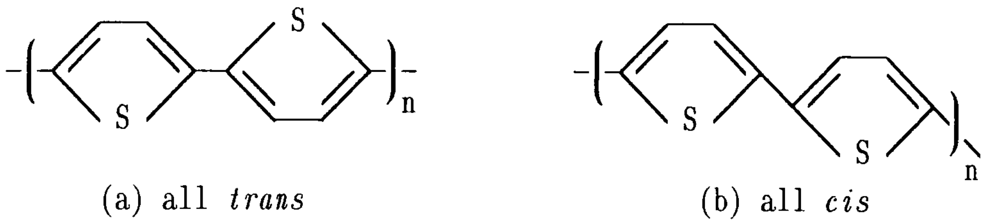
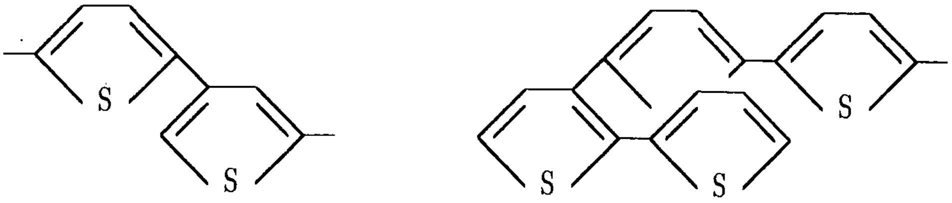


Figure 1.12 *Possible Conformations of Poly(thiophene).*

Street *et al.*[26a] believed that the all *trans* conformation (leading to a linear arrangement) best represented PP based on X-ray structures of the dimer and trimer. Tourillon believed that the all *cis* structure (leading to a helical arrangement) best represented PT based on UV vis observations[48]. The secondary structure of both these polymers is still the subject of debate.

1.4.1 Structural Disorder[20a,26a]

In trying to establish the coupling sites in these polymers, it soon became apparent that miss-linked and cross-linked α,β coupling of the radical cations occurred[49]. These deviations from stereoregularity were observed by X-ray photoelectron spectroscopy XPS[50] and NMR analysis[46def].



Mislinked α-β coupling   Cross-linked coupling

Figure 1.13 *Examples of Structural Disorder in Poly(thiophene).*

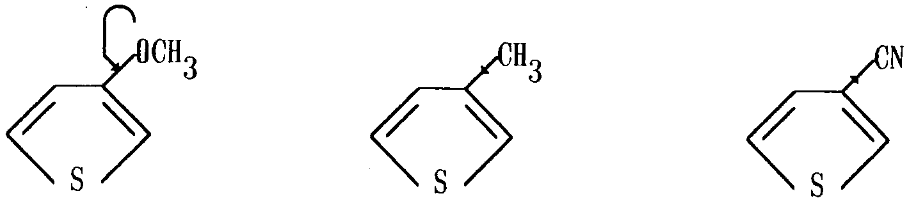
Waltman and Bargon reviewed the π-electron density of many neutral and oxidised (radical cation) organic monomers that electropolymerise in an attempt to explain this phenomenon[33]. In the case of pyrrole, they found that the π electron density of the radical cation was greatest at the α sites, supporting the hypothesis of initial α-α coupling of the radical cations. However, as the chain length of the corresponding oligomer grew, their calculations showed that π electron density at the β site became comparable in magnitude to that at the α site. This meant that radical coupling would no longer overwhelmingly be favoured at the α position. Their calculations demonstrated this important trend. However, the conclusion that they draw is only valid if the criterion for reaction is the unpaired electron density.

1.4.2 Substituent Effects

The stoichiometric electropolymerisation reaction that has just been described is not limited to the unsubstituted parent monomers (M); some substituted derivatives undergo electropolymerisation as well[51], provided the substituent does not dramatically affect the reactivity of the monomer. This substituent can affect the electropolymerisation in one of two ways: either by an electronic or a steric effect.

Electronic Effect

Electron donating groups, through either an inductive (*eg*. 3-methyl thiophene) or a mesomeric (*eg*. 3-methoxy thiophene) effect, tend to lower the oxidation potential of the starting monomer. This is achieved by the raising of the **HOMO** energy level in the monomer which may be associated with the "pumping" of the electron density into the monomer unit. Conversely, 3-cyanothiophene (see Figure 1.14) has a much higher oxidation potential than 3-methoxythiophene (lower **HOMO**) because the group acts inductively as an electron withdrawing group, "pumping" electron density out of the monomer. Generally, it is monomers of lower oxidation potential that yield better quality films with higher conductivities.



Electron Donating Group (Mesomeric).

Electron Donating Group (Inductive).

Electron Withdrawing Group (Inductive).

Figure 1.14 *Demonstration of Electronic Effects Associated With β-Substituted Thiophenes.*

Steric Effect

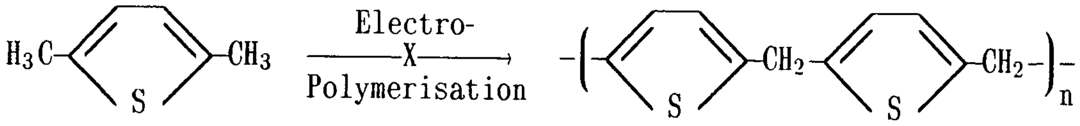
The introduction of any group into the *β* position of thiophene, be it mono-(*β*) or di-(*β*-*β*) substitution, reduces the opportunity for *α*-*β* coupling during the electropolymerisation process. This would therefore lead to a more stereoregular polymer with a correspondingly higher conductivity.

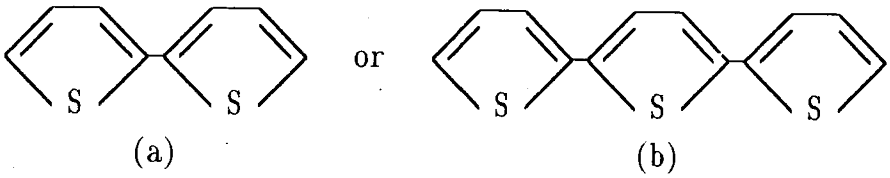
Both electron donating and electron withdrawing substituents when placed at the *β* position also reduce the possibility of cross linked polymer chains.

Another effect that helps determine the nature, morphology and conductivity of these polyheterocyclics is when the the monomer is substituted at the α position.

1.4.3 α-Substituted Monomers

α,α-disubstituted 5-membered ring heterocycles do not undergo electropolymerisation as both the sites of electropolymerisation are blocked[42].





(a) (b)

Figure 1.15 *Types of α-Substituted Thiophene Monomers.*

However, interesting polyheterocyclics can be generated if only one α site is "blocked" with for example another monomer unit *eg.* bipyrrole[53] bithiophene (a) or terthiophene (b)[54,55].

Critical evaluation of these substituted systems is still being undertaken especially to see how the resultant film (PT) differs from PT grown from thiophene itself[56].

The use of substituted monomers is not the only aspect that determines the properties of the resultant polymer film. Electrochemical aspects have to be considered[56b].

1.5 ELECTROCHEMISTRY[57]

The development of conducting polymers has been greatly influenced by the use of electrochemical techniques[58]. The success of the technique lies in the fact that electrogenerated polymers are usually coherent insoluble films that adhere well to the electrode. However, independent workers employing "identical" electrochemical conditions often fail to reproduce polymeric materials of the same quality and conductivity as those cited in the literature[59,60] even when using the same dopant anion. The problems of reproducibility are probably due to inconsistencies in six main areas.

1.5.1 Solvent Parameters[60]

The amount of water present in the solvent used can also adversely affect the film forming process. This has been shown to be the case with thiophene. Water (0.1M) can inhibit polymer formation entirely by the generation of a passivating layer on the working electrode. As some electrolytes can be difficult to dry this may explain why, in some cases, better polymeric films can be grown with a lower electrolyte concentration. S.E.M. studies of films grown under anhydrous conditions and those grown in the presence of < 1% water or other hydroxylic solvent also show differences. A rough surface is recorded in the former case and a smooth (more adherent) surface in the latter[60c].

1.5.2 Temperature Parameters[61]

The higher the temperature of the solvent during electropolymerisation the poorer the quality of the films produced. It appears that lower molecular weight, highly crosslinked PT results from polymerisation at elevated temperatures, however no explanation as to why this should be can be given at this time.

1.5.3 Dopant Parameters[62]

It would not seem unreasonable to assume that the type of anion incorporated into the polymer matrix would also affect the electrical properties of the film. For example, the size and charge on the ion would obviously play a role. Indeed, it has been demonstrated that the very nature of the ion incorporated into the polymer matrix may actually alter chemically after incorporation (see Section 2.7.1).

1.5.4 Monomer Parameters[63]

Work involving the effect of monomer concentration of the resultant polymer has shown that the higher the monomer concentration, the higher the likelihood of forming oligomers. This has a deleterious effect on the stereoregularity and mean conjugation length of the resultant polymer.

1.5.5 Film Thickness

Recently, studies investigating the relationship between film thickness and conductivity have claimed that the conductivity increases to an upper limit (*ca.* 2 x 10^3 S cm^{-1}) as the film thickness grows, before decreasing to almost zero. S.E.M. studies on these films at various thicknesses have shown that the morphology of the polymer films evolve towards an increasing disorder as the thickness increases.

1.5.6 Working Electrode[64]

The preparation, cleaning and type of working electrode also seems to play a significant role in deciding whether or not an adherent polymeric film is produced. Various cleaning procedures and preparation processes have been used but no universal system of working electrode preparation has yet been suggested.

In conclusion, therefore, the technique of electrochemically growing conducting polymeric films, although having gained a good reputation as a facile "method of choice", still presents problems when it comes to reproducibility. However, these studies outlined above have not only helped elucidate the optimum conditions for the electropolymerisation process but they have also accounted for many of the observed inconsistencies shown to exist in the literature.

1.6 CONDUCTION IN EAPS‡†

1.6.1 Doping - the chemical modification of a polymer.

It is generally recognised that for an organic polymer to support electronic conduction the polymer must contain an overlapping set of π molecular orbitals to provide reasonable "carrier mobility" along the

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‡†A more rigourous mathematical approach is given by Moragher (reference 65)

polymer chain. As most organic polymers do not possess intrinsic charge carriers, appropriate charge carriers must be provided by some external source. It was initially thought that the generation of charge carriers in EAPs by "doping" was analogous to the doping of extrinsic semiconductors. This assumption was soon challenged by the discovery that doped conducting polymers could display conductivity which was not associated with unpaired electrons[63]. The partial oxidation or reduction of an organic polymer to generate an EAP is often referred to as doping by analogy with that of an inorganic semiconductor. This is rather misleading when taken in the context of semiconductor physics because doped organic conductors are very different from their inorganic counterparts. Organic conductors possess a much higher doping level several percent units (see section 1.7.3) as opposed to parts per million for their inorganic analogues. EAPs also possess the ability to conduct electricity in one direction (parallel) in preference to any other (perpendicular). This is referred to as quasi one dimensionality and it also makes them very different from their inorganic analogues. Doping of polymers is better seen as a chemical modification of the polymer. It results in the perturbation of the polymer framework, not only due to the physical size of the dopant but also because of the extensive charge transfer which takes place between the polymer chain and the dopant counterion. This causes changes in the geometry of the polymer chain and it is believed that this geometric modification leads to the generation of polarons and bipolarons (*vide infra*). These are believed to be the source of charge carriers in organic conductors. It is with $(CH)_x$ and the concept of the soliton (leading to polaron formation at low doping levels and bipolarons at higher doping levels) that the development of a general principle of conduction for EAPs was defined.

1.7 SOLITONS, POLARONS AND BIPOLARONS[66]

1.7.1 Soliton Formation

It is generally accepted that the carbon-carbon bond lengths alternate along the *trans*-$(CH)_x$ chain. The reason for this lies in terms of a Peierls instability, leading to dimerisation. As a result two degenerate resonance forms of *trans*-$(CH)_x$ exist (Figure 1.16).


Phase (A)

Phase (B)

Figure 1.16 *Degenerate Forms of* $(CH)_x$.

This leads to two energetically equivalent potential energy wells for the isomers (Figure 1.17). This degeneracy is unique amongst conducting polymers and has the consequence that the polymer chains can support stable defects in the bond alternating sequence leading to the formation of neutral solitons.‡‡

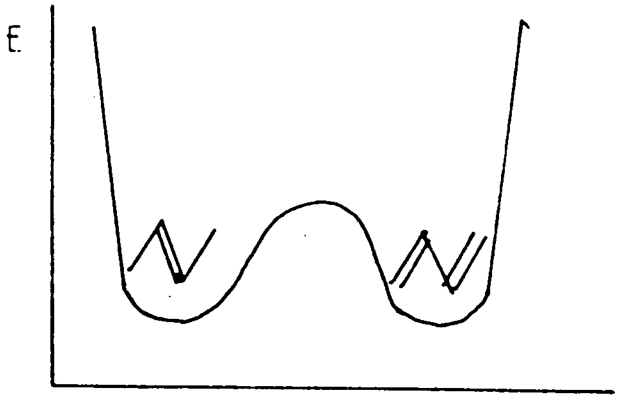

Figure 1.17 *Potential Energy Wells Demonstrating* $(CH)_x$ *Degeneracy.*

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‡‡The term *soliton* is derived from solid state physics, as too are *charged soliton*, *polaron* and *bipolaron*. To the chemist these four terms are known respectively, as radical, radical ion and a doubly charged ion.

The spin density of the soliton is not localised on one carbon atom but spread over several carbons ($\sim$ 14-15), this gives the soliton width^{67} (Figure 1.18).

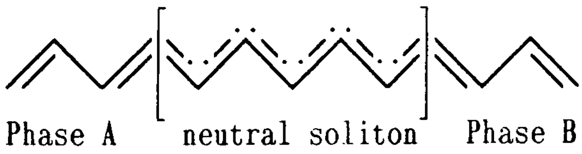

Figure 1.18 *Soliton Formation Within (CH)$_x$.*

The soliton defect can only be created on long conjugated polymers. Topological considerations require that they are created in pairs, so that a sequence greater than 30 carbon bonds would be required to observe well separated and mobile soliton defects [this prerequisite is not satisfied in Durham (CH)$_x$ but probably is in Shirakawa (CH)$_x$]^{67}.

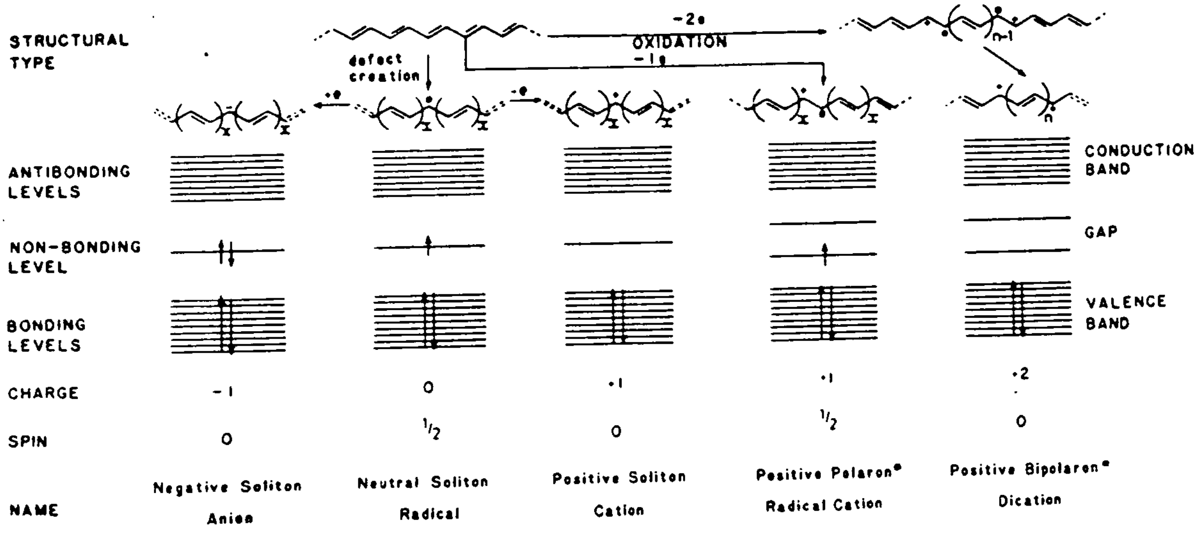

Figure 1.19 *Band Structure and Electronic Configuration for Species Implicated in Conduction Mechanisms in Conjugated Polymers, illustrated for poly(acetylene); *Negative Analogues via Electron Addition.*

Starting from one side of the soliton defect the double bonds gradually get longer and the single bonds shorter so that on arriving at the other side the bond alternation has been reversed. The resulting topological excitation has led from one phase (A) to the other (B). The molecular orbital occupied by the soliton is a localised non bonding orbital midway between the bonding and antibonding orbitals (Figure 1.19).

1.7.2 Polaron Formation

The case for oxidative doping will be described (a similar procedure can be used for reduction doping). On doping, electrons are removed from the HOMO (soliton MO) leading to mobile charged solitons (spinless) in the polymer. If a charged soliton interacts with a neutral soliton the two species combine to form a species possessing spin called a polaron. These are immobile and pinned to the site of formation (see Figure 1.19). Polaron formation is favoured over charged soliton formation, but owing to the presence of an energy barrier to soliton:charged soliton recombination, polarons and charged solitons can coexist at low doping levels. Polarons can also be generated by the removal of an electron from the bonding π orbitals. Either way the generation of a polaron distorts the polymer lattice around the ionisation site and leads to two localised MOs just above and below the bonding and antibonding orbitals of the polymer (see Figure 1.19).

1.7.3 Bipolaron Formation

Additional doping leads to the polymer chains being ionised still further with the result that polaron density increases. This results in the development of a band structure and the formation of bonding and antibonding polaron states (see Figure 1.19). Polaron-polaron interactions increase and if they combine they form bipolarons (spinless charge carriers).

Because both phases in $(CH)_x$ are degenerate, bipolaron formation is not favoured and instead two charged ions become free to move up and down the polymer chain. In the case of any other EAP, the degeneracy is lifted (Figure 1.20) and bipolaron formation is favoured. Thus soliton formation is confined to $(CH)_x$.

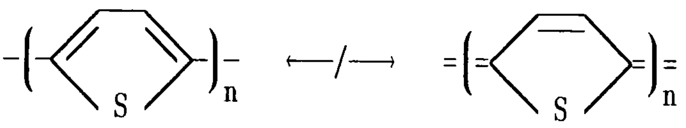

Figure 1.20 *Degeneracy is Lifted in the Case of Poly(thiophene).*

Poly(thiophene) (and its derivatives) possess a non degenerate ground state (above), so soliton formation is not likely. It has been suggested that the stable defect states formed upon doping are polarons (< 1% doping) and/or bipolarons (> 1% doping) depending on the doping level. Evidence to support the existence of both types of defect has been obtained[1c] (Figure 1.21).

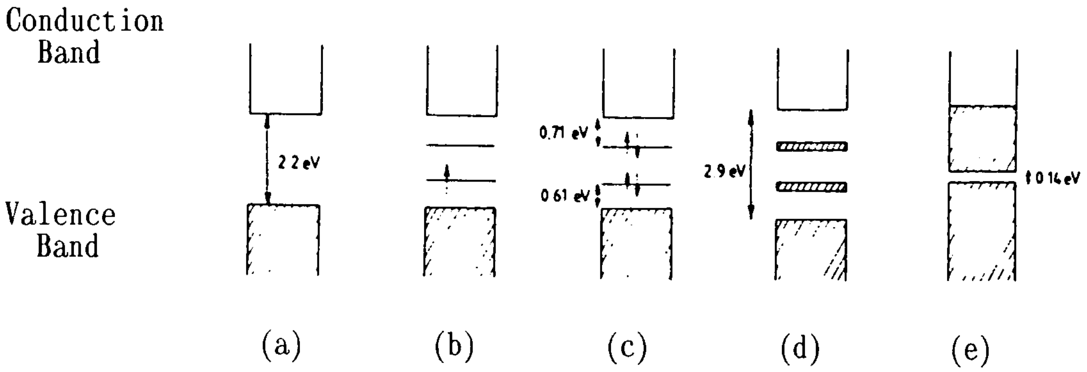

Figure 1.21 *Evolution of the Band Structure of Polythiophene Derivatives on Doping; (a) undoped; (b) 0.1% doping level with polaron states in the gap; (c) few percent doping level, with appearance of bipolaron states; (d) 30% doping level, where the bipolaron states overlap and form two bands and (e) hypothetical 100% doping level, with quasi-metallic behaviour.*

1.7.4 Charge Transport

Although the generation of charge carriers has been discussed with models of conduction on a microscopic level, models to explain macroscopic charge transport tend to conflict with each other and all involve "idealised" systems *eg.* pristine $(CH)_x$ and infinite chain length, which do not exist in reality. However, interchain transport of one or all of the species mentioned has to occur and hopping mechanisms and tunneling mechanisms have been proposed[68].

1.8 APPLICATIONS[69]

The discovery and rapid development of electroactive polymers in the late 1970s and early 1980s offered great possibilities for a new class of material, one that would combine the typical properties of plastics with the electrical conductivity of metals. The prospect of developing processible EAPs that enjoyed the desired mechanical properties and corrosion stability associated with plastics provided much of the impetus for their commercial development. Industrially sponsored research into these materials led rapidly to a wealth of patent literature on the subject and much media speculation into the uses of these materials[70]. However today it seems that many of these uses have been prematurely claimed. The practical realisation of all the enumerated applications based on conductivity depend on the stability of the conducting polymers under environmental conditions[71]. The problem of stability has yet to be overcome along with the problem of processibility, although significant improvements in this area have been made (see section 1.9). Also the employment of existing technologies to provide electrical conductivity to polymer surfaces are so economical and well established that it seems unjustifiable to produce a commercially competing EAP. These dilemmas have contributed to a shift in emphasis concerning the commercial exploitation of these materials.

Their development purely for their conduction properties is no longer the primary objective[72]. Commercially significant applications for EAPs are also likely to stem from their other unique properties, the exact combination of which is not offered by any other material.

1.8.1 Applications Exploiting Conductivity[69c]

The present methods of arc spraying metallation and the use of carbon black filled resins or polymers to provide conducting materials either do not provide uniform conductivity throughout the sample or are not "high performance" systems. So immediate markets exist for the development of new materials which fulfill these two criteria. These can be subdivided as follows:

Electric Power Distribution

A market exists for the provision of conducting sheathing for electrical power cables. At present composites of poly(ethylene) and poly(propylene) containing dispersed carbon black are used. Breaks in uniformity of dispersion of the carbon causes power loss and eventual cracking of the sheathing. As an EAP acquires its conductivity by virtue of its molecular structure, a more uniform conductivity may be available making EAPs a promising alternative.

Antistatic Equipment

The rapid development of the microelectronics industries and changes in the U.S. Governments legislation regarding limits on the levels of interference an electronic device could be subjected to, put pressure on manufacturers to develop new packaging materials, and EAPs have been considered. However, in this field, it still seems unlikely that EAPS will be able to compete with existing materials.

Electromagnetic Interference Shielding (EMI)

A ramification of the electronic conductivity of these materials is their ability to absorb energy at low frequencies. EMI shielding devices were therefore considered a major market for EAPs but the further development in existing technology again eradicated their use in this area. However, extremely effective EMI shielding is unobtainable using conventional technology. This fact coupled with the interest in the use of EAPs to shield electronic equipment against electromagnetic pulses (generated by thermonuclear devices) has meant a continued interest in this area, notably by the defence establishments.

1.8.2 Photovoltaic Devices (P.V.Ds)[73]

Three major areas of application of EAPs in PVDs have been considered.

(1) Their use in the protection against photocorrosion of inorganic semiconductors possessing small band gaps.

(2) The enhancement of oxygen evolution on photo anodes *via* catalysts supported on EAPs.

(3) The use of EAPs as semiconductors in PVDs.

Studies have shown that the problem of photocorrosion can be partially alleviated by the use of EAPs[74]. The high conductivity and high internal surface area of an EAP impregnated with catalysts have enhanced oxygen evolution. However low quantum efficiencies (< 1%) have hampered their use as semiconductor elements.

1.8.3 Applications exploiting the electrochemical reversibility

Electro-optic Devices[75,76]

It is known that thin films of PP and PT change their colour reversibly upon oxidation and reduction. This had led to their potential use in display devices. EAPs would offer several advantages over LCDs *viz.* better optical contrast, wider viewing angles and lower power consumption. These novel optical properties may also be harnessed in fibre optic technology and erasable optical recording devices[77].

Rechargeable Batteries[1d]

The reversibility of electrochemical doping associated with EAPs provides the potential for their use in rechargeable (or secondary) batteries. The types of battery under consideration are the *double polymer* array and the *metal polymer* array[77].

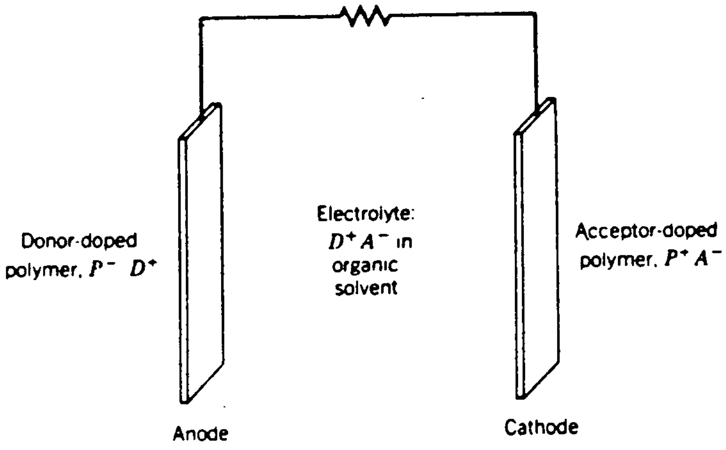

Figure 1.22 *Typical Double Polymer Array.*

Once charged, the double polymer array would behave as a typical battery, the redox reactions being:

$$\text{Anode:} \quad P^-D^+ \rightleftharpoons P + D^+$$

$$\text{Cathode:} \quad P^+A^- \rightleftharpoons P + A^-$$

Figure 1.23 *Electrode Processes for a Double Polymer Array Battery.*

The dopant ions would diffuse in and out of the polymer without changing oxidation state.

Metal Polymer Array

The other type of battery being considered is one where an EAP functions as either the cathode or the anode and a metal (typically lithium) acts as the other electrode. This latter arrangement is the most promising design at this stage of development and would allow polymers that are not amenable to donor doping (*eg.* PP or PA) access as the cathodic element in a battery. The redox reactions in a charged polymer/metal cell (*eg.* lithium) are:

$$\text{Anode:} \quad Li^0 \underset{e^-\ \text{charge}}{\overset{e^-\ \text{discharge}}{\rightleftharpoons}} Li^+$$

$$\text{Cathode:} \quad P^+A^- \rightleftharpoons P^0 + A^-$$

Figure 1.24 *Electrode Processes for a Metal Polymer Array Employing a P-Doped Polymer.*

In a cell employing a donor doped polymer electrochemical doping of the polymer occurs during the discharge cycle.

$$\text{Anode:} \quad Li^0 \underset{e^-\ \text{charge}}{\overset{e^-\ \text{discharge}}{\rightleftharpoons}} Li^+$$

$$\text{Cathode:} \quad P^0 + Li^+ \rightleftharpoons P^-Li$$

Figure 1.25 *Electrode Processes for a Metal Polymer Array Employing an N-Doped Polymer.*

The advantages of such batteries would be their weight, up to ten times lighter than conventional lead-acid batteries. Also, they would in principle be sufficiently flexible to fit into a variety of design configurations. However problems such as self discharging and insufficiently high doping levels, coupled with the stability problems of the electrolyte and solvent have delayed the entry of these high technology batteries into the market place‡††.

1.8.4 Commercially Available EAPs

Poly(vinylidiene fluoride) (PVDF) is now an established[78] piezo-electric and pyroelectric thermoplastic (Figure 1.26).

$$-(CH_2-CF_2)_n-$$

Figure 1.26 *Structure of PVDF.*

It is incorporated into several products. Although the homopolymer itself is not conducting it is rendered active on stretching. The two deficiencies of PVDF are its piezoelectric charge coefficient, which is lower than that of conventional ceramic materials and its low maximum continuous working temperature (70^oC). The only documented commercial application of a true EAP to date is that of an electrostatic brush in copiers made by the Xerox corporation. This dearth in the current number of commercially available EAPs is the subject of the following section (see section 1.9).

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‡††R.S.C. Annual Chemical Congress, 1988, Professor Naarman (BASF) in collaboration with "Varta" produced what he described as a poly(pyrrole) battery which was the first of its type.

1.8.5 Further Applications[79]

New applications of EAPs could be opened in the field of modified electrodes for electrochemical reaction catalysts[80] or chemical sensors[81] (see also Chapter 4). Viable p-n junction diodes[82] and field effect transistors[83] are also entering the arena.

Although many applications of conducting polymers have been proposed, publicised demonstrations have been few. Only two classes of polymer described are now materials of commerce. At this time much work still needs to be done to develop EAPs which are stable and economical to use[84]. However the viability of EAPs has been amply demonstrated and it is only a matter of time before more of these materials enter the market.

1.9 PROCESSING METHODS FOR ELECTROACTIVE POLYMERS[4h,85]

Most of the interest in EAPs has stemmed from their technological applications. However, practical adhibitions of these materials have been extremely limited[86]. This has been due in part to their environmental instability and unsatisfactory mechanical properties. However, in the main, their commercial exploitation has been hampered by their intractability. Attempts to address these problems without unacceptable losses in conductivity have led to several approaches towards the development of melt or solution processible EAPs. Most efforts have been directed towards solution processible materials. Scientifically, solutions can produce well resolved analytical data thereby aiding in the elucidation of molecular configuration and structure. They also provide an amenable form of processing, similar to conventional plastic processing technology. With these views in mind, a summary of the methods employed to fabricate processible EAPs will be presented.

1.9.1 Soluble Pre-Polymer Routes

Ample precedence exists for the solubility of neutral, conducting polymer precursors[17,87] (see also section 1.2.2). This alternative approach to processing has been applied in several cases where a neutral precursor to the doped complex can be dissolved and cast. The cast films can then be *treated* (*eg.* the procurement of heat) to leave the as-cast, neutral target polymer. These neutral films or fibres upon exposure to dopants lead to the final conducting material. Solution cast blends of soluble pre-polymers with other polymeric materials have also been obtained[88]. Heat treatment, followed by doping, once again leads to an electroactive material. Unfortunately the disadvantage of the prepolymer route is that once "treatment" or doping has been effected (even when blended) no further processibility is possible.

1.9.2 Copolymers[89]

When one species of monomer is used in polymer generation, the product is referred to as a *homo*-polymer. If the polymer units are composed of two types of monomer, this polymer is called a *co*-polymer. Copolymers in general exhibit physical and mechanical properties far different from those of the parent homopolymer. Four main types of copolymer exist:

(1) Random - [ABBAAABABB]- where the distribution of the two monomers in the chain is essentially random.

(2) Alternating - [ABABABAB]- with a regular replacement of each monomer along the chain.

(3) Block -[AAAABBBB]- consisting of substantial sequences of each monomer.

(4) Graft -[BB(AAA)BBB(AAA)B]- where blocks of one monomer are grafted onto another.

In general block and graft copolymers possess the properties of both homopolymers whereas the random and alternating structures have characteristics which are more of a compromise between the the extremes. Inspired by the expectation of producing processible EAPs exploiting the copolymerisation technique, the synthesis of random, block and graft copolymers were pursued.

Random Copolymers

Chemically synthesised copolymers of acetylene with other acetylenic moieties[90] (whose homopolymers were soluble)[90c,91] were amongst the first attempts to develop tractable copolymers using this technique. The physical and electrical properties of the product copolymers were heavily dependent upon composition (this being measured indirectly *via* comonomer feed ratios), a feature which has been reflected throughout the entire area of copolymerisation, irrespective of the nature of the starting comonomers. The most environmentally stable and most conducting (σ_{rt} = 50 S cm^{-1}) were those random copolymers with the highest acetylenic content whilst those that tended towards solution processibility (and poor conduction) were the ones with the highest copolymer content.

The chemical copolymerisation of thiophene has also been the subject of many reports[92] (Figure 1.27). Although all copolymers were reported to be solution processible in the neutral state no reports of processible copolymers in the conducting state were given. Molecular weights (determined by either VPO, GPC or end group analysis), like conductivity values, have increased dramatically for these materials, from the earliest reports by Yamamoto *et al.*[92a,b] ($\sigma_{rt} = 10^{-4}$ S cm^{-1}, molecular weight = 1370) to the most recent by Elsenbaumer *et al.*[92d] ($\sigma_{rt} = 50$ S cm^{-1}, molecular weight ≥ 2500). All these copolymers also enjoyed good environmental stability and were a major step towards the commercial realisation of these materials.

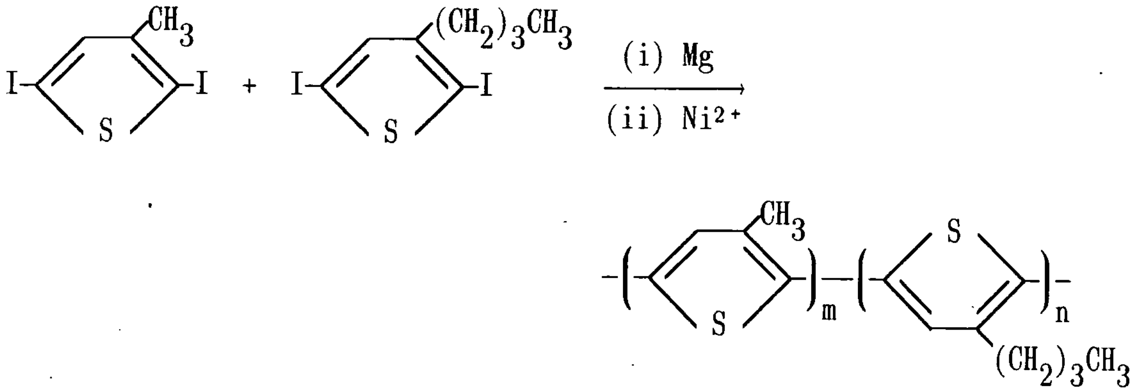

Figure 1.27 *Demonstrating the Typical Methodology for the Synthesis of Thiophene Copolymers - Poly(3-methyl thiophene-co-3'-n-butylthiophene).*

Early studies of electrochemically grown random polymers were hampered because *direct* analysis of the copolymer compositions, like those grown chemically, was not possible[93]. Estimates of composition had previously been made by electrochemical techniques or by comparisons of monomer feed ratios within the electrolyte. Direct analysis was later made possible and has since shown that feed ratio, as a measure of polymer composition, may only be reliable for monomers of similar oxidation potential[94]. Other work on electrogenerated copolymers of this type[95] seems to confirm this finding, even when the starting monomers are not homologues of the same heterocycle[96].

Block Copolymers

The only attempts at chemically generating, solution processible block copolymers, have been the diblock copolymers of $(CH)_x$[97]. Wnek *et al.* demonstrated that blocks of $(CH)_x$ incorporating the soluble carrier polymer, poly(styrene), yielded an insulating but solution processible material[98]. Further work by Aldissi *et al.* led to a $(CH)_x$-poly(isoprene) block copolymer that was solution processible and electroactive (σ_{rt} = 1-10 S cm^{-1}) when doped[99,100]. He also demonstrated a chain length conductivity correlation for electroactive block copolymers (Figure 1.28).[99-102]

CHAIN LENGTH: CONDUCTIVITY CORRELATION IN BLOCK COPOLYMERS	
SHORT ANIONIC CHAINS	NON SOLUBLE COPOLYMER FILM THAT BECOMES SOLUBLE WHEN DOPED.
ANIONIC CHAINS OF MEDIUM LENGTH	SOLUBLE COPOLYMERS BECOME CONDUCTING WHEN DOPED.
LONG ANIONIC CHAINS	SOLUBLE COPOLYMERS REMAIN INSULATING UPON DOPING.

Figure 1.28 *Chain Length Conductivity Correlation for Electroactive Block Co-Polymers.*

Electrogenerated copolymers of this type have been sparse as monomer "blocks" have first to be synthesised and should ideally have similar oxidation potentials to each other.

However, the synthesis of a diverse range of monomer blocks is now available and it seems that electrogenerated block copolymers will soon enter the literature[103]. Although block copolymers have been successful in some respects *viz.* processibility with conduction, the problem of environmental stability [especially with $(CH)_x$] persists.

Graft Copolymers

Graft copolymers of electroactive materials have been synthesised by a variety of methods[104]. Those generated chemically have involved the grafting of $(CH)_x$ segments onto the backbone of poly(isoprene)[104a,b], poly(styrene)[104a,b] or poly(butadiene)[104c] in a more or less systematic manner. All the copolymers were stable and soluble. However, no conductivity data have been reported on any of these materials. Graft copolymers involving polyheterocycles have been synthesised by a combination of chemical and electrochemical procedures[104d]. Although this provided a general method of entry into graft copolymers of this form with good conductivity, (σ_{rt} = 50 S cm^{-1}) solution processibility and environmental stability were not forthcoming.

1.9.3 Composites and Blends[105]

Another method of developing polymeric materials that could combine the desirable properties of one system (*eg.* mechanical strength, conductivity *etc.*) with those of another (*eg.* processibility and stability *etc.*) is the intimate mixing of the two or more systems. The main methods of providing such homogeneous dispersions of materials are summarised below:

(1) In-situ polymerisation
(2) Mechanical mixing of polymers in the melt
(3) Casting blended polymers from solution

Method (1) gives rise to composites, whilst methods (2) and (3) give rise to blends.

Insitu Polymerisation

Considerable effort has been devoted to improving the mechanical properties and processibility of EAPs by the employment of insitu polymerisation methods. The process first requires the homogeneous dispersion of a monomer within the matrix of a host polymer. This is then followed by polymerisation of the monomer either chemically or electrochemically to form a composite. The requirements of the host polymer are that it should possess superior mechanical properties to the polymer held within its matrix and that it should also possess the ability to swell when immersed in solution. This is to allow the monomer greater diffusional access into the host polymer matrix. In the case of electropolymerised composites it also allows for electrical contact to be established between the electrode surface and electrolyte solution.

Early work demonstrated that acetylene could be chemically polymerised within matrices of catalyst impregnated thermoplastics[106] and elastomers[107]. Good conductivity of the materials was achieved on doping. Composites of PA and $(CH)_x$ were also synthesised[100].

While the mechanical properties of all these materials were enhanced, their stability was not. To combat this deficiency, further work in the area centred around composites of PP. Results indicated that the electrogenerated composites did indeed show a marked improvement in stability and mechanical strength[108]. Other features of note were to emerge from these studies. The control of the electropolymerisation time, for example, led to the formation of composites that could be conductive of one side or both. Although the conductivity of the composites has proved similar to that obtained for PP alone (σ_{rt} = 50 S cm^{-1}) the conductivity was not uniform throughout the composite. Further processing of these materials has not been reported. Attempts to obviate the problem regarding the lack of homogeneity of conduction have partially been met by the prior blending of the host polymer with the electrolyte before electropolymerisation[109]. Furthermore attempts to solve the problem of processibility have led to the polymerisation of pyrrole in the presence of lattices[110]. The resultant composites can be ground into small pieces and swollen with shear to give dispersions which can be solution cast to give films with the retention of conductivity (σ_{rt} = 10^{-3} to 10^{1} S cm^{-1}). Another problem with the use of composite materials is that there is no binding (chemical or physical) between the two polymer matrices; this limitation presents problems in the use of such materials in solvents where the host polymer is soluble. The use of polymeric ionomers as the host polymer circumvents this problem and has been reviewed recently[95b]. The involvement of chemically generated composites has led to claims of increased conductivity of the composite PP over chemically generated PP alone[111]. Work has also started on composites of PT[112]; however, although the literature is full of composite electroactive materials, real progress towards processibility and hence applications, once again has not been forthcoming.

Mechanical Mixing in the Melt

In order for this technique to be practicable, the thermal stability and miscibility of the polymers to be blended must be guaranteed. This approach has therefore met with limited success when applied to EAPs. However, Walton *et al.* have developed an electrochemical technique whereby heat-processible conductive films of PP can be fabricated[113]. This has been made possible by the novel use of anodically derivatised polymers as the dopant in the electrochemical synthesis. Another successful method comprised the melt blending of the thermally stable polyphthalocyanines with high performance polymers[114]. However, in general, melt processed blends have not been materials of choice.

Casting Blended Polymers from Solution

Progress in this area has been restricted until recently, even though solution processible polyheterocycles have been claimed since

1983[92a,b]. The first reported blends of these materials with non-conducting processible polymers was reported by Heeger *et al.*[112a] in 1987. Their work demonstrated the possibility of obtaining relatively highly conducting blends with much lower volume fractions of conducting polymer.

1.9.4 Conducting Polymer Solutions[115]

PPPS is a commercially available melt and solution processible thermoplastic[24]. Upon exposure to AsF_5 vapour, PPPS becomes electroactive (see section 1.2.4)[25]. Unfortunately the conductivity was not homogeneous. Attempts to develop a more homogeneous electroactive material led to the discovery in 1983 of a synergistic effect between the dopant AsF_5 and codopant AsF_3 on the uniformity of doping and maximum conductivity of PPPS[116].

The more uniform doping and synergism is explained in terms of oxidation of the polymer by AsF_5 followed by solvation or plasticisation of the doped complex by AsF_3. This effect allows further and simple diffusion of dopant through the outer layers to the inside of the polymer. This eventually leads to a more homogeneously doped material. These encouraging results provided the impetus to develop these materials still further. The AsF_5 doping of PPPS in liquid AsF_3 led to the discovery of the first polymer that was solution processible in its conducting form[117,118]. Upon casting, totally homogeneous films of the EAP were formed.

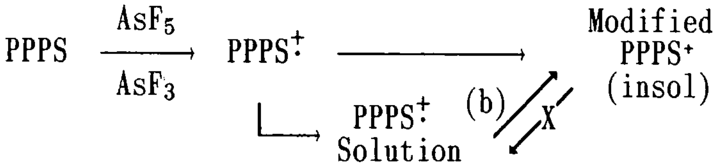

Figure 1.29 *Scheme Depicting the Reaction Pathways for Doping, Solvation and Crosslinking of PPPS.*

These films possessed mechanical and electrical properties far excelling those of similar polymers doped by conventional methods. Additional work with the use of a suitable oxidant and exploiting AsF_3 as a solvent have also led to the simultaneous polymerisation, doping and dissolution of other materials to produce solution processible EAPs[115]. However, the use of such toxic materials has meant that their potential for commercial realisation is virtually nil. Similar techniques have been used employing molten iodine as the medium for the synthesis and dissolution of conducting polycarbazole[119]. Studies directed towards establishing the features common to both AsF_3 and I_2 that enable them to dissolve EAPs have revealed that both reagents are auto-ionising:[120]

$$2\ AsF_3 \rightleftharpoons AsF_4^- + AsF_2^+$$

$$2\ I_2 \rightleftharpoons I^+ + I_3^-$$

Figure 1.30 *Demonstrating Similar Auto-Ionising Behaviour of Both Antimony Pentachloride and Iodine.*

This feature sets them apart from most other solvents. The presence of the ions may contribute to the solvents ability to solvate by enhancing the ionic strength of the solvent. The dissociation process could also be providing a source of intermediate oxidation states which could coordinate the polymer during doping. These suggestions are speculative and have yet to be proven.

1.9.5 Modification of the Monomer Unit

Although the delocalised electronic structure of π-conjugated polymers tends to yield relatively stiff chains with little flexibility and with relatively strong interchain attractive forces, solution processibility can be achieved through the chemical modification of the monomer unit prior to polymerisation. Early experiences with $(CH)_x$ taught that substitution onto the rigid conjugated polymer chains may actually improve processibility but it severely impaired the conductivity of the doped systems.

Poly-N-substituted pyrroles also suffered the fate of reduced conductivity. It was Miller (in 1985) who demonstrated that an electropolymerised β-substituted poly(thiophene) could be made soluble in both the doped and undoped forms[121].

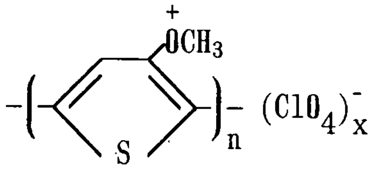

Figure 1.31 *Poly(3-methoxythiophene) - The First Example of a Solution Processible P-Doped Poly(thiophene).*

Although no conductivity data was reported, the impetus was provided for further work in the area of β-substituted polyheteroaromatics. The incorporation of long flexible alkyl chains into the environmentally more stable PT system led to highly conducting solution processible materials[92d,122].

The reduced interchain attractive forces and increased lipophilicity that these side-groups conferred were responsible for the materials solubility. As the substituent did not interfere with the π-electron structure of the polymer backbone, electrical conductivity similar to that obtained of the parent PT was observed.

The ease of fabrication combined with the array of commercially available[123] β-substituted thiophenes soon led to the accoutrement of other side groups into PT[124]. In particular electron donating substituents were found to improve the environmental and thermal stability of the doped polymer especially when compared to the polyalkylthiophenes[125]. The incorporation of many other types of flexible chain with pendent carboxylate or sulphonate groups into the backbone, have led to the development of a new class of EAP, the "auto-doped" EAPs[95b,125]. These are electroactive materials that incorporate the dopant within the polymer and, therefore, do not need to be doped extrinsically. However, it has been argued that the term "auto-doped" should be restricted to the case where there is stoichiometry between the pendent anionic groups and the positive charges (doping level) delocalised on the polymer skeleton[95b].

Furthermore, water soluble EAPs have stemmed from this category of polymer[126].

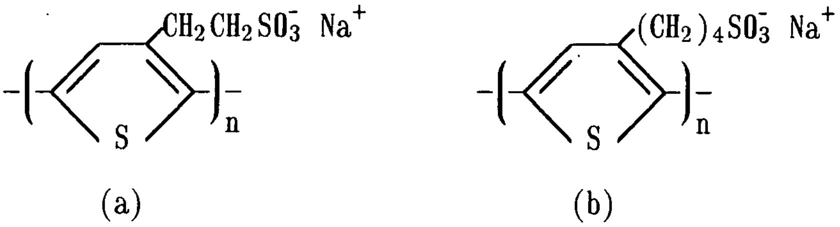

Figure 1.32 *The First Water Soluble (Autodoped) EAP's; (a) Poly-[3-(2-ethanesulphonate)-thiophene] and (b) Poly-[3-(4-butanesulphonate)-thiophene].*

More recently β-substituted thiophenes bearing chiral substituents[127] (able to act as enantioselective sensors), and sulphonate groups[128] capable of exhibiting thermochromism, have been synthesised. The development of β-substituted polyheterocycles over the past three years has seen the rebirth of a field that was rapidly becoming just an academic curiosity.

It is this class of conducting polymer above all others that promises to combine the essential properties of processibility, stability and mechanical strength which are the the key to the development of these materials for device applications.

1.10 SCOPE OF THIS WORK

The work covered so far has mainly been concerned with giving the reader an insight into the vastly dynamic field of organic EAPs, right from their conception in 1977 with $(CH)_x$ to the latest 'state of the art' polymeric systems of 1989.

However when work for this project was started in 1985, no solution processible electroactive poly(thiophenes) had entered the literature, so to all intents and purposes section 1.9.5 did not exist. It was the successful development of that section that concerns the proceeding chapters of this work. Chapter 2 deals with the synthesis, electropolymerisation and CV studies of a series of β substituted thiophenes bearing long, flexible lipophilic chains. Chapter 3 is concerned with similar studies of thiophenes bearing aromatic substituents, including liquid crystalline β-substituted systems. Chapter 4 tackles the synthesis of some derivatised thiophenes bearing macrocyclic groups. CV studies and metal ion complexation studies are also discussed. Chapter 5 concerns future work, whilst Chapter 6 contains the experimental procedures for all the compounds prepared in this work.

CHAPTER TWO

β- LONG CHAINS

2.1 INTRODUCTION

As it became apparent that the parent polymer PT offered several additional advantages over existing polyheterocycles, various techniques designed to enhance its processibility (and hence further its commercial prospects) began to enter the literature[92,121,129]. The following describes our contribution to one such technique, namely, that of chemically modifying the parent polymer by the incorporation of long, flexible, lipophilic chains into the β sites of the monomer prior to polymerisation[124a,c]. The rationale for synthesising these types of molecules has already been expounded in Chapter 1 (see section 1.9.5).

Clearly, if successful in its aims, this project would lead to the large scale preparation of some of the target molecules (or monomers) synthesised herein. Therefore the choice of methodology used to prepare our β substituted thiophenes should not only reflect the chemistry available to the starting materials but should also be:

a) cost effective;
b) simple to perform;
c) amenable to scale up and
d) high yielding.

From the commercially available starting materials 3-methyl- and 3-bromothiophene (Figure 2.1), the target monomers in the following section (Figure 2.2) were prepared†.

3-methylthiophene 3-bromothiophene

Figure 2.1 *Commercially Available Thiophenes Used.*

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†Synthesis of thiophenes bearing long alkyl chains was also considered; however, during the course of the work, these compounds were reported by other groups (Refs: 92c,d and 122b), so we did not proceed with their synthesis.

2.1.1 Target Monomers

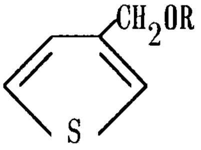
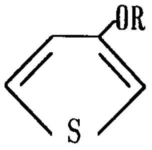
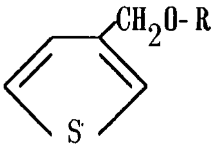
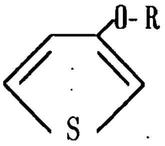
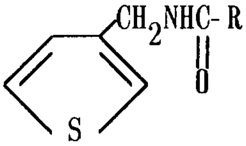
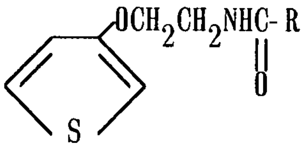
TYPE 1	TYPE 2
 $R = CH_3$ $R = (CH_2)_3CH_3$ $R = (CH_2)_5CH_3$ *Long Chain Ethers*	 $R = (CH_2)_3CH_3$ $R = (CH_2)_5CH_3$ *Long Chain Ethers*
 $R = (CH_2CH_2O)CH_3$ $R = (CH_2CH_2O)_2CH_3$ $R = (CH_2CH_2O)_4(CH_2)_3CH_3$ *Long Chain Polyethers*	 $R = (CH_2CH_2O)CH_3$ $R = (CH_2CH_2O)_2CH_3$ *Long Chain Polyethers*
 $R = CH_3$ $R = (CH_2)_6CH_3$ $R = (CH_2)_{10}CH_3$ *Long Chain Amides*	 $R = (CH_2)_6CH_3$ $R = (CH_2)_{10}CH_3$ *Long Chain Amides*

Figure 2.2 *Target Monomers Synthesised in this Chapter.*

All type 1 monomers were synthesised from 3-methylthiophene and all type 2 monomers were synthesised from 3-bromothiophene. These same starting materials yielded, eventually, all the target monomers described in this thesis.

2.2 SYNTHESIS OF TARGET MONOMERS

2.2.1 Synthesis From 3-methylthiophene

The chemistry of the methyl group in 3-methylthiophene is typical of much of the chemistry of aromatic methyl groups, hence the types of reactions the methyl group can undergo may be summarised as follows:[131,132]

a) Halogenation;
b) Oxidation;
c) Electrophilic attack.

Of these three categories, selective methyl halogenation (usually bromination) offers synthetically, the most useful method of entry into a wide range of β-substituted thiophenes. If N-bromosuccinimide is used as the selective brominating agent, the reaction is known as the *Wohl-Ziegler* reaction and is simple, relatively cheap and readily amenable to scale-up.‡

The product, 3-(bromomethyl)thiophene readily undergoes addition reactions and nucleophilic displacement reactions to form, for example, long chain lipophilic ethers, polyethers and (indirectly) amides.

2.2.1.1 Synthesis of Long Chain Ethers and Polyethers.

The formation of ethers and polyethers followed the *Williamson* route (discovered in 1852) which is the best general method for preparing asymmetrical (or symmetrical) ethers[133]. Complete reaction of the alkali metal with the alcohol prior to the addition of (1) was

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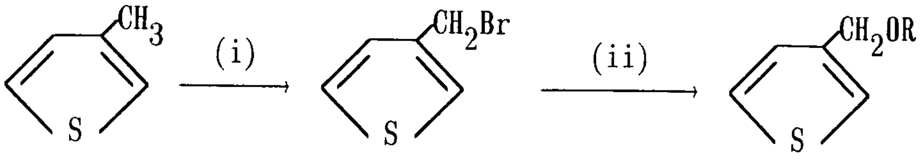
‡The selective bromination of 3-methylthiophene has been successfully performed on a kilogram scale, as a direct result of work pertaining to this thesis.

essential to prevent *Wurtz* type coupling[134].



(1)

ETHERS		
(2)	R = CH_3	(35%)
(7)	R = $(CH_2)_3CH_3$	(49%)
(8)	R = $(CH_2)_5CH_3$	(75%)

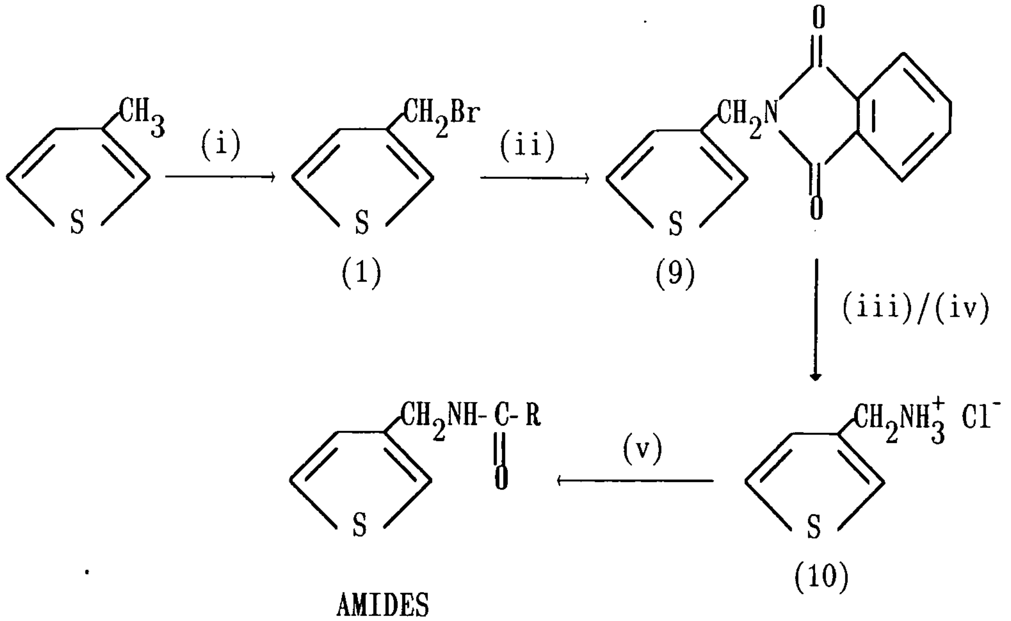
POLYETHERS		
(3)	R = $(CH_2CH_2O)CH_3$	(50%)
(4)	R = $(CH_2CH_2O)_2CH_3$	(46%)
(6)	R = $(CH_2CH_2O)_2(CH_2)_3CH_3$	(57%)

Figure 2.3 *Synthetic Scheme Depicting the Synthesis of Type 1 Ethers and Polyethers. Typical Reagents and Reaction Conditions are: (i) N-bromosuccinimide, AIBN, CCl_4, reflux; (ii) Na^+ or K^+ salt of the appropriate alkoxide, THF or CCl_4, reflux.*

Satisfactory yields of the target monomers above were obtained, ranging from 35% to 75%. However these yields were disappointing when one considered that the major side reaction, that of elimination (from the alkyl halide), was not possible. The highest yields of the target ethers and polyethers were obtained using freshly distilled 3-(bromomethyl)thiophene. Purification of all the target monomers (2) to (8) was carried out by distillation at reduced pressure (10 mm Hg), and when stored at -20°C under nitrogen, these compounds remained stable for up to eight months (see section 2.4.2).

2.2.1.2 Synthesis of Long Chain Amides

The reaction scheme below (Figure 2.4) was modelled around the *Gabriel* synthesis (discovered in 1887)[135]. It is usually the method of choice for generating primary amines for subsequent conversion to primary amides.



AMIDES

(11)	R =	CH_3	(84%)
(12)	R =	$(CH_2)_5CH_3$	(89%)
(13)	R =	$(CH_2)_{11}CH_3$	(92%)

Figure 2.4 *Synthetic Scheme Depicting the Synthesis of Type 1 Amides. Typical Reagents and Reaction Conditions are: (i) N-bromosuccinimide, AIBN, CCl_4, reflux; (ii) K^+ Phthalimide, 18-crown-6 ether, DMF, 80°C; (iii) $N_2H_4.H_2O$, EtOH, reflux; (iv) HCl, reflux; (v) RCOCl, Et_3N, CH_2Cl_2, -5°C.*

The use of freshly distilled 3-(bromomethyl)thiophene leads to a moderately efficient S_N2 displacement of the bromine to form the phthalimide derivative (9) (*ca.* 70%). The original *Gabriel* synthesis stipulates acid or base hydrolysis of the resultant phthalimide derivative to form either the primary amine hydrochloride or free amine respectively. However, the heating of the phthalimide with hydrazine in an exchange reaction, followed by treatment with acid (the *Ing-Manske modification*) is a far more efficient, rapid, way of hydrolysing the pendant phthalimide group to form the desired primary amine as the hydrochloride salt[136]. The *Ing-Manske* procedure has largely, though not entirely, superseded hydrolytic methods. The amine hydrochloride (10) can be recrystallised or used directly for the subsequent N-acylation step [yield > 85% for (11) to (13)] using the desired acyl chloride. The target amides (11) to (13) were stable crystalline solids at room temperature.

2.2.2 Synthesis From 3-bromothiophene

3-Halogenothiophenes, in particular 3-bromothiophene, are readily capable of further chemical modification at the β site. The chemistry of the substituted β site being typified by the following reactions:[131,132]

(a) Nucleophilic Displacement
(b) Halogen Metal Exchange
(c) Formation of Thienyl Radicals

Following the synthesis of a series of ether, polyether and amide derivatives, described above (type 1 target monomers) it was decided to synthesise an analogous series of monomers (type 2 target monomers) in which the oxygen was directly attached to the thiophene ring (Figure 2.5).

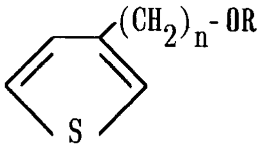
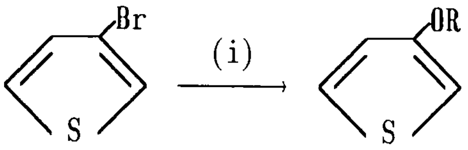


Figure 2.5 *Depicting Both Type 1 Target Monomers (n = 1) and Type 2 Target Monomers (n = 0).*

This would enable comparative studies to be performed between types 1 and 2 monomer and polymer systems. The methods of entry into these systems are limited to nucleophilic displacement reactions (*vide infra*).

2.2.2.1 Synthesis of Long Chain Ethers and Polyethers



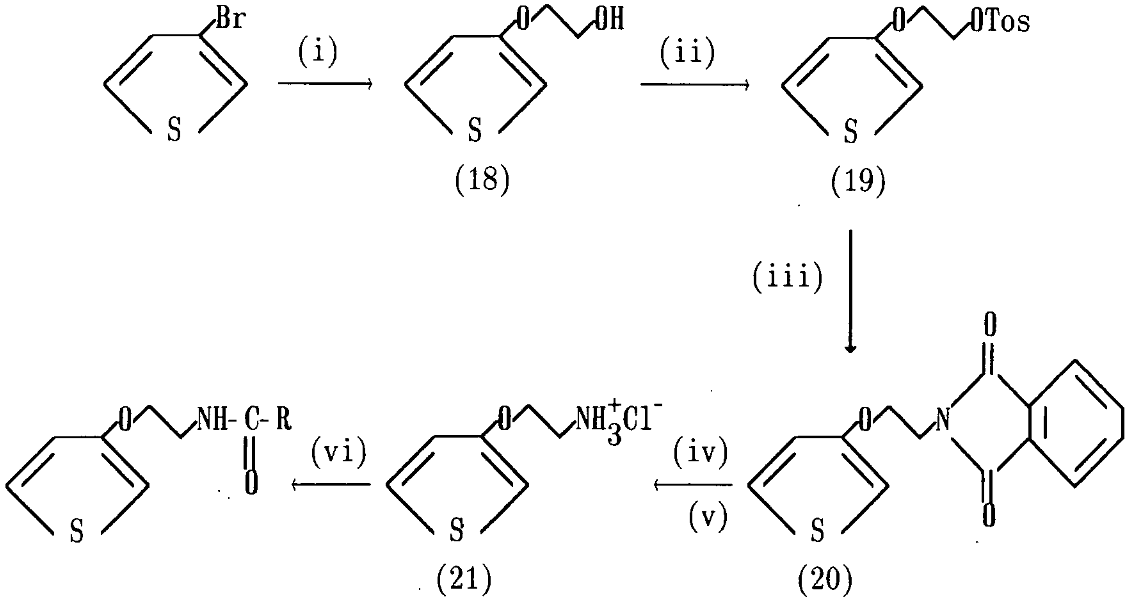
ETHERS		
(14)	R = $(CH_2)_3CH_3$	(42%)
(15)	R = $(CH_2)_5CH_3$	(43%)

POLYETHERS		
(16)	R = $(CH_2CH_2O)CH_3$	(68%)
(17)	R = $(CH_2CH_2O)_2CH_3$	(34%)

Figure 2.6 *Synthetic Scheme Depicting the Synthesis of Type 2 Ethers. Typical Reagents and Reaction Conditions are: (i) Na^+ Alkoxide, CuO, KI, 110°C, 5 days.*

Due to the unactivated nature of the β-bromine substituent the desired nucleophilic displacement reaction only occurs in the presence of copper(I) salts. The reaction conditions involved were similar to those developed by *Gronowitz*[137], *ie.* an excess of copper oxide and a catalytic quantity of potassium iodide (to act as a promoter) were heated in the presence of 3-bromothiophene and an alkoxide/alcohol mixture for 5 days at 110°C. Yields ranging from *ca.* 40-70% were obtained, depending on the starting alkoxide. All of the target ether/polyether derivatives (14) to (17) were less stable than their type 1 homologues, when sealed and stored at -20°C. This may have been due to the lower oxidation potential of the systems bearing the electron donating oxygen directly attached to the ring. After *ca.* one month slight yellow discoloration of the alkoxy monomers (14) and (17) occurred, therefore redistillation of these monomers prior to polymerisation is recommended (see also section 2.4).

2.2.2.2 Synthesis of Long Chain Amides



AMIDES

(22)	R =	$(CH_2)_6CH_3$	(62%)
(23)	R =	$(CH_2)_{10}CH_3$	(48%)

Figure 2.7 *Synthetic Scheme Depicting the Synthesis of Type 2 Ethers and Polyethers. Typical Reagents and Reaction Conditions are: (i)* $(CH_2OH)_2$*,* Na^+*, CuO, KI, 110°C, 5 days; (ii) TsCl, Pyridine, -5°C; (iii)* K^+ *Phthalimide, 18-crown-6, DMF, 80°C; (iv)* $N_2H_4.H_2O$*, EtOH, reflux; (v) HCl, reflux; (vi) RCOCl,* Et_3N*,* CH_2Cl_2*, -5°C.*

Using the same conditions that led to the ether and polyether monomers, (14) to (17) described above, ethylene glycol was reacted with 3-bromothiophene. Nucleophilic displacement yielded alcohol (18) (42%) as a stable crystalline solid. No products were isolated resulting from further reaction of alcohol (18) with a second equivalent of starting material (3-bromothiophene). Alcohol (18) offers great synthetic potential, as the hydroxy group can act as a nucleophile, or, as its tosylate derivative (19) can be displaced. Indeed, compound (19) enabled the simple conversion of the alcohol (18) to the phthalimide derivative (20) in 60% yield over the two steps. Compound (20) then provided the amine hydrochloride which, upon N-acylation yielded two target monomers for comparative studies with those synthesised from 3-methylthiophene, *viz.* (22) and (23).

So far the syntheses of a range of novel β substituted thiophene derivatives has been described. The following section will present and discuss the anodic electrochemistry (studied by cyclic voltammetry) of these target monomers.

2.3 CYCLIC VOLTAMMETRY[57]

Cyclic stationary electrode voltammetry, usually called cyclic voltammetry (CV) is perhaps the most versatile electroanalytical technique available for the mechanistic study of redox systems. In the area of preliminary mechanistic investigation, it is usually the first electroanalytical technique to be applied to a new system of this type.

In the field of EAPs, CV has first and foremost been used as a method of generating coherent, electroactive, thin films, from solutions of the monomer, providing materials for further study and characterisation (ESCA, FTIR, NMR *etc*). It has also found wide ranging application in the analysis of the redox chemistry of these polymeric systems leading, for example, to a greater understanding of conduction mechanisms[138]. The use of CV in monitoring the oxidation potentials of new monomers and the onset of polymer deposition *via* "nucleation overpotentials" has also established the technique as the method of choice for preliminary electrochemical investigations of new systems. In addition, the fact that most applications of EAPs require the polymer to be cycled between the oxidised and reduced states (see section 1.8) means that an electrochemical technique capable of recording such data, should be used in the information gathering process. Again CV is the ideal analytical tool. The following is concerned with the CV behaviour of all the target monomers (2) to (23) synthesised thus far.

The variation of oxidation potential, irreversibility, onset of polymer deposition and polymer formation will be discussed. However, before describing the anodic electrochemistry of these systems, it should be stated that there seems to be no accepted convention concerning presentation of EAP data, obtained from CV. Solvents, temperature, electrodes, electrolytes, are all varied to suit optimum results for individual systems. This tends to create a degree of confusion when one attempts to compare results from different experiments, and more particularly, from different laboratories. This difficulty in quantifying the systems under study, combined with irreproducibility between different research groups, has cast a shadow over the technique. However, some progress has been made towards solving these problems by several workers (see also section 1.5). Therefore it is hoped that before long many of the erroneous results thus far reported, can be corrected. The present research has <u>not</u> tried to optimise conditions for each monomer, in an attempt to grow the best quality films. Our conditions have been based on:

(a) a consideration of the wide range of conditions used successfully for other thiophene derivatives, and

(b) the alacrity of performance and reproducibility in film formation.

2.3.1 Choice of Electrochemical Cell

Because of the low current generation involved in CV (mA), a three electrode, one compartment cell arrangement was chosen (Figure 2.8). This arrangement presents few problems in construction and with respect

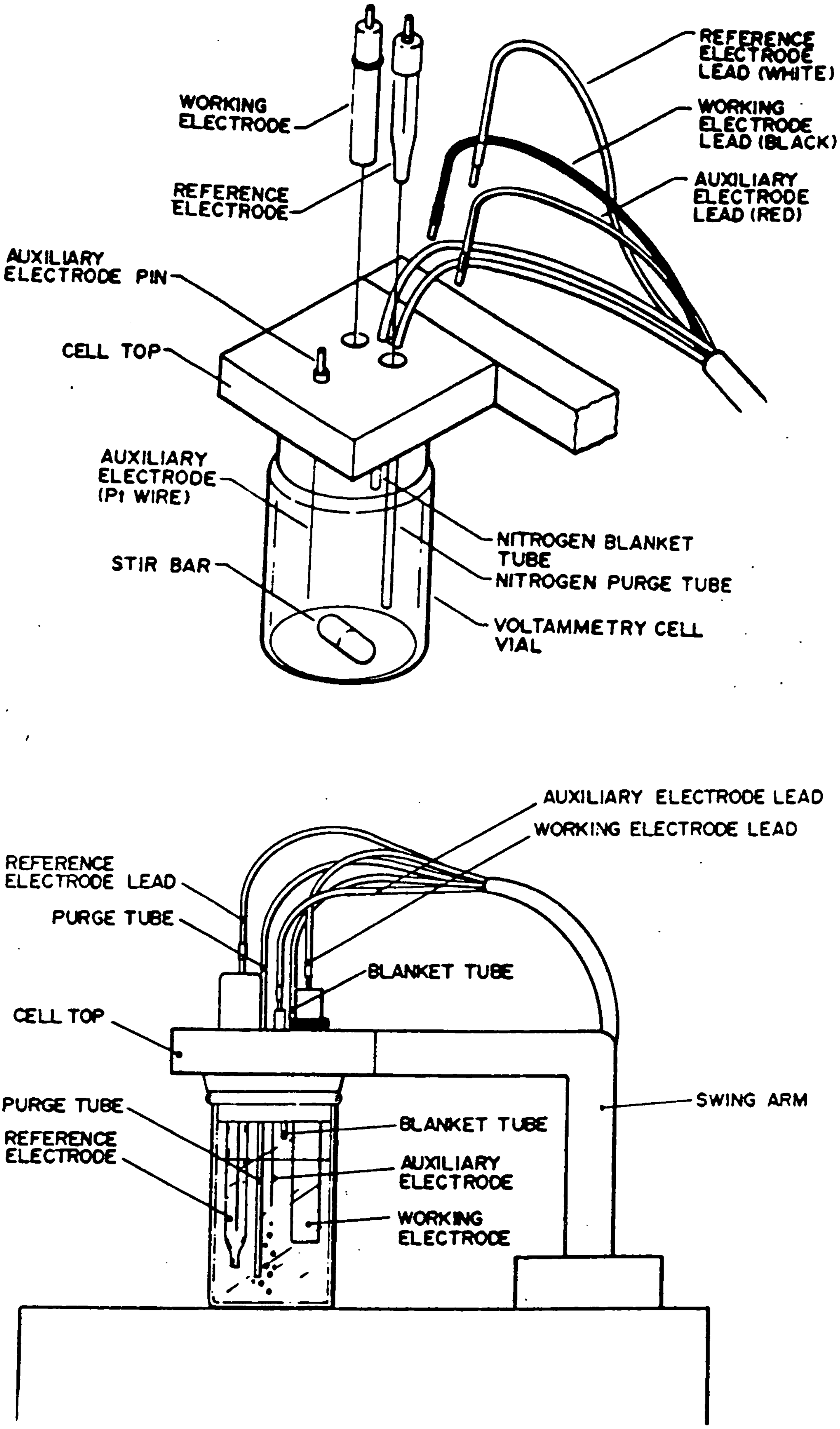


Figure 2.8 *Model C1-B Cell Stand with Electrode Leads Connected.*

to the substances generated at the auxiliary electrode or released from the reference electrode, and it allows all three electrodes to be placed in one single compartment. Although single surface, planar electrodes placed parallel to each other provide the ideal arrangement, satisfactory results may be obtained when the reference electrode is placed close to the working electrode, between the working electrode and auxiliary electrode. The purpose of the auxiliary electrode is two-fold: first, the introduction of this 'independent' reference electrode allows the accuracy of the working electrode to be checked, and second it also acts as an 'electron sink' when electrical current is generated, preventing damage to the reference electrode.

2.3.2 Choice of Working Electrode

The ideal properties of a material for use as a working electrode are that it should possess a wide working potential range, a low electrical resistance and an easily cleaned, smooth surface, capable of surface modification (*eg.* the formation of a coherent oxide layer). The platinum working electrode was considered to be the most suitable, mainly because of the simple manner in which surface modification could be imparted. Although the generation of an oxide layer was not performed prior to the CV studies (see Chapter 5), it was found to be necessary for good quality film formation under constant potential techniques (see section 2.5).

2.3.3 Choice of Solvent

In order to support the passage of an electrical current, the solvent system chosen should have a low electrical resistance and hence a moderately high dielectric constant (≥ 10). The prevalence of ion-pairing and even multiple aggregation in less polar solvents results in low ionic mobility and conductance in such solutions. The solvent should also dissolve a wide range of substances at acceptable concentrations (≤ 0.1 M) while not reacting either with the electroactive material (or with intermediates or products of the electrode reaction) or itself undergoing any electrochemical reaction over the applied potential range. Convenient boiling and freezing and ease of purification are also points for consideration, as well as cost and toxicity. A universal solvent meeting all these requirements does not exist. However, the most widely-used solvent for anodic electrochemistry is acetonitrile (liquid range -45.7 to 81.6^{0}C, dielectric constant = 37.5) and this was the solvent of our choice.

2.3.4 Choice of Base Electrolyte

The base electrolyte used should, therefore, enjoy high solubility in acetonitrile. It should also be stable towards very positive potentials (≤ 3000 mV), ideally, be commercially available in a highly pure form and be non-hygroscopic. In the area of EAPs, one more prerequisite of the base electrolyte has to be satisfied. As the anion of the base electrolyte is actually incorporated into the polymer and the conductivity of the polymer affected by this anion, the base electrolyte should also lead to highly conducting forms of β-substituted thiophenes. The optimum base electrolyte for polyheterocyclic systems is tetrabutylammonium hexafluorophosphate (TBAHFP), which more or less satisfied all the above conditions[139].

2.3.5 Choice of Temperature

To avoid the use of elaborate cooling/heating baths, it was decided to perform all the CV work at room temperature (~18-20^{o}C). It has since been established, however, that better results are obtained using solvents near to their freezing point[140].

2.4 CYCLIC VOLTAMMETRY STUDIES

2.4.1 Introduction

Using the materials and apparatus described above, the behaviour of the monomers was examined systematically by CV using a set of standard conditions (see Section 6.3). The data and observations from these experiments are summarised in Table 2.1.

2.4.2 Results

The primary wave (monomer oxidation potential) shown in Table 2.1 was found to vary according to the nature of the substituent (see also section 1.4.2). This oxidation corresponds to the removal of an electron from the HOMO of the electron rich π system. Alkoxy groups [compounds (14) to (23)] tend to stabilise the product radical cation and raise the monomer HOMO energy, so that oxidation occurs at a lower voltage than with alkyl substituents. The primary oxidation wave of all the systems studied was also irreversible, as defined by the absence of any reverse peaks and the observation that the $|i_0|$ versus $\nu^{1/2}$ (ν = scan rate) correlation was linear. Although other diagnostic tests to demonstrate irreversibility exist, *ie*.

	INITIAL SCAN (ν = 100 mV/s)						MULTISCANS @ 50 mV/s		
CPD	ANODIC SCAN LIMIT (mV)[a]	PRIM.OXID.WAVE E_0/V	$\|i_0\|$/mA	CLR[b]	OTHER PEAKS E/V, $\|i\|$/mA	ANODE COLOUR	I_0(mA)[c]	FILM FORMATION	GENERAL COMMENTS
2	2500	2.21	0.293	0.96		Blue-Black	dec	Thin Gold 10 scans	New peaks @ 2.33 V (scan 2) & 1.97 (scan 3). The former had collapsed by scan 5 when a nucleation loop was observed.
3	2500	2.16	0.188	0.99	Broad wave at ≈ 2.5 V	Blue-Black	dec	No 10 scans	Broad wave at ≈ 2.50 V decreases and disappears after 5 scans.
4	2500	2.11	0.188	0.99	Broad wave at ≈ 2.4 V	None	dec	No 10 scans	Broad wave at ≈ 2.40 V decreases and disappears after 5 scans.
6	3000	2.18	0.110 (sh)	0.99	2.57 0.171 CLR = 0.97	None	dec	No 10 scans	2.57 V peak collapses (scan 3). Shoulder at 2.18 becomes better defined and shifts to E = 2.32 V
7	3000	2.21	0.217	1.00	2.54 0.046	Blue-Black	dec	Thin Gold 5 scans	2.54 V peak decreases as scan rate increases. No film/anode colour with a scan limit of 2500 mV.
8	3000	2.23	0.215	0.98		None	dec	No 5 scans	2.23 V peak structure collapses after 6 scans.
11	3000	1.94	0.040	1.00	2.64 0.088 CLR = 1.00	None	dec	No 4 scans	Peak structure collapses after 4 scans. Crossover seen on reversal.
12	3000	2.20	0.075	1.00	2.84 0.177 CLR = 0.99	None	dec	No 4 scans	Peak structure collapses after 3 scans. Crossover seen on reversal.

Table 2.1 *Cyclic Voltammetric Study of Thiophene Monomers;*

a) The scan range was from +1200 mV to the specified limit;

b) CLR (coefficient of linear regression) was calculated to show the correlation between observed i(o) and $\sqrt{\nu}$ for ν = 50, 100, 200 and 400 mV/s;

c) const = constant; inc = increase; dec = decrease. These terms are used to describe how the current associated with the primary oxidation wave varies with continuous scanning; also sh = shoulder.

CPD	INITIAL SCAN (ν = 100 mV/s)							MULTISCANS @ 50 mV/s			
	ANODIC SCAN LIMIT (mV)[a]	PRIM.OXID.WAVE E_0/V	$\lvert i_0 \rvert$/mA	CLR[b]	OTHER PEAKS E/V	$\lvert i \rvert$/mA	ANODE COLOUR	I_0(mA)[c]	FILM FORMATION	GENERAL COMMENTS
13	3000	2.19	0.048	1.00	2.86	0.127 CLR = 1.00	None	dec	No 4 scans	Peak structure collapses after 3 scans. Crossover seen on reversal.
14	2000	1.56	0.159	0.99			Blue-Green	const	No 10 scans	CV trace invariant - scans 1-10.
	2500						Blue-Green			Extra oxid. peak @ 2.21 V. Crossover seen on reversal.
15	1800	1.67	0.008	0.96	1.61	0.104 (prewave)	None		No 8 scans	
	2500						Blue-Green	const	No 8 scans	Extra oxid. peak at 2.38 V. CV trace invariant - scans 1-8.
16	2000	1.64	0.149	1.00	1.82	weak	Blue-Green	const	No 5 scans	CV trace invariant-scans 1-5. 1.82 V peak only seen < 50 mV/s. Extra peak @ 2.32V when scanned to 2500 mV
17	2000	1.61	0.186	1.00	1.75	0.009	Blue	const	No 5 scans	CV trace invariant - scans 1-5. 1.75 V peak only seen < 50 mV/s.
	2500							dec	Thin Gold	Additional oxidation peak @ 2.21 V & nucleation loop seen on Scan 6.
22	2500	1.61	0.049	1.00	1.75	(sh)	Black	const	No 10 scans	Transient @ 2.21 V (scan 5). One peak @ 1.68 V by scan 10. shoulder at 1.75V decreases as ν increased.
23	2500	1.66	0.095	0.99	1.84	(sh)	Black	const	No 10 scans	CV trace (scans 1-10) almost invariant. Shoulder at 1.84 V decreases as ν is increased.

Table 2.1 (cont'd) *Cyclic Voltammetric Study of Thiophene Monomers;*

a) The scan range was from +1200 mV to the specified limit;

b) CLR (coefficient of linear regression) was calculated to show the correlation between observed i(o) and $\sqrt{\nu}$ for ν = 50, 100, 200 and 400 mV/s;

c) const = constant; inc = increase; dec = decrease. These terms are used to describe how the current associated with the primary oxidation wave varies with continuous scanning; also sh = shoulder.

(1) E_0 shifts $\frac{-60\ \text{mV}}{n}$ per decade increase in ν, and

(2) $E_0 - E_{0/2} = \frac{106\ \text{mV}}{n}$ per decade increase in ν.

(where n = number of electrons transferred)

the accuracy of these methods is dependent upon being able to measure E_0 accurately at high scan rates. This is not always possible as E_0 is usually quite broad at even moderately slow scan rates (100 mV s^{-1}) and widens further with increases in ν. Only minor variations in the monomer oxidation potential with increasing length of the side chain were observed and no distinct pattern in this variation could be established for either the alkoxy or alkyl derivatives; the reasons underlying this fluctuation are open to debate. In compound (15) an irreversible prewave fluctuation was noticed (separated from the main monomer oxidation potential by ~60 mV). This may have been the result of trace amounts of impurities (that could not be detected by micro-analysis or NMR), or possibly a mixture of oligomers were present; their oxidation potential would be lower than the starting monomer, thus accounting for the broad prewave observed. The oligomers could possibly form through the action of trace oxidants or light over several days prior to the CV study. Indeed it was noted that some of the monomers, notably the alkoxy derivatives (14) to (23) began to turn slightly yellow after a few weeks (this would be consistent with the formation of more highly conjugated units, dimers, oligomers *etc*).

Irreversible post oxidation waves, however, were noticed for all the monomers studied (see Figure 2.9). This observation was usually consistent with a distinct blue-black colouration 'streaming' from the anode surface during cycling. Such behaviour is considered to be due to the formation of soluble low molecular weight oligomers which to some extent do not adhere to the electrode surface in the solvent used. It

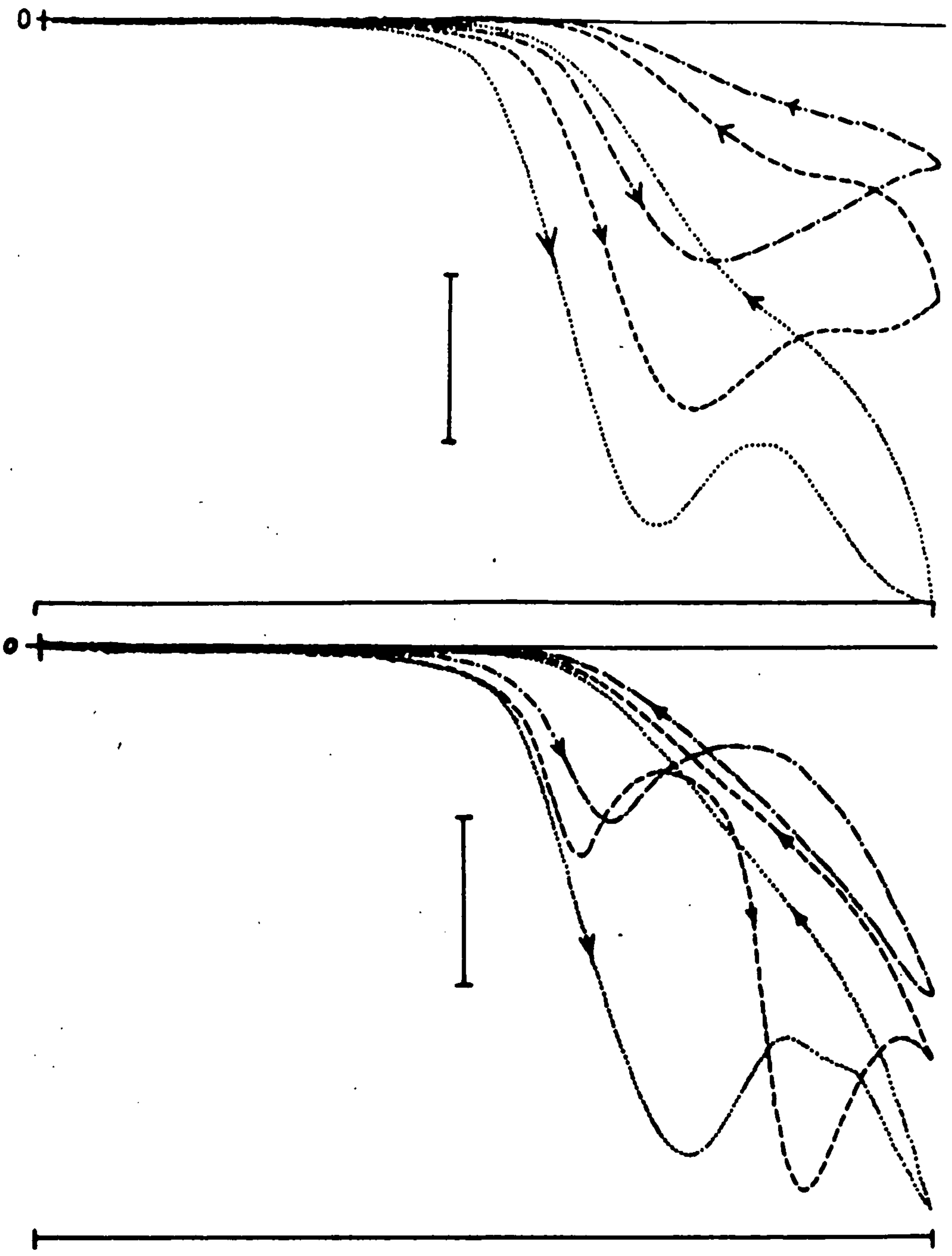


Figure 2.9 *Cyclic voltammograms of monomers (0.02 M in acetonitrile in the presence of 0.1 M Et_4NPF_6; ν = 50 mV s^{-1}; current scale-bar is equivalent to 50 μA; (a) Upper traces are for scans 1,3 and 5 with 3-(methoxyethoxymethyl)-thiophene (8); (b) lower traces are for scans 2,3 and 10 with 3-(methoxymethyl)-thiophene (5). The scan sequence follows the order (····), (- - -) and (- · - ·).*

is known that PT films grown electrochemically, which incorporate this higher post oxidation wave, are different to those grown which only incorporate the primary oxidation peak[141]. What is possibly occurring at these higher electrode potentials is a more intense and less selective (*α-β* or *β-β* or even crosslinking) radical cation coupling process leading to a loss in conjugation[141]. Further study exploiting CV to analyse this post wave was not pursued.

Furthermore, under these standard conditions some monomers gave a 'nucleation overpotential' which in turn led to a 'nucleation loop', *ie.* the anodic sweep upon reversal crossed over the forward sweep. This type of behaviour is often encountered in studies of the deposition of metals onto the working electrode. A possible explanation for the observation of the crossover 'loop' seen for some of the monomers in Table 2.1 [notably the alkyl and alkoxy amides, compounds (11) to (13), and (16) to (17)] can be drawn from other systems (*eg.* the deposition of metals), that demonstrate the same phenomenon. The rationale requires that the adsorptions of thiophene radical cations onto the working electrode (Pt) is a thermodynamically more favourable process, than radical cation coupling to eventually form EAPs. This thermodynamically more favourable process of adsorption also requires an oxidation potential slightly greater than that required to oxidise thiophene (this is the nucleation overpotential). On the reverse sweep, however, deposition of radical cations is now occurring, not on a platinum working electrode surface, but on an electrode bearing several monolayers of adsorbed thiophene radical cations. Further adsorption can be considered as radical cation coupling and this continues at the (true) lower oxidation potential. Hence crossover at some point to form the nucleation loop is inevitable.

However, in the case of EAPs, a nucleation loop does not imply the onset of polymer deposition. This is because any adsorbed species, due to the role of the β substituent, will tend to dissolve away from the electrode surface in its reduced (or even oxidised) form. This may explain why in some cases [compounds (11) to (13)] although repeated nucleation loops were observed, no polymer deposition was noticed even after 10 scans. The only system whereby nucleation loops and polymer deposition were observed under the standard conditions, was compound (2) which bears the shortest (3 atoms) β-chain studied. All other factors being equal, the short chain derivatives are least likely to dissolve away from the electrode surface. Hence a coherent thin gold film was obtained for compound (2). The observation that compound (7) gave no film at a scan limit of 2500 mV, but did produce a gold film at a higher scan limit (3000 mV) is worthy of note: however, no nucleation loop and copious 'streaming' prior to polymerisation at this higher potential was observed [see also compound (17)]. Such behaviour may suggest that for electrodeposition (and polymer formation) to occur under these conditions a large overpotential is essential. Further work on the polymer formed from compound (2) was delayed until research on other monomers (see section 2.5) carried out at Perivale was complete.

Finally, some aspects of the electrochemistry cannot be adequately explained, *eg.* the appearance and disappearance of extra peaks, variations in currents *etc* (see Table 2.1, "General Comments"). However, these observations are reproducible if the working electrode is cleaned (see Section 6.3) prior to repeating the experiment. So, although no detectable film may be observed on the electrode after repeated scanning it is possible that some form of passivating monolayer does cover the electrode surface, and may well be worth investigating at a later date (see Chapter 5).

To sum up, the standard conditions established in this study for the anodic electrochemical study of the monomers, were developed with the intention of producing a series of electroactive, PT films, for further study and characterisation. However aspirations in this direction in all but one example [compound (2)] were not forthcoming. This failure may be due to a variety of reasons associated with the standard conditions employed. The conditions chosen were based on those previously successful for electropolymerisation of PT that did not contain long chain substituents. In retrospect, the *a priori* assumption that thiophenes bearing long chains (> 3-4 atoms) would undergo similar electropolymerisations using our conditions was ill founded and so the conditions had to be modified. This was done largely by Dr. P.K. and Mr. A. Marsh at Cookson Group Research Laboratories at Perivale.

2.5 ELECTROCHEMICAL POLYMERISATION OF THIOPHENE MONOMERS

2.5.1 Introduction

The electrochemical polymerisation of the thiophene monomers was carried out in a single compartment electrochemical cell at a temperature of 10°C under an atmosphere of nitrogen, using TBAHFP as the base electrolyte. The electrochemical technique employed was constant current electrolysis, the anode being either Pt or indium-tin oxide (ITO). Direct current conductivity measurements of the oxidised polymer films were obtained, either while the polymer film was attached to the anode surface (using a two probe mercury contact technique) or with a free standing polymer film that had been peeled off (2 cm x 2 cm) the anode (using a four probe technique). The polymerisation conditions are detailed in Table 2.2. Prior to electropolymerisation, the working

COMPOUND *(a)*	SOLVENT (25ml)	ANODE	MONOMER MOLARITY	TBA-HFP MOLARITY	COULOMBS PASSED	CURRENT DENSITY (mA cm^{-2})	CONDUCTIVITY (σ_{rt} S cm^{-1}) *(b)*
(2)nX	$PhNO_2$	Pt	$1.0x10^{-1}$	$3.0x10^{-2}$	4.35	2.0 ± 0.1	0.31 *(c)*
(3)nX	$PhNO_2$	Pt	$1.0x10^{-1}$	$3.7x10^{-2}$	7.34	1.6 ± 0.15	51 *(c)*
(4)nX	$PhNO_2$	Pt	$2.8x10^{-1}$	$3.1x10^{-2}$	4.10	1.5 ± 0.1	1050 *(d)*
(13)nX	$PhNO_2$: $CHCl_2$ (1:1)	Pt/ITO	$2.0x10^{-2}$	$5.0x10^{-2}$	3.74	2.6 ± 0.1	200 *(c)*
(17)nX	CH_2Cl_2	ITO	$5.2x10^{-2}$	$1.2x10^{-2}$	3.81	2.0 ± 0.15	0.05 *(c)*

Table 2.2 *Polymerisation Conditions;*
a) X=PF_6 (however see Section 2.7.2);
b) Room Temperature;
c) Two-Probe Measurement;
d) Four-Probe Measurement.

electrode (Pt) was subjected to surface modification. A thin oxide layer was grown onto the surface of the electrode by first immersing both the anode and cathode into sulphuric acid (0.5 M) and subjecting the electrodes to a current of 0.5 mA (at +0.8 V) for 30 seconds. The electrodes were then held neutral for a period of 20 seconds before being 'pulsed again for a further 30 seconds (0.5 mA at -0.8 V). After repeating this procedure, the electrodes were deemed to be surface modified (or anodised).

2.5.2 Conductivity Measurements

(1) **Two Probe:**	The two probe conductivity measurement was performed either with two pressure contacts or by the mercury drop method.
(2) **Four Probe:**	The four probe conductivity measurement was performed by four pressure contacts. A Keithley 228 voltage/-current source or Thurlby 30V-2A voltage/current source was used as a current source. The current was measured with a Keithley 160 digital multimeter and voltage monitored by a Keithley 195A digital multimeter.

2.5.3 Results

The conductivity values obtained for compounds (4) and (13) are significantly higher than those reported for most other PT's, and at the time (1987) were some of the highest to enter the literature, notably, compound (4), σ_{rt} 1050 S cm^{-1}. This supported the claim that substituted PT's should be capable of higher conductivities than PP's (this has been further demonstrated by Roncali *et al.*[142] who have obtained films of poly-(3-methylthiophene) with σ_{rt} = 2000 S cm^{-1}.

Work at Perivale also established that all the electrosynthesised polymers (2), (3), (4), (13) and (17) were thermally stable up to 210^{o}C. More importantly, however, the polymer formed from compound (4) was solution processible in its *conducting* state. Slow evaporation of a solution of the polymer in a mixture of tetrahydrofuran:dichloromethane:trichloroethane (4:1:1) regenerated the polymer as a thin film. Unfortunately, this solution casting led to much reduced room temperature conductivity of the material, σ_{rt} (solution cast) = 0.3 S cm^{-1}. This may be due to an internal rearrangement of dopant ions within the polymer matrix during the casting process. Possibly a lower energy matrix-dopant configuration is adopted after casting, and this contributes to the lower conductivity. Unfortunately, further studies concerning the electropolymerisations of the other monomers described in this chapter are still awaiting completion. However, due to the promising results obtained from the electropolymerisation of compound (4) further characterisation of this material was performed and these results are presented and discussed in the proceeding section.

2.6 SCANNING ELECTRON MICROSCOPY (S.E.M.)

2.6.1 Introduction

In its normal mode of imagery the Scanning Electron Microscope (SEM) is used to examine the surface of objects at extremely high magnification. As 100 Å resolution is routinely achieved the technique is ideally suited to the detailed surface examination of electrochemically grown EAPs films. The SEM employed in these studies was a Cambridge Stereoscan 600.

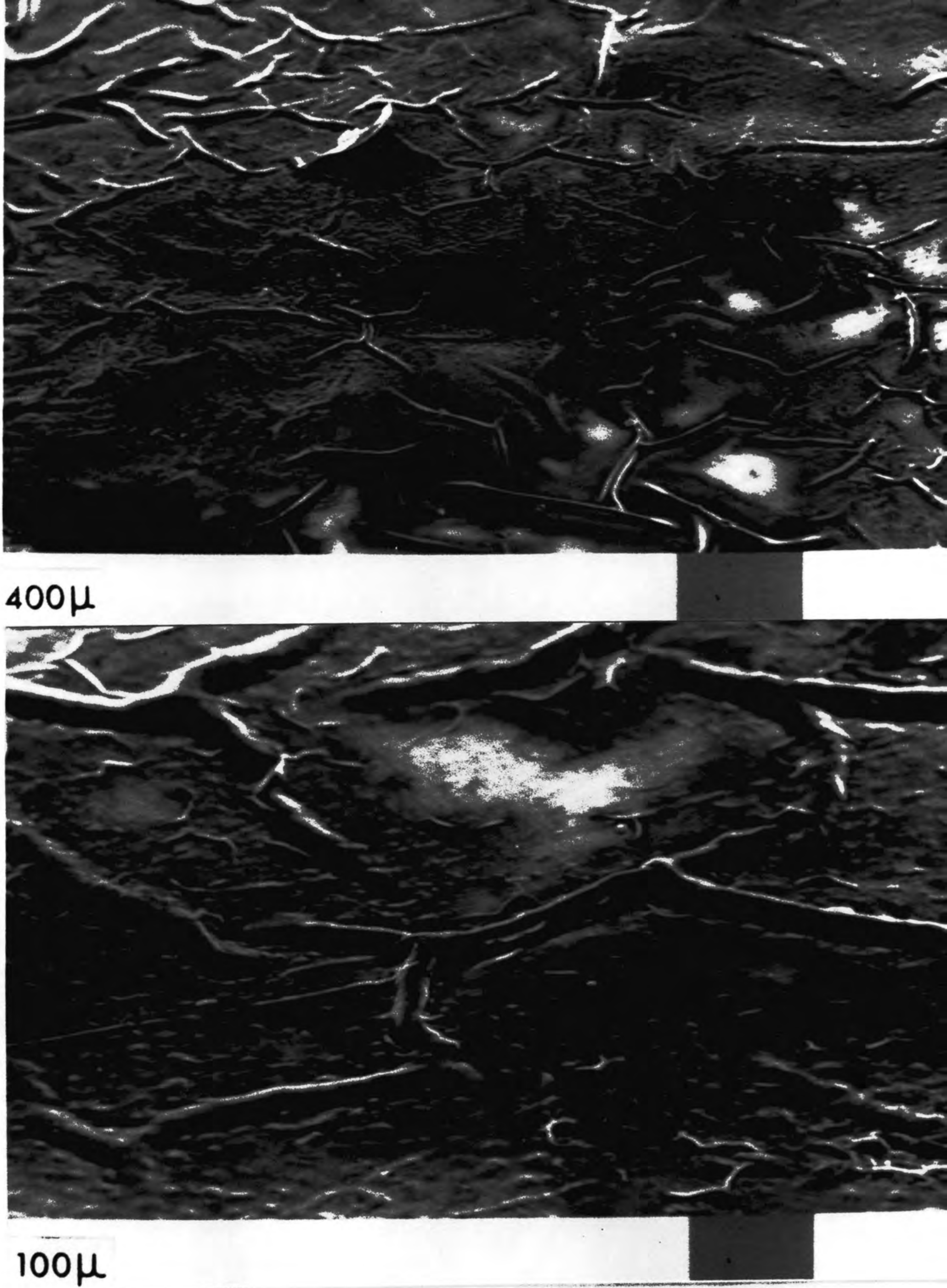


Figure 2.10 *S.E.M. Photographs Depicting the Polymer Surface at Both 400μ (top) and 100μ (bottom).*

2.6.2 Results

The surface morphology of the oxidised form of the polymer [from compound (4)] appears similar to films of other PT's in their oxidised form, that have been grown in a similar manner[1c]. The observed ridges are thought to be the result of film contraction, caused by residual solvent removal from the polymer prior to SEM analysis. Unfortunately, attempts to produce polymer in its reduced form (for a similar SEM study) by the electrochemical de-doping of the oxidised film were not successful. Instead complete solubilisation of the reduced/partially reduced polymer occurred in nitrobenzene to leave a shiny Pt working electrode. If further attempts are to be made to try and obtain a reduced film for SEM analysis, the use of a more weakly solvating solvent, *eg*. tetrachloromethane is suggested (*cf*. nitrobenzene).

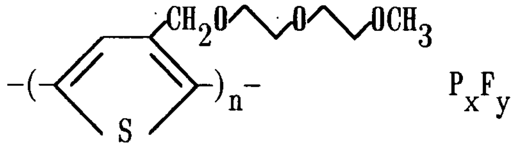
2.7 ELECTRON SPECTROSCOPY FOR CHEMICAL ANALYSIS (E.S.C.A.)[143]

2.7.1 Introduction

The E.S.C.A. technique, otherwise known as X-ray Photoelectron Spectroscopy (X.P.S.) was developed as an analytical tool following the pioneering work of Siebahn *et al*. in the 1950's and 1960's[144,145]. However, its application to the field of organic polymers was developed by Clark *et al*. in the 1970's[146]. E.S.C.A. has proved capable of providing unique information concerning the surface elemental composition and dopant level of EAP's. Thus E.S.C.A. analysis of the polymer of compound (4) was performed. A Kratos ES300 electron spectrometer was used to record the E.S.C.A. spectra, with the sample positioned at an angle of 35° with respect to a plane parallel to the location of the electron analyser slits. MgKα X-radiation was used. Binding energies are quoted relative to hydrocarbon C_{1s} at 285 eV. Surface elemental stoichiometries were obtained from peak area ratios corrected by the appropriate elemental sensitivity factors experimentally determined from standard samples. An error of ±10% can generally be expected in the surface stoichiometries. The E.S.C.A. spectra obtained are presented in Figures 2.11, 2.12 and 2.13.

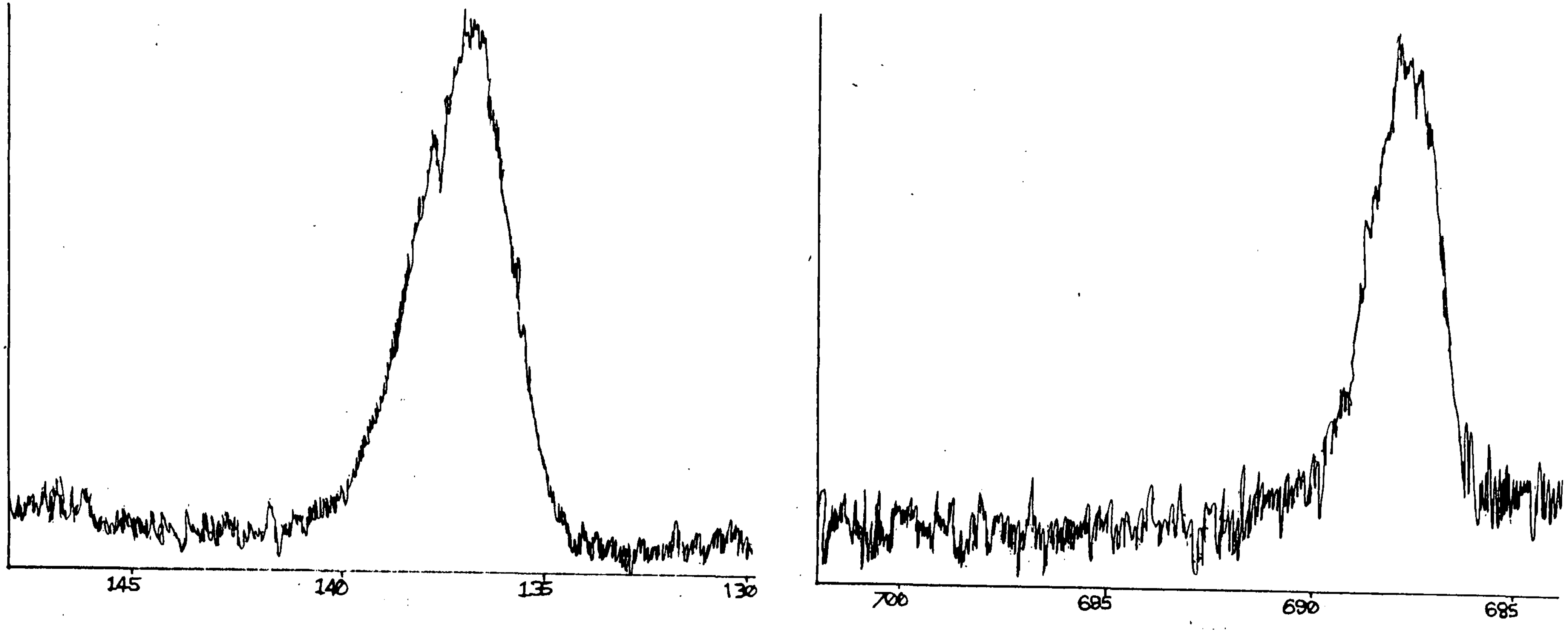
2.7.2 Results

As can be seen from Table 2.3, the ratio of carbon:sulphur is *ca.* 10:1 both from E.S.C.A. and microanalytical data. This is consistent with the structural formula of the monomer, implying that the σ-framework has remained intact on electropolymerisation.



ELEMENT	C(1s)	H(1s)	O(1s)	S(2p)	P(2p)	F(1s)	N(1s)
Binding Energy	288.1	-----	534.6	166.6	134.6	688.0	-----
Elemental Ratio (E.S.C.A.)	10.0	-----	4.0	1.0	0.6	0.4	0.0
Elemental Ratio (Microanalysis)	10.0	14.5	-----	1.2	-----	-----	0.0
Elemental Ratio (Theoretical)	10.0	14.0	3.0	1.0	-----	-----	0.0

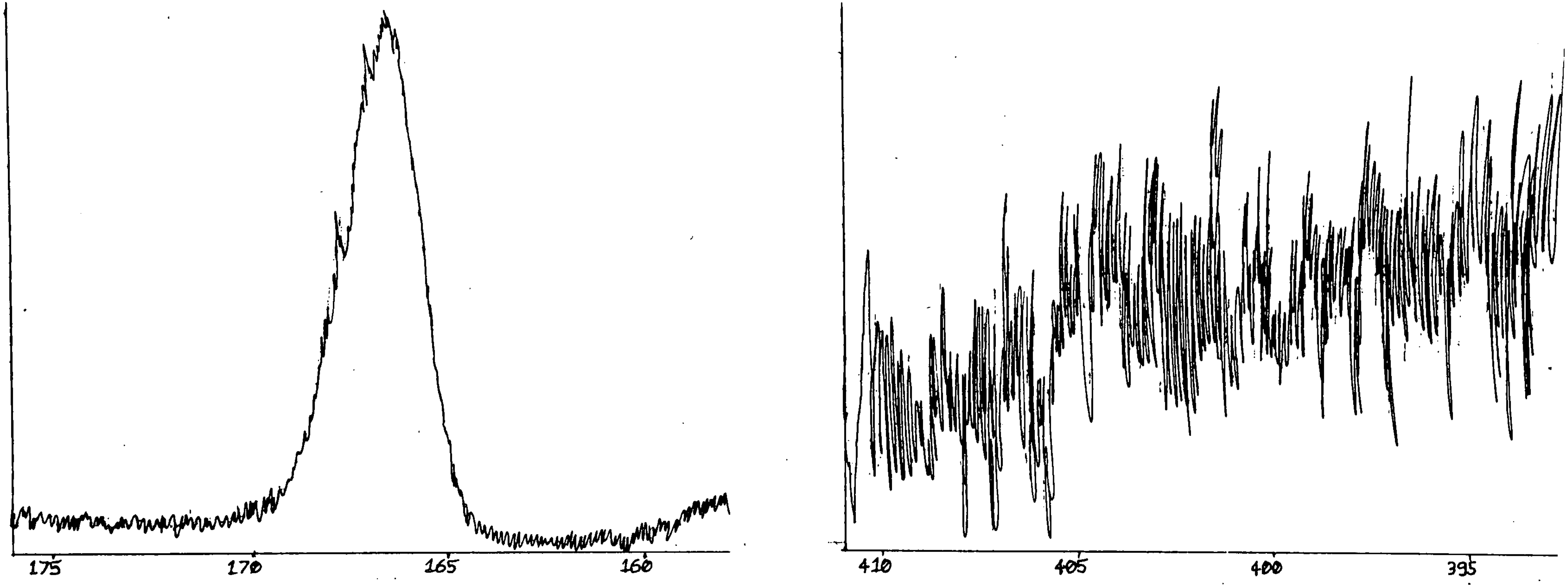
Table 2.3 *E.S.C.A. Results for the Electroactive Polymer of Compound (4).*



(a)

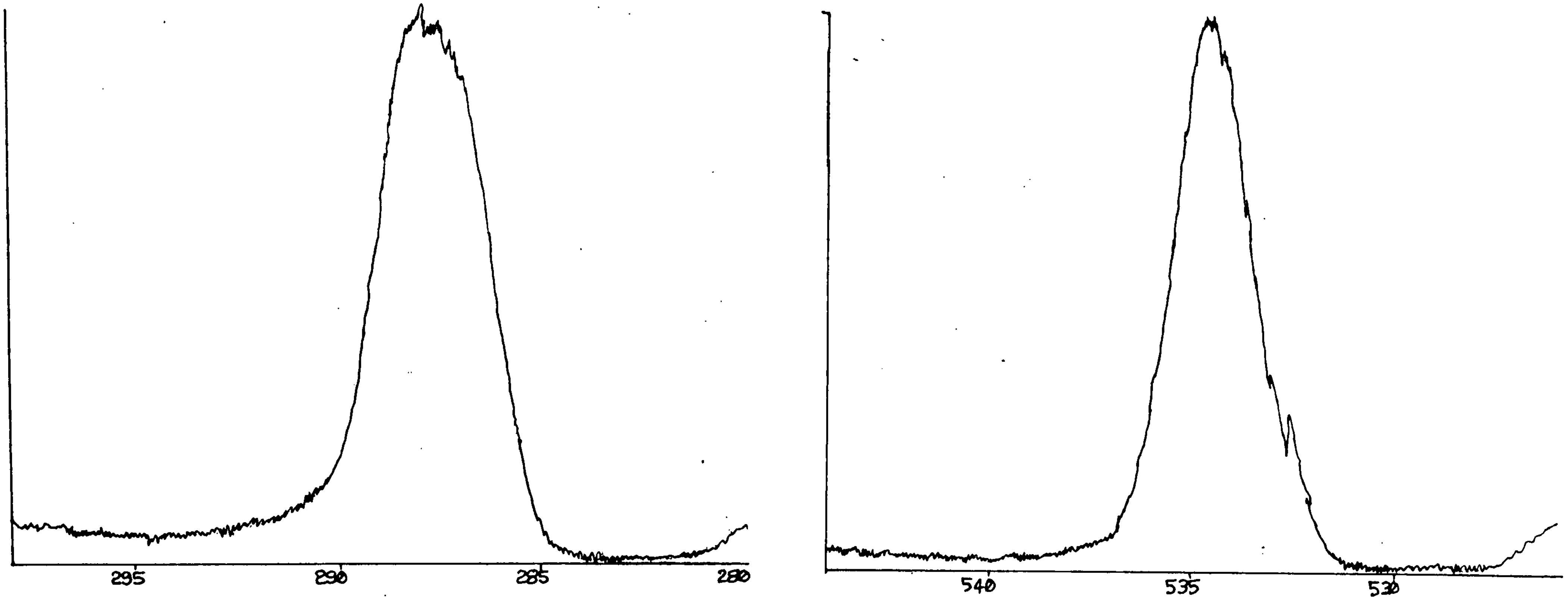
(b)

Figure 2.11 *ESCA Spectra for the Polymer of Compound (4); a)* P_{2p} *b)* F_{1s}



(a) (b)

Figure 2.12 *ESCA Spectra for the Polymer of Compound (4); a)* S_{2p} *b)* N_{1s}



(a)

(b)

Figure 2.13 *ESCA Spectra for the Polymer of Compound (4); a)* C_{1s} *b)* O_{1s}

From the E.S.C.A. analysis the oxygen:sulphur ratio is somewhat high (4:1), however, this is not uncommon and has been observed for many other EAPs as well. The slightly high oxygen count may be due to surface contamination of the sample or it may indicate that the polyether chains reside at the surface of the sample, whilst the thiophene rings are buried further beneath the surface.

Another interesting feature of the spectra obtained is the phosphorus and fluorine analyses. It is clear that the anion incorporated into the polymer is not PF_6^-. This is demonstrated by the calculated binding energy of phosphorus, *viz.* 134.6 eV [after correctional recalibration (*cf.* phosphorus in PF_6^- environment = 137.0 eV)]. Moreover, the P:F ratio obtained is 1:0.6 (*cf.* 1:6 for PF_6^-). These results are in agreement with similar work, performed on PP by Street *et al.*[147,148] and illustrate the danger of assuming that the anions from the electrolyte are necessarily the anions incorporated into the oxidised polymer. The PF_6^- anion, when incorporated into the EAP, appears to undergo an electrochemically initiated transformation the nature of which is obscure. The structure of the resulting anionic species that is incorporated into the polymer is unknown: the ratio of P:S is 0.6:1, *ie.* 3 phosphorus units are associated with every 5 sulphurs. This represents a very high doping level when compared to other PT's. However in similarly prepared samples the conductivity is also much lower.

2.8 FOURIER TRANSFORM INFRARED SPECTROSCOPY (F.T.I.R.)

2.8.1 Introduction

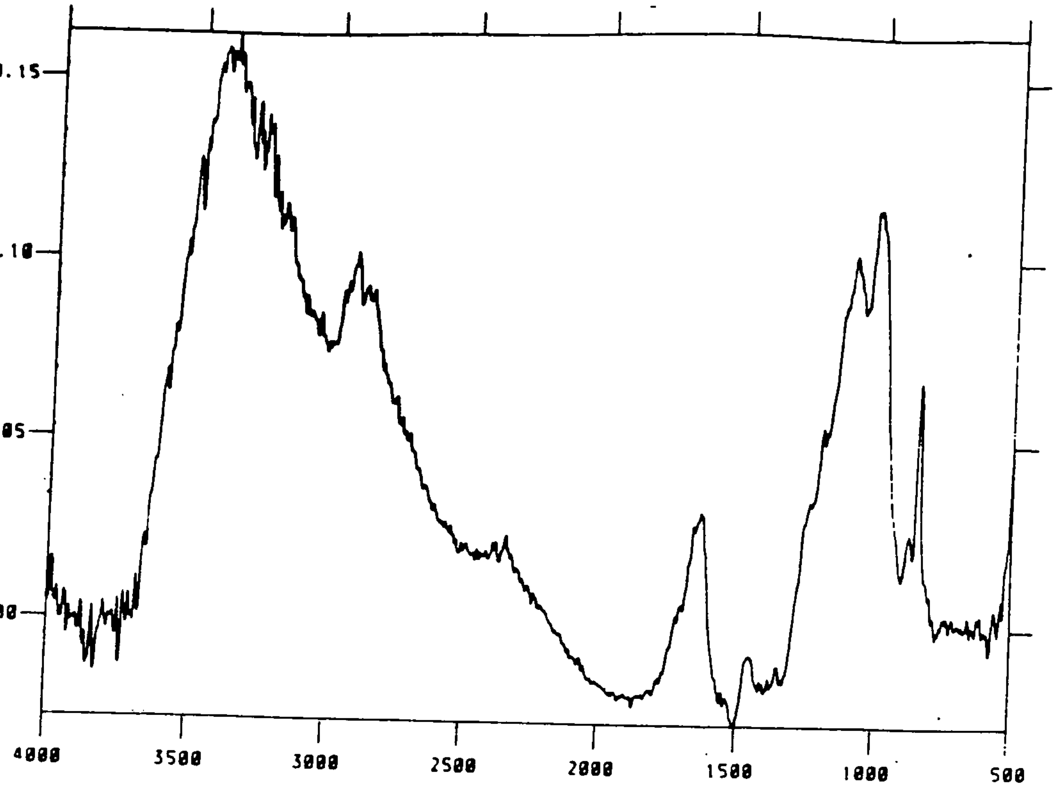
Work carried out by Yamamoto *et al.*[92ab] and more recently by Tourillon *et al.*[38] have established that α-α coupled polythiophene in its neutral form exhibits a ring β C-H out of plane bend at between 785 and 788 cm^{-1} whereas the α-β coupled species exhibits out of plane bends at 820 and 730 cm^{-1}.

Along with the obvious advantages possessed by F.T.I.R., it was hoped that the nature of the polymer (α-α or α-β) could be verified using this infrared technique. The instrument used in these studies was a Mattson Sirius Dixon 100.

2.8.2 Results

Owing to the difficulty of obtaining the polymer in its neutral form (see section 2.6.2), F.T.I.R. was carried out on the polymer in its electroactive (oxidised) form. Figures 2.14 and 2.15 show the spectra of the polymer and monomer for comparison. Before any detailed analysis of the spectra can begin, it must be re-iterated that the main chain polymer backbone is positively charged. This would lead, one might expect, to a lowering of the recorded frequency shifts when compared to the monomer. Also, as electrical neutrality is maintained by the incorporation of anionic species within the polymer matrix, peaks due to these anionic species should also be present in the polymer (compared to the monomer).

From Figures 2.14 and 2.15 it is clear that the polymer has absorbed water (*ca.* 3500 cm^{-1}) otherwise most aspects of the polymer



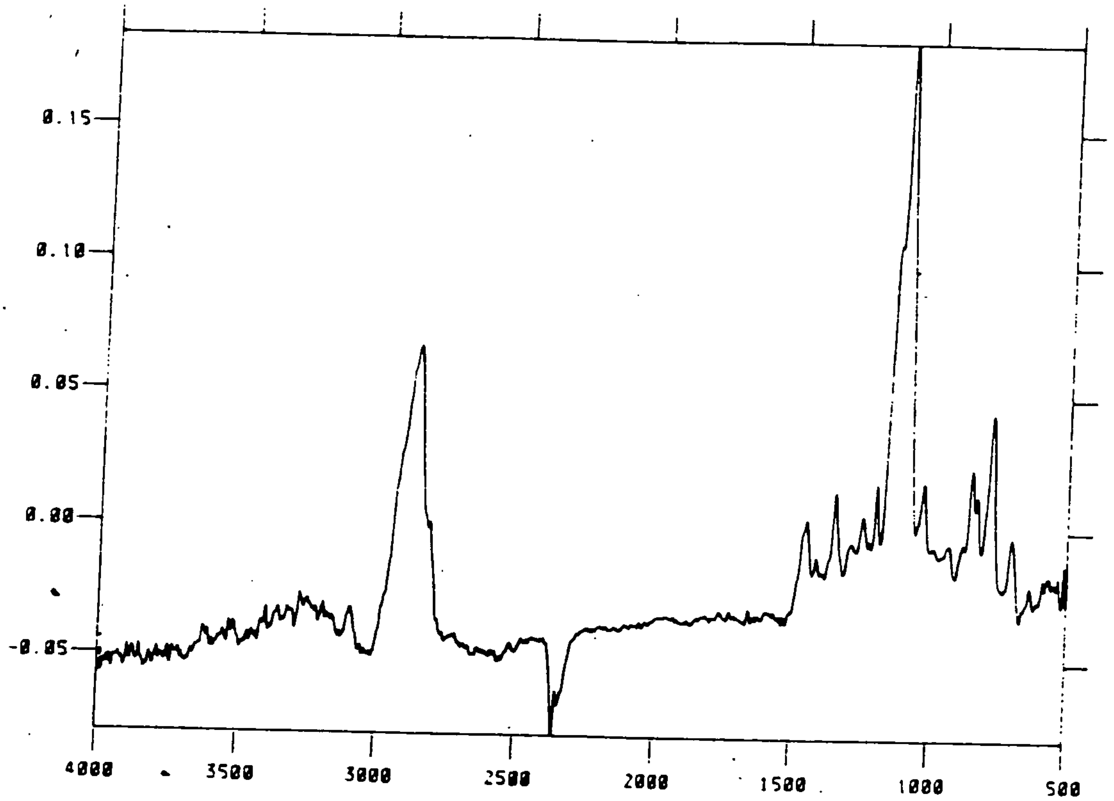


Figure 2.14 *F.T.I.R. Spectrum of a Section of the Polymer (top) and the Monomer (bottom) Between the Scanning Range.*

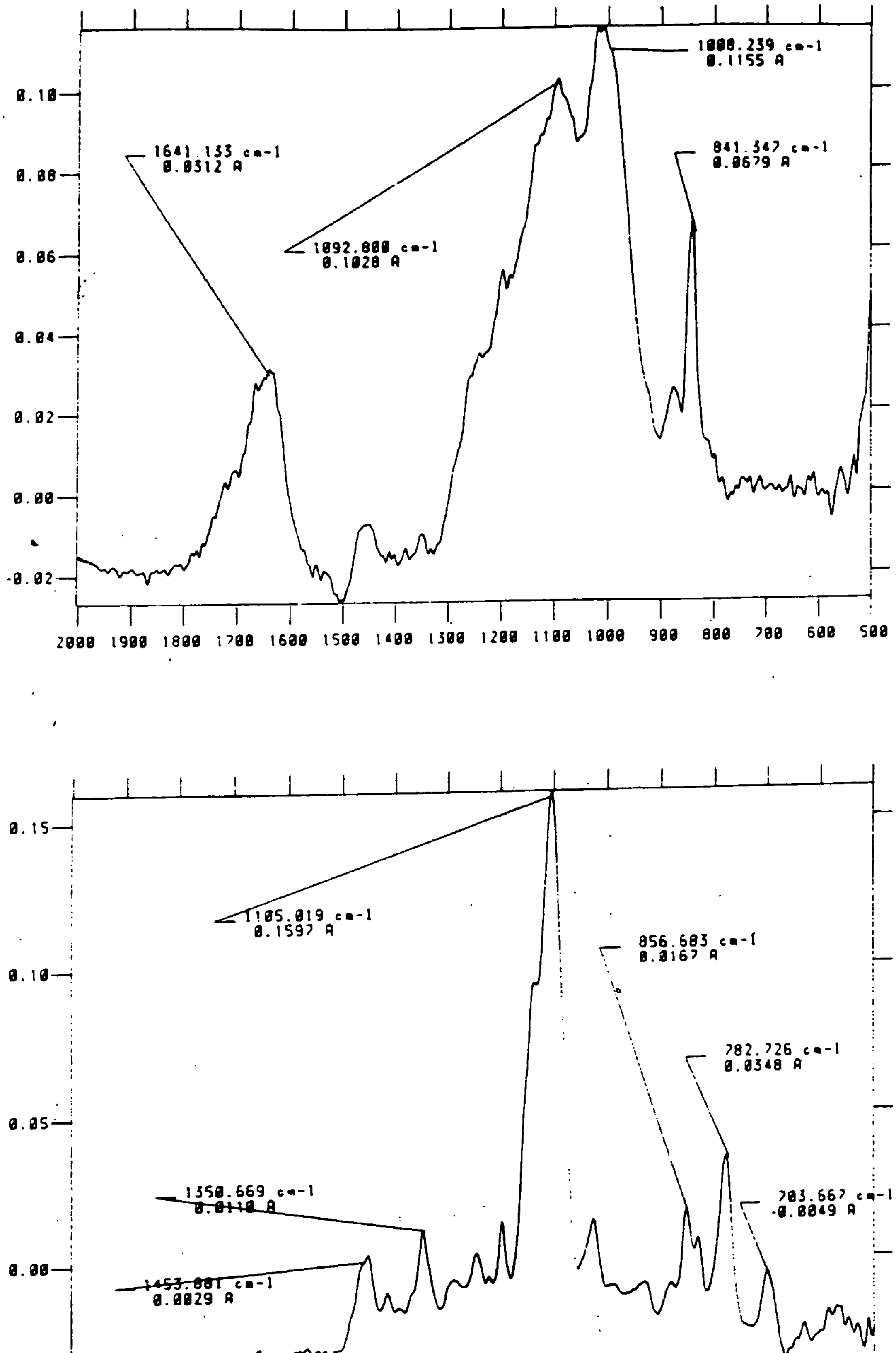


Figure 2.15 *F.T.I.R. Spectrum of the Polymer (top) and the Monomer (bottom) Between the Scanning Range.*

infrared can be detected in the monomer, indicating the preservation of the aromatic moiety and chain.

Unfortunately, as the anionic species incorporated into the polymer cannot be PF_6^- (see section 2.7.2) it is difficult to assign any of the other peaks in the spectrum. The peak at 841 cm^{-1} may be due to a P-F type stretch (the nature of which is unknown), as the C-H out of plane bends for α-α and α-β coupled species come at a lower frequency than 820 cm^{-1} (due to the positively charged main chain). The peak at 1641 cm^{-1} in the polymer is probably again due to the anion and therefore remains unassigned. Unfortunately then, the establishment of the type of linkage within the polymer (in its oxidised form) was not obtainable using this technique.

2.9 CONCLUSION

This chapter has presented a simple method of entry into both alkyl ($-CH_2OR$) and alkoxy ($-O-CH_2R$) β-substituted thiophenes. The synthetic methodology developed in this chapter can be further extended to encompass other types of β-substituent (see proceeding chapters) and it has proved amenable to scale up. For example, compound (4) has been successfully prepared on a 1 Kg scale by Palmer Research. However, at the start of this research, the possibility existed that lengthy β-substituents may interfere with the polymerisation process, either by steric hindrance during the radical cation coupling process, or, through lipophilic interactions that prevent adhesion of polymer to the electrode. In the event, these possibilities, though borne out somewhat during the CV studies, were not crucial in deciding whether electropolymerisation occurred. The overriding factor appeared to be the choice of electropolymerisation conditions. In general, when employing the technique of cyclic voltammetry, only monomers containing a maximum of 3 atoms in the β side-chain seemed to form EAPs (*cf.* β chains > 3 atoms under the standard conditions described herein). Whereas it has been demonstrated that thiophenes bearing β chains of at least 9 atoms in length can be successfully electropolymerised using the constant current technique. The success of this technique may be due to the more 'brutal' approach it provides for the generation of radical cations. Although successful, the technique may have the drawback of reducing the selectivity of α-α linked radical cation coupling. Consequently, the onset of polymer formation employing this technique, may be due to a greater degree of mislinked and crosslinked thiophene units than is the case when cyclic voltammetry is employed. Alternatively, the preferred use of a modified Pt working electrode surface, when using constant current methods may also influence polymer deposition possibly through the preferential adsorption of the thiophene moiety onto the electrode (see Section 3.2.3). This could possibly be verified by performing a separate series of CV experiments using a surface modified Pt working electrode (see Chapter 5). Nevertheless, through the appropriate choice of conditions, thiophenes bearing long chains at the β-position can be electropolymerised to yield highly conducting, thermally stable EAP's, some of which are solution processible in their conducting forms.

CHAPTER THREE

β- PHENOXY ETHER SUBSTITUTED THIOPHENES

3.1 INTRODUCTION

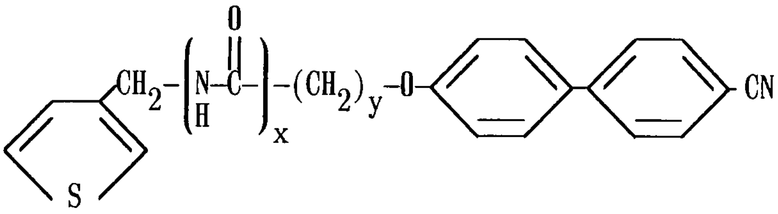
The introduction of β-substituents onto the thiophene ring does not impair the electrical conductivity of the polymer: indeed in some cases, such an introduction may even be beneficial to the conductivity of the polymer. If the β-substituent consists of a long flexible chain, solution processibility may also be imparted to the polymer (Chapter 2). The solution processibility in such a case, is brought about, in the main, by the lipophilic interactions that are established between the polymer chains and the solvent.

Another method of inducing solution processibility through the use of β-substituents is to introduce bulky side groups that physically force the polymer chains apart. This action would reduce the intermolecular attractive forces that exist between the chains making them more amenable to dissolution. This chapter describes the synthesis of such a series of β-substituted thiophene monomers, the bulky pendant side group being provided by a series of substituted phenoxy ethers. These were synthesised employing the methodology established in Chapter 2 (Williamson type coupling), hence the starting materials would be a range of substituted phenols. Phenols were chosen for the following reasons:

a) Cost.	Phenol and its substituted derivatives are relatively cheap, enabling an economical bias towards the large scale development of such systems.
b) Availability	Many substituted phenols exist in the ortho, meta and para positions (or in combinations of the above) leading to a wide range of possible monomers.
c) Synthesis	Monomer synthesis in principle would not be multi-step, lending themselves to an economical method of entry as well as simple method of entry.

3.1.1 Target Monomers

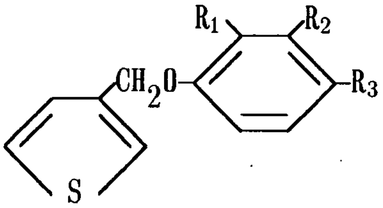
TYPE 1



(25) x=0; y=0
(27) x=1; y=5

Liquid Crystalline Phenoxyethers

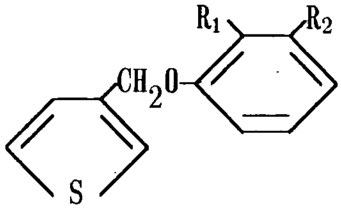
TYPE 2



(28) R_1=H; R_2=H; R_3=H
(29) R_1=CH_3; R_2=H; R_3=H
(30) R_1=H; R_2=CH_3; R_3=H
(31) R_1=H; R_2=H; R_3=CH_3

Alkyl Phenoxy Ethers

TYPE 3



(33) R_1=NH_2; R_2=H
(35) R_1=H; R_2=NH_2

Aniline Phenoxy Ethers

Figure 3.1 *Target Monomers Synthesised in this Chapter.*

The synthesis and electrochemical study of each type of monomer described in this chapter will be dealt with separately. This is convenient because all of the above types of phenoxyether possess their own characteristic electrochemistry and, in contrast to the derivatives synthesised in Chapter 2, the β-substituent itself possesses far more electrochemical activity (Section 3.2). It is the electrochemistry of phenoxyethers that will now be described.

3.2 ELECTROCHEMISTRY OF PHENOXYETHERS[57a]

Phenols and phenoxyethers have played an important role as model compounds for the study of aromatic radical cations, so much information regarding the electrochemistry of these systems has been accumulated.

The presence of the electron donating oxygen in the phenoxyether is responsible for the relative ease of formation of the radical cation, the fate of which is easily monitored by conventional electrochemical techniques.

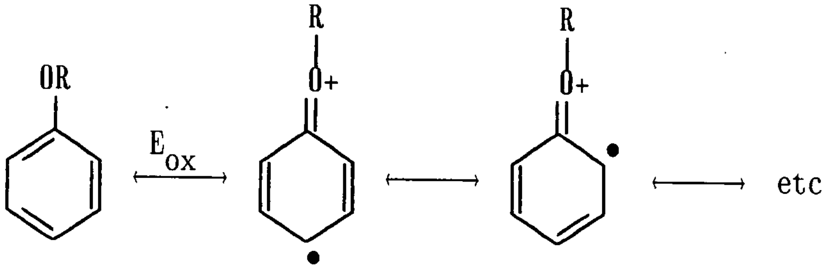


Figure 3.2 *Resonance Structures of Phenoxy Radical Cation.*

As the primary oxidation for all of the above systems to be studied is likely to be that of the phenoxyether moiety (E_{pa} ~ 1.5-1.8 V *cf.* thiophene 2.1 V) the possible fate of such a species must be outlined.

3.2.1 Possible Fates of Phenoxy radical Cations

The end product of a phenoxy radical cation once generated is very dependent upon the reaction conditions. Although electrochemical reversibility can be effected at low enough temperature[150], and reaction with the solvent (if nucleophilic enough) is well documented, it was likely that neither event would occur under the conditions of our C.V. studies. Other outcomes of more direct consequence to our work, like phenoxy coupling or the presence of α-protons on substituents in the ring will however be discussed.

3.2.2 Phenolic Coupling[151]

The possibility exists for two radical cations to couple with each other with the elimination of two protons, *eg.*

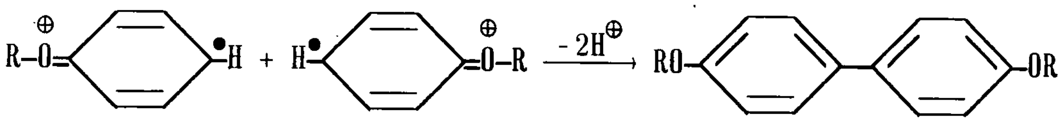


Figure 3.3 *Coupling of Phenoxy Radicals.*

If such an event were to occur, para-para coupling would predominate over ortho-ortho or ortho-para coupling due to the radical cation stability. The resulting biphenyl would then reoxidise rapidly and be subject to attack by solvent or base electrolyte. In cases where this type of coupling has occurred, it has always been a minor side reaction (unless deliberate attempts to initiate such a process have been made).

3.2.3 The Presence of *α*-Protons

α-Proton containing substituents on the aromatic ring are susceptible to ablation upon generation of the radical cation *eg*.

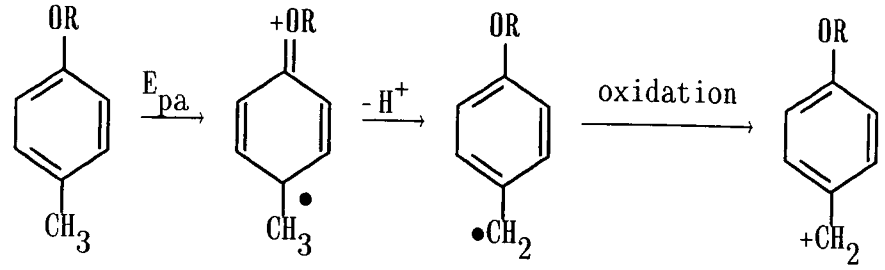


Figure 3.4 *Generation of a Benzylic Cation.*

Once generated, the radical is further oxidised to form the benzylic cation above. This can then go on to react if a nucleophilic solvent *eg*. methanol is present. This information regarding the fate of phenoxyether radical cations would tend to support an argument against their use as pendent moieties to aid the dissolution of poly(thiophene), especially as the thiophene moiety possesses an oxidation potential in excess of the phenoxy moiety. However, there is tentative evidence to suggest that the thiophene moiety is that part of the molecule that is preferentially adsorbed onto the "modified" working electrode (Section 2.4.2). This being the case, the possibility of intramolecular electron transfer from the phenoxy unit to the thiophene unit may occur initiating *α*-*α* coupled poly(thiophene) units. Aside from this, very little work has been done regarding phenoxyethers that contain discrete units that may also undergo electrochemical oxidation. It was with these views in mind that the following research was carried out. The following sections describe in turn, work carried out on liquid crystals, methyl derivatives of phenoxyethers and lastly amino derivatives of phenoxyethers. Each section also contains a brief introduction (where appropriate) to the type of chemistry associated with each type of phenoxyether derivative.

3.3 TYPE 1 MONOMERS

3.3.1 Introduction - Monomeric Liquid Crystals

The existence of liquid crystals has been known since the end of the last century when, for the first time, Reinitzer observed the unusual melting behaviour of certain types of cholesterol[152]. Melting was found not to be a sharp transition from the enantiotropic solid through to the isotropic liquid but rather, to involve intermediate phases known as *mesophases*. This region of intermediate melting was termed the liquid crystalline or mesomorphic region. To date, two types of liquid crystal have been discovered: (i) lyotropic and (ii) thermotropic.

Those characterised as lyotropic exhibit mesomorphic behaviour through the action of a solvent, but those characterised as thermotropic exhibit mesomorphic behaviour through the action of heat. It is this latter category that will be discussed in more detail.

3.3.2 Thermotropic Liquid Crystals[153,154]

The mesophases observed in thermotropic liquid crystals are the result of structural re-ordering of the molecules within the lattice whilst maintaining some semblance of short and long term order. Each mesophase occurs at a definite temperature and is accompanied typically by changes in latent heat (*vide infra*) and colour. However, each type of mesophase is not only dependent upon the temperature, but also upon the structure of the starting liquid crystal (rod, disc or globular). As the synthesis of compounds (25) and (27) specifically deal with rod like liquid crystals, the mesophases associated with such systems will be described.

3.3.3 Mesophases

The two most common mesophases for rod-like mesogens are the smectic and nematic mesophases (Figure 3.5).

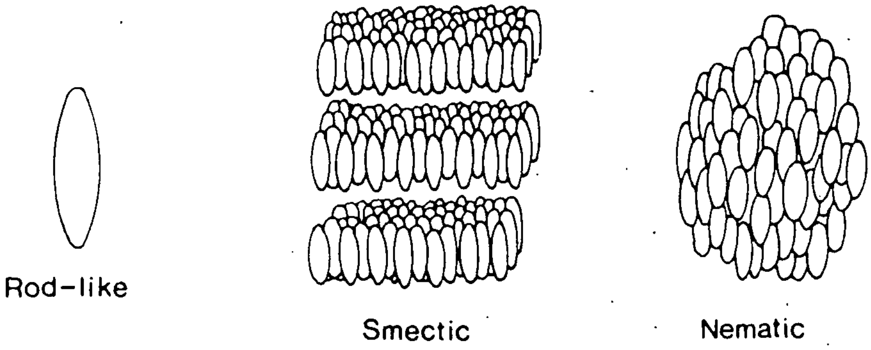


Figure 3.5 *The Most Common Mesophases Associated with Rod Like Mesogens.*

The smectic phase is characterised by a parallelism of molecular long axes and by a layering structure of the molecular centres in two-dimensional sheets. In the nematic phase the long axes of the molecules remain substantially parallel but the positions of the molecule centres are more disorganised. At this moment in time it is impossible to predict with certainty whether or not a given substance will exhibit liquid crystalline behaviour; however, general guidelines exist concerning the requirements for rod-like molecules to exhibit the type of mesomorphic behaviour stated above:[155]

(1) They must be geometrically highly asymmetric with a minimum length of 13-14Å.

(2) They should possess (in most cases) a permanent dipolar group.

(3) The molecules should also present a high anisotropy of polarisability.

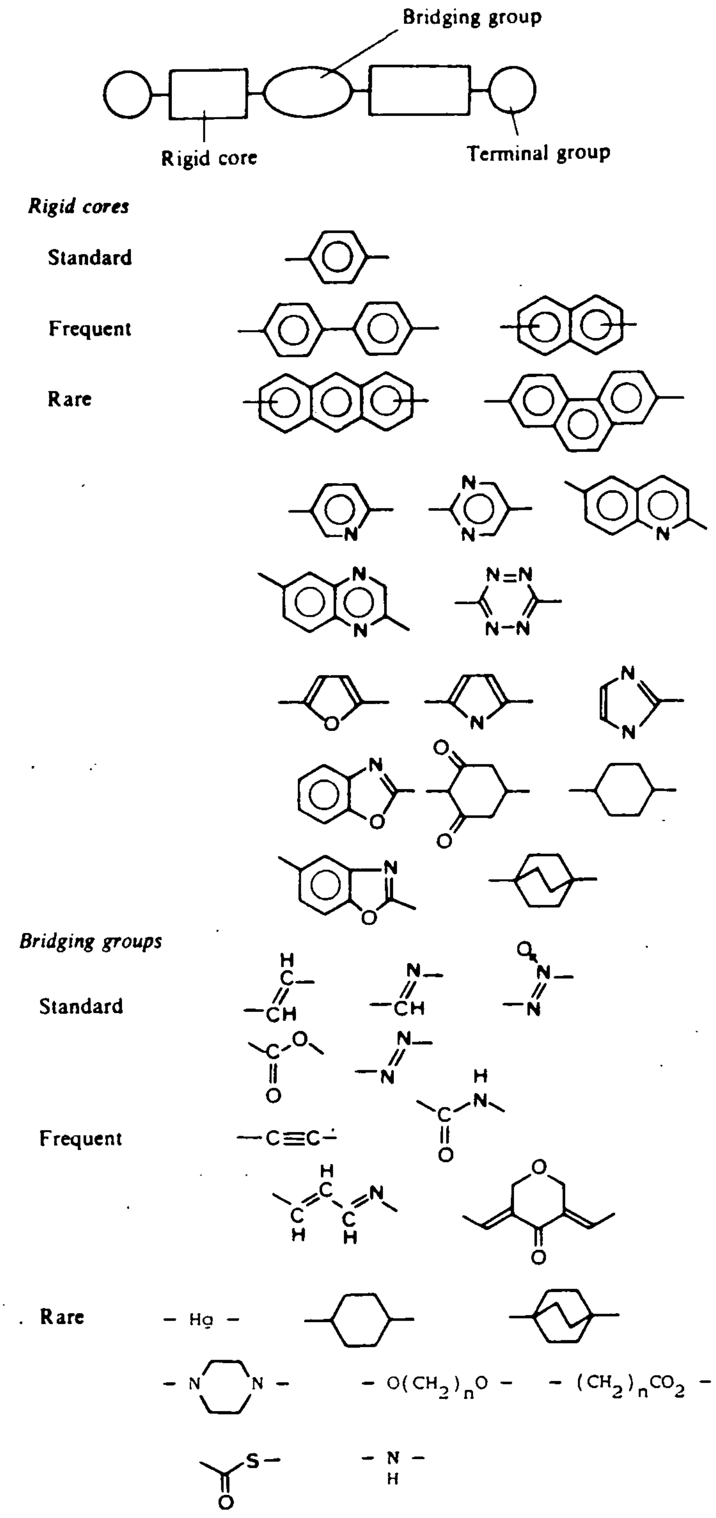
Typical rod-like molecules fulfilling these requirements and possessing liquid crystalline phases usually consist of a rigid core, two terminal end groups and a bridging group (Figure 3.6).

3.3.4 Polymeric Liquid Crystals

When liquid crystals began to be incorporated into polymers, so-called "polymeric liquid crystals", it was noted that in some cases (*eg.* Kevlar) that the resulting polymers possessed superior physical and mechanical properties as the polymers were "locked" into a liquid crystalline phase. There also existed a greater likelihood of melt processibility in a polymer that possessed liquid crystalline sub-units. Hence the branch of "polymeric liquid crystals" developed. Of the two types of "polymeric liquid crystals" developed (main chain and side chain) our work consists potentially of side chain "polymeric liquid crystals".

3.3.5 Side Chain Polymeric Liquid Crystals

The mesogenic groups in typical side chain polymers are separated from the main chain by flexible spacer molecules, the purpose of which



Terminal groups

Standard	$-OR$ $-CN$	$-R$ $-OOCR$	$-CO_2R$	
Frequent	$-Cl$	$-NO_2$	$-COR$	
Rare	$-H$ $-N=C=O$ $-SR$ $-O(CH_2)_nOR$	$-F$ $-OH$ $-COSR$ $-(CH_2)_2OH$	$-Br$ $-CO_2R$ $-HgCl$	$-N_3$ $-NH_2$ $-SiR_3$

Figure 3.6 *Typical Requirements for Rod-like Mesogens.*

is to preserve the delicate interactions between each pendant mesogenic group. This is achieved through the decoupling of the main chain motion from that of the mesogen.

However, it has been demonstrated that the presence of the spacer group need not be necessary to ensure mesomorphic behaviour within the polymer[153]. It has also been demonstrated that incorporating a known mesogenic group into a polymer is no guarantee of ensuring that the polymer itself exhibits similar mesomorphic behaviour. However, spurred on by research being carried out by other groups also combining liquid crystal chemistry with EAP chemistry, the following speculative work, concerning the known mesogenic substance, 4-cyano-4'-methoxybiphenyl was carried out[156].

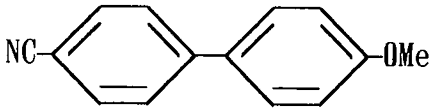


Figure 3.7 *4-cyano-4'-methoxybiphenyl.*

3.3.6 Synthesis of Type 1 Monomers

Two monomers, compounds (25) and (27) were synthesised, both employing a convergent route (Figure 3.8). As the liquid crystalline moiety used is only commercially available as the methyl ether, its cleavage to form the phenol (24) was carried out using a thioethoxide mediated S_N2 displacement according to the method of Feutrill and Mirrington[157]. Effected in good yield (80%) this was then coupled to (1) in the Williamson reaction to give (25) in 81% yield.

In order to synthesise compound (27), a general method of entry *via* compound (10) was established, allowing a degree of autonomy regarding the length of the spacer functionality that could be incorporated. Acetylation of (10) with 6-bromohexanoyl chloride gave compound (26)

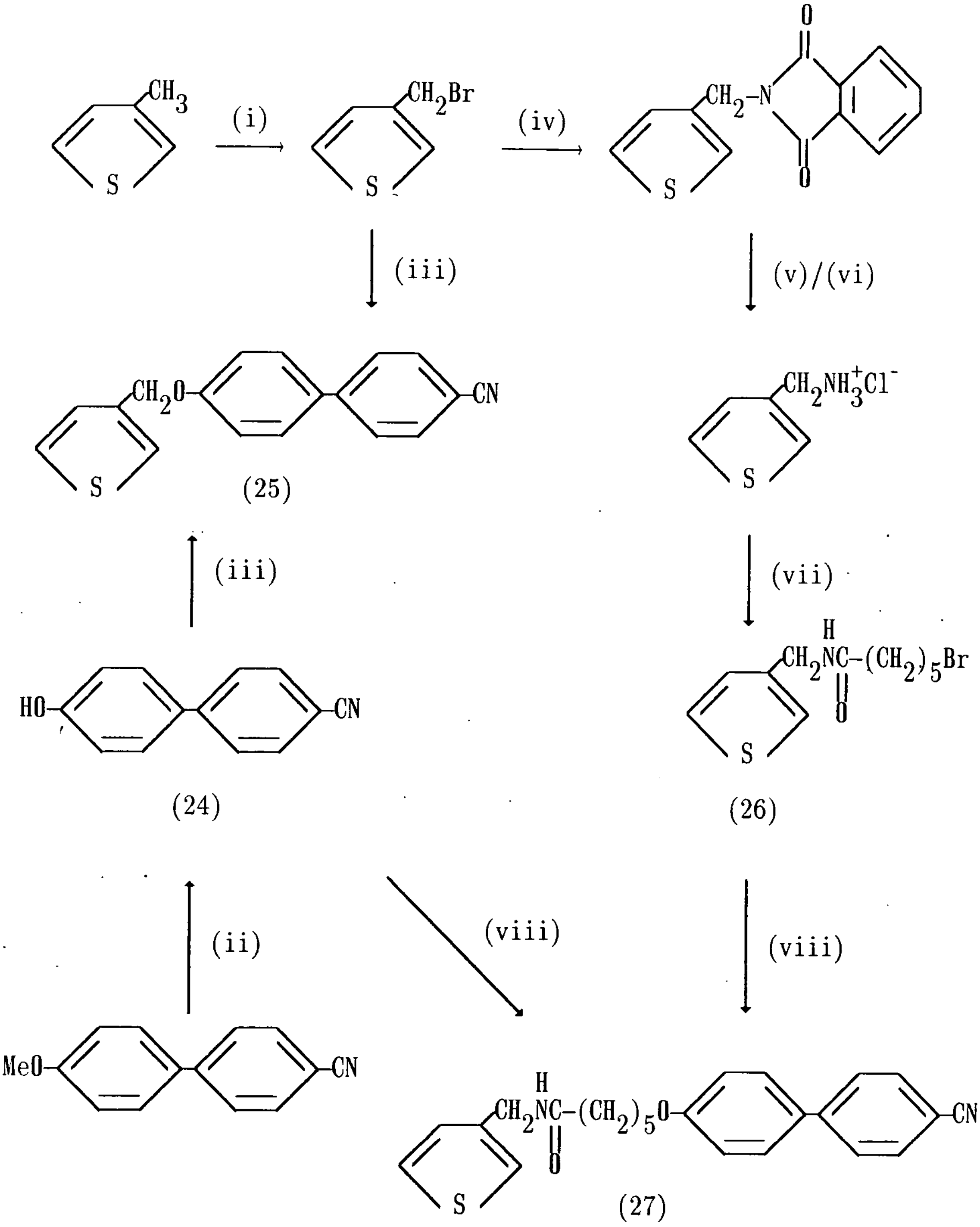


Figure 3.8 *Scheme Depicting the Synthesis of Type 1 Monomers; Typical Reagents and Reaction Conditions are: (i) N-Bromosuccinimide, AIBN, CCl_4, Reflux; (ii) Sodium Ethanthiolate, DMF, 120^0C; (iii) KOH, THF, 18-Crown-6 Ether, Reflux; (iv) K^+ Phthalimide, 18-Crown-6, DMF, 80^0C; (v) N_2H_4, H_2O, EtOH, Reflux; (vi) HCl, Reflux; (vii) 6-Bromohexanoyl chloride, Et_3N, CH_2Cl_2, -5^0C; (viii) Potassium salt of (24), 18-crown-6, DMF, 80^0C.*

PAGE(S) MISSING
NOT AVAILABLE

FIG 3-9

(62% yield) which was coupled with (24) in a similar manner to (1) to yield compound (27) in 30% yield.

3.3.7 Differential Scanning Calorimetry (D.S.C)

DSC studies were carried out on both monomers (25) and (27). The results of this study are illustrated in Figure 3.9. It is clear from Figure 3.9 that compound (25) in its monomeric state does not show any mesomorphic behaviour and only the expected solid-liquid phase transition was observed. The DSC trace of compound (27) however revealed thermal transitions consistent with liquid crystalline behaviour. As stated previously, the fact that compound (25) does not possess any mesomorphic character as the monomer, does not necessarily mean that it will not do so when electropolymerised. Many examples exist in the literature that confirm liquid crystalline behaviour in side chain polymers, whose monomers themselves were not liquid crystalline. This appears to be the case with compound (25). The DSC of the polymer (*vide infra*) clearly illustrates behaviour consistent with a liquid crystalline phase (Figure 3.10).

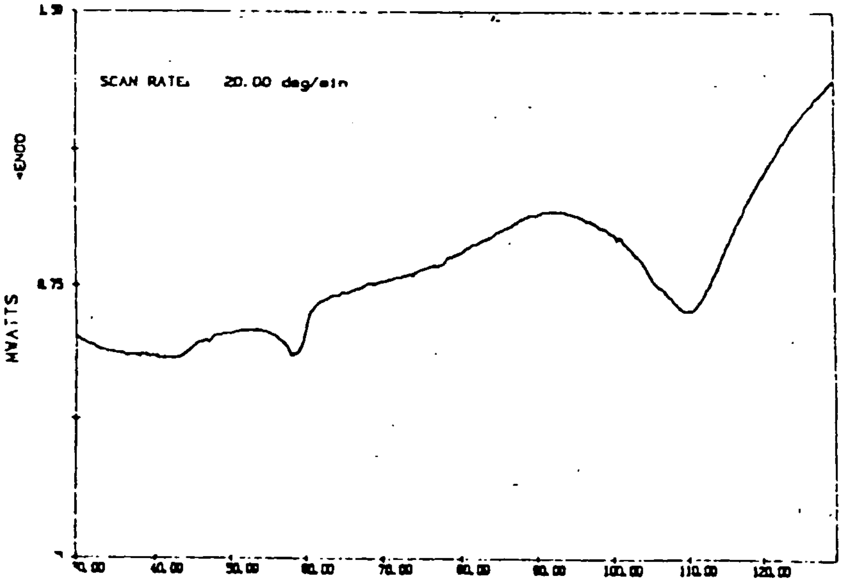


Figure 3.10 *DSC Trace of the Electroactive Polymer of Compound (25).*

Further work concerning these observations is being carried out by B.D.H. (Poole, Dorset) and at Perivale. Compound (27) has yet to be electropolymerised (*cf.* Monomer (25), Section 3.3.9) so no information regarding the DSC of compound (27) in its polymeric form has yet been obtained. Attempts to further characterise the monomers (25) and (27) by polarising microscopy have proved inconclusive, although the rotation of polarised light has been observed for both monomers.

3.3.8 Cyclic Voltammetry Studies

Employing the same methodology developed in the previous chapter, cyclic voltammograms of compounds (25) and (27) were obtained. As it had already been decided (Section 2.3.2) to use a non-modified platinum working electrode for these studies, no adsorption of the thiophene and hence no polymer film was expected. However, as demonstrated in Table 3.1 the presence of nucleation loops are observed for both systems suggesting that some form of adhesion/adsorption may be occurring. The fact that the *para* position of the biphenyl unit was blocked by a cyano group meant that *para-para* coupling of the biphenyls was not possible (any other form of coupling being unlikely). However, as this peak is irreversible, the radical cation must either be reacting with solvent, base electrolyte, or some form of intramolecular electron transfer may be taking place, oxidising the thiophene ring (explaining a lack of a secondary oxidation wave at *ca.* 2.1 - 2.2 V) which is going on to form some low molecular weight oligomeric products.

	INITIAL SCAN (ν = 100 mV/s)							MULTISCANS @ 100 mV/s		
CPD	ANODIC SCAN	PRIM.OXID.WAVE			OTHER PEAKS		ANODE		FILM	GENERAL COMMENTS
	LIMIT (mV)^a	E_0/V,	$\|i_0\|$/mA,	CLR^b	E/V,	$\|i\|$/mA	COLOUR	$\|I_0\|$(mA)^c	FORMATION	
25	2500	1.71	0.16	0.98	None	None	None	inc	None	Nucleation Loops (scan 4) with initial decrease in current. By scan 10 the loops had disappeared.
27	2500	1.73	0.04	0.98	None	None	None	const	None	Nucleation observed (scan 4) but loops had ceased by scan 10.

Table 3.1 *Cyclic Voltammetric Study of Liquid Crystal Thiophene Monomers;*

a) The scan range was from 0.00 V to the specified limit;

b) CLR (coefficient of linear regression) was calculated to show the correlation between observed $|i(o)|$ *and* $\sqrt{\nu}$ *for* ν *= 50, 100, 200 and 400 mV/s;*

c) const = constant; inc = increase. These terms are used to describe how the current associated with the primary oxidation wave varies with continuous scanning.

3.3.9 Electropolymerisation of Monomer (25)

In this study using the constant current technique, compound (25) was successfully electropolymerised to give a "golden yellow-brown" film possessing a maximum room temperature conductivity value of 3.5×10^{-2} S cm^{-1} (two probe mercury drop technique) for *ca.* 20 microns thick film. As an anodised platinum electrode was used and successful electropolymerisation was achieved, evidence to support the idea of preferential thiophene adsorption is taking shape (Table 3.2).

3.4 TYPE 2 MONOMERS

3.4.1 Introduction

Carried out in tandem with the synthesis of the liquid crystalline derivatives were a series of monomers that possessed the bulky phenoxyether group but also bore a pendant methyl moiety in order to lend some lipophilic character to the polymers if successfully electropolymerised. The nature of the methyl groups being benzylic also lent themselves to further reaction *via* the loss of a proton (see Section 3.2.3). It was with these views in mind bearing what was said in Section 3.2 that the following target monomers were synthesised.

3.4.2 Synthesis of Type 2 Monomers

The yields of these reactions (Figure 3.11), though satisfactory, could not be increased, possibly due to the fact that phenoxide anions may act as enolate anions and undergo C- as well as O-alkylation. No attempt was made, however, to isolate any possible C-alkylated product.

COMPOUND	SOLVENT (30ml)	ANODE	MONOMER MOLARITY	ELECTROLYTE MOLARITY [a]	COULOMBS PASSED	CURRENT DENSITY (mA cm^{-2})	CONDUCTIVITY (σ_{rt} S cm^{-1}) [b]
25	$PhNO_2$	Pt	1 x 10^{-2}	1 x 10^{-1}	5.00	1.5 ± 0.1	0.04

Table 3.2 *Polymerisation Conditions;*
a) Tetrabutylammonium hexafluoroborate;
b) Two-Probe Measurement.

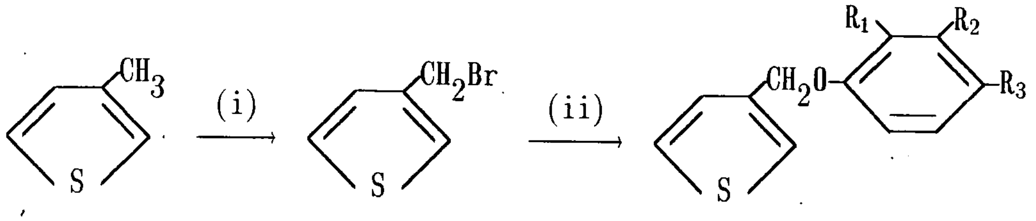
An interesting feature of the resulting monomers (28) and (31) was that they both exhibited thermochromism in the solid state[158]. Thermochromic compounds change colour reversibly with temperature and compounds (28) and (31) are both sky-blue at -20°C and white at 25°C. Of the possible mechanisms responsible for these colour changes:

(a) Thermal equilibrium between two forms *eg*. keto-enol

(b) Thermal structural rearrangement or

(c) Thermal, conformational rearrangements within the crystal lattice,

conformational rearrangements are the only likely explanation[159].



TYPE 2 MONOMERS

(28)	R_1=H; R_2=H; R_3=H	(48%)	(30)	R_1=H; R_2=CH_3; R_3=H	(68%)
(29)	R_1=CH_3; R_2=H; R_3=H	(76%)	(31)	R_1=H; R_2=H; R_3=CH_3	(60%)

Figure 3.11 *Synthetic Scheme Depicting the Synthesis of Type 2 Monomers; Typical Reagents and Reaction Conditions are: (i) N-bromosuccinimide, AIBN, CCl_4, reflux; (ii) Na^+ or K^+ salt of the appropriate phenoxide, THF, Reflux.*

3.4.3 Cyclic Voltammetry Studies

The results of these studies are contained in Table 3.3. From Table 3.3, the oxidation potential of all four monomers occur at a value consistent with the phenoxy moiety oxidising (similar to the biphenyls, Section 3.2). Yet films were formed on the electrode. This may be due to a complex series of coupling reactions involving both the thiophene and phenoxy moieties. Work at Perivale involving FTIR analysis is being carried out (see Section 5.2.2) in order to establish the exact nature of the polymers formed in this instance.

CPD	INITIAL SCAN (ν = 100 mV/s) ANODIC SCAN LIMIT (mV)[a]	PRIM.OXID.WAVE E_0/V	$\lvert i_0 \rvert$/mA	CLR[b]	OTHER PEAKS E/V	$\lvert i \rvert$/mA	ANODE COLOUR	MULTISCANS @ 100 mV/s I_0(mA)[c]	FILM FORMATION	GENERAL COMMENTS
28	2500	1.85	0.110	0.99	2.00 (sh)	0.05	None	dec	Gold-brown	Nucleation loops are seen with consecutive scanning.
29	2500	1.78	0.310	0.99	1.80 (sh)	0.22	None	dec	Gold-brown	Shoulder disappears, replaced by nucleation loop on scan 2; repeated on all subsequent scans.
30	2500	1.80	0.320	0.99	----	----	None	dec	Gold-brown	Nucleation loop seen on scan 1; trace varies in scans 1-5 - multiple oxidation peaks and nucleation loops are observed.
31	2500	1.68	0.240	0.99	1.74 (sh)	0.22	None	dec	Gold-brown	Shoulder disappears by scan 2 and a nucleation loop is observed by the second scan.

Table 3.3 *Cyclic Voltammetric Study of Thiophene Monomers;*

a) The scan range was from +1200 mV to the specified limit;

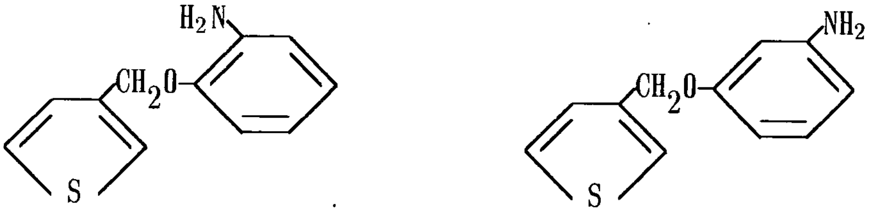
b) CLR (coefficient of linear regression) was calculated to show the correlation between observed $\lvert i(o) \rvert$ *and* $\sqrt{\nu}$ *for* ν *= 50, 100, 200 and 400 mV/s;*

c) const = constant; inc = increase; dec = decrease. These terms are used to describe how the current associated with the primary oxidation wave varies with continuous scanning; also sh = shoulder.

3.5 TYPE 3 MONOMERS

3.5.1 Introduction

At the beginning of this project, poly(aniline) had re-emerged as an interesting electroactive polymer mainly due to its electrochromic nature and thus its applicability in display devices[160]. As the main thrust of this chapter has been the development of phenoxy-substituted thiophene derivatives, a brief look into the chemistry of these systems following the work of the type 2 monomers was felt to be appropriate. Hence the C.V. behaviour of the following phenoxy substituted thiophenes were studied:



(33) (35)

Figure 3.12 *Aniline Derivatives.*

It was felt that these compounds could afford new information concerning the role that substituents could play in the electrochemistry of aniline and its derivatives. It is appropriate to consider briefly the electrochemistry of poly(aniline) at this point.

3.5.2 Poly(Aniline)[161]

This polymer system (first prepared in 1862) differs from other EAPs [*eg.* poly(thiophene)] in that the electronic ground state of the polymer can be controlled through both the variation in the number of electrons per repeat unit (oxidation and reduction) and the number of protons per repeat (acid doping) unit[162].

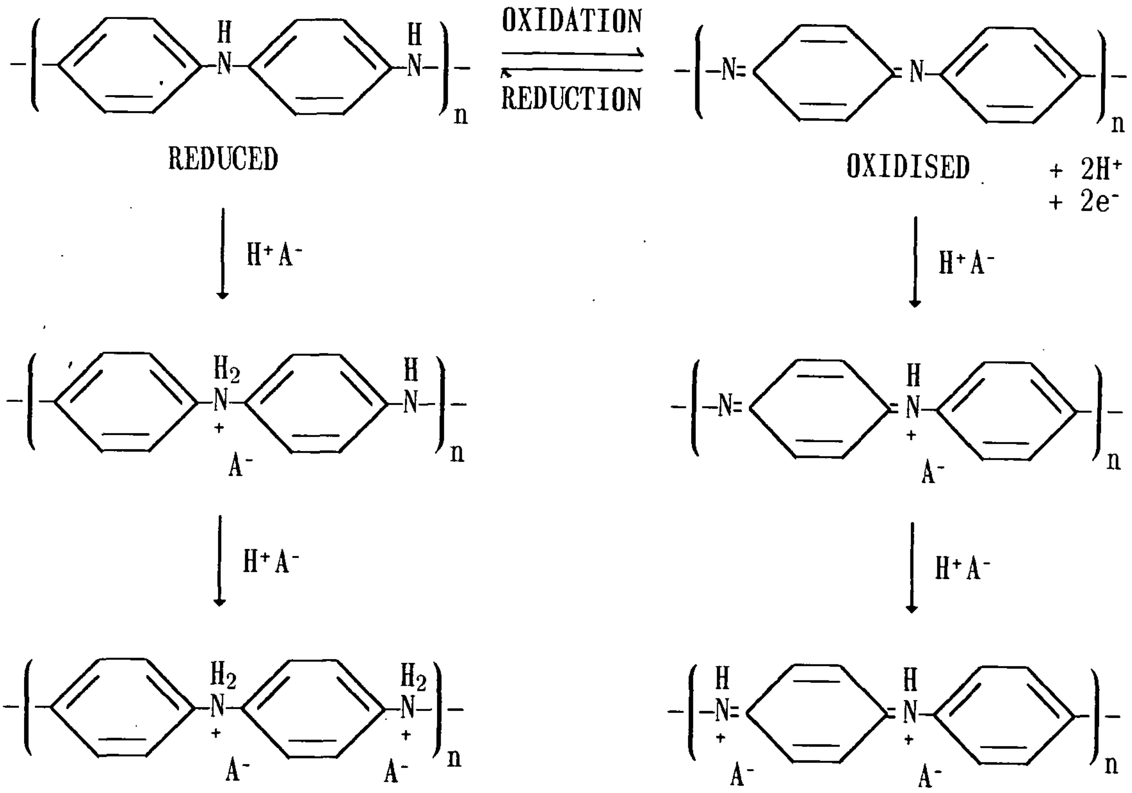
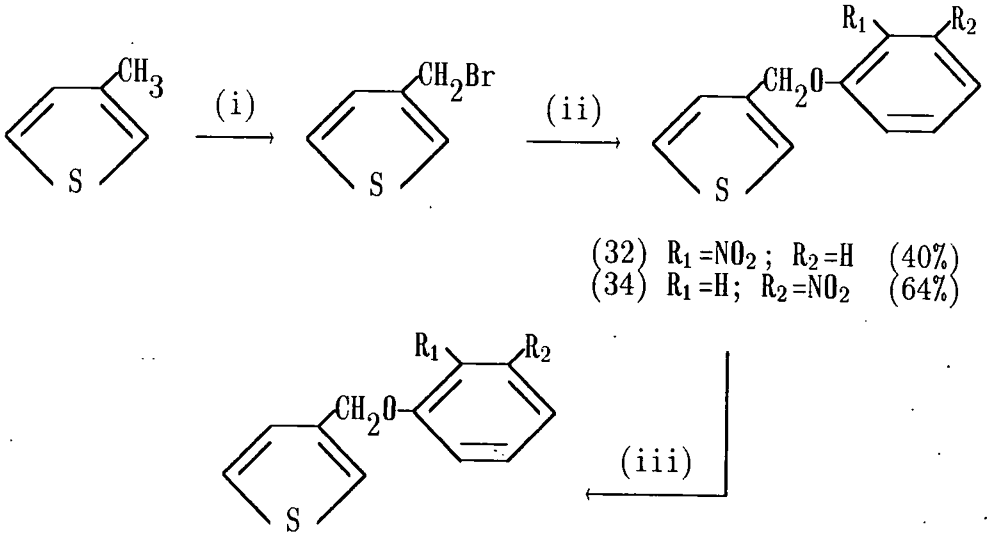


Figure 3.13 *Proposed Forms of Poly(aniline).*

All of these forms of polyaniline have either been speculated or confirmed. Various reaction mechanisms for the oxidation (and reduction) of poly(aniline) films have been proposed[163]. Each mechanism is consistent with some but not all of the experimental results. Thus, this fact of poly(aniline) chemistry is still controversial. The cyclic voltammetric studies of the polymer seem to be somewhat dependent upon the method of synthesis and there is, as yet, no complete understanding or interpretation of exactly what is occurring when poly(aniline) is cycled between the oxidised and reduced states[161].

3.5.3 Synthesis of Type 3 Monomers



(32) $R_1 = NO_2$; $R_2 = H$ (40%)
(34) $R_1 = H$; $R_2 = NO_2$ (64%)

TYPE 3 MONOMERS

(33)	$R_1 = NH_2$; $R_2 = H$	(30%)
(35)	$R_1 = H$; $R_2 = NH_2$	(33%)

Figure 3.14 *Synthetic Scheme Depicting the Synthesis of Type 3 Monomers; Typical Reagents and Reaction Conditions (i) N-bromosuccinimide, AIBN, CCl_4, Reflux; (ii) KOH, THF, appropriate phenol, Reflux; (iii) Pd/C, EtOH, H_2.*

Initial attempts to form compounds (33) and (35) by the direct Williamson type coupling of (1) with either the ortho or para aminophenols only met with partial success, as both oxygen <u>and</u> nitrogen atoms acted as nucleophiles, leading to two products. However, acetylation of the aminophenols, followed by the selective hydrolysis of the ester linkage was successful, yielding both target monomers, however, the number of steps involved made it unlikely to be an acceptable commercial synthesis.

The route finally chosen was the three-step method of entry (Figure 3.14). Hydrogenation led to the low yield of the final product.

3.5.4 Cyclic Voltammetry Studies

The results from the initial studies are given in Table 3.4. A sharp irreversible peak at *ca*. +0.9 V was observed corresponding to aniline being oxidised (scan limit +2000 mV). This wave did not diminish in size even on repeated scanning; this indicates that no passivating, or indeed, electroactive films were being deposited on the electrode. When the scan limit was increased to encompass the oxidation potential of thiophene for both compounds (33) and (35), a second oxidation wave was observed at +2.1 V, indicating that either these types of system can support a radical dication (which is unlikely) or that the radical cation generated at *ca*. +0.7 V has been quenched leaving an electroactive species that can be further oxidised. Intramolecular electron transfer does not take place. We have clearly shown that repeated cycling at this higher voltage leads to a thin film which adheres to the electrode.

However, upon repetitive scanning at this higher voltage, no oxidation wave is observed for the aniline moiety, after the second scan. An oxidation wave at higher potentials is observed; explanations for this reproducible effect however are not readily apparent.

3.5.5 Electropolymerisation of Monomer (33)

Compound (33) has been successfully electropolymerised at Perivale to yield a polymeric substance whose conductivity is of the order of 10^{-3} S cm^{-1}. However the exact nature of the polymer (as is the case

CPD	INITIAL SCAN (ν = 100 mV/s)						MULTISCANS @ 100 mV/s			GENERAL COMMENTS
	ANODIC SCAN	PRIM.OXID.WAVE			OTHER PEAKS		ANODE		FILM	
	LIMIT (mV)[a]	E_o/V,	$\|i_o\|$/mA,	CLR[b]	E/V,	$\|i\|$/mA	COLOUR	$\|I_o\|$(mA)[c]	FORMATION	
33	2300	0.93	0.08	0.99	2.07	0.04	None	dec	None	Nucleation Loops observed on consecutive scanning, however no streaming was observed.
35	2500	0.95	0.03	0.98	1.95	0.02	None	dec	None	Nucleation Loops observed on consecutive scanning, however no streamimg was observed.

Table 3.4 *Cyclic Voltammetric Study of Aniline Derivatives;*

a) The scan range was from 0.00 V to the specified limit;

b) CLR (coefficient of linear regression) was calculated to show the correlation between observed $|i(o)|$ and $\sqrt{\nu}$ for ν = 50, 100, 200 and 400 mV/s;

c) dec = decrease. This term is used to describe how the current associated with the primary oxidation wave varies with continuous scanning.

with all these systems) is still the subject of debate and further work is in progress [including the electropolymerisation of (35)] (see Table 3.5)].

3.6 CONCLUSION

This chapter has seen the further development of the synthetic methodology for β-substituted thiophenes established in Chapter 2.

Although only one 'class' of monomer was described (*ie.* β-phenoxy) three distinct and significantly different types of monomer are included. Although at this time the exact nature of the type of electroactive species formed for each type of monomer is not clear, the following can be said with confidence. In each case the resulting electroactive materials are stable. The studies performed on the monomers have mainly involved cyclic voltammetry. Further work to characterise the polymers derived from the monomers is currently in progress at both Perivale (types 1, 2 and 3) and B.D.H. (type 2).

Most of the device applications for the polymers described in this, and the previous chapter have centred around the polymers conductivity, the action of the β-substituent being merely to impart solution processibility to the polymer. The following chapter hopes to develop a device application for poly(thiophenes) where the β-substituent plays an integral part in the device.

COMPOUND	SOLVENT (40ml)	ANODE	MONOMER MOLARITY	ELECTROLYTE MOLARITY [a]	COULOMBS PASSED	CURRENT DENSITY (mA cm^{-2})	CONDUCTIVITY (σ_{rt} S cm^{-1}) [b]
33	$PhNO_2$	Ni (Foil)	1×10^{-2}	1×10^{-1}	5.00	1.5	4.4×10^{-3}

Table 3.5 *Polymerisation Conditions;*
a) Tetrabutylammonium hexafluoroborate;
b) Four-Probe Measurement.

CHAPTER FOUR

THIOPHENE-SUBSTITUTED MACROCYCLES

4.1 INTRODUCTION

The endeavours of technologically advanced societies are increasingly reliant on the estimation, monitoring and control of chemical species. Increasing concern with environmental and personal protection, together with widespread requirements for more accurate sensitivity has created a need for new improved sensors for both *in vivo* and *in vitro* applications. Prominent amongst the requirements are new sensors that allow for the selective detection, monitoring and binding of mono or divalent metal cations[81]. Research into molecular based devices that might fulfill these requirements have been inspired by recent developments in the fields of organic metals and macrocyclic chemistry.

4.1.1 Organic Metals

Since the discovery of a relatively straightforward electrochemical route into highly conducting polymeric films[29], there has been considerable interest in their use in electronic devices (see section 1.8). Their use as an environmental or biosensor† however has only recently been given serious consideration[164]. Most of the work to date concerning EAPs has centred around the ability of the parent polymer [be it PP or PT], to effect an electrical or visual response upon its exposure to some sort of analyte [*eg.* NH_3(g)][164b]. Recently, pioneering studies into chemically modified EAPs have led to a general method of entry into functionalised PTs (see Chapters 2 and 3). This simple

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†A biosensor is an analytical device that responds to an analyte in an appropriate sample and interprets its concentration as an electrical signal via a suitable combination of a biological recognition system and an electrochemical transducer.

synthetic procedure has culminated in the synthesis of β-substituted thiophene monomers that bear macrocyclic substituents (*vide infra*). As macrocycles can act as sensing devices for metal ions (see proceding section), the development of such potentially polymerisable systems could herald a new generation of chemical sensing devices.

4.1.2 Macrocycles

In 1967, Pederson demonstrated that synthetically prepared macrocycles or *coronands* could also bind certain metals ions[165]. This observation prompted many reports in the literature on the use of coronands as 'selective' *ionophores*‡ for various mono and divalent metal ions[166].

'Ideally an ionophore for a metal ion posing as a spherical guest should provide a cavity of appropriate size, lined with polar σ-donors which give maximum binding through ion-dipole interactions. Several other advantages are offered by coronands over podands (acyclic analogues) in the form of:

i) An increased kinetic inertness towards complex formation in aqueous medium and towards decomposition.

ii) An increase (by orders of magnitude) in thermodynamic stability.

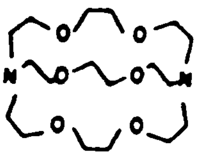
iii) An improved stabilisation of high metal oxidation states.

These factors collectively define what is now known as the macrocyclic effect[167]. The rate and selectivity of ion coronand association both depend on other factors related to the characteristic properties of the

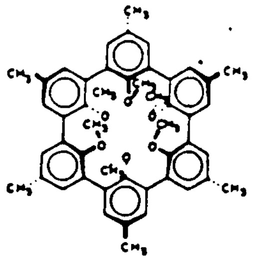
---

‡A *coronand* is the the name given to a macrocyclic compound possessing any heteroatom and an *ionophore* may be defined as a receptor molecule that forms stable lipophilic complexes with charged hydrophilic cations such as K(1+), Li(1+), Cu(2+). Such complexes may be considered as host-guest complexes, where the guest cation resides in the cavity created by the host.

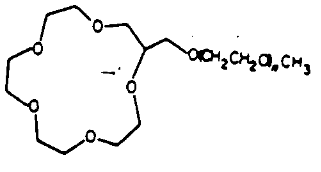
coronand, complexing ion and solvent. All of these have been comprehensively covered in books[168] and extensive review articles[169]. In addition, attempts to further mimic the selectivity and high stability of complexation observed in naturally occurring systems have led to the development of several other types of macrocycle. The main categories being featured as follows:



Cryptands - (from *crypta* meaning cage) are bi and poly-macrocyclic ligands and offer a guest a three dimensional array of binding sites.



Spherands - Unlike coronands and cryptands offer an enforced cavity lined with electron pairs and generally possess superior binding and selective powers.



Lariat Ethers - (from *lariat* meaning lasso). These are macrocyclic ligands possessing side arms with additional donor groups.

Figure 4.1 *Other Categories of Macrocycle (including examples).*

The variation of ring sizes and alteration of the polar binding groups [*eg*. oxygen (hard base) for sulphur (soft base)] along with varying the rigidity of the host also affects the rate and selectivity of ion-macrocycle association. In addition, kinetic stability with respect to cation loss can be obtained if the complex is neutral after binding, as acid mediated dissociation is less likely. Work in this field has led to a wealth of knowledge about the stereochemical and stereophysical behaviour of macrocyclic compounds and has established the field as an independent branch of chemistry. Macrocyclic ligands have been employed in such diverse processes as:

i) separation of ions by transport through artificial membranes
ii) liquid-liquid or solid-liquid phase transfer reactions
iii) dissolution in polar solvents of metal or organic salts
iv) the preparation of ion-selective electrodes (ISEs) and
v) the understanding of some natural processes through the mimicry of metallo-enzymes.

It is the marriage of this branch of chemistry with the knowledge expounded in Chapter 1, that is the subject of the rest of this chapter.

4.1.3 Target Monomers

The synthesis of three target monomers (coronands) will be described (Figure 4.2).

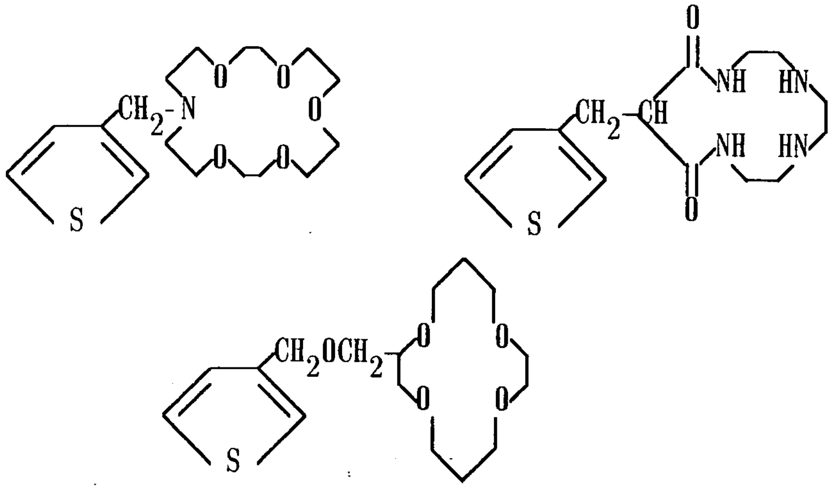


Figure 4.2 *Target Monomers Synthesised in this Chapter.*

Preliminary investigations involving cyclic voltammetry and, where appropriate, metal ion selectivity will be presented for the above compounds.

4.2 16-(3-THIENYLMETHYL)-16-AZA-1,4,7,10,13-PENTAOXACYCLO-OCTADECANE (38)

4.2.1 Introduction

The synthesis of this coronand was the first attempt at functionalising thiophene at the β-position with a macrocyclic unit. Macrocycles of this type (nitrogen containing polyethers) generally possess a lower binding selectivity over their poly-oxa analogues. Although the pendant macrocycle possesses a modest selectivity for potassium ions over other alkali metals, the purpose of synthesising such a monomer was not for its binding ability. Its purpose was to serve as a model compound when compared to the other monomers synthesised.

4.2.2 Synthesis of (38)

The preparation of compound (38) involved a convergent synthesis starting from hexaethylene glycol and 3-methylthiophene (Figure 4.3). Using the methodology of Newcomb *et al.*, hexaethylene glycol was reacted with p-toluenesulphonyl chloride to form the disulphonic ester (36) in moderate yield (*ca.* 69%)[170]. This was readily displaced by iodide ions to form the diiodide (37) employing a variation of the *Finkelstein* reaction[171], in our case, tosylate-halide exchange (*cf.* halide-halide exchange). This reaction proceeded in good yield (82%). Ring closure was then effected by the condensation reaction of compounds (37) and (10) employing the methodology developed by Dale[172]. Sodium ions were present to assist the "templated" synthesis of compound (38) in an attempt to limit the formation of oligomeric side products. Although the ring closure can be performed using the ditosylate (and the

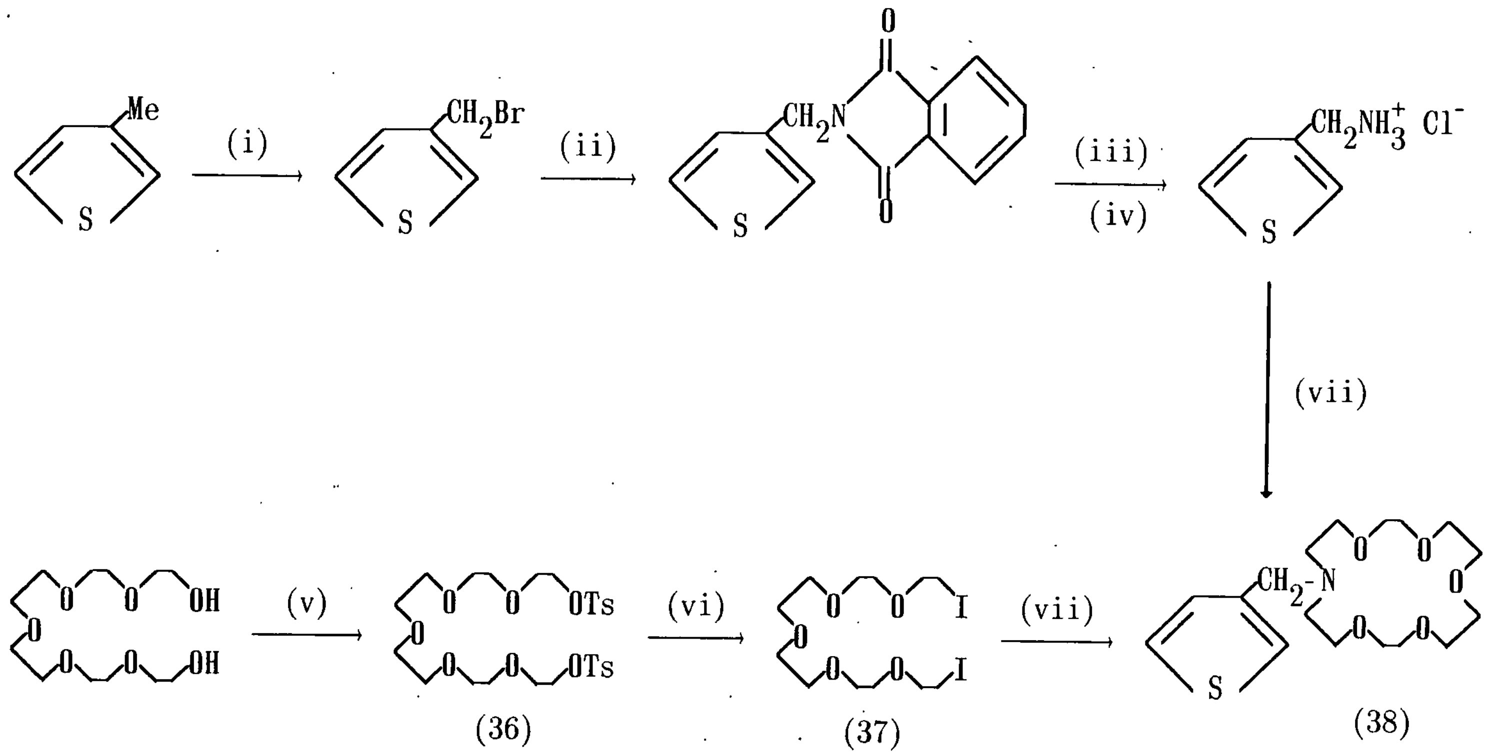


Figure 4.3 *Synthetic Scheme Depicting the Synthesis of Compound (38); Typical reagents and reaction conditions are: (i) N-Bromosuccininmide, AIBN, CCl_4, Reflux; (ii) K^+ Phthalimide, 18-crown-6 ether, DMF, 80^0C; (iii) N_2H_4, H_2O, EtOH, Reflux; (iv) HCl, Reflux; (v) TsCl, Pyridine, -20^0C; (vi) KI, acetone, Reflux; (vii) Na_2CO_3, CH_3CN, Reflux.*

templating procedure), it has been reported that higher yields can be obtained using the dihalide route[173]. Purification of crude (38) afforded (38) in 18% yield.

4.2.3 Cyclic Voltammetry Studies

The C.V. procedures employed for all the compounds synthesised in this chapter mirrored those of the previous two chapters except for compound (40) (see section 4.3.3). The low oxidation potential recorded for (38) (1.05 V) was not due to the oxidation of the thiophene ring. It is likely that irreversible ring nitrogen oxidation occurs (Figure 4.4) by removal of an electron from the nitrogen lone pair (see also Section 3.5.2).

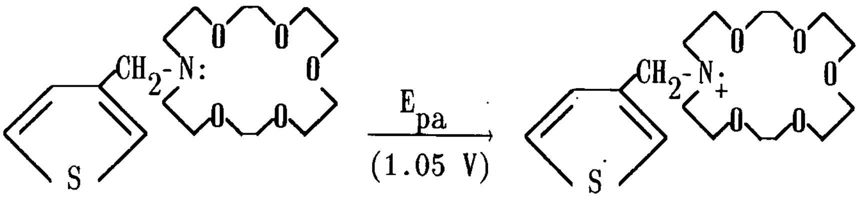


Figure 4.4 *Radical Cation Generation Involving Loss of an Electron from the Nitrogen Atom.*

Irreversible ring nitrogen oxidation and not ring oxygen oxidation is proposed, as the HOMO of the ring nitrogen is intuitively going to be higher than the HOMO of the ring oxygen (due to the increased nuclear charge). To demonstrate this hypothesis, the principles of metal ion binding outlined in section 4.1.2 were applied. Potassium tetrafluoroborate [$K^+BF_4^-$, 1:1 equivalents with respect to (38)] was added to the electrochemical cell containing (38). The addition of potassium ions in this way invokes host guest complexation involving the 5 ring oxygens and ring nitrogen lone pairs (Figure 4.5).

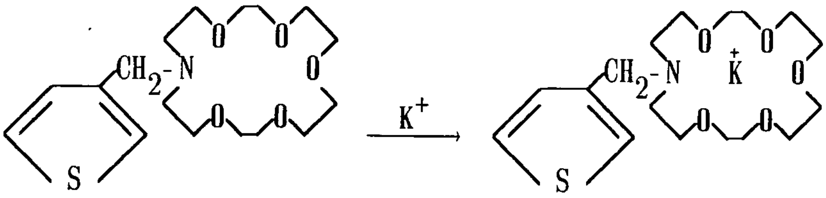


Figure 4.5 *Host Guest Complexation of (38) Employing Potassium ions.*

This host-guest complexation would force the nitrogen lone pair into becoming a "pseudo" bonding orbital, subsequently lowering the HOMO in energy. This being the case one would expect the E_{pa} to rise for the complex (38). This was observed lending credence to the original hypothesis. Further evidence was provided by the cyclic voltammogram of morpholine (an analogous ring system), which again showed an irreversible, ring nitrogen oxidation at 1.10 mV similar to (38).

4.3 12-(3-THIENYLMETHYL)-1,4,7,10-TETRAZACYCLOTRIDECANE-11,13-DIONE (40)

4.3.1 Introduction

The specific solvent extraction of Cu^{2+} ions using carrier molecules was first reported by Schiffer *et al.*[174] employing benzoyl acetone as the carrier molecule. However serious doubt was expressed regarding the selectivity of the process[175]. In 1977, the reported synthesis of dioxotetraaza macrocycles by Tabushi *et al.*[176] and subsequent complexation studies by Kimura *et al.*[177] showed that dioxo-cyclam (Figure 4.6) is capable of forming rigid, stable 1:1 neutral complexes with certain metal ions (Cu^{2+}, Ni^{2+}, Co^{2+}, Pd^{2+} and Pt^{2+}).

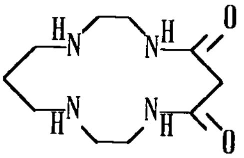


Figure 4.6 *Structure of Dioxocyclam.*

Moreover, Kimura *et al.* have demonstrated that within the pH range 5.7-8.6, dioxocyclam selectively binds Cu^{2+} over a range of mono and divalent metal cations including Ni^{2+}, Co^{2+}, Pd^{2+} and Pt^{2+} [178]. Dissociation of Cu^{2+} from the complex was effected by lowering the pH. The selectivity of Cu^{2+} over other metal cations under these conditions corresponds to the known thermodynamic selectivity of dioxocyclam for Cu^{2+} as reflected in log K values of the complex in water at 35°C: Cu = 1.0, Ni = -5.5, Co = -11.4 [178]. Also the chelation rate of Cu^{2+} under these conditions occurs more rapidly than the above competing ions and this kinetic effect may also contribute to the overall selectivity in binding. Recently Kimura *et al.* have also shown that at pH 3.0, selective complexation of Pt^{2+} over Cu^{2+} occurs[179]. Therefore the potential use of dioxocyclam in removing, concentrating and purifying both Cu^{2+} and Pt^{2+} ions from mixtures looks promising. Its incorporation into an electropolymerisable unit such as thiophene would then potentially allow for the generation of an organic polymer that could act as either a Cu^{2+} or Pt^{2+} sensor or ion selective electrode. In view of the fact that attempts to electropolymerise compound (38) resulted only in irreversible ring nitrogen oxidation, the probability of a similar process occurring with the dioxocyclam system seemed highly likely [dioxocyclam contains two ring nitrogen (amine) lone pairs]. Hopes of avoiding such an event with any thiophene substituted dioxocyclam synthesised were pinned on the complexation of any ligand synthesised with an appropriate metal ion, prior to any attempted electropolymerisation. This would negate any irreversible ring nitrogen oxidation but would not inhibit oxidation of the complexed metal ion. However there is a literature precedent which suggested that because such an oxidation process is *reversible*, it may actually *aid* the electropolymerisation of the thiophene through an ill-defined inter- or intramolecular electron relay mechanism[180]. This may be the case even if the redox couple of the complexed metal ion is lower than the oxidation potential of thiophene. As this proposal is somewhat speculative, and as it is known that the synthesis of 13-membered dioxocyclams bearing pendant aromatic groups have been shown to be facile [when compared to their 14-membered analogues (Figure 4.6)], compound (40) (a 13-membered dioxocyclam) was synthesised[181]. This was to be used in model electrochemical studies prior to the synthesis and electrochemical study of the 14-membered derivative.

4.3.2 Synthesis of (40)

Nucleophilic attack of compound (1) by a five-fold excess of the enolate of diethylmalonate afforded (39) in only a moderate yield (*ca.* 29%). No improvement of this yield was obtained when greater excesses of diethylmalonate were used. An excess had to be used as lower amounts resulted in the formation, almost exclusively, of the disubstituted product (42). This, incidently, failed to couple with TATD under similar reaction conditions to those employed in the formation of (40) (*vide infra*). Condensation of (39) with TATD, employing the technique developed by Tabushi *et al.*, yielded the product macrocycle which precipitated from solution in 5% yield[182]. Literature yields for similar processes range from 5 - 30% (14-membered cycles). The metal ion used to 'complex out' the ring amine nitrogens was Cu^{2+}

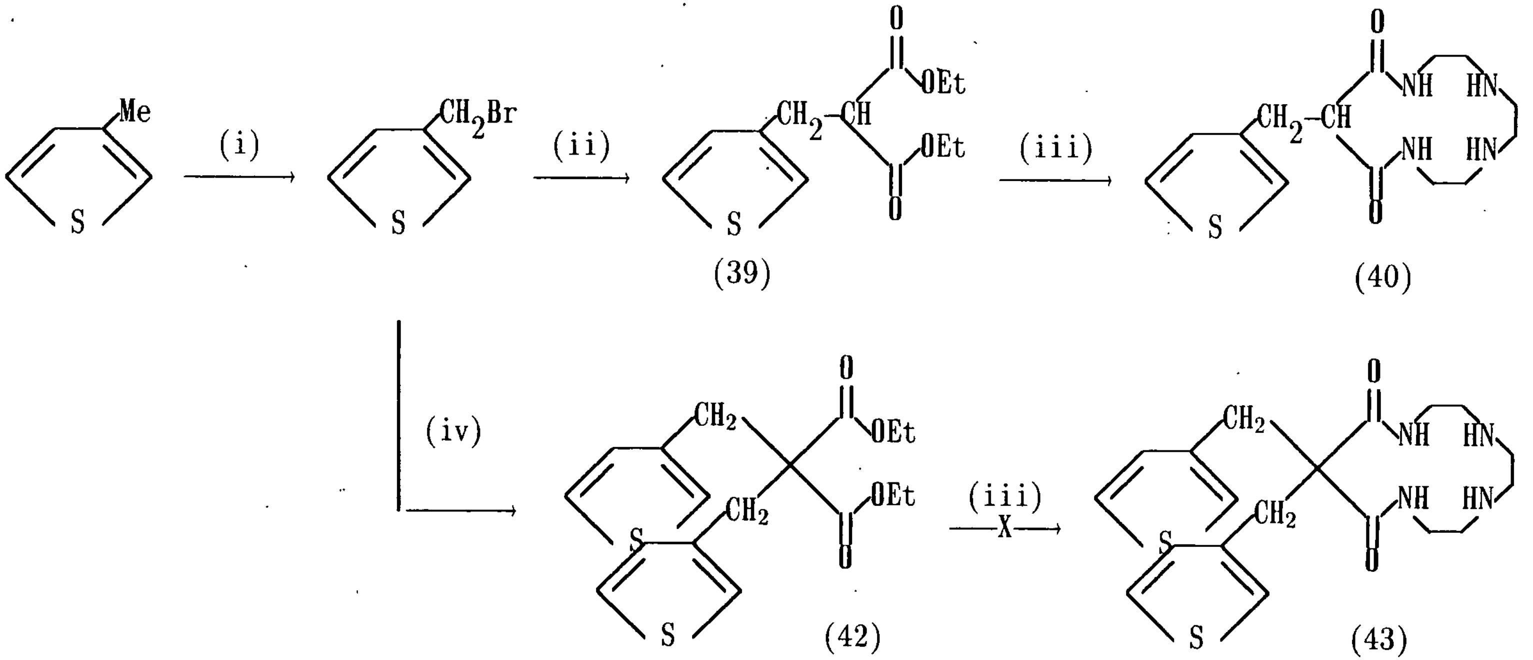


Figure 4.7 *Synthetic Scheme Depicting the Synthesis of Compound (40); Typical reagents and reaction conditions are: (i) N-Bromosuccininmide, AIBN, CCl_4, Reflux; (ii) DEM, NaOEt, EtOH, Reflux; (iii) TATD, EtOH, Reflux; (iv) NaOEt, DEM, EtOH, Reflux.*

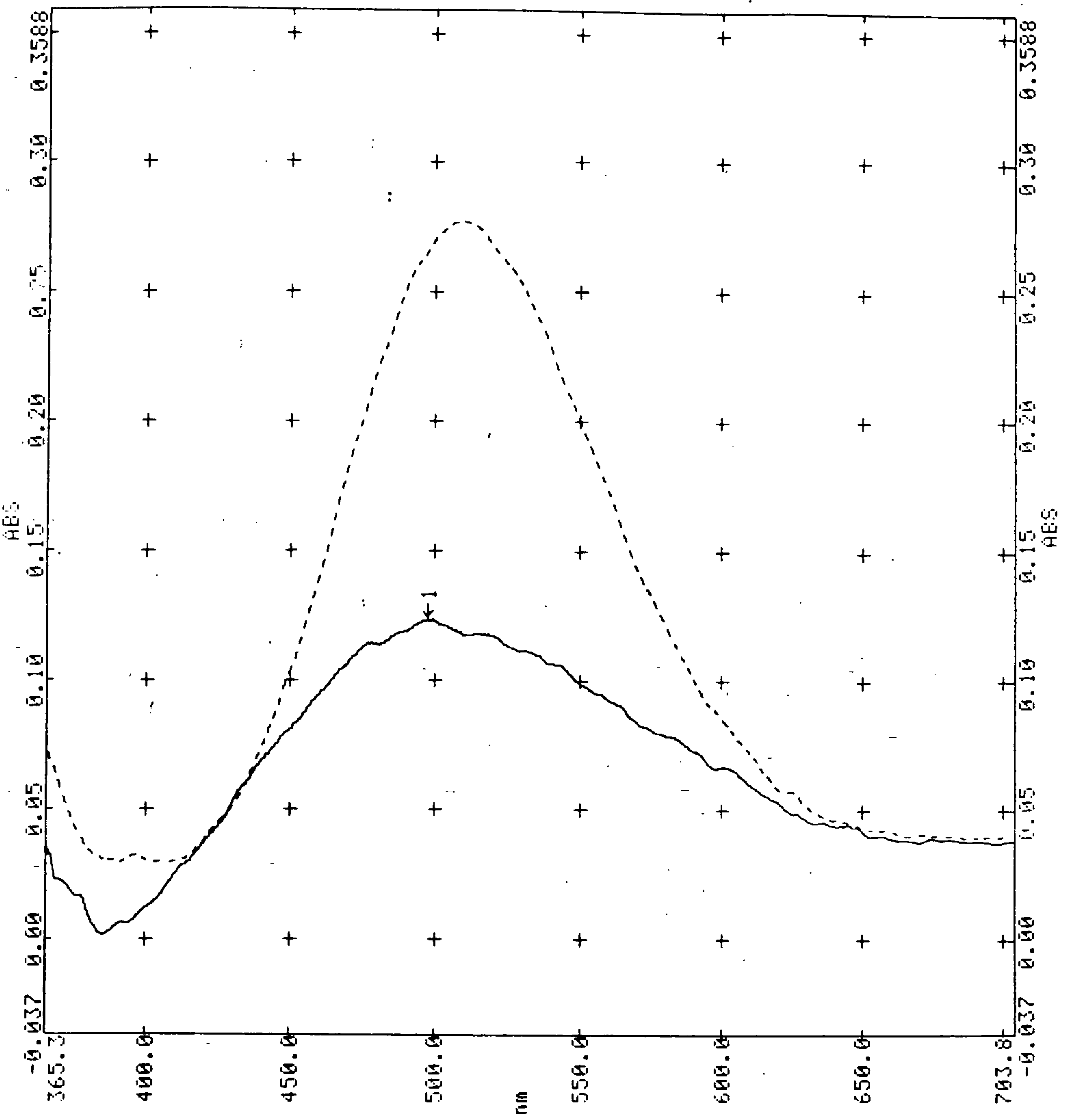


Figure 4.8 *UV-Visible Spectrum of the Copper Complex (41) (---) Compared With the UV-Visible Spectrum of the Copper Complex of the Parent Dioxocyclam (····).*

(in the form of copper perchlorate, $CuClO_4.6H_2O$). Confirmation that the copper complex (41) had formed was initially provided by its UV-visible spectrum (Figure 4.8). Complexation was later confirmed by C.V. analysis of the complex.

The UV/visible spectrum was compared with an identical copper complex of the parent dioxocyclam. Further evidence to demonstrate that complexation had occurred was provided by F.A.B. Mass spectroscopy techniques. Peaks at 373 and 375 were detected showing clearly the two isotopes of copper, in a ratio which showed good agreement with the calculated value.

4.3.3 Cyclic Voltammetry Studies

Initial studies used the methodology developed by Kimura *et al.*, employing water as the solvent and sodium sulphate as the base electrolyte[183]. This was to confirm the results obtained by Kimura concerning the redox couple of the complexed copper species, and also to further demonstrate that copper was complexed to the macrocycle[183]. The results are contained in Table 4.1 with a representative redox couple obtained for the copper complex of (40) being portrayed in Figure 4.9.

From the observed difference between the values of E_{pa} and E_{pc} ($\Delta E > 59$ mV) it was concluded that the unusual redox couple $Cu^{2+/3+}$, which was occurring, was not a reversible process. This conclusion was supported by the failure of other diagnostic tests for reversible behaviour (*eg.* $I_{pa}/I_{pc} = 1$ and E_p being independent of ν). The redox process observed was therefore deemed to be quasi-reversible in nature. Some diagnostic tests for such behaviour are illustrated below:

CPD	SCAN RATE (mV/s)	ANODIC SCAN LIMIT (mV)^a	PRIM.OXID.WAVE			PRIM.RED.WAVE			ΔE_p (mV)^c
			E_o/mV,	$\lvert i_o \rvert$/mA,	CLR^b	E/mV,	$\lvert i_o \rvert$/mA,	CLR^b	
41	10	900	696	0.009	0.97	564	0.005	0.96	132
41	50	900	726	0.016	0.97	537	0.009	0.98	199
41	100	900	741	0.025	0.97	519	0.013	0.97	222
41	200	900	792	0.030	0.97	492	0.015	0.97	300

Table 4.1 *Cyclic Voltammetric Study of (41);*

a) The scan range was from 0.00 V to the specified limit;

b) CLR (coefficient of linear regression) was calculated to show the correlation between $\lvert i(o) \rvert$ *and* $\sqrt{\nu}$ *for* ν *= 10, 50, 100 and 200 mV/s;*

c) ΔE_p $(E_o - E)$ *was calculated to demonstrate the quasi reversibility of (41).*

i) $|I_p|$ increases with, but is not proportional to, $\nu^{1/2}$.

ii) ΔE_p > 59 mV and increases with increasing ν.

iii) E_{pc} shifts negatively with increasing ν.

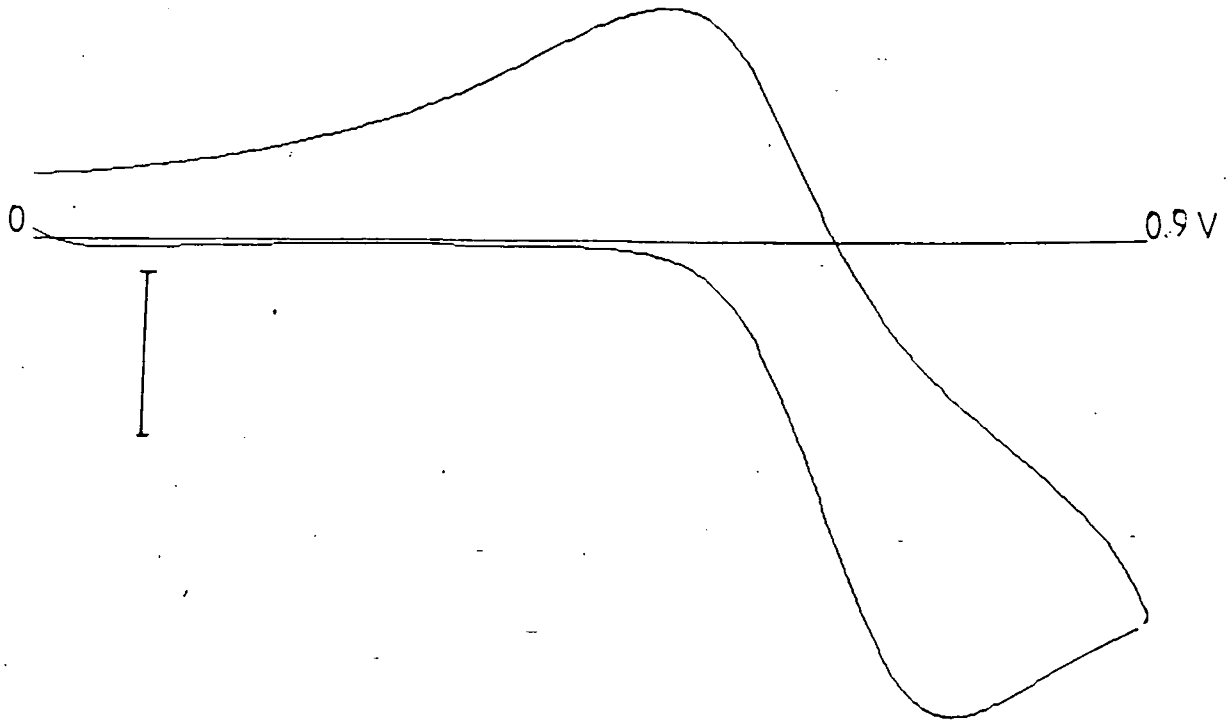


Figure 4.9 *C.V. Trace of the Copper Complex (41) Demonstrating the Cu(2+)/Cu(3+) Redox Couple.*

The results shown in Table 4.1 confirm that the redox behaviour of the copper complex (41) is of a quasi-reversible nature. Quasi-reversibility is observed when the rate of electron transfer with respect to mass transport is insufficient to maintain Nernstian equilibrium at the electrode surface. With regard to (41), the quasi-reversibility observed may be due to the copper's inability to come within direct contact with the electrode surface (due to it being wrapped within a macrocyclic ligand). Therefore any electron transfer process that needs to occur will need to overcome a subsequent energy barrier, not only to penetrate the solvation sheath but to overcome the steric barrier provided by the macrocycle. It is this energy barrier which may explain the slow electron transfer rate and consequently the quasi-reversibility of the redox couple of (41). Unfortunately attempts to electropolymerise the complexed species using identical conditions employed by Parker *et al.*[180] failed to provide an EAP of (41).

4.4 13-METHOXY-(3-THIENYLMETHYL)-1,4,7,11-TETRAOXACYCLOTETRADECANE (46)

4.4.1 Introduction

Currently, there is a great deal of research into the design and development of lithium ion selective electrodes. Such a device would permit the convenient measurement of lithium ion activity in both physiological and environmental systems. Lithium itself is being considered as a blanket material for breeding tritium in thermonuclear reactors. It also expects to see widespread use in the development of high performance low density batteries (see section 1.8.3). Unfortunately, the abundance of lithium ores is relatively low, so to meet the anticipated rise in demand for lithium in the 21st Century, its extraction from sea-water is even under consideration[166a].

As the concentration of lithium in sea-water is small (< 1%) the need for highly selective lithium ionophores is essential. Some of the most successful ionophores have been based on the 14-crown-4-polyether macrocycle (Figure 4.10).

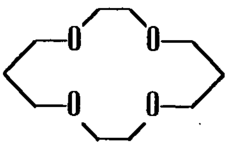


Figure 4.10 *14-Crown-4-Polyether Macrocycle.*

Model studies of such an ionophore bearing a pendant thiophene moiety are worthy of study. There are several reasons for this:

i) Such a system could function as a polymer modified electrode as electropolymerisation of the thiophene onto an electrode would be possible.

ii) Electropolymerising such a system within the matrix of an inert polymer (eg. PVC, see Sections 1.9.3 and 4.7.3) could lead to a cheap, selective lithium ion extractor or I.S.E.

iii) The potential exists to synthesise such a thiophene bearing monomer which possesses superior selective properties over and above the parent polyether (Figure 4.10).

With these views in mind the synthesis of compound (46) with the additional pendant oxygen was attempted. It was hoped that a lariat ether system of this type would result in the monomer (and polymer) possessing superior selective complexation for lithium than the parent compound.

4.4.2 Synthesis of (46)

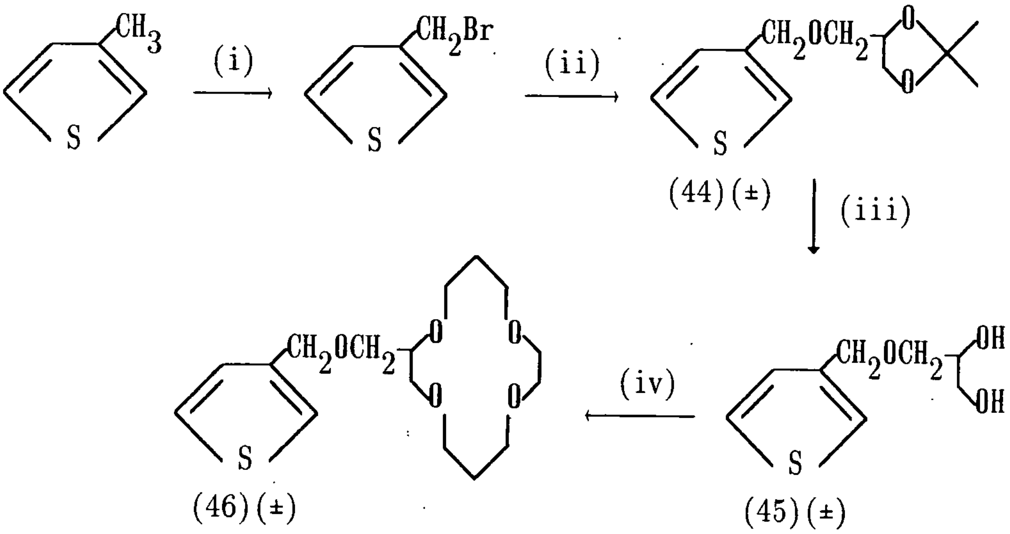


Figure 4.10 *Synthetic Scheme Depicting the Synthesis of Compound (46); Typical Reagents and Reaction Conditions are: (i) N-Bromosuccinimide, AIBN, CCl_4, Reflux; (ii) KOH, 18-crown-6 ether, 2,2-Dimethyl-1,3-dioxalone-4-methanol, Reflux; (iii) Acetone, HCl, Reflux, (iv) t-Butanol, Li, LiBr, 4,7-dioxa-1,10-dichlorodecane, Reflux.*

The synthesis of (46) was a convergent synthesis starting from ethylene glycol and 3-methylthiophene. The provision of some 4,7-dioxa-1,10-dichlorodecane (see acknowledgements) meant that the final ring forming condensation reaction could take place. The use of ±-2,2-dimethyl-1,3-dioxalone-4-methanol in the synthesis of (46) instead of the enantiomerically pure molecule was mainly due to the cost of the material, compared to the pure enantiomer. The complexation properties of the racemate would not be significantly affected.‡† Deprotection of the diol by acid hydrolysis of the acetal gave (45) in 65% yield which was subsequently used in the ring forming condensation with the dichloride to give (46) in 27% yield. The use of lithium ions as a template (similar methodology to that of Dale *et al.*[172]) once again tried to ensure minimal formation of oligomeric side products.

4.4.3 Cyclic Voltammetry Studies

The results of cycling (46) between 0 and 2.5 V (see Table 4.2) was typical of the C.V. behaviour of the long-chain polyethers synthesised in Chapter 1 (see Table 2.1). Although no electropolymerisation occurred under the standard conditions employed, it should be remembered that compound (4) (the polymer of which had a σ_{rt} = 1050 cm^{-1}) also failed to electropolymerise under these conditions.

When either sodium or potassium perchlorate was added to the electrochemical cell, no difference was noted in the oxidation potential of (46). The purpose of adding a 5-fold excess of each salt to solutions of (46) was to ascertain whether this produced an alteration of oxidation potential through complex formation. As stated, sodium and

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‡†Enantiomerically pure 2,2-dimethyl-1,3-dioxolone-4-methanol can be synthesised from S(+)-erythyulose using the methodology of Vanderwalle *et al.* (Reference 184).

	INITIAL SCAN (ν = 100 mV/s)							MULTISCANS @ 50 mV/s		
CPD	ANODIC SCAN	PRIM.OXID.WAVE			OTHER PEAKS		ANODE		FILM	GENERAL COMMENTS
	LIMIT (mV)^a	E_0/V,	$\lvert i_0 \rvert$/mA,	CLR^b	E/V,	$\lvert i \rvert$/mA	COLOUR	I_0 (mA)^c	FORMATION	
46	2500	2.10	0.06	0.98	None	None	None	inc	None	No Nucleation Loops and no streaming was observed.

Table 4.2 *Cyclic Voltammetric Study of Compound (46);*
a) The scan range was from 0.00 V to the specified limit;
b) CLR (coefficient of linear regression) was calculated to show the correlation between observed $|i(o)|$ *and* $\sqrt{\nu}$ *for* ν *= 50, 100, 200 and 400 mV/s;*
c) inc = increase. This term is used to describe how the current associated with the primary oxidation wave varies with continuous scanning.

potassium salt addition had no effect which is in keeping with the known facts that (46) is selective for lithium. Although no electroactive polymer had yet been synthesised from (46), it was felt that more accurate selectivity studies should be performed on the monomer as it offered great potential [*cf*. compound (4)]. This was based on the assumption that the selectivity of the polymer (once grown), be it homo- or copolymeric in nature, would be similar to that of the monomer.

4.5 MEASUREMENT OF SELECTIVITY COEFFICIENTS

4.5.1 Introduction

The stability constant for the formation of a 1:1 complex (usually referred to as the $\log_{10}$ K value) is determined according to the following equations:

$$M + L \rightleftharpoons ML \qquad (4.1)$$

$$K = \frac{[ML]_{eqm}}{[M]_{eqm}[L]_{eqm}} \qquad (4.2)$$

where M is the metal cation, L is the ligand and ML is the complex (the brackets denote equilibrium concentrations). Many workers relate the selectivity of complexation directly to the stability constants of complexes found. Thus selectivity coefficients are given as direct ratios of the log K values. For example, a selectivity coefficient, S for the preference of a ligand for lithium over sodium will be given as:

$$S = K_{Li}/K_{Na}$$

where K_{Li} and K_{Na} refer to the following:

$$L + Li \rightleftharpoons LLi$$

$$L + Na \rightleftharpoons LNa$$

However, this type of selectivity is a *thermodynamic* selectivity and refers to systems under equilibrium conditions [see equation (4.2)]. *Kinetic* selectivity also needs consideration and is related to the relative rates of formation (k_f) and dissociation (k_d) of the complex:

$$M + L \underset{k_d}{\overset{k_f}{\rightleftharpoons}} ML \qquad K = \frac{k_f}{k_d}$$

In order to measure this selectivity, one must use methods in which the dynamics of complexation are studied. As any potential application of ligand bound EAPs will most likely depend upon *thermodynamic* selectivity, it is these techniques that shall be discussed. An important caveat to be considered, when discussing different techniques to measure selectivity, is that no two methods (even after calibration) will give the same selectivity coefficient. For example Kimura *et al.*[185] reported that benzo-13-crown-4 was more selective for sodium ions over lithium ions using a mixed solution potentiometric technique, whereas Olsher and Grodzinski reported that the same macrocycle was more selective for lithium ions than sodium ions using extraction techniques[186]. It is clear then that different methods employed in the determination of selectivity coefficients lead to different apparent selectivities. Therefore, ideally the method of selectivity chosen, should reflect in some way, the use for which the ligand is intended. The two techniques employed to measure the selectivity coefficients of (46) are F.A.B. mass spectroscopy and mixed solution potentiometry. F.A.B. was chosen because it offered a very rapid method of determining selectivity and the mixed solution potentiometric method was used as a more precise "well defined" (but slower) technique. The latter technique is also ideal for studying materials that are potential candidates for ion selective electrodes.

4.6 F.A.B. MASS SPECTROSCOPY

4.6.1 Introduction

Fast atom bombardment mass spectroscopy, first introduced in 1981, was a new method of obtaining high quality mass spectra of molecules which previously had been difficult or impossible to study by ionisation techniques[187]. In 1983, the F.A.B. technique was first used for the direct observation of metal cation selectivity in complexation[188]. This use of the F.A.B. probe is now a routine analytical technique for the study of metal-ligand complexation. In order to determine the selectivity of metal cation complexation, equimolar solutions of a number of cations are made to compete with each other for a similar equimolar solution of complexing ligand. This mixture is then introduced to the F.A.B. probe as a solution in a high boiling point solvent (*eg.* glycerol or 2,2-thiodiethanol) and is bombarded by a beam of high energy atoms (usually xenon or argon). As the cations are competing for a deficiency of the ligand, the resultant F.A.B. spectrum is the acquisition of gas phase abundance signals (at m/e values) representative of the simultaneous complex formation of several metal cations with the ligand in solution. The intensity of these signals, because they closely reflect calculated concentrations of these complexes, enable F.A.B. mass spectroscopy to be used for the determination of selectivity coefficients.

4.6.2 Determination of Selectivity Coefficients

Selectivity coefficients obtained through the F.A.B. mass spectroscopy technique are usually reported in the following manner:

$$S = \log \left(\frac{I(L+A)}{I(L+C)} \right)$$

where I(L+A) is the signal intensity for the most abundant ligand cation complex, and I(L+C) is the signal intensity for the other individual complexes. The selectivity coefficients may be represented in tabular or graphical form (Figure 4.12).

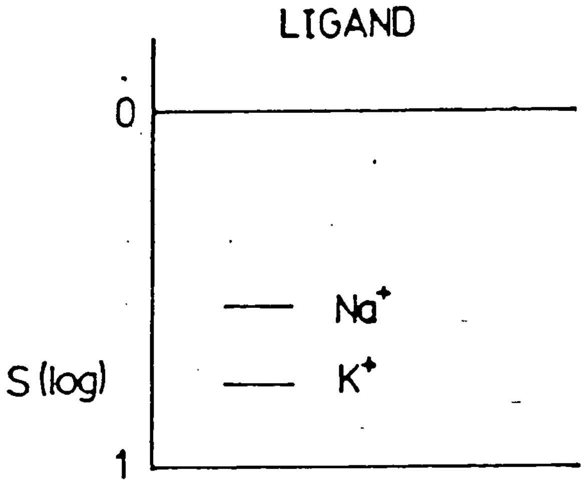

Figure 4.12 *Graphical representation of Selectivity Coefficients.*

A wide range of chemical species can be studied in this way. This wide applicability stems from the fact that F.A.B. mass spectroscopy does not apply heat to the sample under study, allowing the analysis of fragile materials; a feature which has been applied to metal containing species advantageously. The result of the F.A.B. technique applied to compound (46) using the competing ions Li^+, Na^+, K^+ and Cs^+ are presented in Table 4.3.

4.6.3 Results

	H^+	Li^+	Na^+	K^+	Cs^+
COMPLEX	0.38	0.00	0.59	0.98	1.04

Table 4.3 *Selectivity Coefficients of Compound (46); (F.A.B. technique).*

Information regarding the selectivity of (46) for lithium can be found in either Table 4.3 or Figure 4.13.

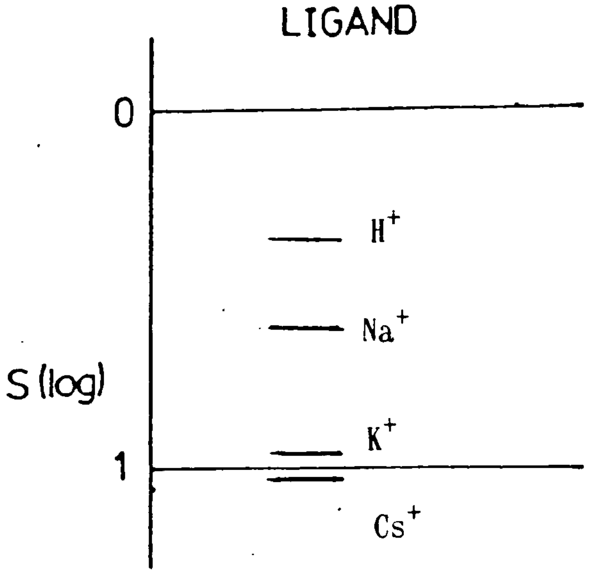

Figure 4.13 *Selectivity Coefficients of Compound (46) (F.A.B. Technique).*

As can be seen, F.A.B. mass spectroscopy indicates that (46) has a greater affinity to bind lithium over any other Group 1A metal cations (all results being reproducible). It is important to point out however that weak peaks in the F.A.B. spectrum associated [ligand + cation + proton] were also observed for each of the complexes. This interference may affect the results reported but as they occurred roughly to the same extent with each complex, it was concluded that this effect could be negated. The mixed solution potentiometric technique (see Section 4.7) uses an ion selective electrode to provide a calibration curve from which the Nicolsky-Eisenman equation can be solved, thus providing the desired selectivity coefficient.

4.7 MIXED SOLUTION POTENTIOMETRY[189]

4.7.1 Introduction

An ideal ion selective electrode produces (for ion A) an electrical potential E (in a solution of ion A) which varies as a function of the concentration of A:

$$E = E^{o} + \frac{2.303RT}{nF} \log_{10} aA \qquad (4.3)$$

This is the Nernst Equation (a = activity of an ion). However no ISE responds exclusively to the ion which it is designed to measure, if another *interfering* ion (ion B) is present in solution (at a concentration that is large with respect to the primary ion A), then the electrical response will be a function of both ions. This function can be represented by the Nicolsky-Eisenman Equation (Equation 4.4).

$$E = E^{o} + \frac{2.303RT}{n_A F} \log_{10} \left(aA + \sum_{B} K_{AB} aB^{(n_A/n_B)} \right) \qquad (4.4)$$

where n_A and n_B are the charges on ions A and B and K_{AB} is the selectivity coefficient for ion A over ion B.

4.7.2 Determination of Selectivity Coefficients

In order to determine the selectivity coefficient K_{AB}, a range of solutions with constant aB and varying aA are first prepared. Then a calibration curve potential as a function of the primary ion (A) concentration is drawn (Figure 4.14).

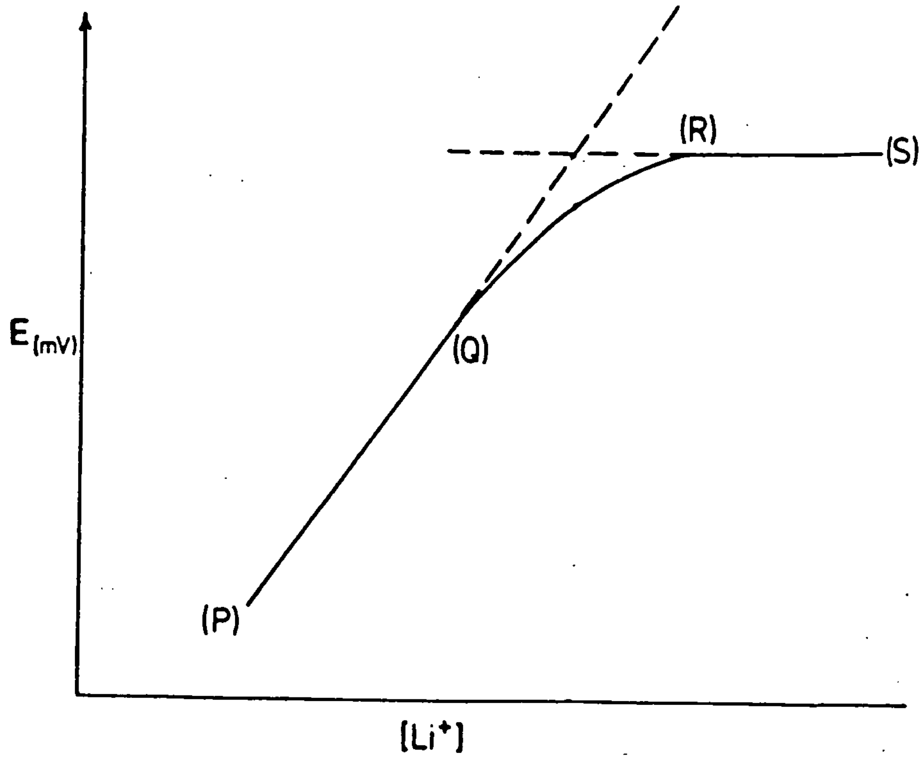

Figure 4.14 *Typical Calibration Curve [Potential vs Primary Ion (A) Concentration].*

From the Nicolsky-Eisenman Equation it can be seen that both ions contribute equally to the electrode response when:

$$aA = K_{AB}aB^{(n_A/n_B)} \tag{4.5}$$

If the activity of primary ion (A) at which this equality occurs is a'A; then the activity of the interfering ion at this equality is a'B (*ie.* a'B = aB = constant concentration) then at equal electrode response, the Nicolsky-Eisenman Equation becomes:

$$E = E^{o} + \frac{2.303RT}{n_A F} \log_{10}\left(a'A + K_{AB}a'B^{(n_A/n_B)}\right) \tag{4.6}$$

Substituting Equation (4.5) into (4.6) reduces the Nicolsky-Eisenman Equation to:

$$E = E^{o} + \frac{2.303RT}{n_{A}F} \log_{10} \left(2a'A\right) \tag{4.7}$$

The response of the electrode in the absence of B is given by the extrapolation of PQ as far as the limit of Nernstian response. The difference between the electrode potentials in solutions of A with activity a'A with and without B at activity a'B is therefore given by subtracting Equation (4.3) from Equation (4.7):

$$\Delta E = \frac{2.303RT}{n_{A}F} \left(\log_{10} 2a'A - \log_{10} a'A\right) = \frac{2.303RT}{n_{A}F} \left(\log_{10} 2\right) = \underset{\text{(at } 37^{o}\text{C)}}{\underline{18.5/n_{A} \text{ mV}}}$$

Thus by finding on the graph the activity of A at which the experimental line QR differs from the extrapolation of PQ by $18.5/n_{A}$ mV (Figure 4.15) the activity a'A can be determined.

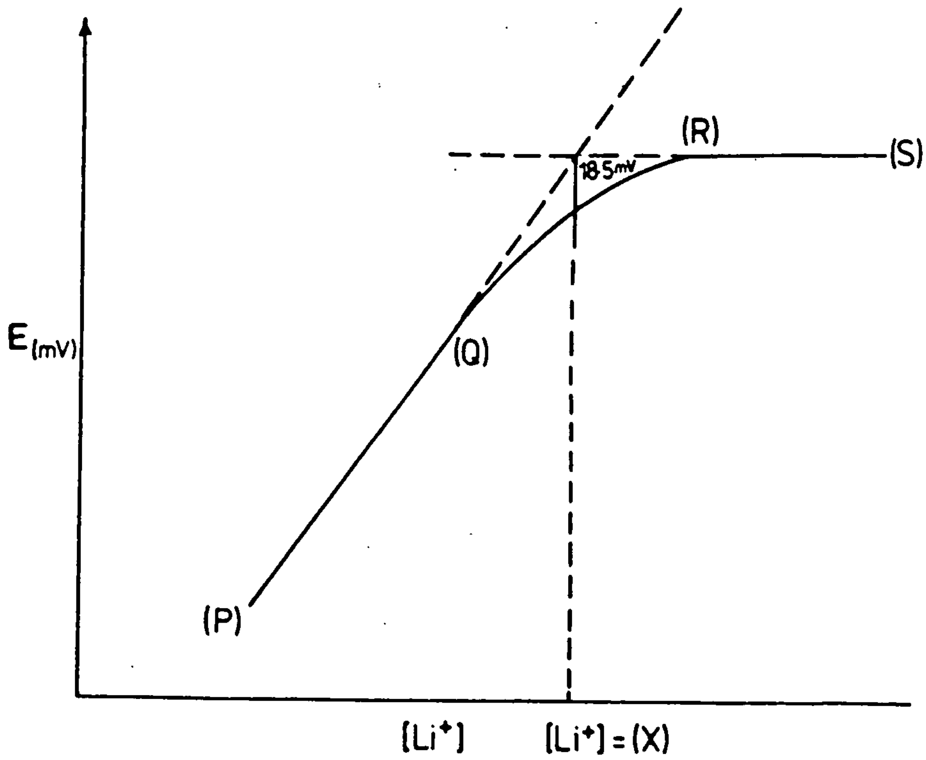

Figure 4.15 *Curve Obtained for Selectivity Coefficient Calculations by Varying the Activity of Primary Ion A, in the Presence of a Constant Background of the Interferent Ion, B.*

The selectivity may be defined as:

$$K_{AB} = \frac{a'_A n_B}{a'_B n_A}$$

thus the selectivity coefficient can be calculated. In addition to the selectivity coefficient, another useful parameter of an I.S.E. called the detection limit can be calculated. This defines, in effect, the minimum concentration of meaningful detection with an I.S.E. The detection limit has been defined in many ways, however IUPAC provisionally recommend that the detection limit be defined as the concentration of the determinant A at which the electrode potential deviates by $18.5/n_A$ mV from the extrapolation of the linear portion of the calibration curve. In order to obtain the selectivity coefficient and detection limit for compound (46), its incorporation into an ion sensing electrode must first be accomplished.

4.7.3 Fabrication of an Ion Sensing Device

Typically the ionophore under study is first dissolved in a solution of a swellable polymer, a plasticiser and a suitable solvent (*eg*. THF). From this a master membrane is cast by the controlled evaporation of the THF (Figure 4.16).

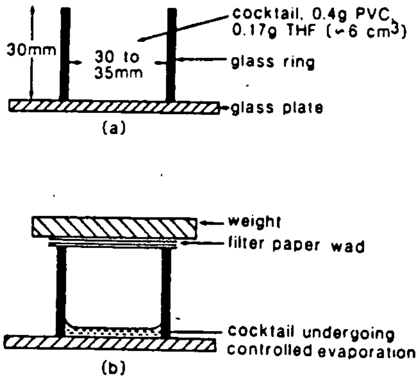

Figure 4.16

From the master membrane a sensor disc can be cut and inserted into a sensing electrode *via* a polished PVC tube (Figure 4.17). The electrode is then ready for the mixed solution potentiometric studies. For compound (46), the membrane consisted of 1.2% (46), 32.8% PVC, 65.5% ortho-nitrophenyloctylether (ONPOE), a plasticiser whose function was to maintain or improve the ion selectivity by reducing the T_g of the resultant polymer, and 0.4% potassium *tetrakis*-(4-chlorophenylborate) (KT_pClPB), a lipophilic anion whose presence reduces the interference by sample anions and reduces the electrical resistance of the membrane.

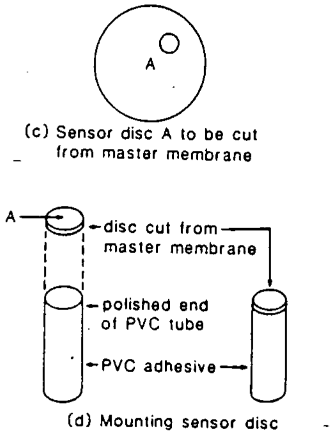

Figure 4.17

4.7.4 Results

The performance of this new thiophene I.S.E. (46) was compared with that of its benzo analogue‡‡ and the commercially available Philips (561-Li^+) I.S.E. Calibration measurements were performed at 37°C for which a Nernstian response predicts a 61.5 mV potential difference per decade change in lithium ion concentration. The electrodes were conditioned prior to examination by immersing for 24h in 10^{-3} M LiCl

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‡‡Prepared by Mr. P.E. Nicholson, University of Durham (Reference 166b).

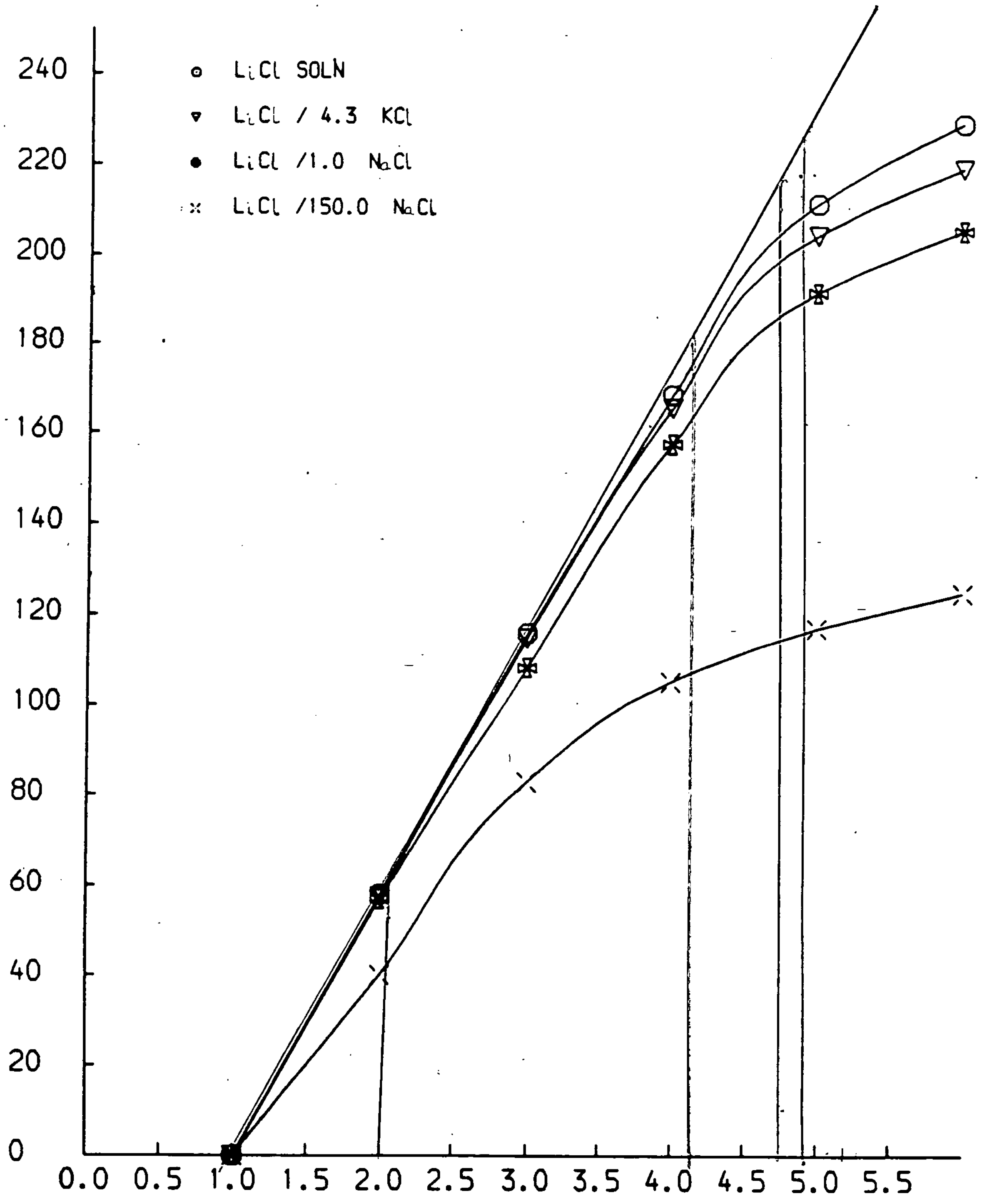


Figure 4.18 *Calibration Curve of the Philips Lithium Ionophore; E/V (Y-axis) plotted against-Log [Li] Concentration (X-axis).*

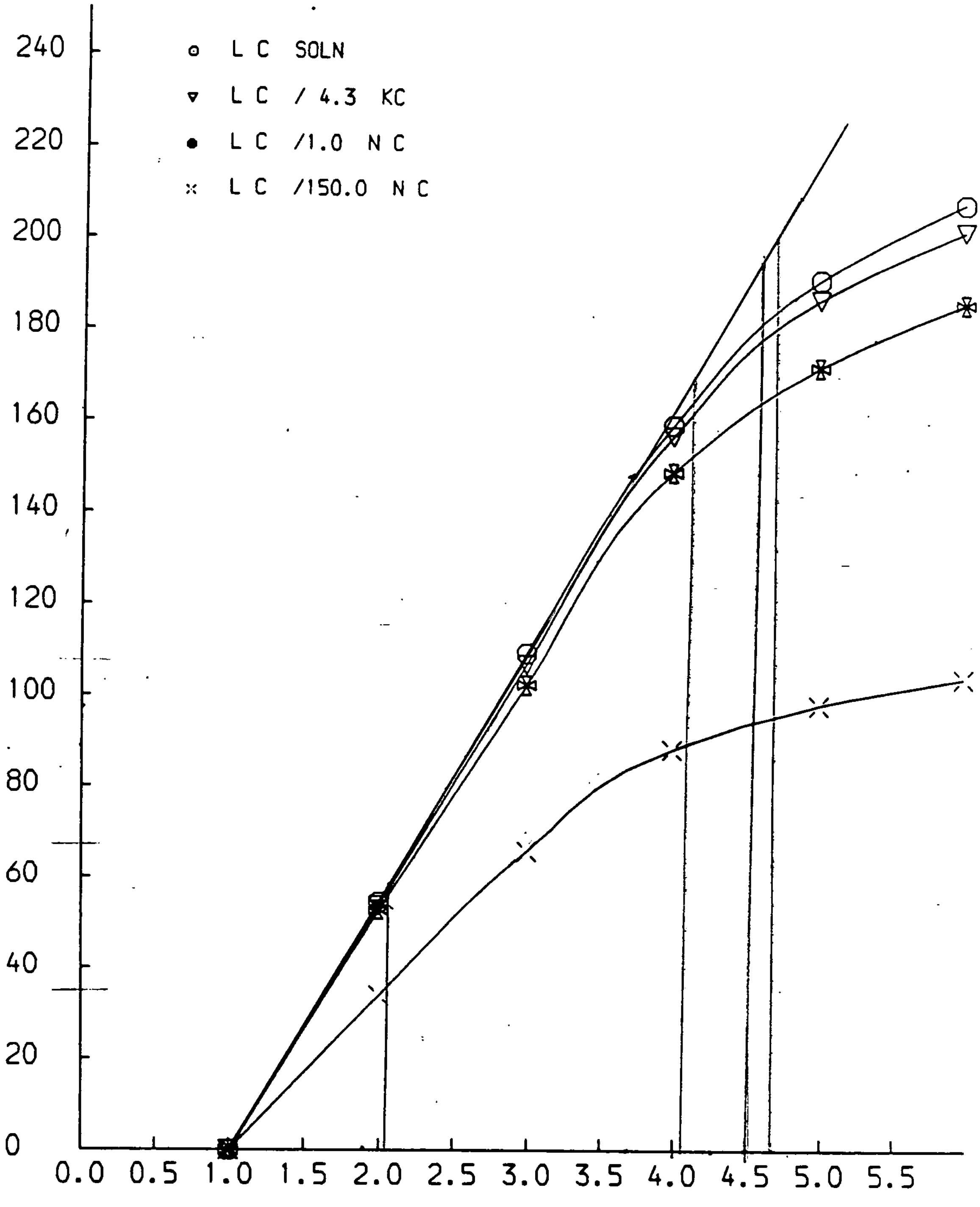


Figure 4.19 *Calibration Curve of the 14-C-4 Benzo Derivative; E/V (Y-axis) plotted against-Log [Li] Concentration (X-axis).*

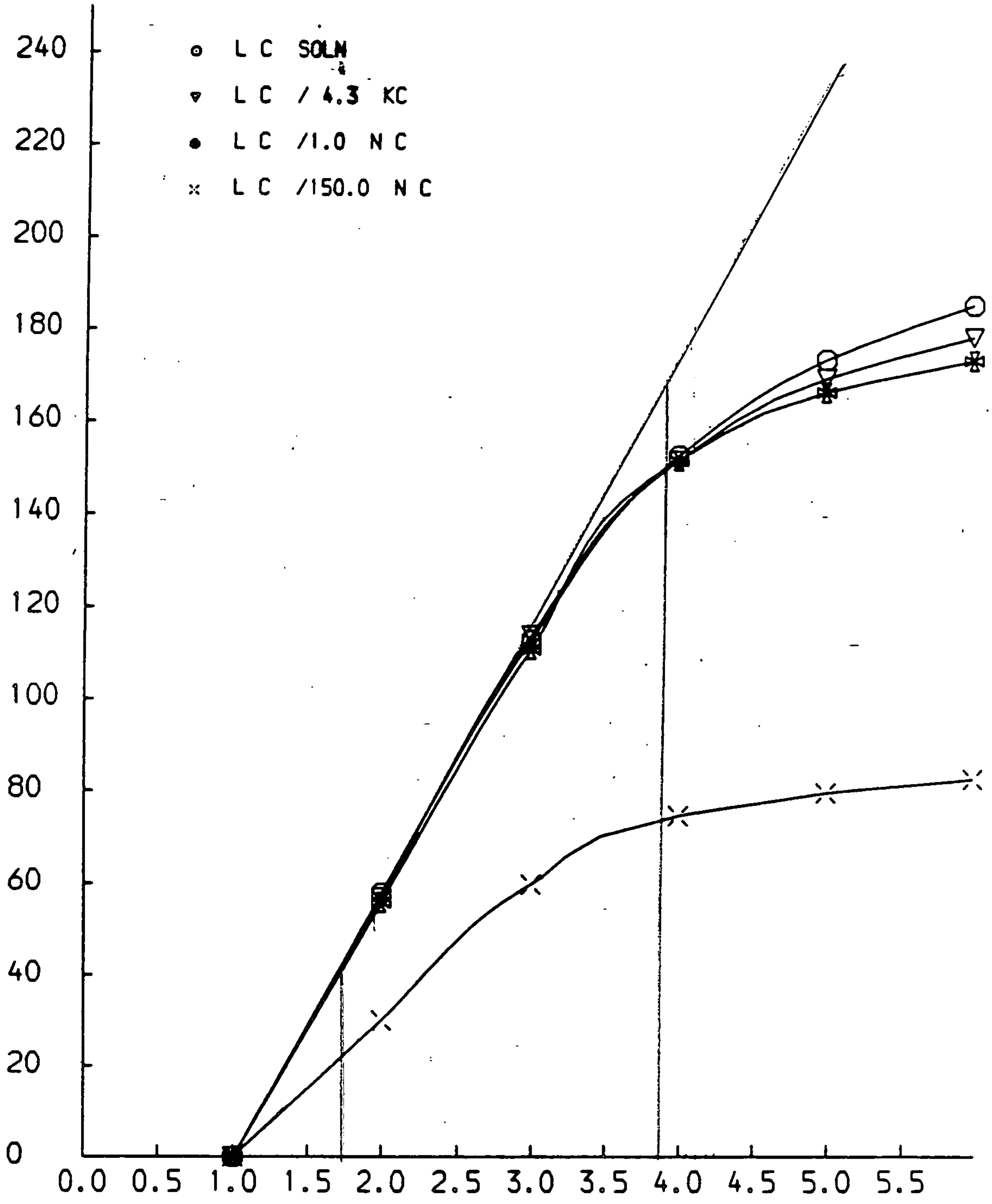


Figure 4.20 *Calibration Curve of the 14-C-4 Thio Derivative; E/V (Y-axis) plotted against-Log [Li] Concentration (X-axis).*

IONOPHORE	SLOPE W.R.T. PURE LiCl Soln. (mV/decade)	DETECTION LIMIT (in Moles)				SELECTIVITY K(AB)	
		PURE LiCl Soln.	4.3 mM KCl Soln.	1.0 mM NaCl Soln.	150 mM NaCl Soln.	Log (Li/K)	Log (Li/Na) [a]
PHILIPS	59.3	1.26×10^{-5}	1.78×10^{-5}	7.08×10^{-5}	1.00×10^{-2}	-2.38	-1.15
14-C-4 BENZO	58.3	2.24×10^{-5}	3.16×10^{-5}	8.90×10^{-5}	7.08×10^{-3}	-2.13	-1.05
14-C-4 THIO	56.5	1.41×10^{-5}	1.41×10^{-5}	1.41×10^{-5}	1.78×10^{-2}	-2.48	-1.85

Table 4.4 *Characteristics of Li Ionophores Obtained from Calibration Curves.*
Ideal Slope at 37°C = 61.5 mV/decade;
a) Selectivity Values obtained w.r.t. 10 mM NaCl solution.

solution. Results of these preliminary studies can be obtained from Figures 4.18-4.20 and are summarised in Table 4.4.

As can be seen from Table 4.4, the slope of (46) is only marginally inferior to the commercial ionophore and the benzo analogue. The detection limit, on the other hand, is in good agreement with both the Philips (561-Li^+) electrode and the benzo derivative. However, the main response, that of selectivity, appears to be better than both the commercially available Philips (561-Li^+) sample and the benzo analogue although the same trend as selectivity (*cf.* F.A.B technique) is being shown for this method of determination.

As the F.A.B technique ostensively measures the selectivity of an ionophore in the presence of many competing ions, whilst the mixed solution potentiometric method only compares two competing ions at any one time the fact that both results correlate with each other is itself a vindication of the F.A.B technique. (46) is at present undergoing further studies in a flow cell (see Appendix I). This can accommodate several interference ions, thereby giving an even more accurate picture of the selectivity coefficient of (46) and therefore its use as an I.S.E.

4.8 CONCLUSION

Several methods of entry into macrocyclic substituted thiophenes have been pursued successfully. The chemistry employed in these syntheses have meant that, by employing the same methodology, various analogues of the three types of derivative can easily be made. This open-ended methodology could be crucial in the fabrication of "working systems" and is worthy of further study. Although (41) could not be made to electropolymerise, it is belief of the author still, that it can be made to electropolymerise, and that this should also be pursued. Regarding (46), the preliminary studies carried out thus far indicate that further work in this area should be more fruitful. Unfortunately the parent 14-crown-4 ionophore (Figure 4.10) is not commercially available, so no F.A.B. or mixed solution potentiometry could be carried out on it. No comparative data to establish whether the chain ether oxygen of (46) either aids or impedes the selectivity is therefore available. However, increased selectivity may be inferred if lariat systems bearing amide linkages are used[166b] (see Section 5.2.3).

As can be seen the selectivity coefficients derived from FAB measurements and those derived from the mixed solution potentiometric methodology do differ, but they both demonstrate the same trend, *ie.* that (46) preferentially binds lithium ions when given a choice of other alkali metal cations.

Although this work has demonstrated that macrocyclic ligands can be successfully attached to thiophene sub-units, no 'working' polymeric systems have yet been developed; nitrogen (amine) free macrocycles potentially offer the best type of system to study and the incorporation of a pendant thiophene moiety, does not detract from the selectivity preference of the parent macrocycle.

CHAPTER FIVE

FUTURE WORK

5.1 INTRODUCTION

The facile method of entry into β-substituted thiophenes developed and built upon over the last three Chapters, has served to further accelerate the commercial realisation of these materials when polymerised.

However, the previous chapters, although complete in their own right, lend themselves to still further development and expansion. It is the purpose of this chapter to outline proposals on the direction that the author thinks these developments should take. The chapter will be split into two sections: the first will concern future work regarding the systems already developed (Chapters 2, 3 and 4), while the second will concern more general future work that should be developed.

5.2 SHORT TERM

5.2.1 Regarding Chapter 2

Attempts should first of all be made to obtain electroactive polymeric films of the remaining monomers that have not yet been polymerised. This would be performed at Perivale, employing the hitherto successful technique of controlled current electrolysis. Furthermore, attempts to grow films at constant potential should also be performed. This would allow a comparative study of films grown at the primary monomer oxidation potential and at the "secondary" monomer oxidation potential. Work that could easily be performed at Durham could include the ESCA study of the working electrode surface after the observed "passivation" of the electrode surface had been established. Although no film could be detected by the naked eye under such circumstances, E.S.C.A. may prove a more reliable analytical tool. As a lot of work has been carried out already on the electroactive form of the polymer of compound (4), it would seem appropriate to carry out some studies on its reduced form. Accordingly, the electrochemical (or chemical)[190] reduction of the polymer in a more weakly solvating solvent, *eg*. tetrachloromethane, should be tried (Figure 5.1).

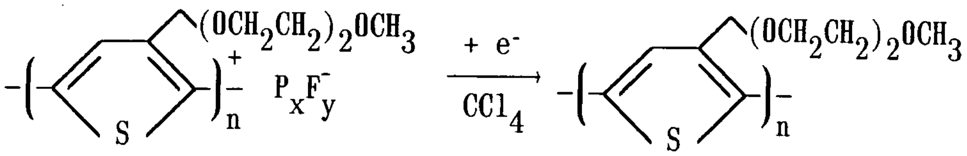


Figure 5.1 *Possible Route into the Electrochemical Reduction of the above Polymers.*

This would hopefully leave a coherent, reduced film on the electrode surface for ESCA analysis (also SEM analysis). In its reduced state, the polymer would also lend itself to a molecular weight determination (*via* the V.P.O. or the G.P.C. technique depending on its molecular weight). FTIR studies of the reduced form for comparison with the oxidised form should also be carried out. Further ESCA studies on the *oxidised* form of the polymer should also be carried out.

Two valuable experiments to perform would include, firstly, the ESCA study of the solution cast film in order to note any difference in the surface composition with the "as grown" film. Secondly, a series of ESCA studies should be performed on oxidised forms of the polymer at different film thicknesses, along with a comparison of conductivity, to see if there is any difference in surface composition and conductivity (see Section 1.5.3).

5.2.2 Regarding Chapter 3

Much needs to be done regarding the characterisation of the polymers formed in this chapter. It is only assumed that the thiophene moiety forms an α-α linked system yet, as stated in Section 3.2.1, the phenolic moiety may take part in the overall bonding of the polymer. Therefore some F.T.I.R. studies should be conducted on the neutral forms of the polymers synthesised in Chapter 3 (excluding the liquid crystal derivatives), as this may help to establish the nature of the polymers in more detail.

Obviously, E.S.C.A. spectra of the liquid crystal systems would be advantageous, if possible at varying temperatures above and below the D.S.C. phase change temperature.

Finally, work to generate poly(anilines) with subsequent polymerisation of the thiophene moiety should also be pursued.

5.2.3 Regarding Chapter 4

Further studies involving the compounds synthesised in this chapter are limited to compounds (40) and (46). Starting with (40), a greater effort should be made to electropolymerise the neutral complex of the material. Variations should be made, therefore, in the choice of metal ion, working electrode *etc.* along with, possibly, variation of the electrochemical technique (Perivale) in an attempt to grow the polymer. In addition to any variation in metal ion, further attempts to grow X-ray crystals of the complexes should be made, in order to establish the nature of the bound ligand. Obviously, once a successful method of entry into the polymer has been established, the synthesis and electropolymerisation of the 14-N-4 analogue should be carried out.

Testing of the polymer as an "ion pump" could then go ahead.

With respect to (46), further emphasis on electropolymerising the compound should be also be made, perhaps in preference to (40) as its electropolymerisation is likely to succeed more rapidly than (40). Similar conditions to those used in the successful electropolymerisation of compound (4) could be used (constant current). Alternatively, if there is still difficulty in obtaining the homopolymer, electropolymerisation with a monomer of similar oxidation polymer could be tried (*eg*. 3, 4 or 6). Again, once a method of entry into the polymer has been obtained (either homo- or co-polymerisation), then the synthesis of pertinent analogues for comparative studies could be made (see work performed by P.E. Nicholson)[166b].

Finally, attempts to synthesise the parent 14-O-4 cycle (Figure 4.10) should be made, so that FAB experiments similar to those carried out with compound (46) can be performed. The results of which should establish whether the presence of the pendant (CH_2O) linkage in (46) acts as a "lariat-type" ether, aiding (or hindering the binding of ions).

5.3 LONG TERM

5.3.1 Electrochemical Polymerisation

At the beginning of this work, it was hoped that Cyclic Voltammetry would not only be used in the study of the monomers synthesised, but would also lend itself to a facile method of entry into the polymers. Therefore, the imposition (in Chapter 2) of a set of stringent conditions regarding the C.V. work seemed appropriate. Indeed it was essential if any meaningful conclusions could be drawn. However, it is now apparent that some of the assumptions made when these conditions were imposed were ill-founded with respect to the formation of EAPs. Although it is the author's belief that these conditions should be maintained as "the bench mark" for any other monomers synthesised, a more flexible approach to film forming using C.V. should be adopted.

For instance, the use of a surface modified electrode platinum working electrode should be considered (see Section 2.3.2) as well as a change in the base electrolyte (see Section 2.3.4). Whereas it was not the original purpose of this work to optimise the film forming conditions (see Section 2.3), a move towards optimisation and characterisation should be made.

5.3.2 Chemical Polymerisation

The synthesis of compound (10) (Figure 5.3) has meant that an extended range of new monomers that possess low oxidation potentials can be synthesised.

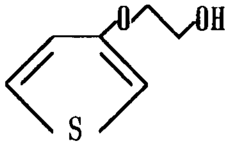


Figure 5.3 *Compound (10).*

This has important implications if the use of chemical oxidants are to be considered in the generation of PTs. As it stands now most chemical oxidants possess oxidation potentials below that of thiophene (*ie.* ≤ +2.1 V) and hence, could not be used to generate the polymer. If on the other hand the oxidation potential of the thiophene monomer could be lowered substantially (*eg.* ≤ +1.6 V), then a far greater range of chemical oxidants could in principle be used to generate the subsequent polymers.

Industrially, the use of chemical oxidants would offer several advantages over the established electrochemical methods:

(a) They would in principle be easier to reproduce.

(b) They would be cheaper (on an industrial scale).

(c) Established solution polymerisation techniques could be employed.

(d) The use of stringent conditions (*ie.* N_2 atmosphere and high purity solvents) are less likely.

Therefore more work to lower the primary oxidation potential of thiophene by the use of electron donating substituents should be considered (Figure 5.4).

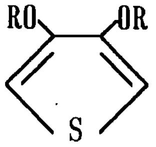


Figure 5.4 *Monomers that will Possess Lower Oxidation Potentials than Compound (10).*

5.3.3 Pharmacological Testing

None of the monomers synthesised thus far have been subjected to any form of pharmacological testing. Although this work has been concerned in the main with developing methods of entry into *β*-substituted thiophenes, studying their C.V. behaviour, forming EAPs and finding secondary end uses should also be considered. This is important from an industrial point of view as one monomer may not offer any potential as an EAP, but it may offer potential in another field (*eg.* agricultural), so all the monomers synthesised should be screened for pharmacological activity.

In conclusion therefore, a less blinkered approach should be adopted as to the possible end uses of these materials, not only from a chemical point of view but from a financial one as well.

CHAPTER SIX

EXPERIMENTAL SYNTHESES

6.1 INTRODUCTION

In the proceeding section which describes the synthetic procedures for all compounds used in this work, alumina refers to Merck alumina (activity II to III) neutralised on ethyl acetate overnight and silica refers to Merck silica (gravity being 70-230 mesh and flash being 230-400 mesh). Thin layer chromatography was carried out using Merck 150 F254 aluminium oxide and Merck silica 60 F254 precoated aluminium sheets.

Melting points were determined using a Reichert-Kofler block and are uncorrected. ^1H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra, were recorded using a Brüker AC250 spectrometer operating at 250.134 MHz for the proton nucleus and 62.896 MHz for the carbon nucleus. Chemical shifts are given in ppm [relative to tetramethylsilane (TMS) at 0 ppm] with J being the scalar coupling constant in Hz. Infrared (IR) spectra were recorded as Nujol mulls between KBr plates and liquid samples were recorded as contact films between KBr plates using a Perkin-Elmer 297 spectrophotometer.

Mass spectra were recorded on a VG 707E mass spectrometer operating at 70 eV with CI, DCI, FAB and EI ionisation modes as stated. C,H,N microanalyses were performed using a Carlo-Erba strumentazione elemental analyser (Model 1106). Analysis for halogens and sulphur were obtained using a Perkin-Elmer atomic absorption spectrophotometer. Differential Scanning Calorimetry (DSC) measurements were performed using a Mettler FP85TA cell and a Mettler FP80 central processor. Ultra-Violet spectra (UV) were determined using a Pye-Unicam 8720 UV/Vis scanning spectrophotometer. Reagents were used as supplied and solvents were dried by standard procedures.

Cyclic voltammetry (CV) measurements were made using either a BAS100 Electrochemical Analyser, a BAS CV1B Voltammograph or a PAR 173276, EG & G Instruments (Cookson Group PLC). In the determination of selectivity coefficients employing the mixed solution technique, the ion selective and reference electrodes were connected to a digital multimeter [Keithley 197 Autoranging Microvolt DMM] *via* a buffer amplifier. The reference electrode was a porous plug, saturated calomel electrode (RE1 Petiacourt). The temperature of the system was maintained at 37^0 using a Techne Tempette junior TE-85 Thermostat bath.

Electrode potentials were measured by dipping both ion selective and reference electrodes into the analyte and recording the limiting potential value. The electrodes were thoroughly rinsed using deionised water between each measurement.

6.2 EXPERIMENTAL

3-Bromomethyl thiophene (1). This was prepared from 3-methyl thiophene according to the method of Gronowitz[191] and was purified by distillation under reduced pressure (Bpt. 97-98 ^oC, 13 mm Hg).

3-(Methoxymethyl)-thiophene (2). A solution of (1) (10.9g, 0.062 mol) in carbon tetrachloride (50 ml) was added dropwise to a solution of sodium methoxide (6.6g, 0.12 mol) in dry methanol (150 ml) and the mixture allowed to reflux (15 min). After cooling to room temperature, the solvent mixture was removed under reduced pressure and the resultant oil dissolved in dichloromethane (100 ml), extracted with distilled water (2 x 100 ml) and dried (K_2CO_3). After removal of the solvent, the crude oil was distilled under reduced pressure to give compound (2) as a colourless oil [2.8g, 35% based on (1)]. Bpt. 56-57 ^oC/10 mm Hg.

Analysis found: C, 55.5; H, 6.0; S, 25.2. Calculated for C_6H_8OS: C, 56.2; H, 6.2; S, 25.0%; IR (Thin Film): 3090, 1495, 1420, 1095 cm^{-1}; EI m/e (Intensity%): 128(25,M^+), 97(100,$C_4H_3S.CH_2^+$); δH($CDCl_3$): 3.37(3H,s), 4.46(2H,s), 7.09-7.11(1H,m), 7.21-7.24(1H,m), 7.26-7.28(1H,m); δC($CDCl_3$): 57.2, 69.4, 121.9, 125.2, 126.6 and 139.3 ppm.

3-(Methoxyethoxymethyl)-thiophene (3). Compound (1) (6.2g, 0.035 mol) in carbon tetrachloride (25 ml) was added to a solution of sodium methoxyethoxide (8.9g, 0.09 mol) in methoxyethanol (90 ml) and the mixture allowed to reflux (2 h). Treatment of the reaction mixture was the same as described for (2). Distillation of the crude oil gave the product, (3) as a colourless oil [3.0g, 50% based on (1)]. Bpt. 100-101 ^{0}C/10 mm Hg. Analysis found: C, 55.7; H, 7.7; S, 18.3. Calculated for $C_8H_{12}O_2S$: C, 55.8; H, 7.0; S, 18.6%; IR (Thin Film): 3095, 2860, 1450, 1200, 1095 cm^{-1}; EI m/e (Intensity%): 172(5,M^+), 97(12,$C_4H_3S.CH_2^+$); δH($CDCl_3$): 3.34 (3H,s), 3.54(4H,m), 4.53(2H,s), 7.05-7.07(1H,m), 7.08-7.13(1H,m), 7.20-7.24(1H,m); δC($CDCl_3$): 59.6, 67.0, 69.7, 72.5, 123.4, 126.4, 127.9 and 140.0 ppm.

3-(Methoxyethoxyethoxymethyl)-thiophene (4). Compound (1) (12.4g, 0.07 mol) in carbon tetrachloride (25 ml) was added to a solution of sodium methoxyethoxyethoxide (29.6g, 0.2 mol) in methoxyethoxyethanol (100 ml) maintained under nitrogen and the mixture was allowed to reflux (12 h). Treatment of the reaction mixture was the same as described above for (2). Distillation of the crude oil gave the product, (4) as a colourless oil [7.0g, 46% based on (1)]. Bpt. 136-138 ^{0}C/10 mm Hg. Analysis found: C, 56.0; H, 7.0; S, 15.1. Calculated for $C_{10}H_{16}O_3S$: C, 55.5; H, 7.4; S, 14.8%; IR (Thin Film): 2995, 2865, 1350, 1200, 1100 cm^{-1}; EI m/e (Intensity%): 216(12,M^+), 97(100,$C_4H_3S.\ CH_2$); δH($CDCl_3$):

3.26(3H,s), 3.40(4H,m), 3.50(4H,m), 4.45(2H,s), 6.96-7.02(1H,m), 7.11-7.13(1H,m), 7.15-7.17(1H,m); δC($CDCl_3$): 58.3, 66.1, 69.2, 70.2, 70.4, 71.7, 121.7, 125.2, 126.7 and 139.6 ppm.

2-(n-Butoxyethoxyethoxyethoxy)-ethanol (5). This was prepared from n-butyl chloride (26 ml, 0.25 mol) and tetraethylene glycol (431 ml, 2.5 mol) according to the method of Gibson[192]. Bpt. 130-145 °C (0.02 mm Hg) in 50% yield.

3-(Butoxyethoxyethoxyethoxyethoxymethyl)-thiophene (6). Compound (5) (25.0g, 0.1 mol) was reacted with potassium metal (3.9g, 0.1 mol) in tetrahydrofuran (100 ml). After 1.5 h compound (1) (17.7g, 0.1 mol) was added dropwise, and the mixture stirred at reflux (24 h). After cooling and filtration, the solvent was removed under reduced pressure, and the residue dissolved in methylene chloride (200 ml), washed with water (2 x 100 ml) and dried (K_2CO_3). Solvent was removed and the crude oil distilled to give (6) as a colourless oil [25.7g, 57% based on (1)]. Bpt. 162-163 °C/0.15 mm Hg. Analysis found: C, 58.6; H, 8.7; S, 9.5. Calculated for $C_{17}H_{30}O_5S$: C, 58.9; H, 8.7; S, 9.3%; IR (Thin Film): 3095, 2860, 1350, 1100 cm^{-1}; EI m/e (Intensity%): 346(9,M^+), 97(100, $C_4H_3S.CH_2^+$), 57(75,C_4H_9); δH($CDCl_3$): 0.91(3H,t), 1.34 (2H,m), 1.53(2H,m), 3.45(2H,t), 3.65 (16H,m), 4.56(2H,s), 7.06(1H,m), 7.20(1H,m), 7.26(1H, m); δC($CDCl_3$): 13.6, 18.9, 31.4, 68.1, 69.0, 69.8, 70.0, 70.3, 122.5, 125.5, 126.7 and 139.1 ppm

3-(n-Butoxymethyl)-thiophene (7). Compound (1) (14.3g, 0.08 mol) in carbon tetrachloride (50 ml) was added dropwise to a solution of sodium butoxide made by dissolving freshly cut sodium (4.6g, 0.2 mol) in n-butanol (100 ml). After stirring at reflux (5 h) the mixture was cooled to room temperature, filtered, and the precipitate washed with carbon tetrachloride (3 x 100 ml). Solvent from the combined filtrate and washings was removed under reduced pressure (80 ^{o}C, 10 mm Hg), and the residue dissolved in methylene chloride (200 ml), washed with water (2 x 100 ml) and dried (K_2CO_3). Methylene chloride was removed, and the residue distilled under reduced pressure. The major fraction collected (Bpt. 96^{o}C/8 mm Hg) was further purified by water washing and redistillation, to give (7) as a colourless oil [6.7g, 49% based on (1)]. Bpt. 93-94 ^{o}C/8 mm Hg. Analysis found: C, 64.2; H, 8.6; S, 18.4. Calculated for $C_9H_{14}OS$: C, 63.5; H, 8.2; S, 18.9%; IR (Thin Film): 2960, 2860, 1155, 1100 cm^{-1}; EI m/e (Intensity%): 170(2,M$^+$), 114(9,$C_4H_3S.CH_3O^+$), 97(100, $C_4H_3S.CH_2^+$); δH($CDCl_3$): 0.98(3H,t), 1.46(2H,m), 1.62(2H,m), 3.54(2H,t), 4.56(2H,s), 7.13(1H,m), 7.26(1H,m), 7.33(1H,m); δC($CDCl_3$): 14.0, 19.4, 21.4, 66.2, 70.2, 122.5, 125.7, 127.4 and 139.9 ppm.

3-(n-Hexyloxymethyl)-thiophene (8). Using a similar method to that described above for (7), compound (1) (19.5g, 0.11 mol) and sodium (4.6g, 0.2 mol) in n-hexanol (100 ml), were reacted. After reflux (5h), cooling and filtration, the filtrate was distilled at reduced pressure to give (8) the second fraction, as a colourless oil [16.4g, 75% based on (1)]. Bpt. 122-123 ^{o}C/9 mm Hg. Analysis found: C, 66.1; H, 9.3; S, 15.8. Calculated for $C_{11}H_{18}OS$: C, 66.6; H, 9.1; S, 15.8%; IR (Thin Film): 2925, 2860, 1150, 1100 cm^{-1}; EI m/e (Intensity%): 198 (1,M$^+$), 114(6,$C_4H_3S.CH_3O^+$), 97(100, $C_4H_3S.CH_2^+$); δH($CDCl_3$): 0.88(3H,t), 1.34(6H,m), 1.59(2H,m), 3.43(2H,t), 4.48(2H,s), 7.06(1H,m), 7.17(1H,m), 7.25(1H,m); δC($CDCl_3$): 14.1, 22.7, 25.9, 29.8, 31.8, 68.2, 70.5, 122.5, 125.8, 127.3 and 139.9 ppm.

3-(N-Phthalimidomethyl)-thiophene (9). Potassium phthalimide (5.7g, 0.03 mol) and 18-crown-6-ether (0.05g) were added to a stirred solution of (1) (5.5g, 0.03 mol) dissolved in dry N,N-dimethylformamide (70 ml), and the mixture heated (3h, 80-90 ^{o}C), then cooled and filtered. The filtrate was poured on crushed ice (ca. 100g), stirred (5h), and filtered to give solid product, which was dried and recrystallised from absolute ethanol to give (9) as a pale yellow solid [5.2g, 72% yield based on (1)]. Mpt. 133-134 ^{o}C. Analysis found: C, 64.8; H, 3.8; N, 5.5; S, 12.7. Calculated for $C_{13}H_9NO_2S$: C, 64.2; H, 3.7; N, 5.8; S, 13.2%; EI m/e (Intensity%): 243(100,M^+), 97(24,$C_4H_3S.CH_2^+$); IR(Nujol): 1760, 1700 cm^{-1}; δH($CDCl_3$): 4.84(2H,s), 7.14-7.35(3H,m), 7.65-7.85 (4H,m); δC($CDCl_3$): 36.2, 123.3, 124.2, 126.2, 128.1, 132.1, 134.0, 136.6 and 167.8 ppm.

3-(Aminomethyl)-thiophene hydrochloride (10). Hydrazine hydrate (1.4 ml, 0.03 mol) was added to a hot solution of (9) (6.4g, 0.026 mol) in absolute ethanol (200 ml), and the mixture was stirred at reflux (12h). Hydrochloric acid was added (5 ml, conc) and reflux continued for a further 30 min. After cooling (0 ^{o}C, 16 h) and filtration, the filtrate was evaporated to recover a white solid. This was dissolved in distilled water (50 ml), the mixture filtered, and the filtrate evaporated under reduced pressure to give a crude yellow solid, which was recrystallised from absolute ethanol to give (10) as a white solid [3.5g, 90% based on (9)]. Mpt. 165 ^{o}C (dec). Analysis found: C, 40.4; H, 5.0; N, 9.6; S, 21.2. Calculated for C_5H_8NSCl: C, 40.1; H, 5.3; N, 9.4; S, 21.4%; IR(Nujol): 3400, 1590, 1240 cm^{-1}; FAB m/e (glycerol): 114(94,M^+); δH(D_2O): 3.80(2H, s), 5.33(s,broad,exchanges in D_2O), 7.04-7.27(3H,m); δC(D_2O): 37.8, 125.9, 127.4, 127.6 and 132.9 ppm.

N-(3-Thienylmethyl)-acetamide (11). Triethylamine (0.46g, 4.5 mmol) was added dropwise to a suspension of (10) (0.6g, 4.0 mmol) in dry dichloromethane (20 ml) maintained at -5 ^{o}C under nitrogen, and the mixture stirred (15 min) before acetyl chloride (0.31g, 4.0 mmol) was added dropwise with continued stirring (3h, -5 ^{o}C). The reaction mixture was then washed sequentially with hydrochloric acid (50 ml, 0.5 M) and sodium hydroxide solution (50 ml, 0.5M). After separation, the organic phase was dried ($MgSO_4$) and the solvent removed under reduced pressure to give the crude product (11). Recrystallisation from hexane gave (11) as white solid [0.52g, 84% based on (10)]. Mpt. 46-47 ^{o}C. Analysis found: C, 53.5; H, 6.2; N, 8.7; S, 20.4. Calculated for C_7H_9NOS: C, 54.2; H, 5.8; N, 9.0; S, 20.7%; IR (Nujol): 3250, 1650, 1550 cm^{-1}; EI m/e (Intensity%): 155(37,M^+), 112(55,$C_4H_3S.CH_2NH^+$), 97(29,$C_4H_3S.CH_2^+$), 83(12,$C_4H_3S^+$); δH($CDCl_3$): 1.93(3H,s), 4.41(2H,d), 6.26(1H,br,s), 6.96-6.98(1H,m), 7.10(1H,m), 7.24-7.26(1H,m); δC($CDCl_3$): 23.1, 38.7, 122.2, 126.3, 127.3, 139.8 and 170.0 ppm.

N-(3-Thienylmethyl)-octanamide (12). Using the same reaction conditions as described above for (11), compound (10) (0.6g, 4.0 mmol), triethylamine (0.46g, 4.5 mmol) and octanoyl chloride (0.76g, 4.0 mmol) were reacted to give (12) as a white solid [0.85g, 89% based on (10)]. Mpt. 72-73 ^{o}C. Analysis found: C, 64.9; H, 8.9; N, 5.7; S, 13.3. Calculated for $C_{13}H_{21}NOS$: C, 65.3; H, 8.8; N, 5.9; S, 13.4%; IR (Nujol): 3290, 1630, 1540 cm^{-1}; EI m/e (Intensity%): 239(19,M^+), 113(35,$C_4H_3S.CH_2NH_2^+$), 97(63,$C_4H_3S.CH_2^+$); δH($CDCl_3$): 0.87(3H,t), 1.28(8H,m), 1.61(2H,m), 2.19 (2H,t), 4.44(2H,d), 5.60(1H,br,s), 7.00-7.03(1H,m), 7.14(1H,m), 7.25-7.31(1H,m); δC($CDCl_3$): 14.2, 22.7, 25.8, 29.1, 29.3, 31.8, 36.9, 38.8, 122.3, 126.5, 127.1, 140.0 and 173.1 ppm.

N-(3-Thienylmethyl)-dodecanamide (13). Using the same reaction conditions as described above for (11), compound (10) (0.6g, 4.0 mmol), triethylamine (0.46, 4.5 mmol) and dodecanoyl chloride (0.86g, 4.0 mmol) were reacted to give (13) as a white solid [1.1g, 92% based on (10)]. Purification was by hexane recrystallisation using hot filtration. Mpt. 89-90 ^{o}C. Analysis found: C, 69.0; H, 10.2; N, 4.2; S, 11.1. Calculated for $C_{17}H_{29}NOS$: C, 69.1; H, 9.8; N, 4.7; S, 10.9%; IR (Nujol): 3300, 1630, 1545 cm^{-1}; EI m/e (Intensity%): 295(18,M^+), 113(100,$C_4H_3S.CH_2NH_2^+$), 97 (46,$C_4H_3S.CH_2^+$); δH($CDCl_3$): 0.87(3H,t), 1.25(16H,m), 1.80(2H,m), 2.20 (2H,t), 4.46(2H,d), 5.80(1H,br,s), 7.01-7.03(1H,m), 7.15(1H,m), 7.30-(1H,m); δC(CD_2Cl_2): 13.6, 22.4, 25.5, 29.1, 29.3, 31.7, 36.4, 38.2, 44.9, 53.6, 121.6, 125.7, 127.0, 140.1 and 174.1 ppm.

3-n-Butoxythiophene (14). Sodium metal (2.0g, 0.087 mol) was completely reacted with n-butanol (125 ml) under an atmosphere of argon. Copper (II) oxide (1.25g, 0.016 mol) and potassium iodide (0.05g, 0.3 mmol) were then added, followed by 3-bromothiophene (5.0g, 0.031 mol). The mixture was stirred (100 ^{o}C, 3d), further potassium iodide added (0.05g, 0.3 mmol), and reaction continued (100 ^{o}C, 2d). After filtration (low porosity sinter), the butanol solution was poured into distilled water (150 ml) and extracted with ether (2 x 100 ml). The combined extracts were dried ($MgSO_4$), the solvent removed under reduced pressure, and the residue chromatographed on a *flash* silica column (15 x 2.5 cm OD) eluted with petroleum ether (Bpt. 40-60). Compound (14) was obtained as a colourless oil [2.0g, 42% based on 3-bromothiophene]. High Resolution MS: 156.00676 (Theoretical: 156.06089); IR (Thin Film): 3120, 1500, 1375, 1240, 1180 cm^{-1}; EI m/e(Intensity%): 156(30,M^+), 100(100,$C_4H_4OS^+$), 57(20,$C_4H_9^+$), 43(21,$C_3H_7^+$); δH($CDCl_3$): 0.93(3H,t), 1.45(2H,m), 1.71(2H, dt), 3.93(2H,t), 6.20-6.22(1H,m), 6.73-6.76(1H,m), 7.13-7.17(1H,m); $\delta C(CDCl_3)$: 13.8, 19.2, 31.3, 69.8, 98.6, 119.5, 124.4 and 158.0 ppm.

3-n-Hexyloxythiophene (15). Using the reaction conditions described above for the preparation of (14), sodium (2.0g) in n-hexanol (125 ml), copper (II) oxide (1.25g) and potassium iodide (0.05g) were reacted with 3-bromothiophene (5.0g, 0.031 mol). After slow filtration of the reaction mixture (using a low porosity sinter), the hexanol solution was washed with water (2 x 50 ml) and vacuum distilled to reduce solvent volume to ca. 10-15 ml. This residue was chromatographed as described above for 3-n-butoxythiophene to give (15) as a colourless oil [2.5g, 43% based on 3-bromothiophene]. Further purification was by vacuum distillation (117 ^{0}C/10 mm Hg). Analysis found: C, 64.9; H, 9.2; S, 17.2%. Calculated for $C_{10}H_{16}OS$: C, 65.2; H, 8.7; S, 17.4. High Resolution MS: 184.09354 (Theoretical: 184.09219); IR (Thin Film): 2950, 1455, 1375 cm^{-1}; EI m/e (Intensity%): 184(64,M^+), 100(100,$C_4H_4OS^+$), 43(50,$C_3H_7^+$); $\delta H(CDCl_3)$: 0.71(3H,t), 1.39(6H,m), 1.70(2H,d), 3.67(2H,t), 6.15-6.16-(1H,m), 7.00-7.03(1H,m), 7.07-7.10(1H,m); $\delta C(CDCl_3)$: 14.0, 22.5, 25.7, 29.2, 31.5, 70.0, 96.7, 119.4, 124.3 and 158.0 ppm.

3-(Methoxyethoxy)-thiophene (16). Using the reaction conditions and method described above for the preparation of (14), sodium (2.0g) in methoxyethanol (125 ml), copper (II) oxide (1.25g) and potassium iodide (0.05g) were reacted with 3-bromothiophene (5.0g, 0.031 mol). Chromatography of the crude product on a *flash* silica column (15 x 2.5 cm O.D.) eluted with diethyl ether gave (16) as a colourless oil [3.3g, 68% based on 3-bromothiophene]. Analysis found: C, 53.1; H, 6.6; S, 20.2. Calculated for $C_7H_{10}O_2S$: C, 53.1; H, 6.3; S, 20.3%; IR (Thin Film): 3110, 2925, 2880, 1550 cm^{-1}; EI m/e (Intensity%): 158(25,M^+), 100(26,

$C_4H_4OS^+$), 59(100,$C_3H_7O^+$), 45(50,$C_2H_5O^+$); δH($CDCl_3$): 3.42(3H,s), 3.70(2H, t), 4.07(2H,t), 6.24-6.25(1H,m), 6.78-6.80(1H,m), 7.13-7.17(1H,m); δC($CDCl_3$): 58.9, 69.2, 70.8, 97.2, 119.4, 124.5 and 157.6 ppm.

3-(Methoxyethoxyethoxy)-thiophene (17). Using the reaction conditions and method described above for the preparation of (14), sodium (2.0g) in methoxyethoxyethanol (125 ml), copper (II) oxide (1.25g) and potassium iodide (0.05g) were reacted with 3-bromothiophene (5.0g, 0.031 mol). Chromatography of the crude product on a *flash* silica column (15 x 2.5 cm O.D.) eluted with diethyl ether gave (17) as a colourless oil [2.1g, 34% based on 3-bromothiophene]. Analysis found: C, 53.3; H, 7.2; S, 16.0. Calculated for $C_9H_{14}O_3S$: C, 53.4; H, 6.9; S, 15.9%; IR (Thin Film): 3110, 2880, 1500 cm^{-1}; EI m/e (Intensity%): 202(3,M^+), 100(9, C_4H_4OS), 59(53,C_3H_7O), 45(12,C_2H_5O); δH($CDCl_3$): 3.34(3H,s), 3.53(2H,dd), 3.65(2H,dd), 3.76(2H,dd), 4.05(2H,dd), 6.22-6.23(1H,m), 6.73-6.76(1H,m), 7.11-7.15(1H,m); δC($CDCl_3$): 58.6, 69.2, 69.4, 70.3, 71.6, 97.2, 119.2, 124.4 and 157.3 ppm.

3-(Hydroxyethoxy)-thiophene (18). Using the reaction conditions and method described above for the preparation of (14), sodium (2.0g) in ethylene glycol (125 ml), copper (II) oxide (1.25g) and potassium iodide (0.05g) were reacted with 3-bromothiophene (5.0g, 0.031 mol). The crude product was placed on a *flash* silica column (15 x 2.5 cm O.D.) and eluted with *(i)* dichloromethane (to remove unreacted starting material) and *(ii)* dichloromethane/methanol (95:5) to give (18) as a white solid [1.9g, 43% based on 3-bromothiophene]. Mpt. 38-39 °C. Analysis found: C, 50.2; H, 5.8; S, 22.5. Calculated for $C_6H_8O_2S$: C, 50.0; H, 5.6; S, 22.3%; IR (Nujol): 3300, 1535, 750 cm^{-1}; EI m/e (Intensity%): 144(100, M^+), 100(47,$C_4H_4OS^+$), 45(17,$C_2H_5O^+$); δH($CDCl_3$): 4.00(4H,m), 6.19(1H,m), 6.73(1H,m), 7.10(1H,m); δC($CDCl_3$): 60.8, 71.4, 97.7, 119.4, 124.8 and 157.4 ppm.

3-(Toluenesulphonylethoxy)-thiophene (19). Solid p-toluenesulphonyl chloride (0.88g, 4.6 mmol) was added in small amounts to a cooled (-5 °C) solution of (18) (0.6g, 4.2 mmol) in dry pyridine (50 ml), the mixture was stirred for 5 mins, then maintained at -20 °C (48 h). The mixture was poured onto crushed ice and stirred (5 h). After filtration, the solid was recrystallised from hot hexane to give (19) as a white solid [1.0g, 83% based on (18)]. Mpt 76-77 °C. Analysis found: C, 52.1; H, 4.5; S, 21.8. Calculated for $C_{13}H_{14}O_4S_2$: C, 52.4; H, 4.7; S, 21.5%; IR (Nujol): 3090, 1590, 1545, 1380, 1180 cm^{-1}; EI m/e (Intensity%): 298 (0.5,M^+), 199(57,Tosyl$OCH_2CH_2^+$), 155(8,$Tosyl^+$), 91(18, $CH_3C_6H_4^+$); δH($CDCl_3$): 2.4(3H,s), 4.0(2H,t), 4.2(2H,t), 6.1(1H,m), 6.5(1H, m), 7.0(1H,m), 7.3-7.7(4H,m); δC($CDCl_3$): 21.3, 67.1, 67.9, 97.7, 118.9, 124.6, 127.6, 129.6, 132.3, 144.7 and 156.3 ppm.

3-N-(Phthalimidoethoxy)-thiophene (20). Potassium phthalimide (0.3g, 1.6 mmol) and (19) (0.4g, 1.4 mmol) were stirred together (85 °C, 12h) with 18-crown-6 ether (50 mg) in dimethylformamide (60 ml). The mixture was cooled to room temperature and stirred into crushed ice (12 h), and the solid filtered and recrystallised from absolute ethanol to give (20) as a white solid [0.26g, 72% based on (19)]. Mpt 146-147 °C. Analysis found: C, 62.2; H, 4.1; N, 4.9; S, 11.8. Calculated for $C_{14}H_{11}NO_3S$: C, 61.5; H, 4.0; N, 5.1; S, 11.7%; IR (Nujol): 1760, 1710, 1550 cm^{-1}; EI m/e (Intensity%): 273(4,M^+), 174(100,phthal-$NCH_2CH_2^+$); δH($CDCl_3$): 4.0(2H,t), 4.1(2H,t), 6.2(1H,m), 6.6(1H,m), 7.0(1H,m), 7.6-7.9(4H,m); δC($CDCl_3$) 37.2, 66.8, 97.9, 119.5, 123.3, 124.7, 132.0, 134.0, 157.0 and 168.1 ppm.

3-(Aminoethoxy)-thiophene hydrochloride (21). Hydrazine hydrate (0.7 ml, 0.015 mmol) was added slowly to a solution of (20) (2.6g, 9.5 mmol) in hot absolute ethanol (200 ml), and the mixture stirred at reflux (12 h) under nitrogen. Hydrochloric acid (5 ml, conc) was carefully added to the system and reflux continued for a further 30 mins. After cooling and filtration, the filtrate was evaporated to dryness (10^{-3} mm Hg, 15^{0}C) to leave a white crystalline solid which was extracted with water (10 ml). Filtration and removal of the water (10^{-3} mm Hg, 15 ^{0}C) gave the product (21) as a white solid [1.5g, 88% based on (20)]. MPt. 135-145 ^{0}C (dec). Analysis found: C, 39.8; H, 5.8; N, 8.1. Calculated for $C_6H_{10}NOSCl$: C, 40.1; H, 5.6; N, 7.8%; IR (Nujol): 3400, 1170, 1060 cm^{-1}; FAB m/e (glycerol): 144(36,M^+); δH($CDCl_3$): 3.00(2H,t), 3.90(2H,t), 6.20(1H,m), 6.70(1H,m), 7.10(1H,m); δC($CDCl_3$): 40.8, 71.5, 96.7, 118.7 and 124.1 ppm.

N-(3-Thienyloxyethyl)-octanamide (22). Triethylamine (1.3 ml, 9.2 mmol) was added (10 mins) to a stirred suspension of (21) (1.5g, 8.4 mmol) in dry dichloromethane (60 ml) cooled to -5 ^{0}C. Octanoyl chloride (1.37g, 8.4 mmol) in dichoromethane (20 ml) was then added dropwise and stirring continued (4h, -5 ^{0}C). The mixture was washed sequentially with hydrochloric acid (2 x 50 ml, 0.1M) and sodium hydroxide (2 x 50 ml, 0.1 M), and dried ($MgSO_4$). Filtration and solvent evaporation resulted in a white solid which was recrystallised from hexane to give (22) as a white solid [1.4g, 62% based on (21)]. Mpt 78-79 ^{0}C. Analysis found: C, 61.9; H, 8.6; N, 4.9. Calculated for $C_{14}H_{23}NO_2S$: C, 62.4; H, 8.5; N, 5.2%; CI m/e (Intensity%): 270(0.5,M^+), 170(100,$C_4H_3SOCH_2CH_2NHCO^+$); IR(Nujol): 3300, 1635, 1545 cm^{-1}; δH($CDCl_3$): 0.88(3H,t), 1.27(8H,m), 1.63(2H,t), 2.19(2H, t), 3.64(2H,m), 4.02(2H,t), 5.93(1H,br,s), 6.27(1H,m), 6.75(1H,m), 7.19(1H,m); δC($CDCl_3$): 13.8, 22.3, 25.4, 28.8, 29.0, 31.4, 36.4, 38.6, 68.7, 97.5, 116.9, 124.7, 157.0 and 173.2 ppm.

N-(3-Thienyloxyethyl)-dodecanamide (23). Triethylamine (1.0 ml, 6.8 mmol) was added to a stirred suspension of (21) (0.8g, 4.5 mmol) in dichloromethane (20 ml) at -5 ^{o}C, followed by addition of dodecanoyl chloride (1.16 ml, 5.0 mmol). After stirring (4 h, -5 ^{o}C) the mixture was washed sequentially with hydrochloric acid (2 x 20 ml, 0.1 M) and sodium hydroxide (2 x 20 ml, 0.1 M), dried ($MgSO_4$) and the solvent removed under reduced pressure to give crude (23) which was recrystallised from hexane to give (23) as a white solid [0.7g, 48% based on (21)]. Mpt 97-98 ^{o}C. Analysis found: C, 66.6; H, 9.9; N, 3.9, S, 9.7. Calculated for $C_{18}H_{31}NO_2S$: C, 66.5; H, 9.5; N, 4.3; S, 9.9%; IR (Nujol): 3295, 1632, 1545 cm^{-1}; CI m/e (Intensity%): 326(7,M$^+$); EI m/e (Intensity%): 226(100,$CH_3(CH_2)_{10}C(O)N(H)CH_2CH_2^+$), 126(5,$C_4H_3S.OCH{=}CH_2^+$), 98(11,$C_4H_3O^+$); δH($CDCl_3$): 0.88(3H,t), 1.24(16H,br), 1.62(2H,t,br), 2.19(2H,t), 3.64(2H,m), 4.02(2H,t), 5.98(1H,br), 6.27(1H,m), 6.74 (1H,dd), 7.19(1H,m); δC($CDCl_3$): 13.7, 22.3, 25.3, 28.9, 29.2, 31.5, 68.6, 97.4, 118.8, 124.5, 156.8 and 173.1 ppm.

4-Cyano-4'-hydroxybiphenyl (24). Sodium ethanethiolate (1.6g, 20 mmol) was added to a stirred solution of 4-cyano-4'-methoxybiphenyl (2g, 10 mmol) in dry dimethylformamide (30 ml). This was allowed to stir at 120 ^{o}C for 2 hours, cooled and poured onto crushed ice. Hydrochloric acid (1.0 M) was added until the pH of the solution was between 1-2. The mixture was filtered and the residue taken up into ether (3 x 50 ml), washed with water (3 x 50 ml), dried ($MgSO_4$) and evaporated to leave crude (24) which was recrystallised from ethanol to give (24) as a white solid [1.6g, 80% based on 4-cyano-4'-methoxybiphenyl]. Mpt. 197-199 ^{o}C. Analysis found: C, 80.1; H, 4.6; N, 6.9. Calculated for $C_{13}H_9NO$: C, 80.0; H, 4.6; N, 7.2%; IR (Nujol): 3355, 2220, 1600, 815 cm^{-1}; EI m/e (Intensity%): 195(100,M$^+$), 166(18,$C_5H_4.C_6H_4.CN^+$), 140(25,$C_3H_2.C_6H_4.CN^+$), 102(15,$C_6H_4.CN^+$); δH(D_3COD_3): 7.01(2H,dd), 7.6(2H,dd), 7.7(4H,s), 8.7(1H,s); δC(D_3COD_3): 110.0, 116.3, 119.0, 127.1, 128.7, 130.3, 132.8, 145.5 and 158.6 ppm.

4-Cyano-4'-(3-thienyloxymethyl)-biphenyl (25). Compound (24) (4.8g, 25 mmol) and potassium hydroxide (1.4g, 25 mmol) in water (5 ml) were stirred together in tetrahydrofuran (100 ml) for 5 hours. The solvent was then evaporated to dryness and a solution of (1) (4.4g, 25 mmol) in dry tetrahydrofuran was added by syringe into the residue along with 18-crown-6 ether (50 mg) and the mixture was stirred at reflux under an atmosphere of nitrogen for 18 hours. The solvent was evaporated and the residue extracted with dichloromethane (5 x 100 ml). The combined organic extracts were washed sequentially with water (2 x 50 ml), 10% potassium hydroxide solution (2 x 100 ml) and water (2 x 50 ml). The solution was dried ($MgSO_4$) and evaporated to leave crude (25). This was recrystallised from tetrachloromethane to give (25) as a white solid [5.9g, 81% based on (1)]. Mpt. 154-156 ^{o}C. Analysis found: C, 74.3; H, 4.4; N, 4.7; S, 11.0. Calculated for $C_{18}H_{13}NOS$: C, 74.2; H, 4.5; N, 4.8; S, 11.0%; IR (Nujol): 2210, 1600, 1245, 820 cm^{-1}; EI m/e (Intensity%): 291(63,M$^+$), 194(12,$C_6H_4O.C_6H_4.CN^+$), 140(42,$C_3H_2.C_6H_4.CN^+$), 97(100,$C_4H_3S.CH_2^+$); δH($CDCl_3$): 5.11(2H,s), 6.98-7.72(11H,m); δC($CDCl_3$): 65.7, 110.1, 115.3, 119.1, 123.2, 126.4, 126.9, 127.1, 128.3, 131.7, 132.5, 137.5, 145.1 and 159.2 ppm.

1-Bromo-(3-thienylmethyl)-hexanamide (26). Triethylamine (5 ml, 36 mmol) was added dropwise to a stirred suspension of (10) (2.5g, 18 mmol) in dichloromethane (50 ml) maintained at -5^{o}C (ice/salt) under nitrogen.

After 10 minutes 6-bromohexanoyl chloride (4g, 18 mmol) was added dropwise to the mixture and this was allowed to stir for a further 5 hours. The dichloromethane layer was then washed sequentially with hydrochloric acid (2 x 20 ml, 0.1M), potassium hydroxide (2 x 20 ml, 0.1M) and dried ($MgSO_4$). The dichloromethane layer was evaporated to leave a tacky semi-crystalline white solid, to which diethyl ether was repeatedly added (10 ml) and evaporated until a powdery white solid resulted. This was recrystallised from hexane/ether (1:1) to give (26) as a white solid [3.2g, 62% based on (10)]. Mpt. 48-49 ^{o}C. Analysis found: C, 45.5; H, 5.6; N, 4.8; S, 10.9; Br, 27.6. Calculated for $C_{11}H_{16}NOSBr$: C, 45.5; H, 5.5; N, 4.8; S, 11.0; Br, 27.6%; IR (Nujol): 3300, 1630, 1535, 1195 cm^{-1}; EI m/e (Intensity%): 291(10,M^+ ^{81}Br), 289(M^+, ^{79}Br), 113(100,$C_4H_3S.CH_2.NH_2^+$), 97(59,$C_4H_3S.CH_2^+$); δH($CDCl_3$): 1.44(2H,m), 1.68(2H,m), 1.78(2H,m), 2.20(2H,t), 4.40(2H,d), 5.90(1H, s,broad), 7.00-7.03(1H,m), 7.13-7.14(1H,m), 7.23-7.31(1H,m); δC($CDCl_3$): 24.8, 27.8, 32.4, 33.5, 36.4, 38.7, 122.4, 126.5, 127.3 and 172.3 ppm.

1-(4-Cyano-4'-phenoxy)-(3-thienylmethyl)-hexanamide (27). Compound (24) (672mg, 3.4 mmol) and potassium hydroxide in water (193mg, 3.4 mmol) (6 ml) were stirred together in tetrahydrofuran (10 ml) for 3 hours. The solvent was then evaporated to dryness and 18-crown-6-ether (~10mg) as a solution in dry dimethylformamide (15 ml) was added to the residue by syringe. (26) (1.0g, 3.4 mmol) was added to the solution in one amount and the mixture stirred at 80 ^{o}C for 5 hours. This was then poured onto crushed ice, allowed to stir until the ice had melted and filtered. The adduct was washed with potassium hydroxide solution (2 x 5 ml, 0.1M) and taken up in chloroform and filtered again. The filtrate was dried ($MgSO_4$) and evaporated to leave a white solid which was recrystallised from ethanol to give (27) as a white solid [0.41g, 30% based on (26)].

Mpt. 132 °C. Analysis found: C, 70.4; H, 6.1; N, 6.4; S, 7.5. Calculated for $C_{24}H_{24}N_2O_2S$: C, 71.3; H, 5.9; N, 6.9; S, 7.9%; IR (Nujol): 3295, 2230, 1630, 1605 cm^{-1}; EI m/e (Intensity%): 404(3,M^+), 210(88,$C_3H_3S.C_8H_{13}NO^+$), 97(100,$C_4H_3S.CH_2^+$); δH($CDCl_3$): 1.56(2H,m), 1.76 (4H,m), 2.25(2H,t), 4.01(2H,t), 4.45(2H,t), 5.76(1H,s,broad), 6.96-7.70 (11H,m); δC($CDCl_3$): 25.4, 25.8, 28.9, 36.5, 38.7, 67.8, 110.0, 115.1, 118.5, 122.3, 126.4, 127.05, 127.1, 128.3, 131.0, 132.5, 138.9, 145.2, 159.6 and 172.5 ppm.

3-(Phenoxymethyl)-thiophene (28). Phenol (10g, 106 mmol) and potassium hydroxide (3g, 106 mmol) in water (5 ml) were stirred together in tetrahydrofuran (100 ml) for 5 hours. The solvent was then evaporated to dryness and a solution of (1) (19g, 106 mmol) in dry tetrahydrofuran was added by syringe into the residue along with 18-crown-6 (50 mg) and the mixture was gently refluxed for 18 hours under nitrogen. The solvent was evaporated and the residue extracted with dichloromethane (5 x 100 ml). The combined organic extracts were washed sequentially with water (2 x 50 ml), 10% potassium hydroxide solution (2 x 100 ml), water (2 x 50 ml), dried ($MgSO_4$) and evaporated to leave a pale yellow solid. This was chromatographed on *gravity* silica (30 x 5 cm O.D.) eluting with toluene to yield (28) as a white solid [9.7g, 48% based on (1)]. Mpt. 50-51 °C. Analysis found: C, 69.1; H, 5.4; S, 16.6. Calculated for $C_{11}H_{10}OS$: C, 69.4; H, 5.3; S, 16.9%; IR (Nujol): 1600, 1240, 840 cm^{-1}; EI m/e (Intensity%): 190(30,M^+), 97(100,$C_4H_3S.CH_2{}^+$), 77(10,$C_6H_5{}^+$); δH($CDCl_3$): 5.0(2H,s), 6.9-7.3(8H,m); δC($CDCl_3$): 65.0, 114.3, 120.5, 122.5, 125.7, 126.5, 137.5 and 158.1 ppm.

3-(2-Methylphenoxymethyl)-thiophene (29). Using the same reaction conditions as described previously for (28), compound (1) (20g, 113 mmol), potassium hydroxide (6.3g, 113 mmol) and 2-methyl phenol (12.2g, 113 mmol) were reacted to give (29) as a pale yellow oil [17.5g, 76% based on (1)]. Analysis found: C, 70.6; H, 5.8; S, 15.4. Calculated for $C_{12}H_{12}OS$: C, 70.6; H, 5.9; S, 15.7%; IR (Thin Film): 3050, 2920, 1605, 1590, 1240 cm^{-1}; EI m/e (Intensity%): 204(5,M^+), 97(83,$C_4H_3S.CH_2^+$), 77(3,$C_6H_5^+$); $\delta H(CDCl_3)$: 2.26(3H,s), 5.05(2H,s), 6.87-6.89(2H,m), 7.10-7.18(3H,m), 7.29-7.32(2H,m); $\delta C(CDCl_3)$: 16.4, 65.8, 111.4, 120.6, 122.3, 126.1, 126.8, 127.1, 130.8, 138.5 and 156.7 ppm.

3-(3-Methylphenoxymethyl)-thiophene (30). Using the same reaction conditions as described above for (28), compound (1) (20g, 113 mmol), potassium hydroxide (6.3g, 113 mmol) and 3-methyl phenol (12.2g, 113 mmol) were reacted to give (30) as a white solid [15.7g, 68% based on (1)]. Mpt. 37-38 ^oC. Analysis found: C, 70.4; H, 5.9; S, 15.7. Calculated for $C_{12}H_{12}OS$: C, 70.6; H, 5.9; S, 15.7%; IR (Nujol): 3020, 1600, 1590, 1260 cm^{-1}; EI m/e (Intensity%): 204(9,M^+), 97(100,$C_4H_3S.CH_2^+$), 77(10,$C_6H_5^+$); $\delta H(CDCl_3)$: 2.30(3H,s), 4.99(2H,s), 6.73-6.78-(2H,m), 7.08-7.29(5H,m); $\delta C(CDCl_3)$: 21.7, 65.6, 111.1, 115.8, 121.9, 123.1, 126.3, 127.1, 129.4, 138.3, 139.6 and 158.8 ppm.

3-(4-Methylphenoxymethyl)-thiophene (31). Using the same reaction conditions as described previously for (28), compound (1) (20g, 113 mmol), potassium hydroxide (6.3g, 113 mmol) and 4-methyl phenol (12.2g, 113 mmol) were reacted to give (31) as a white solid [13.8g, 60% based on (1)]. Mpt. 57-58 ^oC. Analysis found: C, 71.1; H, 6.0; S, 15.9. Calculated for $C_{12}H_{12}OS$: C, 70.6; H, 5.9; S, 15.7%; IR (Nujol): 3090, 1610, 1585, 1235 cm^{-1}; EI m/e (Intensity%): 204(10,M$^+$), 97(100,$C_4H_3S.CH_2^+$), 77(4,$C_6H_5^+$); δH($CDCl_3$): 2.25(3H,s), 4.97(2H,s), 6.83(2H,dd), 7.02(2H,dd), 7.10(1H,m), 7.26(2H,m); δC($CDCl_3$): 20.4, 65.6, 114.6, 122.8, 126.1, 126.9, 129.8, 130.0, 137.5 and 156.5 ppm.

3-(2-Nitrophenoxymethyl)-thiophene (32). Using the same reaction conditions as described above for (28), compound (1) (19g, 110 mmol), potassium hydroxide (6g, 110 mmol) and 2-nitrophenol (15g, 110 mmol) were reacted to give crude (32) which was recrystallised from ether and washed with cyclohexane to give (32) as pale yellow solid [10.3g, 40% based on (1)]. Mpt. 58-59 °C. Analysis found: C, 55.9; H, 3.8; N, 5.6; S, 13.1. Calculated for $C_{11}H_9NO_3S$: C, 56.1; H, 3.8; N, 6.0; S, 13.6%; IR (Nujol): 1605, 1580, 1300 cm^{-1}; DCI m/e (Intensity%): 236(1,M$^+$+1), 139(16,$C_6H_4.NO_3H^+$), 97(100,$C_4H_3S.CH_2^+$); δH($CDCl_3$): 5.22(2H,s), 7.00-7.85(7H,m); δC($CDCl_3$): 67.2, 115.1, 120.6, 123.0, 125.6, 126.4, 126.5, 134.0, 136.4, 140.2 and 151.7 ppm.

3-(2-Aminophenoxymethyl)-thiophene (33). Palladium on carbon (100mg) was added to a solution of (32) (3g, 13 mmol) in dry ethanol (35 ml) and the mixture hydrogenated at room temperature for 18 hours. After filtration, the solvent was evaporated and the residue chromatographed on alumina (15 x 2.5 cm OD) eluting with toluene to give (33) as a red oil [0.8g, 30% based on (32)]. Analysis found: C, 64.6; H, 5.4; N, 6.6; S, 16.1. Calculated for $C_{11}H_{13}NOS$: C, 64.4; H, 5.4; N, 6.8; S, 15.6%; IR (Thin film): 3480, 3440, 1500, 1460 cm^{-1}; EI m/e (Intensity%): 205 (33,M$^+$), 109(3,$C_6H_4.NOH_3^+$), 97(100,$C_4H_3S.CH_2^+$); δH($CDCl_3$): 3.62(2H,s, broad), 5.10(2H,s), 6.41-7.50(7H,m); δC($CDCl_3$): 66.1, 112.3, 115.3, 118.5, 121.6, 123.1, 126.2, 127.2, 136.6, 138.2 and 146.4 ppm.

3-(3-Nitrophenoxymethyl)-thiophene (34). Using the same reaction conditions as described for (28), compound (1) (19g, 110 mmol), potassium hydroxide (6g, 110 mmol) and 3-nitrophenol (15g, 110 mmol) were reacted to give crude (34) which was subsequently used in the next reaction without further purification, 64% conversion. IR (Thin film): 3100, 1608, 1580, 1520 cm^{-1}; DCI m/e (Intensity%): 253(100, M^++NH_4^+), 97(100,$C_4H_3S.CH_2^+$); δH($CDCl_3$): 5.13(2H,s,broad), 7.16-7.44(5H,m), 7.78-7.83(2H,m); δC($CDCl_3$): 66.0, 109.1, 115.8, 121.7, 123.5, 126.5, 126.8, 129.9, 136.6, 149.0 and 158.9 ppm.

3-(3-Aminophenoxymethyl)-thiophene (35). Using the same reaction conditions as described for (33), palladium on carbon and (34) (16.5g, 70 mmol) were hydrogenated to give crude (35) as a red oil which was recrystallised from ethanol to give (35) as a pale yellow solid [4.7g, 33% based on (34)]. MPt. 62-63 ^{0}C. Analysis found: C, 64.5; H, 5.4; N, 6.9; S, 15.9. Calculated for $C_{11}H_{13}NOS$: C, 64.4; H, 5.4; N, 6.8; S, 15.6%; IR (Nujol): 3480, 3380, 1500, 1460 cm^{-1}; EI m/e (Intensity%): 205(33,M^+), 97(100,$C_4H_3S.CH_2^+$); δH($CDCl_3$): 3.75(2H,s,broad), 5.11(2H,s), 6.40-6.55(3H,m), 7.17-7.46(4H,m); δC($CDCl_3$): 65.3, 101.8, 104.6, 108.1, 122.8, 126.0, 127.0, 130.0, 138.1, 147.8 and 159.7 ppm.

Hexaethylene glycol ditosylate (36). This was synthesised according to the method of Newcomb, Moore and Cram[170].

3,6,9,12,15-pentaoxa-1,17-diiodo-heptadecane (37). Potassium iodide (20.0g, 120 mmol) was added to a stirred solution of (36) (14.3g, 24 mmol) in acetone (120 ml) under nitrogen. The mixture was boiled under reflux for 18 hours, the solvent removed and the residue taken up in dichloromethane (3 x 100 ml). The combined organic extracts were washed with water (3 x 50 ml) and dried ($MgSO_4$). Evaporation left a light brown oil and this was chromatographed on alumina (15 x 3 cm OD) eluting with dichloromethane to give (37) as a viscous light brown oil [9.9g, 82% based on (36)]. High Resolution MS: 502.97921 $(M+H)^+$; Theoretical: 502.97915; IR (Thin Film): 2860, 1510, 1350, 1130 cm^{-1}; DCI m/e (Intensity%): 520(100,M^++NH_4^+), 177(11,$(CH_2O)_4H^+$), 133(11,$(CH_2O)_3H^+$), 44(10,CH_2O^+); δH($CDCl_3$): 2.81(4H,t), 3.21(16H,s), 3.33(4H,t); δC($CDCl_3$): 2.9, 70.1, 70.5 and 71.8 ppm.

16-(3-Thienylmethyl)-16-aza-1,4,7,10,13-pentaoxa-cyclooctadecane (38). Compound (10) (2.7g, 20 mmol) was added to a stirred solution of (37) (9.0g, 18 mmol) and sodium carbonate (7g, 66 mmol) in dry acetonitrile (150 ml). Under an atmosphere of nitrogen, the mixture was boiled under reflux (18h), cooled, filtered and the solvent evaporated. The residue was taken up into ether (3 x 100 ml) and the combined organic extracts, washed with water (3 x 100 ml) and dried ($MgSO_4$). Evaporation of the ether layer left a red oil which was acidified by shaking vigorously in a chloroform (30 ml) / hydrochloric acid (0.5M, 30 ml) mixture. The aqueous phase was collected and the water evaporated to leave a tacky red gum which was passed down an ion exchange column to give crude (38). This was chromatographed on alumina (15 x 2.5 cm OD) eluting with dichloromethane to give (38) as a viscous colourless oil [1.3g, 18% based on (10)]. High resolution MS: 359.176645 (Theoretical: 359.176645); IR (Thin film): 3055, 2890, 1650, 1355, 1110 cm^{-1}; EI m/e (Intensity%): 184(15,$C_4H_3S.C_5H_{11}NO^+$), 140(11,$C_4H_3S.C_3H_7N^+$), 126(30,$C_4H_3S.C_2H_5N^+$), 97(100,$C_4H_3S.CH_2^+$); δH($CDCl_3$): 2.76(4H,t), 3.62(23H,m), 7.01-7.03(1H,m), 7.10(1H,m), 7.20-7.23(1H,m); δC($CDCl_3$): 52.9, 53.9, 69.0, 69.4, 69.8, 69.9, 121.4, 124.3, 127.5 and 139.5 ppm.

3-(2,2-bis-ethoxycarbonyl)-ethylthiophene (39). Diethyl malonate (45g, 281 mmol) was added dropwise (over 10 minutes) to a stirred solution of sodium ethoxide (3.8g, 56 mmol) in dry ethanol (300 ml) maintained under nitrogen. After stirring at room temperature for 3 hours, (1) (10g, 56 mmol) was added dropwise over 5 minutes, and the mixture stirred at reflux for 18 hours. The solvent was evaporated and the residue extracted with dichloromethane (3 x 100 ml); the combined organic extracts were washed with water (3 x 50 ml), dried ($MgSO_4$) and evaporated to leave crude (39) as a yellow oil. Upon distillation (120-138^{o}C/1 mm Hg) (39) was obtained as a colourless oil [4.2g, 29% based on (1)]. Analysis found: C, 56.6; H, 6.5; S, 12.4. Calculated for $C_{12}H_{16}O_4S$: C, 56.3; H, 6.3; S, 12.5%; IR (Thin film): 3100, 2980, 1740, 1375 cm^{-1}; EI m/e (Intensity%): 256(92,M^+), 211(32,$C_4H_3S.C_5H_6O_3^+$), 182(100,$C_4H_3S.\ C_5H_7O_2^+$), 137(81,$C_4H_3S.C_3H_2O^+$), 110(20,$C_4H_3S.C_2H_3^+$), 97(100,$C_4H_3S.CH_2^+$); δH($CDCl_3$): 1.21(6H,t), 3.24(2H,d), 3.64(1H,s), 4.16(4H,q), 6.93-6.95 (1H,m), 7.01-7.02(1H,m), 7.21-7.25(1H,m); δC($CDCl_3$): 14.0, 29.2, 53.2, 61.5, 122.0, 125.7, 128.2, 138.0 and 168.8 ppm.

12-(3-Thienylmethyl)-1,4,7,10-tetraazacyclotridecane-11,13-dione (40). Under an atmosphere of nitrogen, compound (39) (22.5g, 80 mmol) and 1,4,7,10-tetraazadecane (12.7g, 80 mmol) were stirrred at reflux in dry ethanol (60 ml) for two weeks. Upon cooling and slow evaporation of the solvent, a white crystalline solid precipitated out of solution. This was filtered, washed with ethanol (2 x 5 ml) and dried to give (40) [1.24g, 5% based on (39)]. Mpt. 217-219 ^{o}C. High Resolution MS: 311.0361 (M^++H), Theoretical: 311.1542 (M^++H); IR (Thin film): 3340, 3315, 1660, 1630, 1550 cm^{-1}; EI m/e (Intensity%): 311(100,M^++H); δH(CD_3SOCD_3): 3.50(8H,s), 3.72(2H,m), 3.87(2H,d), 4.03(1H,t), 4.34(2H,m), 5.58(4H,s), 7.66-7.68 (1H,m), 7.77-7.78(1H,m), 8.00-8.02(1H,m); δC(D_2O): 28.4, 39.7, 46.1, 47.0, 56.2, 122.7, 127.0, 128.8, 137.5 and 171.8 ppm.

[40-Cu(copper complex)] (41). A solution of copper(II) perchlorate hexahydrate (11.3mg, 30.4 mmol) in water (2 ml) was added to a solution of ligand (40) (10mg, 32 μmol) in water (2 ml). An immediate pink/purple colouration was observed and the solution was filtered to leave a clear pink/purple solution. λ_{max}(H_2O) 497.6; λ_{max}(MeOH) 570.4; FAB m/e (glycerol): 373 (0.3,M^+), 375 (0.4,M^+).

3-(2,2-bis-ethoxycarbonyl)-2-(3-thienylmethyl)-ethylthiophene (42). Using the same method described for (40), (1) (20g, 113 mmol), diethyl malonate (9.1g, 56 mmol) and sodium ethoxide (7.7g, 113 mmol) were reacted together to give crude (42) which upon distillation (190-200 ^{0}C/1 mm Hg) gave (42) as a colourless oil [15g, 38% based on (1)]. This crystallised on standing. Mpt. 25-26 ^{0}C. Analysis found: C, 58.0; H, 5.9; S, 18.7. Calculated for $C_{17}H_{20}O_4S$: C, 58.0; H, 5.7; S, 18.2%; IR (Thin film): 3100, 2980, 1735, 1500 cm^{-1}; EI m/e (Intensity%): 352(1, M^+), 97(8,$C_4H_3S.CH_2^+$), 83(8,$C_4H_3S^+$), 28(100,CO^+); δH($CDCl_3$): 1.2(6H,t), 3.23(4H,s), 4.16(4H,q), 6.85(2H,m), 6.98(2H,m), 7.23(2H,m); δC($CDCl_3$): 11.4, 30.6, 56.7, 58.9, 120.8, 122.7, 126.5, 133.7 and 168.4 ppm.

12,12-Bis(3-thienylmethyl)-1,4,7,10-tetraazacyclotridecane-11,13-dione (43). Using the same reaction conditions described above for (41), (42) (14g, 40 mmol) and 1,4,7,10-tetraazadecane (6.4g, 40 mmol) were reacted together in ethanol (40 ml) in an attempt to form (43). After two weeks TLC (silica in methanol) showed only starting material.

5-Methoxy-(3-thienylmethyl)-2,2-dimethyl-1,3-dioxolane (44). Compound (1) (13.0g, 74 mmol) was rapidly added to a stirred solution of 2,2-dimethyl-1,3-dioxalane-4-methanol (10g, 76 mmol), powdered potassium hydroxide (4.1g, 74 mmol) and 18-crown-6-ether (50 mg), in dry tetrahydrofuran (150 ml) maintained under nitrogen. The mixture was allowed to reflux for 18 hours, the solvent removed and the residue taken up into dichloromethane (3 x 100 ml). The combined organic extracts were washed with aqueous potassium hydroxide (0.1M, 2 x 20 ml), water (2 x 20 ml) and dried ($MgSO_4$). The solvent was evaporated and the residue chromatographed on *gravity* silica (30 x 5 cm OD), eluting with toluene to afford (44) as a viscous yellow oil [9.3g, 55% based on (1)]. High Resolution MS: 228.07870 (Theoretical: 228.075307); IR (Thin Film): 2990, 2860, 1380, 1370, 1080 cm^{-1}; EI m/e (Intensity%): 228(6,M^+), 213(11,$C_4H_3S.C_6H_{10}O_3^+$), 113(4,$C_4H_3SCH_2O^+$), 97(100,$C_4H_3S.CH_2^+$); δH($CDCl_3$): 1.34(3H,s), 1.40(3H,s), 3.43(2H,m), 3.67(1H,m), 3.98(1H,m), 4.23(1H,m), 4.54(2H,s), 7.03-7.05(1H,m), 7.11-7.13(1H,m), 7.24-7.28(1H,m); δC($CDCl_3$): 25.0, 28.4, 66.3, 68.2, 70.5, 74.3, 108.9, 122.5, 125.6, 126.8 and 138.8 ppm.

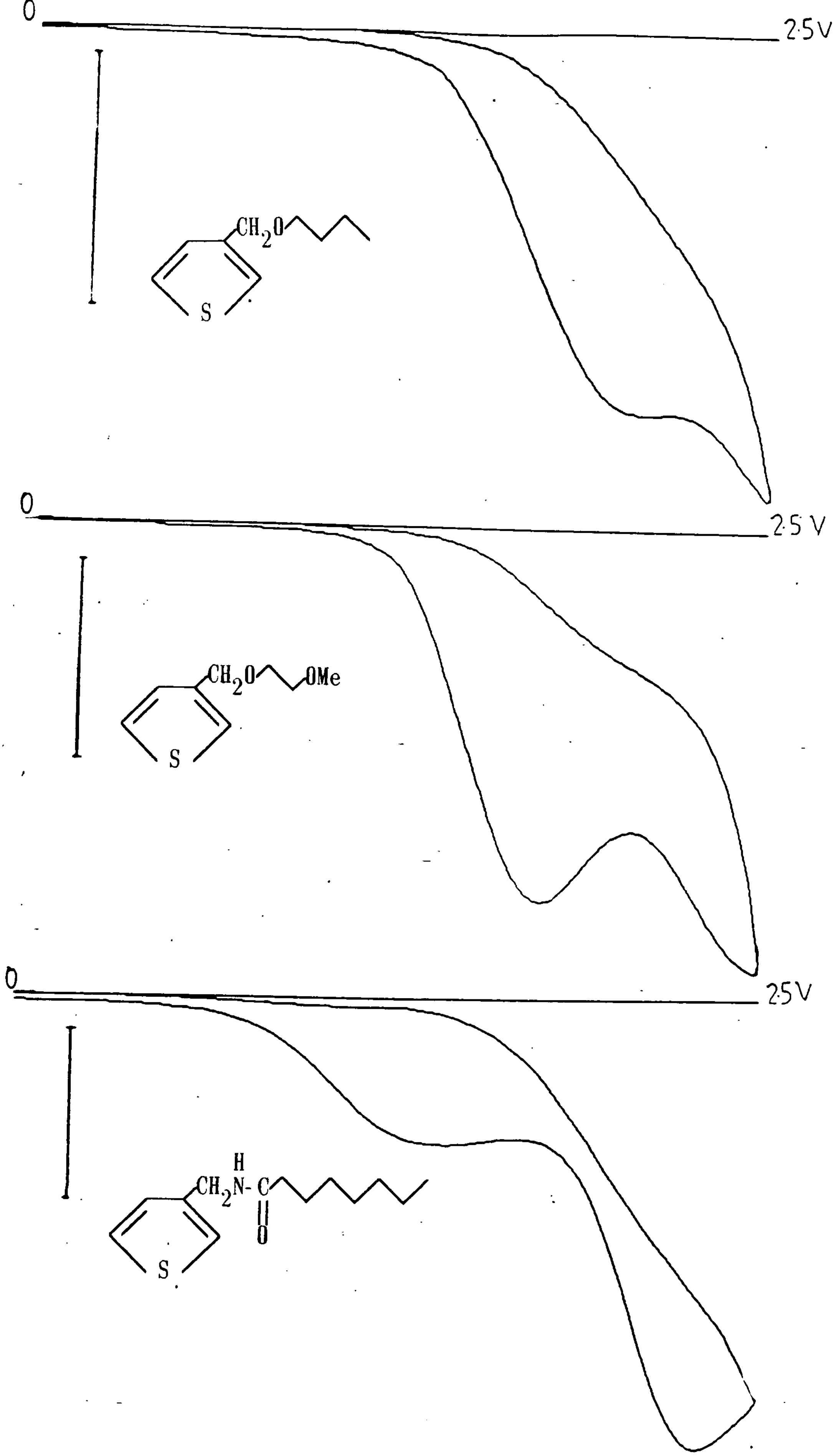
1-Methoxy-(3-thienylmethyl)-ethane-1,2-diol (45). Compound (44) (6.0g, 26 mmol) as a solution in acetone (15 ml) was added to a stirred solution of hydrochloric acid (1.0M, 45 ml). The mixture was allowed to reflux for two hours. The solvent was evaporated and the residue was dried by gentle warming (40 ^{o}C) under reduced pressure (0.01 mm/Hg). The residue was chromatographed on *gravity* silica (15 x 5 cm OD), eluting with ethyl acetate to afford (45) as a light brown viscous oil [3.2g, 65% based on (44)]. High Resolution MS: 188.0471900 (Theoretical: 188.05071672; IR (Thin Film): 3400, 2860, 1415, 1075, 785 cm^{-1}; EI m/e (Intensity%): 188(19,M^+), 113(12,$C_4H_3S.CH_2O^+$), 97(100,$C_4H_3S.CH_2^+$);

δH(CDCl$_3$): 3.46-3.63(5H,m), 4.51(2H,m), 6.96-7.00(1H,m), 7.06-7.13(1H, m), 7.24-7.27(1H,m); δC(CDCl$_3$): 63.6, 68.3, 70.6, 71.2, 122.9, 125.8, 127.1 and 138.7 ppm.

13-Methoxy-(3-thienylmethyl)-1,4,7,11-tetraoxacyclotetradecane (46).
Under an atmosphere of argon, lithium metal (32mg, 4.5 mmol) was added to t-butyl alcohol (45 ml). After reflux (1h), (45) (0.5g, 1.5 mmol) was added dropwise to the heterogeneous mixture, (324 mg, 1.5 mmol) was added followed by lithium bromide (264 mg, 3.0 mmol). The reaction mixture was boiled under reflux for 10 days with vigourous stirring. After the solvent had been removed, water (2 ml) was added to the residue and the mixture neutralised with hydrochloric acid (6 M). Extraction with dichloromethane (3 x 20 ml) gave crude (46) which was chromatographed on *flash* silica (8 x 3 cm O.D.) eluting with *(i)* dichloromethane to remove any unreacted starting materials and side-products and *(ii)* dichloromethane/methanol (9:1) to afford (46) as a viscous colourless oil [134 mg, 27% based on (45)]. High Resolution MS: 330.16181 (Theoretical: 330.15010); IR (Thin Film): 2920, 2850, 1355, 1120, 730 cm^{-1}; EI m/e (Intensity%): 330(7,M$^+$), 97(100,C$_4$H$_3$S.CH$_2^+$); δH(CDCl$_3$): 1.78(4H,m), 3.40-3.96(17H,m), 4.53(2H,s), 7.03-7.07(1H,m), 7.11-7.15(1H,m), 7.24-7.29(1H,m); δC(CDCl$_3$): 30.3, 65.6, 66.5, 66.9, 68.3, 69.7, 69.8, 70.7, 72.3, 77.6, 122.4, 125.6, 126.9 and 139.2 ppm.

6.3 CYCLIC VOLTAMMETRIC STUDY

The behaviour of the monomers presented in this thesis were examined systematically by cyclic voltammetry under a set of standard conditions. For each monomer (unless otherwise stated) these were carried out under argon in a one compartment cell with platinum working and counter-electrodes and a silver-silver chloride (SSC) reference electrode. Measurements were made with a BAS100 electrochemical analyser, scanning the potential range from 0 V to +2500 mV or +1200 mV to +1800-3000 mV as appropriate. For these electrochemical experiments, acetonitrile (Aldrich HPLC grade) was the solvent and was freshly distilled from calcium hydride. The supporting electrolyte was tetraethylammonium hexafluorophosphate (0.1M) which had previously been vacuum and oven dried (120 ^{0}C, 4h, 10^{-2} mm Hg). Monomer concentrations were typically 0.018 M. For each monomer, a series of scans were made, varying the scan rate from 50 to 400 mV s^{-1} and observing the initial scan only. In a second series of experiments, consecutive scans were observed at a fixed scan rate of either 50 or 100 mV s^{-1}. Single scans of monomers (at 100 mV s^{-1}), representative of their series, are presented overleaf to show typical results.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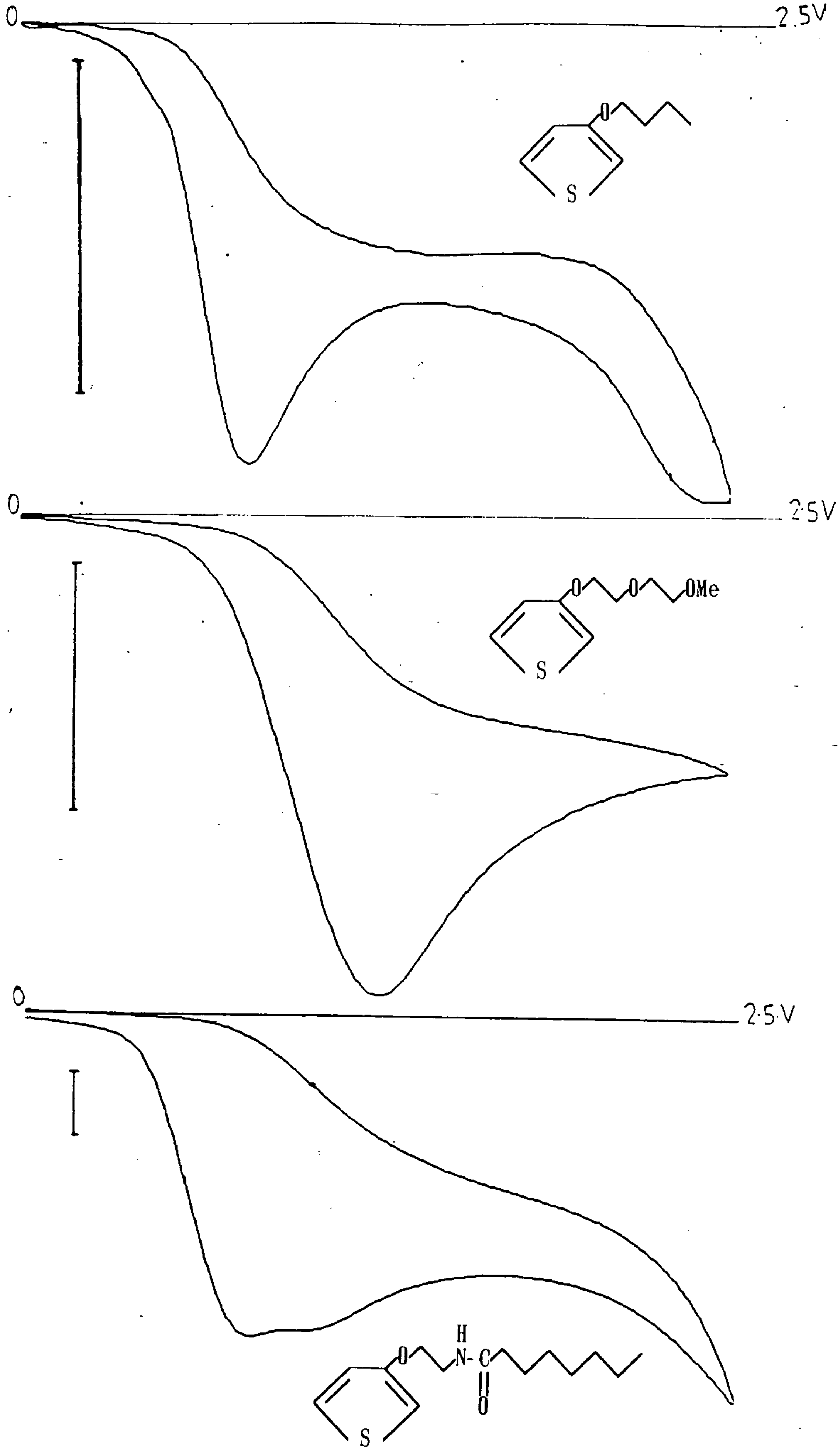
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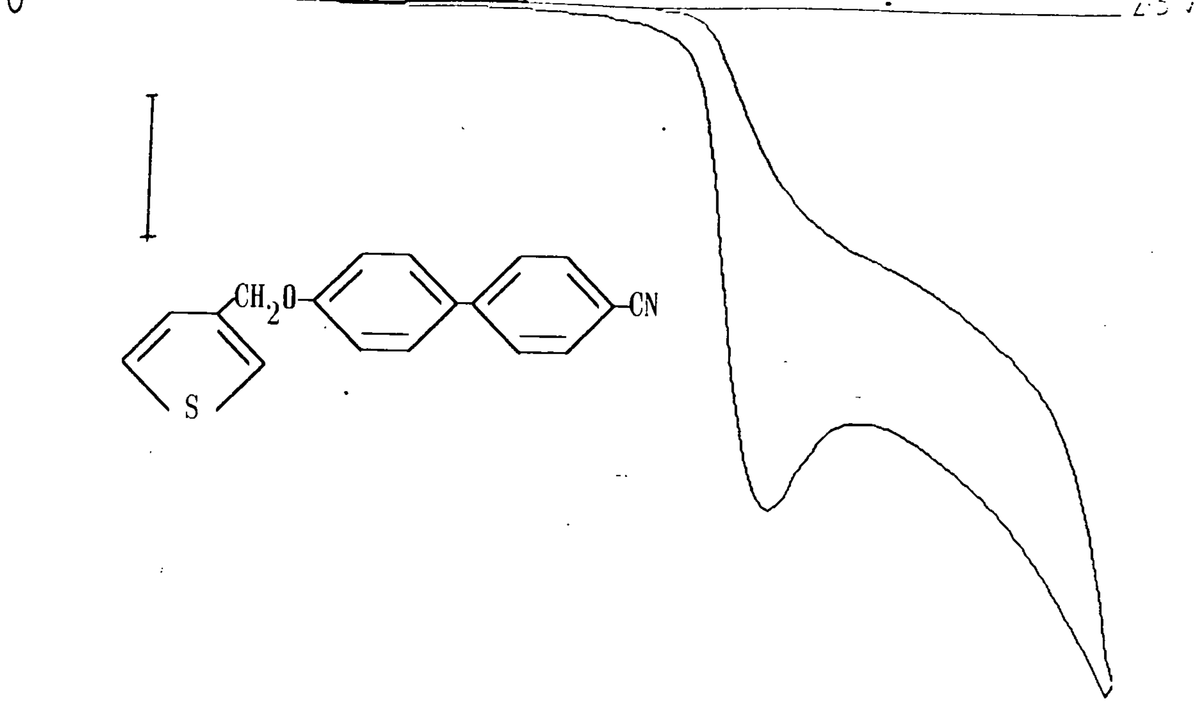
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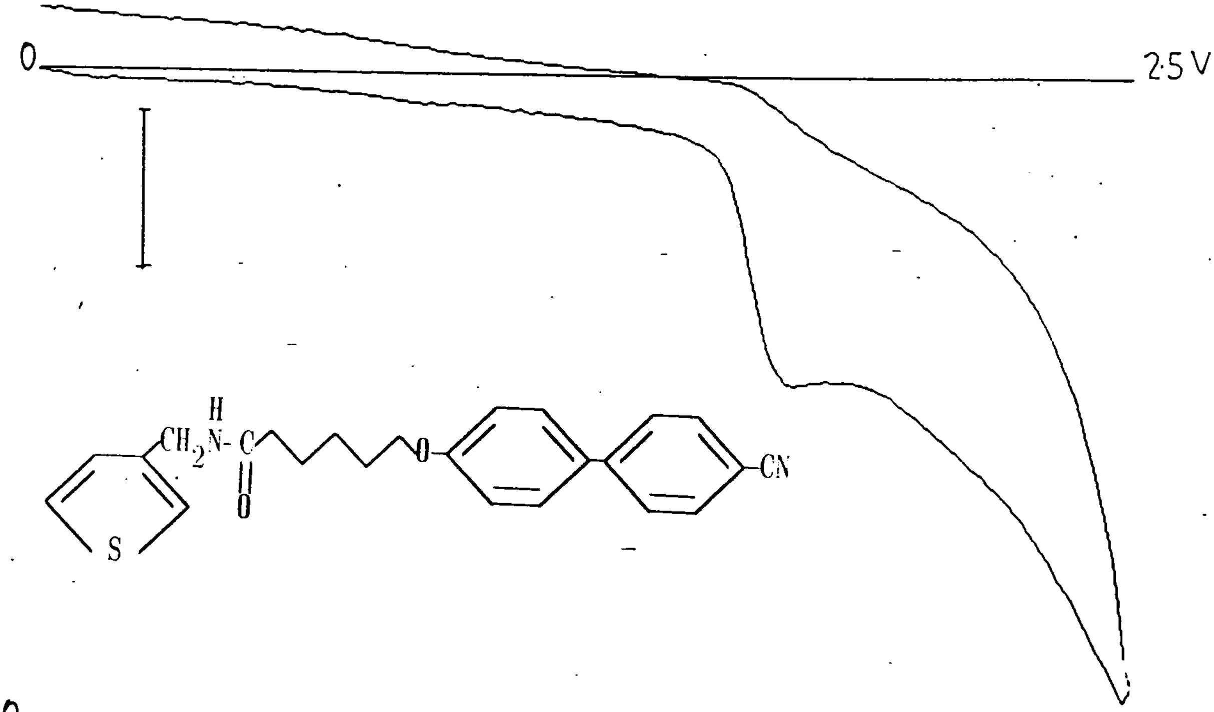
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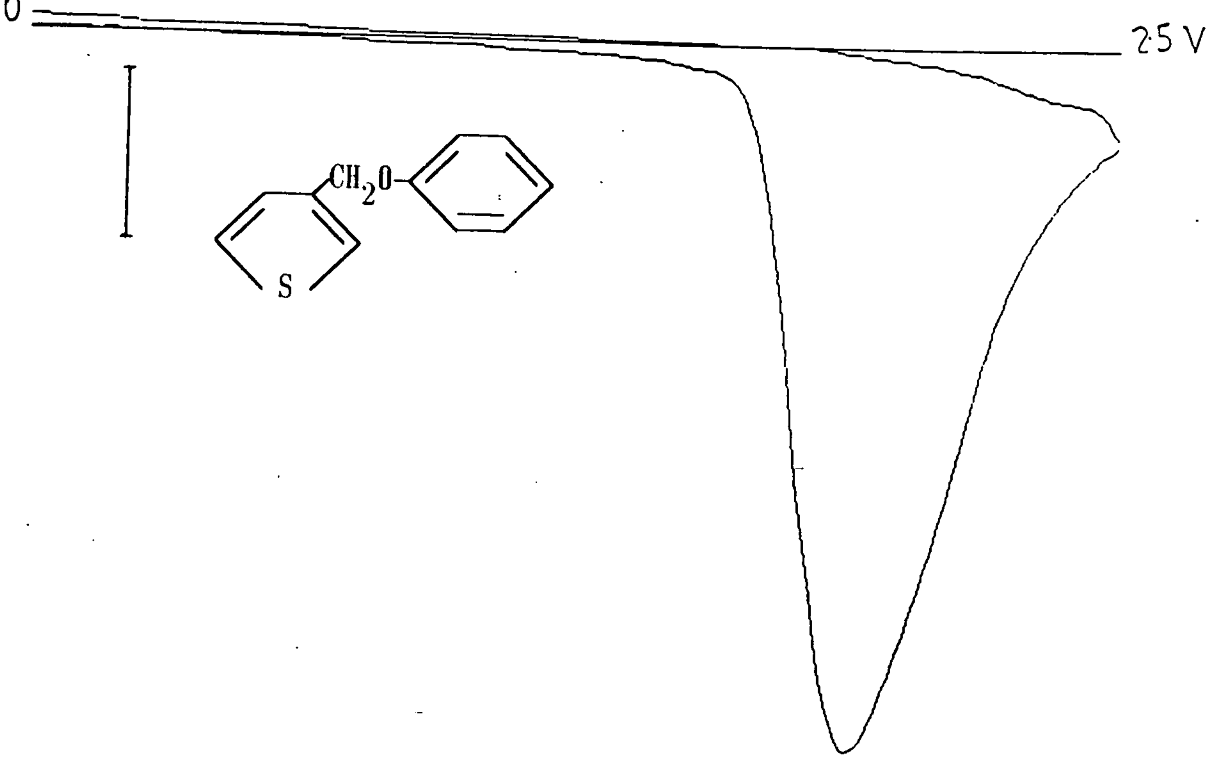
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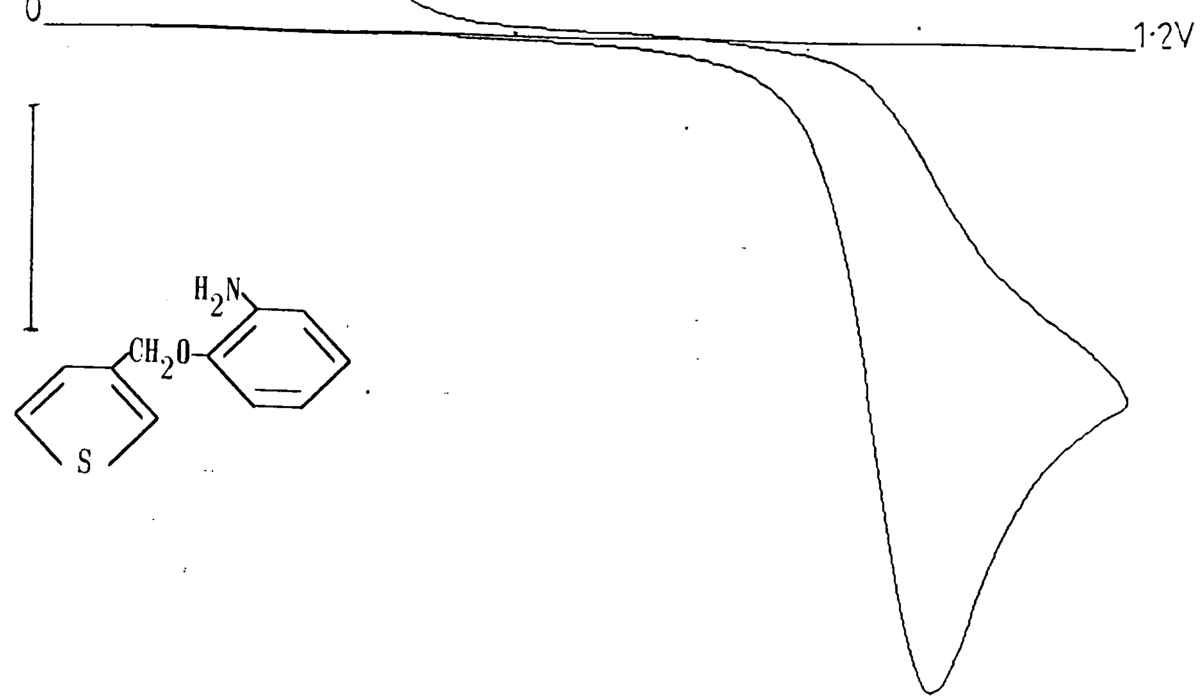
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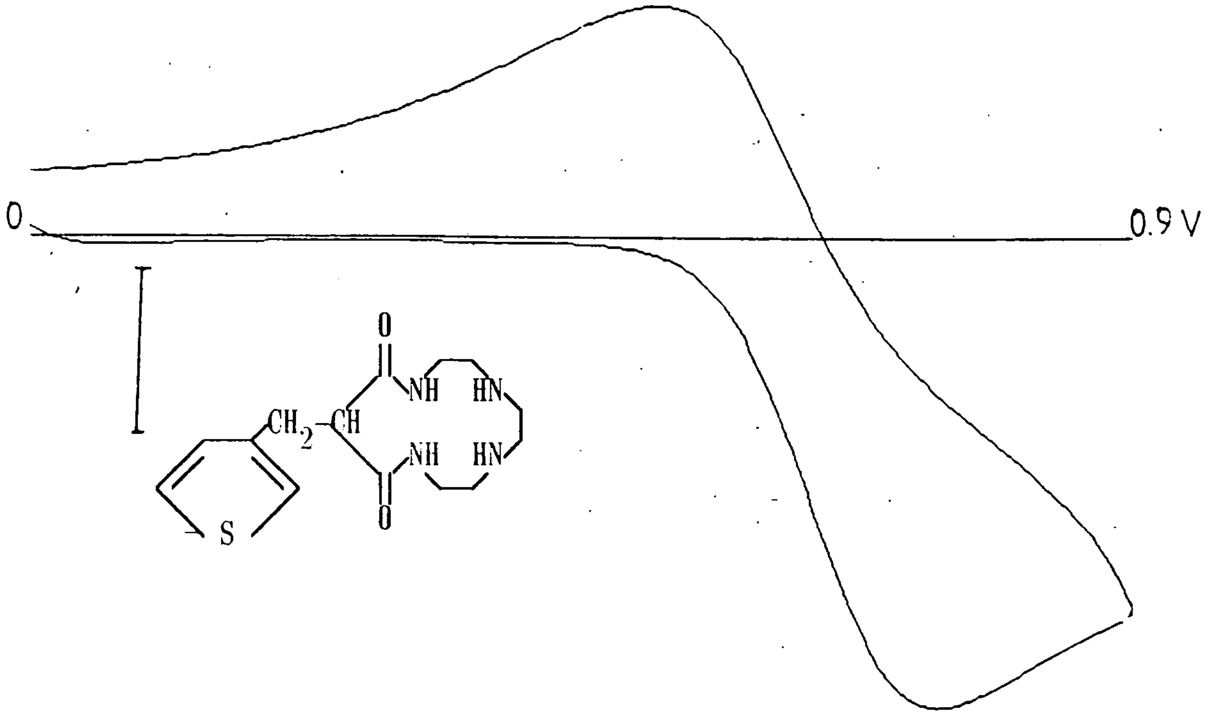
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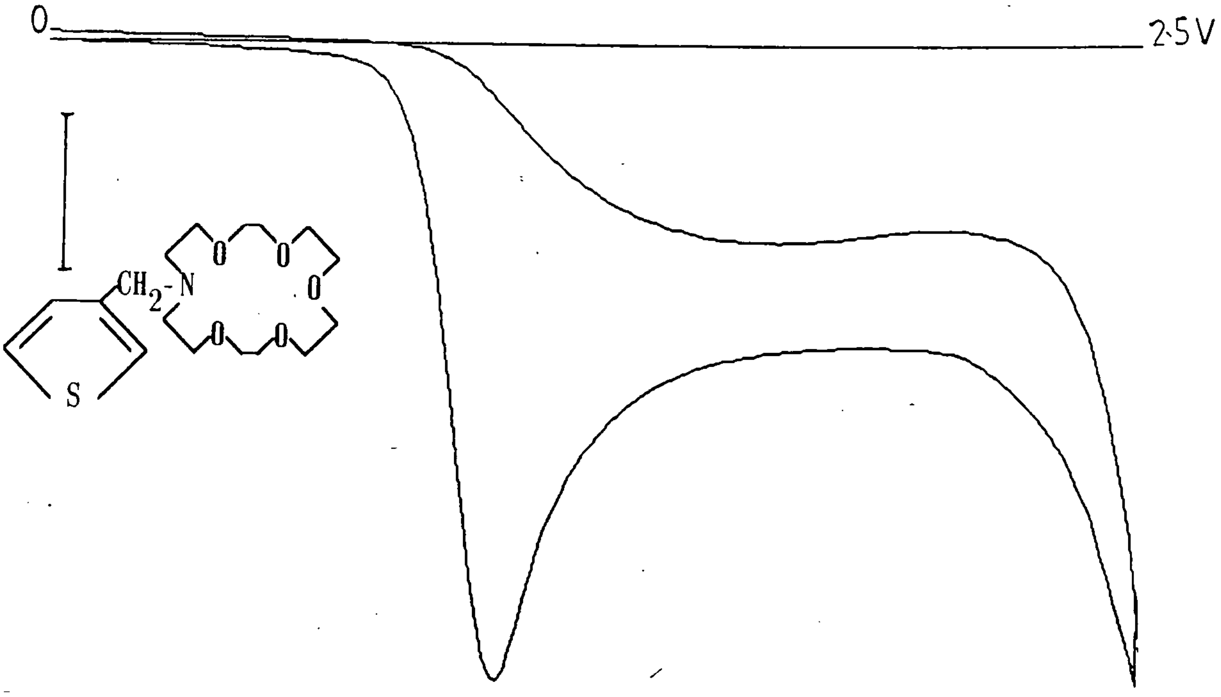
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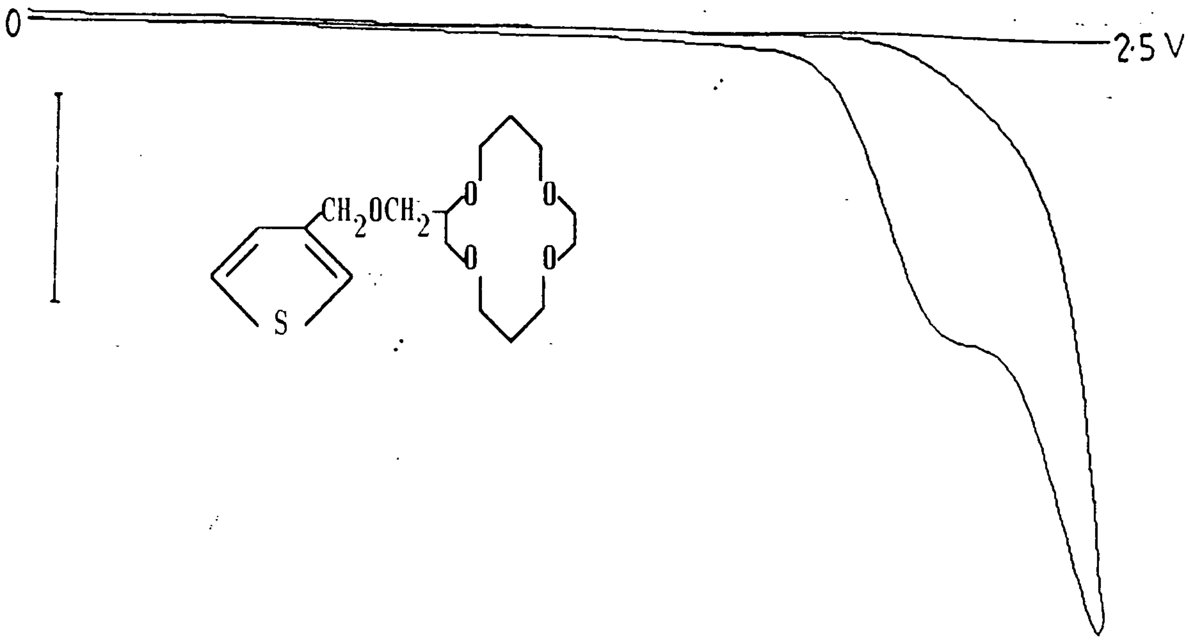
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APPENDICES

APPENDIX I

FLOW CELL EXPERIMENTS

Very recent work carried out in a flow cell has given further results on the selectivity of (46) (see Section 4.7.4).

IONOPHORE	SLOPE WRT PURE LiCl SOLUTION (mV/decade)	DETECTION LIMIT (a)		SELECTIVITY K(AB) log K (Li/Na)
		Pure LiCl Solution	Interference Ions	
Philips	61	$10^{-4.5}$	$10^{-2.15}$	-1.33
14-C4THIO	61	$10^{-5.2}$	$10^{-2.20}$	-1.46

Table A1.1 *Calibration of Electrodes Using a Fixed Interference Method in a Flow Cell (310K); (a) Values have been corrected for the effects of ionic strength and assume Na(1+) to be the primary interferent ion: they therefore represent minimum values for log K (Li/Na).*

As can be seen from the Table, although the Nernstian response is similar to the Philips (561-Li^+) electrode, a value for nearer the theoretical value has been obtained (Theoretical = 61.5 mV/decade at 37°C). The detection limit in pure LiCl solution is superior to that of the Philips electrode. In the presence of a series of competing ions [M^{n+}], where M^{n+} = Na(1+), K(1+), Ca(2+), Li(1+), the selectivity again appears to be better than the commercial ionophore.

APPENDIX II

COLLOQUIA, CONFERENCES AND PUBLICATIONS

COLLOQUIA AND CONFERENCES

The board of studies in Chemistry requires that each postgraduate research thesis contain an appendix listing:

(A) All research colloquia, research seminars and lectures arranged by the Department of Chemistry during the author's period of study.

(B) All research colloquia, research seminars and lectures arranged by the newly formed Centre for Molecular Electronics during the author's period of study.

(C) All research conferences attended and papers presented by the author during their period of study.

(D) Details of the postgraduate induction course.

(E) Publications.

APPENDIX IIA

RESEARCH COLLOQUIA, SEMINARS, LECTURES AND CONFERENCES ORGANISED BY THE DEPARTMENT OF CHEMISTRY DURING THE PERIOD: 1985-1986

* BARNARD, Dr. C.J.F. (Johnson Matthey Group) "Platinum Anti-Cancer Drug Development"	20th February 1986
BROWN, Dr. J.M. (University of Oxford) "Chelate Control in Homogeneous Catalysis"	12th March 1986
CLARK, Dr. B.A.J. (Kodak Ltd.) "Chemistry & Principles of Colour Photography"	28th November 1985
CLARK, Dr. J.H. (University of York) "Novel Fluoride Ion Reagents"	29th January 1986
* DAVIES, Dr. S.G. (University of Oxford) "Chirality Control and Molecular Recognition"	14th November 1985
DEWING, Dr. J. (U.M.I.S.T.) "Zeolites - Small Holes, Big Opportunities"	24th October 1985
ERTL, Prof. G. (University of Munich) "Heterogeneous Catalysis"	7th November 1985
GRIGG, Prof. R. (Queen"s University, Belfast) "Thermal Generation of 1,3-Dipoles"	13th February 1986
HARRIS, Prof. R.K. (University of Durham) "The Magic of Solid State NMR"	27th February 1986
HATHWAY, Dr. D. (University of Durham) "Herbicide Selectivity"	5th March 1986
* IDDON, Dr. B. (University of Salford) "The Magic of Chemistry"	6th March 1986
JACK, Prof. K.H. (University of Newcastle) "Chemistry of Si-Al-O-N Engineering Ceramics"	21st November 1985
LANGRIDGE-SMITH, Dr.P.R.R. (Edinburgh University) "Naked Metal Clusters - Synthesis, Characterisation and Chemistry"	14th May 1986
LEWIS, Prof. Sir Jack (University of Cambridge) "Some more Recent Aspects in the Cluster Chemistry of Ruthenium and Osmium Carbonyls"	23rd January 1986
* LUDMAN, Dr. C.J. (University of Durham) "Some Thermochemical Aspects of Explosions"	17th October 1985
MACBRIDE, Dr. J.A.H. (Sunderland Polytechnic) "A Heterocyclic Tour on a Distorted Tricycle - Biphenylene"	20th November 1985

O'DONNELL, Prof. M.J. (Indiana-Purdue University) "New Methodology for the Synthesis of Amino Acids"	5th November 1985
PARMAR, Dr. V.S. (University of Delhi) "Enzyme Assisted ERC Synthesis"	13th September 1985
* PHILLIPS, Dr. N.J. (Loughborough Univ.Technology) "Laser Holography"	30th January 1986
PROCTOR, Prof. G. (University of Salford) "Approaches to the Synthesis of some Natural Products"	19th February 1986
* SCHMUTZLER, Prof. R. (University of Braunschweig) "Mixed Valence Diphosphorus Compounds"	9th June 1986
* SCHRODER, Dr. M. (University of Edinburgh) "Studies on Macrocyclic Complexes"	5th March 1986
SHEPPARD, Prof. N. (University of East Anglia) "Vibrational and Spectroscopic Determinations of the Structures of Molecules Chemisorbed on Metal Surfaces"	15th January 1986
TEE, Prof. O.S. (Concordia University, Montreal) "Bromination of Phenols"	12th February 1986
TILL, Miss C. (University of Durham) "ESCA and Optical Emission Studies of the Plasma Polymerisation of Perfluoroaromatics"	26th February 1986
* TIMMS, Dr. P. (University of Bristol) "Some Chemistry of Fireworks"	31st October 1985
* WADDINGTON, Prof. D.J. (University of York) "Resources for the Chemistry Teacher"	28th November 1985
WHITTLETON, Dr. S.N. (University of Durham) "An Investigation of a Reaction Window"	30th October 1985
WILDE, Prof. R.E. (Texas Technical University) "Molecule Dynamic Processes from Vibrational Bandshapes"	23rd June 1986
YARWOOD, Dr. J. (University of Durham) "The Structure of Water in Liquid Crystals"	12th February 1986

DURING THE PERIOD: 1986-1987

* ALLEN, Prof. Sir G. (Unilever Research) "Biotechnology and the Future of the Chemical Industry"	13th November 1986
BARTSCH, Dr. B. (University of Sussex) "Low Co-ordinated Phosphorus Compounds"	6th May 1987

BLACKBURN, Dr. M. (University of Sheffield) "Phosphonates as Analogues of Biological Phosphate Esters"	27th May 1987
* BORDWELL, Prof. F.G.(Northeastern University,USA) "Carbon Anions, Radicals, Radical Anions and Radical Cations"	9th March 1987
CANNING, Dr. N.D.S. (University of Durham) "Surface Adsorption Studies of Relevance to Heterogeneous Ammonia Synthesis"	26th November 1986
CANNON, Dr. R.D. (University of East Anglia) "Electron Transfer in Polynuclear Complexes"	11th March 1987
CLEGG, Dr. W. (University of Newcastle-upon-Tyne) "Carboxylate Complexes of Zinc; Charting a Structural Jungle"	28th January 1987
* DÖPP, Prof. D. (University of Duisburg) "Cyclo-additions and Cyclo-reversions Involving Captodative Alkenes"	5th November 1986
DORFMÜLLER, Prof. T. (University of Bielefeld) "Rotational Dynamics in Liquids and Polymers"	8th December 1986
GOODGER, Dr. E.M. (Cranfield Inst.Technology) "Alternative Fuels for Transport"	12th March 1987
* GREENWOOD, Prof. N.N. (University of Leeds) "Glorious Gaffes in Chemistry"	16th October 1986
HARMER, Dr. M. (I.C.I. Chemicals & Polymer Group) "The Role of Organometallics in Advanced Materials"	7th May 1987
* HUBBERSTEY, Dr. P. (University of Nottingham) "Demonstration Lecture on Various Aspects of Alkali Metal Chemistry"	5th February 1987
HUDSON, Prof. R.F. (University of Kent) "Aspects of Organophosphorus Chemistry"	17th March 1987
HUDSON, Prof. R.F. (University of Kent) "Homolytic Rearrangements of Free Radical Stability"	18th March 1987
* JARMAN, Dr. M. (Institute of Cancer Research) "The Design of Anti Cancer Drugs"	19th February 1987
KRESPAN, Dr. C. (E.I. Dupont de Nemours) "Nickel(0) and Iron(0) as Reagents in Organofluorine Chemistry"	26th June 1987
KROTO, Prof. H.W. (University of Sussex) "Chemistry in Stars, between Stars and in the Laboratory"	23rd October 1986

* LEY, Prof. S.V. (Imperial College) "Fact and Fantasy in Organic Synthesis"	5th March 1987
MILLER, Dr. J. (Dupont Central Research, USA) "Molecular Ferromagnets; Chemistry and Physical Properties"	3rd December 1986
MILNE/CHRISTIE, Dr.A./Mr.S.(International Paints) "Chemical Serendipity: A Real Life Case Study"	20th November 1986
NEWMAN, Dr. R. (University of Oxford) "Change and Decay: A Carbon-13 CP/MAS NMR Study of humification and Coalification Processes"	4th March 1987
OTTEWILL, Prof. R.H. (University of Bristol) "Colloid Science a Challenging Subject"	22nd January 1987
PASYNKIEWICZ, Prof. S. (Technical Univ.,Warsaw) "Thermal Decomposition of Methyl Copper and its Reactions with Trialkylaluminium"	11th May 1987
* ROBERTS, Prof. S.M. (University of Exeter) "Synthesis of Novel Antiviral Agents"	24th June 1987
RODGERS, Dr. P.J. (I.C.I. Billingham) "Industrial Polymers from Bacteria"	12th February 1987
* SCROWSTON, Dr. R.M. (University of Hull) "From Myth and Magic to Modern Medicine"	6th November 1986
SHEPHERD, Dr. T. (University of Durham) "Pteridine Natural Products; Synthesis and Use in Chemotherapy"	11th February 1987
THOMSON, Prof. A. (University of East Anglia) "Metalloproteins and Magneto-optics"	4th February 1987
* WILLIAMS, Prof. R.L. (Metropolitan Police Forensic Science) "Science and Crime"	27th November 1987
WONG, Prof.E.H. (University of New Hampshire,USA) "Coordination Chemistry of P-O-P Ligands"	29th October 1986
WONG, Prof.E.H. (University of New Hampshire,USA) "Symmetrical Shapes from Molecules to Art and Nature"	17th February 1987

DURING THE PERIOD: 1987-1988

BIRCHALL, Prof. D. (I.C.I. Advanced Materials) "Environment Chemistry of Aluminium"	25th April 1988
* BORER, Dr. K. (University of Durham Industrial Research Laboratories) "The Brighton Bomb - (A Forensic Science View)"	18th February 1988

BOSSONS, L. (Durham Chemistry Teachers' Centre) "GCSE Practical Assessment"	16th March 1988
* BUTLER, Dr. A.R. (University of St.Andrews) "Chinese Alchemy"	5th November 1987
* CAIRNS-SMITH, Dr. A. (Glasgow University) "Clay Minerals and the Origin of Life"	28th January 1988
DAVIDSON, Dr. J. (Herriot-Watt University) "Metal Promoted Oligomerisation Reactions of Alkynes"	November 1987
GRAHAM, Prof. W.A.G. (University of Alberta, Canada) "Rhodium and Iridium Complexes in the Activation of Carbon-Hydrogen Bonds"	3rd March 1988
* GRAY, Prof. G.W. (University of Hull) "Liquid Crystals and their Applications"	22nd October 1987
HARTSHORN, Prof. M.P. (University of Canterbury, New Zealand) "Aspects of Ipso-Nitration"	7th April 1988
HOWARD, Dr. J. (I.C.I. Wilton) "Chemistry of Non-Equilibrium Processes"	3rd December 1987
JONES, Dr. M.E. (Durham Chemistry Teachers' Centre) "GCSE Chemistry Post-mortem"	29th June 1988
JONES, Dr. M.E. (Durham Chemistry Teachers' Centre) "GCE Chemistry A-Level Post-mortem"	6th July 1988
KOCH, Prof. H.F. (Ithaca College, U.S.A.) "Does the E2 Mechanism Occur in Solution"	7th March 1988
LACEY, Mr. (Durham Chemistry Teacher's Centre) "Double Award Science"	9th February 1988
* LUDMAN, Dr. C.J. (Durham University) "Explosives"	10th December 1987
* McDONALD, Dr. W.A. (I.C.I. Wilton) "Liquid Crystal Polymers"	11th May 1988
MAJORAL, Prof. J.-P. (Université Paul Sabatier) "Stabilisation by Complexation of Short-Lived Phosphorus Species"	8th June 1988
MAPLETOFT, Mrs. M. (Durham Chemistry Teachers' Centre) "Salters' Chemistry"	4th November 1987

NIETO DE CASTRO, Prof. C.A. (University of Lisbon and Imperial College) "Transport Properties of Non-Polar Fluids"	18th April 1988
* OLAH, Prof. G.A. (University of Southern California) "New Aspects of Hydrocarbon Chemistry"	29th June 1988
PALMER, Dr. F. (University of Nottingham) "Luminescence (Demonstration Lecture)"	21st January 1988
PINES, Prof. A. (University of California, Berkeley, U.S.A.) "Some Magnetic Moments"	28th April 1988
RICHARDSON, Dr. R. (University of Bristol) "X-Ray Diffraction from Spread Monolayers"	27th April 1988
ROBERTS, Mrs. E. (SATRO Officer for Sunderland) Talk - Durham Chemistry Teachers' Centre "Links between Industry and Schools"	13th April 1988
ROBINSON, Dr. J.A. (University of Southampton) "Aspects of Antibiotic Biosynthesis"	27th April 1988
* ROSE, van Mrs. S. (Geological Museum) "Chemistry of Volcanoes"	29th October 1987
SAMMES, Prof. P.G. (Smith, Kline and French) "Chemical Aspects of Drug Development"	19th December 1987
SEEBACH, Prof. D. (E.T.H. Zürich) "From Synthetic Methods to Mechanistic Insight"	12th November 1987
SODEAU, Dr. J. (University of East Anglia) Durham Chemistry Teachers's Centre: "Spray Cans, Smog and Society"	11th May 1988
SWART, Mr. R.M. (I.C.I.) "The Interaction of Chemicals with Lipid Bilayers"	16th December 1987
TURNER, Prof. J.J. (University of Nottingham) "Catching Organometallic Intermediates"	11th February 1988
* UNDERHILL, Prof. A. (University of Bangor) "Molecular Electronics"	25th February 1988
WILLIAMS, Dr. D.H. (University of Cambridge) "Molecular Recognition"	26th November 1987
* WINTER, Dr. M.J. (University of Sheffield) "Pyrotechnics (Demonstration Lecture)"	15th October 1987

*.- Indicates Colloquia attended by the author.

APPENDIX IIB

LECTURES AND SEMINARS ORGANISED BY THE CENTRE FOR MOLECULAR ELECTRONICS 1988

* FEAST, Professor W.J. (Chemistry) "Conducting Organic Polymers"	22nd January 1988
PETTY, Dr. M.C. (SEAS) "Langmuir-Blodgett Films"	22nd January 1988
YARWOOD, Dr. J. (Chemistry) "IR/Raman Techniques"	5th February 1988
BANISTER, Dr. A.J. (Chemistry) "Inorganic Polymers"	5th February 1988
MURPHY, Dr. D.J. (Botany) "Biological Membranes"	26th February 1988
MARS, Professor P. (SEAS) "Neural Networks"	26th February 1988
* BRYCE, Dr. M.R. (Chemistry) "Charge Transfer Complexes"	11th March 1988
PARKER, Dr. D. (Chemistry) "Electropolymerisation"	11th March 1988
PURVIS, Dr. A. (SEAS) "Liquid Crystal Devices"	18th March 1988
ABRAM, Dr. R.A. (SEAS) "Theoretical Considerations"	18th March 1988

* - Indicates Colloquia attended by the author.

APPENDIX IIC

CONFERENCES ATTENDED

1.	Graduate Symposium, **UNIVERSITY OF DURHAM**	16th April 1986
2.	Graduate Symposium, **UNIVERSITY OF DURHAM**	27th March 1987
3.	Royal Society of Chemistry, Dalton Division "Inorganic Electrochemistry Workshop" **UNIVERSITY OF SUSSEX**	29th March - 1st April 1988
4.	Royal Society of Chemistry, Perkin Division North East Regional Meeting **UNIVERSITY OF NEWCASTLE UPON TYNE**	15th September 1987
5.	University of Durham Industrial Research Laboratories "Molecular Electronics" **UNIVERSITY OF DURHAM**	29th - 30th September 1987
6.	Royal Society of Chemistry, Annual Chemical Congress. **UNIVERSITY OF KENT AT CANTERBURY**	12th - 15th April 1988
7.	Graduate Symposium, **UNIVERSITY OF DURHAM**	19th April 1988

APPENDIX IID

FIRST YEAR INDUCTION COURSE
OCTOBER 1985

This course consists of a series of one hour lectures in the services available in the department.

1. Departmental Organisation.
2. Safety Matters.
3. Electrical appliances and infrared spectroscopy.
4. Chromatography and Microanalysis.
5. Atomic absoption and inorganic analysis.
6. Library facilities.
7. Mass spectroscopy.
8. Nuclear Magnetic Resonance.
9. Glass blowing techniques.

APPENDIX IIE

PUBLICATIONS

1. Bryce, M.R., Chissel, A.D., Kathirgamanathan, P., Parker, D. and Smith, N.R.M., J.CHEM.SOC., CHEM. COMMUN., 466 (1987)
2. Bryce, M.R., Chissel, A.D., Kathirgamanathan, P., Parker, D. and Smith, N.R.M., EUROPEAN PATENT, E.P. 87306133.7 (1987)
3. Bryce, M.R., Chissel, A.D., Kathirgamanathan, P., Parker, D. and Smith, N.R.M., SYNTH.MET. 26, 153 (1988)
4. Bryce, M.R., Chissel, A.D., Kathirgamanathan, P., Parker, D. and Smith, N.R.M., UNITED KINGDOM PATENT, GB 8813063 (1988)
5. Bryce, M.R., Chissel, A.D., Kathirgamanathan, P., Parker, D. and Smith, N.R.M., UNITED KINGDOM PATENT