TRANSITION METAL ION COORDINATION IN HYDROPHILIC POLYMER MEMBRANES

ANDREW JOHN HALL

Doctor of Philosophy

THE UNIVERSITY OF ASTON IN BIRMINGHAM

September 1994

To my family

THE UNIVERSITY OF ASTON IN BIRMINGHAM

TRANSITION METAL ION COORDINATION IN HYDROPHILIC POLYMER MEMBRANES

Andrew J. Hall

Submitted for the Degree
of Doctor of Philosophy

September 1994

SUMMARY

The research described within this thesis is concerned with the investigation of transition metal ion complexation within hydrophilic copolymer membranes. The membranes are copolymers of 4-methyl-4'-vinyl-2,2'-bipyridine, the 2-hydroxyethyl ester of 4,4'-dicarboxy-2,2'-bipyridine & *bis*-(5-vinylsalicylidene)ethylenediamine with 2-hydroxyethyl methacrylate. The effect of the polymer matrix on the formation and properties of transition metal ion complexes has been studied, specifically Cr(III) & Fe(II) salts for the bipyridyl- based copolymer membranes and Co(II), Ni(II) & Cu(II) salts for the salenH_2-based copolymer membranes. The concomitant effect of complex formation on the properties of the polymer matrix have also been studied, e.g. on mechanical strength.

A detailed body of work into the kinetics and thermodynamics for the formation of Cu(II) complexes in the salenH_2- based copolymer membranes has been performed. The rate of complex formation is found to be very slow while the value of K for the equilibrium of complex formation is found to be unexpectedly small and shows a slight anion dependance. These phenomena are explained in terms of the effects of the heterogeneous phase provided by the polymer matrix.

The transport of Cr(III) ions across uncomplexed and Cr(III)-pre-complexed bipyridyl-based membranes has been studied. In both cases, no Cr(III) coordination occurs within the time-scale of an experiment. Pre-complexation of the membranes does not lead to a change in the rate of permeation of Cr(III) ions. The transport of Co(II), Ni(II) & Cu(II) ions across salenH_2- based membranes shows that there is no detectable lag-time in transport of the ions, despite independent evidence that complex formation within the membranes does occur.

Finally, the synthesis of a number of functionalised ligands is described. Although they were found to be non-polymerisable by the methods employed in this research, they remain interesting ligands which provide a starting point for further functionalisation.

Keywords : **Hydrogel, Complexing Membrane, 2,2'-Bipyridine, SalenH_2**

ACKNOWLEDGEMENTS

First and foremost, I must thank Dr. J.D.Miller for all his massive support, advice, encouragement and enthusiasm over the entire course of this research. It has been a great pleasure to work with him.

I must thank Dr. A.W.P.Jarvie and Dr.C.B.St.Pourcain for their many suggestions regarding organic synthesis and to the latter for also being great to have around the laboratory. Dr.M.C.Perry is to be thanked for the high resolution N.M.R. spectra quoted in this thesis, especially for the COSY, NOESY and ^{15}N spectoscopy that he undertook on my behalf. Thanks are also extended to the other members of staff within the department. For the tensometric studies presented in this thesis I must thank Fiona Lydon, Karen French and James Ma. Large thanks go to Mike Houghton and Denise Ingram for the many extended loans of equipment that they allowed me to have.

S.E.R.C. are to be thanked for their financial support, without which this research would not have been possible.

And now we get to the people who have helped me keep body and soul together for the last four years. Without them, life would have been a lot quieter, but nowhere near as worthwhile.

At the top of this list is Mark Smith, possibly the best friend that a person could ask for. Need I say anything further? Following on are the many occupants of labs 208 & 209, for their warmth, humour and insanity - Babs, Dav, Phil, Monali, Luke, Val, Fred, Karine, Mike, Sue and Robert. Next come the Tighe group for their help with certain aspects of hydrogel polymer chemistry, and to Aisling in particular for her friendship.

Outside of the chemistry, there are a large number of people to thank for just being around to help - Caroline Buckle, Thomas Jackson, Helen Conchie and Liane Davies deserve a special mention. Andy Toft deserves a big mention for managing to persuade me that public musical performance wasn't such a horrible idea and that much fun could be had. This body of work may have been written a little more quickly had he not been quite so persuasive, but I would have missed out on a great deal of enjoyment.

I guess that leaves Helen Savage, another delaying factor, but one that I wouldn't change for the world.

LIST OF CONTENTS

CHAPTER ONE :

CHAPTER TWO :

CHAPTER THREE :

THE MECHANICAL PROPERTIES OF HYDROGEL POLYMER MEMBRANES CONTAINING PHYSICAL AND COORDINATIVE CROSS-LINKS 72

Page

LIST OF TABLES

LIST OF FIGURES

Page

Figures 1.1, 1.6, 1.7, 2.6, 2.7 and 5.1 have been reproduced, with permission, from reference 21, while Figure 2.4 has been reproduced, with permission from reference 36.

LIST OF ABBREVIATIONS

HEMA	Hydroxyethyl Methacylate
EDMA	Ethylene Dimethacrylate
GMA	Glycidyl Methacrylate
PHEMA	Poly(Hydroxyethyl Methacrylate)
EWC	Equilibrium Water Content
W_h	Weight of Hydrated Hydrogel Membrane
W_d	Weight of Dehydrated Hydrogel Membrane
bipy	2,2'-Bipyridine
salenH_2	*Bis*(salicylidene)ethylenediamine
VSAL	5-Vinylsalicylaldehyde
DVSALEN	*Bis*(5-Vinylsalicylidene)ethylenediamine
MVSALEN	(N-Salicylidene-N'-5-Vinylsalicylidene)ethylenediamine
MF	Microfiltration
UF	Ultrafiltration
MWCO	Molecular Weight Cut-Off
RO	Reverse Osmosis
J	Flux per unit area
D	Diffusivity
NMR	Nuclear Magnetic Resonance Spectroscopy
VBPY	4-Methyl-4'-Vinyl-2,2'-Bipyridine
mp	Melting Point
DHBPY	DiHEMA Ester of 4,4'-Dicarboxy-2,2'-Bipyridine
bp	Boiling Point
AIBN	Azo-*bis*-isobutyronitrile
EGDM	Ethylene Glycol Dimethacrylate
TM	Transition Metal
d	Optical Density

I_o	Intensity of Incident Light
I	Intensity of Emergent Light
ε	Molar Absorption Coefficient
c	Concentration
l	Path Length
UV	Ultra-Violet
σ	Tensile Strength
E	Young's Modulus
ε_b	Elongation to Break
$acac^-$	Acetyl Acetate
A_{inf}	Observed Maximum Absorbance
K_a	Overall Equilibrium Constant for Complex Formation
k_1	Rate Constant for Complex Formation
k_{-1}	Rate Constant for Complex Dissociation
t	time (in minutes)
K_b	Equilibium Constant Describing the Partition of Copper(II) Ions between the Aqueous Phase and the Imbibed Water in the Copolymer Membranes
K_c	Equilibrium Constant Describing the Partition of Copper(II) Ions between the Imbibed and Non-Freezing Water in the Copolymer Membranes
K_d	Equilibrium Constant Describing Ligand Deprotonation
K_e	Equilibrium Constant Describing Reorientation of the Ligand from "Rest" to "Available" States
K_f	Equlilibrium Constant Describing the Interaction between Copper(II) Ions in the Freezing Water of the Copolymer and the Ligand in its "Available State
CCMC	Charge-Coupled Mobile Carrier
TOA	Trioctylamine

EDTA	Ethylenediamine Tetraacetic Acid
P_c	Permeability Coefficient
dm/dt	Rate at which moles of permeant pass across Membrane Aperture
L	Membrane Thickness
A	Cross-Sectional Area of Membrane Aperture
C	Concentration of Source Solution
S_m	Partition Coefficient
r^c	Crystal Radius
r^s	Stoke's Radius
r^h	Hydrodynamic Radius
BUBPY	4-Butenyl-4'-Methyl-2,2'-Bipyridine
DABPY	DiAllyl Ester of 4,4'-Dicarboxy-2,2'-Bipyridine
DASALEN	*Bis*(3-Allylsalicylidene)ethylenediamine
Ni[CR]	2,12-Dimethyl-3,7,11,17-Tetraaza*bicyclo*(11.3.1)Heptadeca-1(17),2,11,13,15-Pentaene-Nickel(II)
COSY	Correlation Spectroscopy
NOESY	Nuclear Overhauser Effect Spectroscopy

CHAPTER ONE

INTRODUCTION

1. 1 Introduction

Interest in metal-containing polymeric systems has increased rapidly over the last thirty years. While they have been used primarily as supported catalysts, with virtually every known catalyst having been immobilised on some kind of polymer support, they have found enormously wide-ranging applications from anti-tumour treatment to solar energy conversion.[1-4]. In the case of some metallo-enzymes, the reactivity of the metal complex active site is known to be controlled by the conformation of the macromolecular protein chain. This illustrates the extreme importance of the polymer-metal interactions within these systems. More recently, metal-containing polymers have been used as pre-heat shield targets for internal confinement nuclear fusion[5,6,7].

Traditionally, polymer chemists have confined their interests to the preparation of polymers containing the elements C, H, N, O, S, P, Cl and Br. As the number of readily available metals is well over forty, it is hardly surprising that research into metal-containing polymers was eventually initiated, beginning in the early 1960s with the polymerisation of vinylic transition metal complexes, e.g. ferrocene derivatives[8]. The potential for metal-containing polymers is enormous, limited only by the need for synthetic routes to polymerisable ligands.

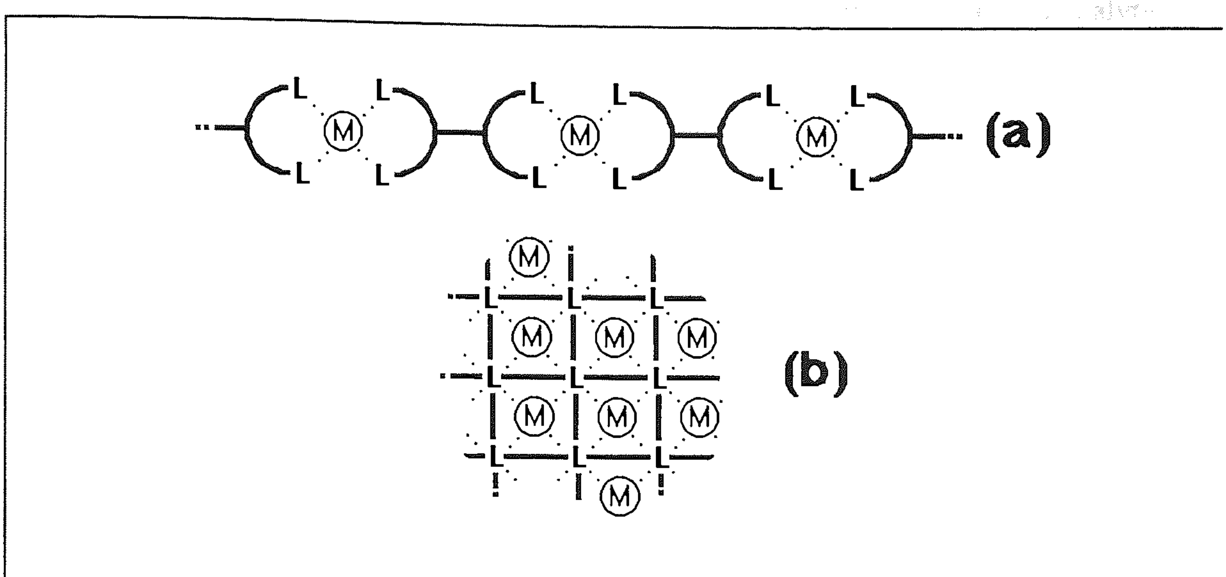
While classical inorganic polymers, such as polymeric sulphur, selenium and silica are well documented[9], polymers where the metal is complexed to organic moieties offer a far broader range of traditional synthetic procedures. Also, more manageable products may be obtained. There are two methods by which we may achieve the synthesis of such polymers. Firstly, we may derivatise preformed polymers using suitable ligands or complexes. For example, a great deal of work has centred upon the use of chloromethylated poly(styrene) as the polymer matrix, ligands being appended to the polymer *via* reaction with the chloromethyl function. The second option is the derivatisation of ligands or complexes, such that they may be homo- or co- polymerised.

The latter option allows a more precise knowledge of both the amount of the organometallic function within the polymer and its position within the system.

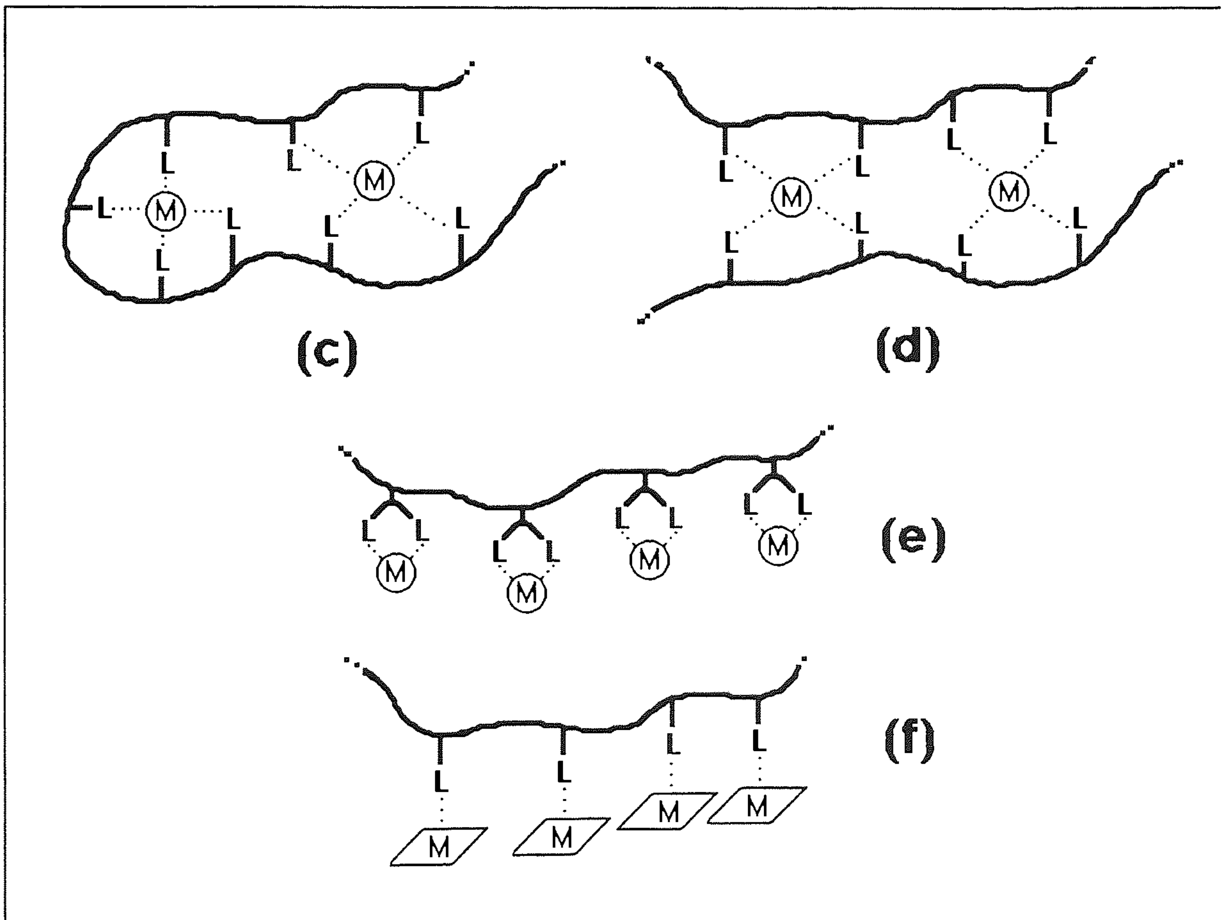
A convenient summary of polymer types is provided by a combination of the classification schemes of Tsuchida *et al.*[10] and Hodgkin[11] (see Figure 1.1). When a metal ion is complexed by bifunctional ligands, the formation of a polymer in which the metal ion is an integral part of the polymer backbone may be formed (Figure 1.1(a)). This complexation step is analogous to a condensation polymerisation, and has led to such products being labelled 'polycondensation coordination polymers'. 'Network-coordinated polymers' result from reaction between functional groups on the ligand, made possible by a *template-effect* induced by coordination to a metal ion (Figure 1.1(b)). A classic example of such polymers are the poly(metallo-phthalocyanine) chelated-type structures.

The other broad class of chelating polymer is that in which the ligands are present as pendant groups along the length of the polymer backbone (Figure 1.1(c)-(f)). Ion-exchange resins are included in this class of polymer. In these polymers, the coordinated metal may be removed from the polymer, leaving the macromolecular structure intact. Thus, the polymeric ligand is regenerated. Complexation of a metal ion may involve a number of ligands, either from the same chain, to give an intramolecular bridge (Figure 1.1(c)), or from different chains to produce intermolecular bridging structures (Figure 1.1(d)), as long as the valency of the metal will permit the further coordination. If the pendant ligand is polydentate in nature (Figure 1.1(e)), chelation to a metal will produce complexes of high stability. In this study, the polymers produced fall into the categories described by Figure 1.1(c)-(e). The final type of chelating polymer is produced from the coordination of metal ions or complexes with only one labile position by monodentate pendant ligands (Figure 1.1(f)). Enhanced solubility often results from the absence of bridging structures and the coordination structure within the polymer is very clear.

Figure 1.1 Classes of Metal-Containing Polymers



Chain-Linked by Metal Ion Complexation



Chelate-Forming Type

Chelating agents are used in a wide range of applications including the separation of metal ions by ion-exchange materials[12-14], as medicinal therapeutic agents[15,16], and in analytical chemistry[17]. Such uses have drawn attention to the need to design ligands to selectively complex metal ions in solution[18]. Donor atoms may be selected for specific purposes, with reference to Pearson's hard and soft acid and base principle[19]. Also, the pioneering work of Lehn and others[20] on molecular architecture has lead to the design of ligands that are 'tailor-made' for a particular metal ion.

Such knowledge, combined with the polymer technology at Aston, was used by Lewis[21] in the design of hydrophilic copolymers capable of complexing to transition metals in an aqueous environment. His use of pyridine-based ligands produced polymers which can interact reversibly with transition metal ions (hence the use of pyridine-based ligands in many commercial ion-exchange resins), while his use of bipyridine- based ligands lead to polymers where the coordination step was, although not irreversible, very slow in its completion. This effectively irreversible coordination step produced new polymers due to coordinative cross-linking.

It was the author's aim, in carrying out the work described here, to extend this previous study on transition metal ion complexation in hydrophilic polymers by both the use of other ligand systems and the examination of the interaction of different metal ions with the bipyridine-based polymers.

1. 2 Hydrogel Polymers

The replacement of the more traditional hydrophobic supports, such as poly(styrene), by hydrophilic porous polymers as polymeric matrices for ion-exchange materials has gathered pace in recent years. Copolymers of hydroxyethyl methacrylate/ethylene dimethacrylate (HEMA-EDMA), known as SPHERON, have been used to obtain sorbents with salicylic acid[22,23], thiol[24] and 8-hydroxyquinoline groupings[25-28]. Also, glycidyl methacrylate/ethylene dimethacrylate (GMA-EDMA) copolymers with appended ethylenediamine, iminodiacetate and mercapto groups have been used as materials for metal ion separations[29,30]. The attainment of equilibrium during sorption with such materials is very rapid due to their hydrophilicity, large internal surface area and high degree of porosity. The ability of these materials to swell in polar solvents has been exploited by their use as matrices for a series of immobilised rhodium hydrogenation catalysts[31,32].

At Aston, exhaustive research into hydrophilic polymers has been carried out by the Speciality Materials Research Group.

The term hydrogel is a generic term for the family of synthetic polymers in which the matrix swells, but does not dissolve, in water. In this study, copolymers of 2-hydroxyethyl methacrylate (HEMA), as employed in SPHERON sorbents, were used. Such materials have been well characterised by the group[33-35] and the monomer is readily available. It has been proven that the interstitial water present in the gel provides a medium for the transport of species through the polymer matrix and for the coordination of metal ions to ligands immobilised on the polymer backbone[21,36]. Copolymers in the form of membranes, prepared by free-radical bulk polymerisation, were employed in my investigation. This form ensured both reproducibility in the results of both transport and coordination studies in the ligand-modified systems, and also allowed a direct comparison with previous studies[21,35,36].

It is the chemical components of poly(HEMA), PHEMA, that enable it to interact with water. This is achieved through hydrogen-bonding by the hydroxyl groups and other polar functions on the chain. The imbibed water in this system can be thought of as ranging between two extremes[37]. Close to the polymer backbone, water is intimately associated with the polymer due to the action of the polar functional groups. This water is tightly bound and is referred to as 'bound' or 'non-freezing' water. Further away from the backbone, as the structuring effects of the polar groups diminish, the water is more mobile. This water, in the bulk interstitial spaces of the gel, is termed 'freezing' water.

When a hydrogel is left to reach equilibrium in water, it absorbs a specific amount of water. The equilibrium water content (EWC) of the gel is the ratio of the weight of water in the gel to the weight of the gel at hydration, given by equation 1.1,

$$\mathbf{EWC} = (\{\mathbf{W_h - W_d}\}/\mathbf{W_h}) \times \mathbf{100} \qquad \text{Equation 1.1}$$

where W_h is the weight of the hydrated membrane and W_d is the weight of the dehydrated membrane. The EWC is a convenient measure of an extremely important feature, as the amount of imbibed water influences many of the gel's properties, such as the mechanical and transport properties.

In swollen PHEMA membranes, typically around 40% of the polymer weight is due to imbibed water. This bulk water provides a medium for the diffusion of metal ions into the polymer matrix. The subsequent coordination with the appended ligands in the chelating membrane will then take place in what is still an essentially aqueous environment. This should allow direct comparison with the more traditional solution studies of coordination chemistry , which have generally been performed in polar environments. Previous studies[38,39] have shown that, in chelating polymer systems, the rate may be determined either by diffusion, by chemical reaction, or a by combination of both these processes. This will obviously depend upon the properties of the polymer, metal ion, nature of the ligand and sorption conditions.

1. 3 The Ligands

The aim of this research was to investigate both the complexation of metal ions by chelating polymer systems and the way in which the immobilised ligands affected the transport of metal ions across the chelating hydrogel membranes. Following the work of Lewis[21], derivatives of the ligand 2,2'-bipyridine (bipy) were employed in further studies. In order to extend the work, ligands based on *bis*(salicylidene)ethylenediamine, usually given the trivial name salenH$_2$, were also prepared. Routes to the functionalisation of these ligands have been reported in the literature, and so the preparation of ligands possessing a vinyl function, for subsequent copolymerisation with HEMA, is possible.

1. 3. 1 2,2'-Bipyridine

The chelating ligand, 2,2'-bipyridine (bipy, Figure 1.2), its derivatives and its structural relatives (1.10-phenanthroline and 2,2',6',2''-terpyridine), show great versatility in complexing a large number of metal ions[40-43].

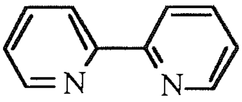


Figure 1.2 Structure of 2,2'-Bipyridine

The conjugated bidentate ligand, abbreviated to bipy, achieves coordination to metal ions *via* the two basic nitrogen atoms in the heterocyclic rings. These function as effective π-acceptors in back-bonding, as can be seen in the resonance structures in Figure 1.3.

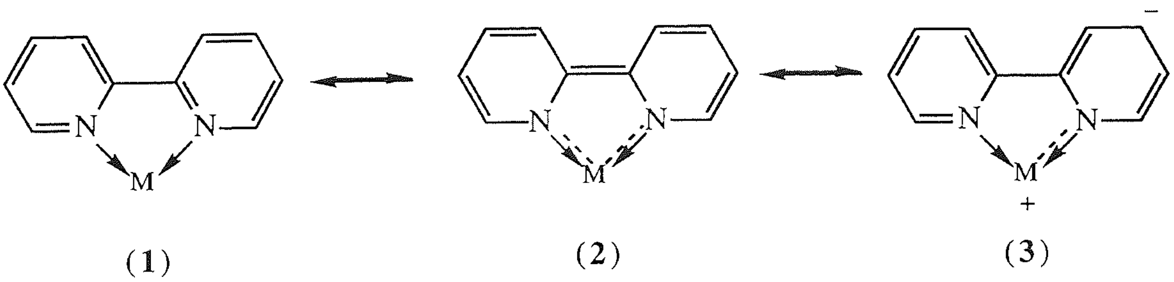


Figure 1.3 Bonding in 2,2'-Bipyridine Complexes

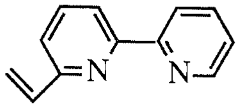
It is argued that the diimine structure (**1**) is crucial. Diimine itself has been isolated, although only as a coordinated ligand. However, in addition, ten dipolar structures such as (**3**) may be drawn, indicating that negative charge, transferred to the ligand in synergic interactions, is spread around all ten carbon atoms. However, in all these structures, aromaticity in either or both the heterocyclic rings is destroyed. Thus, the delocalisation of the electrons on the metal ion can only occur at the expense of the delocalisation in the rings.

Amongst other properties, it is the excellent metal ion binding capacities, the ability to stabilise unusual oxidation states and the potential to form complexes of versatile photoactivity which make this ligand desirable for immobilisation on a polymer backbone.

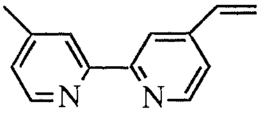
A vast amount of work concerning the immobilisation of bipy as a pendant group on a poly(styrene) matrix has been reported. The subsequent reaction of such polymers with ions of metals such as palladium[44-46] and tungsten[47] has produced a series of polymer-bound catalysts for hydrogenation reactions[48-51]. Bipy derivatives have also been incorporated directly into the polymer backbone, e.g. the diaminobipyridine-TDI polymers of Neckers *et al.*[52,53] and the dicarboxybipyridine-based polyesters of Miller and Morton[54].

The predominant method for obtaining polymers with pendant bipy groups is the direct homo- or co- polymerisation of a vinyl-functionalised bipy derivative. Extensive studies on the electropolymerisation of vinyl polypyridyl ligands have been performed by Murray, Meyer, Calvert and others[55-62]. A number of vinyl-functionalised 2,2'-bipyridine compounds have been reported in the literature (Figure 1.4). The first of these, 6-vinyl-2,2'-bipyridine, was synthesised by Woltermann in 1976[63]. Since then, synthetic routes to 4-methyl-4'-vinyl-2,2'-bipyridine by Ghosh and Spiro[64] , 6,6'-dimethyl-5-vinyl-2,2'-bipyridine by Newkome[65] and 6-methyl-4-vinyl, 3-methyl-6-vinyl- and 4-methyl-4'-vinyl-2,2'-bipyridine by Kaschig and Lohmann[66] have been published. The synthesis of 4-

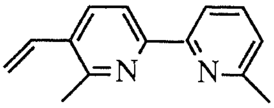
methyl-4'-vinyl-2,2'-bipyridine, as used in this study, was achieved using the later improved method reported by Abruna *et al.*[67].



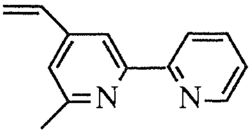
6-Vinyl-2,2'-bipyridine



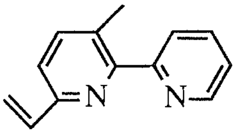
4-Methyl-4'-vinyl-2,2'-bipyridine



6,6'-Dimethyl-5-vinyl-2,2'-bipyridine



6-Methyl-4-vinyl-2,2'-bipyridine



3-Methyl-6-vinyl-2,2'-bipyridine

Figure 1.4 Series of Vinyl Bipyridines

It should be noted that these bipy derivatives have been drawn in the *cis*-configuration, i.e. that which is required for complex formation. In the free organic molecules, bipy (and its simple derivatives) adopt the *trans*-configuration. This may have a bearing on the copolymer structures whose descriptions follow.

Polymers made from these materials and their applications as supports for catalytic complexes and to metal ion-specific absorption in solution studies are well documented[66,68-73]. The aforementioned bipy derivatives have been copolymerised with HEMA previously[66], but only the work of Lewis[21] has employed the membrane form.

1. 3. 2 *Bis*(salicylidene)ethylenediamine

Bis(salicylidene)ethylenediamine (salenH_2, Figure 1.5) is an example of the class of compounds called Schiff bases, which have been known for over a hundred years. The first transition metal complexes formed by salenH_2, Cu^{II}(salen) and Ni^{II}(salen) respectively, were isolated by Dubsky and Sokol[74] in 1931. In the same year, Pfeiffer and co-workers began a systematic synthetic study of Schiff base complexes, producing a prodigious number and variety of complexes over the following eleven years[75-87]. The properties of the many complexes formed by salenH_2 have been reviewed in great detail by Holm *et al.*[88].

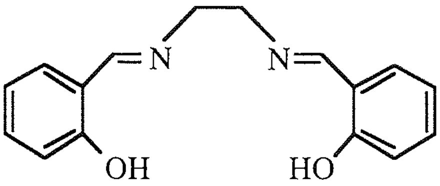


Figure 1.5 Structure of *Bis*(salicylidene)ethylenediamine (salenH_2)

SalenH_2 is a tetradentate chelating agent. On complexation to a metal ion, the phenolic functions are deprotonated and the ligand coordinates to the metal ion *via* the two phenolate oxygen atoms and the two imine nitrogen atoms.

Perhaps the greatest incentive for the preparation of salenH_2 and its derivatives has been the demonstrated ability of their Co(II) complexes to bind small molecules. Tsumaki[89] observed that red Co(II)(salen) blackened in air due to the absorption of oxygen, an observation first noted in the laboratories of Pfeiffer in 1931[76]. Tsumaki also found that the absorbed oxygen could be driven off by heating the complex in a stream of carbon dioxide. A great deal of research into the oxygen-carrying ability of these complexes followed these observations[90-94] and the scope of the research was extended by the discovery that other molecules could be bound by these complexes, e.g. carbon monoxide, carbon dioxide (both reversibly)[95,96] and nitrous oxide (irreversibly)[97,98] The oxygen-containing complexes are also known for their catalytic activity in the oxidation of organic molecules, e.g. phenols, indoles and *bis*hydrazones[99-101].

Syntheses for the preparation of vinyl-functionalised salenH_2 molecules have been reported[102-104]. In every case, the necessary precursor has been the relevant functionalised salicylaldehyde derivative. Although other vinyl derivatives have been reported[105], the most commonly used of these precursors has been 5-vinylsalicylaldehyde, VSAL, which was first reported by Wulff and Akelah[106]. This molecule may itself be directly homo- or co- polymerised, after protection of the aldehydic function[103]. The resulting polymer may then be de-protected and the formation of the polymeric Schiff base effected by reaction with the desired polyamine. This is, essentially, a cross-linking reaction.

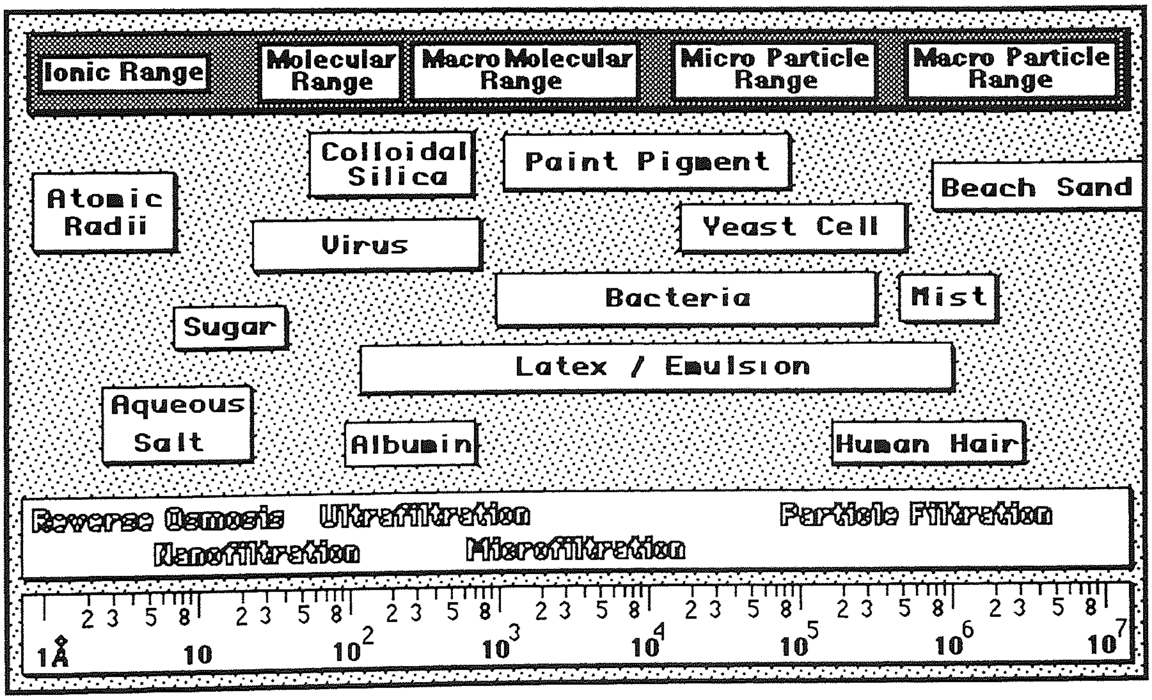
Alternatively, the monomeric divinyl Schiff base, *bis*-(5-vinylsalicylidene) ethylenediamine, DVSALEN, may be formed by the reaction of VSAL with the desired polyamine, and subsequently polymerised[102-104]. In this case, the monomer may also act as a cross-linker, due to the presence of the two vinyl functions in the molecule. A method for the preparation of non-symmetrical quadridentate Schiff bases has been reported by Mandal and Nag[107] but there have been no reports of a mono-vinyl salenH_2 molecule, such as (N-salicylidene-N'-5-vinylsalicylidene)ethylene diamine, MVSALEN. The preparation of such a compound has been achieved during this study and is described in Chapter 2. 5. 2.

The polymers obtained from these monomers have been subjected to a number of investigations. Wohrle *et al.*[104] have studied the dioxygen binding properties and catalytic activity of polymer bound cobalt complexes, while Akelah *et al.*[102] have investigated the possibility of using polymeric Schiff bases for the separation of metal ions from solution. In all these reported instances of polymers containing salenH_2 as a pendant function, the comonomer employed has been styrene. This leads to a hydrophobic polymer. The copolymerisation of DVSALEN with HEMA, as achieved in this work, produces a hydrophilic polymer, thus providing an aqueous environment in which the coordination of metal ions can occur. As in the work of Lewis[21], the membrane form of the polymer has been employed in the subsequent investigations of complexation and transport.

1. 4 Membrane Processes

We may define a membrane as a barrier exhibiting some variety of selectivity towards solutes, generally on the basis of size[108]. Thus, if we regard membranes as possessing pores of specific size, the 'bulk flow' of solutes smaller in size than the pores will be permitted, while those species larger than the pore size will not be allowed to flow.

Figure 1.6 Membrane Filtration Spectrum



Microfiltration (MF) membranes, with pore sizes in the range 0.02-10μm, are able to remove suspended materials such as bacteria, cells and some pigments, while ultrafiltration (UF) membranes have smaller pores, 1-20nm in size. The latter are characterised by the molecular weight of the largest species that may be transported, i.e. a molecular-weight cut-off (MWCO). Those membranes employed in reverse osmosis (RO or hyperfiltration) separations possess a different morphology to the previous two types of membrane. RO uses a semi-permeable membrane that is capable of transmitting solvent but not dissolved solutes. Such membranes are considered to possess a continuous thin active layer, rather than a fixed pore system. The solvent may dissolve and diffuse through the matrix *via* a network of transient pores, which are produced by the fluxional polymer chain. Presumably, the solutes are less soluble in the polymer phase than in solution, and so they are excluded from transport. For all the above mentioned processes, an applied pressure across the membrane is required to drive the separation and achieve respectable fluxes.

Hydrogel polymers do not possess a fixed porous structure and membranes of these materials are deemed to be homogeneous in nature. The highly mobile polymer chain segments are plasticised by the large amount of 'freezing water' in the gel, giving a series of randomly altering, water-filled spaces. It is here that the difference between hydrogel membranes and RO-type polymer films occurs. While solutes are not permitted to pass through the RO polymeric barrier, the hydrogel offers a medium into which salts may dissolve and diffuse. This concept is known as the solution-diffusion theory.

This study follows the transport of transition metal salts across membranes in the absence of an external pressure, with only the influence of a concentration gradient driving the diffusion. Thus the fluxes through the membrane will be low, with transport resulting purely as a result of mass transfer of a species from a high concentration to a lower one. This phenomenon is governed by Fick's First Law of Diffusion[109] (Equation 1.2), which states that the diffusional flux is proportional to the concentration gradient.

$$J = -D(dc/dx) \qquad \text{Equation 1.2}$$

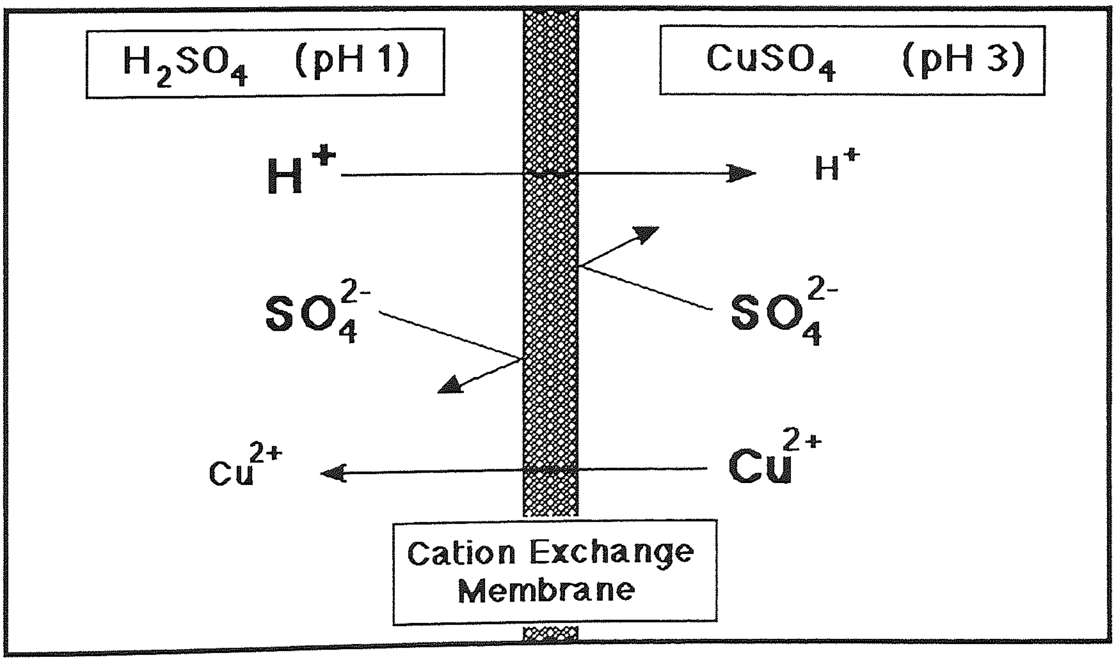
where J = Flux per unit area, D = Diffusivity and dc/dx = Concentration Gradient

Diffusion in gels is described by a mathematical theory which is notoriously complex[110], but on a simple level, equation 1.2 is sufficient to derive those expressions necessary for the calculation of permeability coefficients for the permeating transition metal-ion species in this study (see later chapters).

1. 4. 1 Membrane Separations of Transition Metal Ions

The separation and pre-concentration of metal ions using a membrane-based technique is most commonly achieved by Donnan-dialysis[111] across an ion-exchange membrane[112-115], the principles of which will now be described with reference to Figure 1.7, which shows the separation of two solutions of $CuSO_4$ and H_2SO_4 by a cation exchange membrane.

Figure 1.7 The Principle of Donnan Dialysis



On the H_2SO_4 solution side, the $[H^+]$ is much greater than in the $CuSO_4$ solution. Thus, the proton gradient will act as the driving force for the flow of H^+ across the membrane. The membrane is specific in its permeability of cations only and so electrical neutrality is maintained by the counter-flow of Cu^{2+} ions in the opposite direction. If the $[H^+]$ is kept at a constant level in the H_2SO_4 phase, the transport of Cu^{2+} ions will continue, even against their own concentration gradient, until the level of Cu^{2+} ions is equivalent to that of the H^+ ions. This is the Donnan-effect.

Despite its wide use, Donnan-dialysis through ion-exchange membranes suffers from the fact that the process is not selective enough to distinguish between different metal ions in solution. Liquid membranes have been employed by a number of groups in the investigation of more specific transport effects. They have used either linear chelating compounds[116-118] or macrocyclic ligands[119-121] in their studies to achieve the desired selectivity. These systems also have their limitations, namely their lack of stability and the tendency for the metal-carrier complex to leach from the organic to the aqueous phase. Often, it is necessary to append some kind of lipophilic function to the carrier to increase its affinity for the organic phase.

Various groups have studied the transport of metal ions across polymeric membranes and the potential use of such membranes for metal-ion separations. This includes work involving hydrogels by the Speciality Materials Group at Aston[122-126]. Hamilton[35] discovered that the anions associated with the metal ions play a vital role in the permeation of the metal ions. The anion is found to have a dominant influence over the cations in their rate of permeation through hydrogel membranes.

Research conducted by Oxley[36] centred on the immobilisation of crown compounds in hydrogels to control the transport of alkali and alkaline earth metal ions, while the work of Lewis[21] looked at the transport of transition metal ions through hydrogel membranes containing immobilised pyridine and bipyridine functions. Generally, however, there are few reports of chelating polymer membranes to be found in the literature[127,128], thus leaving an opportunity for a more extensive study of the design, synthesis and application of chelating membrane systems.

1. 5 Summary of Objectives

In this chapter, the factors that have influenced the use of certain materials in this study, where the aim has been to produce hydrophilic polymers with the ability to coordinate to a variety of transition metal ions, have been explained. In writing this chapter, the purpose of the author is to give a brief introduction to the work, which is rather multi-disciplinary in nature and requires the connection of information from different areas of chemistry. Each chapter that follows will begin with a further introductory section, to complement the information contained in this chapter.

In the following chapters the synthesis of monomeric ligands will be described. This will be followed by a description of how the coordination of metal ions affects the physical properties of the polymer, and *vice versa*. The techniques employed will be familiar to all chemists.

The hydrophilic polymeric matrix used in this study is formed by the hydrogel poly(2-hydroxyethyl methacrylate) (PHEMA). This polymer is used in the manufacture of soft contact lenses and, as such, membranes made with this material are optically clear in the visible region. Many transition metal form complexes with both bipyridyl and salen groups that are coloured. As the polymer will not interfere with absorptions in the visible region of the spectrum, visible spectroscopy may be used to characterise the complexes obtained.

An extension of this idea has lead to a kinetic study of the coordination-kinetics of copper (II) salts with the salen-based membranes, thus obtaining more subtle data concerning the ligand-metal-polymer interactions. Here, information regarding the coordinating ability of the hydrogel membranes, along with the influential role of the counter-anion in the transport of metal salts into the membranes, is acquired.

Subsequently, the transport of transition metal ions across the ligand-modified membranes is discussed. Here the counter-anion is kept constant, leading to information on the effect of the cations employed.

CHAPTER TWO

MATERIALS AND METHODS.

2. 1 Introduction

This chapter is divided into two sections. The first of these sections deals with the synthesis and purification of the vinyl monomers used in subsequent copolymerisations. Where possible, spectroscopic evidence is used in the analysis of the products. The method for preparing and characterising copolymers in membrane form is then described. The second section is given over to those techniques which have been used to study transition metal ion binding within the hydrogel membranes. Also, the apparatus and methods used in the study of the mechanical properties of copolymer membranes is discussed. Finally, the design and operation of equipment employed for the study of transition metal ion transport through the membranes is covered.

Further synthetic work, detailing the preparation of various allyl-substituted ligands, will be discussed separately in a later chapter.

Section (A) : Polymerisable Ligand Synthesis and Polymer Preparation

2. 2 Chemicals and Analysis

2. 2. 1 Reagents and Solvents

The reagents used in the preparation of the vinylic ligands described in the subsequent sections are listed in Table 2. 1. With the exception of diisopropylamine, all reagents were used as received from their respective suppliers. Purification of diisopropylamine was effected by standing it over calcium hydride overnight and then distilling it from the calcium hydride under a nitrogen atmosphere. The material purified in this manner was used immediately.

Table 2. 1 Reagents used in Monomer Synthesis

REAGENT	M_r	SUPPLIER
Diisopropylamine	101.19	Aldrich Chemical Company
Calcium hydride	64.06	Janssen Chimica
4,4'-Dimethyl-2,2'-bipyridine	184.24	Aldrich Chemical Company
(Chloromethyl)methyl ether	80.51	Aldrich Chemical Company
Sodium hydrogen carbonate	84.01	Aldrich Chemical Company
Potassium t-butoxide	112.22	Aldrich Chemical Company
Sodium sulphate (anhydrous)	142.04	Aldrich Chemical Company
Silica gel (flash grade & 230-400 mesh)	-	Aldrich Chemical Company
Potassium permanganate	158.04	Hopkin and Williams Ltd.
Hydrochloric acid	36.46	Fison's
Thionyl chloride	118.97	Aldrich Chemical Company
2-Hydroxyethyl methacrylate	130.14	
Magnesium sulphate (anhydrous)	120.37	Aldrich Chemical Company
Salicylaldehyde	122.12	Aldrich Chemical Company / Janssen Chimica
Paraformaldehyde	-	Aldrich Chemical Company
Triphenylphosphine	262.29	Aldrich Chemical Company / Janssen Chimica
Sodium hydroxide	40.00	Fison's
37% Aqueous formaldehyde	30.03	Fison's
Sodium	23.01	Aldrich Chemical Company
Copper(II) perchlorate hexahydrate	370.53	B. D. H.
1,2-Diaminoethane	60.10	B. D. H.
Triethylamine	101.19	Aldrich Chemical Company
Iron (II) sulphide	87.91	Aldrich Chemical Company

The solvents used in the syntheses to be described are listed in Table 2. 2. All solvents were used as received unless otherwise stated. Pure, dry tetrahydrofuran (THF) was prepared by first standing it over sodium wire for at least one day, and then distilling from sodium/benzophenone. Once purified, the dry THF was used immediately. Dry benzene was prepared by distillation, the first 10% of the distillate being discarded.

Table 2. 2 Solvents used in Monomer Synthesis

SOLVENT	M_r	SUPPLIER
Tetrahydrofuran	72.11	Fison's
Benzophenone	182.22	Aldrich Chemical Company
Diethyl ether	74.12	Fison's
Distilled water	18.02	Laboratory distillation
Benzene	78.11	Fison's
Chloroform	120.39	Fison's
Acetone	58.08	Ellis and Everard (U.K.) Limited
Petroleum ether (60-80°C)	-	Fison's
Petroleum ether (40-60°C)	-	Fison's
Methanol	32.04	Ellis and Everard (U.K.) Limited
Ethanol	46.07	Hayman Limited

2. 2. 2 Analytical Techniques

2. 2. 2. 1 Nuclear Magnetic Resonance (NMR) Spectroscopy

All the NMR spectra quoted in the following sections were obtained on a Bruker AC-E 300MHz spectrometer. In ^{13}C NMR, the ^{13}C-^{1}H coupling constant is large (125-200 MHz for directly bonded protons). This leads to overlapping multiplets that complicate the spectra and render them more difficult to analyse. Therefore, all the ^{13}C spectra quoted are proton noise-decoupled, each peak appearing as a sharp singlet. While this increases the sensitivity of the technique with regards the accuracy of chemical shifts, information derived from spin-spin splitting patterns is lost. However, the Bruker spectrometer possesses software that can combine the proton noise-decoupling with another multi-phase technique, known as the *J*-modulated spin-echo sequence (*J*-mod). This permits the identification of different types of carbon atom by employing the ^{13}C-^{1}H couplings and the intensities they generate[129]. The use of this technique causes an inversion of the peaks due to methylene and quaternary carbons, i.e. CH_3 and CH point up (+), while CH_2 and C point down (-) on graphical representations.

2. 2. 2. 2 Elemental Analysis

All elemental analyses were performed by MEDAC Limited at the University of Brunel, London.

2. 2. 2. 3 Melting Points

All melting points were determined using Gallenkamp melting point apparatus and are uncorrected.

2. 3 The Preparation of 4-Methyl-4'-Vinyl-2,2'-Bipyridine

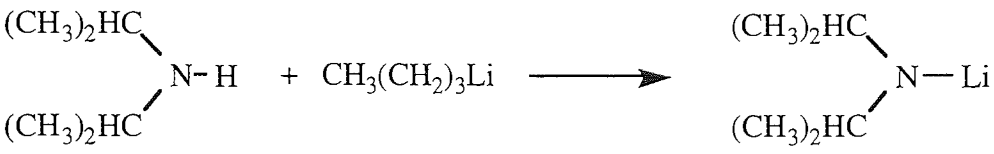
The first reported multigram synthesis of 4-methyl-4'-vinyl-2,2'-bipyridine, VBPY, was that of Ghosh and Spiro[64] in 1980. Many groups subsequently found this procedure difficult to execute and, in 1984, Abruna *et al.*[67] published a modified synthesis allowing multigram preparation of VBPY. The VBPY used in this work was therefore produced via this improved method, which remains the simplest and most effective route to VBPY, despite various attempts to improve both the yield and the purity[130,131].

The synthesis of Abruna *et al.* involves two stages which will now be discussed in greater detail. A summary of the ^1H and ^{13}C NMR spectra for the products of each stage is then provided.

2. 3. 1 The preparation of 4-methoxyethyl-4'-methyl-2,2'-bipyridine

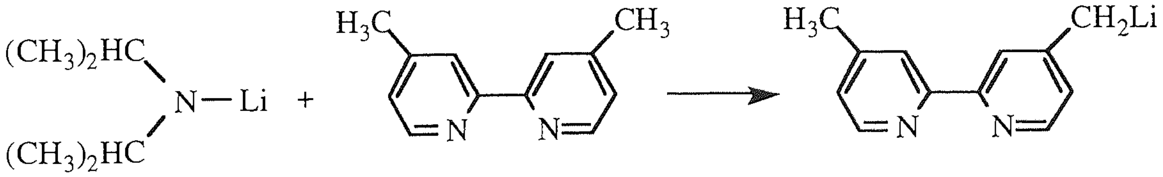
The reagents used in this synthesis were purified as follows. Diisopropylamine was distilled over calcium hydride under nitrogen, while dry tetrahydrofuran (THF) was obtained by distillation over sodium/benzophenone. All other reagents were used as received from the Aldrich Chemical Company.

The first stage of the reaction is the generation of the strong base lithium diisopropylamide (LDA) (**3**). This was achieved by the reaction of a THF solution of diisopropylamine (**1**) [11.4cm^3 (81mmol) in 90cm^3] with 1.5M butyllithium (**2**) (in hexanes) [54.3cm^3 (81.5mmol)] at 0°C under a nitrogen atmosphere. [SCHEME 2.1]



(**1**) (**2**) (**3**)

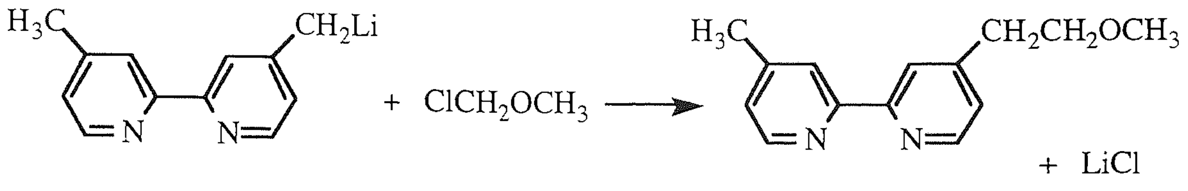
To this mixture was added, dropwise, a THF solution of 4,4'-dimethyl-2,2'-bipyridine (**4**) [15g (81.5mmol) in 350cm^3].*{It should be noted that 4,4'-dimethyl-2,2'-bipyridine does not readily dissolve in THF and that agitation and elevated temperatures are required for dissolution}.* Each mole of (**3**) reacts with one methyl group of (**4**) to yield the lithiated intermediate (**5**). [SCHEME 2.2]



(**3**) (**4**) (**5**)

The lithiated intermediate gave the THF solution a deep brown colour. This solution was stirred for 15 minutes at 0°C under nitrogen.

A THF solution of (chloromethyl)methyl ether (**6**) [6.9cm^3 (90.9mmol) in 60cm^3] was then added dropwise, yielding a homogeneous, pale yellow reaction mixture, which was stirred for a further 30 minutes at 0°C under nitrogen. The ether product (**7**) is formed during this stage by the nucleophilic attack of the lithiated side-chain on the chlorine-carrying carbon of **(6)** [SCHEME 2.3]



(5) **(6)** **(7)** **(8)**

The reaction solution was then quenched by the addition of distilled water [90cm^3], and partitioned between saturated sodium hydrogen carbonate [50cm^3] and diethyl ether [150cm^3]. Two additional diethyl ether extractions were carried out [150cm^3 aliquots] and the combined ethereal layers were dried over sodium sulphate.

Concentration of the combined ethereal layers afforded a pale yellow oil, which was then filtered through flash grade silica gel (ether elution) and concentrated. On standing for one week, all remaining traces of the starting material **(4)** were deposited as white crystals. *{While Abruna et al. recommend standing for 2-3 days only, the extended period employed here ensures complete precipitation of the starting material}.*

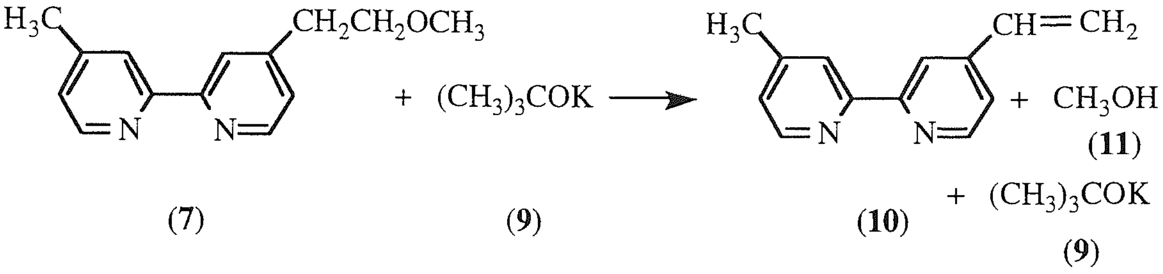
The product was then isolated by filtration, to give a pale yellow, almost colourless oil in 62% yield [literature[67] 12.6g, 68% yield]. The literature reports the product as a colourless oil, which implies that the product here is still slightly impure. In repeat experiments, consistent yields of pure product have been achieved in the range of 38-56%.

ELEMENTAL ANALYSIS : For $C_{14}H_{16}N_2O$

	C	H	N
Calculated	73.65%	7.06%	12.27%
Found	73.07%	7.27%	11.33%

2. 3. 2 The preparation of 4-methyl-4'-vinyl-2,2'-bipyridine

A THF solution of potassium t-butoxide (**9**) [12.4g (110.4mmol) in 210cm^3] was added dropwise to a THF solution of (**7**) [12.6g (52.2mmol) in 325cm^3] at -78°C under nitrogen. (**9**) causes the elimination of methanol from (**7**) to give the vinyl derivative (**10**). [SCHEME 2. 4]



The reaction mixture was stirred for 90 minutes at -78°C and for a further 15 minutes at room temperature, before the reaction was quenched with distilled water [150cm^3] and then extracted three times with diethyl ether [300cm^3 aliquots]. The combined ethereal layers were dried over sodium sulphate and then stripped to yield a pale yellow solid. Polymeric residue was removed by filtration through a 2-inch column of 230-400 mesh silica gel [ether elution] to afford a yellow solid. Recrystallisation from hexane/diethyl ether yielded the product as a white, crystalline solid [4.6g, 30% overall yield; literature[67] 35% overall yield].

ELEMENTAL ANALYSIS : For $C_{13}H_{12}N_2$:

	C	H	N
Calculated	79.56%	6.16%	14.28%
Found	79.32%	6.27%	13.96%

2. 3. 3 NMR Spectroscopy for Bipyridine Derivatives

The NMR data for all the bipyridine derivatives described throughout this thesis will make reference to the numbering scheme in Figure 2.1, which shows the hydrogen, carbon and substituent positions on the bipyridyl molecule.

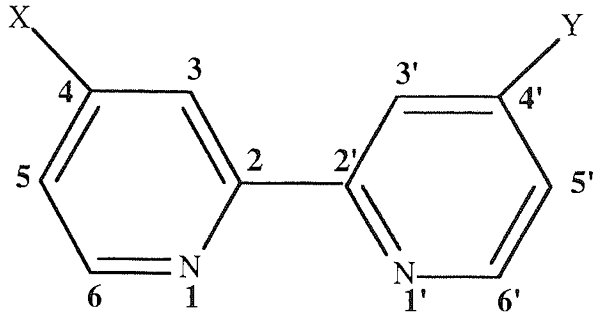


Figure 2.1 Numbering Scheme in Bipyridine Derivatives

X = Y = CH_3 --- 4,4'-dimethyl-2,2'-bipyridine

X = CH_3 Y = $CH_2CH_2OCH_3$ --- 4-methoxyethyl-4'-methyl-2,2'-bipyridine

X = CH_3 Y = CH=CH_2 --- 4-methyl-4'-vinyl-2,2'bipyridine

2. 3. 3. 1 4-methoxy-4'-methyl-2,2'-bipyridine

^{1}H N.M.R. (in $CDCl_3$)	8.31/8.33/8.35/8.37δ(**H6/6'**); 8.03/8.08δ(**H5/5'**); 6.85/6.89/ 6.96/7.01δ (**H3/3'**); 3.43/3.45/3.48δ(OC**H**$_2$: position 4); 3.12δ(OC**H**$_3$: position 4); 2.71/2.74/2.76δ(C**H**$_2$: position 4); 2.18δ(C**H**$_3$: position 4')

^{13}C N.M.R. (in $CDCl_3$)	155.7/155.9δ(**C2/2'**); 148.8/149.0δ(**C6/6'**); 147.8/149.1δ(**C4/4'**); 124.1/124.5δ(**C5/5'**); 121.4/121.8δ(**C3/3'**); 71.9δ(OCH_2 : position 4); 58.5δ(OCH_3 : position 4); 35.5δ(CH_2 : position 4); 20.9δ(CH_3 : position 4')

2. 3. 3. 2 4-methyl-4'-vinyl-2,2'-bipyridine

^{1}H N.M.R. (in $CDCl_3$)	8.49/8.55δ(**H6/6'**); 8.20/8.35δ(**H5/5'**); 7.08/7.27δ(**H3/3'**); 6.67/6.7/6.72/6.76δ(=**CH**$_2$: position 4'); 5.45/5.56δ, 6.01/6.07δ(=**CH** : position 4'); 2.39δ(**CH**$_3$: position 4)

^{13}C N.M.R. (in $CDCl_3$)	155.8/156.8δ(**C2/2'**); 148.87/149.3δ(**C6/6'**); 145.7/148.1δ(**C4/4'**); 134.9δ(=**CH** : position 4'); 121.9/124.7δ(**C5/5'**); 118.7δ(=CH2 : position 4'); 118.4/120.5δ(**C3/3'**); 21.1δ(CH3 : position 4)

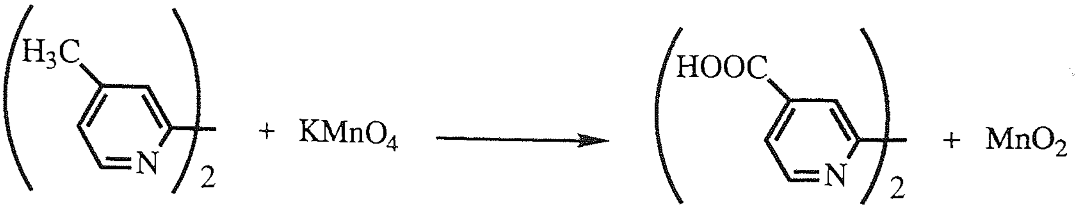
2. 4 The Preparation of the DiHEMA Ester of 4,4'-Dicarboxy-2,2'-Bipyridine (DHBPY)

This molecule was synthesised in order to investigate both the effect of increasing the distance of the ligand centre from the polymer backbone and any additional cross-linking effect introduced by the molecule.

The preparation of this molecule follows the procedure of Sprintschnik *et al.*[132] for the synthesis of diesters of 4,4'-dicarboxy-2,2'-bipyridine. The synthesis proceeds in two stages which will now be discussed.

2. 4. 1 The preparation of 4,4'-dicarboxy-2,2'-bipyridine

4,4'-dimethylbipyridine (**1**) [16.8g (86.8mmol)] and potassium permanganate (**2**) [50g] were heated at reflux in distilled water [560cm^3] for 12 hours. (**2**) causes the oxidation of the methyl side chains of the aromatic bipyridine molecule, yielding 4,4'-dicarboxy-2,2'-bipyridine (**3**). [SCHEME 2.5]

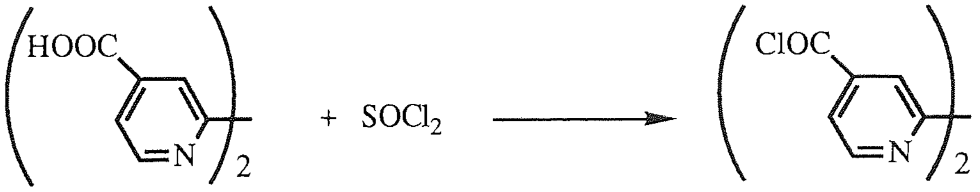


(1) (2) (3)

The brown precipitate of manganese dioxide was removed by filtration to yield a slightly yellow solution, which was extracted with diethyl ether [3 x 100cm^3 aliquots] to remove any unreacted **(1)**. Addition of concentrated hydrochloric acid precipitated white crystals, which were well washed with distilled water. As reported, the crystals were found to be insoluble in all organic solvents. The reaction yielded 5g [38%] of the di-acid (no yield is quoted by Sprintschnik *et al.*) with melting point > 340°C [literature[133] mpt > 360°C].

2. 4. 2 The preparation of DHBPY

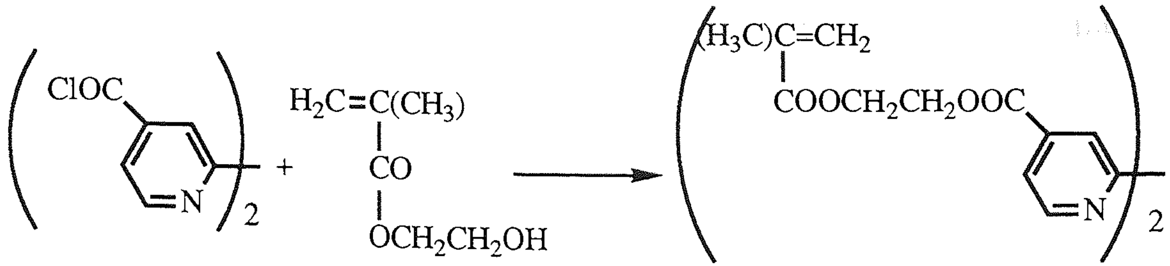
(3) [1g (4.6mmol)] and thionyl chloride **(5)** [10cm^3 (84mmol)] were refluxed for 3 hours, resulting in a yellow solution. During this period, the di-acid is converted to its dicarbonyl chloride **(6)** by the action of **(5)**. [SCHEME 2.6].



(3) (5) (6)

All excess thionyl chloride was removed by evaporation under vacuum and the residue was dried under vacuum for 2 hours.

Dry benzene [20cm^3] was added and the solution was then treated with a slight excess of 2-hydroxyethylmethacrylate (HEMA) **(7)** [1.3g (10mmol)]. The reaction mixture was refluxed for 2 hours, during which time **(6)** reacts with **(7)** to produce the diHEMA ester **(8)**. [SCHEME 2.7]



(6) (7) (8)

Chloroform [60cm^3] was added and the mixture was then treated with cold, aqueous sodium hydrogen carbonate [40cm^3]. The organic phase was separated and dried over anhydrous magnesium sulphate, before being evaporated to dryness. Recrystallisation of the solid residue from acetone/chloroform yielded the product as white crystals [0.6g, 31% yield].

ELEMENTAL ANALYSIS : For $C_{24}H_{24}N_2O_8$:

	C	H	N
Calculated	61.53%	5.16%	5.98%
Found	59.72%	5.01%	5.80%

2. 4. 3 NMR Spectra for DiHEMA Ester

As in chapter 2. 3. 3., the NMR data that follow make reference to the numbering scheme shown in Figure 2.1., where

$$X = Y = COOCH_2CH_2OOCC(CH_3){=}CH_2$$

^{1}H N.M.R. (in $CDCl_3$ + DMSO-D_6)	8.68/8.70δ(**H6/6'**); 8.60/8.63δ(**H5/5'**); 7.64/7.66δ(**H3/3'**); 5.33/5.87δ(=CH_2 position 4/4'); 4.35-4.42δ and 4.24-4.34δ (two triplets OCH_2CH_2O : position 4/4');1.68δ(CH_3 : position 4/4')

^{13}C N.M.R. (in $CDCl_3$ + DMSO-D_6)	164.1δ and 166.4δ(Ar-C=O and =C-C=O : position 4/4'); 155.5δ(**C2/2'**); 149.5δ(**C6/6'**); 137.9δ(**C4/4'**); 135.2δ(=**C** : position 4/4');125.6δ(=CH_2 :position4/4'); 122.8δ(**C5/5'**); 120.1δ(**C3/3'**); 61.5δ and 62.9δ (OCH_2CH_2O : position 4/4'); 17.6δ(CH_3 : position 4/4')

2. 5 The Preparation of (N-salicylidene-N'-5-vinylsalicylidene) ethylenediamine and *Bis*(5-vinylsalicylidene) ethylenediamine

The preparation of (N-salicylidene-N'-5-vinylsalicylidene) ethylenediamine, MVSALEN, is based upon the method of Mandal and Nag[107] for the synthesis of non-symmetrical quadridentate Schiff bases, while *bis*(5-vinylsalicylidene) ethylenediamine,DVSALEN, is prepared by the method of Akelah *et al.*[102]. In the synthesis of both molecules, the crucial precursor is 5-vinylsalicylaldehyde, VSAL, which is prepared by the method of Wulff and Akelah[106], a three stage synthesis from salicylaldehyde itself.

The synthesis of 5-vinylsalicylaldehyde and the subsequent synthesis of both the mono- and di- vinyl Schiff bases will now be discussed further.

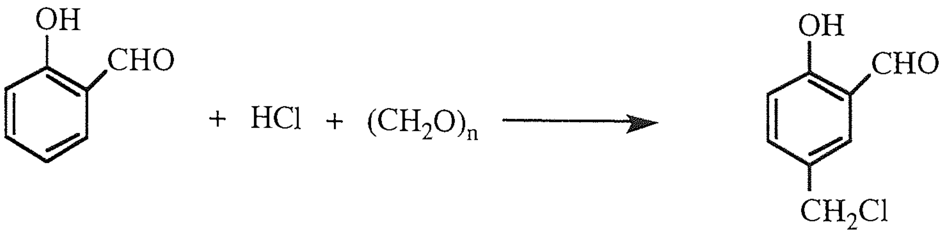
2. 5. 1 The preparation of 5-vinylsalicylaldehyde

The method of Wulff and Akelah proceeds in three steps from salicylaldehyde. The first step is the chloromethylation of salicylaldehyde. The chloromethylated product is converted into its triphenylphosphine chloride, which is then converted to the desired vinyl product under modified Wittig conditions.

2. 5. 1. 1 The preparation of 5-chloromethylsalicylaldehyde

This simple preparation was effected by stirring a mixture of salicylaldehyde (**1**) [30.5g (0.25mol)], paraformaldehyde (**3**) [13.5g (0.15mol)] and concentrated hydrochloric acid

(2) [150cm^3] at room temperature for 48 hours. During this time, 5-chloromethylsalicylaldehyde (**4**) precipitated out of solution. [SCHEME 2.8].

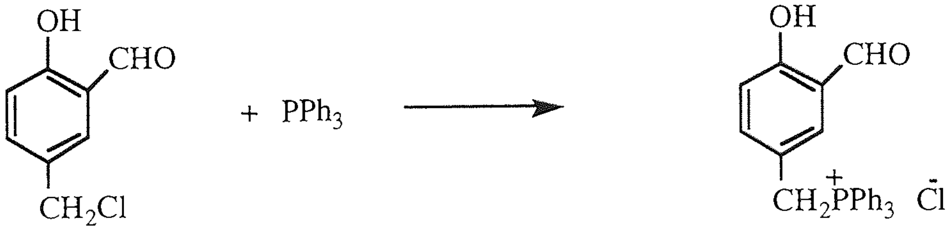


(1) (2) (3) (4)

The precipitated product was filtered off, washed with 0.5% aqueous sodium hydrogen carbonate [100cm^3] and then washed with water until neutral, before being dried in vacuum. Recrystallisation from benzene/petroleum ether gave pure 5-chloromethylsalicylaldehyde [36.2g, 85% yield, mpt 85-86°C; literature[106] 91.5% yield, mp[134] 88°C].

2. 5. 1. 2 The preparation of 3-formyl-4-hydroxybenzyl(triphenylphosphonium)chloride

A mixture of (**4**) [34.8g (0.2mol)] and triphenylphosphine (**5**) [52.4g (0.2mol)] in benzene [500cm^3] was refluxed for 1 hour. [SCHEME 2.9]

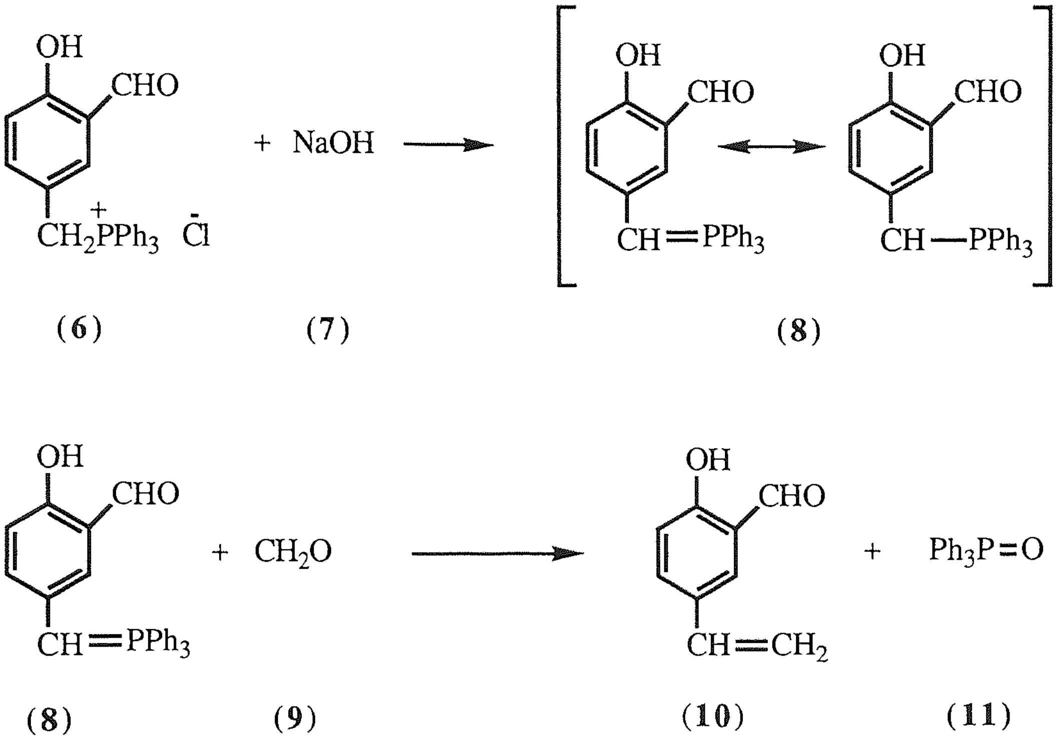


(4) (5)

The reaction mixture was then allowed to cool to room temperature, during which time the phosphonium salt (**6**) precipitated. The precipitated salt was then filtered, washed with diethyl ether and used without further purification [82.2g, 95% yield, mpt 297-299°C; literature[106] 98% yield, mpt 303-305°C].

2. 5. 1. 3 The preparation of 5-vinylsalicylaldehyde

The final stage of this preparation follows a variation of the Wittig reaction reported by Broos and Anteunis[135]. Here, the phosphorane (or ylide) (**8**) is generated *in situ* by the action of sodium hydroxide (7) on the phosphonium salt (**6**) in the presence of a large excess of aqueous formaldehyde (**9**), to give the product (**10**). [SCHEME 2.10]



To a vigorously stirred suspension of (6) [77.85g (0.18mol)] in 40% aqueous formaldehyde [600cm^3] was added, dropwise, a 12.5M aqueous solution of sodium hydroxide [195cm^3]. The addition was carried out at such a rate that the reaction temperature never exceeded 40°C. The reaction mixture was stirred for a further 2 hours and then extracted with benzene (to remove triphenylphosphine oxide). The deep yellow aqueous phase was neutralised with dilute hydrochloric acid, under cooling, and then extracted with diethyl ether [4 x 250cm^3 aliquots]. The diethyl ether was evaporated and the residue was extracted with petroleum ether (40-60°C) [6 x 50cm^3 aliquots]. Evaporation of the petroleum ether yielded the product as a viscous yellow oil. Purification was achieved by reduced pressure distillation (74°C/2mmHg) to give a viscous yellow oil which crystallised on cooling to 5°C [7.5g, 28% yield; literature[106] 58% yield, mp 19-20°C].

{Despite claims by Wulff and Akelah as regards the simplicity of this final stage, it has repeatedly proven to be difficult to execute, giving only small yields of the product}.

ELEMENTAL ANALYSIS : For $C_9H_8O_2$:

	C	H
Calculated	72.96%	5.44%
Found	72.43%	5.21%

2. 5. 1. 4 NMR Spectra for the 5-Vinylsalicylaldehyde

The NMR data presented here will make reference to the numbering scheme shown in Figure 2.2, which shows the positions of the hydrogens, carbons and substituents on the salicylaldehyde molecule.

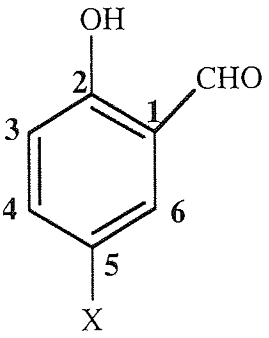


Figure 2.2 Numbering Scheme for Salicylaldehyde Derivatives

(i) X = H --- Salicylaldehyde

(ii) X = $CH=CH_2$ --- 5-vinylsalicylaldehyde

(ii)	^{1}H N.M.R. (in CDCl3)	10.94δ(O**H** : position 2); 9.74δ(C**H**O : position 1); 7.46/7.47/7.49/7.50δ(**H6**); 7.38/7.39d(**H4**); 6.82/6.85/6.87δ(**H3**); 6.50/6.53/6.56/6.59δ(=C**H** : position 5); 5.12/5.16δ and 5.53/5.59δ(=C**H**$_2$: position 5)

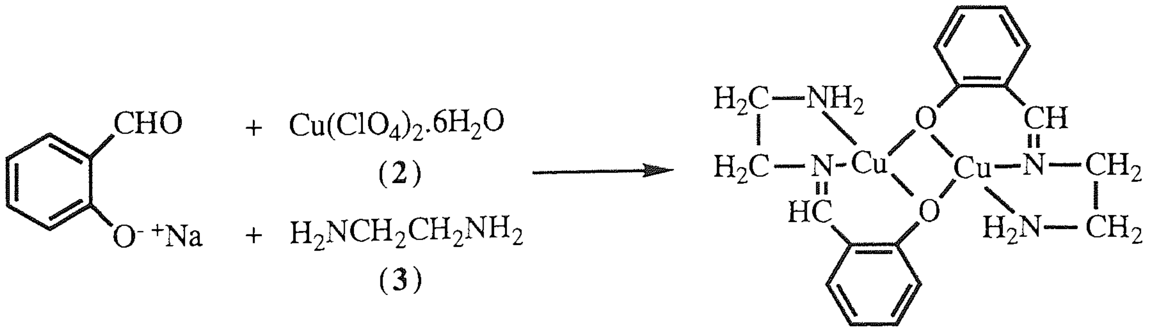
(ii)	^{13}C N.M.R. (in CDCl$_3$)	196.2δ(CHO : position 1); 160.8δ(**C2**); 134.5δ(=CH : position 5); 133.9δ(**C4**); 131.0δ(**C6**); 129.5δ(**C5**); 120.0δ(**C1**); 117.5δ(**C3**); 112.8δ(=CH$_2$)

2. 5 . 2 The preparation of (N-salicylidene-N'-5-vinylsalicylidene) ethylenediamine

This preparation, based on that of Mandal and Nag[107], comprises three steps. The formation of a phenoxo-bridged dicopper(II) complex is the first step. This is followed by the conversion to the copper(II)-monovinylsalen complex. The free ligand is achieved by the action of hydrogen sulphide on the copper(II)-MVSALEN complex.

2. 5. 2. 1 The preparation of the phenoxo-bridged dicopper(II) complex

A solution of copper(II) perchlorate hexahydrate (**2**) [2.7g (7.5mmol)] in 1:1 water-methanol [20cm^3] and 1,2-diaminoethane (**3**) [0.45g (7.5mmol)] were added quickly to a boiling solution of the sodium salt of salicylaldehyde (**1**) [0.61g (5mmol)] in methanol [500cm^3]. The resulting solution was refluxed for 2 hours and then filtered. The filtrate was reduced to 100cm^3 by rotary evaporation and filtered once more. Further concentration of the filtrate, to 50cm^3, was performed and the solution was left to stand overnight, during which time crystallisation of the product occurred. Recrystallisation from 1 : 1 water-methanol afforded the product (**4**) [0.95g, 83% yield; literature[107] 90% yield]. [SCHEME 2.12]

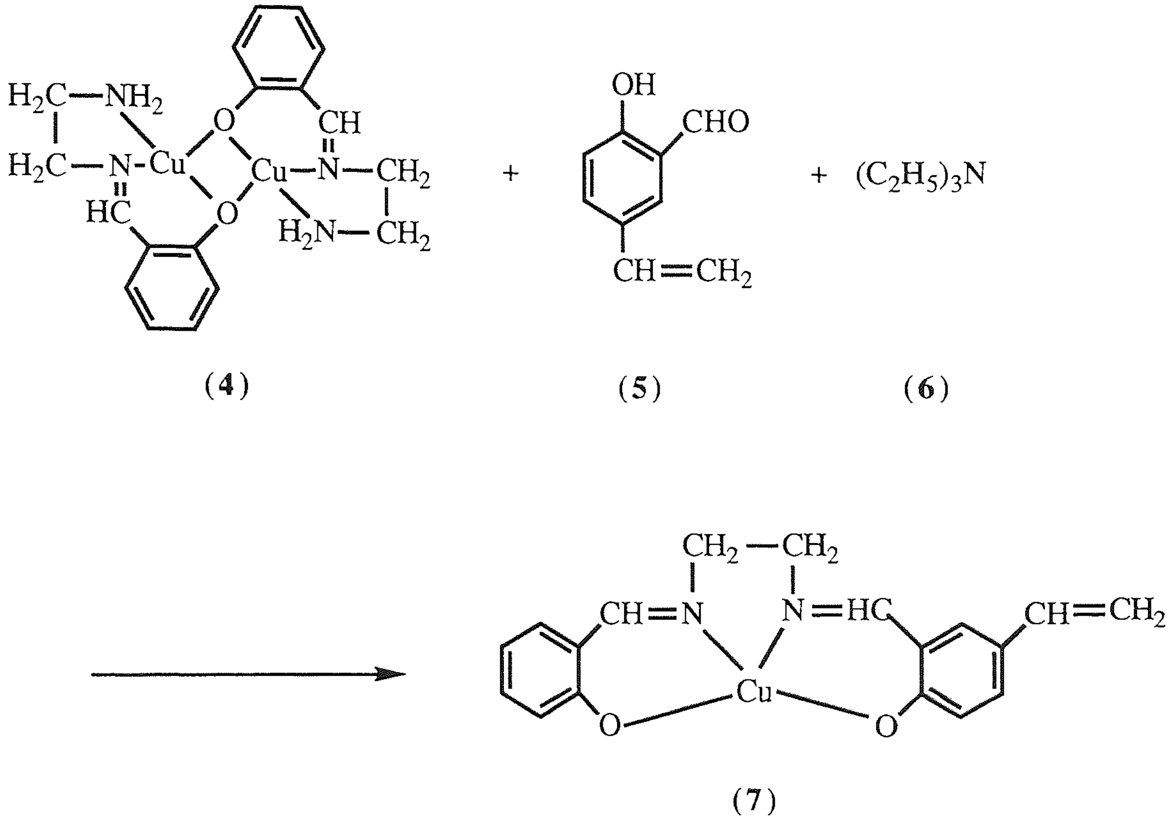


(1)

(4)

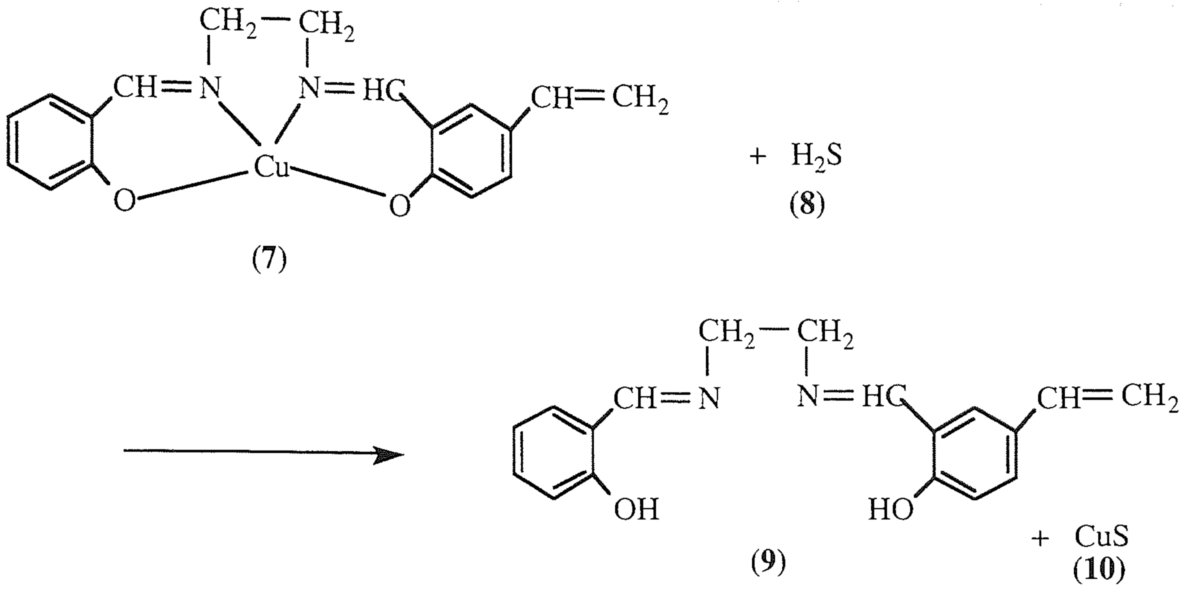
2.5.2.2 The preparation of (N-salicylidene-N'-5-vinylsalicylidene) ethylenediamine

During this stage, (**4**) is reacted with 5-vinylsalicylaldehyde (**5**) to yield monovinylsalen (**7**). [SCHEME 2.13]



5-vinylsalicylaldehyde (**5**) [0.59g (4mmol)] and triethylamine (**6**) [0.4g (4mmol)] were added to a solution of (**4**) [0.91g (2mmol)] in methanol [$30cm^3$]. After the solution had been refluxed for 3 hours, it was concentrated to half its original volume. On slow evaporation of the solvent, crystals separated and were collected by filtration. The collected crystals were washed several times with water to remove any unreacted (**4**). Recrystallisation from methanol afforded the copper(II)-MVSALEN complex (**7**). [0.57g, 80% yield].

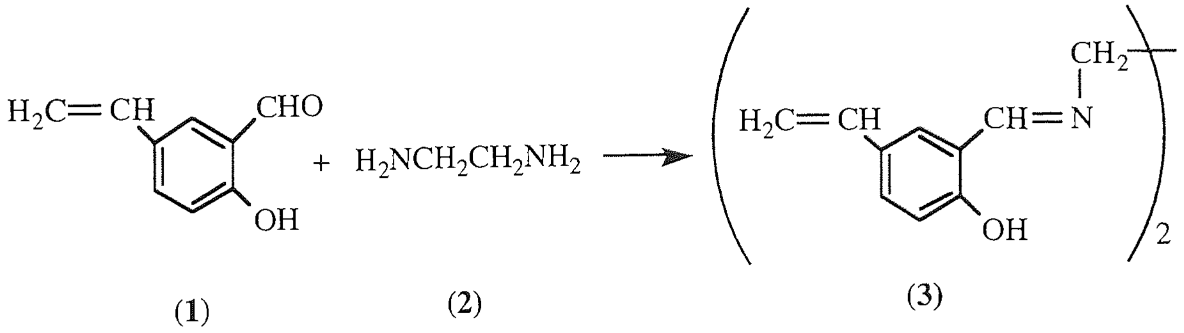
To remove the metal from the complex and hence obtain the free monomeric ligand (**9**), hydrogen sulphide (**8**), produced by the action of dilute hydrochloric acid on iron (II) sulphide, was passed through a stirred solution of (7) in methanol [$150cm^3$]. [SCHEME 2.14]


(7) + H_2S (8) → (9) + CuS (10)

Copper(II) sulphide, precipitated during the reaction, was removed by filtration through a fine sinter. Methanol was evaporated off to yield the free ligand as a yellow solid. Recrystallisation from ethanol gave MVSALEN (**9**) as yellow crystals [0.45g, 94% yield].

2. 5. 3 The preparation of *bis*(5-vinylsalicylidene) ethylenediamine

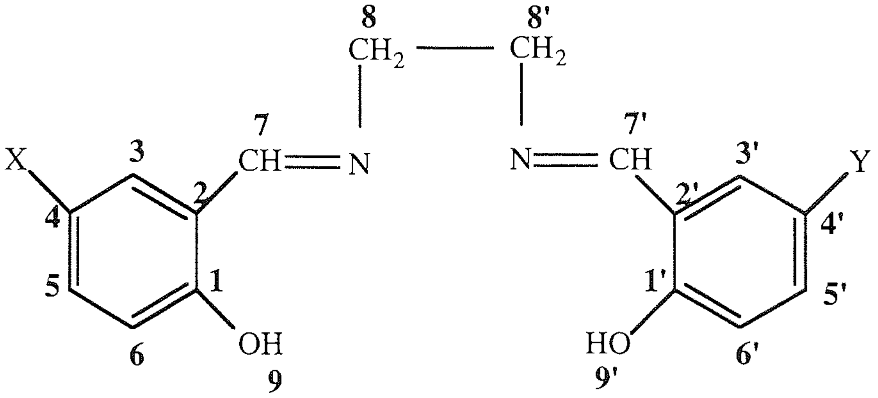
Following the method of Akelah *et al.*[102], this compound was prepared simply by the reaction of 5-vinylsalicylaldehyde (**1**) with 1,2-diaminoethane (**2**). [Scheme 2.15]


(1) + $H_2NCH_2CH_2NH_2$ (2) → (3)

1,2-Diaminoethane (**2**) [0.15g (2.5mmol)] in hot ethanol (15cm^3) was added to 5-vinylsalicylaldehyde (**1**) [0.74g (5mmol)] in hot ethanol (15cm^3). The product precipitated immediately as a yellow solid, which was filtered and then recrystallised from ethanol to give N,N'-ethylene-bis(5-vinylsalicylaldimine) (**3**). [0.8g, 85% yield, mp 167-170°C; literature[102] 90% yield, mp 168-170°C].

2. 5. 4 NMR Spectra for SalenH$_2$ derivatives

The NMR data that follow will make reference to the numbering scheme in Figure 2.3, which shows the positions of the hydrogens, carbons and substituents on the salenH$_2$ derivatives.



2.3 Numbering Scheme in SalenH$_2$ Derivatives

X = H , Y = CH=CH$_2$ --- (N-salicylidene-N'-5-vinylsalicylidene) ethylenediamine

X = Y = CH=CH$_2$ --- *bis*(5-vinylsalicylidene) ethylenediamine

2.5.4.1 (N-salicylidene-N'-5-vinylsalicylidene) ethylenediamine

In the ^{1}H spectrum of (N-salicylidene-N'-5-vinylsalicylidene) ethylenediamine, the fact that the mono- vinyl compound has been formed is indicated by the integrals of both the vinyl protons and the aromatic protons with respect to the imine protons, **H7/7'**. There are three vinyl protons and seven aromatic ring protons compared with the two imine protons. In addition to this, examination of the ^{13}C spectrum reveals that the carbons **C4** and **C4'** are different, **C4'** being a quarternary carbon while **C4** is not.

^{1}H N.M.R. (in $CDCl_3$)	13.19δ(**H9/9'** - very broad); 8.33δ(**H7/7'**); 6.80-7.38δ(**H3/3', H4, H5/5', H6/6'** - complicated multiplets); 6.54/6.58/6.60/6.64δ(=CH : position 4')); 5.07/5.12δ and 5.52/5.58δ(=CH_2 : position 4'); 3.86δ(**H8/8'**)

^{13}C N.M.R.(in $CDCl_3$)	166.4δ(**C7/7'**); 160.9δ(**C1/1'**); 135.6δ(=CH : position 4'); 131.4/132.4δ(**C5/5'**); 129.4/130.0δ(**C3/3'**); 129.0δ(**C4'**); 118.7δ(**C4**); 118.0δ(**C2/2'**); 116.9/117.2δ(**C6/6'**); 111.6δ(=CH_2 : position 4'); 58.4δ and 59 6δ(**C8/8'**)

2.5.4.2 *Bis*(5-vinylsalicylidene) ethylenediamine

In the case if *bis*(5-vinylsalicylidene) ethylenediamine, the di- vinyl compound is again confirmed by comparison of the integrals in the ^{1}H spectrum. We see two imine protons, **H7/7'**, six vinylic protons and six aromatic ring protons. Also, there is only one peak in the ^{13}C spectrum corresponding to **C4/4'**. This carbon atom now appears only as a quarternary carbon, again proving the di- vinyl compound.

^{1}H N.M.R. (in $CDCl_3$)	13.25δ(**H9/9'** - very broad); 8.33δ(**H7/7'**); 7.35/7.36/7.38/7.39δ(**H3/3'**); 7.22/7.23/7.24δ(**H5/5'**); 6.88/6.91δ(**H6/6'**); 6.56/6.59/6.61/6.65δ(=CH : positions 4/4'); 5.09/5.12 and 5.54/5.59δ(=CH2 : positions 4/4'); 3.93δ(**H8/8'**)

^{13}C N.M.R.(in $CDCl_3$)	166.4δ(**C7/7'**);160.8(**C1/1'**); 135.6δ(=CH : positions 4/4'); 130.0δ(**C5/5'**); 129.4δ(**C3/3'**); 128.6δ(**C4/4'**); 118.3δ(**C2/2'**); 117.2δ(**C6/6'**); 111 6δ(=CH2 : positions 4/4'); 59.7δ(**C8/8'**)

2. 6 Polymer Preparation

2. 6. 1 Reagents

The reagents used in the preparation of the hydrophilic polymers are as follows. The monomer 2-hydroxyethyl methacrylate, HEMA, was obtained as the pure optical grade and required no further purification. The ligand-based monomers were prepared as discussed in the preceding sections. The free-radical polymerisation initiator and the cross-linking agent were both used as supplied. All reagents were stored in a refrigerator until needed.

2. 6. 2 Preparation of Hydrogel Membranes

The following method of preparing hydrogel polymer membranes was developed within the Speciality Materials Group at Aston[33]. The desired monomer mixture, plus 0.5% w/w AIBN and 1% w/w EGDMA, was degassed with nitrogen for 10 minutes. The total reaction mixture was approximately 6g. The mixture was then injected by syringe into the membrane mould design shown in Figure 2.4. The mould comprises two glass plates (10 x 12.5cm), each with a poly(ethylene terephthalate) (melinex) sheet fixed to the inner surface to aid the removal of the membrane.

The cavity in the mould is formed by sandwiching two poly(ethylene) gaskets with a rectangular hole (8.75 x 11.25cm) between the glass plates. The sandwich is secured by eight bulldog clips, and the degassed polymerisation mixture was transferred to the mould *via* a G18 needle inserted between the plates. While the mixture was being injected, the mould was allowed to stand upright on two of the bulldog clips. This enables all the air in the mould cavity to be displaced by the reaction mixture. The 6g sample did not completely fill the cavity and, on removal of the needle, excess liquid was expelled as the plates squeezed together and the cavity was completely filled.

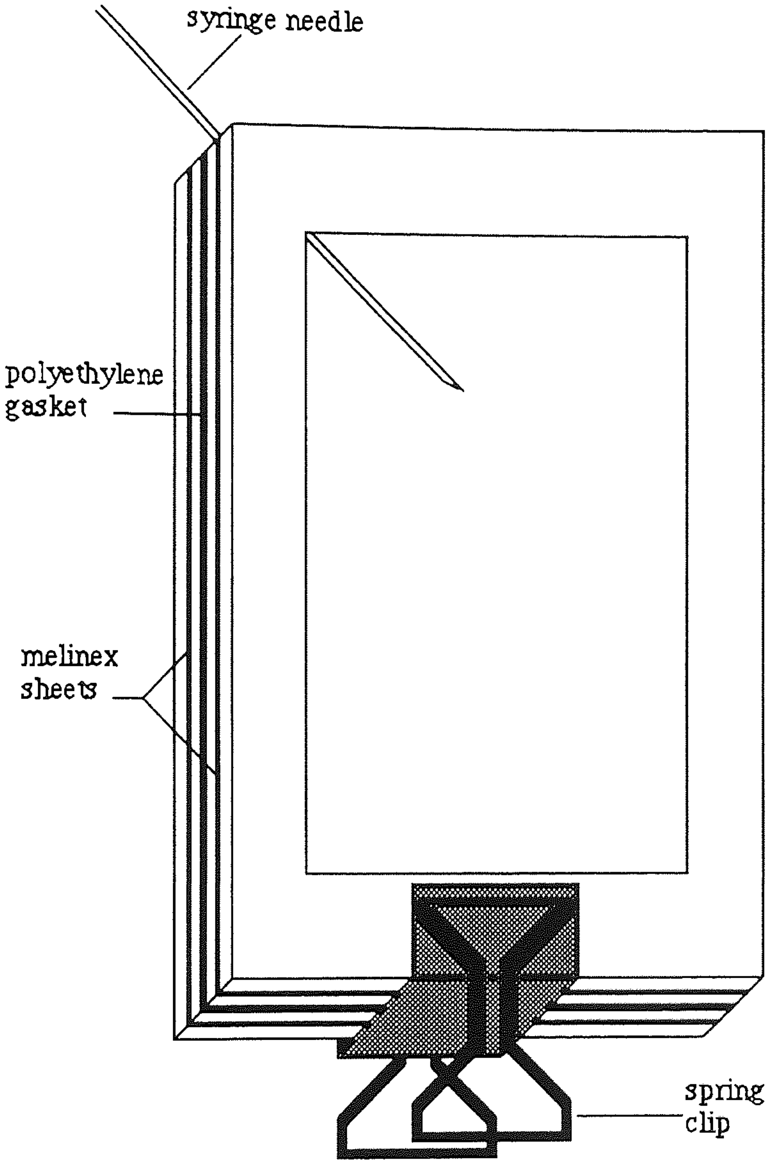


Figure 2.4 Membrane mould

The mould was then placed horizontally in an oven at 60°C for 3 days. During this time, bulk polymerisation occurred. After this period, the mould was placed in an oven at 90°C for 3 hours for post-curing purposes. The mould was dismantled while still hot, the plates being separated by running a sharp knife along the edges. The melinex sheet was removed carefully and the membrane was peeled gently from the sheet. The membrane was then allowed to hydrate in distilled water for 2 weeks, the water being changed each day to allow leaching of unpolymerised material.

2. 6. 3 Equilibrium Water Content (EWC) Measurement

Five samples were cut from each hydrated membrane under test using a No. 8 cork borer. Any excess surface water was removed by carefully blotting the membrane samples with filter paper. The samples were then weighed immediately to give the hydrated weight, W_h. Dehydration of the samples was achieved by placing in a 600 watt microwave oven, on cook, for 12 minutes, a method used as standard within the group in the measurement of EWC.

The dehydrated samples were immediately weighed to give the dehydrated weight, W_d. It was essential that the dehydrated samples be weighed immediately, as the hydrogel membrane can absorb water from the atmosphere. The EWC could then be calculated from equation 2.1.

$$\mathbf{EWC = (\{W_h - W_d\}/W_h) \times 100} \qquad \text{Equation 2.1}$$

where W_h is the weight of the hydrated membrane, and

W_d is the weight of the dehydrated membrane

A statistical treatment of the error involved in the EWC determination by this technique using poly(HEMA) gives a standard deviation of $\sigma_{n-1} = 0.4$, an error of roughly 3%.

Section (B) : Techniques Used in the Study of Transition Metal Ion Interactions in Ligand-Modified Hydrogel Polymers

2. 7 Introduction

In this study of the interaction of transition metal (TM) ions with polymer-appended ligand groups, the use of hydrogel polymers provides an essentially aqueous environment into which the TM ions may permeate and coordinate with the ligand. While this approximates to the more conventional environment for the study of TM complexes, many of the usual physical and spectroscopic techniques cannot be employed successfully with such polymers, e.g. infrared spectral detail is largely obscured by intense, broad water bands.

The techniques used in this study are summarised below and will be discussed in greater detail in the subsequent sections.

(i) Many of the TM complexes of the ligands under study are highly coloured. As poly(HEMA) produces optically clear ligand-based copolymer membranes (hence its use in the production of contact lenses), the rate and extent of TM coordination can be monitored by observing the UV/Visible absorption spectra of the complexes.

(ii) Tensometric studies have been performed in order to investigate the potential cross-linking abilities of the divinyl ligand-based monomers described previously.

(iii) The transport of TM ions through ligand-modified copolymer membranes has been studied using a "permeation rig" where the flow of ions from one side of the membrane to the other has been monitored by the change in conductivity.

2.8 Ultraviolet and Visible Absorption Spectroscopy

The ions of both the first and second row transition elements, along with the complexes formed by them, generally absorb visible radiation in at least one of their oxidation states. Broad absorption bands are seen due to *d-d* electronic transitions, and these bands are strongly dependent upon the chemical environment in which the metal finds itself. These bands tend to be weak and have small molar absorptivities, as such transitions are forbidden.

In many TM complexes, much stronger *charge-transfer* absorption bands are seen. Here, one component of the complex acts as an electron donor, while the other acts as an electron acceptor. On absorption of radiation, an electron is transferred from a donor orbital to one largely associated with the acceptor. As a result, the excited state is the product of an internal redox process. These *charge-transfer* absorptions are allowed transitions and, as such, have very large molar absorptivities. Therefore, they provide an extremely sensitive means for the detection and determination of absorbing species.

The technique of UV/Visible spectroscopy is thus a very important, non-destructive tool for both the qualitative and quantitative determination of TM complexes within hydrogel polymers.

A spectrophotometer measures optical density (**d**) as a function of wavelength, as given in equation 2.2.

$$\mathbf{d} = \log_{10} (\mathbf{I_o/I}) \qquad \text{equation 2.2}$$

where I_O is the intensity of light incident to the sample and I is the intensity of the emergent light. The molar absorption coefficient (ε) is given by equation 2.3, which, on rearrangement, gives the most useful form of the equation, namely Beer's law (equation 2.4)

$$\varepsilon = d/cl \qquad \text{equation 2.3}$$

$$d = \varepsilon cl \qquad \text{equation 2.4}$$

where c is the concentration of the absorbing species, conventionally quoted in units of mol. dm^{-3}, and l is the path length, measured in cm.

2. 8. 1 Instrumentation

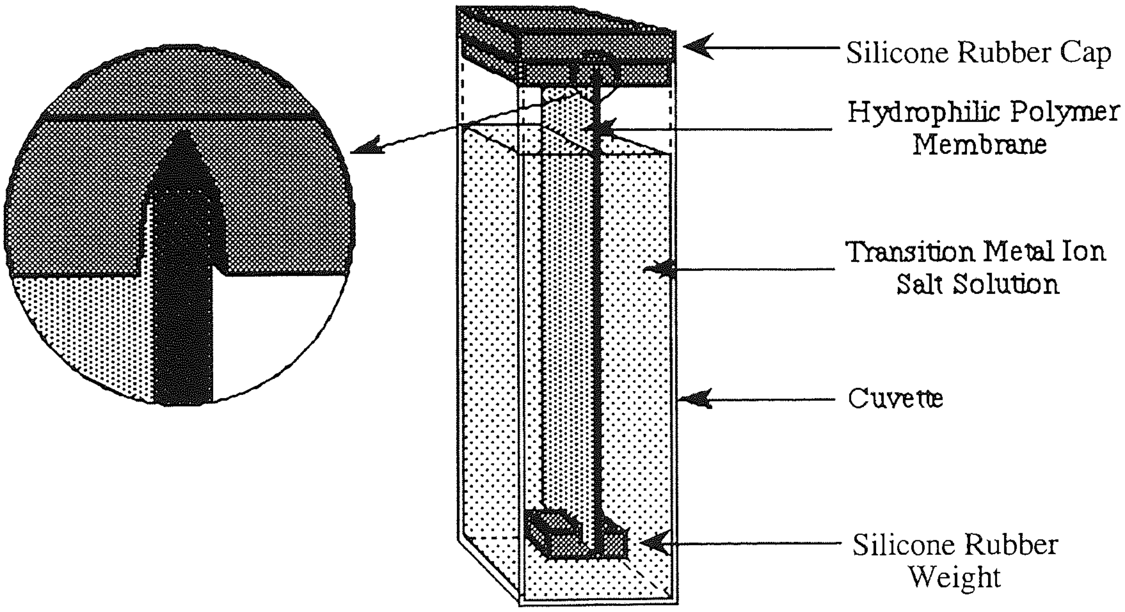
In this study, the UV/Visible spectrophotometer used was a Pye-Unicam SP8-100 double beam instrument.. This instrument possesses a wavelength range of 190-890nm and a variable band width of 0.2-1mm. In a previous study[21], the instrument was interfaced with a BBC micro-computer for data collection and storage purposes. The computer was dispensed with during this study in favour of fitting a four-cell carriage, capable of being thermostatted, into the spectrophotometer. While this meant that manual data collection had to be employed, the time saved by being able to run four experiments concurrently more than compensated for the operator time consumed by the method.

2. 8. 2 Membrane Studies using UV/Visible Spectroscopy

The membranes produced by the copolymerisation of the vinylic bipyridine compounds with HEMA are optically clear, absorbing radiation only in the UV region of the spectrum (<300nm). Those membranes produced with divinylsalen as comonomer with HEMA possess an absorption, due to the ligand at around 340nm. When placed in a TM saltsolution, the membranes may be expected to coordinate TM ions and thus give rise to new absorption bands. This is indeed the case.

In the previous study[21], difficulty was found in keeping the hydrogel samples (membrane strips of dimension 4cm x 1cm) flat and upright within the cuvettes, regardless of their path length. As a result, the samples were allowed to adhere to the cuvette surface. Using this technique, spectra and absorption readings had to be taken quickly to avoid dehydration of the membranes, caused by warming from the sample beam and the general instrument conditions. The dehydration of the membranes led to their contracting away from the surface of the cuvette and hence they did not remain square to the sample beam. Here, the hydrogel samples were fixed into cuvettes containing the appropriate TM salt solution (or distilled water) by means of caps and weights made of silicone rubber, as shown in Figure 2.5. This arrangement ensured that the membrane remained square to the sample beam for the course of the experiment.

Figure 2.5 Arrangement for holding Membrane Samples in Cuvette



2. 8. 3 Ion-binding Studies Using UV/Visible Spectroscopy

When complex formation gives rise to a visible absorption, if Beer's law (equation 2.4) is obeyed, the concentration of the species causing that absorption is proportional to the absorbance observed. By choosing a region of the spectrum where the absorption is due to one species only, the coordination process can be followed spectrophotometrically by making absorbance measurements at that particular wavelength as a function of time.

Using the arrangement described previously, membrane strips (4cm x 1cm) could be placed in cuvettes containing the appropriate TM salt solution. This assumes that the salt solution did not itself possess an absorption which would interfere with that of the complex under study. The membrane is held rigidly by the arrangement and does not move when placed in the thermostatted cell carriage. In this way, the sample could remain in the spectrophotometer and the absorbance reading could be read simply from the spectrophotometer LCD display.

This method has obvious advantages over that used previously[21], where the membrane strips were removed from thermostatted bottles containing the appropriate TM salt solution, their absorbances read, and the strips returned to the salt solution. The earlier procedure introduced further error associated with the absorbance readings and was difficult to execute.

2. 9 Mechanical Property Measurement

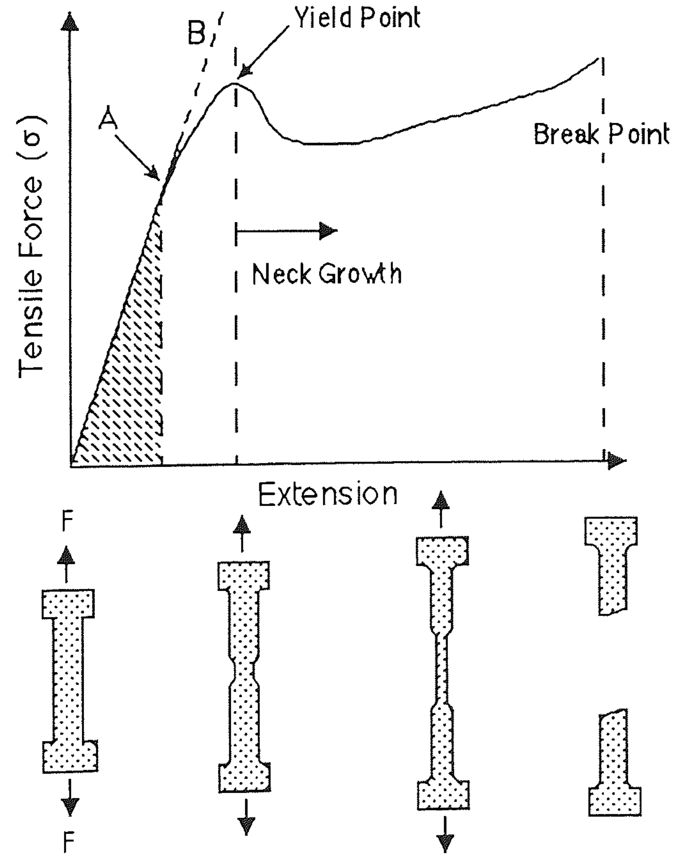
The investigation of the mechanical properties of hydrogel-based polymers is a well-characterised area of research at Aston[34]. These studies include simple tension and, to a lesser extent, shear and uniform compression studies. Such experiments are of limited use within this study. However, noticeable changes in mechanical properties do occur as the degree of cross-linking changes. The data that may be obtained from stress-strain measurements are important here, as they provide information on the modulus, brittleness, ultimate strength and yield strength of the material. It is these properties that alter significantly with the degree of cross-linking. These studies were undertaken in order to evaluate the cross-linking abilities of the divinyl ligand monomers synthesised as described previously.

2. 9. 1 Instrumentation and Procedures

A 20KM Hounsfield Tensometer with a 10N load cell was employed for the tensile testing of the copolymers. This is interfaced with an IBM 55SX computer, which drives the equipment and facilitates data handling via customised software.

When a 'dumbbell-shaped' sample is subjected to a tensile force applied at a uniform rate, a trace resembling the hypothetical curve in Figure 2.6 can be obtained.

Figure 2.6 Hypotheical Stress-Strain Curve



The tensile strength of a material (σ) is a measure of the force per unit area (F/A), while the strain (or elongation) (ε) is defined as the extension per unit length. The two are related by equation 2.5, where E is a proportionality constant known as Young's modulus.

$$\sigma = E\varepsilon \qquad \text{equation 2.5}$$

The slope of the initial linear portion of the curve is used to obtain E. Point A defines the point after which a brittle material will fracture, the shaded area under the curve being proportional to the amount of energy needed for brittle fracture to occur. In tougher materials, fracture does not occur at this point and the curve proceeds through a maximum known as the yield point. From this point until the sample reaches its ultimate extension and hence its breaking point, 'necking' occurs. The energy required for tough fracture is defined by the area under the curve to this point.

Many factors can affect the shape of such curves, and all parameters must remain constant if any significant comparisons are to be drawn from the data obtained. Previous investigations[34] have defined the fixed parameters and these parameters were chosen for this study. They include:

<u>(i) Temperature</u>	Room Temperature (~21°C) is the standard temperature.
<u>(ii) Humidity</u>	To obtain consistency in the tensile strength readings for hydrogel polymers, it is essential that they be kept in a hydrated state. As underwater testing would be impractical, a fine mist of water is sprayed periodically onto the sample. This appears to maintain the water content balance of the sample, providing 100% humidity.

(iii) Strain rate	A constant strain rate of 200%/minute was used in this study. The rate at which samples under tension are stretched affects the mechanical properties. Faster rates of extension lead to higher observed strengths, but lower extensions.
(iv) Sample dimensions	A constant sample size was employed. Membrane thickness was measured by micrometer to allow stress-strain calculations. The dumbbell shape was chosen as it produces a more uniform stress field. The wider portions of the sample fit within the tensometer jaws and the gauge length (the distance between the wider end portions) was 8mm.

2. 10 Transition Metal Ion Permeation Studies

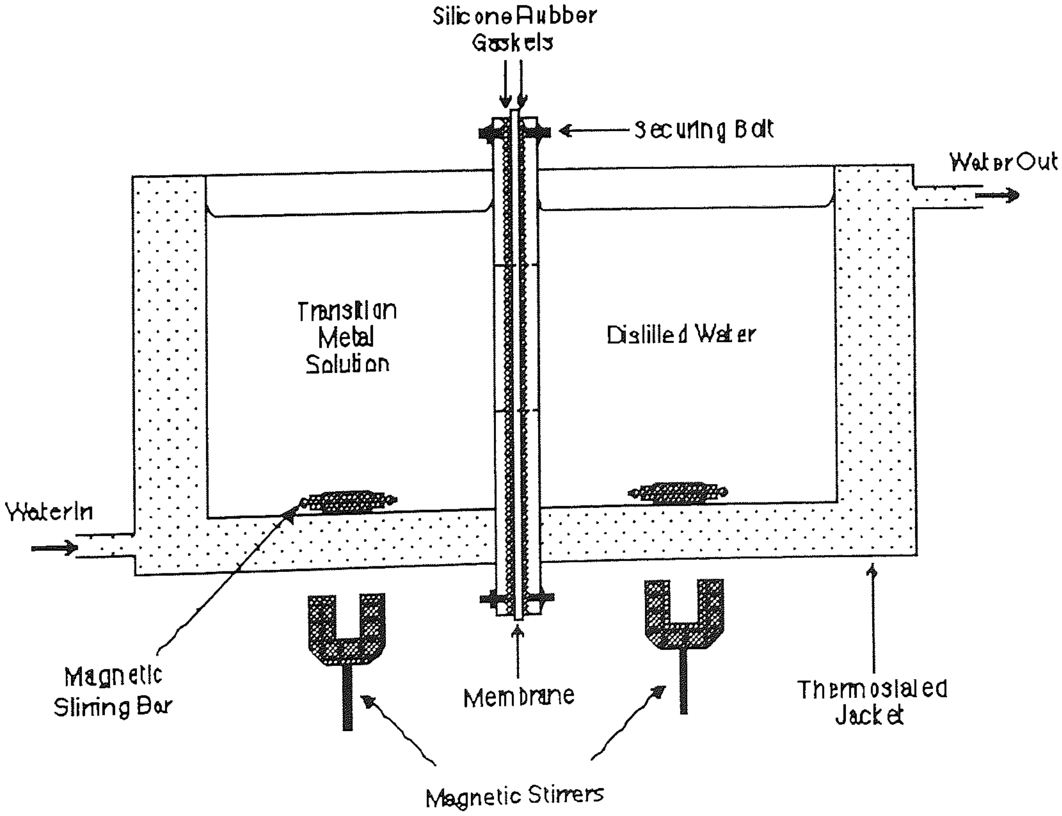
Previous work within the Speciality Materials Research Group at Aston has studied the transport of alkali and alkaline earth metal ions through crown ether modified poly(HEMA)[36]. A second study[21] examined the transport of first-row transition metal ions through poly(HEMA)-based membranes with pyridine and 2,2'-bipyridine as the appended modifying ligands. The former study identified the potential for ion-selective transport and separation, while the latter indicated anti-selective transport of the metal ions. During this work, the transport of first-row transition metal ions through salenH_2-modified poly(HEMA) membranes has been studied, along with the permeation of chromium (III) through bipyridine modified poly(HEMA) membranes.

The construction of a suitable permeation cell is of paramount importance to the success of such transport studies. The design must take account of many experimental variables (temperature, concentrations, stirring rates and ease of sampling) along with membrane parameters (thickness, area and integrity). Many cell prototypes may be found in the literature[124], despite the constraints imposed. They are usually classed by the manner of membrane placement, i.e. horizontal or vertical. The permeability cell used in this study will now be described.

2. 10. 1 Permeability Cell Design

The main features of the cell used in this study are shown in Figure 2.7. This cell design was employed by Lewis[21] when investigating the transport of mixed metal solutions. The apparatus was found to be suitable for the study of single metal ion permeation. The only alteration was the use of a dip conductivity cell, as opposed to the flow-through conductivity cell employed by Lewis for single ion transport and the atomic absorption technique that he utilised for multiple ion transport.

Figure 2.7 Permeability Rig



The permeability cell was fabricated from perspex. This allowed the condition of the fragile membranes to be examined during the course of each experiment. The cell itself comprised two chambers (8cm ht x 7cm lg x 5cm dp), with one side of each chamber acting as a backing plate (15cm x 14cm with a 4cm diameter hole). The membrane under test was placed between two silicone rubber gaskets of the same dimensions as the backing plates. The backing plates were then bolted 'back-to-back' around the gaskets to complete the membrane sandwich. A water jacket surrounded the chambers on all sides, the temperature being set by a thermostatically controlled circulating water bath connected to the jacket. The top of each chamber was left open, enabling the conductivity cell and accompanying thermocouple to be placed in the low concentration chamber. While the vertical positioning of the membrane overcomes problems with hydrostatic pressure build up and the collection of air bubbles found when the membrane is horizontally oriented, stirring near to the membrane in this array is rendered more difficult. To ensure prevention of an electrical double-layer build-up close to the membrane due to ion migration, stirring at the bottom of each chamber was employed and found to be satisfactory.

Cells of similar design have since been reported in the literature. Indeed, an identical stirring mechanism was used in the apparatus of Uragami *et al.* [124].

2. 10. 2 Conductometric Study of TM Ion Transport

The permeability cell was assembled with a membrane disc, minimum diameter 5cm, sandwiched between the silicone rubber gaskets as described previously. The conductivity cell (cell constant k= 1) was connected to an AGB-1000 conductivity meter (Canterbury Scientific Instruments). The conductivity meter was interfaced with a BBC microcomputer, *via* the chart recorder output. The conductivity apparatus had been previously calibrated using a 1mM KCl solution as per the instructions provided. The conductivity cell was placed in one chamber of the empty permeability rig, along with its accompanying thermocouple. This chamber was designated as the low concentration side. Into this chamber was poured deionised water, while the TM ion test solution was poured into the remaining chamber at the same time. Each chamber contained the same volume of liquid so as to maintain an equal hydrostatic pressure on the membrane. Unequal hydrostatic pressures would cause the membrane to bulge to one side, potentially leading to damage of the membrane and affecting its transport properties. The stirrers were operated and the permeation process was followed by the BBC microcomputer, which used a BASIC program called CONDUCTIPLOT, as written by Lewis[21], to collect and store the conductivity meter readings at specified time intervals.

2. 10. 3 Conductivity Cell Calibration

Calibration of the conductivity cell with solutions of known concentration was necessary in order to convert the observed changes in conductivity with the concentration of TM salt permeating through the membranes. The change in TM salt concentration in the low concentration side of the permeability rig was always relatively small during the time period used for these studies. In this range, conductivity varies linearly with concentration, and a number of standard solutions were used to construct a calibration graph for each of the TM salts involved in the transport studies. The gradient of the graph allows the conversion from conductivity (in μsiemens) to concentration (in $mMdm^{-3}$).

Calibration was achieved by simply dipping the conductivity cell into the standard solution (along with the thermocouple) and the reading taken from the meter. The cell was well washed with deionised water and the procedure repeated to see if a constant reading could be attained.

CHAPTER THREE

THE MECHANICAL PROPERTIES OF HYDROGEL POLYMER MEMBRANES CONTAINING PHYSICAL AND COORDINATIVE CROSS-LINKS

3.1 Introduction

During the course of this research, monomeric ligands possessing two potentially polymerisable vinyl functions were prepared, namely *bis*-(5-vinylsalicylidene)-diaminoethane, DVSALEN, and the DiHEMA ester of 4,4'-dicarboxy-2,2'-bipyridine, DHBPY (Figures 3.1 and 3.2).

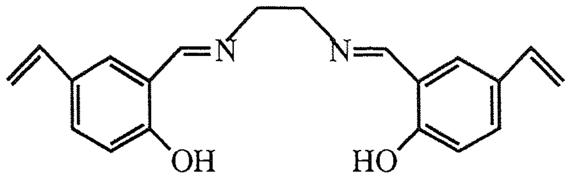


Figure 3.1 *bis*-(5-vinylsalicylidene) ethylenediamine(DVSALEN)

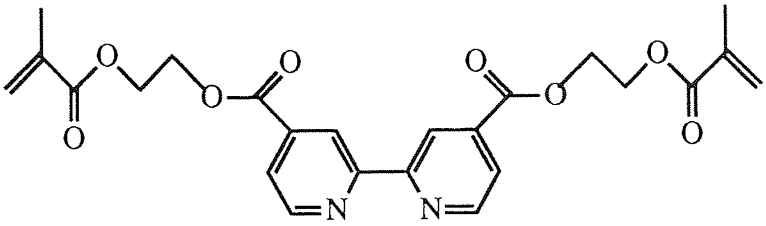


Figure 3.2 DHBPY

It is known that the amount of cross-linking agent employed in the fabrication of poly(HEMA) membranes has a significant effect on the properties of the polymer, for example on the equilibrium water content (EWC) and mechanical properties of the gel. It was anticipated that the copolymerisation of the aforementioned divinyl monomers with HEMA would lead to a measurable increase in cross-linking within the polymers.

Both monomers were found to be relatively insoluble in HEMA. As a result of this, the maximum ligand loadings were 1% DVSALEN and 0.5% DHBPY respectively. It is uncertain whether such low loadings are capable of producing significant effects on the properties of the copolymers. Certainly, the changes in polymer properties will be lower than those found by Lewis[21], using pyridine- and 2,2'-bipyridine- modified polymers, where the maximum ligand loadings were 16% and 8% respectively.

There is a possibility of further cross-linking, *via* coordination to metal ions, in the case of DHBPY. It has been demonstrated that the formation of *tris*-iron(II) complex centres in VBPY-HEMA copolymers leads to an increase in mechanical strength, an effect also observed for *tetrakis*- copper (II) complex centres of polymer-immobilised pyridine ligands[136]. Such coordinative cross-linking has been reported by Kopeikin[137] in chelating polymers containing the acetylacetate (acac$^-$) group, and by Eichinger *et al.*[138], who have developed spectroscopic means for examining the *bis*- and *tris*-complexes formed by these polymers with Cu(II), Fe(III) and Cr(II). Their work has also extended to include a novel approach to the investigation of the effects of "coordination cross-linking", *via* a study of the mechanical properties of the polymers[139]. This remains one of the few reports of its kind.

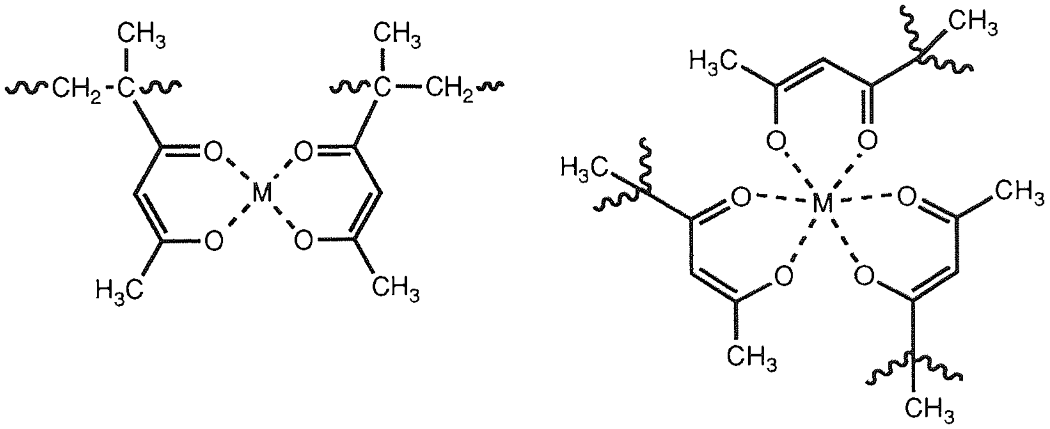


Figure 3.3 Polymer Immobilised *bis*- and *tris*- (acac) Complexes[137]

The chance of coordinative cross-linking is unlikely in the case of DVSALEN, as this chelating ligand generally coordinates to transition metal ions in a tetradentate manner. There remains a slight possibility for such cross-linking, but only if each ligand group behaves in a bidentate manner towards each of two metal ions.

In addition to the investigation of mechanical properties of these polymers, the effect of chromium(III) coordination on the properties of VBPY-modified membranes has also been studied.

Due to the wide use of hydrogels in the contact lens industry, there has been extensive use of mechanical characterisation techniques for the study of the physical properties of cross-linked gels[34]. Such approaches are obviously applicable to the chelating membranes prepared during this project. The tensometric methods used in the study of the mechanical properties of these polymers have been described in Chapter 2.9, and were employed to investigate the physical traits shown by the ligand-HEMA copolymers.

3. 2 Membrane Composition and its Effects on Mechanical Properties

In the fabrication of the homo- and co- polymers based on HEMA described in Chapter 2.6, 1% w/w of the cross-linking agent ethylene glycol dimethacrylate, EGDM, was routinely employed. With this low percentage of cross-linker, the polymers produced have relatively poor mechanical properties. They are soft materials which are capable of moderate elongation prior to failure, with typical tensile strengths of 0.5MPa and elongations to break (ε_b) of around 200%. If no cross-linking agent is employed in the polymerisation process, then linear polymers are formed which cannot exist in a membrane form. These linear polymers, on addition of water, give rise to milky solutions. However, it is found that there is almost always some residual cross-linker in samples of 'pure' HEMA.

Copolymerisation of HEMA with more hydrophobic monomers, e.g. styrene and methyl methacrylate, causes an increase in tensile strength (σ) and a reduction in ε_b. This occurs as the polymer changes from being flexible to behaving in a more rigid manner, due to the decrease in the plasticising bulk 'freezing' water content of the gels.

Lewis showed that the copolymerisation of HEMA with his vinylpyridine and vinylbipyridine derivatives has a different effect[21]. As the ligand content of the copolymer increases, only slight decreases in EWC, consistent with the addition of more hydrophobic components, occurred. However, for both sets of copolymers, an increase in ligand comonomer concentration led to an increase in both σ and ε_b. He attributed these observations to the hydrogen-bonding abilities of the heterocyclic nitrogen atoms. Temporary cross-links may be formed via weak hydrogen-bonding interactions between polymer chains leading to an improved strength and an increased elongation to break. The presence of the two hydroxyl functions in DVSALEN may also give rise to such an effect, although it may not be noticed due to the low ligand loadings.

3. 3 The Mechanical Properties of DVSALEN-HEMA Copolymer Membranes

It was thought that the DVSALEN ligand, by way of its two polymerisable vinyl groupings, may act as a cross-linking agent when copolymerised with HEMA. To test this hypothesis, two sets of copolymer membranes were fabricated:-

(i) Membranes made using the standard technique, i.e. the copolymerisation mixture contained 1% EDGM as cross-linking agent.

(ii) Membranes made without 1% EDGM included in the copolymerisation mixture, i.e. leaving DVSALEN as the only potential cross-linker.

The equilibium water contents (EWC) of each membrane were also calculated. There is no significant variation in EWC with increasing DVSALEN content for either set of copolymers, although those membranes containing both EDGM and DVSALEN have lower EWC than those polymers that do not contain EDGM, the values being around 37.5% and 39.5% respectively. The results obtained from testing both sets of polymers are shown in Table 3.1.

Table 3.1 Mechanical Property Data for DVSALEN-HEMA Membranes

Membrane Polymer Type	Modulus (E_{25}, %)	Tensile Strength (σ, MPa)	Elongation to Break (ε_b, %)
EDGM Added			
0% DVSALEN	0.49 ± 0.01	0.64 ± 0.11	166 ± 28
0.1% DVSALEN	0.46 ± 0.02	0.72 ± 0.11	196 ± 34
0.25% DVSALEN	0.45 ± 0.02	0.69 ± 0.13	192 ± 39
0.5% DVSALEN	0.43 ± 0.03	0.64 ± 0.17	190 ± 58
1% DVSALEN	0.5 ± 0.04	0.85 ± 0.19	204 ± 47
No EDGM Added			
0.1% DVSALEN	0.15 ± 0.1	1.26 ± 0.17	745 ± 63
0.25% DVSALEN	0.16 ± 0.01	1.13 ± 0.11	692 ± 47
0.5% DVSALEN	0.16 ± 0.02	1.61 ± 0.2	758 ± 65
1% DVSALEN	0.14 ± 0.001	1 58 ± 0.06	814 ± 11

Examination of the data shows that the addition of up to 1% DVSALEN to the copolymer mixture has little or no effect on the mechanical properties of those copolymers which already contain EDGM as a cross-linker. Within experimental error, the ε_b values are consistent, in the region of 200%, and there is little variation in σ or in the modulus (E) for these copolymers. In those copolymers where EDGM was not employed, we find an increase in σ and a marked increase in ε_b. This is accompanied by an appreciable lowering of the modulus. The marked differences between the two types of polymer are shown graphically in Figures 3.4 (a), (b) and (c) respectively.

Figure 3.4 (a) Effect of Cross-Linker on E in DVSALEN-HEMA Copolymers

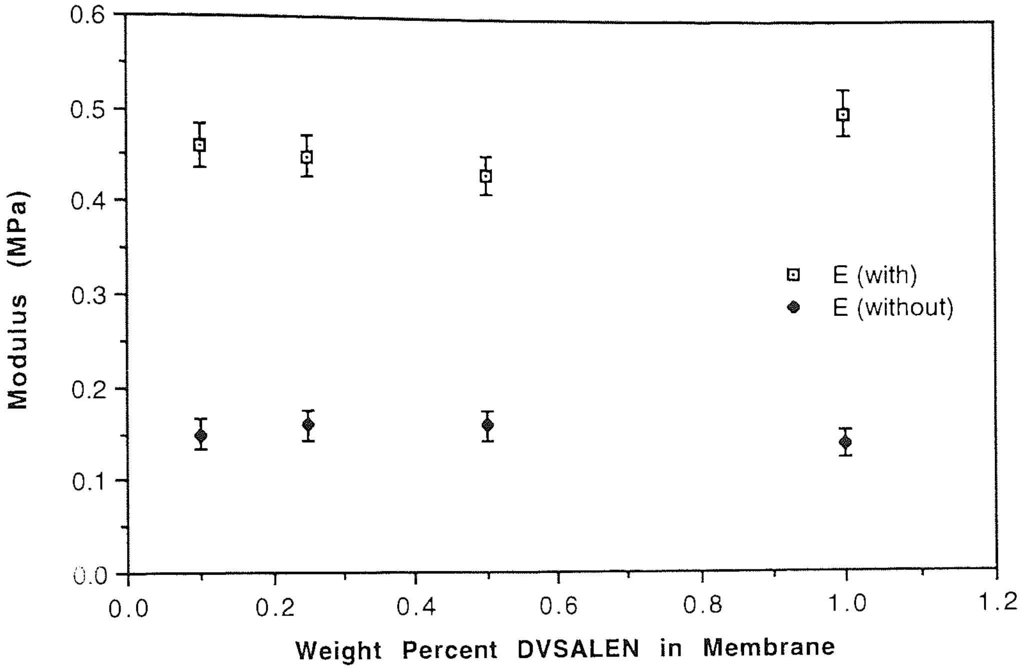


Figure 3.4 (b) Effect of Cross-Linker on σ in DVSALEN-HEMA Copolymers

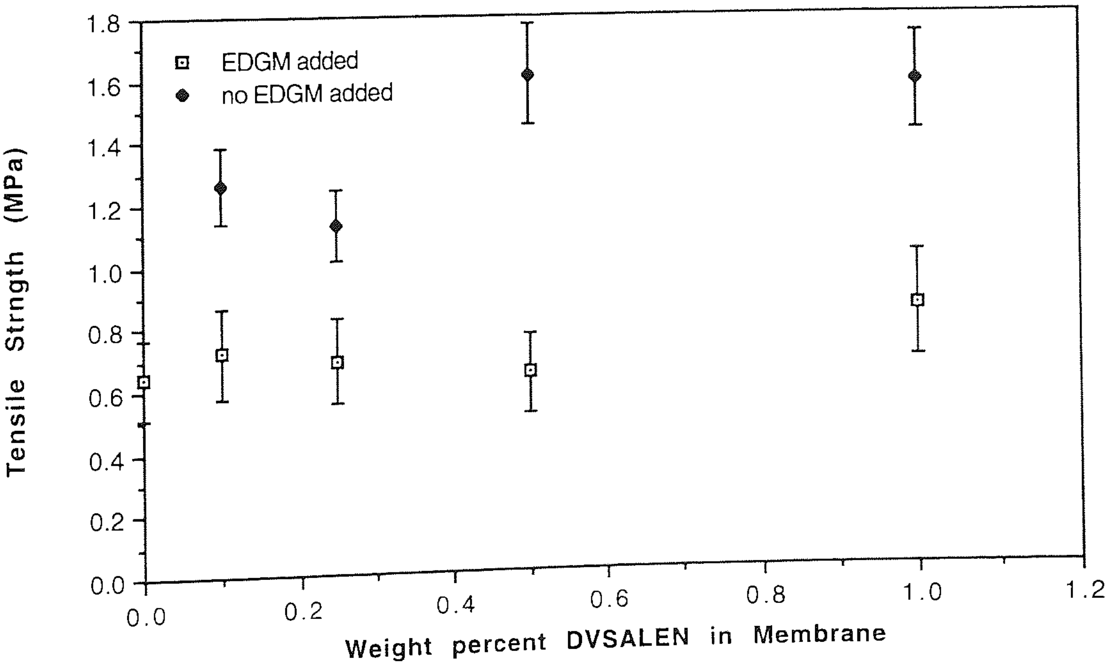
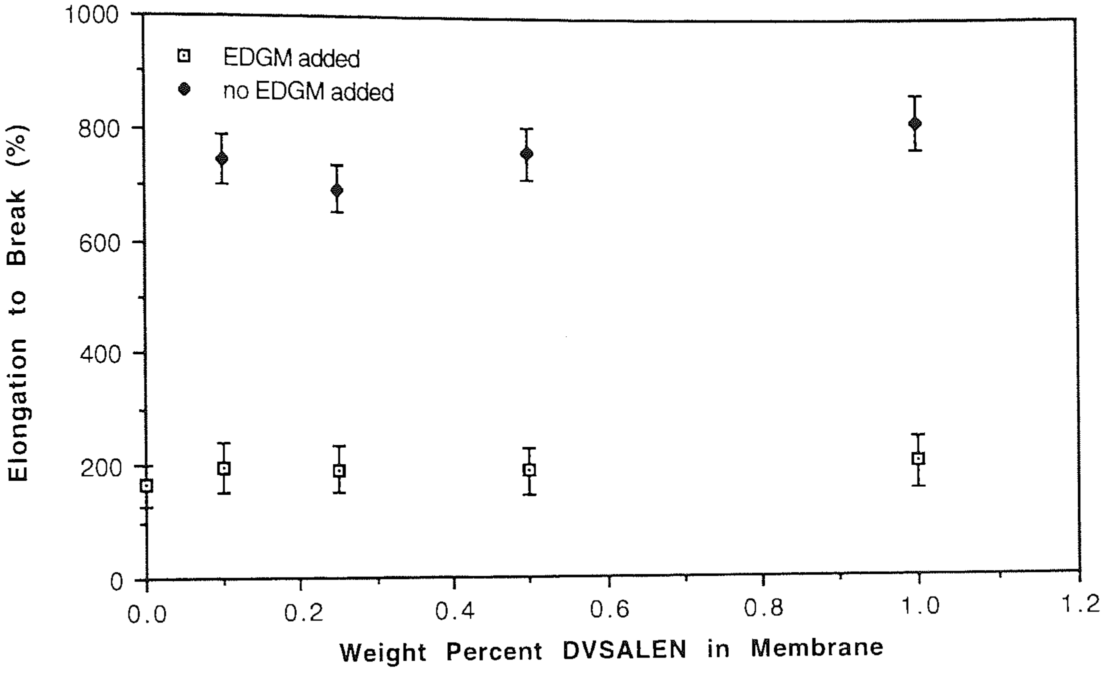


Figure 3.4 (c) The Effect of Coss-Linker on ε_b in DVSALEN-HEMA Copolymers



When no EDGM is added to the copolymerisation mixture, the resulting polymer behaves in an elastomeric manner. This is indicated by both the sharp decrease in the value of the modulus and the load versus elongation curves, where the breaking point of the polymer occurs long after the yield point has been passed. For the EDGM-containing polymers, the modulus is greater and the curves are indicative of a more rigid material, i.e. there is little deformation between the yield point and the breaking point of the material.

All the evidence implies that DVSALEN shows either no or only a slight ability to act as a cross-linking agent in these sytems. The large values of ε_b found for those materials where no EDGM is present point to materials which are very flexible, with the scant mechanical strength possessed by these materials perhaps being due to residual cross-linker present in the HEMA monomer and a small contribution from DVSALEN itself. Also, the fact that there is no significant change in the properties of those copolymers where EDGM is present as the proportion of DVSALEN increases, implies that little or no additional cross-linking has occurred as a result of the presence of DVSALEN.

3. 4 The Mechanical Properties of DHBPY-HEMA Copolymer Membranes

The ligand DHBPY was initially prepared to investigate the effect of a 'spacer' group, between the polymer chain and the active ligand site, on the coordination of metal ions by copolymers containing the ligand. The surprising insolubility of the monomer in HEMA limited its use during this research. However, copolymers containing 0.5% w/w DHBPY were prepared. As in the case of the DVSALEN membranes, in one case EDGM was omitted from the copolymerisation mixture in order to gauge the effectiveness of the ligand as a cross-linking agent.

Additionally, for these copolymers, the membranes were allowed to soak in an aqueous iron(II) solution. Visible and spectroscopic examination of the membranes showed that formation of the iron(II) *tris*-2,2'-bipyridine complex had occurred, an absorbance maximum for the soaked membranes appearing at 543nm, c.f. λ_{max}=535nm for free *tris*-VBPY-Fe(II) and λ_{max}= 534nm for polymer bound *tris*-VBPY-Fe(II).

0.5% DHBPY COPOLYMER	**ABSORBANCE AT 543nm**	**[FeL_3] in membrane** (moles/cm^2)
Uncomplexed - no added EDGM	0	0
Uncomplexed - EDGM added	0	0
Pre-Complexed - no added EDGM	1.1	1.3×10^{-7}
Pre-Complexed - EDGM added	0.85	1.1×10^{-7}

The absorbances for the copolymers are given above. For iron(II)-*tris*(bipy) complexes in solution $\varepsilon \approx 8000 M^{-1} cm^{-1}$. Using this value of ε and applying it to the DHBPY-HEMA membranes gives the concentration of *tris*-complex within the membrane. In a 0.5% DHBPY copolymer membrane, there will be 3.4×10^{-7} moles of monomeric ligand per cm^2 of membrane. The above absorbance measurements therefore suggest that most or all of the appended ligand groups are present in *tris*-complexes.

As can be seen, the absorbance values are very similar. The lower value for the pre-complexed membrane which also contains EDGM as a cross-linker, can perhaps be attributed to the physical cross-links provided by the added EDGM hindering the formation of the *tris*-centres in comparison with the copolymer made without the addition of EDGM. After this soaking period, the mechanical properties of the complexed membranes were tested. The results of the testing of both uncomplexed and pre-complexed membranes are shown in Table 3.2.

In contrast to DVSALEN, the DHBPY ligand appears to have the ability to act as a cross-linking agent. At the 0.5% w/w loading and with no EDGM present, the ε_b is far lower than those values obtained for the DVSALEN copolymers, while both the modulus and σ are greater. When EDGM is present along with DHBPY, the mechanical properties are of the same order as those found for membranes where EDGM is the sole cross-linker. There is, however, a fall in the value of ε_b, indicating a slightly more brittle material than one might expect if only EDGM were acting as cross-linker. It can be seen that although DHBPY confers some cross-linking ability, it is not as effective as EDGM as a cross-linking agent.

Table 3.2 Mechanical Property Data for DHBPY-HEMA Membranes

Membrane Polymer Type	Modulus (E_{25}, %)	Tensile Strength (σ, MPa)	Elongation to Break (ε_b, %)
Uncomplexed			
No Added EDGM			
0.5% DHBPY	0.31 ± 0.02	0.61 ± 0.03	285 ± 26
EDGM Added			
0% DHBPY	0.49 ± 0.01	0.64 ± 0.11	166 ± 28
0.5% DHBPY	0.53 ± 0.02	0.59 ± 0.05	147 ± 21
Pre-Complexed			
No Added EDGM			
0.5% DHBPY	0.23 ± 0.005	1.76 ± 0.29	626 ± 53
EDGM Added			
0.5% DHBPY	0.49 ± 0.05	1.12 ± 0.27	252 ± 45

The results obtained from the iron(II)-soaked copolymers are somewhat surprising. In contrast to the findings of Lewis, for VBPY-HEMA copolymers, the addition of iron(II) does not appear to improve the mechanical strength of the polymers. The existence of iron(II) *tris*-2,2'-bipyridine centres within the polymer matrix is indicated by the ruby colour of the membranes. However, the effect of these coordination centres on the strength of the membrane appears to have been swamped. Indeed, the presence of the complexes has the effect of making the materials less rigid and behave in a more elastomeric manner, indicated by the increase in both σ and ε_b and the decrease in the modulus.

The difference in ligand must be taken into account when trying to explain the findings of these experiments. For VBPY-HEMA copolymers, the amount of polymer rearrangement required for the formation of *tris-* complexes will be far lower than the rearrangement required in DHBPY-HEMA copolymers, where the ligand grouping is more bulky. Also, for this latter group of copolymers, the reorientation of the ligand will also affect its ability to act as a physical cross-linking agent in its own right.

It should be remembered that the presence of the coordination centres within the polymer matrix leads to an increase in the amount of water associated with the polymer. Additional quantities of water will now be present, which are associated with the metal cation and its counter anions. As water within the gel acts as a plasticising agent, the increase in the amount of imbibed water should lead to the material behaving in a more elastomeric fashion.

It is perhaps a balance of these factors that leads to the more elastomeric behaviour of the iron(II)-soaked DHBPY-HEMA copolymer membranes, namely

(i) that the presence of cordination sites, be they mono-, bis-, or tris-, causes an increase in the bulk water within the gel ,leading to a plasticising effect.

(ii) the presence potential cross-linking provided by the metal-centred cross-links is replacing the original, more effective "form" of cross-linking, i.e. that complex formation has, along with introducing plasticising water, detrimentally affected the way in which the DHBPY ligand acts as a cross-linker.

3. 5 The Mechanical Properties of VBPY-HEMA Copolymer Membranes Containing Chromium (III) Metal Ions

The work of Lewis[21] clearly demonstrated the existence of coordinative cross-linking in his pyridine- and bipyridine- modified polymer membranes, with copper(II) and iron(II) respectively as the coordinated metal ions. As chromium(III) is known to form a very stable *tris*-complex with 2,2-bipyridine, this coordinative cross-linking should again be evident.

The copolymers were tested in an uncomplexed state and were then soaked for nine months in 0.25M solutions of chromium(III) nitrate. This extended period of soaking was employed to ensure that the ligand substitution reaction on the chromium(III) ions, which is extremely slow, was allowed to occur. It is also known that ligand substitution reactions in polymeric matrices are far slower than in solution, e.g. $[Fe(bipy)_3]^{2+}$ formation occurs in milliseconds in solution, but takes around half an hour within VBPY-HEMA copolymers[21]. Visible inspection of the copolymer membranes indicated that coordination of chromium within the gels had occurred, with a red colouration, indicative of chromium(III) *tris*-2,2'-bipyridine centres, appearing. The visible spectra of the respective complexed membranes show a broad absorption band with $\lambda_{max} \approx 535$nm. The visible spectrum absorption around 535nm has been measured and we find that the absorbances for the various copolymers are as given below.

LIGAND LOADING	**ABSORBANCE AT 535nm**
1%	**0.23**
2%	**1.68**
4%	**2.98**

Greater *tris*-centre formation is obviously being encouraged at higher ligand loadings, as would be expected purely from an equilibrium point of view. It is possible to calculate the concentration of complex centres within the membrane if values of ε are known. For the parent $[Cr(bipy)_3]^{3+}$ complex, $\varepsilon=91$[140]. Using this value, the maximum absorbance possible for the membranes tested would be 0.15, 0.3 and 0.6 respectively. If we invoke the principle of equivalent extinction coefficient, $\varepsilon\varepsilon_l$, as defined by Lewis & Miller[141], then we can use the obseved absorbance values and find a value of $\varepsilon\varepsilon_l \approx 500M^{-1}cm^{-1}$. This would give a value for a *tris* complex of $e \approx 1500M^{-1}cm^{-1}$. This implies that the coordination centres being formed cannot be *tris* in nature. The large value of ε also implies that the complexes have less than octahedral geometry.

The mechanical properties of the complexed copoplymer membranes were then tested. The results of the mechanical testing of both sets of copolymer are shown in Table 3.3.

For the uncomplexed membranes, there appears to be no significant rise in the value of σ as the VBPY content increases, a trend which was observed by Lewis. There is a jump in the value of ε_b from PHEMA to the copolymers, again confirming Lewis's observation, but there is no discernible trend in the values.

When the membranes have been allowed to soak in chromium(III), there is an obvious increase in the mechanical strength of the materials. There is, as the ligand loading increases, an increase in both the modulus and σ, while there is a concomitant decrease in ε_b. This is consistent with the materials becoming stronger and more brittle. This must be due to the effect of the coordinative cross-linking introduced by the chromium(III) complexes formed by the ligand-modified polymers.

Table 3.3 Mechanical Property Data for VBPY-HEMA Copolymer Membranes - Uncomplexed and Chromium(III) Pre-Complexed

Membrane Polymer Type	Modulus (E_{25}, %)	Tensile Strength (σ, MPa)	Elongation to Break (ε_b, %)
Uncomplexed			
0% VBPY	0.49 ± 0.01	0.64 ± 0.11	166 ± 28
0.5% VBPY	0.50 ± 0.01	0.73 ± 0.11	186 ± 25
1% VBPY	0.49 ± 0.03	0.75 ± 0.11	196 ± 30
2% VBPY	0.51 ± 0.01	0.70 ± 0.05	177 ± 13
4% VBPY	0.48 ± 0.04	0.71 ± 0.05	194 ± 22
Pre-Complexed			
0% VBPY	0.52 ± 0.04	0.81 ± 0.08	192 ± 26
1% VBPY	0.61 ± 0.01	1.01 ± 0.09	185 ± 12
2% VBPY	0.66 ± 0.04	1.06 ± 0.08	177 ± 14
4% VBPY	0.94 ± 0.07	1.36 ± 0.1	144 ± 7

Figures 3.5 (a), (b) and (c) show the effect on mechanical properties caused by increasing the VBPY content of the membrane.

Figure 3.5 (a) Effect of Cross-Linking on Modulus for VBPY:[Cr(III)] Polymers

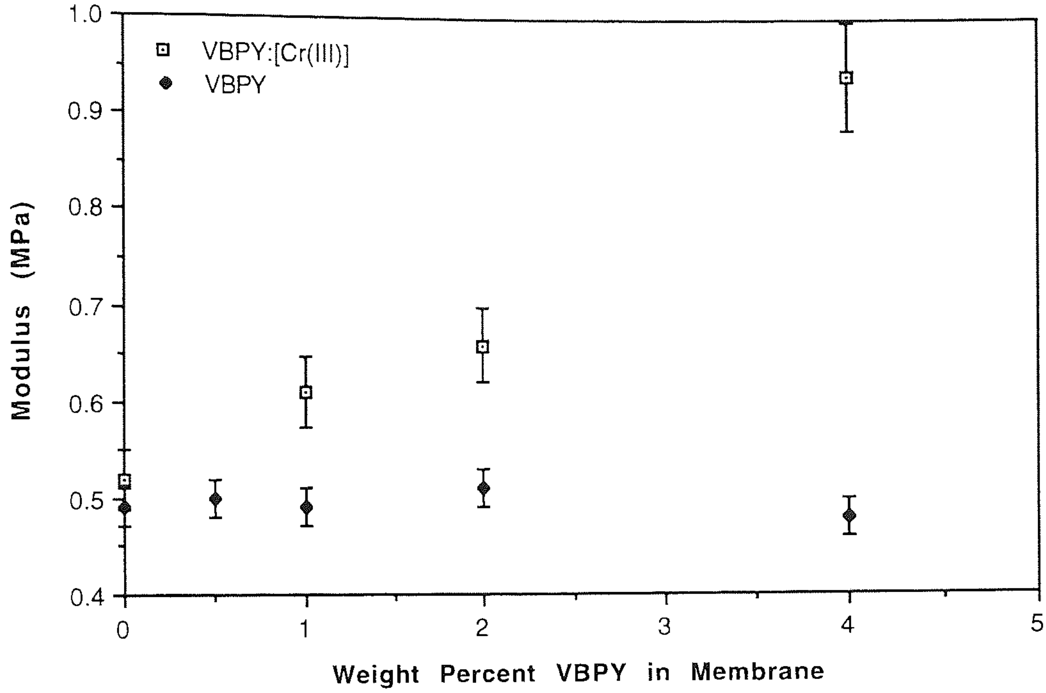


Figure 3.5 (b) Effect of Cross-Linking on σ for VBPY:[Cr(III)] Polymers

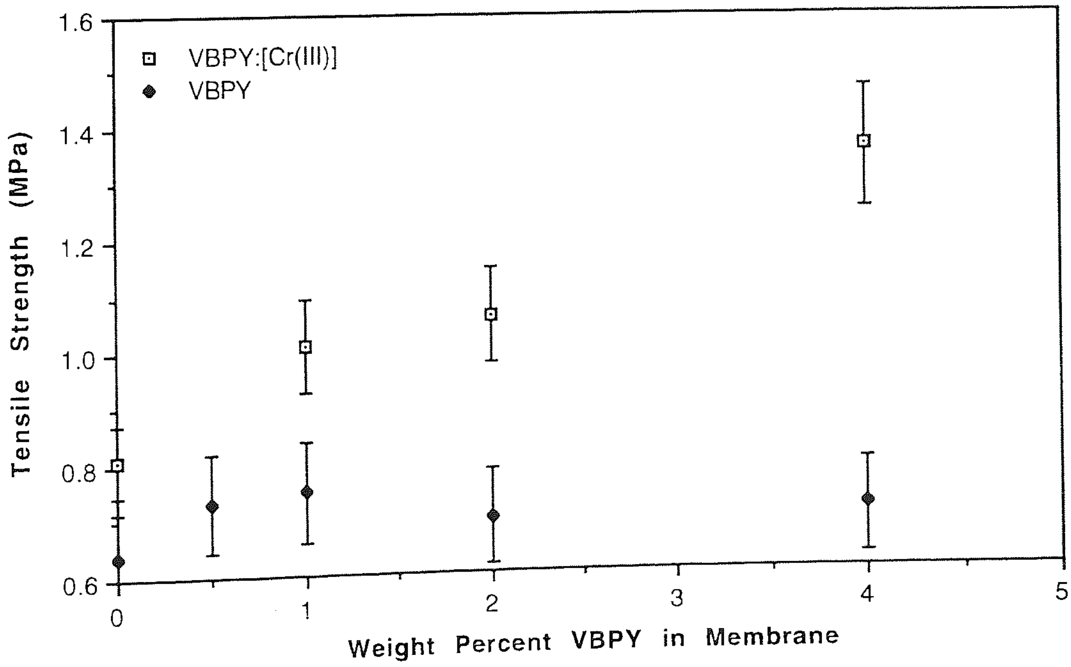
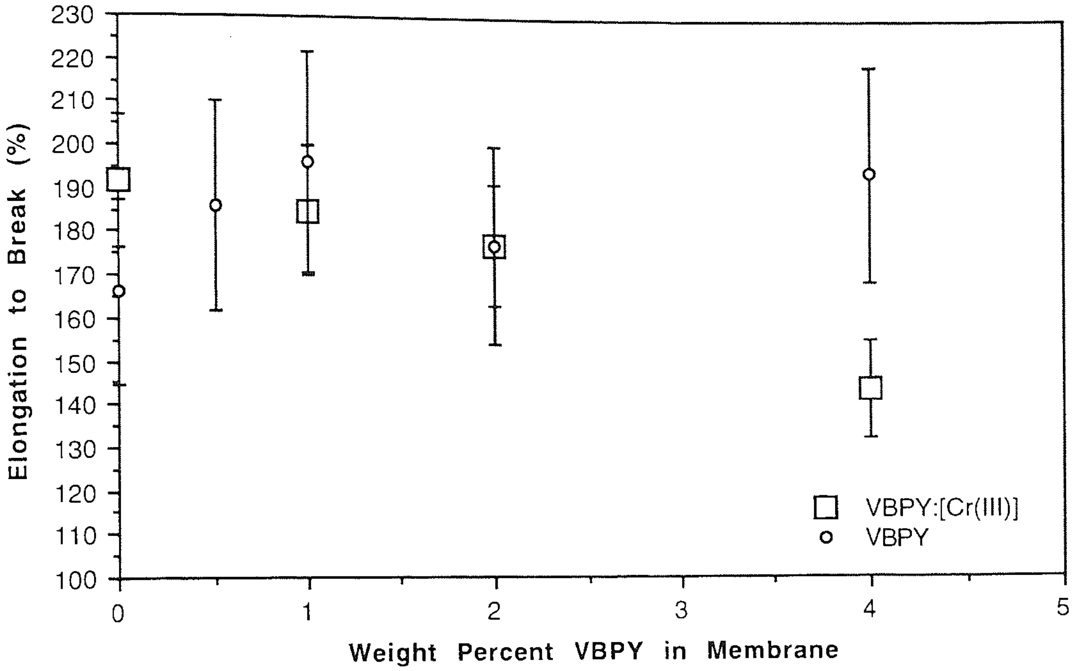


Figure 3.5 (c) Effect of Cross-Linking on ε_b for VBPY:[Cr(III)] Polymers



For the chromium(III)-containing VBPY-HEMA copolymers, the coordinative cross-linking effect is not as great as that observed by Lewis when he allowed iron(II) complexation to occur in the same family of polymers. In that case the materials became extremely brittle, while for the Cr(III) cross-linked polymers the trend towards increased rigidity is less pronounced. This lesser trend towards rigidity can perhaps be explained in the same manner as the elastomeric behaviour of the iron(II)-soaked DHBPY-HEMA copolymers, namely the incorporation of the large amounts of solvating water molecules into the structure.

The greater complex formation being encouraged at higher ligand loadings, as would be expected purely from an equilibrium point of view, presumably leads to the increase in rigidity through the series of copolymers. However, it is not known precisely what kind of complexes have been formed. The rate of ligand substitution around chromium(III) is very slow and the process will be further hindered by the need for the polymer to rearrange so that the ligand molecules are correctly oriented. When comparing iron(II) with counter anions for the latter metal ion and that this will cause a larger amount of water to be imbibed by the polymer. This plasticising water will have a great dominance over the mechanical properties of the copolymer membrane. Thus, there will be a balance between the plasticing tendencies of the imbibed water and the cross-linking abilities of the metal-centred cross-links.

3.6 Summary

The mechanical properties of copolymers of HEMA with two divinyl monomers have been studied. In the case of DVSALEN-HEMA copolymers, little or no mechanical strength is conferred by the ligand monomer, leading one to conclude that DVSALEN is, at best, a very inefficient cross-linking agent.

When dealing with DHBPY-HEMA copolymers, the ligand does show the ability to act as a cross-linking agent. However, on complexation with iron(II) ions, there is a decrease in the mechanical strength of the copolymers, despite the formation of *tris-* complexes which might be expected to provide additional cross-linking and, hence, extra mechanical strength. This phenomenon has been explained via a mixture of potential causes. These are (i) that physical cross-linking can impede metal ion complexation, (ii) that metal ion complexation introduces plasticising water into the polymer matrix, and (iii) that the effect of coordination is to replace the original, more effective cross-linking of the ligand monomer.

Additionally, the mechanical properties of uncomplexed and chromium(III) nitrate pre-complexed VBPY-HEMA copolymers have been investigated. Here, coordinative cross-linking is seen to occur and confer additional mechanical strength to the copolymers. The effect is not as pronounced as that found in iron(II) complexed VBPY-HEMA copolymers. This is attributed to the slow rate of complex formation exhibited by chromium in oxidation state III not permitting full *tris*- complex formation and to the effect of an additional counter anion (and its associated hydration sphere) entering the polymer matrix.

CHAPTER FOUR

THE COORDINATION OF COPPER (II) SALTS IN SALENH$_2$-MODIFIED HYDROPHILIC POLYMER MEMBRANES

4. 1 Introduction

The copper(II) complex of *bis*-(salicylidene)ethylenediamine, Cu(salen), has been known for many years, having been first isolated by Dubsky and Sokol in 1931[74], along with the nickel(II) analogue. Following this work, an enormous number of related quadridentate Schiff base complexes have been prepared and studied, for example in the extensive work of Pfeiffer *et al.* from 1931-1942[75-87]. Further studies, mainly in the 1960s, elucidated the structures of these molecules, e.g. Waters *et al.*[142] The dark green Cu(salen) complex is known to exist as dimers in the solid state. The dimers are caused by intermolecular Cu-O bonding, leading to *penta*-coordinated copper(II) possessing a pyramidal coordination sphere.

The spectral behaviour of Cu(salen) has also been studied[143], and it is found that a very intense absorption band appears in the region of 400nm. The value of the extinction coefficient (ε) for the band suggests that the band is *charge-transfer* in nature, as ε is around 10^4. Another, far weaker absorption is found at 560-610nm, with an extinction coefficient of around 300. This may be attributed to forbidden *d-d* transitions. Both transitions are sensitive to changes in solvent.

The ligand *bis*-(5-vinylsalicylidene)ethylenediamine, DVSALEN, has previously been copolymerised by a number of other groups[102-104], usually with styrene as the comonomer. Akelah *et al.*[102] have examined such copolymers as potential metal complexing agents for the separation of metal ions. They measured the visible spectrum of Cu(DVSALEN) and also found a strong absorption band in the region of 400nm. This points to the use of this band in monitoring the reaction between copper(II) ions and the appended Schiff base ligand in the hydrophilic polymer membranes prepared during this research.

During this work, the visible spectra of the copolymers were obtained, using a pure PHEMA membrane as the reference. The ligand itself gives rise to a strong absorption band at around 400nm. This phenomenon was also observed by Akelah *et al.*[102] in their DVSALEN-styrene copolymers, the position of the maximum absorption being pH dependant. The copolymers were then left to stand in 0.25M copper(II) nitrate solutions and their visible spectra again measured using the relevant copolymer as the reference in each case. An absorption maximum between 396nm and 402nm was observed for the DVSALEN-HEMA copolymers. Having confirmed the existence of this absorption band in my copper-coordinated copolymers, the reaction of Cu(II) ions with the DVSALEN-modified copolymers was monitored at 400nm.

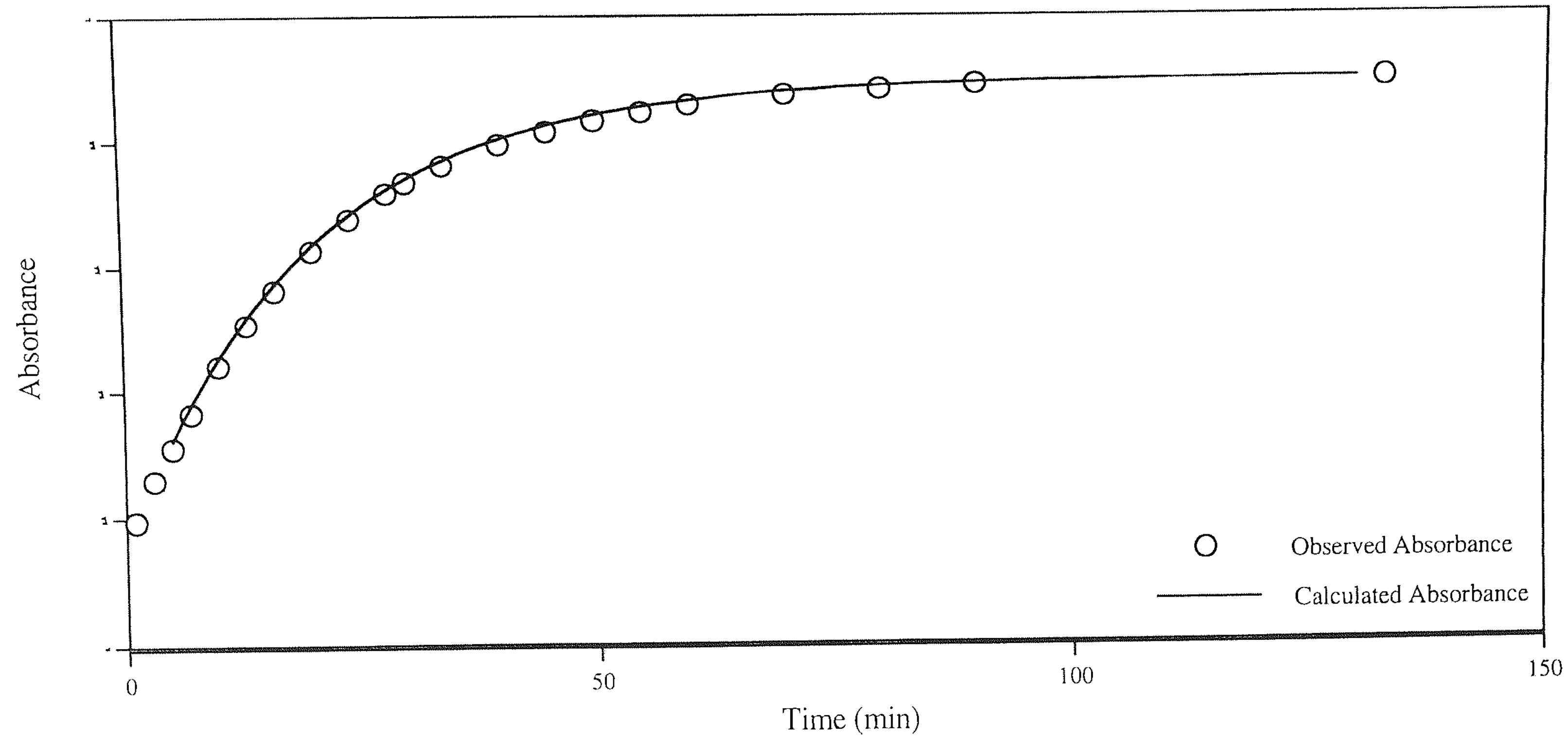
The data fitting which was performed on the raw data was all carried out using the software package Sigmaplot^{TM} 4.11.

4. 2 Preliminary Studies of Copper(II) Coordination

The first set of experiments performed were as follows. For each of the four different ligand loadings in the copolymers, i.e. 0.1%, 0.25%, 0.5% and 1%, experiments using four different copper(II) concentrations were employed, namely 0.025M, 0.05M, 0.1M and 0.25M. Such sets of "4 by 4" experiments were performed separately using nitrate, chloride and sulphate as the counter anions. All the runs were performed at a constant temperature of 25°C. The results of a typical set of experiments are shown graphically in Figure 4.1.

Although these initial experiments were subject to significant experimental errors, plots of the observed maximum absorbance, A_{inf}, versus [Cu(II)] indicate that the best fit to the data is almost certainly a curve of some description.

Figure 4.1 Typical Experiments of Copper(II) Coordination in SalenH$_2$-Modified Hydrogel Copolymers



Diffusion always presents an additional complication when attempting to define the kinetics of transition metal ion coordination within ligand-modified hydrogel polymers. The transition metal ion must permeate into the membrane before any coordination process can take place. Therefore there is a delay in the onset of coordination, which means that the starting time for the reaction cannot be defined as it could be for a simple homogeneous reaction. Trial and error indicate that diffusion is the dominant factor in the development of the colour centres only during the first few minutes. For this reason, the data for the first five minutes of each run were ignored in the calculations that follow, and A_0, the value of the absorbance extrapolated to the experimental time t=0, is treated as an unknown constant to be determined during data fitting.

4. 3 More Detailed Studies of Copper(II) Coordination

In order to confirm the findings of the preliminary experiments, i.e. that the A_{inf} versus [Cu(II)] plots are best described by curves, further experiments were required. Therefore, one ligand loading of copolymer was chosen (1%w/w), along with one counter anion (nitrate), and the interacting copper(II) concentration was varied from 0.005M to 0.5M in a much larger set of experiments. Overall twenty data points were obtained, from which a more reliable curve fit for the A_{inf} versus [Cu(II)] plot could be obtained. The raw experimental data are presented in Appendix One.

Examination of this plot indicated that some kind of saturation effect was being observed in this system, i.e. an equilibrium was being set up. The A_{inf} versus [Cu(II)] data was successfully described using a saturation curve fit, i.e.

$$A_{inf} = A_{max}K[Cu^{2+}]/(1 + K[Cu^{2+}]) \qquad \text{equation 4.1}$$

where A_{max} is the calculated maximum value for the absorbance and K is the equilibrium constant for the system. The plot is shown in Figure 4.2. From this treatment, a value of $K=23M^{-1}$ was obtained. For a polydentate ligand such as salenH_2, this is an amazingly small value for a stability constant.

The raw data for the reaction profile during colour development was then analysed in an attempt to obtain values for the rate constants of the equilibrium. A straight line plot was obtained when the data were fitted to a *pseudo*-first order rate equation. A system where A_0 is not at $t \neq 0$, is described mathematically by the equation,

$$A_t = [(A_\infty - A_0)(1 - e^{-kt})] + A_0 \qquad \text{equation 4.2}$$

It is found that this *pseudo* first-order data fit is a very good representation of the kinetics of the system. As can be seen in Figure 4.3, the data are well described by the linear plot, and values for the observed rate constant were thus obtained. The equilibrium which is being described by equation 4.2 can be written as,

$$\textbf{Ligand} + \textbf{Metal} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \textbf{Complex}$$

The observed *pseudo*-first order rate constant, k_{obs}, is made up of two components in such a system and is defined by the equation,

$$k_{obs} = k_1[Cu^{2+}] + k_{-1} \qquad \text{equation 4.3}$$

where k_1 is the rate constant for the forward reaction and k_{-1} is the rate constant for the back reaction. Plotting k_{obs} against $[Cu^{2+}]$ leads to the values of $k_1=0.15mol^{-1}dm^3s^{-1}$ and $k_{-1}=0.025s^{-1}$. It should be noted that the rate constant for the reaction is extremely slow. A similar phenomenon was also observed by Lewis[21] in his studies of the complexation of iron(II) salts by bipyridine-modified membranes. This slow rate of complex formation in

Figure 4.2 A_{inf} versus $[Cu^{2+}]$ for $Cu(NO_3)_2$ in 1% DVSALEN-HEMA

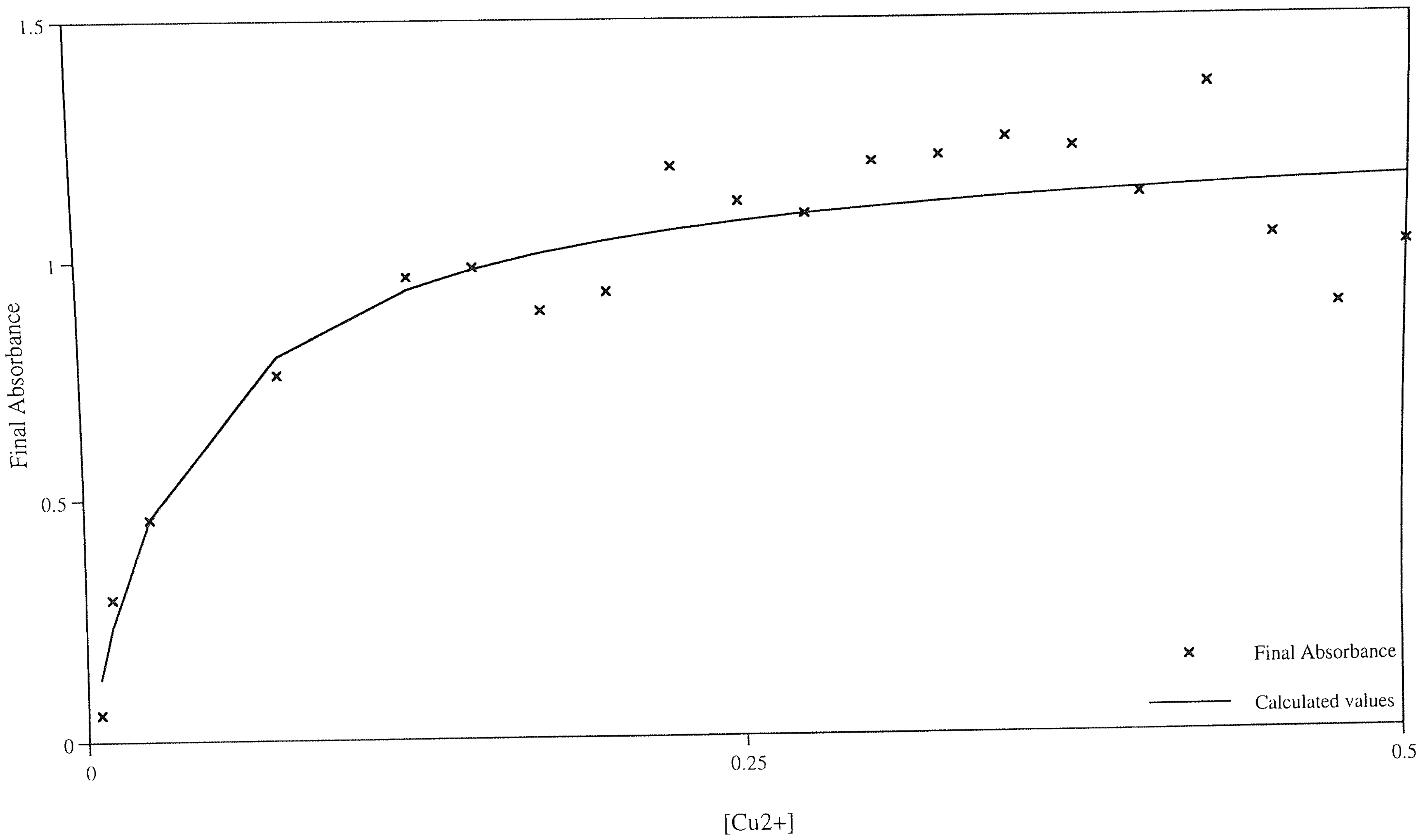
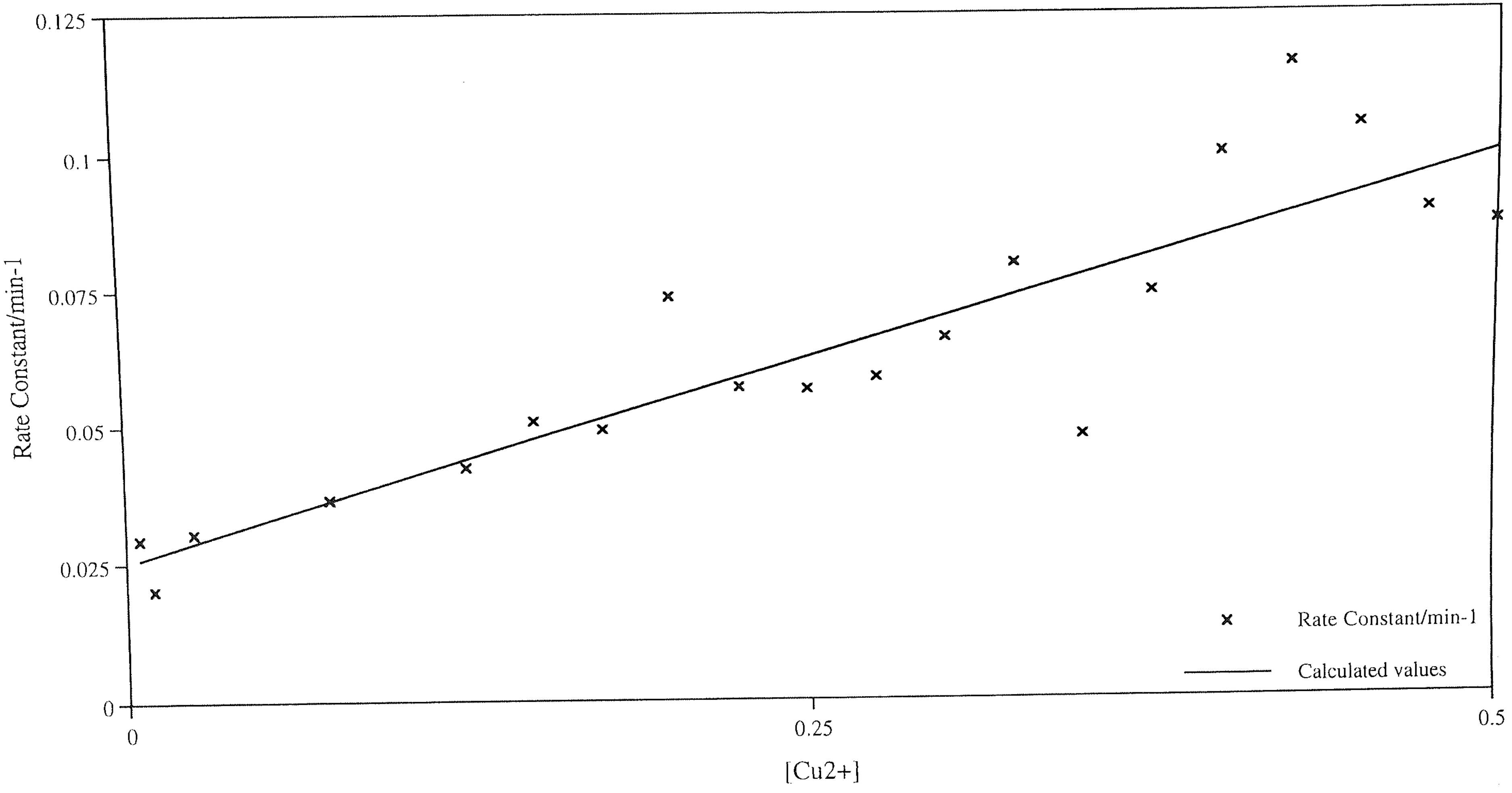


Figure 4.3 k versus $[Cu^{2+}]$ for $Cu(NO_3)_2$ in 1% DVSALEN-HEMA



copolymer membranes compared with complex formation in solution is undoubtedly due to the heterogeneous nature of the system and the need for the ligand to attain the correct orientation and environment before coordination can occur.

The rate constants and the equilibrium constant for the system are related by the equation,

$$\mathbf{K = k_1/k_{-1}} \qquad \text{equation 4.4}$$

and hence the kinetically determined value of $K=6M^{-1}$. This value is obviously different from that obtained from the thermodynamic data treatment, but is still of the same order of magnitude and is exceptionally small for a ligand such as salenH_2. Therefore, from the results of both the thermodynamic and kinetic data fitting we can say that for the coordination of copper(II) nitrate in these systems,

$$\mathbf{6M^{-1} \leq K \leq 23M^{-1}}$$

It seems reasonable to suggest that these values of K are the same within the experimental error likely to prevail for a heterogeneous system such as that employed here.

If we take the geometric mean of these independently obtained values of K(=12) and use that value in curve-fitting for the A_{inf} versus [Cu(II)] plots, a good, though in neither case the best, fit is obtained. Therefore it is reasonable to deduce that the same equilibrium is affecting both the kinetic and the thermodynamic parameters.

The same curve-fitting techniques were then applied to the data obtained when the different anions, i.e. chloride and sulphate, were used. Once more, the saturation curve defines the A_{inf} versus [Cu(II)] plots and values for the equilibrium constants were obtained. Again, these equilibrium constants are much smaller than would be anticipated for the salenH_2 coordination site. For chloride, a value of $K=20M^{-1}$ was obtained for the equilibrium constant, while for sulphate, a value of $K=44M^{-1}$ was obtained. From these values, it is fair to say that the chloride system exhibits similar behaviour to the nitrate system, the equilibrium constants not being statistically different for these two salts. However, in the case of the sulphate system, the difference in the determined constant may indicate that K is weakly anion-dependant.

It is also noticeable in these cases that the observed final absorbance is lower than that found for the nitrate system, and that the rate of complexation is slower. While this is not quite so marked in the chloride case, complex formation in the sulphate system appears to be very slow. This may be due to a phenomenon related to the anion dependence of the rate of permeation into the membrane via the ability of the copper(II) within ion pairs to reach the ligand sites within the membrane, but since the period in which permeation is important has been excluded from the calculations it is not due to diffusional effects. The order in which the anions permeate through the PHEMA-based membranes is,

$$NO_3^{2-} > Cl^- > SO_4^{2-}$$

The overall equilibrium for the complexation reaction is more informatively written as,

$$\text{salenH}_2 + \text{Cu}^{2+}{}_{aq}.2\text{X}^-{}_{aq} \underset{}{\overset{K}{\rightleftharpoons}} \text{Cu(salen)} + 2\text{H}^+{}_{aq}.\text{X}^-{}_{aq}$$

Given the existence of such ion pairs in the system, it is evident that the anion must have some influence over the value of K.

4. 4 Interpretation of the Determined Equilibrium Constants

It has already been mentioned that the values obtained for the equilibrium constant in all the systems studied here are very small in comparison with those prevailing for the solution chemistry of such systems. Coordination of transition metal ions by salenH_2 normally gives rise to large equilibrium constants, indicating the great stability of the chelate complexes formed. Therefore, in the systems described here other unfavourable reactions, which render the overall equilibrium constant for the reaction small, must occur.

The general equilibrium of complex formation is,

$$\textbf{Ligand} + \textbf{Metal Ion} \overset{K_a}{\rightleftharpoons} \textbf{Complex}$$

In the present case this summarises several linked equilibria. Firstly there will be an equilibrium between the copper(II) ions in solution around the membrane and the copper(II) ions in the imbibed water within the membrane, i..e. a partitioning of the copper(II) ions into the membrane. This can be described by,

$$Cu^{2+}(aq) \overset{K_b}{\rightleftharpoons} Cu^{2+}(imb)$$

Also there may be an equilibrium set up between the copper(II) ions in the imbibed water as a whole, and those in the non-freezing water more closely associated with the copolymer chain and hence the ligand groupings. It is the copper(II) ions in the immediate environment of the ligands that will take part in complexation.

$$Cu^{2+}(imb) \overset{K_c}{\rightleftharpoons} Cu^{2+}(non\text{-}freezing)$$

We must also consider the ligand groupings and their environment when discussing the complexation reaction. There is an equilibrium involving the deprotonation of the ligand to leave it in its anionic coordinating state, i.e.

$$LH_2 \overset{K_d}{\rightleftharpoons} L + 2H^+$$

A further, crucial equilibrium will involve the various possible orientations of the ligand groups in the copolymer, not all of which will be suitable for coordination to copper(II) ions. As the rate of copper(II) complexation is also slow, it seems certain that a significant degree of atomic/molecular movement is needed to orientate the ligand groups from their rest state to one in which they are capable of complexation. Therefore, the following equilibrium must occur,

$$\mathbf{L(rest)} \xrightleftharpoons{\mathbf{K_e}} \mathbf{L(available)}$$

It is only when all the necessary conditions for complexation have been met that the reaction may actually occur. This then leaves us with the final equilibrium involving copper(II) ions in the correct environment and the ligand in such a state that it may readily participate in the coordination reaction.

$$\mathbf{Cu^{2+}(non\text{-}freezing)} \quad + \quad \mathbf{L(available)} \xrightleftharpoons{\mathbf{K_f}} \mathbf{Complex}$$

Thus in the heterogeneous system described in this work, the overall equilibrium constant for the reaction will be governed by all or some of those equilibria, i.e.

$$\mathbf{K_a} = (\mathbf{K_b})(\mathbf{K_c})(\mathbf{K_d})(\mathbf{K_e})(\mathbf{K_f}) \qquad \text{equation 4.5}$$

The equilibrium constant for the final step, K_f, is known to be large in solution studies and there is no reason to suspect that it would not be so in these heterogeneous systems. Similarly, the ligand deprotonation step, governed by K_d, is not dominant in solution studies, and so probably does not cause the dramatic reduction of the overall value of K seen here. The equilibrium involving the copper(II) ion in the surrounding water and that in the imbibed water is less than unity, $K_b \approx 0.25M^{-1}$ [35], but this is not sufficient to reduce K to the minuscule value observed here.

Therefore the equilibria responsible for getting the two reacting species into the correct state for coordination, i.e. K_c and K_e, must be the unfavourable factors. It is likely that the ligand moieties, by virtue of the hydrophobic groupings within the molecule, would adopt a position close to the polymer backbone and hence be in a conformation that would preclude coordination. Thus, for coordination to occur, the ligand groupings must reorientate to allow close approach of the copper(II)ions. This close approach of the copper(II) ions will be hindered by the solvation sphere around both the copper(II) ion and its closely associated counter anions. The ligand groups will resist entering into this hydrophilic environment and so K_e will be small.

There appears to be some kind of dependence of K with the anion type. The monovalent anions, chloride and nitrate, exhibit very similar values for K, while for sulphate, the value is doubled. The counter anions must accompany the copper(II) ions to the coordination site and their presence must influence the overall value of K. It is presumably more difficult for a copper(II) ion accompanied by two hydrated monovalent anions to approach the coordination site than it is for a copper(II) ion accompanied only by one divalent anion. Hence, K_c must also be important in the overall process.

It is reasonable to deduce that it is these two equilibria that play the important role in greatly diminishing the value of K from that occurs in solution studies. The difficulty in attaining the correct ligand orientation, via segmental rotation in the polymer backbone and movement of the ligand itself, and environment for coordination is undoubtedly a property of the heterogeneous system under study here. The hydrophobicity of the ligand also appears to diminish its availability for coordination in the hydrophilic environment provided by both the copolymer membrane in general and the hydration sphere presented by the copper(II) ion and its closely associated counter anions.

4.5 SUMMARY

The coordination of copper(II) salts, namely nitrate, chloride and sulphate, to polymer appended salenH_2 groups has been followed spectrophotometrically and has been shown to obey *pseudo-* first-order kinetics. Rate constants for the formation (k_1) and dissociation (k_{-1}) of the complexes formed have been derived. The equilibrium constant (K) for complex formation/dissociation has been derived both kinetically and thermodynamically. The order of magnitude for the two, independently derived values for K is the same within the experimental error likely within such heterogeneous systems. The unexpectedly and exceptionally small value of K that has been obtained has been attributed to processes needed to occur within the polymer matrix before complex formation can take place.

CHAPTER FIVE

THE TRANSPORT OF TRANSITION METAL NITRATES THROUGH LIGAND-MODIFIED HYDROGEL MEMBRANES

5. 1 Introduction

The use of such techniques as electrodialysis, Donnan-dialysis and charge-coupled mobile carrier (CCMC) dialysis for the pre-concentration and/or separation of metal ions in solution has reflected the growing interest in membrane processes in recent years. Donnan-dialysis through liquid membrane systems has formed the majority of the initial work in this area. Here, an ionic gradient across an ion-exchange membrane phase establishes a potential that drives the appropriately charged analyte from lower (sample) to higher (receiver) ionic strength (μ) solutions[112,113]. That this technique leads to only modest separation factors has led to the incorporation of mobile carriers into the membrane phase, thus aiding the removal of ions from the sample[116-118,121].

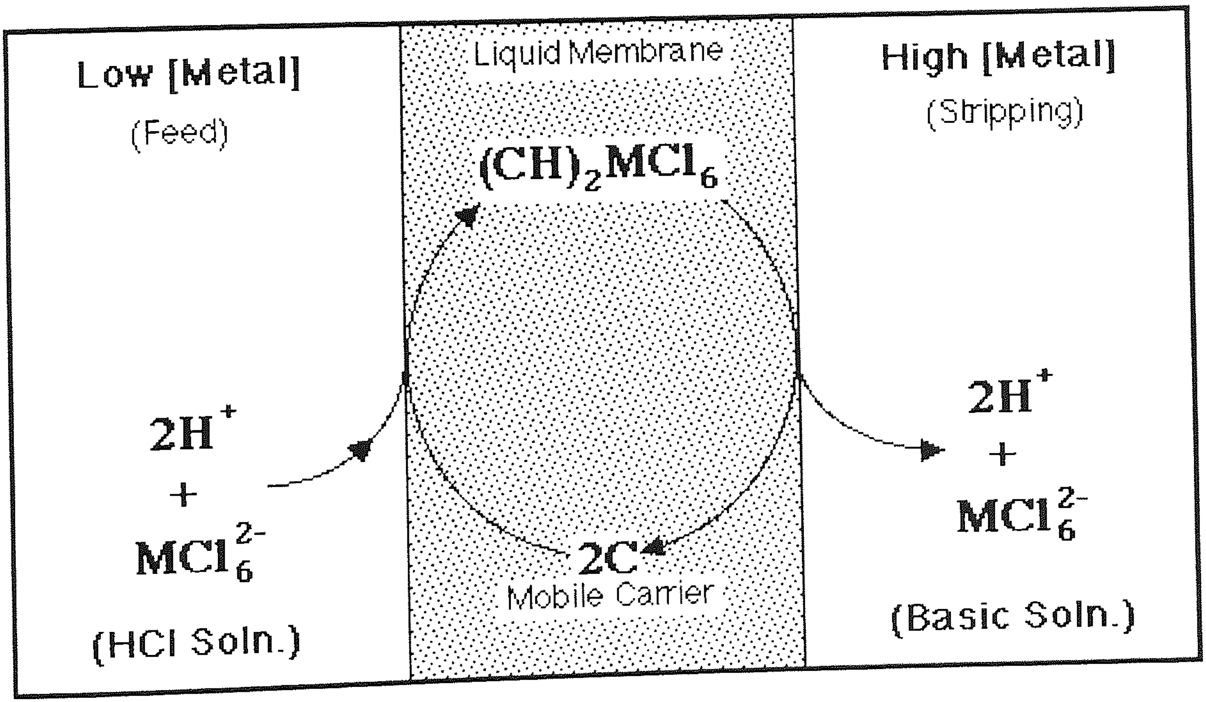


Figure 5.1 Permeation Mechanism for CCMC Dialysis in a Liquid Membrane

The separation of platinum ions as $[PtCl_6]^{2-}$, which is particularly slow in its substitution reactions, has been achieved using a system such as that shown above. The carrier is trioctylamine (TOA) in a xylene membrane. Often, the driving force in such cases is a pH gradient or the presence of a chelating agent in the stripping solution, e.g. ethylenediamine tetraacetic acid (EDTA). However, liquid membranes are severely unstable, preventing the large-scale use of the technology and limiting its analytical applications. Work on the substitution of liquid phases by polymeric membranes has begun to be developed for this reason.

Ideally, for Donnan-type processes, membranes possessing a high ion-exchange capacity and which allow site-to-site diffusion are needed. Cross-linking should be below 15%, and the polymer backbone should have sufficient flexibility to allow a continuous polyelectrolyte network throughout the bulk of the polymer matrix[114].

As their physical properties are ideal for such applications and can be modified by altering the degree of hydrophilicity and cross-link density, hydrogel polymers are an obvious potential starting point for such chelating membranes. In aqueous media, the hydrogel is swelled by osmotic forces. This causes a concomitant increase in permeant concentration, leading to increased mobility of polymer chain segments due to an enhancement of the permeant-polymer interactions[144,145].

Lewis[21] described examinations of the transport of a range of transition metal salts across pyridine- and 2,2'-bipyridine- modified hydrogel membranes, with the aim of achieving selective separation and transportation. He found that these chelating ligands displayed an "anti-selective" nature in the separation of transition metal ions, thus rendering them unsuitable for the applications mentioned earlier. The ligand loading of the polymer was found to have a marked effect on the transport of ions through the membranes. The amount of ligand in the polymer affected not only the rate at which ions permeated through the membranes, but also led to induction periods, before which transport did not occur. As these induction periods, or 'lag-times', depend upon the ligand loading within the polymer matrix, it is obvious to attribute the phenomenon to complexation of the permeating species by the polymer. The transport behaviour of the transition metal salts was also found to be highly dependent on the counter-anion associated with the metal ion. Sulphate was found to be the slowest permeant, while perchlorate and hexafluorophosphate were the fastest, for reasons that will be discussed in the following section. Between this range lie nitrate and chloride.

In the present work, the transport of chromium(III) nitrate through VBPY-modified membranes was examined, to observe the permeation of a metal ion which will be essentially non-coordinating over the time-scale of the experiment.

{*Chromium in the oxidation state III is renowned for the slowness of its ligand substitution reactions. For example, for water exchange on the hexa-aquo chromium(III) ion, the rate constant is* $k=2.4x10^{-6}s^{-1}$}.[146]

Additionally, the transport of copper(II), cobalt(II) and nickel(II) nitrates through DVSALEN-modified membranes was studied to see if the effects of this new ligand were similar to those of the VBPY-modified membranes, and to assess the ability of these chelating polymers to separate transition metal ions.

5. 2 Transport Phenomena in Hydrogel Membranes

Previous work at Aston by Hamilton[35] has involved detailed studies of EWC, partition coefficient (S_m), water-structuring and hydrodynamic radii to develop a model to describe the behaviour of hydrogel polymers in the transport of alkali and alkaline-earth metal ions. He concluded that the observed permeabiliy order for cations and anions through poly(HEMA) membranes could not be explained simply in terms of hydrodynamic size. Anions were found to have a dominant influence over these cations, when considering permeability behaviour. This phenomenon is best described by a comparison of the permeability order of the salts with the Hofmeister (or lyotropic) series. This is an arrangement of the ions according to the influence they exert on reactions in colloidal solution and on their powers of coagulation. The comparison yields a very similar order:

$$ClO_4^- > SCN^- \sim NO_3^- > Cl^- > SO_4^{2-}$$

The ionic structures of the various anions influence the surrounding water to differing degrees. It is believed that small ions and multivalent ions cause electrostriction of water molecules beyond the primary hydration shell of the ion. This induces a long-range ordering of the water molecules, and effectively causes an increase in the viscosity of the water. Therefore, ions such as SO_4^{2-} are considered to be 'structure-makers', and their permeation is slow. If the anion is large and monovalent, ClO_4^- for example, then the electrostatic field generated by the anion is much weaker. These anions are termed 'structure-breakers' as they leave much of the bulk water unperturbed and 'fluid', allowing faster permeation rates. Such arguments can be used to explain permeation rates which are not obviously explicable on the basis of size alone.

5. 3 Collection of Permeability Data

The apparatus used in the collection of permeability data has been described in Chapter 2. 10. The techique yields two pieces of information:

(i) The induction period, or 'lag-time', is a measure of the time taken for the permeant solution to be transported through the membrane and to appear on the low concentration side of the apparatus. This parameter gives an indication of the degree of interaction between the immobilised ligands and the permeating ions.

(ii) The permeability coefficient, P_c, is a parameter that allows comparison of the rate at which different permeants cross a membrane. It may be obtained from the gradient of the $[M2+]_{\text{low side}}$ versus time plot by the implementation of equation 5.1, previously derived from Fick's first law of diffusion in solution (equation 1.2)[33,109,110].

$$\mathbf{P_c = \{dm/dt\}.L/AC} \qquad \text{Equation 5.1}$$

where L = membrane thickness,

A = cross-sectional area,

C = concentration of source solution, and

dm/dt is the rate at which moles of permeant pass across the membrane aperture

5. 4 Permeation of Transition Metal Ions Through Poly(HEMA) Membranes

Prior to the investigation of the permeation behaviour of transition metal ions through ligand-modified membranes, it was necessary to study their transport properties using pure poly(HEMA) membranes. This would then set a base-line for the data obtained from the later experiments and allow the separation of those properties inherent to the polymer matrix and those introduced by the appended ligands.

For the purpose of this study, it was decided to use a range of transition metal nitrates in the permeation runs, as previous knowledge indicated that this anion would lead to permeation at such a rate that experiments could be conveniently followed.

In his study, Lewis[21] employed a range of metal chlorides, Ca^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} respectively, to investigate permeation behaviour in both pure poly(HEMA) and in his ligand-modified poly(HEMA) membranes. He also investigated the effect of different anions on transport behaviour using a range of Co(II) salts, SO_4^{2-}, Cl^-, NO_3^-, SCN^-, ClO_4^-, PF_6^- respectively. He found no great inconsistencies with the theory described earlier in this chapter to explain the influence of the anion on permeation.

Similar experiments were performed during this work and the comparison between these experiments and those of Lewis can be seen in Table 5.1.

Table 5.1 Permeation Data for Metal Nitrates through PHEMA Membranes

Metal Nitrate	**Induction Period** /(minutes) **(Lewis[21])**	**Induction Period** /(minutes) **(Hall)**	**P_c** /($cm^2.min^{-1}$) **(Lewis[21])**	**P_c** /($cm^2.min^{-1}$) **(Hall)**
Cobalt(II)	**30**	**28**	**3.76×10^{-6}**	**9.76×10^{-6}**
Copper(II)	**25**	**25**	**5.71×10^{-6}**	**7.48×10^{-6}**
Nickel(II)	**28**	**25**	**4.9×10^{-6}**	**7.05×10^{-6}**
Chromium(III)	-	**22**	-	**3.56×10^{-5}**

Lewis found that when the cations used were allowed to permeate through poly(HEMA) membranes the rate of permeation followed the order

$$Ca^{2+} > Cu^{2+} > Ni^{2+} > Mn^{2+} \geq Co^{2+}$$

This order has not been seen in the case of those experiments carried out during this research. While the power of the values for P_c is the same, the value for cobalt(II) nitrate is much higher than was anticipated. This can perhaps be explained by differences in membrane morphology[147].

These differences in the degree of hydration of poly(HEMA) membranes are due to the varying extents of interaction between the permeant ions and water within the membrane. This can be related to the partition coefficient, S_m, a measure of the extent to which the salt partitions into the membrane phase. The different ions swell or de-swell the membranes, affecting the thickness of the membranes. When comparing changes in anion, the effect is more dramatic. The relationship between the partition and permeability coefficients, S_m and P_c respectively, is expressed in equation 5.3, where D is the diffusivity of the permeant:

$$\mathbf{P_c = S_m.D} \qquad \text{equation 5.2}$$

Thus, the EWC imposed on the membrane by the salt does indeed influence its transport across the polymer. The 'lag-time', the time taken for the permeant to appear on the low concentration side, may also be thought of as a function of EWC and the permeability coefficient.

The permeability process is governed by two separate components, as shown in equation 5.2. There is a thermodynamically-controlled stage, expressed by S_m, that accounts for the solubilisation of the salt into the membrane. This is followed by a kinetically-controlled stage, represented by D. In previous work[35], it has been shown that diffusion across the membrane can demonstrate size effects, when the hydrated size of the cation is greater than that of the counter-anion, as long as the effect of dissolution of the salt is taken into account. In the work of Lewis[21] and in the current study, all the cations have larger hydrodynamic and Stoke's radii than the anions employed. This is shown in Table 5.2.

In this work, the transport of metal nitrates has been examined. The salt concentrations have been 0.25M with respect to the metal, and so the anion concentration has been 0.5M in the case of studies involving DVSALEN-modified membranes and 0.75M in the study of chromium(III) transport through VBPY-modified membranes. At this level, the anion has a significant affect on the transport processes, and this should be remembered when interpreting the permeability data obtained when using ligand modified polymers.

Table 5.2 Crystal (r^c), Stoke's (r^s) and Hydrodynamic (r^h) Radii for Some Ions[148]

Ion	r^c (Å)	r^s (Å)	r^h (Å)
Ca^{2+}	0.99	3.10	4.12
Mn^{2+}	0.80	3.68	4.38
Cr^{3+}	??? ①	??? ②	??? ③
Co^{2+}	0.72	3.35	4.23
Ni^{2+}	0.70	2.92	4.04
Cu^{2+}	0.72	3.25	4.19
Cl^-	1.81	1.21	3.32
SO_4^{2-}	2.90	2.30	3.79
NO_3^-	2.64	1.29	3.35
ClO_4^-	2.92	1.35	3.38

① 0.62

5. 5 Permeation of Chromium (III) Salts through 2,2'-Bipyridine-Modified Hydrogel Membranes

The work of Lewis[21] examined the transport of two varieties of transition metal ion across ligand-modified membranes, namely those that would coordinate strongly to the appended ligand groups, e.g. Cu^{2+}, and those that would coordinate only weakly to the appended ligand groups, e.g. Mn^{2+}.

Chromium in the oxidation state (III) is renowned for its kinetic inertness with respect to ligand substitution reactions. However, the reactions will take place if sufficient time is given for them to reach completion. This is indeed the case with the reaction of aqueous chromium (III) with the 2,2'-bipyridine ligand. If the reaction is allowed to reach completion a stable *tris*-complex is eventually formed, but over the time scale of a permeation run, no appreciable complexation of chromium (III) by the appended 2,2'-bipyridine groups will occur.

It was decided to investigate the transport of chromium (III) nitrate through three types of hydogel membrane:

(i) pure poly(HEMA), to establish a base-line for the subsequent experiments using the 2,2'-bipyridine-modified polymers.

(ii) copolymers of HEMA and VBPY, where the w/w % of VBPY was varied, which had not previously been in contact with chromium (III) ions.

(iii) the copolymers from (ii) after they had been allowed to stand for one month in 0.25M aqueous solutions of chromium (III).

Evidence of some chromium(III) coordination to the appended 2,2'-bipyridine ligands in test group (iii) was found, the visible absorption spectrum showing a broad band with a maximum around 535nm. The absorbance measured at this wavelength does not however correspond with that would be expected for the *tris* complex, and so it is uncertain what kind of complex has actually been formed within the copolymer membranes. Due to the slowness of chromium(III) in ligand substitution reactions and the reduction of the rate of substitution imposed by the need for the polymer matrix to assume the correct orientation, it is by no means certain as to what kind of complex the chromium(III) is present as.

By performing these experiments, any change in the permeation behaviour of the chromium (III) ions caused by the pre-complexation would be seen, without any complications due to coordination of the permeating species. The data obtained from each experiment is presented in Table 5.3, and represented graphically in Figures 5.2 and 5.3 respectively.

Table 5.3 Permeability Data for Chromium (III) Nitrate Transport through VBPY-HEMA Copolymer Membranes

% Ligand (by weight)	**Transition Metal Salt**	**Concentration** /(mol.dm^{-3})	**Thickness *** /(cm)	**dm/dt** /(molmin^{-1})	**Time Lag** /(minutes)	**Permeability Coefficient** /(cm^2.min^{-1})
Uncomplexed						
0% VBPY	$Cr(NO_3)_3$	0.25	0.033	$2.60e^{-6}$	22	$3.57e^{-5}$
1% VBPY	$Cr(NO_3)_3$	0.25	0.038	$2.17e^{-6}$	19	$3.43e^{-5}$
2% VBPY	$Cr(NO_3)_3$	0.25	0.035	$2.16e^{-6}$	25	$3.15e^{-5}$
4% VBPY	$Cr(NO_3)_3$	0.25	0.033	$1.95e^{-6}$	37	$2.67e^{-5}$
Pre-Complexed						
0% VBPY	$Cr(NO_3)_3$	0.25	0.033	$2.77e^{-6}$	-8	$3.79e^{-5}$
1% VBPY	$Cr(NO_3)_3$	0.25	0.038	$2.19e^{-6}$	1	$3.46e^{-5}$
2% VBPY	$Cr(NO_3)_3$	0.25	0.035	$2.47e^{-6}$	-12	$3.59e^{-5}$
4% VBPY	$Cr(NO_3)_3$	0.25	0.033	$2.05e^{-6}$	-4	$2.81e^{-5}$

* with transition metal present

Figure 5.2 The Transport of Chromium(III) Nitrate through Uncomplexed VBPY-Modified Membranes

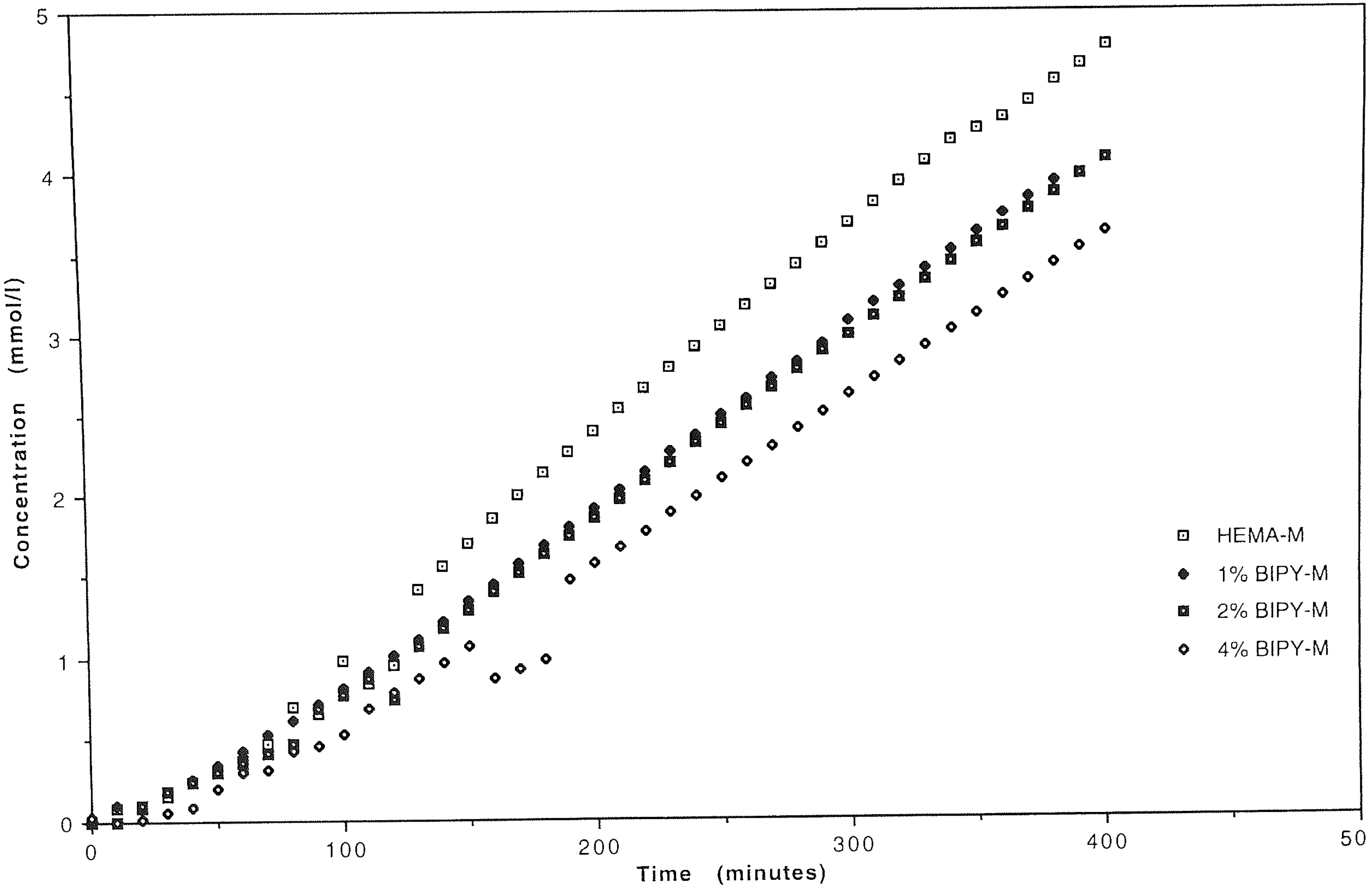
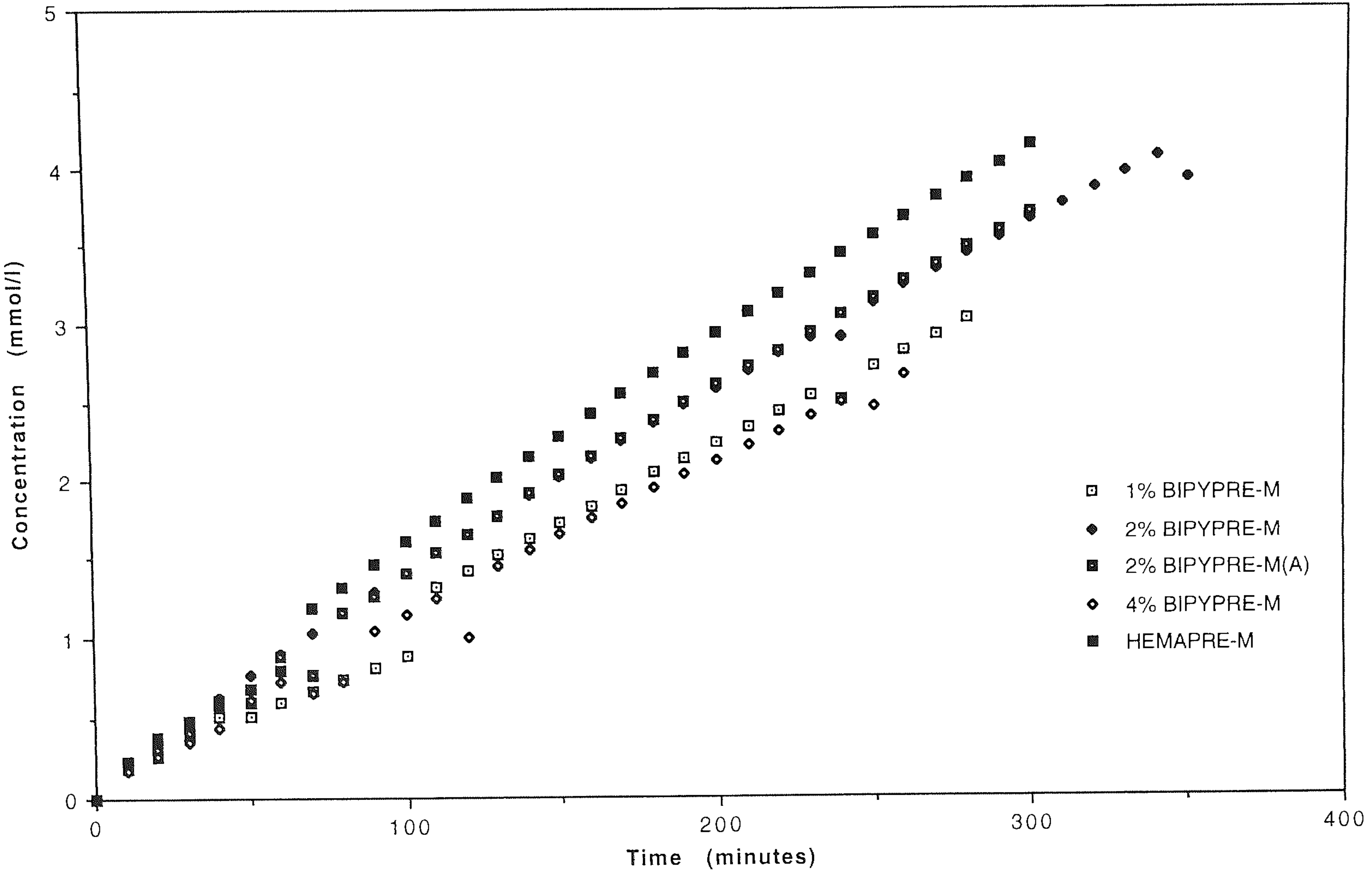


Figure 5.3 The Transport of Chromium(III) Nitrate through Pre-Complexed VBPY-Modified Membranes



As can be quite clearly seen from the data presented, the belief that the transport of chromium(III) ions would not be complicated by any competing complexation reaction appears to be true. The 'lag-times' for the permeation runs using the uncomplexed VBPY-modified membranes, an obvious feature in the work of Lewis[19] with such polymers, are of the same order as the 'lag-time' found when pure poly(HEMA) is used as the barrier. Within experimental error, it is reasonable to say that the 'lag-times' are constant, with a value of 26±4 minutes. This implies that negligible coordination of the metal by the chelating ligands occurs over the time of the transport study. The change in permeation rate with varying ligand loading also appears to be small, with no significant trend apparent.

When using the pre-complexed VBPY-modified membranes, the rate of permeation appears not to have been greatly affected by the presence of complexed chromium(III) ions, although there is a slight increase in permeation rate. Again, no significant trend can be seen. Another observation is that the 'lag-time' has completely disappeared, the transport of chromium(III) ions beginning immediately. Again, within experimental error, the value for the 'lag-times' with this group of polymers can be considered as a constant with a value of -6±3 minutes. This loss of lag-time is not surprising, as any induction period caused by the need for the ions to diffuse into the membrane is no longer present, due to the pre-equilibrium that has been allowed to occur within the membrane.

5. 6 Permeation of Transition Metal Nitrates through DVSALEN-Modified Hydrogel Membranes

Having performed the experiments detailed in the preceding section, it was decided to investigate the effect of the immobilised Schiff base, DVSALEN, on the transport of transition metal ions through hydrophilic membranes. It was thought that these polymers would show similar phenomena to those observed by Lewis[21] with 2,2'-bipyridine-modified polymers. The salts chosen for this study were Co(II)nitrate, Cu(II)nitrate and Ni(II) nitrate respectively. The complexes Co(salen, Cu(salen) and Ni(salen) are well documented and have been the subject of intensive research since their discovery in the 1930s. Poly(DVSALEN) and its copolymers with styrene have been used in the separation of transition metal ions from solution[102].

The data obtained from each experiment is presented in Table 5.4, and represented graphically in Figures 5.4, 5.5 and 5.6 respectively.

Perhaps the most surprising feature of the results is the non-appearance of an appreciable induction period before the permeation of these salts through the ligand-modified membranes begins. As already mentioned, all three metal ions are known to form coordination compounds with such ligands and indeed, the kinetics and thermodynamics of the coordination of Cu(II) nitrate by these ligand-modified polymers have been followed spectrophotometrically during the course of this research (see Chapter Four).

Additionally, the permeation rates of each salt through the ligand-modified membranes show no significant variation with the ligand loading of the respective polymer membranes.

There are also only slight differences between the permeation rates of the respective metal nitrates through the membranes, and while the transport of the Cu(II) salt remains the fastest of the three, the Co(II) and Ni(II) salts appear to have very similar permeation rates.

Therefore, under the conditions employed during this study, the appended salenH_2 ligand has no effect on the transport of the transition metal ions through the hydrophilic membranes.

Table 5.4 Permeability Data for the Transport of Selected Transition Metal Nitrates through DVSALEN-HEMA Copolymer Membranes (* with transtion metal present)

% Ligand (by weight)	**Transition Metal Salt**	**Concentration** /(mol.dm^{-3})	**Thickness *** /(cm)	**dm/dt** /(molmin^{-1})	**Time Lag** /(minutes)	**Permeability Coefficient** /(cm^2.min^{-1})
Cobalt(II) Nitrate Transport						
0% DVSALEN	$Co(NO_3)_2$	0.25	0.036	6.52 x10^{-7}	28	9.76 x10^{-6}
0.1% DVSALEN	$Co(NO_3)_2$	0.25	0.035	4.94 x10^{-7}	29	7.19 x10^{-6}
0.25% DVSALEN	$Co(NO_3)_2$	0.25	0.037	6.40 x10^{-7}	26	9.85 x10^{-6}
0.5% DVSALEN	$Co(NO_3)_2$	0.25	0.038	5.25 x10^{-7}	21	8.30 x10^{-6}
1% DVSALEN	$Co(NO_3)_2$	0.25	0.036	5.01 x10^{-7}	40	7.50 x10^{-6}
Copper(II) Nitrate Transport						
0% DVSALEN	$Cu(NO_3)_2$	0.25	0.040	4.50 x10^{-7}	25	7.48 x10^{-6}
0.1% DVSALEN	$Cu(NO_3)_2$	0.25	0.035	6.69 x10^{-7}	34	9.74 x10^{-6}
0.25% DVSALEN	$Cu(NO_3)_2$	0.25	0.037	6.21 x10^{-7}	41	9.55 x10^{-6}
0.5% DVSALEN	$Cu(NO_3)_2$	0.25	0.038	6.42 x10^{-7}	29	1.01 x10^{-5}
1% DVSALEN	$Cu(NO_3)_2$	0.25	0.036	5.08 x10^{-7}	27	7.60e x10^{-6}
Nickel(II) Nitrate Transport						
0% DVSALEN	$Ni(NO_3)_2$	0.25	0.040	4.24 x10^{-7}	25	7.05 x10^{-6}
0.1% DVSALEN	$Ni(NO_3)_2$	0.25	0.035	5.05 x10^{-7}	31	7.35 x10^{-6}
0.25% DVSALEN	$Ni(NO_3)_2$	0.25	0.037	4.84 x10^{-7}	35	7.45 x10^{-6}
0.5% DVSALEN	$Ni(NO_3)_2$	0.25	0.038	4.97 x10^{-7}	38	7.85 x10^{-6}
1% DVSALEN	$Ni(NO_3)_2$	0.25	0.036	3.53 x10^{-7}	10	5.28 x10^{-6}

Figure 5.4 Cobalt (II) Nitrate Transport through DVSALEN-HEMA Copolymer Membranes

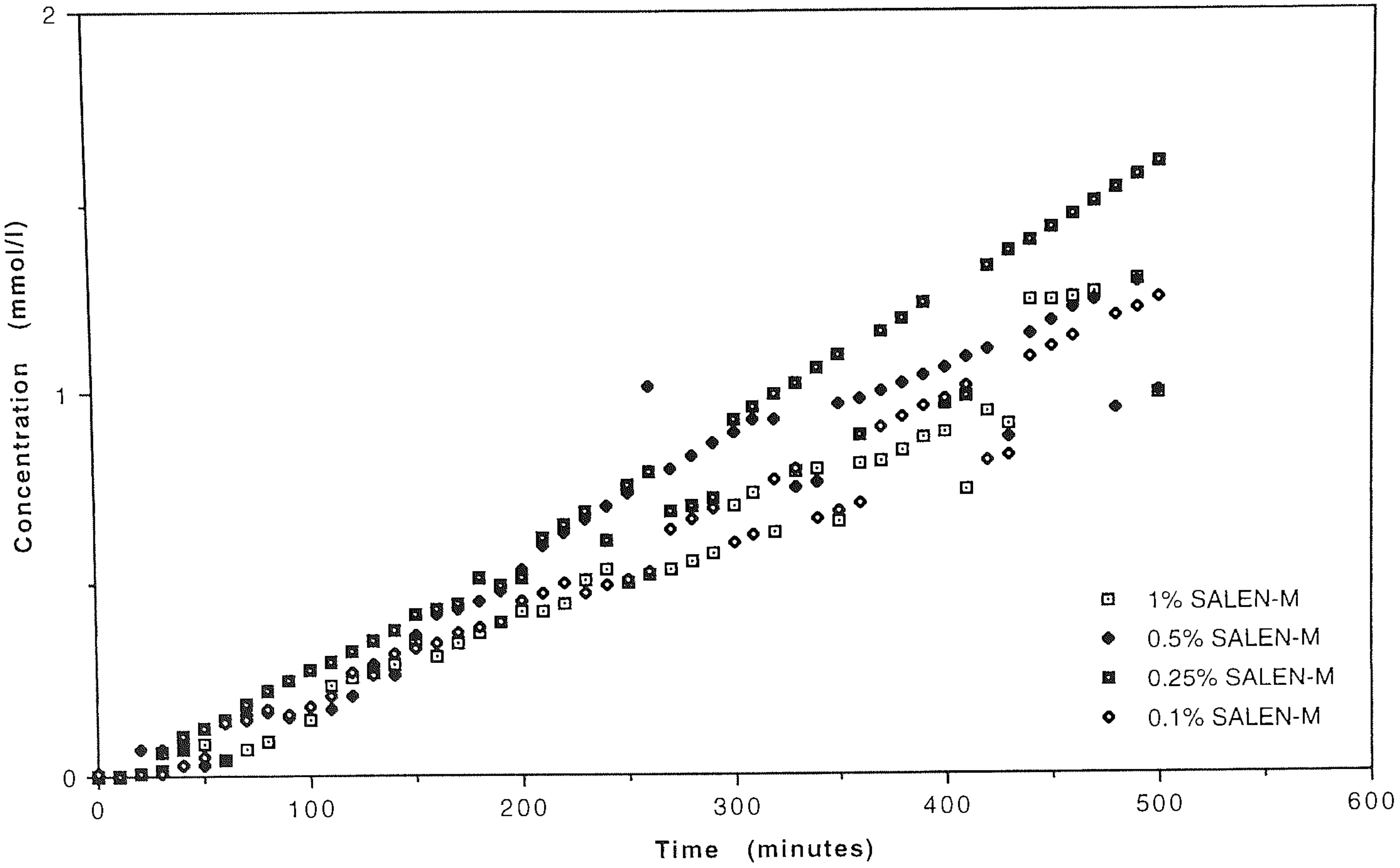


Figure 5.5 Copper (II) Nitrate Transport through DVSALEN-HEMA Copolymer Membranes

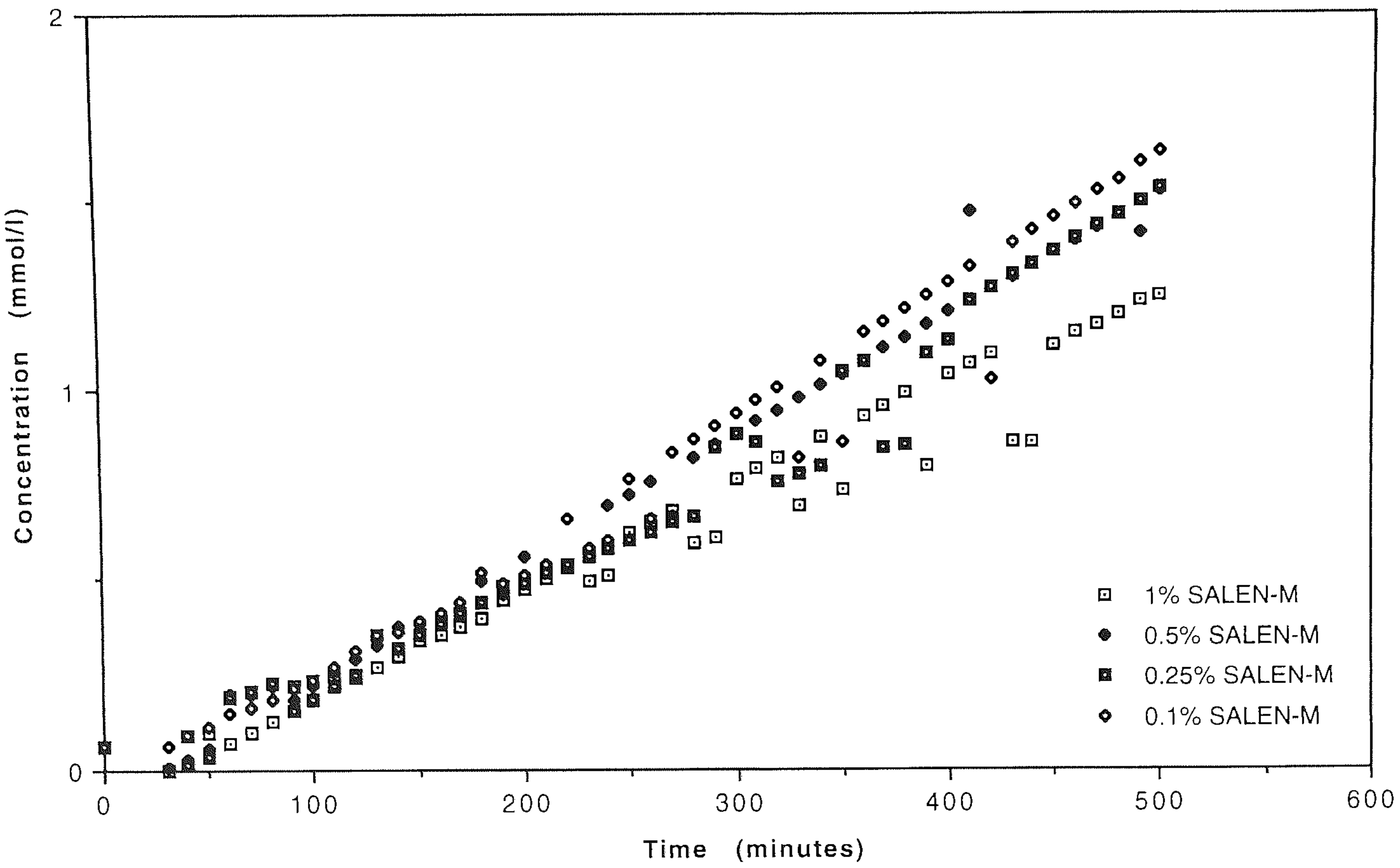
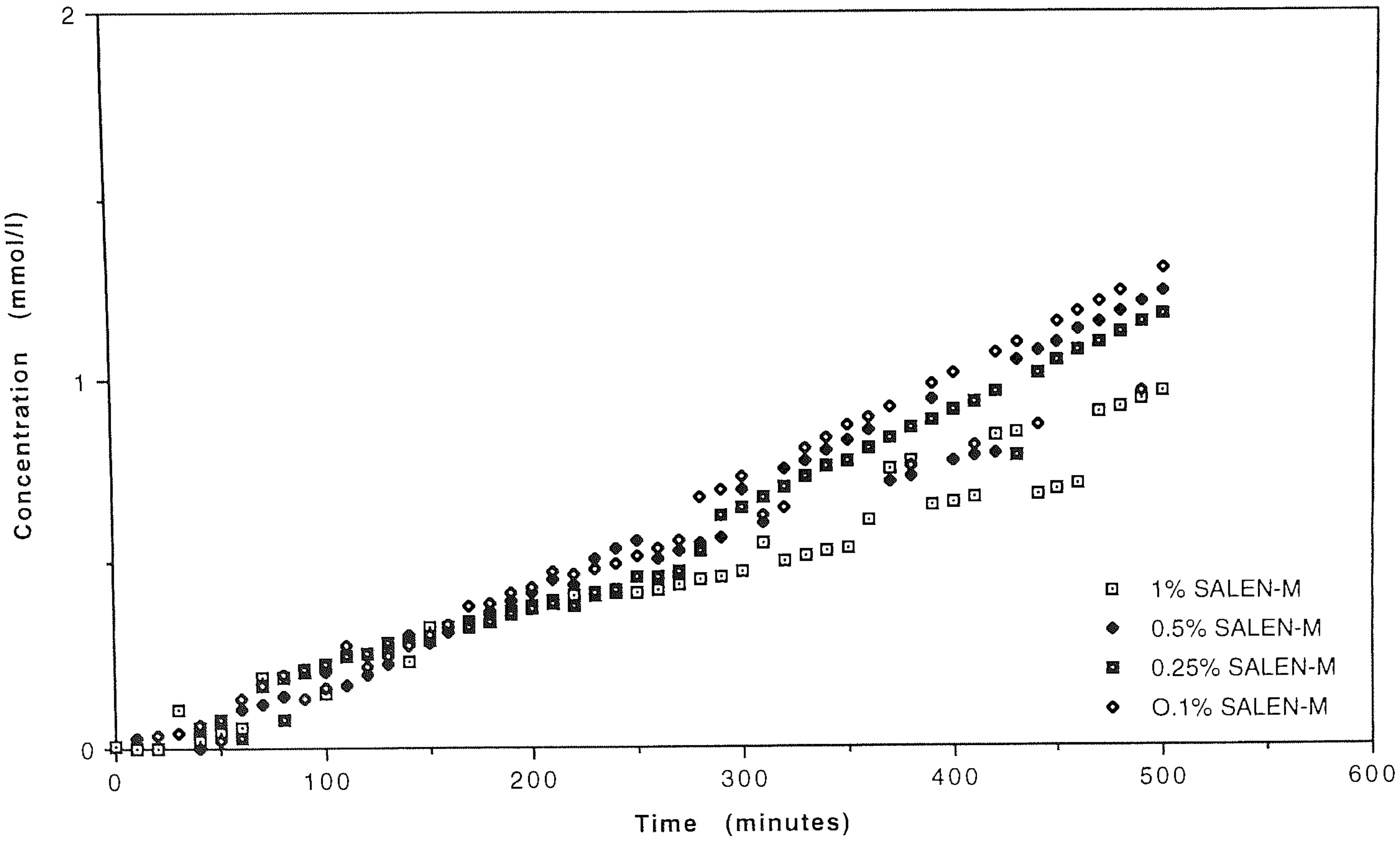


Figure 5.6 Nickel (II) Nitrate Transport through DVSALEN-HEMA Copolymer Membranes



In the future, it may be interesting to study the reaction further at a different pH, e.g. pH=8, to see if there is any difference in the results obtained when the exchanging species are both metal cations rather than H^+ and a metal cation.

5.7 Summary

The transport of chromium(III) nitrate through VBPY-HEMA copolymer membranes has been shown to be unimpaired by the presence of coordinated chromium(III) nitrate within the polymer matrix.

The transport of cobalt(II), nickel(II) and copper(II) nitrates through DVSALEN-HEMA copolymer membranes has been studied. No “lag” in permeation greater than that for pure HEMA membranes has been observed for any of these metal ions, despite the knowledge that complexes are formed between the functionalised copolymers and the metal ions employed. Also, no appreciable variation in P_c is observed with change in ligand density in the copolymer or with a change in metal ion.

CHAPTER SIX

FURTHER LIGAND SYNTHESES

6.1 Introduction

In this chapter the attempts to prepare ligand molecules containing different functional groups to those ligands introduced in Chapter Two are described. The synthesis of molecules based on 2,2'-bipyridine (bipy) and the Schiff base *bis*(salicylidene)ethylenediamine (salenH_2) will be described first. Details of the preparation of some macrocyclic compounds with functional pendant arms will then follow, along with attempts to prepare a functional diamine for later use in the synthesis of Schiff base molecules and Lindoy *et al.*[149] type macrocycles. Where possible, the syntheses are supported by spectroscopic evidence.

The nature of the compounds described in this chapter renders them unlikely to participate in free radical polymerisation, hence the decision to separate the description of their preparation in this separate chapter.

6. 2 Chemicals and Analysis

6. 2. 1 Reagents and Solvents

The reagents used in the preparation of the vinylic ligands described in the subsequent sections are listed in Table 6. 1. With the exception of diisopropylamine, all reagents were used as received from their respective suppliers. Purification of diisopropylamine was effected by standing it over calcium hydride overnight and then distilling it from the calcium hydride under a nitrogen atmosphere. The material purified in this manner was used immediately.

Table 6. 1 Reagents used in Ligand Synthesis

REAGENT	M_r	SUPPLIER
Diisopropylamine	101.19	Aldrich Chemical Company
Calcium hydride	64.06	Janssen Chimica
Sodium	23.01	Aldrich Chemical Company
Butyllithium	64.06	Janssen Chimica
4,4'-Dimethyl-2,2'-bipyridine	184.24	Aldrich Chemical Company
Allyl bromide	120.98	Aldrich Chemical Company
Sodium hydrogen carbonate	84.01	Aldrich Chemical Company
Sodium sulphate (anhydrous)	142.04	Aldrich Chemical Company
Potassium permanganate	158.04	Hopkin and Williams Limited
Hydrochloric acid	36.46	Fison's
Thionyl chloride	118.97	Aldrich Chemical Company
Allyl alcohol	58.08	Aldrich Chemical Company
Magnesium sulphate (anhydrous)	120.37	Aldrich Chemical Company
Salicylaldehyde	122.12	Aldrich Chemical Company / Janssen Chimica
Potassium carbonate (anhydrous)	138.21	Aldrich Chemical Company
Calcium sulphate (anhydrous)	136.14	Aldrich Chemical Company
1,2-Diaminoethane	60.10	Aldrich Chemical Company
Triethylenetetraamine	146.24	Aldrich Chemical Company
Diethylallyl malonate	200.23	Lancaster
Silica gel (flash grade)	-	Aldrich Chemical Company
2,6-Diacetylpyridine	163.18	Aldrich Chemical Company
3,3'-Imino*bis*propylamine	131.22	Aldrich Chemical Company
Nickel (II) chloride hexahydrate	237.71	B.D.H. Limited
Sodium perchlorate	122.44	Hopkin and Williams Limited
Iron (II) sulphide	87.91	Aldrich Chemical Company

The solvents used in the syntheses to be described are listed in Table 6. 2. All solvents were used as received unless otherwise stated. Pure, dry tetrahydrofuran (THF) was prepared by first standing it over sodium wire for at least one day, and then distilling from sodium/benzophenone. Once purified, the dry THF was used immediately. Dry benzene was prepared by distillation, the first 10% of the distillate being discarded. Anhydrous ethanol was prepared as follows, e.g. for one litre of anhydrous ethanol. Magnesium (5g) is added to 50cm^3 ethanol, then iodine is added and the mixture refluxed until the iodine colour has disappeared. The mixture is made up to 1000cm^3 with ethanol, refluxed for 30 minutes under an inert atmosphere. Pure, anhydrous ethanol is then distilled. The material so prepared was used immediately.

Table 6. 2 Solvents used in Ligand Synthesis

SOLVENT	M_r	SUPPLIER
Tetrahydrofuran	72.11	Fison's
Benzophenone	182.22	Aldrich Chemical Company
Diethyl ether	74.12	Fison's
Distilled water	18.02	Laboratory distillation
Benzene	78.11	Fison's
Chloroform	120.39	Fison's
Acetone	58.08	Ellis and Everard (U.K.) Limited
Methanol	32.04	Ellis and Everard (U.K.) Limited
Ethanol	46.07	Hayman Limited

6. 2. 2 Analytical Techniques

6. 2. 2. 1 Nuclear Magnetic Resonance (NMR) Spectroscopy

All the NMR spectra quoted were obtained as described in Chapter 2. 2. 2. 1, with the exception of the ^{15}N spectrum quoted in Chapter 6.7.2, which was obtained using the PENDANT technique (Polarisation Enhancement that is Nurtured During Attached Nucleus Testing)[150].

6. 2. 2. 2 Elemental Analysis

All elemental analyses were performed by MEDAC Limited at the University of Brunel, London.

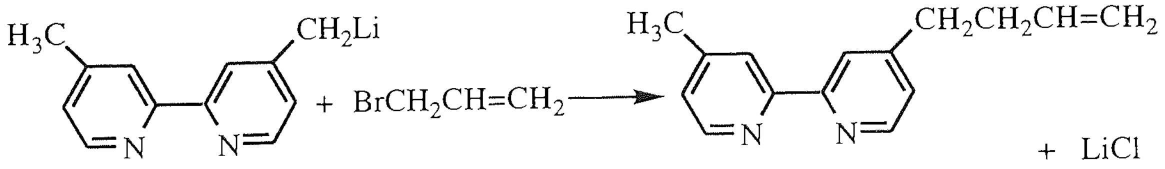
6. 2. 2. 3 Melting Points

All melting points were determined using Gallenkamp melting point apparatus and are uncorrected.

6. 3 The preparation of 4-butenyl-4'-methyl-2,2'-bipyridine

This preparation is a modification of the method of Abruna *et al.*[67], used in the synthesis of 4-methyl-4'-vinyl-2,2'-bipyridine described in Chapter 2. 3. 1. Again, the first step is the generation of lithium diisopropylamide (LDA), which is then reacted with 4,4'-dimethyl-2,2'-bipyridine to yield the lithiated intermediate (**5**), which gave the reaction solution a deep brown colour.

A THF solution of allylbromide (**6**) [11cm^3 (90.9mmol) in 60 cm^3] was added dropwise to the reaction, and the mixture was stirred for a further 30 minutes at 0°C under nitrogen. During this stage, the product (7) is formed by the nucleophilic attack of the lithiated side-chain on the bromine-carrying carbon of (**6**). [SCHEME 6.1]



(5) (6) (7) (**8**)

The reaction was quenched by the addition of distilled water [90cm^3] and then partitioned between saturated sodium hydrogen carbonate [50cm^3] and diethyl ether [150cm^3]. Two further diethyl ether extractions were performed [150cm^3 aliquots] and the combined ethereal layers were dried over sodium sulphate.

Concentration of the ethereal layers yielded the product (7) as a brown oil [11.9g, 65% yield].

ELEMENTAL ANALYSIS : For $C_{15}H_{16}N_2$:

	C	H	N
Calculated	80.32%	7.19%	12.49%
Found	80.08%	7.48%	11.65%

6. 3. 1 NMR of 4-butenyl-4'-methyl-2,2'-bipyridine

As in Chapter Two,the NMR data that follow will make reference to the numbering scheme in Figure 2.1, where

$$X = CH_2CH_2CH{=}CH_2, \quad Y = CH_3$$

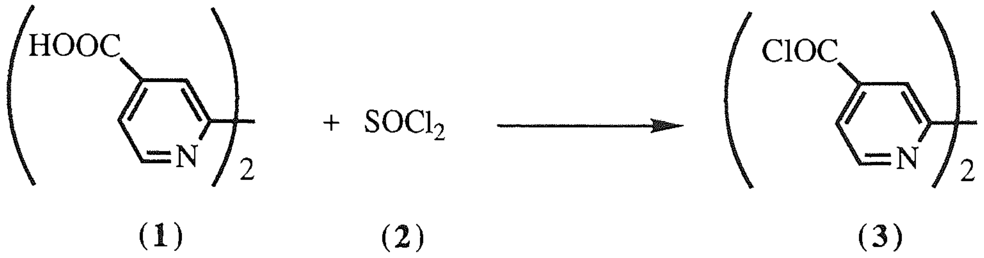
^{1}H N.M.R. (in CDCl3)	8.28/8.32δ(**H6/6'**); 8.01/8.05d(**H5/5'**); 6.82/6.86δ(**H3/3'**); 5.52-5.86δ(=**CH** : position 4); 4.74-4.85δ(=**CH2** : position 4); 2.17-2.23d and 2.49-2.55δ(**CH2CH2** : position 4); 2.14δ(**CH3** : position 4')

^{13}C N.M.R. (in CDCl3)	155.6/155.8δ(**C2/2'**); 148.5/148.6δ(**C6/6'**); 147.6/151.3δ(**C4/4'**); 136.7δ(=**CH** : position 4); 123.5/124.3δ(**C5/5'**); 120.9/121.6δ(**C3/3'**); 115.2δ(=**C**H2 : position 4); 33.9δ and 34.5δ(**CH2**CH2 : position 4); 20.8δ(**C**H3 : position 4')

6. 4 The preparation of the DiAllyl Ester of 4,4'-Dicarboxy-2,2'-Bipyridine (DABPY)

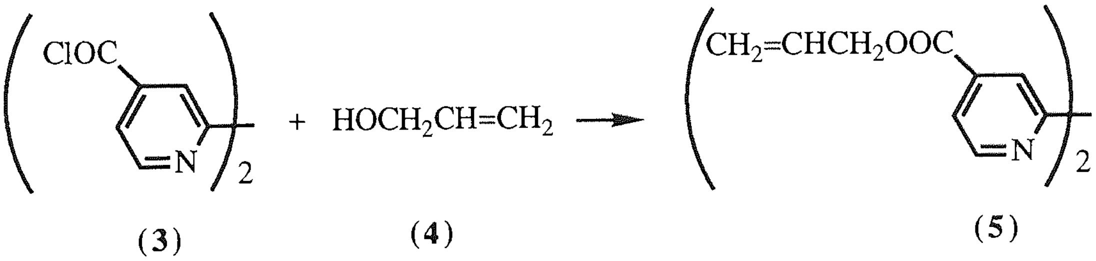
This preparation follows the method of Sprintschnik *et al.* [132] for the preparation of diesters of 4,4'-dicarboxy-2,2'-bipyridine. The first stage , the preparation of the dicarboxylic acid by the reaction of 4,4'-dimethyl-2,2'-bipyridine with potassium permanganate, has been discussed previously (in Chapter 2. 4. 1.).

The diacid **(1)** [1g (4.6mmol)] was refluxed with excess thionyl chloride **(2)** [10cm^3 (84mmol)] for three hours resulting in a yellow solution. Here the dicarbonylchloride **(3)** is formed. [SCHEME 6.2]



All excess thionyl chloride was removed under vacuum and the residue was dried for a further 2 hours under vacuum.

Dry benzene [20cm^3] was added and the solution was treated with a slight excess of allyl alcohol **(4)**[0.58g (10mmol)]. The reaction mixture was refluxed for 2 hours, during which time **(3)** reacts with **(4)** to produce the diallyl ester **(5)**. [SCHEME 6.3]



Chloroform was added and the mixture was then treated with cold, aqueous sodium hydrogen carbonate [40cm^3]. The organic phase was separated and dried over anhydrous magnesium sulphate, before being evaporated to dryness. Recrystallisation of the solid residue from acetone/chloroform yielded the product as white crystals [0.6g, 11% yield from 4,4'-dimethyl-2,2'-bipyridine].

ELEMENTAL ANALYSIS : For $C_{18}H_{16}N_2O_2$:

	C	H	N
Calculated	66.65%	4.97%	8.64%
Found	66.80%	5.42%	7.92%

6. 4. 1 NMR of DABPY

The NMR data that follow will make reference to the numbering scheme in Figure 2.1, where

$$X = Y = COOCH_2CH=CH_2$$

^{1}H N.M.R. (in CDCl3)	8.94/8.95δ(**H6/6'**); 8.85δ(**H5/5'**); 7.88/7.91δ(**H3/3'**); 5.98-6.11δ(=**CH** : positions 4/4' : quartet); 5.30/5.33δ and 5.40/5.46δ(=**CH2** : positions 4/4'); 4.86/4.88δ(OC**H2** : positions 4/4')

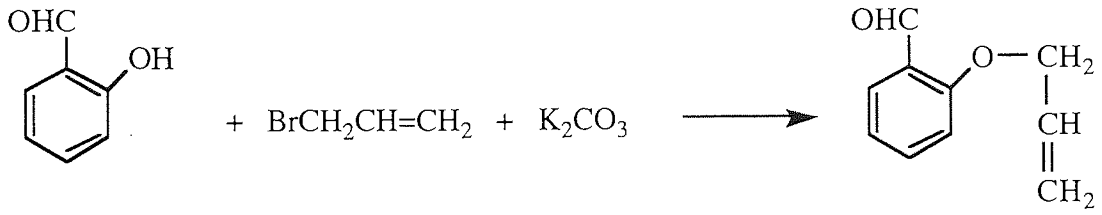
^{13}C N.M.R. (in CDCl3)	156.2δ(**C2/2'**); 149.8δ(**C6/6'**); 138.4δ(**C4/4'**); 131.3δ(=CH : positions 4/4'); 122.9δ(**C5/5'**); 120.3δ(**C3/3'**); 118.8δ(=CH2 : positions 4/4'); 68.0δ(OCH2 : positions 4/4')

6. 5 The preparation of N,N'-ethylene-bis(3-allylsalicylaldimine)

The preparation of this ligand is achieved in three stages from salicylaldehyde. The first two steps are the synthesis of the allyl ether of salicylaldehyde, followed by the rearrangement of this molecule to give 3-allyl salicylaldehyde. The first step is an example of the Williamson ether synthesis, while the second step is an example of a Claisen rearrangement. The synthesis of 3-allyl salicylaldehyde was first demonstrated by Claisen and Eisleb in 1913[151]. In my work, the modified synthesis described by Schlesinger *et al.*[152] was used. Diallylsalen is then prepared simply by the method described in Chapter 2. 5. 3, which is a general method for the preparation of such Schiff bases.

6. 5. 1 The preparation of 2-allyloxy benzaldehyde

Salicylaldehyde (**1**) [122g (1mol)], anhydrous potassium carbonate (**2**) [140g (1mol)] and freshly distilled allyl bromide (**3**) [121g (1mol)] were well mixed in anhydrous ethanol [175cm^3]. The reaction mixture was refluxed for 4 hours with stirring. The formation of the allyl ether (**4**) occurs as the phenolate anion attacks the bromine-bearing carbon of (**3**). [SCHEME 6.4].

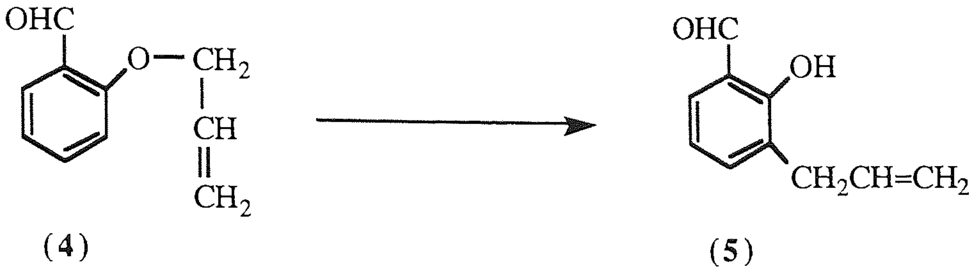


(1) (2) (3) (4)

The reaction mixture was allowed to cool to room temperature and distilled water [1000cm^3] was added. The resulting mixture was extracted with diethyl ether [3 x 125cm^3 aliquots] and the combined ethereal layers were dried over anhydrous calcium sulphate. Filtration of the drying agent and evaporation of the ether gave the raw product which was distilled under reduced pressure to give pure 2-allyloxy benzaldehyde (**4**) [137g, 85% yield, b_{10} 129-130°C; literature[152] 90% yield, b_{10} 130°C].

6. 5. 2 The preparation of 3-allyl salicylaldehyde

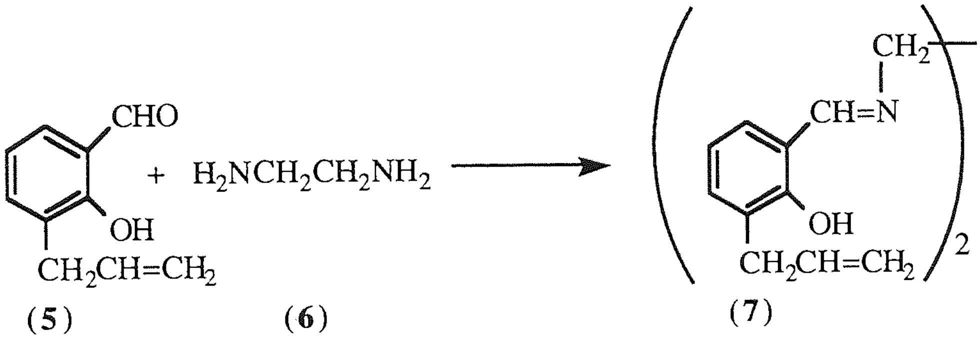
2-allyloxy benzaldehyde (**4**) [81.09g (0.5mol)] was heated slowly to 210-220°C. An exothermal reaction occurred in this temperature range, at which point the external heating was removed until the reaction became smoother. The reaction mixture was then heated again so that the temperature was maintained at 225-230°C for 1 hour. During this time, the intramolecular rearrangement of 2-allyloxy benzaldehyde occurs to yield the product 3-allyl salicylaldehyde (**5**). [SCHEME 6.5].



The reaction mixture was allowed to cool to 50°C before distillation at reduced pressure yielded the product 3-allyl salicylaldehyde (**5**) [61g, 70% yield, b_{10} 110-111°C; literature [152] 80% yield, b_{10} 111°C].

6. 5. 3 The preparation of *bis*(3-allylsalicylidene) ethylenediamine

Following the method of Akelah *et al.*[102], this compound was prepared simply by the reaction of 3-allylsalicylaldehyde (**5**) with 1,2-diaminoethane (**6**). [Scheme 6.6]



1,2-Diaminoethane (**2**) [1.67cm^3 (25mmol)] in hot ethanol (50cm^3) was added to 3-allylsalicylaldehyde (**1**) [8.11g (50mmol)] in hot ethanol (50cm^3). The product precipitated immediately as a yellow solid, which was filtered and then recrystallised from ethanol to give *bis*(3-allylsalicylidene) ethylenediamine (**7**).

ELEMENTAL ANALYSIS : For $C_{22}H_{24}N_2O_2$:

	C	H	N
Calculated	75.83%	6.94%	8.04%
Found	75.35%	6.93%	8.01%

6. 5. 4 NMR

6. 5. 4. 1 NMR of salicylaldehyde derivatives

In the NMR data presented here, the numbering of the benzene ring positions starts at the position of the carbonyl function. In both compounds the typical splitting pattern of the allylic function is observed. The conversion of salicylaldehyde to 2-allyloxybenzaldehyde and the subsequent formation of 3-allylsalicylaldehyde is shown by the diasppearance of the hydroxyl peak in the ^1H spectrum of 2-allyloxybenzaldehyde and its reappearance in the ^1H spectrum of 3-allylsalicylaldehyde. Additionally, in the ^{13}C spectra of the two compounds, we see two quarternary aromatic carbons for 2-allyloxybenzaldehyde and three quarternary aromatic carbons for 3-allylsalicylaldehyde. This is consistent with the Claisen rearrangement having occurred. The ^1H and ^{13}C shifts for the methylene grouping of the C_3H_5 chain also vary. When the methylene is attached to oxygen, as in 2-allyloxybenzaldehyde, both the proton and carbon peaks are shifted downfield with respect to the corresponding peaks in 3-allylsalicylaldehyde.

(i) 2-allyloxy benzaldehyde

^1H N.M.R. (in $CDCl_3$)	10.47δ(**CHO** : position 1); 7.75-7.78δ(1H), 7.43-7.49δ(1H) and 6.89-6.97δ(2H) (aromatic **H3/4/5/6**); 5.94-6.07δ(=**CH** : position 2); 5.25-5.43δ(=$\mathbf{CH_2}$: position 2); 4.57-4.59δ(O-$\mathbf{CH_2}$-C= : position 2)

^{13}C N.M.R. (in CDCl3)	189.5δ(**CHO** : position 1); 160.7δ(aromatic **C2**); 135.7δ(**=CH** : position 2); 132.2δ(aromatic **C4**); 131.3δ(aromatic **C6**); 124.8δ(aromatic **C1**); 120.6δ(aromatic **C5**); 117.8δ(**=CH$_2$** : position 2); 112.7δ(aromatic **C3**); 68.9δ(O-**CH$_2$**-C= : position 2)

(ii) 3-allyl salicylaldehyde

^{1}H N.M.R. (in CDCl$_3$)	11.46δ(**OH** : position 2); 9.75δ(**CHO** : position 1); 6.81-7.46δ(aromatic **H4/5/6**); 5.90-6.04δ(=**CH** : position 3); 5.07-5.15δ(=**CH$_2$** : position 3); 3.38-3.42δ(=C-**CH$_2$** : position 3)

^{13}C N.M.R. (in CDCl$_3$)	196.4δ(**CHO** : position 1); 158.9δ(aromatic **C2**); 136.6δ(=**CH** : position 3); 135.3δ(aromatic **C4**); 131.5δ(aromatic **C6**); 128.2δ(aromatic **C3**); 119.8δ(aromatic **C1**); 119.5δ(aromatic **C5**); 115.9δ(=**CH$_2$** : position 3); 32.6δ(=C-**CH$_2$** : position 3)

6. 5. 4. 2 NMR of N,N'-ethylene-bis(3-allylsalicylaldimine)

The NMR data presented here will make reference to the numbering scheme shown in Figure 6.1, which shows the positions of the hydrogens, carbons and substituents on the salicylaldehyde molecule.

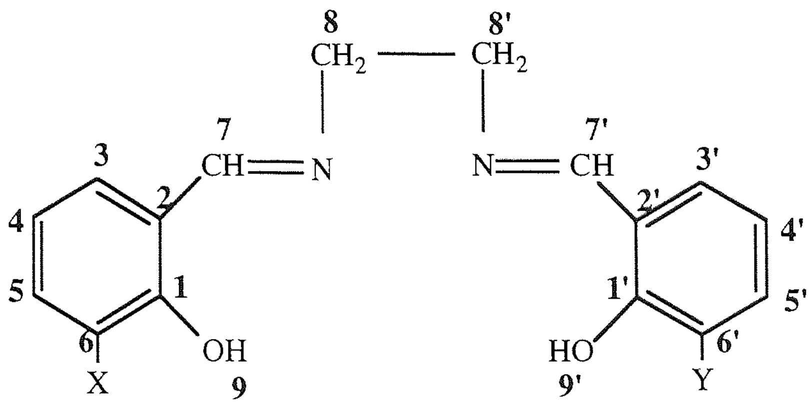


Figure 6.1 Numbering Scheme for Salen Derivatives

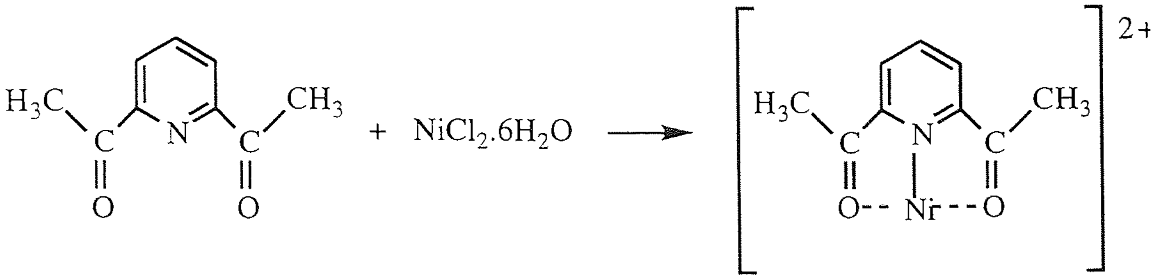
X = Y = CH2CH=CH2 --- *bis*(3-allylsalicylidene) ethylenediamine

^{1}H N.M.R. (in $CDCl_3$)	13.52δ(**H9**); 8.34δ(**H7**); 7.16-7.19δ(**H3**); 7.08-7.11δ(**H5**); 6.78-6.83δ(**H6**); 5.95-6.08δ(=**CH** : position 6/6'); 5.04-5.11δ(=**CH**$_2$: position 6/6'); 3.91δ(**H8**); 3.41/3.42/4.46δ(=C-**CH**$_2$:position 6/6')

^{13}C N.M.R. (in $CDCl_3$)	166.8δ(**C7**); 158.4δ(**C1**); 138.5δ(=**CH** : position 6/6'); 132.8δ(**C5**); 129.8δ(**C3**); 127.7δ(**C4**); 118.3δ(**C6**); 118.1δ(**C2**); 115.6δ(=CH$_2$: position 6/6'); 59.6δ(**C8**); 33.5δ(=C-CH$_2$: position 6/6')

6. 6 The Preparation and Subsequent Attempts at Functionalisation of 2,12-Dimethyl-3,7,11,17-tetraazabicyclo(11.3.1)heptadeca-1(17),2, 11,13,15-pentaene-nickel(II) (Ni[CR])

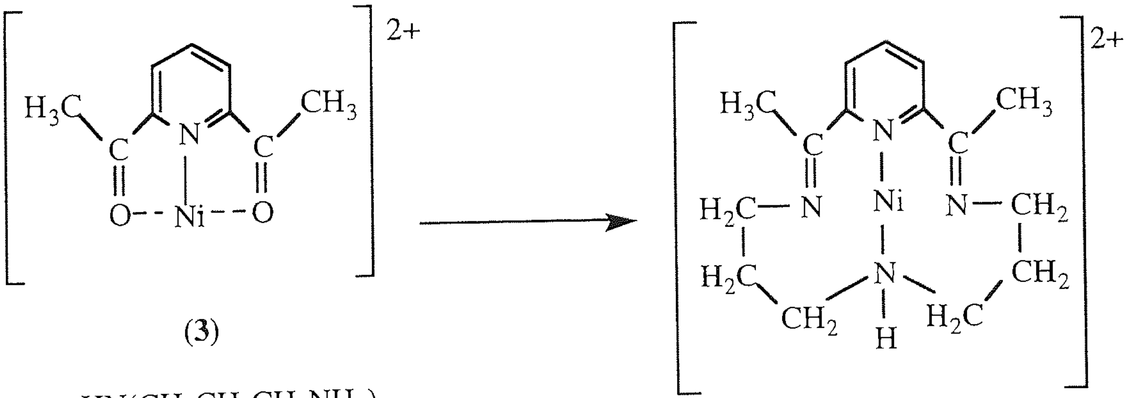
This molecule was synthesised by the method of Busch and Karn[151]. The macrocycle is formed *via* a template reaction around a nickel (II) cation. Diacetylpyridine (**1**) [16.32g (0.1mol)], nickel (II) chloride hexahydrate [23.77g (0.1mol)] (**2**) and 3,3'-diamino-dipropylamine [14cm^3, (0.1mol)] (**4**) were refluxed in 50:50 water:ethanol [500cm^3] for 6 hours. The first stage of the reaction is the formation of the nickel (II) - diacetylpyridine complex (**3**). [SCHEME 6.7]



(1) (2) (3)

(In the complex (3), it is thought that the two carbonyl functions coordinate to the metal ion which has been brought close enough for such an interaction due to coordination to the pyridine nitrogen, although this is unconfirmed. For this reason, the coordinate bonds to the carbonyl functions are shown as dotted lines) .[154]

The complex **(3)** then reacts with the triamine to form the product **(5)**. [SCHEME 6.8]



(3)

+ $HN(CH_2CH_2CH_2NH_2)_2$

(4)

(5)

When the reflux period was over, the ethanol was removed by evaporation. The product was precipitated as its perchlorate salt by the addition of concentrated aqueous sodium perchlorate. Recrystallisation from water yielded grey-brown needles of the dihydrate complex. The coordinated water was removed *in vacuo* to yield brick red needles of the perchlorate salt of **(5)** [16.8g, 53% yield]

6. 6. 1 NMR data for Ni[CR]

In this complex, the Ni^{2+} ion adopts a square planar geometry, which is diamagnetic. If this is indeed the case, then it should be possible to obtain NMR data for the complex by the use of Magic Angle Spinning NMR (MASNMR). For the scrupulously dry product this was indeed the case. The ^{1}H and ^{13}C NMR spectra obtained are shown in Figures 6.2 and 6.3 respectively. The square planar arrangement is destroyed if any water is present, as the complex contains unhindered axial sites at which water (and other ligands) may coordinate, leading to a paramagnetic tetragonal geometry. The loss of the square planar geometry results in a loss of the NMR spectra. No formal, specific assignment of the peaks in either the ^{1}H or ^{13}C are suggested, although the ^{13}C peaks have been separated from their associated "spinning side-bands". In order to make specific assignments for the peaks, a detailed study of Ni(II) complexes would be required. Such an exercise was not appropriate within the time-scale of this research.

6. 6. 2 Attempted functionalisation of Ni[CR]

Due to the insolubility of the perchlorate salt of Ni[CR], prepared earlier, in suitable organic solvents, it was decided to remove the metal ion by the action of hydrogen sulphide (as described in Chapter 2. 5. 2), to leave the uncoordinated ligand. Once this had been achieved, an attempt was made to react the secondary amine function of [CR] with allyl bromide to give the allylated ligand. NMR analysis of the products obtained from these attempts showed that the preparation had not been achieved, the absence of the typical allylic splitting pattern in the ^{1}H NMR proving this.

Figure 6.2 1H Spectrum of Ni(CR)

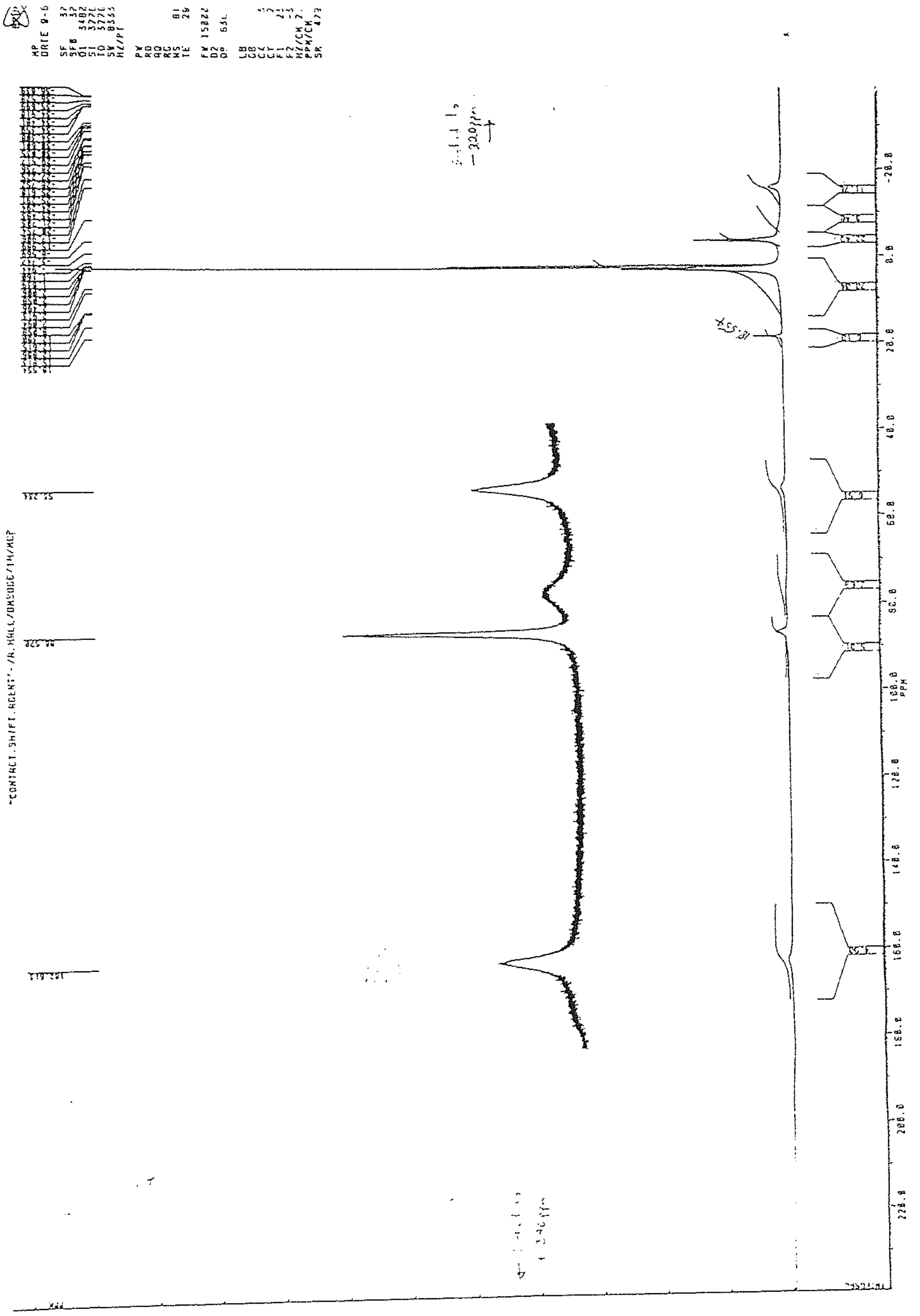
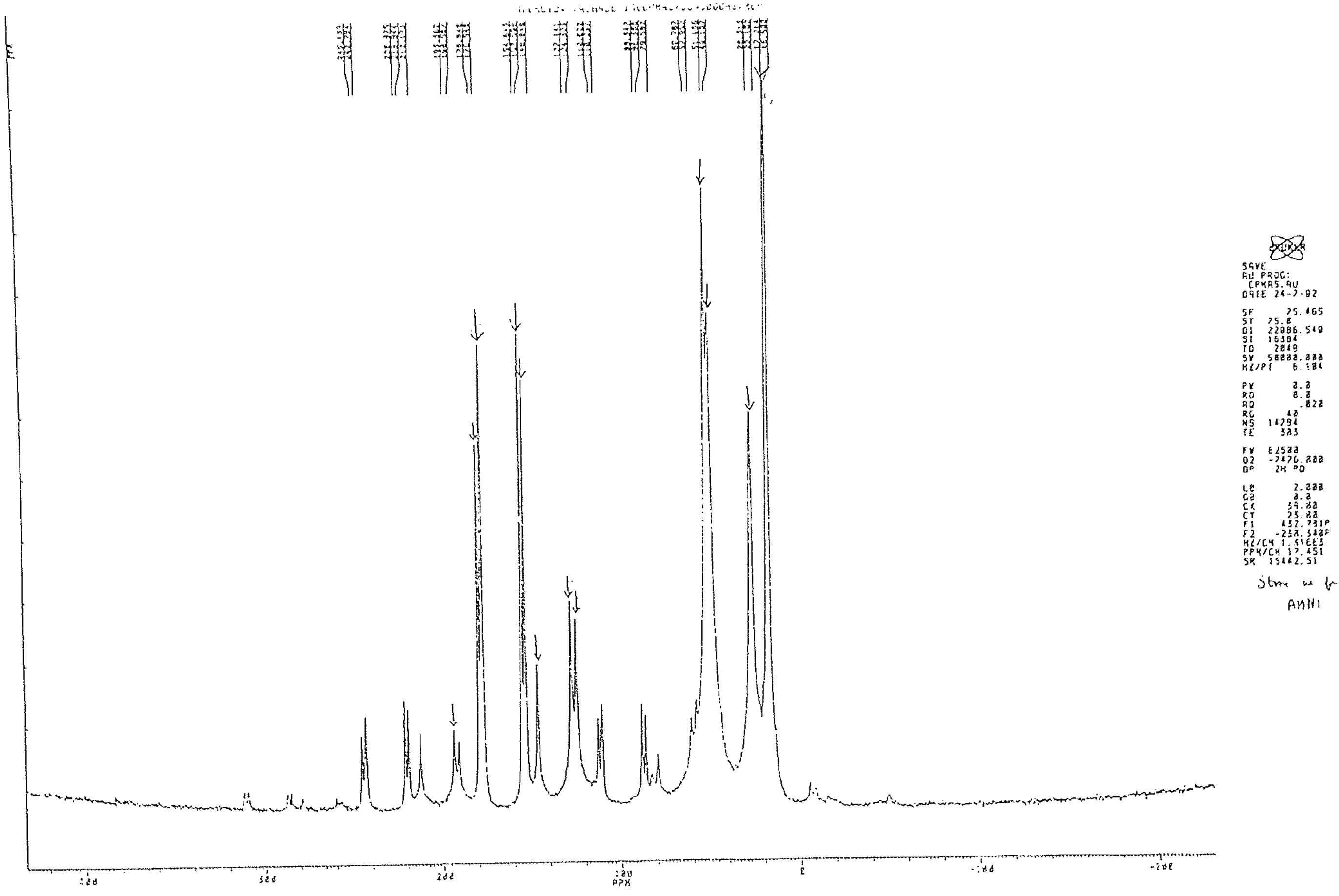


Figure 6.3 13C Spectrum of Ni(CR)



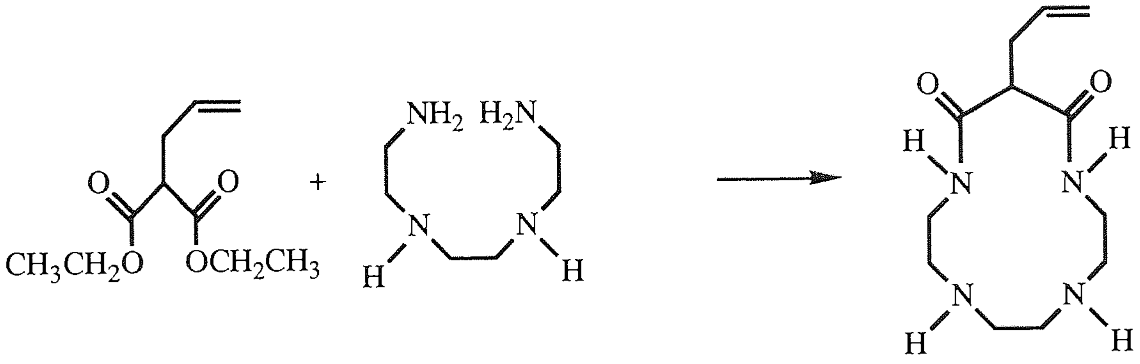
```
SAVE
AU PROG:
 CPMAS.AU
DATE 24-7-92

SF      75.465
SY  75.0
O1  22086.549
SI  16384
TD   2049
SW  50000.000
HZ/PT    6.104

PW       0.0
RD       0.0
AQ         .020
RG      40
NS  14294
TE     303

FW  62500
O2  -2470.000
DP   2H PO

LB       2.000
GB       0.0
CX      39.00
CY      23.00
F1     432.731P
F2    -250.540P
HZ/CM 1.516E3
PPM/CM 17.451
SR  15442.51
```

ANNI

6. 7 The Preparation of 3-Allyl-2,4-dioxo-1,5,8,11-tetraazaterdecane

This compound may be conveniently prepared by the method of Tabushi *et al.*[153] for the synthesis of C-alkylated macrocyclic polyamides/polyamines. The reaction is achieved by the ammonolysis of a suitable C-alkylated diethylmalonate with the desired polyamine. The reaction occurs under normal conditions, with regards concentration, solvent and temperature, unlike many macrocyclic syntheses, where inconvenient high-dilution techniques or template reactions must be employed.

Thus, diethyl allylmalonate (**1**) [24.8cm3 (0.1mol)] and triethylenetetraamine (**2**) [19.7cm3 (0.1mol)] were refluxed in ethanol [100cm3] for 3 days. The condensation between (**1**) and (**2**) occurs during this period to yield the crude product (3). [SCHEME 6.9]



(1) (2) (3)

The pure product, 3-allyl-2,4-dioxo-1,5,8,11-tetraazaterdecane (**3**), was isolated through silica gel chromatography (chloroform:methanol [5:1] elution), and was recrystallised from ethanol [5g, 20%yield].

ELEMENTAL ANALYSIS : For $C_{12}H_{22}N_4O_2$:

	C	H	N
Calculated	56.57%	8.72%	22.03%
Found	56.31%	8.43%	21.86%

6. 7. 2 NMR of 3-allyl-2,4-dioxo-1,5,8,11-tetraazaterdecane

The NMR data that follow will make reference to the numbering scheme in Figure 6.4, which shows the hydrogen, carbon and substituent positions on the 3-allyl-2,4-dioxo-1,5,8,11-tetraazaterdecane molecule. In addition to the ^{1}H and ^{13}C spectra, ^{1}H-^{1}H and ^{1}H-^{13}C COSY (Correlation Spectroscopy) and ^{1}H-^{1}H NOESY (Nuclear Overhauser Effect Spectroscopy) spectra were obtained to help in the elucidation of the rather complicated spectra. The NOESY spectrum indicates through-space interaction between the amino- and amido- protons, but there is no evidence of interaction between these protons and the pendant vinylic function, indicating that, in the free molecule, the vinyl group is oriented away from the macrocyclic cavity. In addition, a ^{15}N spectrum was also obtained, and this clearly shows the presence of two different nitrogen atoms within the molecule. The ^{15}N spectrum was using pyridine as the solvent and the shifts quoted are therefore relative to pyridine. Nitromethane is generally used as the reference in nitrogen N.M.R., and pyridine has a shift range of roughly 0 to -60δ. Thus, the shifts quoted for the two types of nitrogens are comparable to literature values for amino and amido nitrogens. The COSY, NOESY and ^{15}N spectra are shown in Figures 6.5, 6.6, 6.7 and 6.8 respectively.

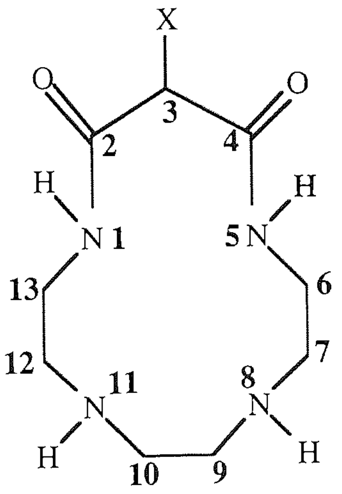


Figure 6.3 Numbering Scheme for 3-allyl-2,4-dioxo-1,5,8,11-tetraazaterdecane

X = $CH_2CH=CH_2$

^{1}H N.M.R. (in CDCl$_3$)	7.41-7.50δ(**H1** and **H5**); 5.67-5.80δ(=C**H** : position 3); 4.948-5.12δ(=C**H2** : position 3); 3.2 – 3.5δ(multiplet [**5H**] : **H3**, **H6** and **H13**); ~2.7δ(multiplet [**10**] : **H7**, **H9**, **H10**, **H12** and -C**H$_2$** at position 3); 2.18δ(**H11** and **H8**)

^{13}C N.M.R. (in CDCl$_3$)	170.2δ(**C2** and **C4**); 134.8δ(=CH : position 3); 116.9δ(=CH$_2$: position 3); 54.8δ(**C3**); 47.8, 46.5 and 39.2δ(**C6/13**, **C7/12**, **CC9/10**); 32.9δ(-CH2 : position 3)

^{15}N N.M.R. (in pyridine)	-200.9δ(**N1** and **N5**); -290.8δ(**N8** and **N10**)

Figure 6.5 ^{1}H-^{1}H COSY Spectrum for 12-Allyl-2,4-Dioxo-1,5,8,11-Tetraazaterdecane

Figure 6.6 ^{1}H-^{13}C COSY Spectrum for 12-Allyl-2,4-Dioxo-1,5,8,11-Tetraazaterdecane

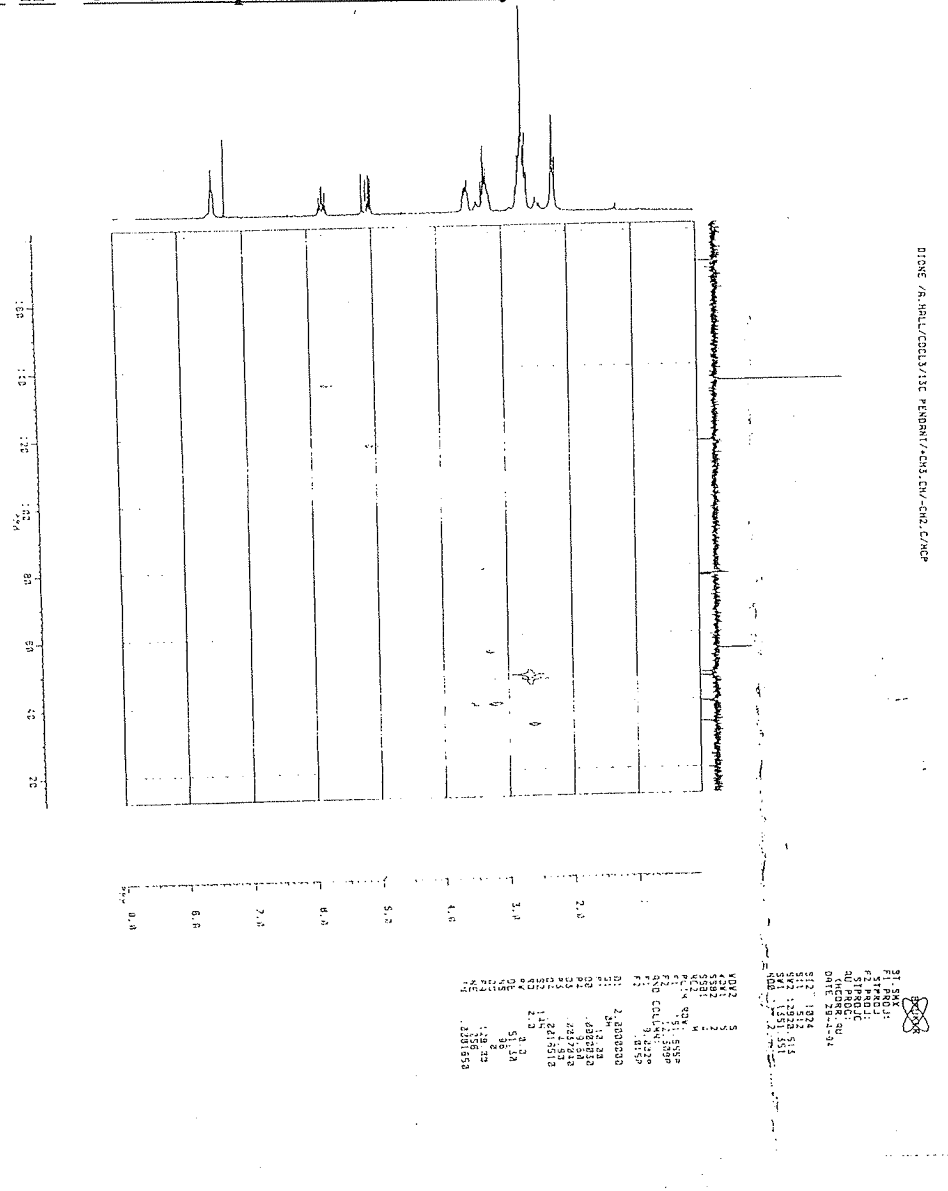


Figure 6.7 ^{1}H-^{1}H NOESY Spectrum for 12-Allyl-2,4-Dioxo-1,5,8,11-Tetraazaterdecane

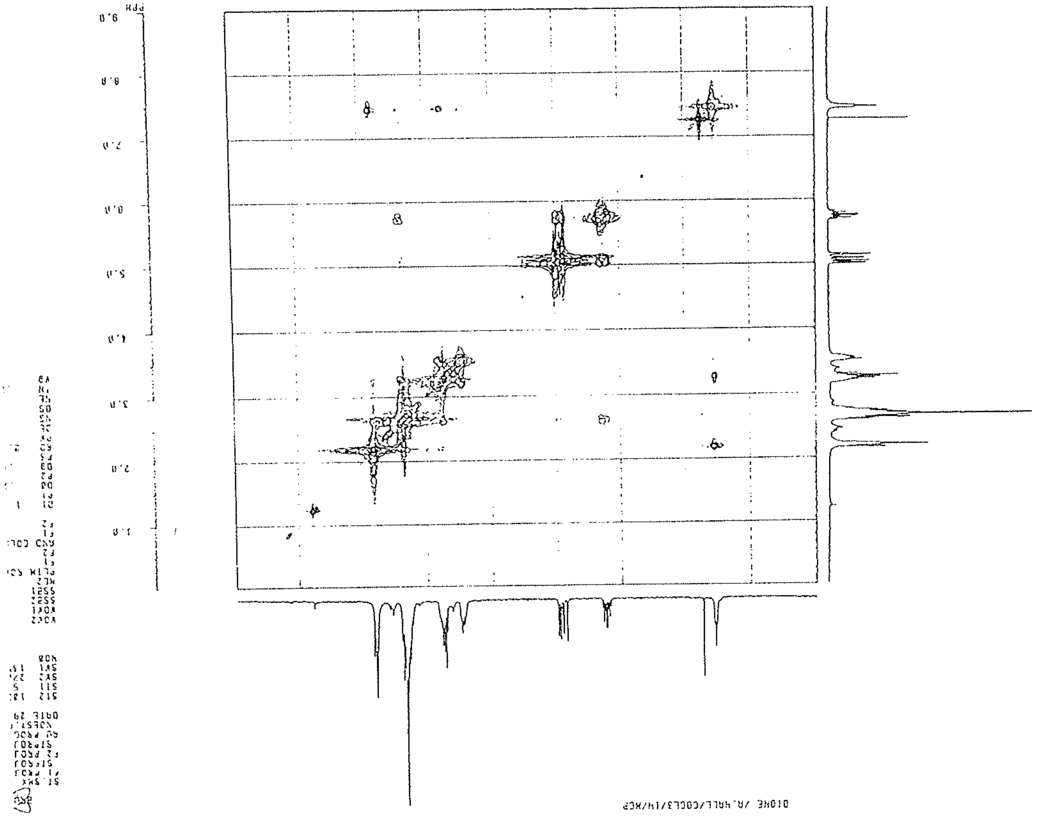
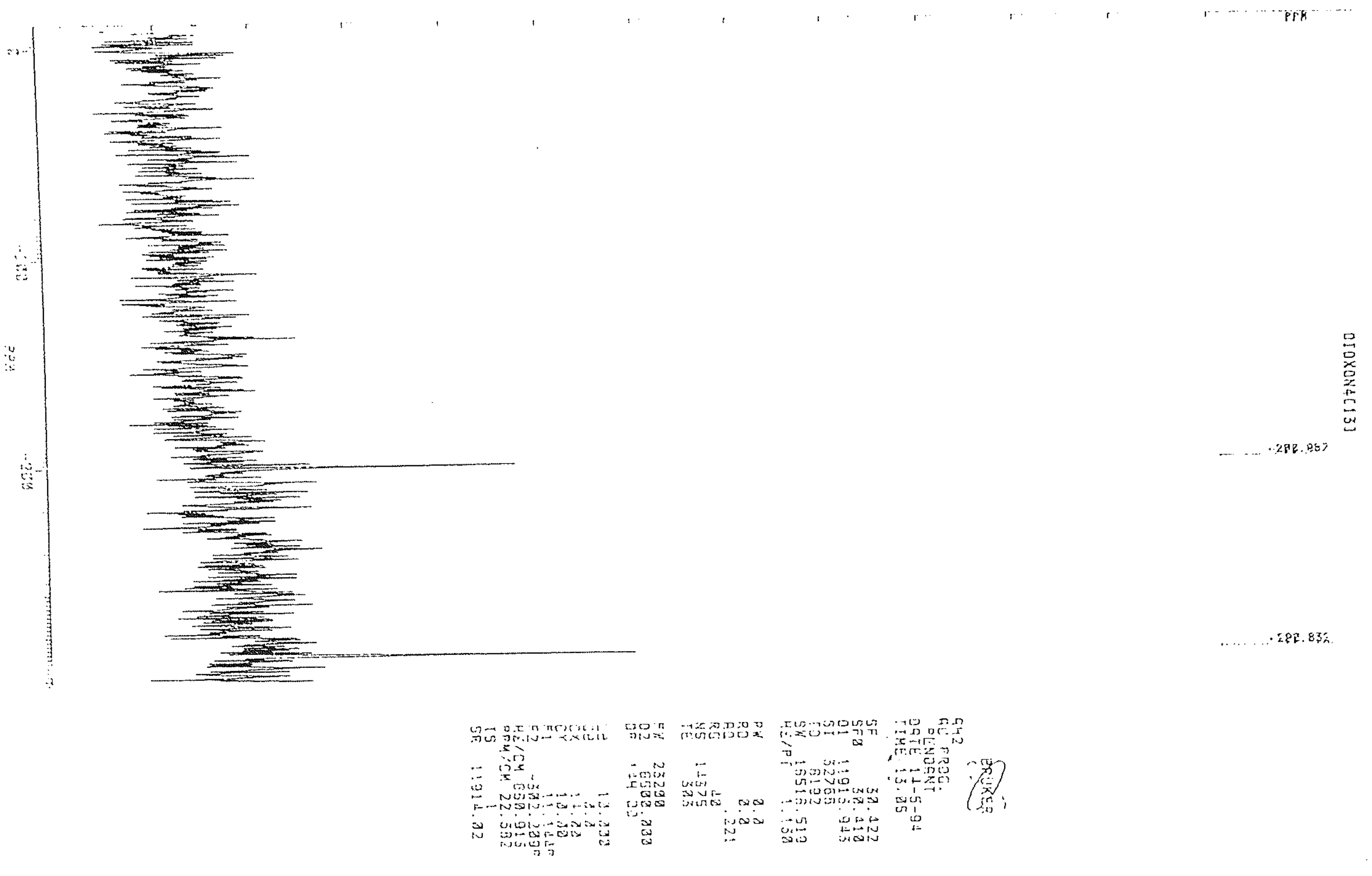
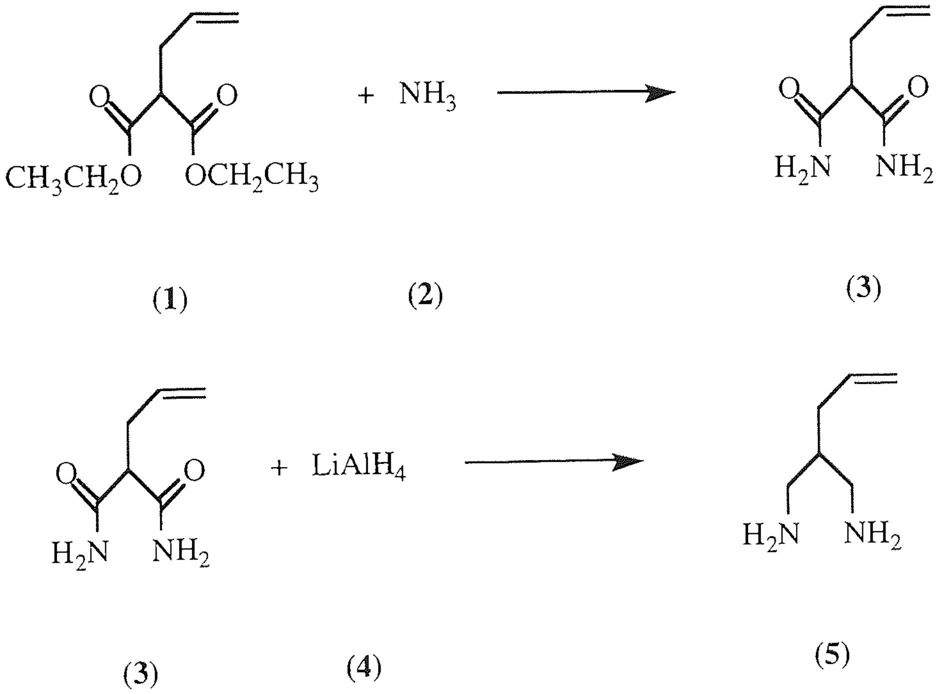


Figure 6.8 ^{15}N Spectrum for 12-Allyl-2,4-Dioxo-1,5,8,11-Tetraazaterdecane



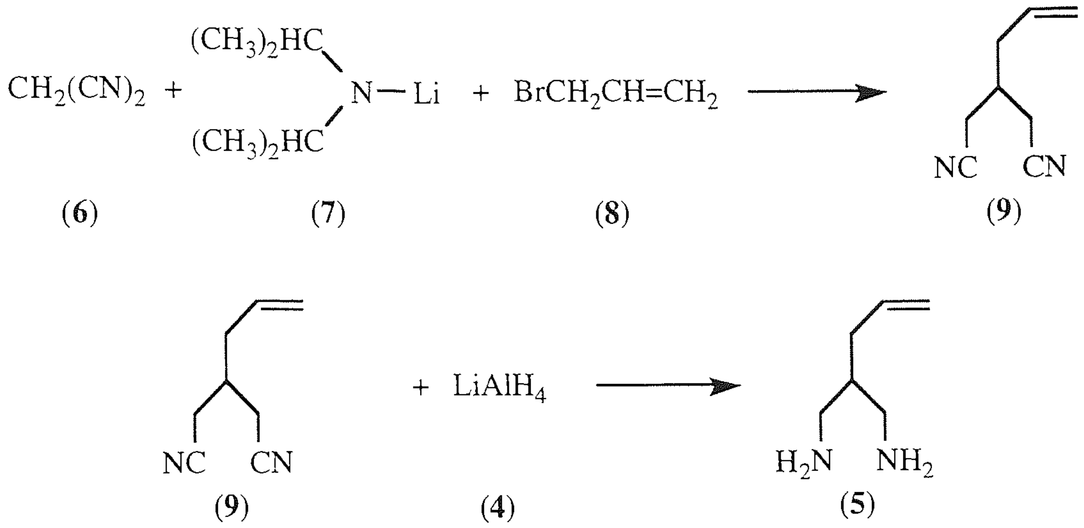
6. 8 Attempted Preparation of 2-allyl-1,3-diaminopropane

Attempts at the synthesis of this functional diamine were performed in the hope that it could be subsequently used in the synthesis of polymerisable Schiff base molecules and Lindoy *et al.*[149] type macrocycles. Two synthetic strategies were followed in the course of these attempts. The first route involved the ammonolysis of allyl diethylmalonate, yielding 2-allylmalonamide as reported by Russell in 1950[156], and the subsequent reduction of the diamide to the desired diamine. [SCHEME 6.10]



While the synthesis of the diamide was achieved relatively easily *via* the literature method, it was found to be insoluble in all organic solvents suitable for carrying out the reduction stage of the preparation. Thus, no further progress was made from this first strategy. Also, the insolubilty of the diamide precluded any N.M.R. studies, as sufficient quantities for solid state N.M.R. spectroscopy were not synthesised.

In the second route, malononitrile is allylated by the method of Toshimitsu *et al.*[157] and the functionalised dinitrile compound is then reduced to yield the diamine. [SCHEME 6.11]



A mixture of dicyano- compounds resulted from the first stage of the reaction scheme shown above. The product mixture was a viscous brown oil and it was decided to use this mixture in the second stage, i.e. the reduction, as the separation of the diamines should be easier to achieve *via* a simple reduced pressure distillation.

The preparation abandoned at this stage, due to both the realisation that the proposed compounds would not participate in free radical polymerisation and the constraints of time.

6.9 Summary

This chapter has dealt with the synthesis of a variey of ligands which were initially thought to be of use as monomers for radical polymerisation. This did not prove to be the case, but in certain cases, novel molecules have been synthesised, while in other cases, interesting phenomena expressed by the molecules have been reported.

While the ligands prepared here are not monomers for radical polymerisation, they do possess a potentially useful functional moiety. The vinyl groups possessed by these molecules will be able to undergo further modification to give ligands that may be polymerisable or of use in coordination studies.

CHAPTER SEVEN

DISCUSSION AND CONCLUSIONS

7.1 Thesis Summary

During the course of the research described in this thesis, those factors affecting the complexation of a number of first-row transition metal ions within three separate series of ligand-modified hydrogel polymers has been examined. The copolymers were based on 2-hydroxyethyl methacrylate, with the ligand modification provided by the ligand comonomers:-

(i) 4-methyl-4'-vinyl-2,2'-bipyridine (**VBPY**)
(ii) the 2-hydroxyethyl methacrylate ester of 4,4'-dicarboxy-2,2'-bipyridine (**DHBPY**)
(iii) *bis*(5-vinylsalicylidene)ethylene diamine (**DVSALEN**)

The synthesis of these ligand-comonomers has been described, alnog with the preparation of a novel mono- vinyl salenH_2 compound - namely (N-salicylidene-N'-5-vinylsalicylidene)ethylene diamine (**MVSALEN**) - although this latter compound was not used in the preparation of copolymer membranes.

Several properties of the copolymer membranes have been studied. In the first instance, the equilibrium water contents (EWC) of the membranes was measured. The VBPY-HEMA membranes prepared in this study were found to follow the trend of those prepared by Lewis[21], while there was no significant variation in EWC for the DVSALEN-HEMA and DHBPY-HEMA membranes, their EWC's being roughly the same as that for pure poly(HEMA).

The mechanical properties of the copolymer membranes have also been tested. The ligands DHBPY and DVSALEN were thought to be potential cross-linking agents, by virtue of their divinyl nature. DVSALEN exhibits no great ability to act as a cross-linker, the mechanical properties of the DVSALEN-HEMA membranes being very poor. When no additional cross-linking agent, EDGM, is employed in the fabrication of these membranes, the materials behave in an extremely elastic manner.

In contrast, DHBPY appears to act as a cross-linker, the mechanical strength of its copolymers with HEMA being enhanced by the presence of DHBPY. On formation of [Fe(bipy)3]2+ centres within these membranes, the expected enhancement of mechanical strength, through coordinative cross-linking, was not observed. This has been explained in terms of the amount of plasticising water being introduced into the polymer matrix on complex formation and also by the possibility that the cooordinative cross-links formed disturb the more effective physical cross-links of the ligand monomer in a manner detrimental to the mechanical strength of the membranes.

The coordination of copper(II) salts, namely nitrate, chloride and sulphate, in DVSALEN-HEMA membranes has been studied. The reaction has been followed using visible spectroscopy and has been found to obey *pseudo*-first-order kinetics. The rate constants for the formation and dissociation of the complex formed have been derived. The rates of both the forward and back reaction are very slow, as would be expected due to the heterogeneous system in which complex formation is occurring. The equilibrium constant, K, for complex formation/dissociation has also been derived, both from a kinetic and thermodynamic standpoint. The two independently obtained values of K are of the same order of magnitude and are within the experimental error likely within such heterogeneous systems. For a ligand such as salenH_2, the values of K obtained during this work are exceptionally small. This has been attributed to the processes needed to occur within the polymer matrix before complex formation can take place. The value of K also shows a weak anion dependance, the value for the divalent sulphate anion being double that for the monovalent nitrate and chloride anions.

The transport of transition metal salts through the various copolymer membranes was examined. In the transport of chromium(III) nitate through VBPY-HEMA membranes, no coordination of the metal ion occurred within the time-scale of a permeation experiment. This was expected due to the kinetic inertness of Cr(III) in substitution reactions. The transport of Cr(III) ions through membranes pre-complexed in Cr(III) solution for nine months was not impaired by the formation of Cr(III) complexes within the polymer matrix.

The transport of cobalt(II), nickel(II) and copper(II) nitrates through DVSALEN-HEMA membranes was also studied. In all cases, no lag-time greater than that for the transport of these salts through pure poly(HEMA) was observed, despite the fact that complexes are formed between the ligand-modified copolymers and the metal ions employed. The permeability coefficient, Pc, showed no apprecible variation with change in the ligand density of the copolymer, or with a change in metal ion.

Finally, a further series of ligands were synthesised in the hope that they too could act as ligand comonomers. The allylic nature of the ligands precluded their use as monomers for radical copolymerisation. However, these ligands do possess potentially useful functional moieties and so could feasibly used as starting points for further modification to give other interesting and useful ligands. Some interesting NMR spectra have been obtained from these molecules. The square planar nature of Ni(CR) renders the metal ion diamagnetic, and so ^1H and ^{13}C could be obtained. The spectra were lost as soon as the square planarity of the complex was destroyed, e.g. by the addition of moisture to the complex. For the N_4 macrocycle, 3-allyl-2,4-dioxo-1,5,8,11-tetraazaterdecane, a ^1H-^1H NOESY spectrum indicates a through space interaction between the amine and amide protons in the macrocyclic cavity. There is no interaction between the pendant allylic protons and the amine or amide protons.

7.2 Suggestions for Further Work

The work presented in this thesis has concerned itself with the use of only one hydrogel monomer, namely HEMA. There are many other readily available monomers, e.g. N-vinylpyrrolidone (NVP), that could also be employed in such work. This would lead to the ability to vary the water content of the copolymers.

There is further scope for the investigation of complex formation within DVSALEN-HEMA copolymer membranes. The copper(II) system has been described here, but the formation of other metal ion complexes are open to examination.

The use of different ligands is also a way in which this work could be extended. Certainly, the use of these systems in the selective separation of metal ions would require a large degree of sophistication in the ligand employed. Perhaps the major difficulty in achieving this suggestion is not so much in the synthesis of the active ligand, but in making it polymerisable.

There remains the potential to examine in closer detail the properties of many interesting complexes formed by the copolymers described in this thesis. Certainly, the ability of cobalt(II) complexes of salenH_2 to reversibly bind dioxygen would certainly be worth examining. Lewis[21] found that Co(I) species could be stabilised in VBPY-HEMA membranes simply by dehydrating the membrane and hence removing the imbibed water through which oxygen travels in these polymers. This is still an area which could provide an valuable means of de-oxygenating systems.

The use of these copolymers in the detection and separation of metal ions is an obvious suggestion. The distinctive colour produced by $[Fe(bipy)_3]^{2+}$ centres within VBPY-HEMA membranes make the copolymers useful in the detection of iron(II). The DVSALEN-HEMA membranes form coloured complexes with a range of transition metal ions and so their use for detection purposes can also be envisaged. For use in separation processes, it is better that the polymer be in the form of a bead rather than in the membrane form. This is due to the low surface area of the membrane form in comparison with beads. It is possible to fabricate these copolymers in the bead form. Ligand design must also be taken into account in order to obtain selectivity from the system.

The use of other metal ions in coordination and immobilisation studies is another way in which to continue this work. It is possible to immobilise ruthenium on VBPY-HEMA copolymers[21], the *tris* complexes fromed being of interest as 'water-splitting' catalysts for th production of hydrogen and oxygen by photoreduction of water.

REFERENCES

1 Pittman, C.U., Jr., Carraher, C.E. and Reynolds, J.R., "Organometallic Polymers", Enc. Polymer Sci. and Engineering, **10**, 541-594, 2nd Edition, Edited by Mark, H.F., Bikales, N.M., Overberger, C.G. and Menges, G., J.Wiley N.Y. (1987), ISBN 0-471-88789-7.

2 Hartley, F.R., "Supported Metal Complexes - A New Generation of Catalysts", D.Reidel Pub. Co. (1985).

3 Carraher, C.E., Sheats, J.E. and Pittman, C.U., Jr., " Metal-Containing Polymeric Systems", Plenum Press N.Y. (1985).

4 Carraher, C.E., Sheats, J.E. and Pittman, C.U., Jr., "Organometallic Polymers", Academic Press N.Y. (1978).

5 Carraher, C.E., Sheats, J.E. and Pittman, C.U., Jr., "Metal-Containing Polymeric Systems", Plenum Press, New York, (1985).

6 Frank, A.J. and Honda, K., "Polymer-Modified Electrodes, Catalysis and Water-Splitting Reactions", *J. Photochem.*, **29**, 195-204, (1985).

7 Kaneko, M. and Yamada, A., "Solar Energy Conversion by Functional Polymers", *Adv. Polym. Sci.*, **55**, 1-47, (1984).

8 Arimato, F.S. and Haven, A.C., "Derivatives of Dicyclopentadienyliron", *J. Am. Chem. Soc.*, **77**, 6295, (1955).

9 Ray, N.H., "Inorganic Polymers", Academic Press, New York, (1978).

10 Kaneko, M. and Tschida, E., "Formation, Characterisation and Catalytical Activity of Polymer-Metal Complexes", *J. Polym. Sci., Mac. Rev.*, **16**, 397-522, (1981).

11 Hodgkin, J.H., "Chelate-Forming Polymers", in reference [1], **3**, 363-381 (1987).

12 Sahni, S.K. and Reedijk, J., "Coordination Chemistry of Chelating Resins and Ion Exchangers", *Coord. Chem. Rev.*, **59**, 1-139, (1984).

13 Schmuckler, G., "Chelating Resins-Their Analytical Properties and Applications", *Talanta*, **12**, 281-290, (1965).

14 Warshawsky, A., "Selective Ion-Exchange Polymers", *Die Angew. Makromol. Chemie*, **109/110**, 171-196, (1982).

15 May, P.M. and Bulman, R.A., "The Present Status of Chelating Agents in Medicine", *Progr. Medicinal Chem.*, **20**, 225-336, (1983).

16 Bulman, R.A., "The Chemistry of Chelating Agents in Medical Science", *Struct. & Bonding*, **67**, 91-141, (1987).

17 Myasoedova, G.V. and Savvin, S.B., "Chelating Sorbents in Analytical Chemistry", *CRC Critical Review in Anal. Chem.*, **17** (1), 1-63, (1986).

18 Hancock, R.D. and Martell, A.E., "Ligand Design for Selective Complexation of Metal Ions in Aqueous Solution", *Chem. Rev.*, **89**, 1875-1914, (1989).

19 Pearson, R.G., "Hard and Soft Acids and Bases", *J. Am. Chem. Soc.*, **85** (22), 3533-3539, (1963).

20 Lehn, J.M., "Supramolecular Chemistry-Scope and Perspective, Mplecules, Supermolecules and Molecular Devices (Nobel Lecture)", *Angew. Chem., Int. Ed. Engl.*, **27**, 89-112, (1988).

21 Lewis, A.L., "Transition Metal Ion Coordination In Hydrophilic Polymer Membranes", PhD Thesis, Aston University, (1991).

22 Slovak, Z and Docekal, B., "Sorption of Arsenic, Antimony and Bismuth on Glycomethacrylate Gels with Bound Thiol Groups for Direct Sampling in Electothermal Atomic Absorption Spectrometry", *Anal. Chim. Acta.*, **117**, 293-300, (1980).

23 Slovak, Z., Smrz, M., Docekal, B. and Slovakova, S., "Analytical Behaviour of Hydrophilic Glycomethacrylate Gels with Bound Thiol Groups", *Anal. Chim. Acta.*, **111**, 243-249, (1979).

24 Slovak, Z., Slovakova, S. and Smrz, M., "Analitsche Eigenschaften von Hydrophilen Glykomethacrylate Gelen mit Chemish Gebunder Salicylsaure", *Anal. Chim. Acta.*, **87**, 149-155, (1976).

25 Slovak, Z. and Slovakova, S., "Use of Hydrophilic Glycomethacrylate Gels with Bound 8-Hydroxyquinoline in Trace Analysis", *Z. Anal. Chem.*, **292**, 213-215, (1978).

26 Slovak, Z., Slovakova, S. and Smrz, M., "Analitsche Eigenschaften von Hydrophilen Glykomethacrylate Polymeren mit Chemish Gebunder 8-Oxychinolin", *Anal. Chim. Acta.*, **75**, 127-138, (1976).

27 Slovak, Z. and Toman, J., "Use of Hydrophilic Glycomethacrylate Gels with Bound 8-Hydroxyquinoline in Trace Analysis, *Z. Anal. Chem.*, **278**, 115-120, (1976).

28 Hock, P.J. and Reedijk, J., "Coordination of Transition Metals by Chelating Cation-Exchange Resins: Co(II), Ni(II) and Cu(II) Coordinated by the 8-Quinolinoyl Group in Spheron Oxine 1000", *J. Inorg. Nucl. Chem.*, **42**, 1759-1765, (1980).

29 Kálal, J., Kálalová, E., Jándrova, L. and Svec, F., "Reactive Polymers, 45; Use of Macroporous Glycidyl Methacrylate-Ethylene Dimethacrylate Copolymer Modified by Diethylamine, for the Separation of Pt(IV), Pd(II) & Rh(II)", *Angew. Makromol. Chem.*, **115**, 13-22, (1983).

30 Janák, K. and Janák, J., "Chelating Ion Exchangers with Bonded 8-Quinolinol on a Glycidyl Methacrylate Gel", *Collect. Czech. Chem. Communs.*, **48**, 2352-2360, (1983).

31 Baker, G.L., Fritschel, S.J., Stille, J.R. and Stille, J.K., "Transition Metal-Catalysed Asymmetric Organic Syntheses via Polymer-Attached Optically Active Phosphine Ligands 5: Preparation of Amino Acids in High Optical Yield via Catalytic Hydrogenation", *J. Org. Chem.*, **46**, 2954-2960, (1981).

32 Baker, G.L., Fritschel, S.J. and Stille, J.K., "Asymmetric Hydrogenation with a Polymer Catalyst Containing Optically Active Pendant Alcohols", *J. Org. Chem.*, 46, 2960-2965, (1981).

33 Pedley, D.G. and Tighe, B.J., "Water Binding Properties of Hydrogel Polymers for RO and Related Applications", *Br. Polym. J.*, **11**, 130-136, (1979).

34 Corkhill, P.H., "Novel Hydrogel Polymers", PhD Thesis, Aston University, (1988).

35 Hamilton, C.J., "Transport Phenomena in Hydrogel Membranes", PhD Thesis, Aston University, (1988).

36 Oxley, H.R., "Crown-Mediated Transport in Hydrogel Membranes", PhD Thesis, Aston University, (1991).

37 Corkhill, P.H., Jolly, A.M., Ng, C.O. and Tighe, B.J., "Synthetic Hydrogels: 1. Hydroxyalkyl Acrylate and Methacrylate Copolymers - Water Binding Studies", *Polymer*, **28**, 1758-1766, (1987).

38 Orlova, N.N., Tolmachev, V.N. and Simonenko, E.A., "Investigation of Sorption Kinetics of Metal Ions by Means of Complexing Oxinrescorcinol-Formaldehyde Resin", *Vysokomol. Soed.*, **14B**, 335-338, (1972).

39 Svec, F., Kálal, J., Kálalová, E. and Marek, M., "Reactive Polymers, XXVII: Kinetics of Chemical Reactions of Metal Ions with Functional Groups of Glycidyl Methacrylate-Ethylene Dimethacrylate Copolymers and Ethylenediamine", *Angew. Makromol. Chem.*, **87**, 95-117, (1980).

40 Brandt, W.W., Dwyer, F.P. and Gyarfas, E.C., "Chelate Complexes of 1,10-Phenanthroline & Related Compounds", *Coord. Chem. Revs.*, **2**, 173-193, (1954).

41 Irving, H. and Mellor, D.H., "The Stability of Metal Complexes of 1,10-Phenanthroline & Its Analogues Pt.1: 1,10-Phenanthroline & 2,2'-Bipyridine", *J. Chem. Soc.*, 5222-5237, **(1962)**.

42 Lindoy, L.F. and Livingstone, S.E., "Complexes of Fe(II), Co(II) & Ni(II) with Diimine Related Bidentate Ligands", *Coord. Chem. Revs.*, **2**, 173-193, (1967).

43 Miller, J.D. and McWhinnie, W.R., "The Chemistry of Complexes Containing 2,2'-Bipyridine, 1,10-Phenanthroline or 2,2',6,2"-Terpyridine as Ligands", *Adv. Inorg. Chem. Rad. Chem.*, **12**, 135-215, (1969).

44 Card, R.J. and Neckers, D.C., "(Polystyrylbipyridine)Palladium(0)- Catalysed Isomerisation of Quadricyclene", *J. Org. Chem.*, **43** (15), 2958-2960, (1978).

45 Card, R.J. and Neckers, D.C., "(Polystyrylbipyridine)Palladium(0)-Heterogeneous Catalyst for the Mild Hydrogenation of Dienes to Monoenes", *Isr. J. Chem.*, **17** (4), 269-273, (1979).

46 Card, R.J., Liesner, C.E. and Neckers, D.C., "(Polystyrylbipyridine)Palladium Complexes as Heterogeneous Catalysts for Hydrogenation of Alkenes and Alkynes", *J. Org. Chem.*, **44** (7), 1095-1098, (1979).

47 Tamagaki, S., Card, R.J. and Neckers, D.C., "(Polystyrylbipyridine)(Tetracarbonyl) Tungsten. An Active, Reusable Heterogeneous Catalyst for Metathesis of Internal Olefins", *J. Am. Chem. Soc.*, **100** (21), 6635-6639, (1978).

48 Card, R.J. and Neckers, D.C., "Preparation of Polymer-Bound Bipyridine and some of its Transition Metal Complexes", *J. Am. Chem. Soc.*, **99** (23), 7733-7734, (1977).

49 Card, R.J. and Neckers, D.C., "(Polystyrylbipyridine): Synthesis and Formation of Transition Metal Complexes and Some of Their Physical, Chemical and Catalytic Properties", *Inorg. Chem.*, **17** (9), 2345-2349, (1978).

50 Neckers, D.C., "Polymeric Bipyridines as Chelating Agents and Catalysts", in reference [3], pg. 385-403.

51 Neckers, D.C., "Polymeric Metal Catalysts and Reagents", *J. Macromol. Sci.*, **A24** (3-4), 431-448, (1987).

52 Zhang, K. and Neckers, D.C., "Diaminobipyridine-TDI Polyureas: Synthesis, Metal Complexes, and Catalytic Activity", *J. Polym. Sci., Polym. Chem. Ed.*, **21** (11), 3115-3127, (1983).

53 Zhang, K. and Neckers, D.C., "Diaminobipyridine-TDI Polyureas: Synthesis, Metal Complexes, and Catalytic Activity", *Polym. Mater. Sci. Eng.*, **49**, 207-209, (1983).

54 Miller, J.D. and Morton, D.S., "Complex Formation Between Polymers Containing the 2,2'-Bipyridine Group & Iron (II)", *J. Chem. Soc., Dalton Trans.*, 1511-1514, **(1983).**

55 Calvert, J.M. and Meyer, T.J., "Polypyridyl Complexes of Ru (II) Bound to Poly(4Vinylpyridine). Synthesis, Characterisation & Thin-Film Electrochemistry of a Series of Bis(Bipyridyl) Metallopolymers", *Inorg. Chem.*, **21**, 3978-3989, (1982).

56 Denisevich, P., Abruna, H.D., Leidner, C.K., Meyer, T.J. and Murray, R.W., "Electropolymerisation of Vinylpyridine & Vinylbipyridine Complexes of Iron (II) & Ru (II)", *Inorg. Chem.*, **21** (6), 2153-2161, (1982).

57 Ellis, C.D., Margerum, L.D., Meyer, T.J. and Murray, R.W., "Oxidative Electropolymerisation of Polypyridyl Complexes of Ru (II)", *Inorg. Chem.,* **22**, 1283-1291, (1983).

58 Kelly, J.M., Long, C., O'Connell, C.M., Vos, J.G. and Tinnemans, A.H.A., "Preparation, Spectroscopic Characterisation and Photochemical & Electrochemical Properties of Some Bis(2,2'-Bipyridine) Ru (II) & Tetracarbonyl W(0) Complexes of 6-p-Tolyl 2,2'-Bipyridine and of 6-p-Styryl 2,2'-Bipyridine & its Copolymers", *Inorg. Chem.*, **22**, 2818-2824, (1983).

59 Calvert, J.M., Schmehl, R.H., Sullivan, B.P., Facci, J.S., Meyer, T.J. and Murray, R.W., "Synthetic & Mechanistic Investigation of the Reductive Electrochemical Polymerisation of Vinyl-Containing Compounds of Fe (II), Ru (II) & Os (II)", *Inorg. Chem.*, **22** (15), 2154-2161, (1983).

60 Potts, K.T., Usifer, D.A., Guadalupe, A. and Abruna, H.D., "4-Vinyl, 6-Vinyl, 4'-Vinyl 2,2',6',2"-Terpyridine Ligands: Their Synthesis & the Electrochemistry of Their Transition Metal Coordination Compounds", *J. Am. Chem., Soc.*, **109**, 3961-3967, (1987).

61 Leidner, C.R., Sullivan, B.P., Reed, R.A., White, B.A., Crimmins, M.T., Meyer, T.J. and Murray, R.W., "Synthesis & Electropolymerisation of Distyryl Bipyridine & Methyldistyryl Bipyridine Compounds of Fe, Ru, Os, Re & Co", *Inorg. Chem.*, **26**, 882-891, (1987).

62 Elliott, C.M., Baldy, C.J., Nuwaysir, L.M. and Wilkins, C.L., "Electrochemical Polymerisation of 4-Methyl-4'-Vinyl-2,2'-Bipyridyl-Containing Metal Complexes. Polymer Structure & Mechanism of Formation", *Inorg. Chem.*, **29**, 389-392, (1990).

63 Woltermann, A., Kauffmann, T. and König, J., "Protophane und Polyaromaten XXII: Nucleophile Alkylierung und Arylierung des 2,2'-Bipyridyls", *Chem. Ber.*, **109**, 3864-3868, (1976).

64 Ghosh, P.K. and Spiro, T.G., "Photoelectrochemistry of tris(bipyridyl) Ruthenium (II) Covalently Attached to n-Type SnO2", *J. Am. Chem. Soc.*, **102**, 5543-5549, (1980).

65 Newkome, G.R. and Yoneda, A., "Synthesis, Characterisation & Complex Formation of Poly(5-Vinyl-6,6'-Dimethyl-2,2'-Bipyrdine)", *Makromol. Chem., Rapid Commun.*, **4**, 575-581, (1983).

66 Kashig, J. and Lohmann, D., "Vinyl-Substituted 2,2'-Bipyridine Compounds", U.S. Patent 4,424,859, (1985).

67 Abruna, H.D., Breikss, A.I. and Collum, D.B., "Improved Synthesis of 4-Vinyl 4'-Methyl-2,2'-Bipyridine", *Inorg. Chem.*, **24**, 987-988, (1985).

68 Gupta, S.N. and Neckers, D.C., "Template Effects in Chelating Polymers", *J. Polym. Sci., Polym. Chem. Ed.*, **20** (6), 1609-1622, (1982).

69 Furue, M., Nozakura, S.I. and Sumi, K., "Synthesis & Luminescence Properties of *tris*(Bipyridyl) Ruthenium (II)- Containing Vinyl Polymers", *Chem. Lett.*, 1349-1352, (**1981**)

70 Furue, M., Nozakura, S.I. and Sumi, K., "Properties of Poly(Vinyl-2,2'-Bipyridine) & Complex Formation with Various Metal Ions", *J. Polym. Sci., Polym. Lett. Ed.*, **20**, 291-295, (1982).

71 Furue, M., Nozakara, S.I. and Sumi, K., "Preparation & Luminescence Properties of tris(Bipyridyl) Ru (II)-Containing Polymers: Ru(Bipy)2 (Poly-6-Vinyl-2,2'-Bipy)Cl2 & Ru(Bipy)2 (Poly-4-Methyl-4'-Vinyl-2,2'-Bipy)Cl$_2$", *J. Polym. Sci., Polym. Chem. Ed.,* **22**, 3779-3788, (1984).

72 Kaschig, J., Finter, J. and Freiburg, D.E., "Strahlungsempfindliche, Metallkomplex bildende Polymere, Verfahren zur Polymerisation von Acetylen und beschichetes Material", Ger. Offen., DE 3510133 A1, (1985).

73 Pitt, C.G., Bao, Y. and Seltzman, H.H., "The Synthesis of Polymers Containing the 2,2'-Bipyridine Ligand", *J. Polym. Sci., Polym. Lett. Ed.*, **24**, 13-16, (1986).

74 Dubsky, J.V. and Sokol, A., "Inner Complex Salts of Cu and Ni from the Prodcut of the Condensation of *o*-Hydroxybenzaldehyde with Ethylenediamine", *Collection Czech. Chem. Commun.*, **3**, 548-549, (1931). [C.A. **26** : 1538]

75 Pfeiffer, P., Bucholz, E. and Bauer, O., "Inner Complex Salts from Hydoxyaldimines and Hydroxyketimines", *J. Prakt. Chem.*, **129**, 163-177, (1931). [C.A. **25** : 2131]

76 Pfeiffer, P., Breuth, E., Lubbe, E. and Tsumaki, T., "Tricyclische orthokondensierte Nebenvalenzringe", *Ann.*, **503**, 84-130, (1933).

77 Pfeiffer, P. and Pfitzinger, H., "High-atomic Partial-Valence Rings with *m*- and *p*- condensations", *J. Prakt. Chem.*, **145**, 243-256, (1936). [C.A. **30** : 5197^1]

78 Pfeiffer, P.,, Hesse, T., Pfitzinger, H., Scholl, W. and Thielert, H., "Inner Complex Salts of the Aldimine and Azo Series", *J. Prakt. Chem.*, **149**, 217-296, (1937). [C.A. **32** : 5127^7]

79 Pfeiffer, P., and Thielert, H., "Complex Titanium Salts", *Chem. Ber.*, **71B**, 119-123, (1938). [C.A. **32** : 2862^5]

80 Pfeiffer, P., Christeleit, W., Hesse, T., Pfitzinger, H. and Thielert, H., "Stereochemistry of Spiranlike Complex Salts - Cotton Effect", *J. Prakt. Chem.,*, **150**, 261-316, (1938). [C.A. **32** : 5783^2]

81 Pfeiffer, P., , Thielert, H. and Glaser, H., “Reciprocal Interchange of Metals in Inner Complexes”, *J. Prakt. Chem.*, **152**, 145-156, (1939) [C.A. **33** : 4544^4].

82 Pfeiffer, P. and Glaser, H., “Exchange of the Amine Residue in the Inner Complex Salts of Schiff Bases”, *J. Prakt. Chem.*, **153**, 265-284, (1939). [C.A. **34** : 87^5]

83 Pfeiffer, P. and Krebs, H., “Stereochemistry of Inner Complex Cu Salts”, *J. Prakt. Chem.*, **155**, 77-114, (1940). [C.A. **34** : 3710^1]

84 Pfeiffer, P. and Saure, S., “Optically Active Chrome Lakes”, *Chem. Ber.*, **74B**, 935-941, (1941). [C.A. **35** : 6936^6]

85 Pfeiffer, P., “The Structural Principles of Inner [Metalloorganic] Complex Salts”, *Angew. Chem.*, **53**, 93-948, (1940). [C.A. **34** : 4723^7]

86 Pfeiffer, P., Offermann, W. and Werner, H., “Inner Complex Salts from Esters of α-Amino Acids”, *J. Prakt. Chem.*, **159**, 313-333, (1942). [C.A. **37** : 3686^9]

87 Thielert, H. and Pfeiffer, P., “Luminescence Phenomena in the Oxidation of Luminol”, *Chem. Ber.*, **71**, 1399-1403, (1938). [C.A. **32** : 8394^6]

88 Holm, R.H., Everett Jr., G.W. and Chakravorty, A., "Metal Complexes of Schiff Bases and B-Ketoamines", *Progr. Inorg. Chem.*, **7**, 83-214, (1966).

89 Tsumaki, T., "Nebenvalenzringverbindungen. IV. Uber Einige Innerkonplexe Kobaltsalze der Oxyaldimine", *Bull. Chem. Soc. Japan*, **13**, 252-260, (1938).

90 Martell, A.E. and Calvin, M., “Chemistry of the Metal Chelate Compounds”, Prentic-Hall, New York, (1952), pp 337-352.

91 Vogt, L.H., Jr., Faigenbaum, H.M. and Wilberley, S.E., “Synthetic Reversible Oxygen-Carrying Chelates”, *Chem. Rev.*, **63**, 269-277 (1963).

92 Floriani, C. and Calderazzo, F., “Oxygen Adducts of Schiff’s Base Complexes of Cobalt Prepared in Solution”, *J. Chem. Soc. (A)*, 946-953, (**1969**).

93 Jones, R.D., Summerville, D. A. and Basolo, F., "Synthetic Oxygen Carriers Related to Biological Systems", *Chem. Rev.*, **79**, 139-179, (1979).

94 Smith, T.D. and Pilbrow, J.R., "Recent Developments in the Studies of Molecular Oxygen Adducts of Cobalt (II) Compounds and Related Systems", *Coord. Chem. Rev.*, **39**, 295-383, (1981).

95 Fachinetti, G., Floriani, C., Zanazzi, P.F. and Zanzari, A.R., "Isolation of the Ion Pair $NaCo(CO)_4$ Promoted by an Inorganic Ligand : Structure and Properties of $[Co(salen)_2NaCo(CO)_4THF]$", *Inorg. Chem.*, **17**, 3002-3007, (1978).

96 Gambrotta, S., Arena, F., Floriani, C. and Zanazzi, P.F., "Carbon Dioxide Fixation : Bifunctional Complexes Containing Acidic and Basic Sites Working as Reversible Carriers", *J. Am. Chem. Soc.*, **104**, 5082-5092, (1982).

97 Clarkson, S.G. and Basolo, F., "Study of the Reaction of Some Cobalt Nitrosyl Complexes with Oxygen", *Inorg. Chem.*, **12**, 1528-1534, (1973).

98 McCleverty, J., "Reactions of Nitric Oxide Coordinated to Transtion Metals", *Chem. Rev.*, **79**, 53-76, (1979).

99 Nishinaga, A. and Tomita, H., "Model Catalytic Oxygenations with Cobalt (II) - Schiff Base Complexes and the Role of Cobalt-Oxygen Complexes in the Oxygenation Process", *J. Mol. Cat.*, **7**, 179-199, (1980).

100 Zombeck, A., Drago, R.S., Corden, B.B. and Gaul, J.H., "Activation of Molecular Oxygen. Mechanistic Studies of the Oxidation of Hindered Phenols with Cobalt-Dioxygen Complexes", *J. Am. Chem. Soc.*, **103**, 7580-7585, (1981).

101 Inada, A., Nakamura, Y., Morita, Y., "An Effective Oxidation of Dihydrazones to Acetylenes with Cobalt (II) Schiff's Base Complexes", *Chem. Pharm. Bull.*, **30**, 1041-1042 (1982).

102 Akelah, A., Abbasi, M.M. and Awad, M.K.H., "Preparation and Studies of Polymeric Schiff Bases of Bis-(5-vinylsalicylidene)diamine Derivatives and Their Metal Complexes", *Ind. J. Chem.*, **25A**, 923-928, (1986).

103 Wohrle, D., Bohlen, H. and Meyer, G., "Polymeric Schiff's Base Chelates and Their Precursors. 5a). Copolymerisation of 2-Hydroxy-5-Vinylbenzaldehyde and Synthesis of Covalently Polymer Bound Cobalt Chelates", *Polym. Bull.*, **11**, 143-150, (1984).

104 Wohrle, D., Bohlen, H. and Meyer, G., "Polymeric Schiff's Base Chelates and Their Precursors. 6a). Covalently Polymer Bound Cobalt Chelates from Divinylsalenes and Their Dioxygen Binding and Catalytic Activity", *Polym. Bull.*, **11**, 150-158, (1984).

105 Kamogawa, H., Watanabe, M., Tsuchiya, H., Oka, S., Hayashi, M. and Nansawa, M., “Synthesis of Novel Organic Functional Substances. I. New Phenol Derivatives Bearing Vinyl Group”, *Kenkyu Hokuku - Asahi Garasu Kogyo Gijutsu Shoreikai*, **44**, 35-41, (1984).

106 Wulff, G. and Akelah, A., “Enzyme-Analogue Built Polymers, 6a) : Synthesis of 5-Vinylslicylaldehyde and a Simplified Synthesis of Some Divinyl Derivatives”, *Makromol. Chem.*, **179**, 2647-2651, (1978).

107 Mandal, S.K. and Nag, K., “Synthesis of Phenoxo-bridged Dicopper (II) Complexes of N-(2-Aminoalkyl)salicylaldimines and Their Use in the Formation of Monohalogeno-complexes and Non-symmetrical Quadridentate Schiff-base Complexes”, *J. Chem. Soc., Dalton Trans.*, 2839-2841, (1984).

108 Isreal, C., "Membranes", in reference [1], **9**, 509-578, (1987).

109 Hwang, S.T. and Kammermeyer, K., Techniques of Chemistry Vol. VII, "Membranes in Separation", John Wiley & Sons, N.Y. (1975).

110 Spacek, P. and Kubin, M., "Diffusion in Gels", *J. Polym. Sci.* (Part C), **16**, 705-714, (1967).

111 Based on the 'Osmonics Filtration Spectrum', Osmonics Inc., 5951 *Clearwater* Drive, Minnetonka, Minnesota, 55343, USA.

112 Cox, J.A. and DiNunzio, J.E., "Donnan Dialysis Enrichment of Cations", *Anal. Chem.*, **49** (8), 1272-1275, (1977).

113 Cox, J.A., Oibrych, E. and Brajter, K., "Separation of a Mixture of Cations by Donnan Dialysis", *Anal. Chem.*, **53,** 1308-1309, (1981).

114 Cox, J.A., Gajek, R., Litiwinski, G.R. and Carnahan, J., "Optimisation of Ion-Exchange Membrane Structures for Donnan Dialysis", *Anal. Chem.*, **54**, 1153-1157, (1982).

115 Cox, J.A., Brajter, K. and Slovawska, K., "Separation of Pt-Group Metal ions by Donnan Dialysis", *Anal. Chem.*, **57**, 2405-2407, (1985), and references therein.

116 Nishiki, T. and Bautista, R.G., "Pt(IV) Extraction with Supported Liquid Membranes Containing Trioctylamine Carrier", *A. I. Ch. E. J.*, **31** (12), 2093-2095, (1985).

117 Maruyama, K., Tsukube, H. and Araki, T., Highly Selective Membrane Transport of Copper (II) Ions by Synthetic Linear Oligomer Carriers, *J. Chem. Soc., Dalton Trans.,* **7**, 1486-1491, (1981).

118 Dohno, R. and Hakushi, T., "Solvent Extraction and Liquid Membrane Transport of Transition Metals by Non-Cyclic Diamides", *Senryo to Yakuhin*, **34** (12), 336-347, (1989).

119 Peppas, N.A., Moynihan, H.J. and Lucht, L.M., "The Structure of Highly Cross-Linked PHEMA Hydrogels", *J. Biomed. Mater. Res.*, **19**, 397-411, (1985).

120 Kobuke, Y., Hanji, K., Horriguchi, K., Asuda, M., Nakayama, Y. and Furikawa, J., "Macrocyclic Ligands Composed of THF for the Selective Transport of Monovalent Cations through Liquid Membranes", *J. Am. Chem. Soc.*, **98**, 7414-7419, (1976).

121 Di Casa, M., Fabbrizzi, L., Perotti, A., Poggi, A. and Riscassi, R., "Ligand Field Effects on the Transport of 3d Metal Ions Across a Bulk Liquid Membrane by Lipophilic Tetraamine Carriers", *Inorg. Chem.*, **25** (22), 3984-3987, (1986).

122 Hasegawa, M. and Kawakutsu, K., "Active Transport & Selective Transport of Alkali Metal Ions through Poly(3-Vinyl-1,4-Butyrolactone-co-Acrylonitrile) Membranes", *Macromol.*, **14,** 170-175, (1981).

123 Shimidzu, T., Yoshikawa, M. and Ohtani, B., "Synthesis of Poly(3-(4-Vinylphenoxy) Phthalide-co-Acrylonitrile) & the Selective Transport Properties of its Membranes", *Macromol.*, **14**, 506-509, (1981).

124 Uragami, T., Watanabe, S., Nakamura, R., Yoshida, F. and Sugihara, M., "Studies on the Synthesis & Permeability of Special Polymer Membranes XLVIII- Active Transport & Selective Transport of Metal Ions through Membranes of Poly(Isobutylene-alternate co-Maleic Anhydride) & PVA", *J. Appl. Polym. Sci.*, **28** (5), 1613-1623, (1983).

125 Uragami, T., Watanabe, S., Nakamura, R., Yoshida, F. and Sugihara, M., "Studies on the Synthesis & Permeability of Special Polymer Membranes 50-Transport of Metal Ions Against their Concentration Gradient through Water-Insoluble Poly(Styrene-Sulphonic Acid) Membranes", *Polymer*, **24** (5), 559-564, (1983).

126 Dohno, R., Takeshita, J., Kinugasa, M. and Hakushi, T., "Active Transport of Transition Metal Ions through Poly(Vinyl Alcohol) & Poly(Acrylic Acid) Blend Membranes", *Maku*, **12** (6), 351-356, (1987)

127 Cox, J.A., Dabek-Zlotorzynska, E. and Brajter, K., "Preparation of a Chelating Polymeric Membrane and Application to Uphill Transport", *Anal. Lett.*, **20** (8), 1149-1156, (1987).

128 Oyobikawa, E., "Separation of Solutes by Complex-Forming Polymer Films", *Kobunshi Kako*, **35** (10), 475-480, (1986).

129 Saunders, J. and Hunter, B., "Modern NMR Spectroscopy- A Guide for Chemists" Ch.3: Multi-Pulse Experiments, Oxford University Press (1987), ISBN 0-19-855202-5.

130 Guarr, T.F. and Anson, F.C., "Electropolymerisation of Ruthenium Bis(1,10-Phenanthroline)(4-Methyl-4'-Vinyl-2,2'-Bipyridine) Complexes through Direct Attack on the Ligand Ring System", *J. Phys. Chem.*, **91**, 4037-4043, (1987).

131 Terasawa, I. and Kawakatsu, T., "Process for the Preparation of High Purity 4-Methyl-4'-Vinyl-2,2'-Bipyridine as a Material for Organic Semiconductors", Japanese Patent, *Jpn. Kokai Tokkyo Koho*, JP 86-295291, 5pp, (1988).

132 Sprintschnik, G., Sprintschnik, H.W., Kirsch, P.P. and Whitten, D.G., “Preparation and Photochemical Reactivity of Surfactant Ruthenium (II) Complexes in Monolayer Assemblies and at Water-Solid Interfaces”, *J. Am. Chem. Soc.*, **99**, 4947-4954, (1977).

133 Case, F.H., “The Synthesis of Certain 2,2’-Bipyridines”, *J. Am. Chem. Soc.*, **68**, 2574-2577, (1946) ; Maerker, G. and Case, F.H., “The Synthesis of Some 4.4’-Disubstituted 2,2’-Bipyridines“, *J. Am. Chem. Soc.*, **80**, 2745-2748, (1958).

134 Broos, R. and Anteunis, M., “A Simplified Wittig Synthesis of Substituted Styrenes”, *Synth. Commun.*. **6**, 53-??, (1976).

135 Stoermer, R. and Behn, K., *Ber. Dtsch. Chem. Ges.*, **34**, 2455, (1901).

136 Lewis, A.L. and Miller, J.D., “Coordinative Crosslinking of Pyridyl- and Bipyridyl- Based Hydrogel Polymer Membranes”, *Polymer*, **34**(11), 2453-2457, (1993).

137 Kopeikin, V.V., “Polymeric 1,3-Dicarbonyl Compounds & Their Derivatives”, *Acta Polymerica*, **34** (6), 307-315, (1983).

138 Yeh, H.C., Eichinger, B.E. and Andersen, N.H., “Metal Ac-Ac Chelate Cross-Linked Gels”, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 2575-2602, (1982).

139 Ning, Y-P., Mark, J.E., Iwamoto, N. and Eichinger, B.E., “Elastomeric Properties of Some Isoprene-Styrene Networks Cross-Linked through Metal-Acetylacetonate Chelation”, *Macromolecules*, **18**, 55-57, (1985).

140 Mandal, J.N. and De, G.S., "Kinetics of Substitution of Aquo Ligands from Hexaaquochromium(III) Ion by 2,2'-Dipyridyl in Water-Ethanol Mixture", *Ind. J. Chem.*, **16A**, 580-582, (1978).

141 Lewis, A.L. and Miller, J.D., "Synthesis, Characterisation and Complexation Behaviour of a Series of Pyridyl- and Bipyridyl- based Hydrogel Membranes", *J. Mater. Chem.*, **3**(8), 897-902, (1993).

142 Hall, D. and Waters, T.N., "The Colour Isomerism and Structure of Some Copper Co-ordination Compounds. Part IV. The Structure of NN'-Disalicylidene-ethylenediaminecopper", *J. Chem. Soc.*, 2644-2648, (**1960**).

143 Csaszar, J., "Studies of Spectral Behaviour of Copper(II) Complexes of Aromatic Schiff Bases and of Secondary Amines", *Acta Phys. Chem.*, **30**(1-2), 61-69, (1984).

144 Kojima, Y., Furuhata, K. and Miyasaka, K., "Diffusive Permeabilities of Solutes in Poly(Vinyl Alcohol) Membranes as a Function of the Degree of Hydration", *J. Appl. Polym. Sci.,* **29**, 533-546, (1984).

145 Kim, S.W., Cardinal, J.R., Wisinowski, S. and Zentner, G.M., "Solute Permeation through Hydrogel Membranes in Water", in *Polymer*, (Ed. Rowland, S.P.), ACS Symposium Series 127, ACS, Washington D.C. (1980), 347.

146 Wilkins, R.G., "Kinetics and Mechanism of Reactions of Transition Metal Complexes", VCH, Weinheim, (1991).

147 Noble, R.D., "Generalized Microscopic Mechanism of Facilitated Transport in Fixed Site Carrier Membranes", *J. Membrane. Sci.*, **75**, 121-129, (1992).

148 Nightingale, Jr., E.R., "Phenomological Theory of Ion Solvation. Effective Radii of Hydrated Ions", *J. Phys. Chem.*, **63**, 1381-1387, (1959).

149 Lindoy, L.F., in "Progress in Macrocyclic Chemistry, Vol. 3 : Synthesis of Macrocycles - The Design of Selective Complexing Agents", (Eds. Izatt, R.M. and Christensen, J.J.), J. Wiley and Sons, New York, (1987), pp 53-92

150 Homer, J. and Perry, M.C., private communication; *J. Chem. Soc., Perkin Trans.*, accepted for publication, (1994).

151 Claisen. L. and Eislieb, O., "Uber die Umlagerung von Pneolallylathern in die isomeren Allylphenole", *J. Liebig's Annalen der Chemie*, **401**, 21-119, (1913).

152 Schlesinger, A. , Weiner, N. , Gordon, S.M. , "Mercurial Diuretic", United States Patent 2,667,442, January 26th 1954.

153 Karn, J.L. and Busch, D.H., “Nickel (II) Complexes of the Tetradentate Macrocycle 2,12-Dimethyl-3,7,11,17-Tetraazabi*cyclo* (11.3.1) Heptadeca-1(17),2,11,13,15-Pentaene”, *Nature*, **211**, 160-162, (1966).

154 Lindoy, L.F., "The Chemistry of Macrocyclic Ligand Complexes", Cambridge University Press, Cambridge, (1989).

155 Tabushi, I. , Taniguchi, Y. and Kato, H., "Preparation of C-Alkylated Macrocyclic Polyamines", *Tetrahedron Letters*, **1977** (12), 1049-1052, (1977).

156 Russell, P.B., “The Conversion of Monosubstituted Malonic Esters to Malondiamides”, *J. Am. Chem. Soc.*, **72**, 1853-1854, (1950).

157 Toshimitsu, A., Terao, K. and Uemera, S. “Intramolecular Amidoselenation of N-Alkenylamides : Formation of Nitrogen Heterocycles”, *J. Org. Chem.*, **51**, 1724-1729, (1986).

APPENDIX ONE

Amax VERSUS [Cu2+] IN DVSALEN-HEMA

Amax	**[Cu^{2+}]** (moldm^{-3})
0.056	0.005
0.293	0.01
0.458	0.025
0.761	0.075
0.965	0.125
0.986	0.15
0.893	0.175
0.933	0.2
1.195	0.225
1.122	0.25
1.095	0.275
1.204	0.3
1.216	0.325
1.253	0.35
1.233	0.375
1.134	0.4
1.362	0.425
1.046	0.45
0.897	0.475
1.027	0.5