

**Synthesis and Characterisation of Some Ruthenium
Containing Metallopolymers**

by

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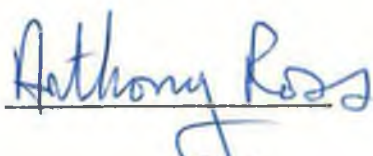
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DECLARATION

I declare that the work described within this thesis is all my own work.

A handwritten signature in blue ink that reads "Anthony Ross". The signature is written in a cursive style with a horizontal line underneath the name.

Anthony G. Ross.

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N. I. H. E. D.

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ABSTRACT

Poly 4(5)vinylimidazole (PVI_m) and a series of copolymers of 4-vinylpyridine and methylmethacrylate (PVP-MMA) were prepared and reacted with hydrated bis(2,2'-bipyridyl)ruthenium dichloride [Ru(bpy)₂-Cl₂·2H₂O]. The mole ratio of 4-vinylpyridine units to methylmethacrylate (4VP:MMA) was varied between 1:5 to 6:1 and the mole ratio of 4VP to ruthenium (4VP:Ru) varied between 1:15:1 to 106:1. In this work the spectroscopic and electrochemical properties of the metallopolymer thus formed both as coatings on electrode surfaces and in solution are described. It is shown that depending on the reaction conditions and the polymer backbone, different types of ruthenium-polymer complexes are formed. The spectroscopic and electrochemical properties of the ruthenium-(PVI_m) metallopolymer are compared to those of mononuclear 4-methylimidazole compounds of Ru(bpy)₂. Chronocoulometry was used to obtain an indication of the ease of charge transport across a film of metallopolymer attached to a glassy carbon electrode. It was found that as the amount of MMA in the copolymer backbone increases, the activation energy for charge transport (E_a) increases and hence charge transport becomes more difficult. The values of E_a obtained both for the (PVP-MMA) and (PVI_m) metallopolymer suggest that some movement of the polymer chains is necessary for charge transport. Electrodes modified with these metallopolymer were found to mediate the oxidation of Fe^{II} in solution at potentials where the ruthenium-polymer complex was reduced. As the amount of MMA in the copolymer backbone increased, it was found that the mediation became less efficient. The results for the photolysis of these metallopolymer in various solvents and as thin films on electrodes are similar to those obtained for Ru(bpy)₂-(poly 4-vinylpyridine or poly N-vinylimidazole).

CHAPTER 1

INTRODUCTION

1.1 Applications and Uses of Ruthenium

The principal use of ruthenium is for hardening alloys with palladium and platinum. Alloys with platinum (12% ruthenium content) find applications as electrical contacts and alloys with both platinum and palladium are used for jewellery and fountain pen nibs. Of increasing interest, however, are the application of ruthenium compounds in catalysis. Ruthenium metal is an active catalyst for the hydrogenation of alkenes and ketones¹ and research into the use of supported ruthenium for the catalytic reduction of nitrous oxide in automobile exhausts has been carried out².

The recent chemistry of ruthenium has, since 1976, been dominated by investigations based on the $[\text{Ru}(\text{bpy})_3]^{2+}$ complex and its derivatives³.

The reason for this reflects a unique combination of photochemistry, electrochemistry and chemical stability which has resulted in these species being considered as potential photocatalysts for the visible light photo-induced decomposition of water into hydrogen and oxygen. Most of this work has been directed⁴ towards the electron transfer reactions of $[\text{Ru}(\text{bpy})_3]^{2+}$ in its electronically excited state which is thermodynamically (although not kinetically) capable of reducing water. Whitten et. al. claimed⁵ in 1976 the successful photocleavage of water by a monolayer assembly of two surfactant derivatives of $[\text{Ru}(\text{bpy})_3]^{2+}$ coated onto glass slides. This was reasoned to be due to the monolayer assembly either lowering the barrier of the electron transfer process or increasing the barrier to the back reaction. This result has proved unrepeatable in a number of laboratories and Whitten and his coworkers have also been unable to repeat their observations and subsequently reported that the initial samples contained numerous impurities⁶. It is possible that an unidentified complex was responsible for the results or that a combination of identified complexes within the monolayer occurred. However if the

kinetic barrier can be overcome the $[\text{Ru}(\text{bpy})_3]^{2+}$ species offers some hope for the conversion of solar energy into stored chemical energy in the form of hydrogen.

1.2 Emission and Absorption Properties of $\text{Ru}^{\text{II}}(\text{bpy})$ Complexes

The photophysics and photochemistry of $[\text{Ru}(\text{bpy})_3]^{2+}$ and related complexes have been widely investigated⁷⁻¹⁰, however there still does not exist an unambiguously correct assignment of either the electronic absorption or the luminescence spectra¹¹. In 1959 Paris and Brandt¹² reported the first observation of the luminescence from $[\text{Ru}(\text{bpy})_3]^{2+}$ and assigned this luminescence to the decay of an excited state of the molecule created by an MLCT absorption $(t_{2g})^6 \rightarrow \pi^*$. The first detailed study of the absorption and emission spectra of $[\text{Ru}(\text{bpy})_3]^{2+}$ was reported by Crosby¹³, who assigned the emission to $(t_{2g})^5(\pi^*)^1 \rightarrow (t_{2g})^6$. The vibrational fine structure was assigned to a perturbed skeletal vibration of the aromatic ring, due to the removal of the π^* electron. The luminescence lifetimes of these complexes were reported by Demas and Crosby¹⁴ who suggested that the decay of the excited state is too slow for a spin allowed (singlet-singlet) transition and too fast for a spin forbidden (triplet-singlet) transition. However for ruthenium, the large value of the spin-orbit coupling constant implies that the terms singlet and triplet can no longer be applied, and the observed lifetimes are consistent with heavy-atom perturbed spin-forbidden transitions. Thus, the transition $(t_{2g})^5(\pi^*)^1 \rightarrow (t_{2g})^6$ may be considered as a $^3\text{CT} \rightarrow ^1\text{A}_{1g}$ band. Recently, Crosby and coworkers showed that the emission arises from three closely spaced electronic states with symmetries A_1 , E_1 and A_2 , in order of increasing energy^{15, 16}. These states are in rapid equilibrium and the emission properties of the excited states are primarily determined by

the properties of the A_2 state except at very low temperatures (less than 25K).

Both the quantum yield for efficiency and the excited state lifetimes are strongly temperature dependent. Substitution of the ligand when the compound is in its excited state can occur because the triplet 3CT state can undergo thermal activation to an antibonding metal-based orbital, $d\sigma^*$. The structural consequences of electron occupation of the $d\sigma^*$ orbital includes large distortions along the metal ligand axes and a subsequent weakening of the Ru-ligand bonds¹⁷ which can lead to photosubstitution of the ligand.

1.3 $Ru^{II}(bpy)_2$ Metallopolymers.

It has been demonstrated that as an electron donor, essentially all the excitation energy of $[Ru(bpy)_3]^{2+}$ can be quenched and an electron can be transferred to a long lived species. Although this reaction occurs rapidly and efficiently in solution, the use of $[Ru(bpy)_3]^{2+}$ as a catalyst is prevented by rapid back reactions to the unexcited species. Immobilisation of the complex on a support such as a polymer backbone by a covalently bonding ligand should inhibit non productive back reactions and promote efficient energy capture by the substrate. Hence there has been interest in polymers containing the $Ru(bpy)_3$ chromophore such as¹⁸ $[Ru(bpy)_2-(vbpy)]^{2+}$ (where vbpy is 4 vinyl-4'methyl-2,2'bipyridine) and in $Ru^{II}(bpy)_2$ -polymers like poly 4-vinylpyridine (PVP) bound $Ru^{II}(bpy)_2$ complexes^{19, 20}. It was found¹⁹ for the PVP metallopolymers that two species could be produced: mono $[Ru(bpy)_2(PVP)Cl]^+$ and bis $[Ru(bpy)_2(PVP)_2]^{2+}$ substituted ligands, depending on the reaction conditions. When the bis substituted species is formed, the vinylpyridine ligands may be on the same or different polymer chains. In the latter case

the metal centre acts as a cross linking agent which in turn can affect the solubility of the metallopolymer.

The use of synthetic polymers as catalysts for reactions has received considerable attention^{21, 22} since these reactions can be used as models for complex enzymatic processes. Although less efficient than enzymes, these polymeric catalysts have several analogous characteristics such as higher reactivities than their corresponding monomers and specificity towards substrates. Synthetic macromolecules containing pendant imidazole groups such as poly 4(5)vinylimidazole (PVI_m) have been used²³ as catalysts for the hydrolysis of esters. The synthesis and characterisation of Ru(bpy)₂-(PNVI_m), where PNVI_m is poly N-vinylimidazole, has been reported recently by Geraty and Vos^{24, 25}. As with the PVP metallopolymer, two species (the mono and bis substituted) were produced. However the PNVI_m metallopolymers have different photochemical and electrochemical properties indicating that the polymer backbone has an affect on the chemical properties of these complexes. It has been shown that the composition and stabilisation of polymer complexes can differ widely from those of their monomeric analogues²⁶. for example, the polymer environment around the metal complex can affect its reactions with other species in solution. Introducing substituent groups into the aromatic rings of the bipyridyl ligand can²⁷ change both the absorption maxima and the extinction coefficient of the MLCT transition without affecting its nature. Hence changes in the backbone of a polymer containing the Ru^{II}(bpy)₂ complex may offer the possibility of "tuning" the photochemical reactivity of the complex²⁸. Hence a systematic variation of the polymer backbone should give information on the affect of the polymer backbone on the chemical properties of the bound complex. Irradiation of these metallopolymer in solution has shown^{25, 28} a photosubstitution of

the polymer ligands by solvent molecules which eventually lead to removal of the complex from the polymer backbone. Such reactions are of interest since photosubstitution changes the chemical properties of the complex and can provide a route to changing the redox potential of an electroactive metallopolymer. Furthermore compounds which may not be prepared easily by normal synthetic routes may be prepared by photosubstitution.

1.4 Polymer Modified Electrodes.

In 1975, Murray and coworkers²⁹ introduced the term 'chemically modified electrodes' to describe electrodes that had foreign molecules deliberately immobilised on their surfaces. Research on surface modified electrodes has involved studies of the electrochemistry of the attached molecules, the catalysis and inhibition of various electrochemical processes and specific applications such as photoelectrodes and analytical determinations. A great deal of this research is devoted to the preparation and characterisation of polymer coated electrodes and to an understanding of the charge transport mechanism within the polymer film. Electroactive polymers can be attached to electrodes by the following methods:

- (a) adsorption onto the electrode surface of the preformed polymer which may contain either covalently or electrostatically bound electroactive groups³⁰.
- (b) electrosorption, where redox active molecules containing vinyl groups are polymerised directly at the electrode surface³¹.
- (c) covalently bound linkages using silane reagents³².
- (d) glow discharge polymerisation.

These polymer films have been observed to retain their own chemical behaviour, such as catalytic properties when attached to the electrode

surface. The coatings offer a three dimensional arrangement of reacting centres as opposed to the two dimensional dispersion found at bare electrodes but monolayer surfaces can be produced by method (c) above. Hence high local concentrations of catalytic sites at the electrode can be achieved even though the total amount of catalyst remains small. The electroactive groups can be part of the polymer, as in the case of polyvinylferrocene, or they can be inserted into the polymer by electrostatic binding through ion exchange or by covalent linkages.

Anson and Oyama³³ pioneered work using poly 4-vinylpyridine for polymer modified electrodes. When the polymer is placed a solution of low pH, the pyridine units become protonated and the matrix essentially becomes a polyelectrolyte with fixed positive charges and mobile counter anions. Ionic redox centres such as IrCl_6^{2-} or $\text{Ru}(\text{edta})^-$ can be introduced into the film by anion exchange to bind strongly, so that the assembly thus formed can be removed from the exchange solution and be used in a different solution that does not contain dissolved complex. The polymers used for anion exchange that have received the most attention are protonated poly 4-vinylpyridine³⁴, quarternized poly 4-vinylpyridine and a copolymer involving poly L-lysine.

Electrostatic binding offers synthetic simplicity and facilitates experimentation but these systems are instable because of leaching of the redox centres from the film. The most permanent way to bind a redox centre to a polymer is to make it a part of the polymer through covalent linkages. Poly 4-vinylpyridine bound $\text{Ru}^{\text{II}}(\text{bpy})_2$ complexes have been of interest³⁵ because of their photochemical and electron transfer properties and their potential role as electrocatalysts.

The most striking feature of these systems is that often they can be electrochemically oxidised and reduced completely. Hence every

exchanged redox centre can be cycled between its oxidation states in a short time, even though most of the centres are remote from the electrode surface. Charge transfer directly across the film is not possible, but there is clearly some mechanism for propagation of charge in these matrices provided an external electrolyte is present. The way in which charge propagation through the layer is taking place is not clearly understood. Anson et al³⁴ proposed the "electron hopping" mechanism. As the fully reduced film becomes oxidised, a few sites near the electrode surface become oxidised directly by the electrode. They can undergo electron exchange with outer neighbouring sites, so they become reduced again and the neighbouring sites become oxidised. The electrode then is able to remove once again electrons from nearby sites so there is lasting oxidation of the neighbouring sites. These sites oxidise their neighbouring site in a similar fashion and this wave of oxidation continues until the remotest sites are converted even though none of the redox centres except the closest actually move to the electrode surface. However in other systems, conversion of the film from the oxidised to reduced form seems to involve physical diffusion of redox sites to the electrode. Others involve an interaction of diffusion of compensating ions in the film and electron exchange.

The importance of the polymer modified electrodes lies in their ability to act as transducers. The polymer layer is able to interact efficiently with both the electrode surface and the electrolyte solution. But, at the same time the layer is acting as a control mechanism. Electron transfer from the electrode to a redox couple in solution can be mediated through the coating. This means that the potential at which the solution is oxidised or reduced depends on the electrochemical properties of the coating. This can lead to either activation or passivation of specific electrochemical

reactions. Modified electrodes might therefore be used to increase the efficiency of fuel cells and electrochemical cells.

In this work, the synthesis of a series of ruthenium containing polymers is reported. It was hoped that a study of these metallopolymers would provide information on how the polymer backbone and the reaction conditions for the formation of the metallopolymer would affect the physical and chemical properties of the metallopolymers formed.

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CHAPTER 2

THEORETICAL CONSIDERATIONS OF THE TECHNIQUES EMPLOYED.

2. 1: Ultraviolet/Visible and Emission Spectroscopy.

2. 1. 1: General UV/Vis Spectroscopy

The theory of ultraviolet/visible spectroscopy is well covered in standard texts^{1, 2}. However a brief description of this theory is given in this section. When a quantum of light impinges upon a molecule it is absorbed in about 10^{-15} seconds and a transition to a higher electronic state takes place. This absorption of light is highly specific and radiation of a particular wavelength is absorbed only by a characteristic structure. These ground to excited state transitions are responsible for the visible and ultraviolet absorption spectra observed for molecules.

2. 1. 2: Luminescence Spectroscopy.

When light is absorbed either entirely or in part by matter, energy is transferred to the molecule. However, absorption of energy must occur in integral units called quanta. Every molecule possesses a series of closely spaced energy levels and an electron can go from a lower to a higher energy level by the absorption of a discrete quantum of light equal in energy to the difference between the two energy levels.

During the time the molecule can spend in the excited state, some energy in excess of the lowest vibrational energy is rapidly dissipated. The lowest vibrational energy of the excited state is attained. If all the excess energy is not further dissipated by collisions with other molecules, the electron returns to the ground electronic state with the emission of energy in the form of light. This phenomenon is called fluorescence (fig. 1). Because some energy is lost in the brief period before emission, the emitted energy is of longer wavelength than the energy that was absorbed.

Any fluorescent molecule has two characteristic spectra: the excitation

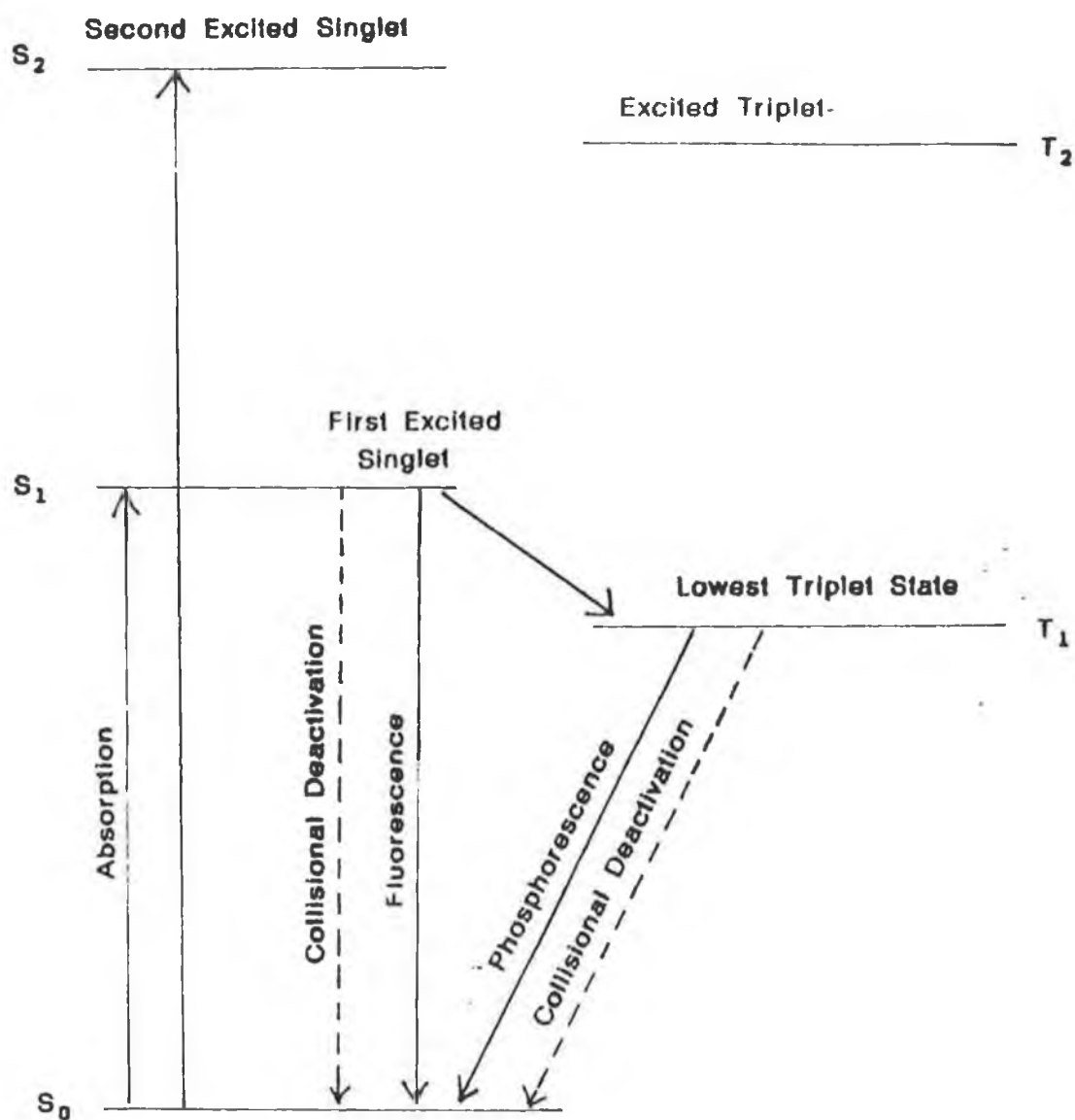


FIG. 1: Schematic Energy-Level Diagram for Fluorescence

spectrum (which is a measure of ability of the different wavelengths of exciting radiation to cause fluorescence) and the emission spectrum (which is the relative intensity of radiation emitted at various wavelengths). The wavelength which gives maximum emission is normally chosen and the fluorescence peak will usually be at the same wavelength regardless of the excitation wavelength, however the intensity of fluorescence will vary with the relative strength of absorption.

It should be noted that the excited state of a molecule differs from the ground state of a molecule in chemical and physical properties. The excited state possesses a different geometry with different diatomic distances and a different dipole moment. Even geometric effects like cis and trans isomers can be introduced and changes in acidity can result in going from the ground to the excited state.

The temperature of a liquid sample plays an important part in the emission spectrum. The rates of radiative and radiationless decay of the excited molecules in a liquid solution are usually dependent on the temperature. The following represent some of the ways in which temperature can affect emission:

- (a) The rate of collisional quenching decreases as the viscosity of the medium is increased. Thus collisional quenching of the emission in liquid media tends to become less serious as the temperature is lowered.
- (b) Other chemical processes involving excited singlet states (e.g. intermolecular hydrogen bonding) occur more slowly as the temperature decreases. The positions of the excited state equilibria also shift slightly with temperature.
- (c) At sufficiently high temperatures intersystem crossing from one

excited state to a higher excited state can occur by thermal excitation. In such systems, the molecules are said to exhibit delayed fluorescence and this fluorescence increases in intensity with increased temperature.

Luminescence spectra obtained at low temperatures often contain well resolved vibrational fine structure not observed in liquid solution. It is usually observed that the fluorescence spectrum of a compound is blue-shifted in a rigid medium relative to the spectrum obtained in liquid medium. This shift results from the fact that solvent and anion reorientation after excitation is considerably less easy in a rigid medium than it is in solution. For complexes where the electron is transferred from the metal and is localised on one ligand, the formation of an induced dipole occurs^{3, 4}. This dipole provides an electrostatic basis for reorientation of the anions on the side of the complex away from the ligand containing the excited electron. Hence the inability of this reorientation of anions in rigid media fixes the excited state into an energy level higher than if it was in solution (fig. 2). Complexes exhibiting this kind of blue-shift are said to undergo rigidochromism⁵.

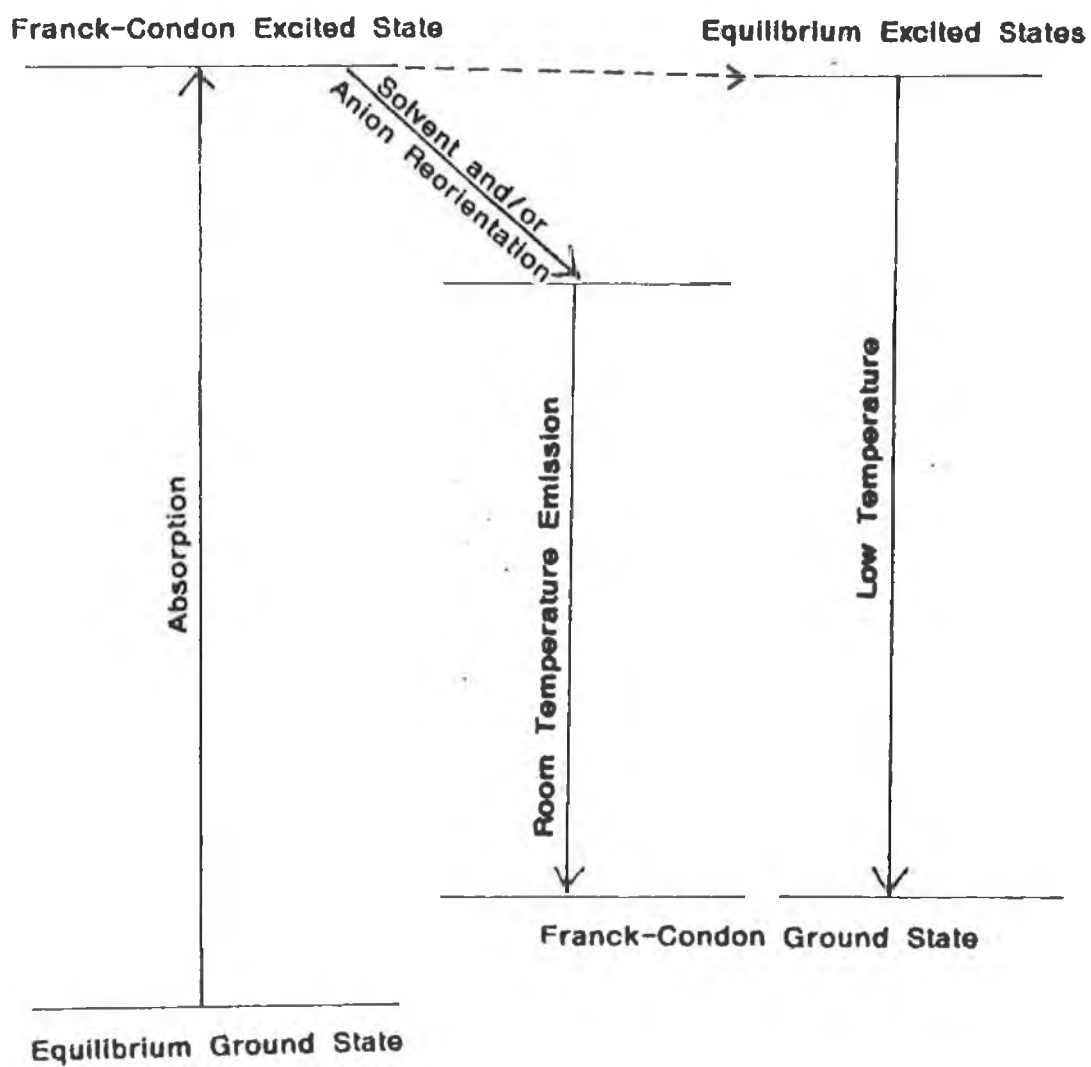


FIG. 2: Schematic representation of Equilibrium and Franck-Condon Electronic States at room and low temperatures.

2. 2: Electrochemistry

2. 2. 1: Cyclic Voltammetry

Cyclic voltammetry is perhaps the most versatile electroanalytical technique for the study of electroactive species because information about complicated reactions over a wide range of time scales can be obtained. Cyclic voltammetry employs the conventional 3-electrode system of working electrode, reference electrode and counter electrode. The potential of the stationary working electrode is changed linearly with time starting from a potential where no electrode reaction occurs (E_0) and moving to potentials where reduction or oxidation of the material being studied occurs (fig. 3). When the final potential is reached (E_λ) the scan direction is reversed to scan back to the original potential.

Since the potential is changed linearly with time, the potential may be written as:

$$E = E_0 + \nu t \quad (1)$$

where E_0 is the initial potential, ν the potential sweep rate in mVs^{-1} and t the time in seconds. For a simple n electron reversible system:



the non-steady state current-potential (I/E) relationship has been derived by Nicholson and Shain⁶. As the potential (E) is increased a peak will appear in the I/E plot becoming more and more prominent (fig. 4). The anodic peak (i_{pa}) for reactants in solution is caused by a combination of the increasing net rate of oxidation, as the potential is made more positive and the development of a thickening depletion layer across which reactants

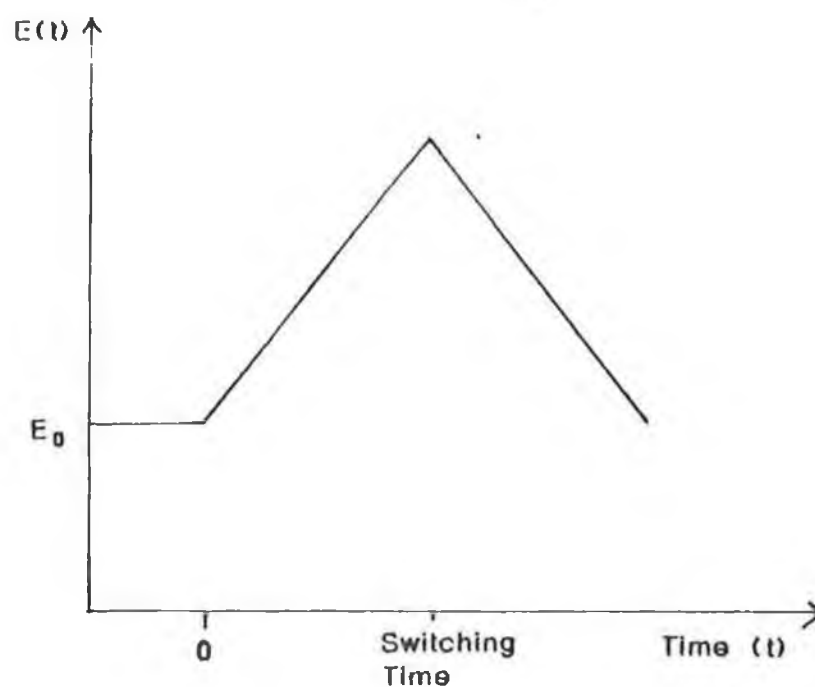


FIG. 3: Schematic representation of the Cyclic Potential Sweep.

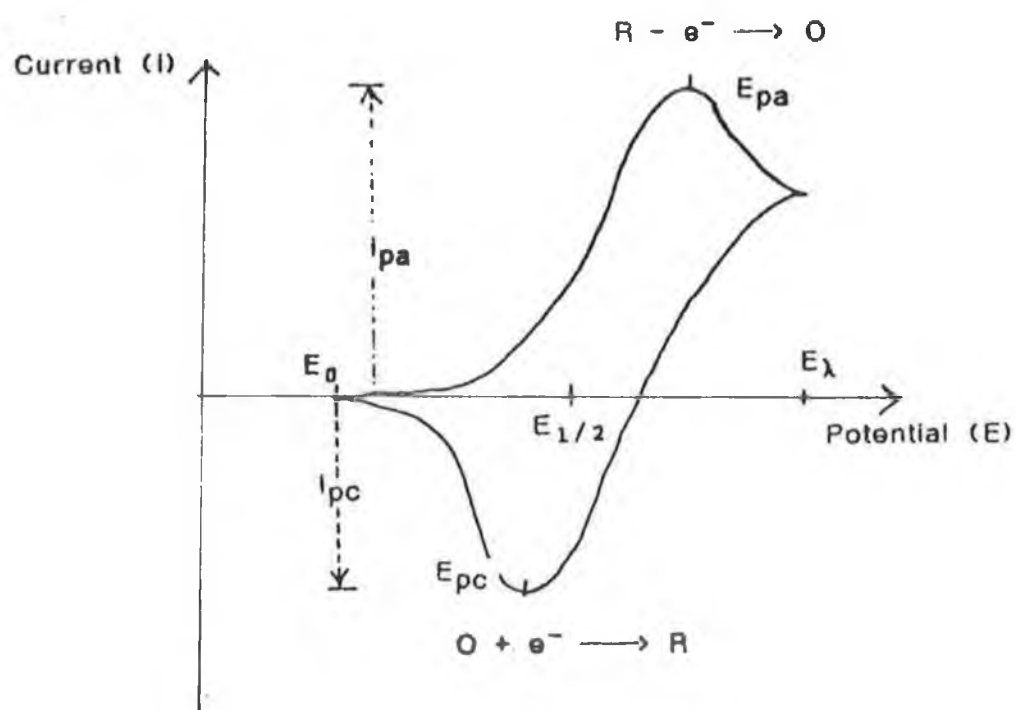


FIG. 4: Typical Cyclic Voltammogram.

must diffuse. If the rate of electron transfer is sufficiently high so that a nernstian equilibrium can be maintained at the electrode surface (a reversible reaction), then the peak current is given by⁷:

$$i_p = (2.69 \times 10^5) n^{3/2} A D_0^{1/2} \nu^{1/2} C_0 \quad (3)$$

where C_0 is the concentration of reduced species in the bulk solution in mol cm^{-3} , D_0 is the diffusion coefficient of the electroactive species, A is the area of the electrode surface in cm^2 and n is the number of electrons involved in the reaction.

Providing the oxidised species (O) is stable, when the potential is reversed at E_λ the reverse sweep will produce a cathodic peak which is equal in height but opposite in sign and is obtained for reasons which are analogous to those underlying the anodic peak: the surface concentration of O becomes small and the current is limited by the rate of return of O to the electrode. The cyclic voltammogram is characterised by several important parameters, the anodic (i_{pa}) and cathodic (i_{pc}) peak currents, the anodic (E_{pa}) and cathodic (E_{pc}) peak potentials and the half wave potential ($E_{1/2}$). For a fast reversible process and at sufficiently slow scan rates the peak separation, ΔE_p , is found to be $59/n$ mV. This relationship can be used to evaluate n , however when the sweep rate is increased to the point where nernstian equilibrium is not maintained, then ΔE_p will begin to increase with ν .

Another situation is when the electroactive species is contained within a thin layer of polymer on the working electrode surface (i.e. a polymer-modified electrode). In this case the peak current is given by⁷:

$$i_p = (9.39 \times 10^5) n^2 \nu V C_\Gamma \quad \text{at } 25^\circ\text{C} \quad (4)$$

where V is the metallopolymer volume in cm^3 and C_T is the concentration of electroactive species in the polymer film in mol cm^{-3} . In this case the anodic peak is caused by the increase in the rate of oxidation and the depletion of unoxidised species in the film.

A comparison of cyclic voltammetry for reactants in bulk solution and reactants confined to a thin layer at the surface can be made by comparing equations (3) and (4). It can be seen from equation (3) that for reactants in bulk solution, the peak current is proportional to $\nu^{1/2}$ and the total charge under the I/E curve is dependent on ν . However, from equation (4) it can be seen that in an ideal case for reactants attached to the electrode surface, the peak current is proportional to ν and the charge under the I/E curve is independent of ν . Hence it is possible to distinguish between the two processes by plots of i_p vs ν and i_p vs $\nu^{1/2}$.

Although quantitative data such as peak currents and potentials can be obtained from cyclic voltammetry, the technique's major use has been in the rapid qualitative elucidation of reaction mechanisms. In a single experiment, intermediates can be directly observed and their possible identification implied by the potential at which they oxidise or reduce. One can often gain immediate information about the reaction mechanism from peak separation, peak height ratios, the absence of reversible peaks and the appearance of new peaks on subsequent scans.

2.2.2: Chronocoulometry

Chronocoulometry is a powerful technique for investigating the properties of the electrode/electrolyte interfaces. All the important events in electrochemistry take place at the interface between the conducting solid electrode and the liquid electrolyte solution. This is where the ionic

current is transferred into electronic current by an electrode reaction. The chronocoulometric method was developed by Anson⁸ and co-workers and the technique consists of rapidly stepping the potential from a point where no reaction takes place to a potential where reduction or oxidation of the material being studied takes place. The electric charge (Q) that flows as a result of this potential step is measured as a function of time (t).

Consider a homogeneous polymer film containing an electroactive species R attached to a planar electrode which is held at some potential E_i , where insignificant electrolysis takes place. At $t=0$, the potential is shifted to E_f which is sufficiently positive to oxidise the species and enforce a diffusion-limited current. Then the resulting current is given by the Cottrell equation:

$$i = nFAC_{\Gamma} \left[\frac{D_{app}}{\pi t} \right]^{1/2} \quad (5)$$

where F is the Faraday (96,487 coulombs per equivalent), t is the time following the potential step, D_{app} is the apparent diffusion coefficient, C_{Γ} is the volume concentration of reactant confined to the polymeric coating and the other parameters are as defined previously.

The current is actually composed of two components: the faradaic current given by equation (5) plus a "charging current", i_c , that flows to charge up the double layer that is always present at electrode/electrolyte interfaces. Figure 5 shows the current and charge that results from a potential step. The total charge passing through the electrode is the time integral of the two current components:

$$Q = \int nFAC_{\Gamma} \left[\frac{D_{app}}{\pi t} \right]^{1/2} dt + \int i_c dt \quad (6)$$

$$Q = 2nFAC_{\Gamma} \left[\frac{D_{app}t}{\pi} \right]^{1/2} + Q_c \quad (7)$$

where Q_C is the charge due to the interfacial capacitance when the electrode potential is stepped from E_i to E_f .

From equation (7) it can be seen that plots of Q vs $t^{1/2}$ (fig. 7), should be linear with intercepts Q_C and at any temperature T , the slopes (S_T) proportional to the square root of the diffusion coefficient

$$S_T \propto D_{app}^{1/2} C_T \quad (8)$$

Chronocoulometry has found application in the study of the diffusion of charge through polymer modified electrodes^{9, 10}. Significant quantities of attached complex remain unoxidised under cyclic voltammetric conditions and the magnitude of the peak does not provide a reliable measure of the apparent diffusion coefficient. However, the slopes of a linear chronocoulometric charge-(time)^{1/2} plots give a reliable measure of D_{app} . The temperature dependence of the apparent diffusion coefficient exhibits an Arrhenius type of behaviour:

$$D_T = D_0 \exp(-E_a/RT) \quad (9)$$

where D_T is the apparent diffusional coefficient at temperature T , E_a is the energy of activation for charge transport, D_0 is the preexponential factor and R is the gas constant. The slopes obtained from the Q vs $t^{1/2}$ plots can be used to evaluate E_a , since:

$$\ln \frac{S_T}{S_{298}} = \frac{1}{2} \ln \frac{D_T}{D_{298}} \quad (10)$$

where S_{298} is the slope at 298K and D_{298} is the apparent diffusion

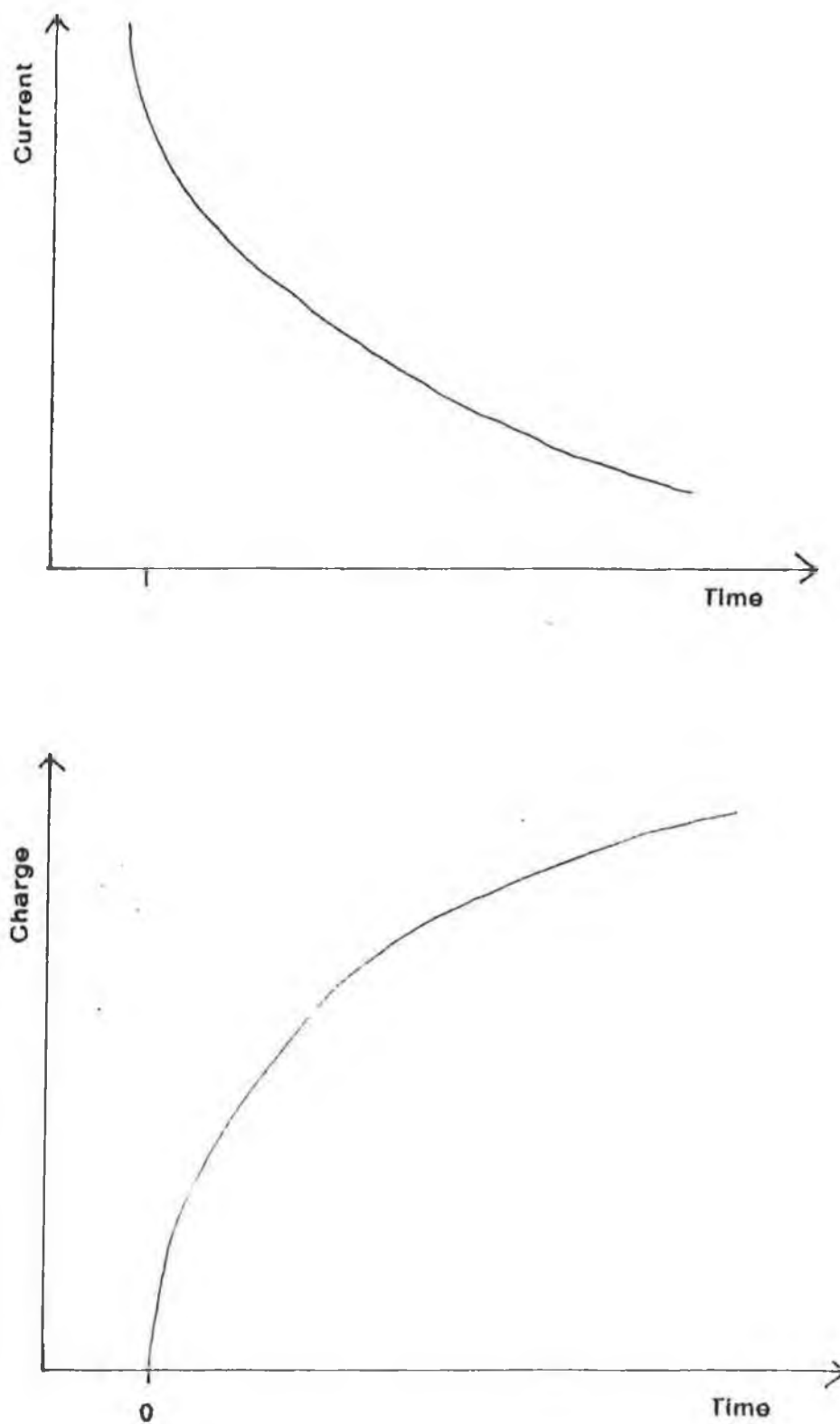


FIG. 5: The behaviour of electrode current and charge in response to a potential step.

coefficient at 298K.

From equation (9) and (10):

$$\frac{D_T}{D_{298}} = \frac{D_0 \exp(-E_a/RT)}{D_0 \exp(-E_a/298R)} \quad (11)$$

Hence substituting equation (20) into (19) gives:

$$\ln \frac{S_T}{S_{298}} = -\frac{E_a}{2RT} + \frac{E_a}{596R} \quad (12)$$

Simplifying equation (21) gives:

$$\ln \frac{S_T}{S_{298}} = -\frac{E_a + 2.018 \times 10^{-4} E_a}{2RT} \quad (13)$$

Therefore it can be seen from equation (13) that a plot of $\ln(S_T/S_{298})$ against $1/T$ should give a straight line with slope $-E_a/2R$ (fig. 4). From this the activation energy can be determined.

The activation energy, E_a , gives a measure of the energy barrier or the difficulty associated with charge transport within the polymer layer to the electrode surface.

2.2.3: Rotating Disk Electrodes.

The method of rotating disk electrode experiments involves the rotation of an electrode surface at a known rotation rate (r) in sec^{-1} , causing controlled stirring of the solution. In the case of fast electron transfer, the mass transfer process from bulk solution is dominated by forced convection rather than by diffusion and a steady state situation is quickly achieved. Current-potential (I/E) curves recorded under such conditions of mass

transport are relatively insensitive to scan rates (below 5 mV/s) unlike voltammetric methods applicable to stationary electrodes. The measurement of I/E curves under these conditions is referred to as hydrodynamic voltammetry.

When polymer-modified electrodes, where catalysts are confined to the electrode surface, are used in hydrodynamic voltammetry it has been found that electrocatalysis of reagents can occur (fig. 5). However the realisation of high intrinsic redox reactivities in such systems requires that the accessibility as well as the reactivity of the bound complex is maintained.

Under conditions where the convective terms are dominant, the limiting current, i_a , is governed by the rate of rotation of the electrode. The following equation for the limiting current holds¹¹:

$$i_a = 0.62nFAC_a D^{1/2} \omega^{1/2} \nu^{-1/6} \quad (14)$$

Where C_a is the bulk concentration of the substrate, D is the diffusion coefficient of the substrate in solution, ν is the kinematic viscosity in cm^2s^{-1} and ω is the angular velocity of the disk given by: $\omega = 2\pi r$.

For situations where the current is limited by relatively slow exchange at the electrode surface the total current, i , is controlled by kinetic phenomenon occurring at the surface and inside the film as well as by the transport of reactants in the bulk solution.

$$\frac{1}{i} = \frac{1}{i_a} + \frac{1}{i_f} \quad (15)$$

where i_f is the 'film current' due to kinetic effects in the polymer film.

From equation (23) and (24):

$$\frac{1}{i} = \frac{1}{i_f} + \frac{1}{0.62FAC_a D_s^{1/2} \omega^{1/2} \nu^{-1/6}} \quad (16)$$

It can be seen from this equation that a plot of i vs. $\omega^{1/2}$ will be curved and tend towards the limit $i=i_f$ as $\omega^{1/2} \rightarrow \infty$. A plot of $1/i$ vs. $1/\omega^{1/2}$ should be linear and can be extrapolated back to $1/\omega^{1/2}=0$ to yield $1/i_f$.

The kinetics of electrochemical reactions mediated by redox polymer films have been considered in a number of studies in recent years¹²⁻¹⁵. In particular the theory in the case of an irreversible cross-exchange reaction (fig. 6):



where equation (17) is for the attached redox couple and equation (18) shows the subsequent cross-exchange reaction with the substrate (A), has been rigorously detailed¹². The four characteristic currents that are measures of the four possible rate-limiting factors are as follows:

i_a is the Levich current¹¹ that corresponds to the limiting current that would be obtained at a bare electrode.

i_s is the current arising from the diffusion of the substrate through the coating to the electrode in response to changes in applied potential; where S is the electrode surface area, κ is the partition coefficient of the substrate between the film and solution, D_s is the diffusion of the substrate in the film and Φ is the film thickness.

$$i_s = FSC_a \kappa D_s / \Phi \quad (19)$$

i_e is the current arising from the diffusion-like electron transport by interactions of the surface bound reactant along the polymer chain; where

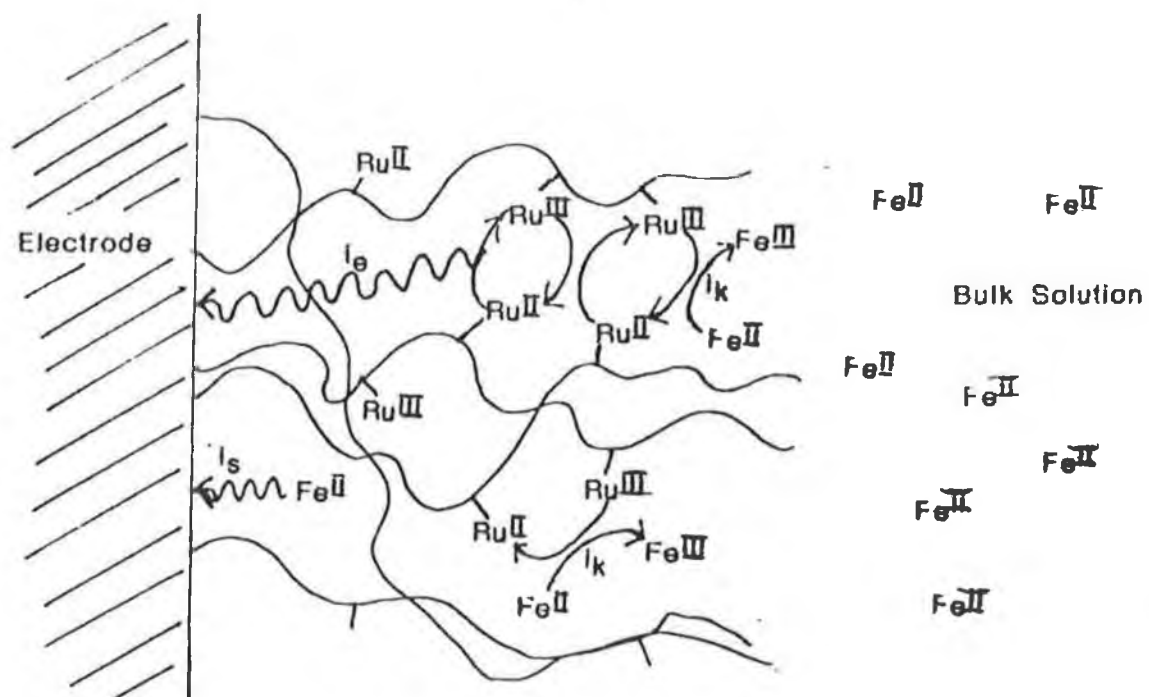


FIG. 6: Diagram representing the three electrode processes i_e , i_k and i_s .

C_T is the concentration of electroactive species in the coating, D_e is the "diffusion coefficient" for the diffusion like propagation of electron in the film.

$$i_e = FSC_T D_e / \Phi \quad (20)$$

i_k is the current that arises from the cross-exchange reaction (eqn. (18)); where k_1 is the second order rate constant of the reaction between the substrate and the active form of the mediator in the film.

$$i_k = FSC_a k_1 C_T \Phi \quad (21)$$

Using the diagnostic criteria developed by Saveant et. al.¹², the limiting behaviour of the system where $[Ru(bpy)_2(PVP)Cl]^{2+}$ is the mediator in the copolymer film and $[Fe(H_2O)_6]^{2+}$ is the substrate, can be determined. This system could be an SR case, that is, the film current is controlled by the rate of the cross-exchange reaction and the diffusion of the substrate in the film or an S case, where the film current is controlled purely by the kinetic current i_k . The film electron diffusion-like transport current, i_e , is so much faster than the Levich current (that is: $i_e \gg i_a$), that it is not a rate limiting factor. In the SR case there is mutual compensation of the cross-exchange reaction and the diffusion of substrate. Hence for any particular SR case the product of i_k and i_s is a constant value. However it is usual to assume that the rate of the cross-exchange reaction is much faster than the rate of diffusion of the substrate through the coating (that is: $i_k \gg i_s$). The total current for an SR case is given by the following relationship¹⁵:

$$\frac{1}{i} = \frac{1}{i_a} + \frac{1}{(i_k i_s)^{1/2}} \quad (22)$$

and in an S case:

$$\frac{1}{i} = \frac{1}{i_a} + \frac{1}{i_k}$$

(23)

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CHAPTER 3

EXPERIMENTAL

3. 1: APPARATUS AND MATERIALS

3. 1. 1: Instrumentation

Infrared Spectra were recorded using a Perkin Elmer 983G Infrared Spectrometer. Samples were prepared as a KBr disc or in the case of the polymers and metallopolymers coated as a film from dichloromethane onto KRS-5 or NaCl plates. Nuclear Magnetic Resonance Spectra were recorded on a Perkin Elmer 60 MHz Nuclear Magnetic Resonance Spectrometer R12B with Me_4Si as an internal standard. Ultraviolet spectra were recorded using a Shimadzu UV-Visible Spectrophotometer UV-240 coupled to a Shimadzu Graphic Printer PR-1. Samples and reference were placed in 1cm matching Quartz Cells. Both room temperature and low temperature Luminescence Spectra were recorded on a Perkin Elmer LS-5 Luminescence Spectrophotometer coupled to a Perkin Elmer 561 recorder and a Low Temperature Accessory 5212-6000. Measurements were not corrected for photomultiplier response.

Measurements of pH were made with a Phillips digital pH meter PW9140 with an Orion combination pH electrode 91-05 and a temperature compensating device. The pH meter was calibrated with standardised buffer solutions of pH 4, pH 7 and pH 9. Melting points were obtained on a Gallenkamp Melting Point apparatus and are uncorrected. Photochemical experiments were carried out using an Applied Photophysics Quantum Yield Photoreactor Model QYR25 with a 240V power source and 1cm Quartz cells.

Electrochemical measurements were carried out using an EG&G Princeton Applied Research (PAR) Model 174A Polarographic Analyzer and an EG&G PAR model 175 Universal Programmer and recorded on a EG&G PAR model RE 0074 X-Y recorder. A conventional thermostatted 3-electrode cell

system consisted of a counter electrode of platinum wire, a reference electrode which was a Coleman saturated calomel electrode and the working electrode. The working electrode was a pyrolytic graphite disk (diameter 0.5 cm) sealed into glass tubing with epoxy and heat shrinkable tubing and electrical contact made to the rear face of the disk with a drop of mercury and a copper wire¹. A glassy carbon electrode (diameter 0.75cm) was also used as the working electrode.

In addition to the equipment listed above, chronocoulometric experiments were carried out using an EG&G PAR Digital Coulometer Model 379 with a JJ Instruments PL3 XY/t recorder and rotating disc electrode measurements obtained in conjunction with a Pine Instrument Company Analytical Rotator (Model ASRE) and a Pine Instrument Company ASR Speed Control Unit.

The Photolysis experiments carried out in conjunction with Cyclic Voltammetry used a Kodak Slide Projector as a light source shone through a beaker of water to filter the associated heat and a concave mirror of focal length 100mm to focus the light onto the working electrode surface. No efforts were made to optimise the light intensity.

3.1.2: MATERIALS

3.1.2.1: Materials used in Synthesis

In the synthesis of poly 4(5)-vinylimidazole, all reagents were of general purpose grade and the fructose, basic cupriccarbonate, triphenylmethyl chloride, triethylamine and methyl triphenylphosphonium bromide were obtained from Riedel de Haen and were used without further purification. Precipitated manganesedioxide was prepared from solutions of manganoussulphate, sodiumhydroxide, and potassiumpermanganate according to

a modified Attenburrow Procedure². The manganesedioxide was then activated by azeotropic removal of water using toluene³. Column Chromatography was performed for organic compounds using Kieselgel S 0.032-0.063 mm and for inorganic compounds using Aluminium Oxide S (Active, Neutral) both obtained from Riedel de Haen. TLC was performed for organic materials using DC-cards SI F 10X20 cm silica gel with fluorescent indicator 254nm on aluminium cards; and for inorganic materials using DC-cards AL F 10X20 cm aluminium oxide with fluorescent indicator 254nm on aluminium cards. For polymerisations α, α' -azoisobisbutyronitrile (AIBN) was acquired from Riedel de Haen and was recrystallised twice from methanol. 4-vinylpyridine and methylmethacrylate obtained from Riedel de Haen were purified by vacuum distillation and were stored in the dark at -20°C . 4-methylimidazole was obtained from Aldrich and was used as received. $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ was prepared⁴ using $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, 2,2'-bipyridine and LiCl (all obtained from the BDH Chemical Company).

3.1.2.2: Solvents and Materials used in Physical Measurements

Water used to make up solutions was distilled before being passed through a Waters Millipore System to remove metal and organic impurities. Acetonitrile was obtained from Koch-Light Limited and was of spectroscopic grade and was dried over molecular sieve Type 4A. Triethylammonium perchlorate (TEAP) was synthesised⁵ from triethylammonium bromide and perchloric acid, recrystallised from boiling water and dried in vacuum. A 0.1 M solution of TEAP in Acetonitrile was used as electrolyte for the model compounds. All chemicals used to make up the buffers were of analytical grade. A stock solution of Britton-Robinson Buffer (pH 1.8), composed of a mixture of boric acid, orthophosphoric acid and glacial

acetic acid all 0.04 M was prepared. Addition of a 0.2 M solution of sodium hydroxide gave a range of buffers from 1.8 to 13. The buffer used in the Chronocoulometric experiments was a 0.1 M solution of sodium trichloroacetic acid (from BDH) which was added to a 0.2 M solution of sodium trichloroacetate (from Merck) to give a buffer of pH 2. For hydrodynamic experiments an Fe^{2+} solution of ammonium ferrous sulphate (from Riedel de Haen) made up in a 0.9 M sodium sulphate (from BDH)/0.1 M H_2SO_4 buffer solution was used.

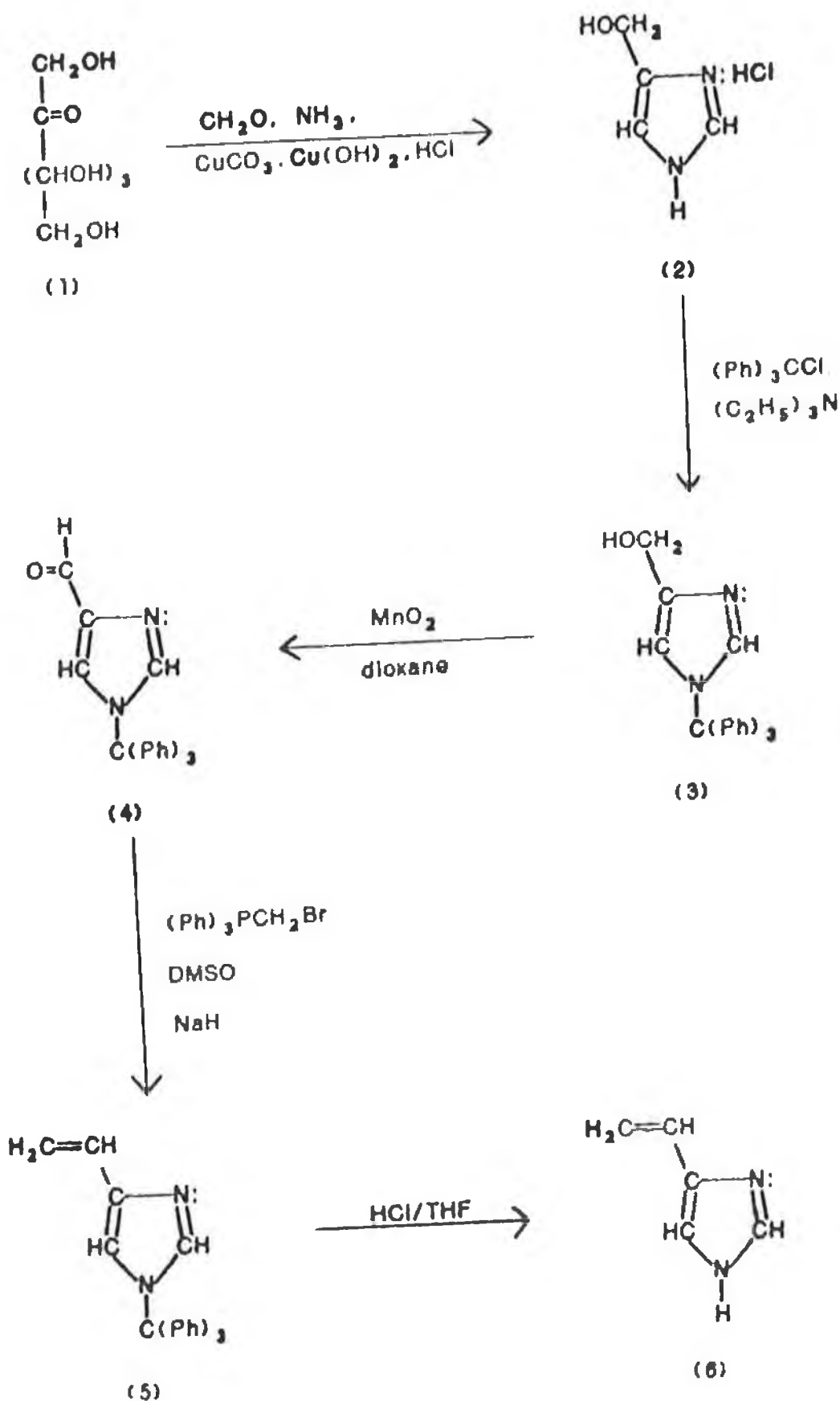
3.1.2.3: Materials Synthesised

4(5)-(Hydroxymethyl)imidazole hydrochloride (2). This compound was prepared from fructose (1) in 48% yield by the procedure outlined by Darby and Trotter⁶. mp 102-104°C (lit.⁶ 107-109°C).

1-(Triphenylmethyl)-4-(hydroxymethyl)imidazole (3). The N-H group of (2) was blocked with the Triphenylmethyl group according to a literature procedure⁷. The progress of the reaction was followed by TLC and it was found necessary to carry out the reaction for at least 2 hours (lit.⁷ 1hr) in order to ensure complete conversion: yield 92% (lit.⁷ 88%); mp 215-217°C (lit.⁷ 219-221°C); IR (KBr) 3200cm^{-1} ($\nu\text{O-H}$), 1600cm^{-1} (νC): NMR (CD_3OD): δ 7.2-7.7(m, 15H, Ph_3), 6.7(s, 1H, Im H), 4.5(s, 2H, CH_2OH), 2.92(s, 1H, CH_2OH).

1-(triphenylmethyl)-4-imidazolecarboxaldehyde (4). The hydroxyl group of (3) was preferentially oxidised using MnO_2 according to the literature procedure⁷; yield 91% (lit.⁷ 91%); mpt 189-193°C (lit.⁷ mpt 189-192°C); IR (KBr) 1692cm^{-1} ($\nu\text{C=O}$); NMR (CD_3COCD_3): δ 7.0-7.6(m, 15H, Ph_3), 6.7 (s, 1H, Im H), 9.8 (s, 1H, CHO).

1-(triphenylmethyl)-4-vinylimidazole (5). The desired vinyl group was produced by a Wittig reaction on compound (4) according to the literature



Scheme 1: Synthesis of 4(5)-Vinylimidazole.

procedure by Kokosa et al⁸. The final reaction mixture was stirred for 6 hours (Instead of 4 to 5 hours) and the reaction product, starting material residue and Ph_3PO were separated by dissolving the mixture in CHCl_3 (30g in 25cm^3) and chromatographed on a $4\text{cm} \times 1.5\text{m}$ glass column containing silica gel and using $\text{CH}_2\text{Cl}_2/\text{Pet Ether}$ (65/35) for elution. The product was isolated to yield pure (5); yield 90% (lit.⁸ 80%). An analytical sample was recrystallised from $\text{CHCl}_3/\text{Hexane}$; mp $196-200^\circ\text{C}$ (lit.⁸ $202-204^\circ\text{C}$); IR (KBr) 3086cm^{-1} (Ar H), 1630cm^{-1} ($\text{C}=\text{C}$); NMR (CDCl_3): (H_g refers to the vinyl proton geminal to the Im ring at C-1, H_t refers to the vinyl proton trans to the Im ring at C-2, H_c refers to the vinyl cis to the Im ring at C-2): δ 5.0-5.2 (dd, 1H, H_g , $J_{cg}=10\text{Hz}$, $J_{gt}=2\text{Hz}$), 5.6-6.0 (dd, 1H, H_t , $J_{ct}=18\text{Hz}$), 6.3-6.5 (dd, 1H, H_c , $J_{cg}=10\text{Hz}$), 6.8- (s, 1H, Im H-5), 7.1-7.9 (m, 16H, Ph_3 , Im H-4).

4(5)-Vinylimidazole (6). The Triphenylmethyl blocking group was removed by acid hydrolysis according to the literature procedure⁸; yield 42% mpt $78-80^\circ\text{C}$ (lit.⁸, 86°C); IR (KBr) 3124cm^{-1} ($\nu\text{N-H}$), 1640cm^{-1} , ($\nu\text{C}=\text{C}$), 1585cm^{-1} ($\delta\text{N-H}$); NMR (CDCl_3): δ 4.9-5.1 (dd, 1H, H_g , $J_{cg}=10\text{Hz}$), 5.4-5.7 (dd, 1H, H_t , $J_{ct}=18\text{Hz}$), 6.3-6.8 (dd, 1H, H_c), 6.9 (s, 1H, Im H-5), 7.5 (s, 1H, Im H-2).

Polymerisation of 4(5)-Vinylimidazole. 4(5)-Vinylimidazole (0.949g, 10.6 mmoles) and 2 mg of azobisisobutyronitrile (AIBN, 0.1 mole %) were dissolved in 20cm^3 of dry benzene in a 25cm^3 round bottomed flask fitted with a stop-cock. The solution was frozen in liquid nitrogen, evacuated to 0.1 mm Hg, closed to the vacuum and allowed to thaw to room temperature. After this procedure had been repeated three times, the flask was filled with a dry nitrogen atmosphere and sealed. The flask was then placed in a water bath at 65°C and it was noted that polymer began to precipitate out after 1 hour. After 24 hours at 65°C the flask was opened

and poured into 100ml of benzene and stirred for an hour. The polymer was isolated by filtration, dissolved in methanol and precipitated in tetrahydrofuran. The polymer was then dried in vacuum to yield 0.474g (47% yield) of poly 4(5)-vinylimidazole.

Copolymerisation of 4-Vinylpyridine and Methylmethacrylate. Four copolymers of 4-vinylpyridine and methylmethacrylate in the ratios given in Table 1 have been prepared. The monomer feed ratios were chosen according to monomer reactivity ratios reported in the literature⁹. The radical copolymerisation reactions using AIBN were carried out in toluene solution at 65°C for 7 hours under a nitrogen atmosphere. The reaction mixture had been de-gassed by the freeze-thaw method prior to copolymerisation. The conditions and yields of the reaction are given in Table 1. The copolymers were purified by dissolving them in dichloromethane and precipitating in the solvents given in Table 1. They were subsequently dried in vacuo for 24 hours at room temperature.

Analysis calcd. for:

Polymer 1 (16.75% 4VP), C, 63.4; H, 7.8; N, 2.3. Found C, 63.1; H, 8.0; N, 2.3.

Polymer 2 (23.9% 4VP), C, 65.0; H, 7.7; N, 3.3. Found C, 65.2; H, 7.7; N, 3.3.

Polymer 3 (49.85% 4VP), C, 67.3; H, 7.4; N, 6.5. Found C, 67.8; H, 6.8; N, 6.6.

Polymer 4 (85.7% 4VP), C, 77.1; H, 6.8; N, 11.5. Found C, 73.9; H, 6.5; N, 11.0.

Metallopolymers

Preparation of $[\text{Ru}(\text{bpy})_2(\text{PVP-MMA})_n\text{Cl}_m]\text{Cl}_n$ ($m, n = 0.2; 1, 1$)

Several $\text{Ru}(\text{bpy})_2$ -containing redox polymers of the copolymers of 4-

4-vinylpyridine content in feed in mole%	AIBN mole%	Solvent/monomer ratio ml/mole	Precipating solvent	Conversion %	4-Vinylpyridine ^a content in copolymer in mole %
12.9	0.261	241	Pet ether	61.9	16.8
24.91	0.261	343	Pet ether	76.68	23.9
44.97	0.261	343	Diethyl ether	32.15	49.9
79.98	0.261	343	Toluene	42.7	85.7

a - Based on calculations of C/N ratios obtained from C.H.N microanalysis

TABLE 1 The reaction conditions in the preparation of 4-Vinylpyridine and Methylmethacrylate Co-polymers.

vinylpyridine and methylmethacrylate (PVP-MMA) were made by the thermal displacement of the chloride ligands of $\text{Ru}(\text{bpy})_2\text{Cl}_2^{10}$. The copolymers were refluxed with various quantities of $\text{Ru}(\text{bpy})_2\text{Cl}_2$ in either ethanol or an ethanol/water mixture, with the conditions of reaction shown in Table 2. The progress of the reaction was followed by UV/vis spectroscopy. The metallopolymer thus formed were evaporated to dryness, dissolved in about 10 cm^3 of dichloromethane and precipitated in 200 cm^3 of 40/60 pet ether. The material was then isolated by filtration and dried in vacuo at room temperature overnight.

Preparation of $[\text{Ru}(\text{bpy})_2(\text{PVI})_n\text{Cl}_m]\text{Cl}_n$. ($m, n = 0.2: 1.1$)

Five $\text{Ru}(\text{bpy})_2$ - containing redox polymers of poly 4(5)-vinylimidazole (PVI) were made by refluxing the polymer with an amount of $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ calculated to give a 1:5 (4VIm:Ru) loading. The polymers made and conditions of reaction are shown in Table 3. The progression of the reaction was followed by UV/vis spectroscopy and formation of the products observed in this way. The reaction mixture was evaporated down to about 10 cm^3 and added dropwise into 200 cm^3 of THF. The metallopolymer precipitated out and was isolated by centrifugation, stirred in 50 cm^3 of THF before filtration, washed with diethyl ether and dried in vacuo at room temperature overnight.

Model Compounds

Preparation of $[\text{Ru}(\text{bpy})_2(4\text{MIm})\text{Cl}](\text{PF}_6) \cdot \text{H}_2\text{O}$ $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (- 0.39g: 0.75mmol) and 4-methylimidazole (4MIm, 0.0615g: 0.75mmol) were dissolved in 50 cm^3 of methanol and the mixture was refluxed for 3 hours. The reaction product was then isolated by addition of 0.5 g of NH_4PF_6 in 10 cm^3 of water to the reaction mixture. The volume was then reduced to 20 cm^3 and left overnight in the dark at 4°C . The mixture was

Co-Polymer Ratio 4VP: MMA	PVP: Ru Ratio	Code	Solvent Mixture EtOH/H ₂ O	Reflux Time (hrs)	Yield %
1:5	1.15:1	PM1R1	100/0	86	86.2
1:5	4.61:1	PM1R2	100/0	72	96.9
1:5	4.48:1	PM1R3	75/25	74	73.5
1:5	21.5:1	PM1R4	75/25	74	77.9
1:5	4.48:1	PM1R5	100/0	72	98.3
1:3.2	2.6:1	PM2R1	100/0	72	99.8
1:3.2	10.3:1	PM2R2	100/0	72	95.7
1:3.2	3.85:1	PM2R3	75/25	74	79.4
1:3.2	15.4:1	PM2R4	75/25	74	74.6
1:1	8:1	PM3R1	100/0	72	98.4
1:1	31.9:1	PM3R2	100/0	72	99.1
1:1	5.4:1	PM3R3	75/25	74	87.6
1:1	21.5:1	PM3R4	75/25	74	88.5
6:1	22.3:1	PM4R1	100/0	42	99.6
6:1	106:1	PM4R2	100/0	24	98.3
6:1	5.7:1	PM4R3	75/25	74	91.2
6:1	23:1	PM4R4	75/25	74	90.4
6:1	5.7:1	PM4R5	100/0	72	93.5

TABLE 2: The conditions of reaction between Ru(bpy)₂Cl₂ and copolymers of 4-vinylpyridine and methylmethacrylate.

Polymer Code	4VIm: Ru Ratio	Solvent Mixture MeOH/H ₂ O	Reaction Time	Yield %
AR1	5.37:1	100/0	72	95.7
BR1	5.37:1	75/25	76	95.97
ER1	5:1	100/0	48	75.4
FR1	5:1	100/0	24	68.3
GR1	5:1	100/0	12	58.6

TABLE 3: The reaction conditions for synthesis of metallopolymers from poly-4(5)-Vinylimidazole and Ru(bpy)₂Cl₂·2H₂O.

then filtered and the crystalline product obtained, dried in vacuo to give 0.30 g (yield 60.3%). TLC (alumina oxide/methanol) shows the product to be pure. UV/Vis (methanol) $\lambda_{\max}$ (log ϵ) 510nm (3.75), 353nm (3.73). Analysis Calcd. for $C_{24}H_{24}N_6ClPF_6ORu$: C, 41.4; H, 3.4; N, 12.1. Found: C, 41.4; H, 3.3; N, 11.9.

Preparation of $[Ru(bpy)_2(4Mim)_2](PF_6)_2 \cdot H_2O$ $Ru(bpy)_2Cl_2 \cdot 2H_2O$

(0.13g, 0.25mmol) and 4-methylimidazole (0.197g, 2.4mmol) were refluxed in the dark and in 40 cm³ of a 60/40 methanol/water solution for 5 hours. The reaction product was precipitated by the addition of 0.5 g of NH_4PF_6 in 5 cm³ of water. The volume of the mixture was reduced to 10 cm³ and left in the fridge overnight. The precipitate formed was separated by filtration and dried in vacuo overnight. The material was purified by recrystallisation in acetone/water to give 0.171g (78.8% yield). The product is pure as indicated by TLC (alumina oxide/methanol). UV/Vis (methanol) $\lambda_{\max}$ (log ϵ): 343nm (3.86), 488nm (3.0). Analysis calcd. for $C_{28}H_{30}N_8P_2F_{12}ORu$: C, 36.9; H, 3.3; N, 12.6. Found: C, 36.9; H, 3.1; N, 12.8.

Preparation of $[Ru(bpy)_2(4Mim)(H_2O)]^{2+}(PF_6)_2 \cdot H_2O$ 50 cm³ of distilled water in a 100ml round bottomed flask was degassed by bubbling through oxygen-free nitrogen for 15 minutes. 0.24 g of $[Ru(bpy)_2(4Mim)Cl]PF_6$ was added and the mixture was refluxed in the dark for 20 minutes. The solution was then placed in a 100ml beaker and 0.5 g of NH_4PF_6 in 10cm³ of water was added while the solution was still hot. The mixture was allowed to cool whereupon some solid precipitated out. The mixture was then moved to the fridge and left at 4°C over the weekend. The solid precipitate was separated by filtration and dried in vacuo to give 0.143g (60.6% yield). TLC on alumina oxide with methanol as the mobile phase indicated. UV/Vis (methanol) $\lambda_{\max}$ (log ϵ): 491nm (3.82);

342nm (3.74). Analysis calcd. for $C_{24}H_{40}N_6OPF_6O_8Ru$: C, 35.1; H, 3.16; N, 10.2; Found C, 35.2; H, 3.1; N, 10.3.

3.2: Experimental Procedures.

3.2.1: Spectroscopic Techniques.

3.2.1.1: Electronic Spectra

Where ultraviolet spectroscopy was used to observe chemical changes over a period of time or at different pH's, overlay spectra were obtained. At the beginning of each experiment, the spectrometer was allowed to equilibrate for 15 minutes before proceeding. The spectra were obtained between 300 nm and 600 nm.

In ascertaining the photochemical behaviour of the model compounds in different solvents, the quantum yield reactor was used in conjunction with the ultraviolet spectrometer. The model compounds were made up to 10^{-4} M in three different solvents: acetone, methanol and acetonitrile. These solutions were protected from premature photolysis by covering the volumetric flasks with aluminium foil and storing them in the dark. The quantum yield reactor was allowed to warm up for at least 30 minutes. The high intensity light beam produced by the lamp was filtered of ultraviolet light and heat by placing a water filter in the path of the beam. After the sample had been irradiated for a set period of time, the cell was transferred to the ultraviolet spectrometer and a spectrum was immediately recorded. This was repeated until it appeared that the compound was completely photolysed, and in this way the photolysis of the compound in different solvents could be observed.

Ultraviolet techniques were also used to follow the degree of reaction of the $\text{Ru}(\text{bpy})_2\text{Cl}_2$ complex with the different polymers. Depending on the concentration of $\text{Ru}(\text{bpy})_2\text{Cl}_2$ complex in the reaction mixture, between 0.25 and 1 cm^3 of the reaction mixture was pipetted out during the reaction and placed in a 1 cm quartz cell. The sample was then diluted with ethanol or an ethanol/water mixture (depending on the composition of the reaction solvent) to 3.5 cm^3 and the ultraviolet spectrum recorded. The sample was then discarded. Hence the progress of the reaction can be followed by observing the shift of λ_{max} at 505–515 nm to higher energies.

3.2.1.2: Luminescence Methods

In obtaining the emission spectrum of the metallopolymer and the model compounds, all compounds were made up to 10^{-4}M (for the metallopolymer this was based on $\text{Ru}(\text{bpy})_2\text{Cl}_2$ concentration) with analar methanol and for room temperature spectra were placed in 1 cm quartz fluorescence cells. The luminescence spectrometer was allowed to warm up for at least 30 minutes before the spectrum was obtained. Between spectra the excitation shutter, which cuts off the excitation beam, was closed to protect the samples from any photochemical decomposition. However this shutter could not be used when the low temperature accessory was attached and in this case the cell holder was rotated to take the sample out of the direct path of the beam. The samples were excited at the λ_{max} for absorption of the lowest energy metal to ligand charge transfer band of the species.

For obtaining spectra at low temperature, the low temperature accessory was attached, which uses as a coolant liquid nitrogen. At low temperatures methanol is a suitable solvent for, as well as dissolving all

the metallopolymer. It does not expand when frozen and it forms a perfect glass at low temperatures. The samples were contained in a quartz capillary cell, 4 mm outside diameter, 2 mm inside diameter and 75 mm in length. When placing the sample in the tube, care was taken to ensure that no bubbles formed in the cell. The capillary cell was then placed in the accessory and the fluorescence spectrum at temperatures 77K were obtained.

3.2.2: Electrochemical Methods

3.2.2.1: Cyclic Voltammetry Methods.

The cyclic voltammograms of the metallopolymer were obtained using a fresh surface on the graphite disk working electrode which was produced by cleaving the disk with a scalpel and applying between 1–6 μl of a 1% (w/w) solution of the metallopolymer in methanol to the surface and allowing the resulting film to dry overnight. The electrolytes used were 1M H_2SO_4 , 1M HClO_4 , 1M HCl and 0.1M TEAP/acetonitrile which when placed in the cell were de-aerated using a steady stream of oxygen-free nitrogen and after degassing a blanket of nitrogen was kept over the solutions. The graphite disk working electrode were placed in each acid in turn and the cyclic voltammograms obtained between +200 mV and +1300 mV (vs SCE). The cyclic voltammograms of the model compounds were obtained by dissolving 30 mg of the compounds in 30 cm^3 of 0.1M TEAP/acetonitrile. The cell was screened from light by covering it with aluminium foil. The working electrode in this case was a bare polished glassy carbon electrode (diameter 0.75 cm) and the voltammogram as obtained between -1.9 mV and +1.2 mV (vs SCE). In all cases the initial potential was 0.0 mV.

3. 2. 2. 2: Chronocoulometric Methods

A solution of the metallopolymer was made up to 10^{-4}M (based on $\text{Ru}(\text{bpy})_2\text{Cl}_2$ concentration) in methanol and $100\mu\text{l}$ of it was placed on a bare polished glassy carbon electrode. The film was allowed to dry for a week. The $\text{CCl}_3\text{COOH}/0.2\text{ M CCl}_3\text{COONa}$ buffer was placed in a thermostatted cell containing a thermometer and was allowed to equilibrate to the initial temperature while the solution was degassed with oxygen-free nitrogen for about 15 minutes. The potential jump was accomplished by scanning the potential from 0.5 mV to 1.0 mV at a scan rate of 1000Vs^{-1} . This extremely fast scan rate gives an almost instantaneous step and is the nearest to a potential jump that can be achieved with the equipment used. The recorder was set to record the signal at 2 minutes in 10 cm and the coulometer sensitivity set at 10^{-4} Coulombs. Chronocoulometric plots were recorded at different temperatures.

3. 2. 2. 3: Hydrodynamic Methods

$100\mu\text{l}$ of a 10^{-4}M solution of the metallopolymer in methanol was dried onto a bare polished glassy carbon electrode and left in the dark for a week to ensure complete drying. The rotating disc electrode was calibrated and it was found that the true rotation speed was 1.078 times the apparent rate. 50 cm^3 of the $2 \times 10^{-3}\text{M}$ ammonium ferrous sulphate solution in the $0.9\text{M Na}_2\text{SO}_4$ in $0.1\text{M H}_2\text{SO}_4$ buffer was placed in the thermostatted cell and was degassed with oxygen-free nitrogen. It was found that at temperatures below 15°C the sodium sulphate in the buffer crystallises out; hence all measurements were carried out above 15°C . The rotation speed was varied between 100 r.p.m. to 3000 r.p.m. and the solution was scanned from 200 mV to 900 mV at a scan rate of 2 mVs^{-1} . Current-

potential curves were obtained at temperatures ranging from 15°C to 45°C for each metallopolymer. The concentration of the cell solution was increased by the addition of measured aliquots of a 0.1M $(\text{NH}_4)_2\text{FeSO}_4$ in 0.1M H_2SO_4 / 0.9M Na_2SO_4 buffer and further measurements recorded.

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CHAPTER 4

SYNTHESIS AND SPECTROSCOPIC CHARACTERISATION

4.1: Synthesis

4.1.1: Synthesis of 4(5)-Vinylimidazole

The monomer was synthesised according to procedures described by Kokosa, Szafasz and Tagupa¹ and Kelley, Millar and McLean² which offered a workable synthesis of pure compound in quantities greater than 5 grams. However it was found necessary to modify parts of these syntheses in order to achieve or improve the reported yields.

4.1.1.1: N-(Triphenylmethyl)-4-(hydroxymethyl)imidazole (3)

This compound was produced from 4(5)-(hydroxymethyl)imidazole hydrochloride by the method described by Kelley², which protects the N-H group from further reactions by removing the hydrogen and replacing it with the triphenylmethyl group. This method resulted in yields of impure compound (3) of 36% (lit.² 88%). Therefore it was decided to follow the reaction by TLC on silica gel and with a solvent system of hexane/ethyl acetate/methanol (20/10/1). The TLC results are given in fig. 1 and show that at 20°C and for a reaction time of 0.5 hour, the reaction had not been completed, but after a period of 2 hours the starting material was completely transformed into the product. The TLC also shows that during the reaction, an intermediate is formed, the nature of which was not further investigated. It was found to be important to add all the triphenylmethylchloride at once, since when precipitation of the product occurs this causes poor mixing of the reactants. The extended reaction time and improved reaction conditions increased the yield to 92% of a pure product.

Although the literature procedure² does not state the temperature at which the reaction was carried out, a small difference in temperature may have an effect on the yield and hence explain the need for a longer reaction

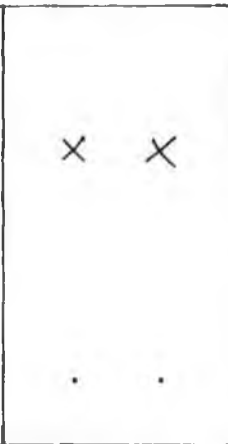
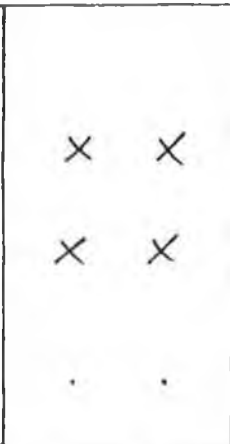
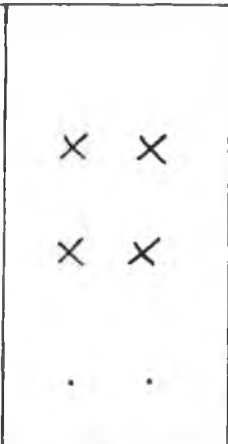
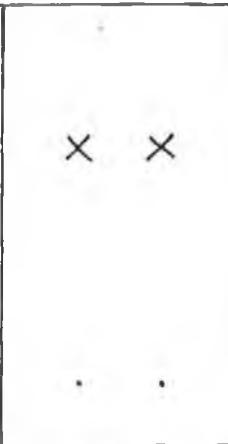
				
(Ph) ₃ CCl	Product	Reaction Time t = 0	t = 0.5hr	t = 2hr

FIG. 1: TLC on silica gel using Hexane/EtOAc/MeOH (20/10/1) as eluent showing the progress of the formation of 1-(triphenylmethyl)-4-(hydroxymethyl)imidazole from 4(5)-(hydroxymethyl)imidazole hydrochloride.

time at a room temperature of 20°C.

4.1.1.2: N-(Triphenylmethyl)-4-imidazolecarboxaldehyde (4)

This compound was prepared from (3) according to the literature procedure² at 92% yield (lit², 91%) by the selective oxidation of 1-(triphenylmethyl)-4-(hydroxymethyl)imidazole using manganese dioxide. Manganese dioxide has found³ appreciable use in the oxidation of alcohols to aldehydes. This reagent preferentially attacks allylic and benzylic hydroxyl groups⁴ and hence exhibits a useful degree of selectivity. However in order to achieve the above yield it was found essential to further activate the precipitated MnO₂. The precise reactivity of MnO₂ depends⁵ on its mode of preparation with the 'active' form being precipitated from a reaction of manganese sulphate, potassium permanganate and sodium hydroxide. The level of activity is dependent on the extent of drying, and azeotropic drying by benzene recommended by Goldman⁶ was used. Compound (4) produced had a melting point of 189-193°C which is higher than that quoted by Kokosa¹ (165-181°C), but the same as that given by Kelley². The attainment of a pure product with a high yield, therefore, seems to be dependent on the level of activity of the manganese dioxide.

4.1.1.3: N-(triphenylmethyl)-4-vinylimidazole (5)

Compound (5) was produced from (4) by a Wittig reaction according to the method of Kokosa¹. The reaction mixture became so viscous that the recommended¹ stirring bar was ineffective and a mechanical stirrer was used instead. An extension of the reaction time at 70°C from 4.5 to 6 hours was found to give improved conversion to the product. But there was still incomplete conversion (Kokosa claims complete conversion) as was indicated by TLC on silica gel plates with chloroform used as the mobile phase.

The reported mobile phase (chloroform) used for the separation of the mixture by column chromatography was found to be inefficient since although it separated the starting compound and product from the Ph_3PO it would not separate the starting compound from the product. A number of mobile phases were tested to find the most suitable and efficient system. Hence it was found that using this system of a mobile phase of CHCl_3 /(Pet Ether(40-60)) (65/35) and a stationary phase of silica gel gives the required separation and gives a yield of 90% (lit.¹ 80%).

4.1.1.4: 4(5)-Vinylimidazole, (6)

Attempts to synthesise this compound from (5) by repeating the method described by Kokosa¹ which involves cleaving the triphenylmethyl group from (5) by mild acid hydrolysis, produced an impure oil from which pure product crystallised in a yield of 42% (lit.¹ 86%). The reaction product was confirmed by N.M.R. and Infrared spectroscopy (see figures 2 and 3). This infrared spectrum corresponds with the spectrum shown by Morita et al.⁷ for 4(5)-vinylimidazole.

The use of water as the reaction solvent and in the work-up leads to the added difficulty in the effective removal of it from the hygroscopic product. The relatively high temperatures (50°C) and high vacuum used for the removal of the water may have led to decomposition of the product. There should be no polymerisation during the reaction as a by-product of the reaction, triphenylmethanol, is an inhibitor of polymerisation. Attempts to use solvent extraction with diethylether and chloroform proved unsuccessful as the product has more affinity for water.

Three other deblocking reactions were considered. Mild acid hydrolysis using 6N HCl and acetone for a reaction period of 3 hours proved unsuccessful. Catalytic reduction using either hydrogen and palladium black or sodium and ammonia solution were ruled out because these

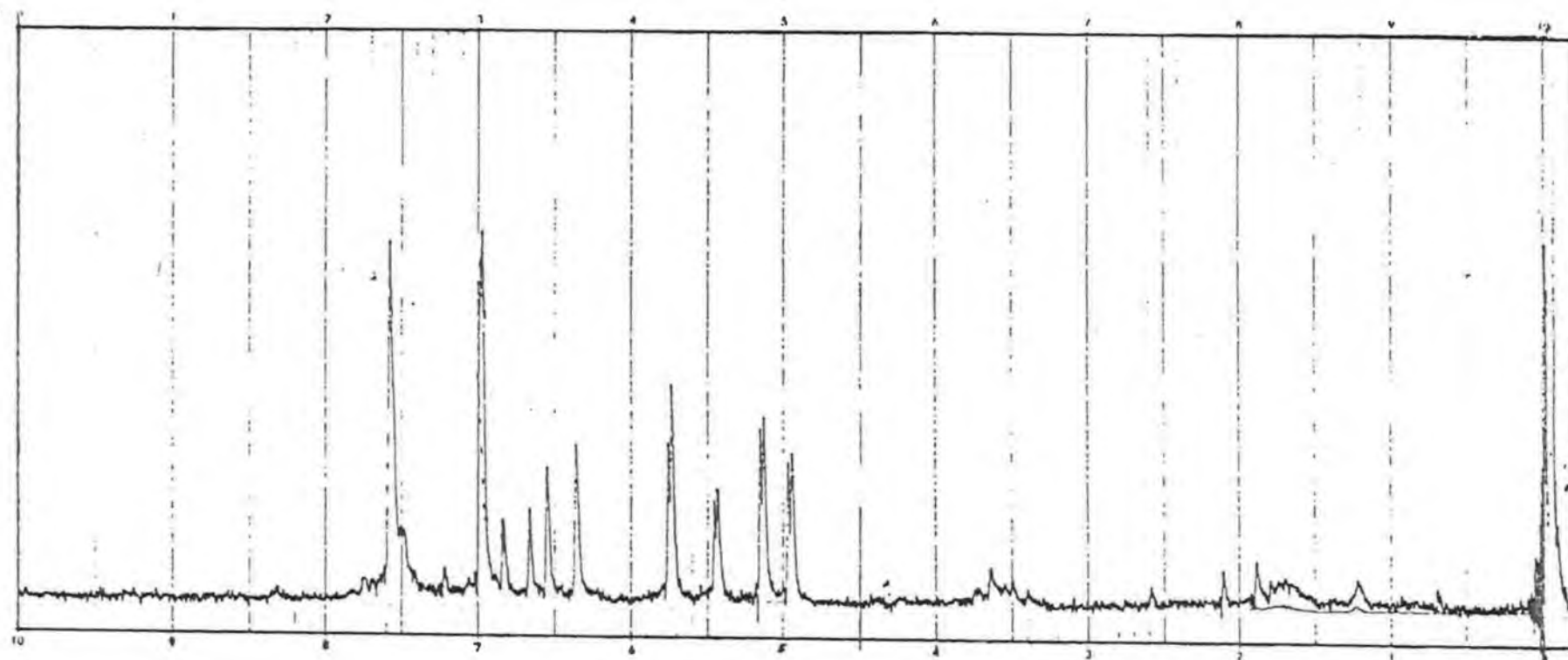


FIG. 2: Nuclear Magnetic Resonance spectrum of 4(5)-Vinylimidazole prepared in CD_3OD .

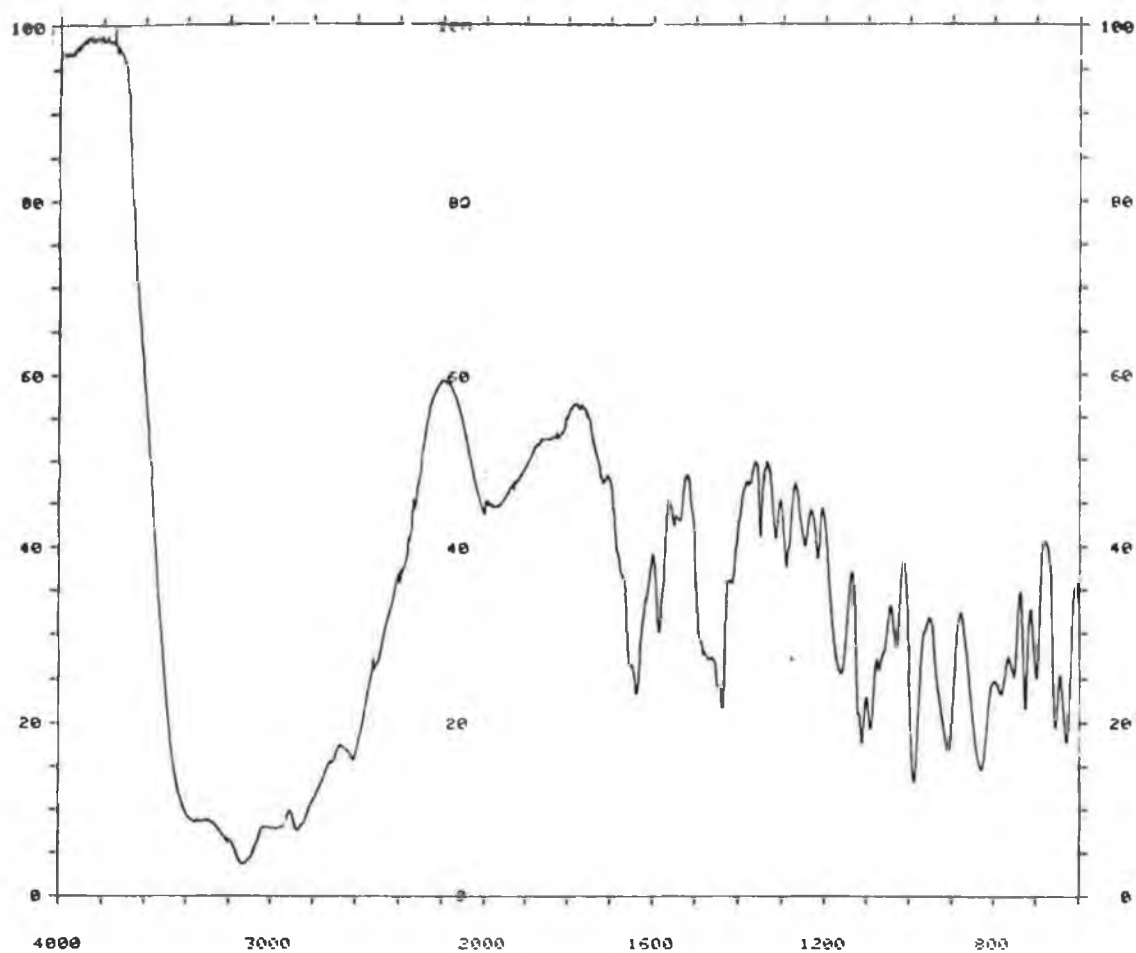


FIG. 3: Infrared spectrum of 4(5)-Vinylimidazole prepared as a KBr disc.

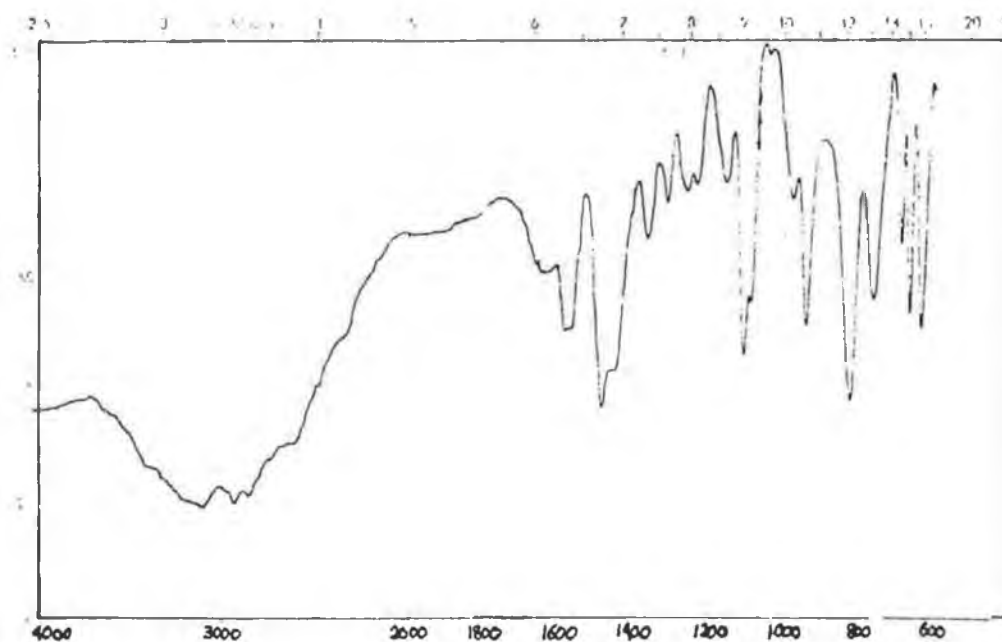


FIG. 4: Infrared spectrum of Poly-4(5)-Vinylimidazole prepared as a KBr disc.

reactions may also reduce the vinyl group.

It seems that although the triphenylmethyl group reacted selectively at one reactive site in a good yield and blocked the nitrogen from further reactions, it cannot be selectively removed in a good yield by reagents that will not attack the vinyl group.

4.1.2: Polymerisation of 4(5)-Vinylimidazole

The technique used by Overberger et al.⁸ which involves free-radical polymerisation in benzene using AIBN as initiator was used for polymerising the 4(5)-vinylimidazole monomer. However the reported⁸ yield of 80% was not attained (yield attained was 42%). When the chain length reaches the point where the polymer is insoluble in the benzene reaction solvent it precipitates out and after about 5 hours this precipitate fills the volume of the solution completely. This precipitate prevents adequate mixing of the solution for further polymerisation. When the polymer is produced using methanol as solvent, there is no precipitation and the yield is increased to 60%.

The polymer produced has an infrared spectrum (fig. 4) identical to that for poly-4(5)-vinylimidazole shown by Morita et al.⁷. It should be noted that even after prolonged drying by heating to 50°C under a high vacuum for 24 hours, the infrared spectrum still suggests the presence of water. Overberger and Vorcheimer⁹ have reported that half a mole of water per mole of polymer remains bound to the polymer and could not be removed by prolonged heating at 100°C over phosphorous pentoxide.

4.1.3: Copolymerisation of 4-Vinylpyridine and Methylmethacrylate

The copolymers of 4-vinylpyridine and methylmethacrylate were produced by solution polymerisation in toluene using the reactivity ratios and

procedure described by Orbay et al.¹⁰ which involves free-radical polymerisation of the two monomers in toluene. However they recommend adding the monomer mixture to the reaction vessel at a very slow rate in order to achieve higher degrees of conversion without altering the monomer composition during polymerisation. Solution polymerisation was used instead, since with careful choice of the solvent the polymer will precipitate out after reaching a certain composition and/or chain length. This strategy keeps the chain length and hence the solubility of the polymer within useable limits.

Using the monomer reactivity ratios ($r_{4vp} = 1.05$ and $r_{mma} = 0.54$), where 4vp refers to 4-vinylpyridine and mma refers to methylmethacrylate, described in the literature¹⁰, the monomer feed ratios were calculated to give the following ratios for 4VP/MMA copolymers: 1/4, 1/2, 1/1, 4/1. These reactivity ratios give some indication of the composition of the copolymers formed. Since 4-vinylpyridine has a reactivity ratio greater than one, a radical chain ending with 4-vinylpyridine would prefer to add more 4-vinylpyridine rather than methylmethacrylate. Furthermore, methylmethacrylate with a reactivity ratio less than one, prefers to add 4-vinylpyridine rather than itself. This means that one needs an excess of methylmethacrylate in the monomer feed mixture. The amount needed to give a required copolymer composition can be calculated by using the following equation:

$$F_{4vp} = \frac{r_{4vp}f_{4vp} + f_{4vp}f_{mma}}{r_{4vp}f_{4vp} + 2f_{4vp}f_{mma} + r_{mma}f_{mma}} \quad (1)$$

Where f_{mma} and f_{4vp} are the monomer feed ratios of methylmethacrylate and 4-vinylpyridine respectively and F_{4vp} is the ratio of 4

vinylpyridine in the copolymer. Since the product of the reactivity ratios is less than one, there would be a tendency for the monomer residues in the copolymer to alternate.

The actual ratios obtained are shown in Table 1 of the experimental section and from these results it can be seen that the monomer feed ratios were nearly correct. It can be seen that under identical reaction conditions conversion increases from PM1 to PM2 but then decreases for PM3 before rising for PM4. This decrease may be due to the fact that there was no precipitation of copolymer when PM1 and PM2 were produced, but there was precipitation of copolymer for PM3 and PM4. Precipitation causes incomplete mixing of the reactants and leads to lower conversion.

4.1.4: Synthesis of The Metallopolymers and Model Compounds

The formation of ruthenium containing polymers can be achieved by two methods¹¹:

(i) A ruthenium halide complex can be reacted with a pre-made polymer in an appropriate solvent.

(ii) A ruthenium monomer complex can be synthesised and then subsequently copolymerised with either the same monomer or other monomers.

Method (i) offers the advantage that since the polymer is synthesised and characterised before reaction with the metal complex, the resulting metallopolymer is to some extent controlled since the polymer chain length, tacticity, composition and solubility are known in advance of forming the metallopolymer. However the disadvantages incurred by this method are:

(a) A metal complex like $\text{Ru}(\text{bpy})_2\text{Cl}_2$ initially reacts with a solvent

molecule to form the solvent-chloro complex: $[\text{Ru}(\text{bpy})_2(\text{S})\text{Cl}]^+$. The labile solvent ligand can be substituted so that a coordinate bond with a polymer (P) is formed:

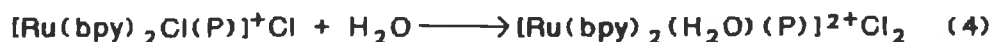


The remaining chloride ligand can be substituted so that a further coordinate bond with a polymer ligand is formed:



The products formed from reaction (2) and (3) are called in this work the 'chloro' substituted and 'bis' substituted species respectively.

(b) Since some of the reaction solvents used were either methanol/water or ethanol/water mixtures (see experimental chapter), there is the possibility that the formation of an 'aquo' substituted species can occur¹¹.



(c) The structure of a polymer formed by copolymerisation may be uncertain and a metallopolymer with an extremely non-uniform distribution of metal complexes can occur.

The method of preparation (ii) mentioned above has the advantage that since a change in co-ordination sphere of the ruthenium-monomer complex is very unlikely during polymerisation, the structure of the complex on the polymer backbone is more clearly defined and only one ruthenium-polymer species is formed. However extensive interchain crosslinking occurs when polymerising the 'bis' substituted monomer compound making

it insoluble in most solvents, thus preventing the study of this species by UV/vis spectroscopy and electrochemistry. Also since the reactivity of the vinylpyridine-ruthenium complex is unknown, the structure of a copolymer formed would be uncertain. For these reasons it was decided to use the first method for the formation of metallopolymers. The metallopolymers produced contain the 'bis' species as a mixture with the 'chloro' species mainly as intrachain crosslinks. It can be assumed that these metallopolymers are not initially heavily cross-linked as they are soluble in suitable organic solvents. It was observed that it becomes more difficult to redissolve some of the metallopolymers with time. From electrochemical measurements it was noticed that the relative amount of 'bis' species increases with time even when the dry metallopolymer is stored in the dark.

4.1.4.1: 4-Vinylpyridine-Methylmethacrylate Metallopolymers.

Various copolymers of 4-vinylpyridine and methylmethacrylate were allowed to react with $\text{Ru}(\text{bpy})_2\text{Cl}_2$ in ethanol or an ethanol/water mixture to give a metallopolymer with an predetermined metal complex loading (see table 2, experimental chapter). According to the reaction scheme outlined in equations (2) and (3) above, the reaction should proceed as follows:



Some indication of the progressive formation of the two species can be gained from an observation of the reaction with time by UV/Vis spectroscopy. The λ_{max} at about 505nm (which is the absorption maximum

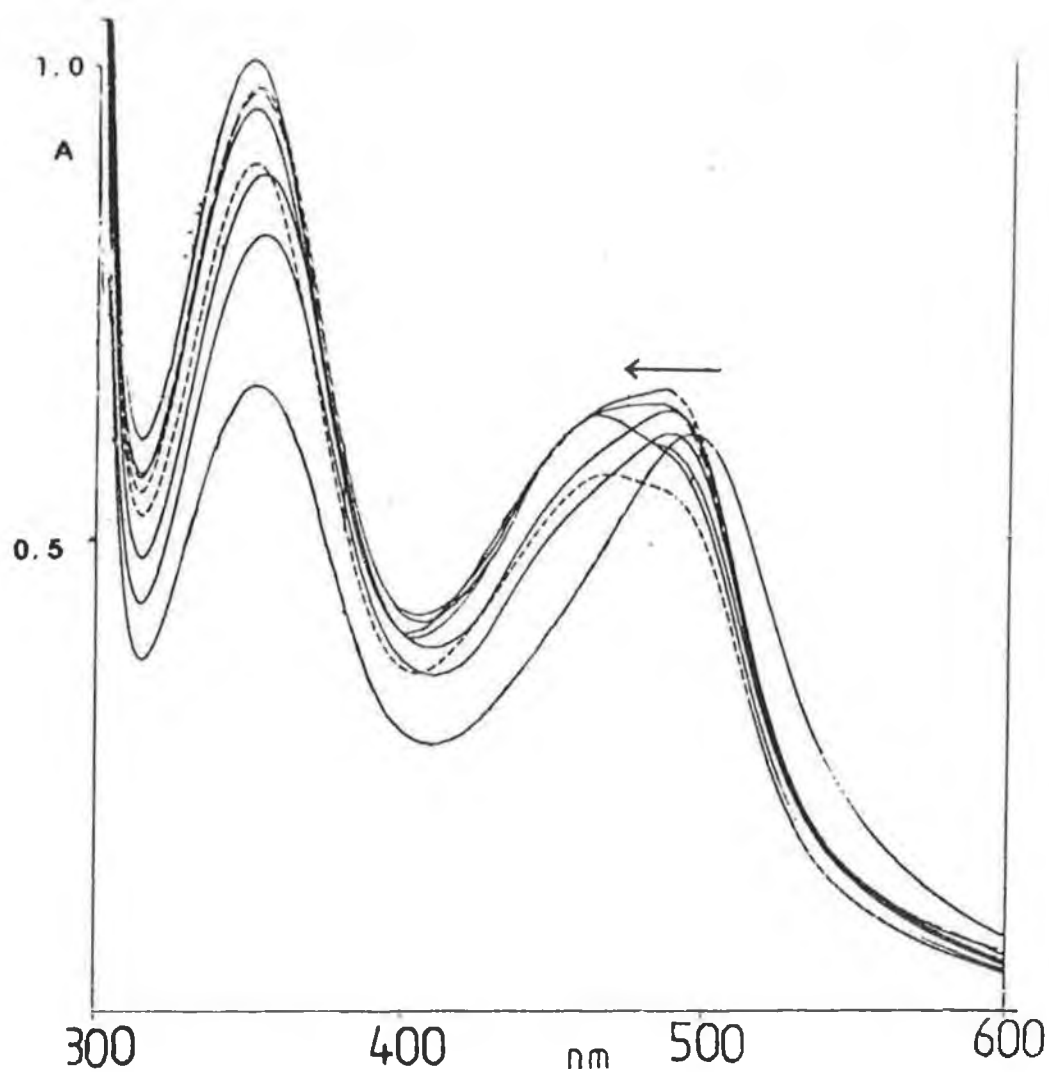


FIG. 5: Ultraviolet/visible spectra of the reaction mixture showing the progress of the reaction between the $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ complex and Poly-4-Vinylpyridine-Methylmethacrylate.

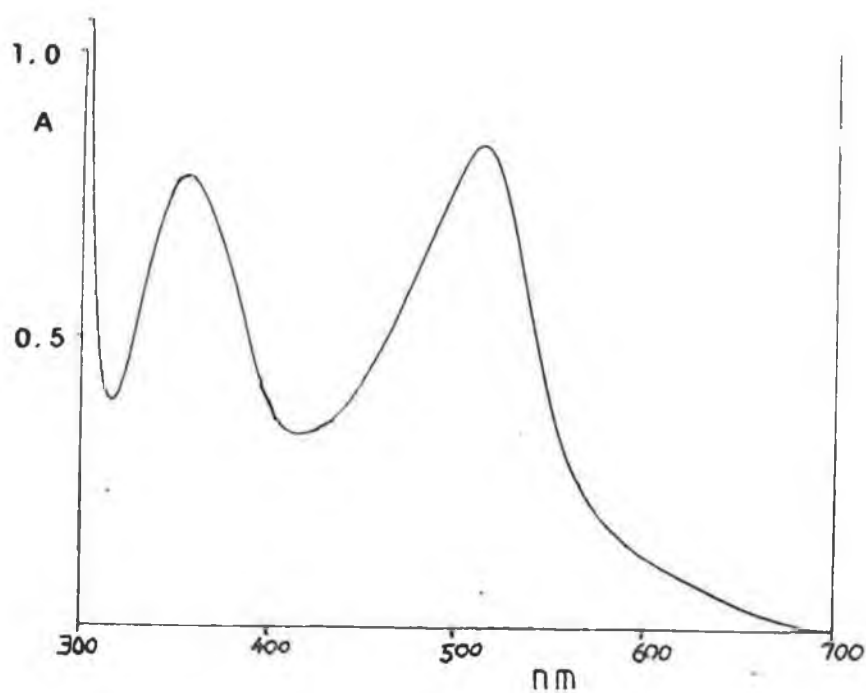


FIG. 6: Ultraviolet/visible spectrum of $[\text{Ru}(\text{bpy})_2(4\text{MIm})\text{Cl}]^+(\text{PF}_6)$ in methanol.

for the solvent chloro complex) is seen to decrease whilst simultaneously a higher energy peak increases as the reaction proceeds (see fig. 5). This shows the progress of the reaction scheme (eqns. 5, 6 and 7) as the disubstituted species is formed which absorbs strongly at 470nm¹².

4.1.4.2: Poly-4(5)-Vinylimidazole Metallopolymers.

$\text{Ru}(\text{bpy})_2$ -containing polymers were obtained by reaction of poly-4(5)-vinylimidazole with $\text{Ru}(\text{bpy})_2\text{Cl}_2$ in a similar way as described for the corresponding poly-4-vinylpyridine-methylmethacrylate metallopolymers. The reaction conditions were set so as to produce a 5:1 (PVIm:Ru) metallopolymer, but with varying degrees of mono-substituted ($[\text{Ru}(\text{bpy})_2(\text{PVIm})\text{Cl}]^+\text{Cl}^-$) and bis-substituted ($[\text{Ru}(\text{bpy})_2(\text{PVIm})_2]\text{Cl}_2$) species—see table 3, experimental chapter. The progress of the reaction can be followed by uv/visible spectroscopy as the MLCT peak at 510nm shifts steadily to 485nm.

4.1.4.3: Model Compounds

In order to identify the different species contained in the $\text{Ru}(\text{bpy})_2$ -containing poly-4(5)-vinylimidazole and to obtain an indication of the properties of the different species in isolation; a number of model compounds were made (see experimental section). The ligand used for these model compounds was 4-methylimidazole, which should approximate very closely the properties of the polymer. The ultraviolet spectra of these compounds were measured in methanol and show that the compound which should mimic the chloro-substituted species $[\text{Ru}(\text{bpy})_2(4\text{MIm})\text{Cl}]\text{PF}_6$ has its lowest MLCT band at about 510 nm (fig. 6), whilst the compound approximating the disubstituted species $[\text{Ru}(\text{bpy})_2(4\text{MIm})_2](\text{PF}_6)_2$ has its lowest MLCT band at 488 nm. The model compound for the aquo species $[\text{Ru}(\text{bpy})_2(4\text{MIm})(\text{H}_2\text{O})](\text{PF}_6)_2$ has a lower MLCT band at 492 nm. The lowest MLCT bands of the disubstituted and aquo species for these model

compounds are very close and this may explain why the progression of the chloro species to the aquo species cannot be seen using UV/visible spectroscopy.

4.2: Characterisation of the Metallopolymers.

The metallopolymers of the vinylpyridine-methylmethacrylate copolymers and the poly-4(5)-vinylimidazole polymers were characterised by ultraviolet/visible and fluorescence spectroscopy.

4.2.1: $\text{Ru}(\text{bpy})_2$ -Poly-4VP-MMA Metallopolymers

4.2.1.1: Ultraviolet/visible Spectral Studies

The UV/Vis spectra of the products formed show in all cases (table 1) an absorption peak at 495nm which agrees closely with that obtained¹¹ for $[\text{Ru}(\text{bpy})_2(\text{PVP})\text{Cl}]\text{Cl}$, and this indicates the predominant presence of the 'chloro' species. However it can be seen (table 1) that depending on the reaction conditions some products show an absorption peak near 470nm which concurs with the spectrum obtained¹² for $[\text{Ru}(\text{bpy})_2(\text{py})_2]^{2+}$, suggesting a mixture of 'chloro' and 'bis' species can occur.

It can be seen in table 1, that the relative concentrations of the two species for the 4-vinylpyridine/methylmethacrylate copolymers is dependent on a number of factors¹². The UV spectral data suggests that the relative amount of disubstituted species increases with the amount of methylmethacrylate in the polymer backbone. This might be due to the reduced steric hindrance which the smaller methylmethacrylate units contribute, making the approach of the ruthenium complex easier. Also an increase in the amount of water used in the reaction solvent and a

Code	Copolymer Ratio ¹ 4VP: MMA	PVP: Ru Ratio	MLCT λ_{max} (nm)
PM1R1	1:5	1.15:1	352.495
PM1R2	1:5	4.61:1	352.463(sh).495
PM1R3	1:5	4.48:1	350.470(sh).495
PM1R4	1:5	21.50:1	345.463.495(sh)
PM2R1	1:3.2	2.00:1	352.495
PM2R2	1:3.2	10.30:1	352.495
PM2R3	1:3.2	3.85:1	350.470(sh).495
PM2R4	1:3.2	15.40:1	345.403.495(sh)
PM3R1	1:1	8.00:1	350.495
PM3R2	1:1	32.00:1	352.470(sh).495
PM3R3	1:1	5.40:1	350.495
PM3R4	1:1	21.50:1	349.405.495(sh)
PM4R1	0:1	22.30:1	352.495
PM4R2	0:1	106.0:1	352.470(sh).495
PM4R3	0:1	5.70:1	350.470(sh).495
PM4R4	0:1	23.00:1	350.465.495(sh)

Table 1: Ultraviolet/visible spectral data for $\text{Ru}(\text{bpy})_2$ containing Poly-4-vinylpyridine-methylmethacrylate measured in methanol.
(1 - obtained from CHN analysis)

decrease in the amount of ruthenium to pyridine units has been found to increase the amount of 'bis' species formed. Water facilitates the displacement of the chloride ligand and the formation of the aquo intermediate, thus increasing the amount of disubstituted species formed. Figure 7 compares the spectra of a copolymer possessing a high ruthenium loading with that of a copolymer with a low loading. This behaviour may be explained by the fact that the reduced ruthenium:pyridine ratio leaves more neighbouring pyridine groups available for disubstitution to take place.

4.2.1.2: Emission Studies

The fluorescence spectral data for the $\text{Ru}(\text{bpy})_2$ -containing poly-4-vinylpyridine-methylmethacrylate copolymers are given in Table 2. The copolymers containing both $[\text{Ru}(\text{bpy})_2(\text{PVP})\text{Cl}]^+$ and $[\text{Ru}(\text{bpy})_2(\text{PVP})_2]^{2+}$ centres show emission from both sites. Solutions of the metallopolymers in methanol were excited at the excitation wavelength for the lower energy MLCT band for the chloro (500 nm) and bis (460 nm) species. The characteristic emission spectra for the two species were then obtained (fig. 8). Excitation at 500 nm produces the dominant emission spectrum for the $[\text{Ru}(\text{bpy})_2(\text{PVP})\text{Cl}]^+$ species which has a room temperature emission maximum λ_{max} at 705 nm and a low temperature (77K) λ_{max} at 662 nm. On excitation at 460 nm, the emission due to the $[\text{Ru}(\text{bpy})_2(\text{PVP})_2]^{2+}$ species is predominant and produces a room temperature λ_{max} at 603 nm and a low temperature λ_{max} at 585 nm. These emission spectra obtained show the same trend that was observed with the absorption spectra, with the formation of the two species being closely dependent on the reaction conditions. However since the quantum yield of emission for the two species is unknown, it is impossible at this

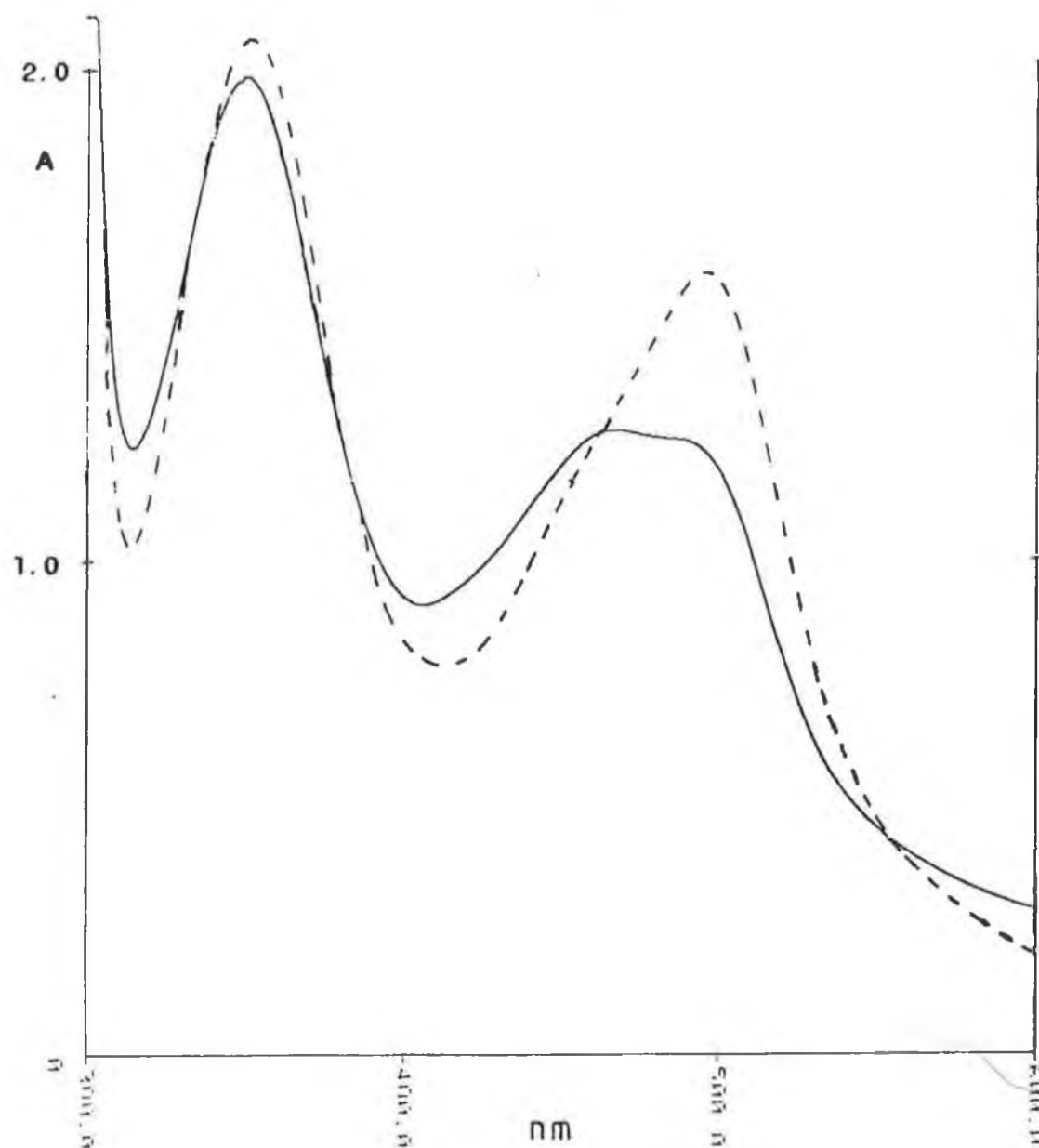


FIG. 7: Ultraviolet/violet spectra of copolymer PM1R1 (---- containing 1.15:1 PVP:Ru ratio) and copolymer PM4R2 (— containing 106:1 PVP:Ru ratio) in methanol at identical concentrations.

Polymer Code	Room Temp. Ex. 460nm	Emission Ex. 500nm	Low Temp. Ex. 460nm	Emission. Ex. 500nm
PM1R1	705	705		
PM1R2	603, 705	705		
PM1R3	603, 705	603, 705	586, 666	584, 666
PM1R4	603	603		
PM2R1	702	702		
PM2R2	700	700	580, 666	666
PM2R3	603, 702	702	588, 670	584, 669
PM2R4	603	603, 703	586	583
PM3R1	700	702		
PM3R2	602, 705	705	585	584
PM3R3	602, 703	603, 705	582	583, 662
PM3R4	602, 705	603, 705		
PM4R1	695	705		
PM4R2	605, 695	705	582	587, 662
PM4R3	606, 705	702		
PM4R4	605, 705	605, 702	585	586, 658

Table 2: Maximum emission wavelengths for the Ru(bpy)₂-containing poly-4-vinylpyridine-methylmethacrylate copolymers. All emission data obtained were in methanol solutions.

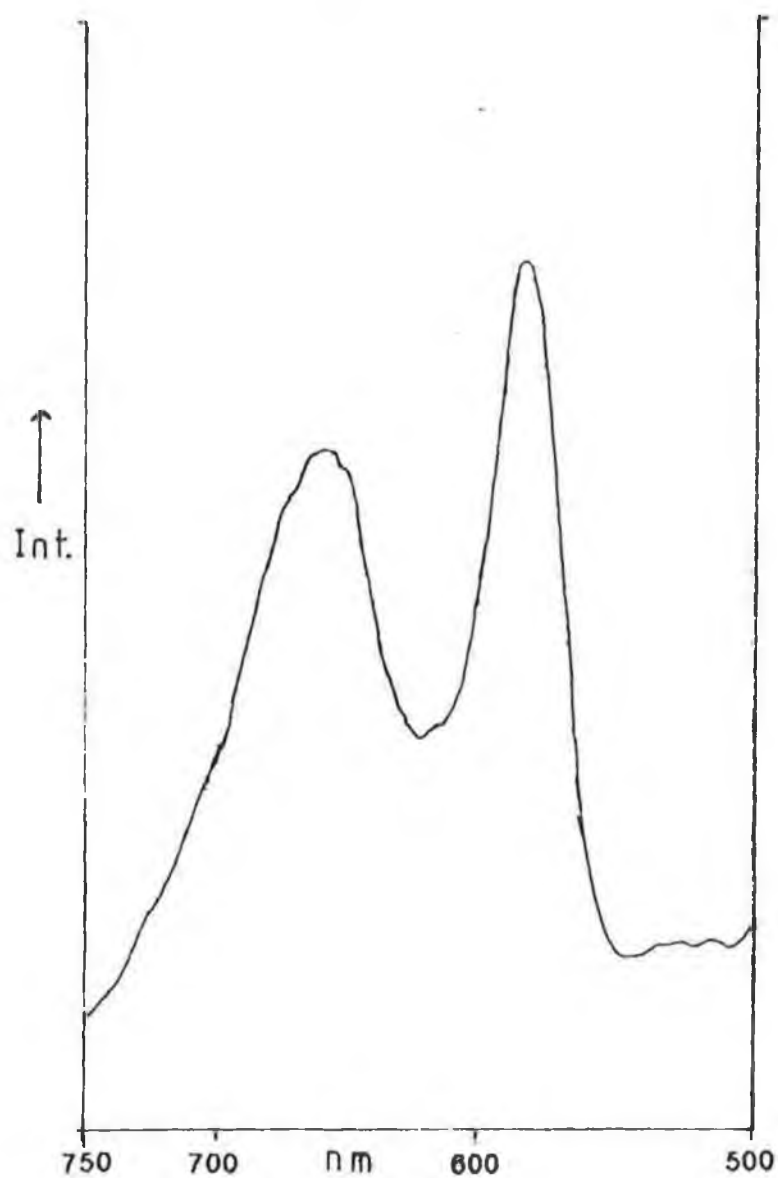


FIG. 8: Low temperature emission spectrum of PM1R3 in methanol excited at 460 nm.

stage to determine the relative concentrations of each species in a particular metallopolymer. Calvert¹⁶ has reported that the excited state emission of $[\text{Ru}(\text{bpy})(\text{trpy})(\text{PVP})]^{2+}$ depends on the degree of metallation which as it increases forces the distance between the metal centres to decrease and causes the emission spectrum to be red-shifted by 20–25 nm. This phenomenon was not observed for these metallopolymer (table 3), which may be due to the fact that the copolymers do not create significant steric problems. At low temperature the spectra were more intense, better resolved and had the emission maxima blue shifted by about 30–40 nm.

4.2.2 $\text{Ru}(\text{bpy})_2$ -Poly-4(5)VIm Metallopolymer.

4.2.2.1: Ultraviolet/visible Spectral Studies.

The model compounds show that the chloro species $[\text{Ru}(\text{bpy})_2-(4\text{MIm})\text{Cl}]\text{PF}_6$ has a lower MLCT band at about 510 nm, whilst the compound approximating the disubstituted species: $[\text{Ru}(\text{bpy})_2(4\text{MIm})_2](\text{PF}_6)_2$ has a lower MLCT band at 488 nm. Metallopolymer BR1 and ER1 have their lower λ_{max} peaks located at 488 nm, which is at a higher energy than for the other polyvinylimidazole metallopolymer and corresponds to the same λ_{max} obtained for the disubstituted model compound. Compound GR1 has a lower energy MLCT band located at 505 nm, and from the evidence given by the model compounds this suggests that it has more mono-substituted species than the other compounds.

It can be seen that from an analysis of the lower MLCT band of ER1, FR1 and GR1 that the amount of bis-substituted species increases with an increase in the length of the reaction time. The metallopolymer produced contain different amounts of bis-substituted species as shown by their lower energy MLCT bands. The reaction times for AR1 and BR1 are almost

Polymer Code	MLCT ^a $\lambda_{\max}$ (nm)	Reaction time (hrs)	Solvent mixture ratio MeOH/H ₂ O
AR1	348.495	72	100/0
BR1	345.488	76	75/25
ER1	345.488	48	100/0
FR1	350.498	24	100/0
GR1	350.505	12	100/0

Table 3: Ultraviolet/visible spectral data for the Ru(bpy)₂-containing poly-4(5)-vinylimidazole metallopolymers.

a - all measurements were made on a 1×10^{-4} M solution in methanol.

	Emission Maximum ($\lambda_{\max}$ /nm)	
	Ex. 470 nm	Ex. 510 nm
[Ru(bpy) ₂ (4MIm)Cl] PF ₆	—	685
[Ru(bpy) ₂ (4MIm) ₂](PF ₆) ₂	645	640
[Ru(bpy) ₂ (4MIm)(H ₂ O)](PF ₆) ₂	642	638
Ru(bpy) ₂ -poly-4(5)VIm Metallopolymer	640	650

Table 4: Room temperature emission data for the model compounds and metallopolymer.

the same. but the solvent mixture for the reaction of BR1 contained water. This suggests that, as with the copolymers, the presence of an appreciable amount of water in the reaction mixture leads to the formation of the aquo $[\text{Ru}(\text{bpy})_2(\text{PVIm})(\text{H}_2\text{O})]\text{Cl}_2$ intermediate species, which can facilitate the formation of the disubstituted species.



It appears that the disubstituted species $[\text{Ru}(\text{bpy})_2(\text{PVIm})_2]\text{Cl}_2$ for the vinylimidazole polymer is formed more easily than the corresponding species for the copolymer 4-VP and MMA and the homopolymer poly-4-vinylpyridine¹². A disubstituted species is not formed in the reaction of $\text{Ru}(\text{bpy})_2\text{Cl}_2$ with poly-4-vinylpyridine¹². It should be noted that this phenomenon has also been observed¹³ for the reaction of $\text{Ru}(\text{bpy})_2\text{Cl}_2$ and poly-N-vinylimidazole. The positions of the lowest MLCT bands in table 2 are also close to the positions of the lowest MLCT bands reported¹³ for $\text{Ru}(\text{bpy})_2$ -containing poly-N-vinylimidazole. This ease of the formation of the disubstituted species with poly-4(5)-vinylimidazole in relation to the difficulty of poly-4-vinylpyridine could be due to steric factors which have been shown to be important in the formation of the bis-species with copolymers. Since imidazole is a σ electron donor and pyridine is a π electron acceptor, the poly-vinylimidazole ligand does not compete with the bipyridyl π acceptor ligands of the complex as does polyvinylpyridine. Hence there would be less repulsion to the approach of the imidazole ligand to form the metallopolymer.

There is no evidence from the uv/vis spectra to indicate the presence of any aquo species. However the lowest MLCT band for the aquo species

would be expected between the band for the mono and bis species. Since there is only a 20 nm difference between the lowest MLCT bands for the mono and bis species, and different mixtures can occur any place in between it would be impossible to resolve the peak if it was present.

4.2.2.2: Emission Studies

The room temperature emission spectra of the model compounds in methanol are given in table 4. The data suggest that the emission maximum for the $[\text{Ru}(\text{bpy})_2(\text{PVIm})\text{Cl}]^+$ species appears at 685 nm whereas the emission due to the $[\text{Ru}(\text{bpy})_2(\text{PVIm})_2]^{2+}$ centre appears at 640 nm. The $\text{Ru}(\text{bpy})_2$ -containing poly-4(5)-vinylimidazole metallopolymers weakly fluoresce in methanol to give emission spectra (fig. 9) with maximum emission peaks (λ_{max}) at about 640 nm for an excitation at 470 nm (the absorption maximum for the $[\text{Ru}(\text{bpy})_2(\text{PVIm})_2]^{2+}$ species), and 650 nm for an excitation at 510 nm (the absorption maximum for the $[\text{Ru}(\text{bpy})_2(\text{PVIm})\text{Cl}]^+$ species). The small difference between the emission spectra of these metallopolymers indicates that if there are characteristic spectra for the two species then their λ_{max} are close to one another and hence cannot be resolved.

It is expected that the aquo compound does not emit and as the λ_{max} for absorption for this compound is identical to that obtained for the disubstituted compound the presence of emission at 640nm indicates that there is some contamination of the disubstituted species present in the aquo compound.

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CHAPTER 5

ELECTROCHEMICAL PROPERTIES

5.1 Cyclic Voltammetry

The $\text{Ru}(\text{bpy})_2$ -containing poly-4-vinylpyridine-methylmethacrylate (PVP-MMA) and poly-4(5)-vinylimidazole (PVIIm) metallopolymer were further characterised by electrochemical methods. Cyclic voltammetry (CV) has been widely used in recent years to study the electrochemical properties of surface coated metallopolymer^{1, 2}. When coated on an electrode surface, metallopolymer can be electrochemically reduced or oxidised. It should be noted that metal centres which are not in direct contact with the electrode surface are electroactive, since electron transfer from the electrode to outlying attached metal sites and from there to a redox couple in solution, at certain potentials, is mediated by the coating. As the relationship between the redox potential of a $\text{Ru}(\text{bpy})_2$ compound and the electronic properties of the ligands is well established³, electrochemical analysis of these polymer-modified electrodes and in particular a study of their redox potentials can give information on the chemical nature of species present.

5.1.1 $\text{Ru}(\text{bpy})_2$ -Poly-4VP-MMA Metallopolymer

The PVP-MMA metallopolymer are expected to have electrochemical properties similar to those observed for the poly-4-vinylpyridine(PVP) metallopolymer. The electrochemical properties of poly-4-vinylpyridine containing $\text{Ru}(\text{bpy})_2$ centres have attracted much attention^{3, 4} because of possible applications of such materials in solar power conversion systems. The $E_{1/2}$ values for $[\text{Ru}(\text{bpy})_2(\text{PVP})\text{Cl}]^+$ have been found at 0.675 V (vs SCE) in 1M H_2SO_4 and at 0.64 V (vs SCE) in 1M HClO_4 ⁴. The $E_{1/2}$ values for the species $[\text{Ru}(\text{bpy})_2(\text{PVP})_2]^{2+}$ has been observed⁴ in 1M HClO_4 at 1.03V (vs SCE).

It is expected that the systematic variation of the PVP-MMA copolymer

backbone and of the degree of metallation should have an effect on the chemical properties of these metallopolymer. The half-wave potentials ($E_{1/2}$) of the metallopolymer obtained by cyclic voltammetry are given in Table 1. The $E_{1/2}$ of the oxidation of the polymer bound Ru^{II} to Ru^{III} can be seen from the data to vary between +0.60 and +0.63 V (vs SCE) for measurements made in 1M $HClO_4$. The second peak for the bis or aquo species observed in 1M H_2SO_4 is less well defined in 1M $HClO_4$. For measurements in 1M H_2SO_4 , half wave potentials between +0.65 and +0.68 V and one centered at +1.05 V were observed (fig. 1). The lower $E_{1/2}$ values agree well with the $E_{1/2}$ values reported for the $[Ru(bpy)_2(PVP)Cl]^+$ species³, hence these peaks correspond to the oxidation of the $[Ru(bpy)_2(PVP)Cl]^+$ species whereas the peak with the $E_{1/2}$ centred at 1.05 V indicates oxidation of the $[Ru(bpy)_2(PVP)_2]^{2+}$ species.

Modified electrodes were prepared by applying 2 - 4 μ l of a 1% (w/w) solution of the metallopolymer in methanol on the electrode, but because the concentration of metal centres in the metallopolymer varies between polymers, there is a variation in the concentration of the electroactive species in the attached metallopolymer. As the degree of metallation in the metallopolymer decreases, the resistance of the film increases since charge propagation by electron transfer between metal sites is more difficult and is more dependent on the motions of the polymer. The effect of a decrease in the ease of charge propagation in the polymer film should lead to a positive shift in the half-wave potentials. This may explain the small variations observed in $E_{1/2}$ values for the different metallopolymer in a particular acid.

The peak to peak separations (E_p) of these cyclic voltammograms also vary considerably, however this parameter depends on a number of

Metallopolymer Code	Half-Wave Potentials ($E_{1/2}$) ^a	
	1M HClO ₄ Solution	1M H ₂ SO ₄ Solution
PM1R1	0.625	0.68
PM1R2	0.6	0.675
PM1R3	0.61	0.685
PM1R4	0.6	0.685
PM2R1	0.63	0.69
PM2R2	0.63	0.675
PM2R3	0.63	0.68, 1.05
PM2R4	0.63	0.67, 1.10
PM3R1	0.62	0.67
PM3R2	0.6	0.65
PM3R3	0.625	0.67, 1.04
PM3R4		0.66, 1.075
PM4R1	0.615	0.66
PM4R2	0.615	0.675
PM4R3	0.605	0.66
PM4R4		0.66, 1.04
PM4R5	0.605	0.66, 1.04

TABLE 1: Half-Wave potential values obtained from the cyclic voltammograms of electrodes coated with poly-4-Vinyl-pyridine-Methylmethacrylate containing Ru(bpy)₂ metallopolymers. (a - all figures are positive vs SCE and are in Volts)

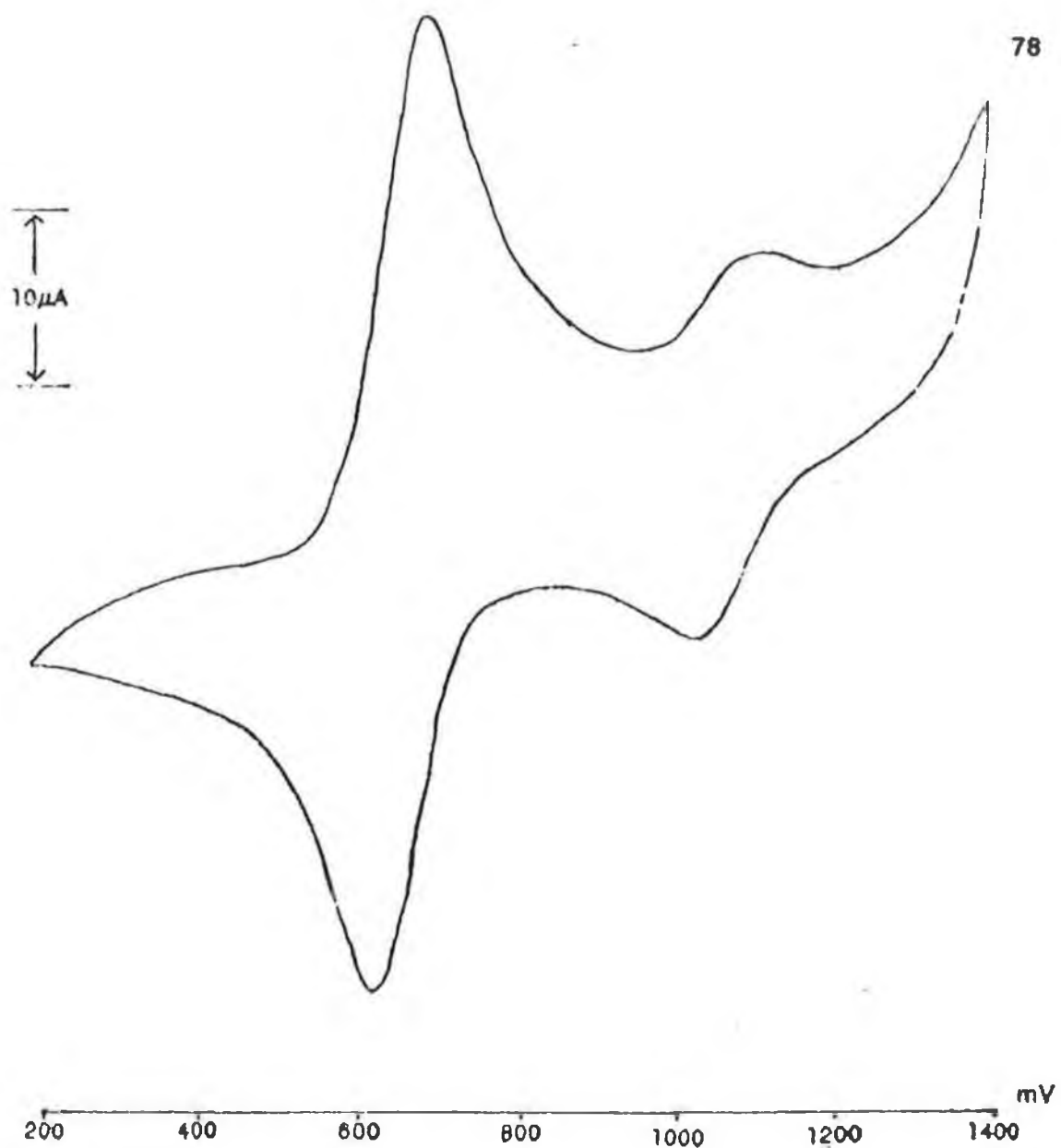


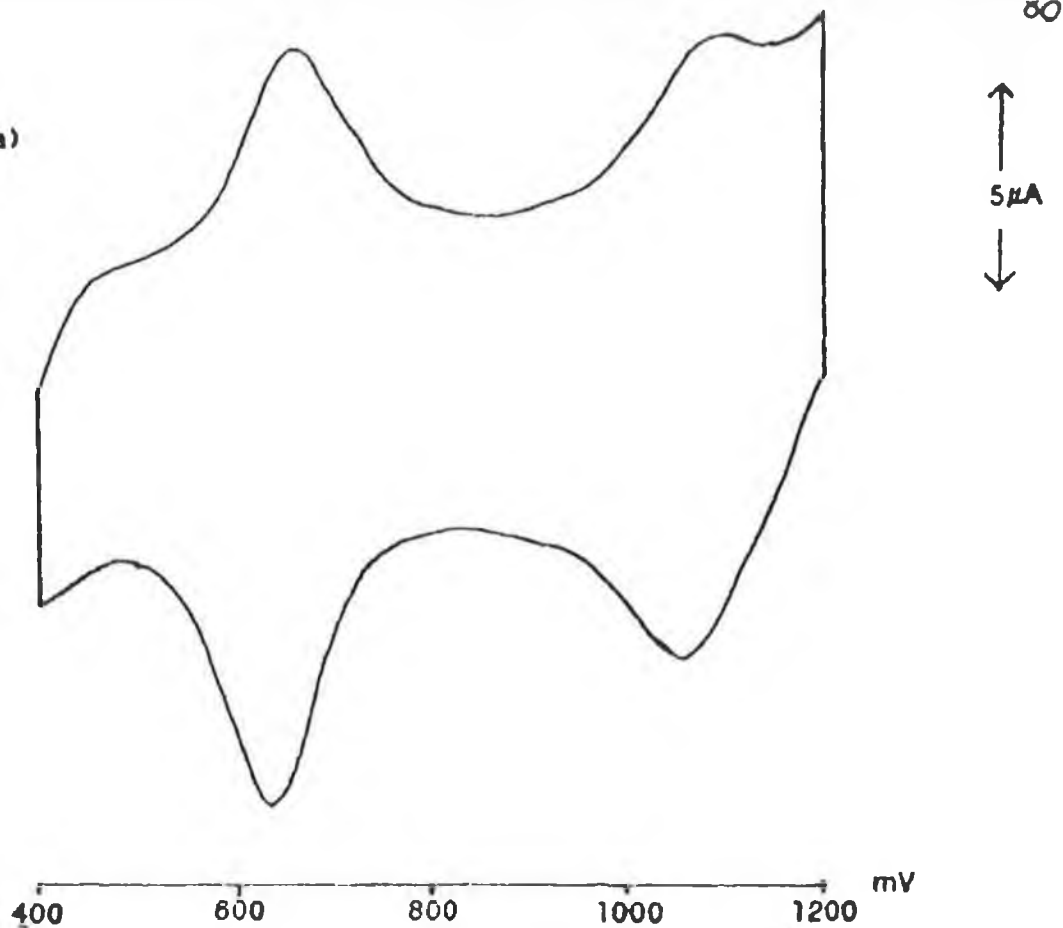
Figure 1: Cyclic Voltammogram of an electrode coated with metallopolymer PM2R3 at a scan rate of 100 mVs^{-1} .

factors: the degree of metallation, the layer thickness, the surface coverage and the scan rate⁵. Making comparisons between samples with different degrees of metallation is difficult and requires assumptions to be made about the groups surrounding the metal.

Although emission spectroscopy indicates the presence of the bis species $[\text{Ru}(\text{bpy})_2(\text{PVP})_2]^{2+}$ in most of the metallopolymers, cyclic voltammetry only shows its presence in six of the metallopolymers with an $E_{1/2}$ between +1.04 and +1.07 V in 1M H_2SO_4 (vs SCE). Some of the other metallopolymers have small waves at this potential but the presence of the bis species for these metallopolymers cannot be stated conclusively by electrochemical means. The cyclic voltammogram (in 1M H_2SO_4) and emission spectrum of the metallopolymer PM2R4 are shown in figure 2. Analysis of the areas under the current peaks indicates that this metallopolymer contains about 25% of the metal centres in the $[\text{Ru}(\text{bpy})_2(\text{PVP})_2]^{2+}$ state (fig. 2(a)). However at room temperature emission from this species completely dominates the emission spectrum for this metallopolymer (fig. 2(b)). This indicates that as expected $[\text{Ru}(\text{bpy})_2(\text{PVP})_2]^{2+}$ is a stronger emitting species than $[\text{Ru}(\text{bpy})_2(\text{PVP})\text{Cl}]^+$. For this reason the analysis of emission spectra is a more viable analytical technique for the detection of the bis species than electrochemical methods.

In 1M H_2SO_4 the electrochemical signals have smaller peak widths and are more intense, however the $E_{1/2}$ of the signals obtained in 1M HClO_4 are about 50 to 80 mV less positive. This implies that electron transfer through the polymer when it is in contact with 1M HClO_4 is easier, possibly because the polymer is not soluble in HClO_4 . Therefore the polymer layer is more compact and the electroactive centres are closer together and charge transfer through the layer is dominated by inter-site

(a)



(b)

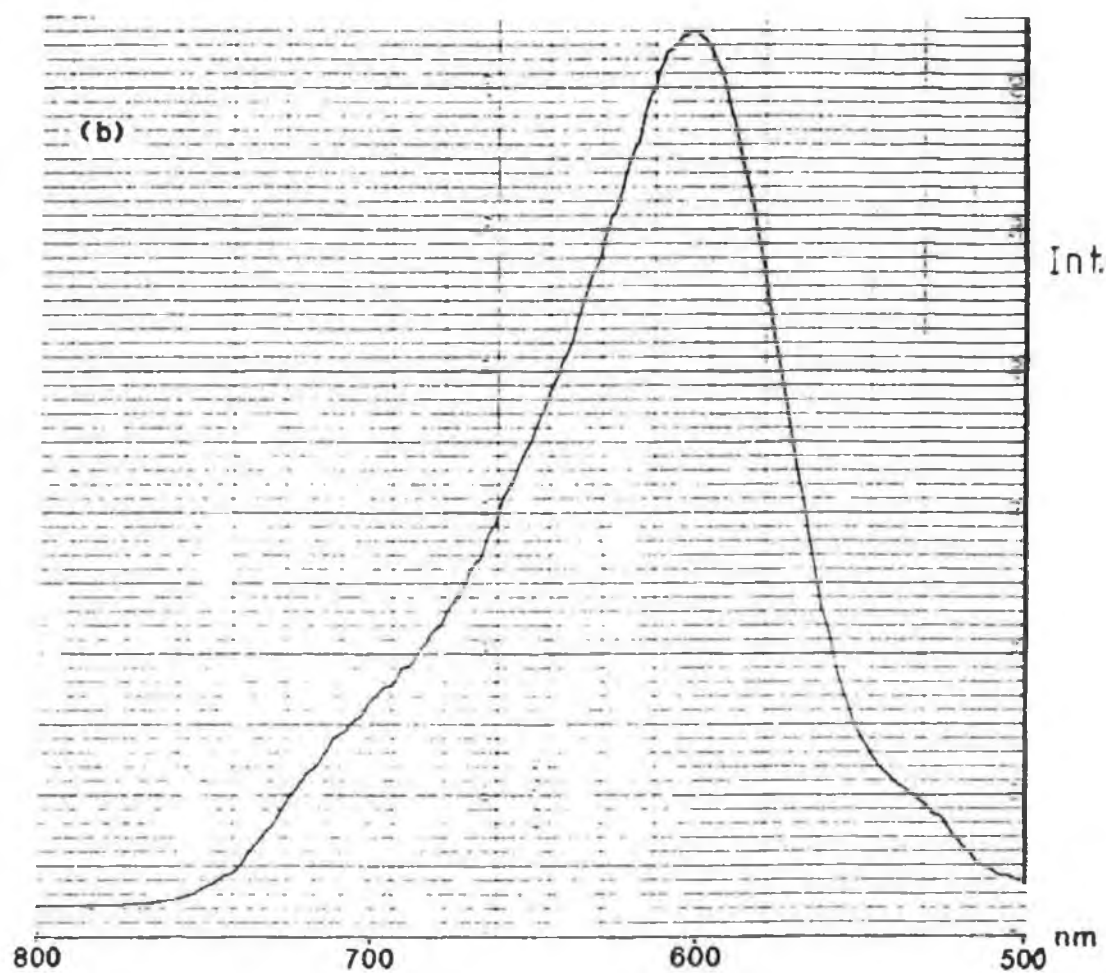


Figure 2: (a) cyclic voltammogram of an electrode coated with metallopolymer PM2R4 at a scan rate of 100 mV/s. (b) emission spectrum of PM2R4 in methanol at room temperature excited at 460 nm.

communication. The two metallopolymer at the extremes of the vinylpyridine concentration range (PM1R1 and PM4R5), for example, show no change in peak position of the cyclic voltammograms with pH but do show a decrease in peak current with increasing pH⁴. It is expected that the metallopolymer between these extremes would behave similarly. This can be explained by the fact that the concentration of anions that are electrostatically held within the protonated copolymer layer will be relatively insensitive to the ionic strength of the supporting electrolyte but highly sensitive to the pH⁶. Therefore an increase in pH should decrease the anion concentration in the film producing a less charged structure and a subsequent decrease in current. Also increasing the protonation of the poly-4-vinylpyridine tends to stretch apart the chains to minimise coulombic repulsions⁷ which leads to a structure through which ions can move more easily. The $E_{1/2}$ values associated with an acid electrolyte are not affected if the electrode is first cycled in 1M HClO₄ and then transferred to 1M H₂SO₄ (or vice versa). This implies that if an electrode is transferred from one to another of the acids, the anions in the film are quickly replaced by the anions of the new acid. There is no significant difference, therefore, in ion mobility in the polymer layer for these two anions.

A plot of peak current (i_L) against (scan rate)^{1/2} (fig. 3) gives a straight line for most of the metallopolymer coatings. With sufficiently heavy coatings, the peak currents exhibit this relationship which is typical for diffusing reactants⁶, but with thin polymer coatings the peak currents are proportional to the scan rate which is expected for thin layers of attached reactants⁶.

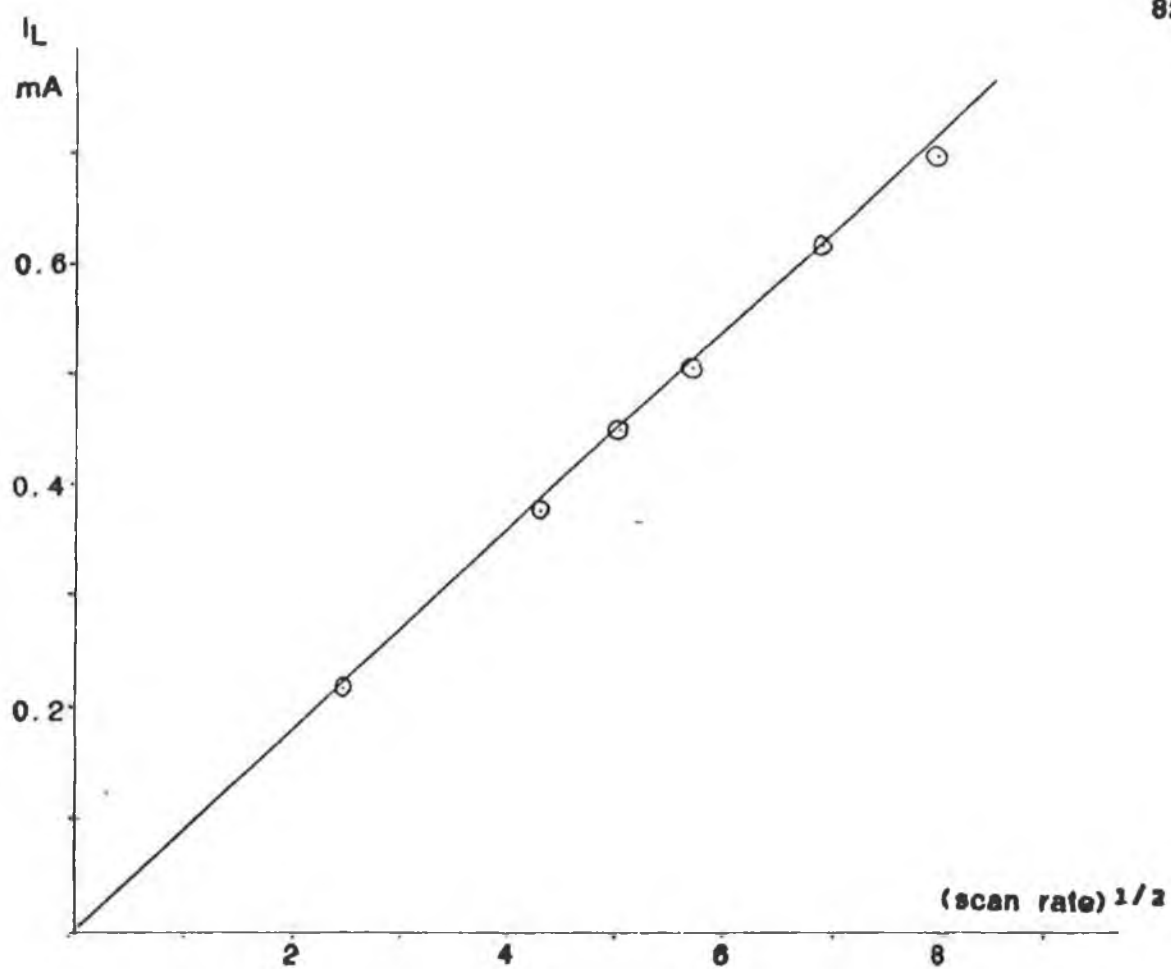


Figure 3: Plot of peak current (I_L) against $(\text{scan rate})^{1/2}$ for an electrode coated with metallopolymer PM4R5 in 1M H_2SO_4 .

5. 1. 2 $\text{Ru}(\text{bpy})_2$ -Poly-4(5)Im Metallopolymers

The half wave potentials of the metallopolymers and model compounds in different electrolytes are given in Table 2. The CV of $[\text{Ru}(\text{bpy})_2 - (4\text{MIm})\text{Cl}]\text{PF}_6$ (fig. 4), which is a model compound for the chloro species in the metallopolymer, shows surprisingly two peaks in 0.1M TEAP/ CH_3CN at equal intensity at +0.3 V and +0.63 V (vs SCE). The two peaks are of equal intensity making it unlikely that one peak represents an impurity. Furthermore the C,H,N elemental analysis indicates a pure compound. This behaviour cannot be explained at present and requires further study. The CV of $[\text{Ru}(\text{bpy})_2(4\text{MIm})_2](\text{PF}_6)_2$ (fig. 5) is straightforward in that it produces a single signal at +0.925 V (vs SCE) in 0.1M TEAP/ CH_3CN . The CV of $[\text{Ru}(\text{bpy})_2(4\text{MIm})(\text{H}_2\text{O})](\text{PF}_6)_2$ (fig. 6) shows two peaks at respectively +0.94 V and +1.135 V (vs SCE). The peak currents were initially of equal intensity but it was noticed that the peak at 0.94 V decreased whilst the peak at 1.135 V simultaneously increased with time. Geraty et. al.⁷ have reported the $E_{1/2}$ under the same conditions for the species $[\text{Ru}(\text{bpy})_2(\text{NMIm})(\text{H}_2\text{O})](\text{PF}_6)_2$ (where NMIm is N-methyl-imidazole) at 0.95 V and they have also observed the formation of $[\text{Ru}(\text{bpy})_2(\text{NVIIm})(\text{CH}_3\text{CN})]^{2+}$ with an $E_{1/2}$ at 1.15 V in $\text{CH}_3\text{CN}/\text{TEAP}$ from the corresponding aquo species. The developing peak in this CV could likewise be explained by ligand substitution of the aquo complex to give $[\text{Ru}(\text{bpy})_2(\text{CH}_3\text{CN})(4\text{MIm})](\text{PF}_6)_2$ with an $E_{1/2}$ at 1.135 V which is close to the value for this species reported by Geraty et. al. It is likely that the aquo complex is located at 0.94 V which may explain why it is not distinguished in the metallopolymers from the bis-imidazole complex which has a peak potential of 0.92V. The same phenomenon was not observed for the bis-imidazole model compounds which would indicate that in CH_3CN , 4MIm is more difficult to replace than water.

Compound	Half-Wave Potentials ($E_{1/2}$)			
	0.1M TEAP/ CH_3CN	1M HClO_4	1M H_2SO_4	1M HCl
$\text{Ru}(\text{bpy})_2\text{-Poly 4(5)VIm}$	0.635, 0.92	0.51, 0.695	0.56, 0.755	0.57, 0.745
$[\text{Ru}(\text{bpy})_2(4\text{MIm})\text{Cl}]\text{PF}_6$	0.3, 0.63			
$[\text{Ru}(\text{bpy})_2(4\text{MIm})_2](\text{PF}_6)_2$	0.925			
$[\text{Ru}(\text{bpy})_2(4\text{MIm})(\text{H}_2\text{O})](\text{PF}_6)_2$	0.94, 1.135			

TABLE 2: Electrochemical data for the model compounds and the poly-4(5)-VIm metallopolymer.

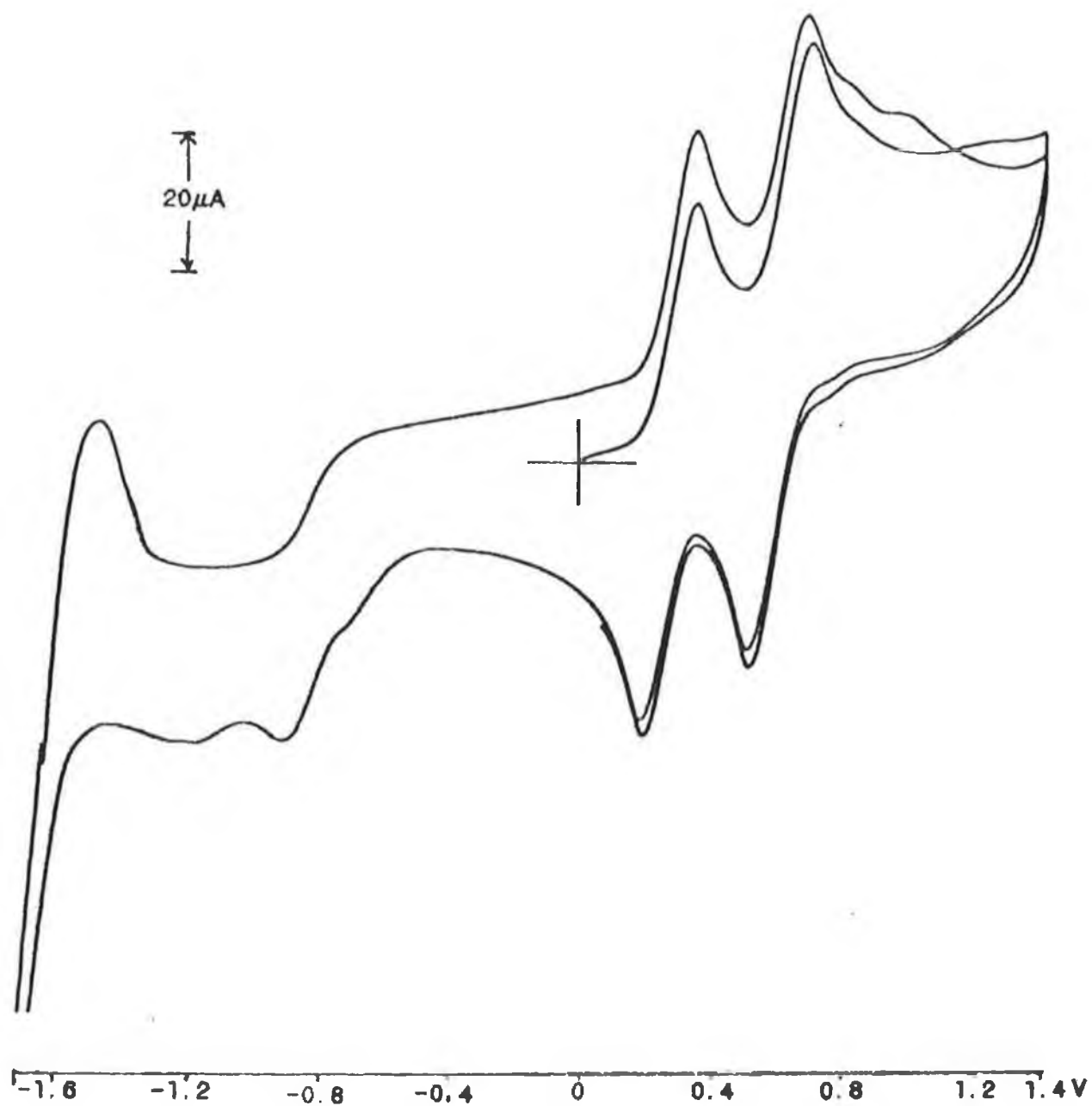


Figure 4: Cyclic voltammogram of model compound $[\text{Ru}(\text{bpy})_2(4\text{Mim})\text{Cl}]^+$ in 0.1M TEAP/ CH_2CN at a scan rate of 100 mV/s.

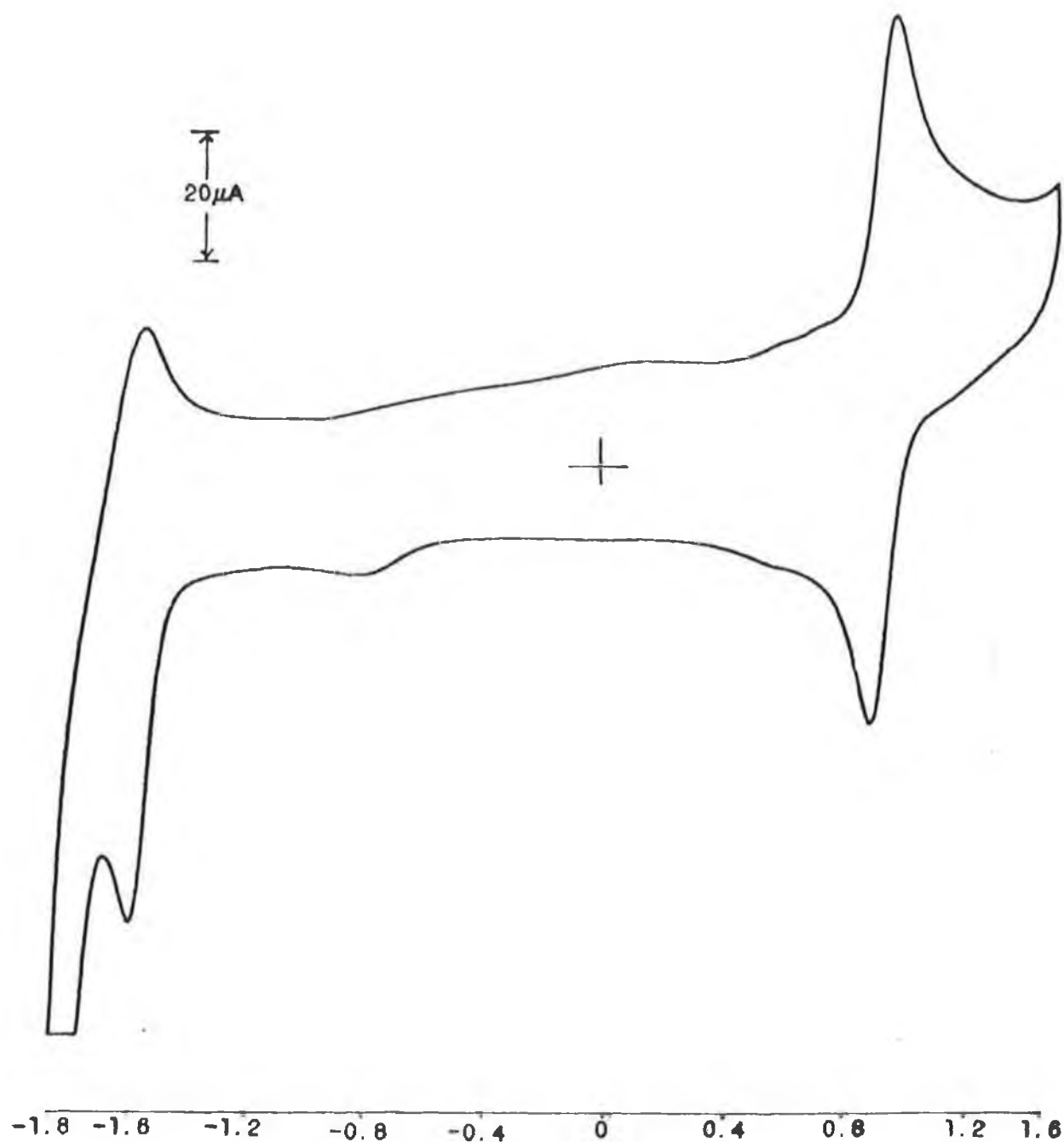


Figure 5: Cyclic voltammogram of model compound $[\text{Ru}(\text{bpy})_2(4\text{Mim})_2]^{2+}$ in 0.1M TEAP/ CH_3CN at a scan rate of 100 mV/s.

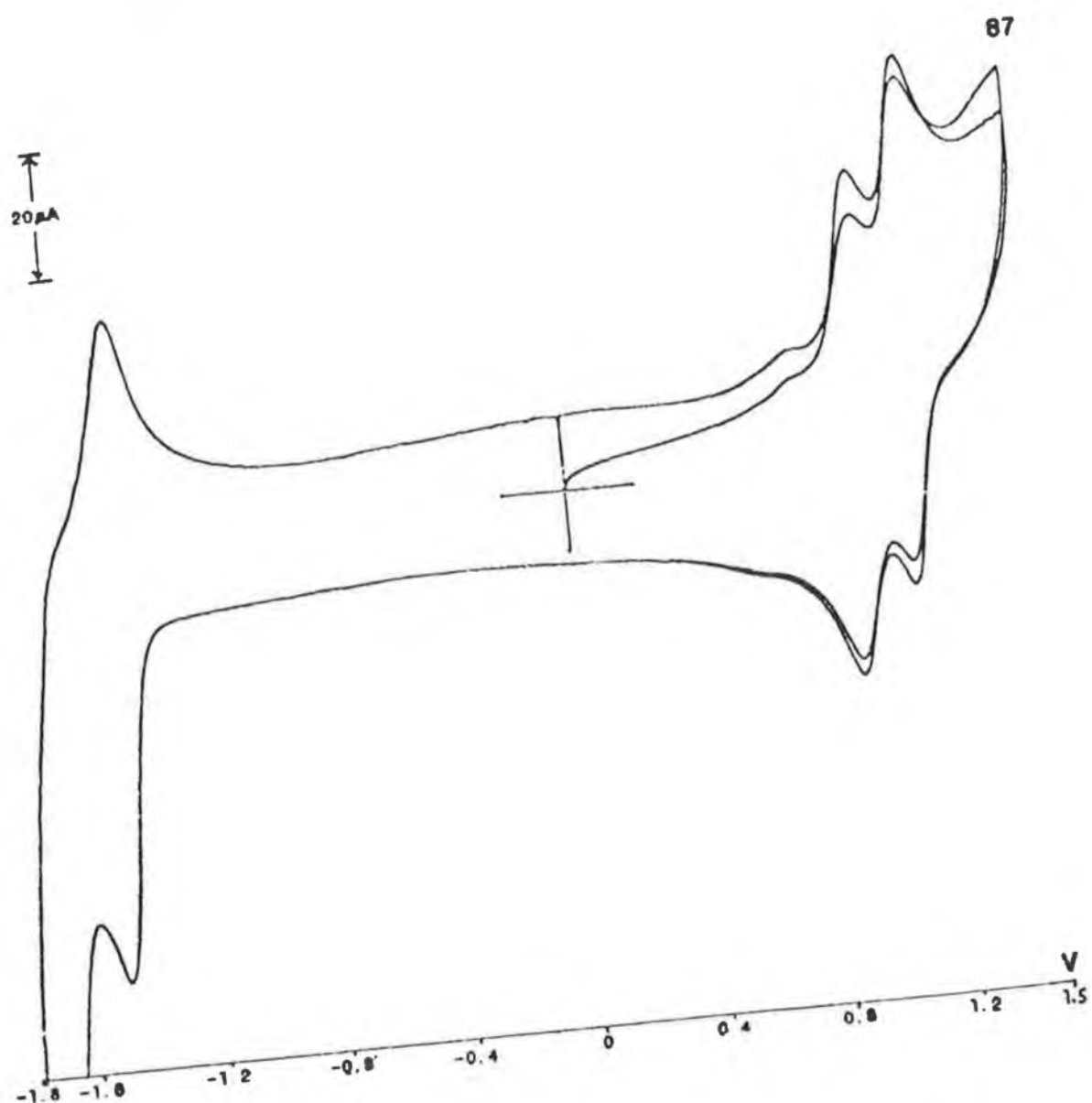


Figure 6: Cyclic voltammogram of model compound $[\text{Ru}(\text{bpy})_2(4\text{Mim})(\text{H}_2\text{O})]^{2+}$ in 0.1M TEAP/ CH_3CN at a scan rate of 100mV/s.

The CV of the metallopolymer BR1 (fig. 7) in 0.1M TEAP/CH₃CN produces two signals at 0.635 V and 0.92 V (vs SCE). The peak at 0.92 V corresponds well with that obtained for the bis-imidazole model compound and the peak at 0.635 V can be explained by the presence of the peak at 0.63 V obtained for the chloro model compound. So by comparison with electrochemical data obtained for the model compounds the presence of the chloro and bis-imidazole species in the metallopolymer can be confirmed. However the presence of the aquo species is uncertain as its $E_{1/2}$ is at +0.94V which is too close to be distinguished from that of the bis compound at +0.92V.

The polymers AR1 to GR1 are grouped together under the heading Ru(bpy)₂-Poly 4(5)VIm in table 2 because their metal centres are in similar environments. Under the reaction conditions investigated, two species appear to have been produced in significant concentrations in all 5 polymers.

It can be seen from the data presented that the $E_{1/2}$ and peak to peak separation (ΔE_p) of the metallopolymer depend on the electrolyte used. In this case the degree of metallation was the same for each metallopolymer and hence direct comparisons between polymers with the same surface coverage should be possible. It was found that the polymers were more soluble in HCl than H₂SO₄ or HClO₄ since if the polymer was cycled for any length of time in HCl the signal decreased steadily indicating removal of the metallopolymer film from the electrode. The $E_{1/2}$ values become more positive as the acid's ability to dissolve the polymer complex from the electrode i. e. for the $E_{1/2}$ values HCl > H₂SO₄ > HClO₄.

The more negative half wave potential for HClO₄ suggests that oxidation of the metallopolymer film in this electrolyte is easier. Replacement of anions in the polymer film by anions of a new electrolyte occurs quickly and

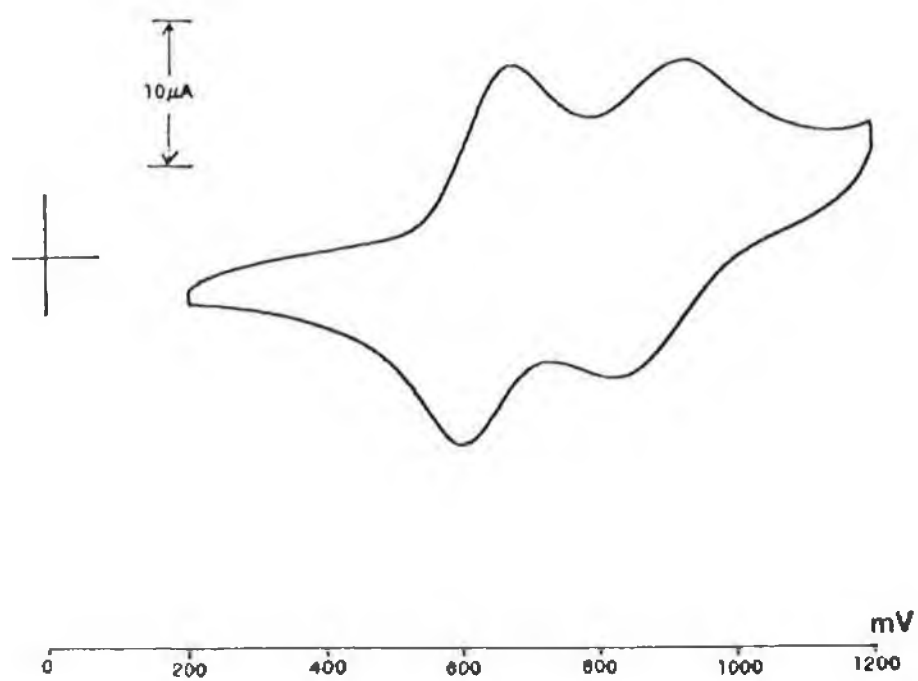


Figure 7: Cyclic voltammogram of a solution of metallopolymer BR1 in 0.1 M TEAP/ CH_3CN at a scan rate of 100 mV/s.

easily and the changed environment of the metal complexes produces the characteristic $E_{1/2}$ values for that particular acid.

These cyclic voltammetry experiments show that the nature of the polymer bound metal complex obtained from the reaction between $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ and the copolymers of 4-vinylpyridine and methylmethacrylate depend strongly on the reaction conditions. The formation of at least two species for these copolymers agrees with the results obtained by Clear et. al.²¹. The amount of $[\text{Ru}(\text{bpy})_2(\text{PVP})_2]^{2+}$ present can be judged best by electrochemical means. For the polymer bound complex obtained from the reaction between $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ and poly 4(5)-vinylimidazole, the formation of at least two species is obtained which is similar to results obtained by Geraty⁷ for poly N-vinylimidazole. The use of model compounds has shown that the chloro species $[\text{Ru}(\text{bpy})_2(\text{PVIm})\text{Cl}]^+$ is formed but the second peak observed could be due to either the aquo or bis substituted species or both.

It has been shown by spectroscopic methods that the chloro and bis substituted species are present in these metallopolymer but the presence of the aquo complex has not been conclusively proven either by spectroscopy or cyclic voltammetry, as it has similar spectral and electrochemical properties to the bis species.

5.2 Chronocoulometry

Chronocoulometry was used to obtain information about the apparent diffusion coefficient (D_{app}) of charge across the metallopolymer films when attached to glassy carbon electrodes. For thin polymer films, chronocoulometry is preferable to chronopotentiometry and cyclic voltammetry for the measurement of diffusion coefficients, and especially at longer experimental times⁹ because the double layer charging current is ignored under these conditions. However, the value found at longer times may be effected by what happens at the outer edges of the polymer. When experiments are carried out over a range of temperatures, an estimate of the activation energy for charge transport, E_a , can be obtained. This can provide valuable information about the effect of the polymer backbone, degree of metallation and the proportion of cross-linking on the ease of charge transport across the film. It should be noted that polymer coatings with large diffusion coefficients for charge transport are required to realise the full possibilities for electrocatalysis by surface confined mediators.

All metallopolymer films were cast from a $10^{-4}M$ solution in methanol onto a polished glassy carbon disk and chronocoulometric experiments were conducted in a $CCl_3COOH/0.2 M CCl_3COONa$ buffer solution at pH 2. Initially, a cyclic voltammogram was recorded, which showed at first a decrease in the signal which stabilised after about 5 minutes. This behaviour could be due to some initial loss of metallopolymer or rearrangement of the metallopolymer chains and a general swelling of the film. Chronocoulometric plots were measured over 6 minutes at the following temperatures: 15, 25, 35 and 45°C. The relatively long step time of 6 minutes ensures that almost all of the electroactive sites in the polymer film are oxidised and hence participating in charge propagation.

For the vinylimidazole metallopolymer, GR1 was studied since it was the least cross-linked of the vinylimidazole metallopolymer and it was anticipated that charge transport would be easier as a result.

The process of charge transport within the coating can be described in terms of an apparent diffusion coefficient (D_{app}), a value which incorporates three modes of charge transport. Charge is thought^{10, 11, 13} to be transported through the polymer coating by:

- (1) electron hopping between redox couples or sites,
- (2) counterion diffusion and
- (3) diffusion of electroactive substrates within the layer if substrate is present in solution.

The polymer can be soluble enough in the electrolyte to achieve a "solution like" state¹² where segments can have enough vibrational mobility to reach a minimum free energy state at equilibrium. Diffusion can proceed by the polymer segments rotating and separating in order to accommodate charge transfer, by any of the three methods outlined above. In general, factors which decrease the segmental mobility decrease the diffusion rate¹³, thus crosslinking, chain stiffness and crystallinity tend to reduce the rate of diffusion. Plots of the charge (Q) versus $t^{1/2}$ should exhibit straight lines with slopes (S_T) proportional to D_{app} where:

$$S_T = \frac{2nFAC_{\Gamma}D_{app}^{1/2}}{\pi^{1/2}} \quad (1)$$

From this equation:

$$C_{\Gamma}D_{app}^{1/2} = \frac{S_T}{48097.8} \quad (2)$$

where C_{Γ} is the volume concentration of reactant confined to the polymeric coating. It is difficult to determine C_{Γ} since although 100 μ l of a 10^{-4} M

solution (based on $\text{Ru}(\text{bpy})_2\text{Cl}_2$, this is $2.2635 \times 10^{-8} \text{ M cm}^{-2}$), was applied to the electrode surface in each case. there is always some spillage of solution over onto the insulating sheath around the disk when coating. such spilled material may not participate in the electrode reaction. Also some metallopolymer is lost depending on the electrolyte during the initial equilibration of the film in the electrolyte. Furthermore the area of the peak in cyclic voltammetry cannot be relied on as a measurement of C_T since in a metallopolymer film significant quantities of attached complex can remain unoxidised under cyclic voltammetric conditions. Because of the reasons outlined above it is very difficult to obtain an accurate value for D_{app} .

5.2.1 $\text{Ru}(\text{bpy})_2$ - Poly-4VP-MMA Metallopolymer.

Chronocoulometric charge vs (time)^{1/2} plots of the copolymers are shown in figure 8. The charge values used here are those of the metallopolymer less those measured when similar experiments were carried out with metal free polymer. In this way the double layer charging contribution was, to some extent, compensated for. Straight lines were obtained in the temperature range from 15 to 45°C. Values for the variation of the term $C_T D_{\text{app}}^{1/2}$ with temperature are shown in table 3. Assuming C_T to be constant during the experiment, it can be seen from this table that D_{app} increases with temperature in all cases. This is to be expected since an increase in temperature increases the physical motion of the polymer chains with the attached reactant electroactive groups which in turn increases the rate of inter-complex electron transfer¹⁴. The diffusion of the corresponding counter ions through the polymer film to sites where the anchored metal complexes are to be oxidised is also increased by an increase in temperature.

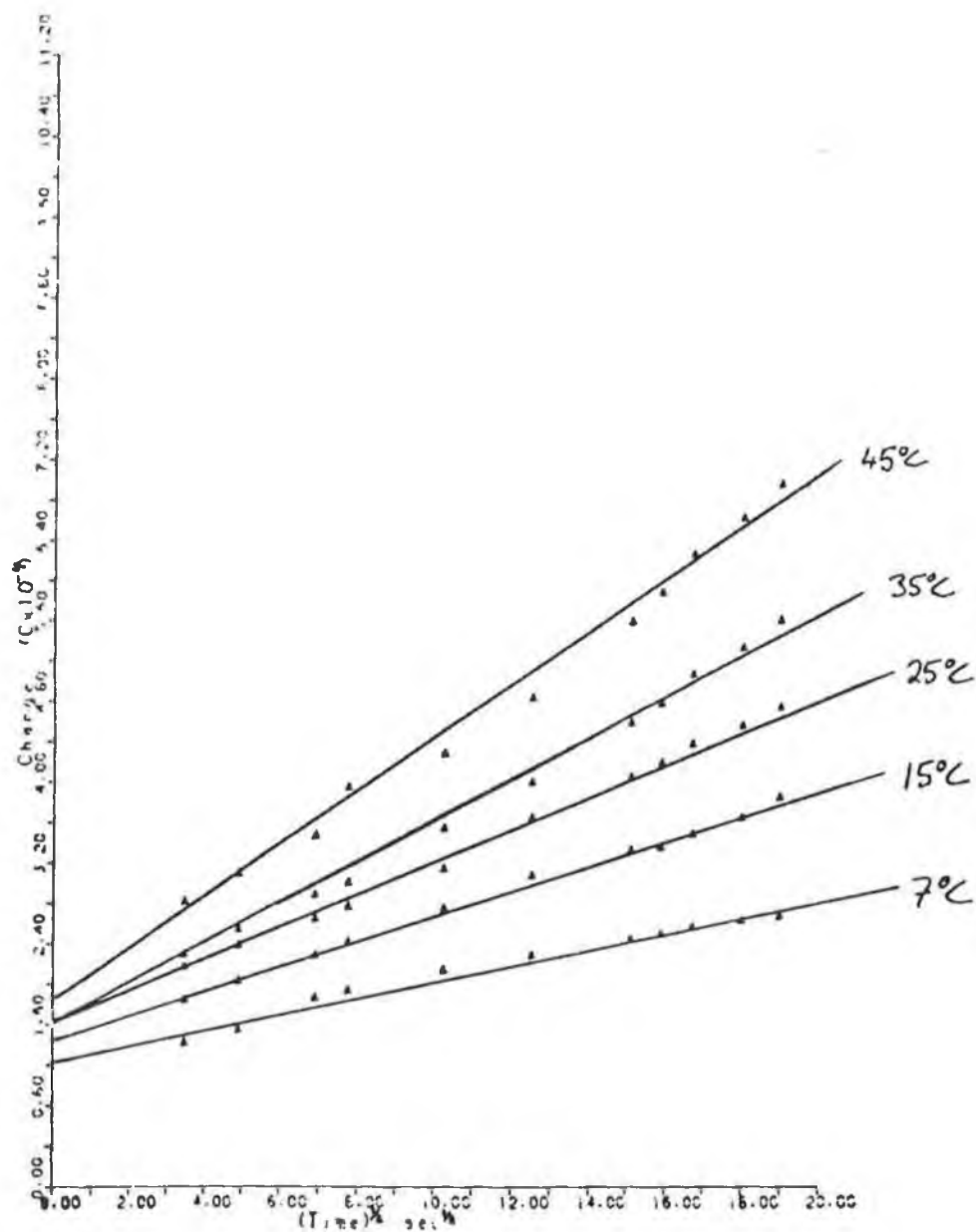


Figure 8: Chronocoulometric (Charge) vs. (time)^{1/2} plots at different temperatures for Ru(bpy)₂-poly-4VP-MMA metallopolymer PM4R5.

Temperature (°C)	$C_T D_{app}^{1/2} \times 10^{-10}$		
	PM2R1	PM3R1	PM4R5
15	2.95	1.35	2.64
25	4.32	1.725	3.51
35	6.44	2.37	4.42
45	9.144	3.445	5.47

TABLE 3: The variation of $C_T D_{app}$ with temperature for the $Ru(bpy)_2$ -poly-4VP-MMA metallopolymer: PM2R1, PM3R1 and PM4R5.

Polymer	Calculations for E_a (kJmol ⁻¹)	
	Slope	Intercept
PM2R1	57.9	58.0
PM3R1	43.1	43.3
PM4R5	36.7	36.7

TABLE 4: Comparison of E_a calculated from slope and intercept of plots of $\ln(S_t/S_{298})$ vs. $1/T$.

The systematic variation of the copolymer backbone of $\text{Ru}(\text{bpy})_2$ -poly 4VP-MMA metallopolymers by dilution of the vinylpyridine units with methylmethacrylate might allow the effect of this dilution on charge transport through the film to be studied. A trend for the apparent diffusion coefficient with the amount of 4-vinylpyridine in the copolymer cannot be observed in table 3. However this inconsistency in the table could be due to the uncertainty of the volume concentration of electroactive species (C_F) in the polymer films. The thickness of the film varies due to different degrees of swelling for each copolymer in solution and also because of the different concentrations per gram of the electroactive complex for each copolymer. Oyama and Anson have reported¹⁶ for a polyvinylpyridine incorporating various metal complex anions that D_{app} does not depend on film thickness but does depend on the concentration of incorporated electroactive material (when it is less than 1M).

A measurement of E_a will show the effect that the amount of 4-vinylpyridine in the polymer backbone or the degree of crosslinking has on the diffusion of charge. Moreover an estimate of the diffusion activation energy (E_a) allows the nature of the charge transport process to be elucidated. For example, activation energies up to 33.5 kJ/Mol are typical of counterion movement in polymers and values of 167 kJ/Mol are typical of movement of large chain segments¹⁵. From relative measurements of D_{app} at different temperatures the activation energy can be measured from the Arrhenius relationship:

$$D_{\text{app}} = D_0 e^{-E_a/RT} \quad (3)$$

where D_0 is the diffusion at a certain temperature. And from this it can be shown that (see theoretical chapter):

$$\ln \left\{ \frac{S_T}{S_{298}} \right\} = -\frac{E_a}{2RT} + \frac{E_a}{596R} \quad (4)$$

The method by which this is calculated removes the C_T factor from the equation and provides two measurements for E_a from the slope and intercept of a plot of the left hand side of the equation (4) against $1/T$. Plots for the three copolymers studied are shown in figure 9 and measurements of the diffusional energy of activation determined from slopes and intercepts are given in table 4.

There are a number of properties of these metallopolymer to emerge from this data. the first being that as expected there is good correlation between the E_a values calculated from slopes and intercepts. It can also be noted that the diffusional activation energy increases from a low value for metallopolymer PM4R5 to a high value for PM2R1. These values are slightly higher than those reported¹⁵ for the diffusion of TEAP ions (between 8.4 and 33.5 kJ/Mol) in poly-4-vinylpyridine and suggests that some movement of metallopolymer segments is contributing to charge transport.

The diffusional activation energy is a measure of the difficulty or energy barrier associated with charge transport across the polymer films. It can be seen from table 4 that E_a increases with increasing concentration of methylmethacrylate in the copolymer backbone. Oyama and Anson¹⁶ have reported E_a values for $Ru^{III}(edta)$ complexes electrostatically bound in poly 4-vinylpyridine in a CF_3COOH/CF_3COONa electrolyte as 19.25kJ/Mol which is less than the figures obtained for these copolymers. They concluded that charge transport for their system results from ion movement only. It seems therefore that diluting the vinylpyridine polymer with methylmethacrylate has lead to an increase in the diffusion activation energy. An increase in methylmethacrylate in the copolymer increases the inter site distances thus making the movement of polymer chains necessary for charge transport between sites. Also vinylpyridine units within the

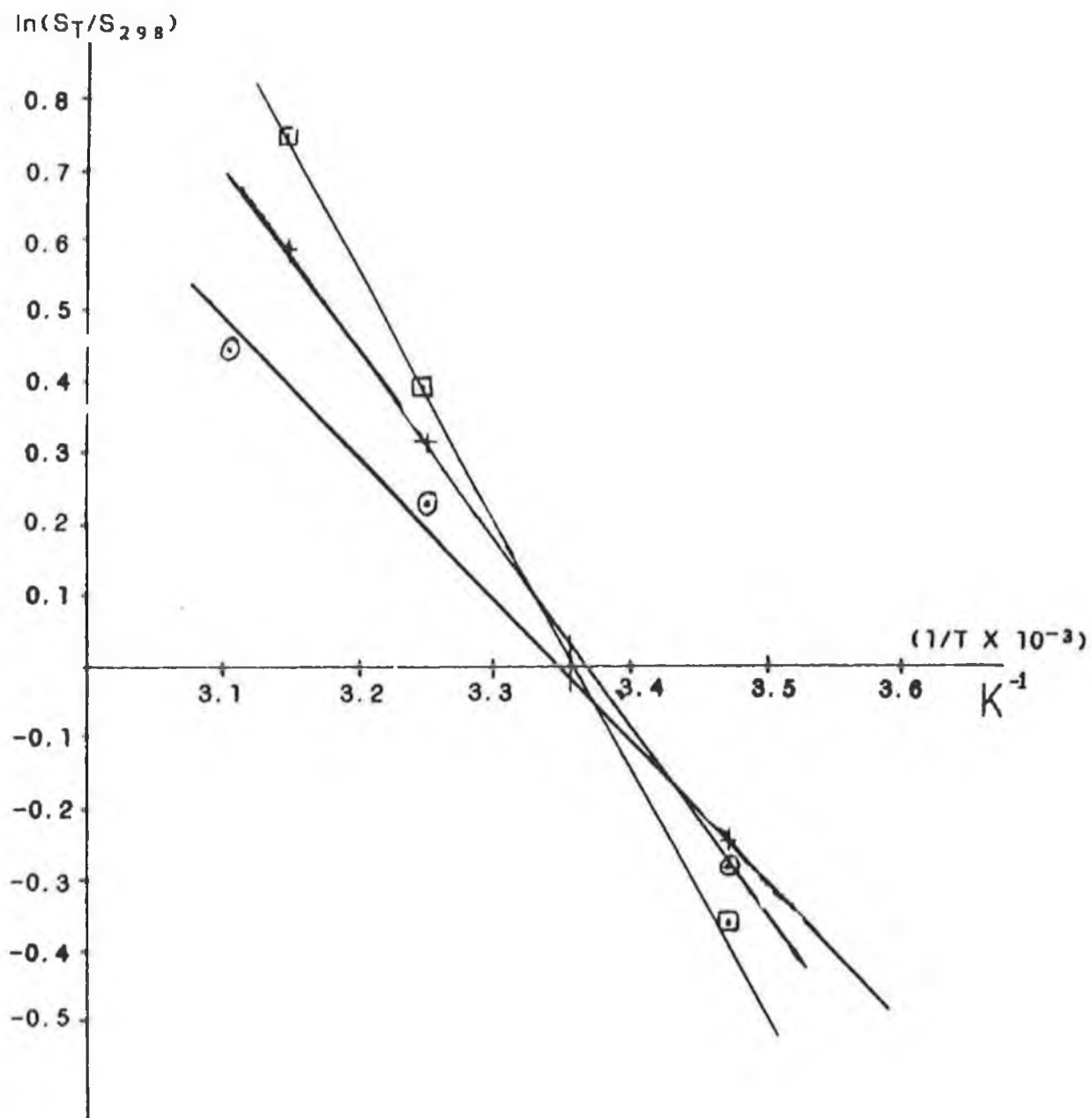


Figure 9: Plots of $\ln(S_T/S_{298})$ vs $1/T$ for $\text{Ru}(\text{bpy})_2$ -Poly-4VP-MMA metallopolymers: PM2R1 (□), PM3R1 (+) and PM4R5 (○).

copolymer repel one another when protonated in acids leading to a porous structure in the film facilitating substrate diffusion and enabling increased mobility of the polymer chains with attached electroactive groups which in turn facilitates electron transfer between sites. Therefore an increase in the amount of vinylpyridine in the copolymers increases the degree of repulsion and also the porosity of the film, which leads to an increase in the efficiency of the electrochemical reactions.

5.2.2 $\text{Ru}(\text{bpy})_2$ -Poly-4(5)VIm Metallopolymers.

A chronocoulometric charge/(time)^{1/2} plot for GR1 is shown in figure 10. From the slopes of the lines, values for $C_T D_{app}$ were determined and are shown in table 5. It can be seen that GR1 behaves in a similar fashion to the PVP-MMA copolymers since D_{app} increases with temperature. This is consistent with the fact that increasing temperature will increase the segmental mobility of the polymer thus allowing the diffusing species to penetrate more easily into the layer¹⁷. Also the greater segmental motion allows interaction between sites to be more frequent. The diffusional activation energy (E_a) for this metallopolymer can be evaluated from the plot of $\ln(S_T/S_{298})$ against $1/T$ as shown in figure 11. The values of E_a determined from the slope and from the intercept is 45.1 kJmol^{-1} .

This value suggests that charge transport is not solely the result of ion movement within the layer, but that some movement of the polymer chains occurs which contributes to charge transport. This metallopolymer (GR1) contains a significant amount (approximately 10% as measured by cyclic voltammetry) bis substituted sites and therefore more crosslinking which would restrict the amount of movement of ions in the polymer and thus contribute to the difficulty in charge transport.

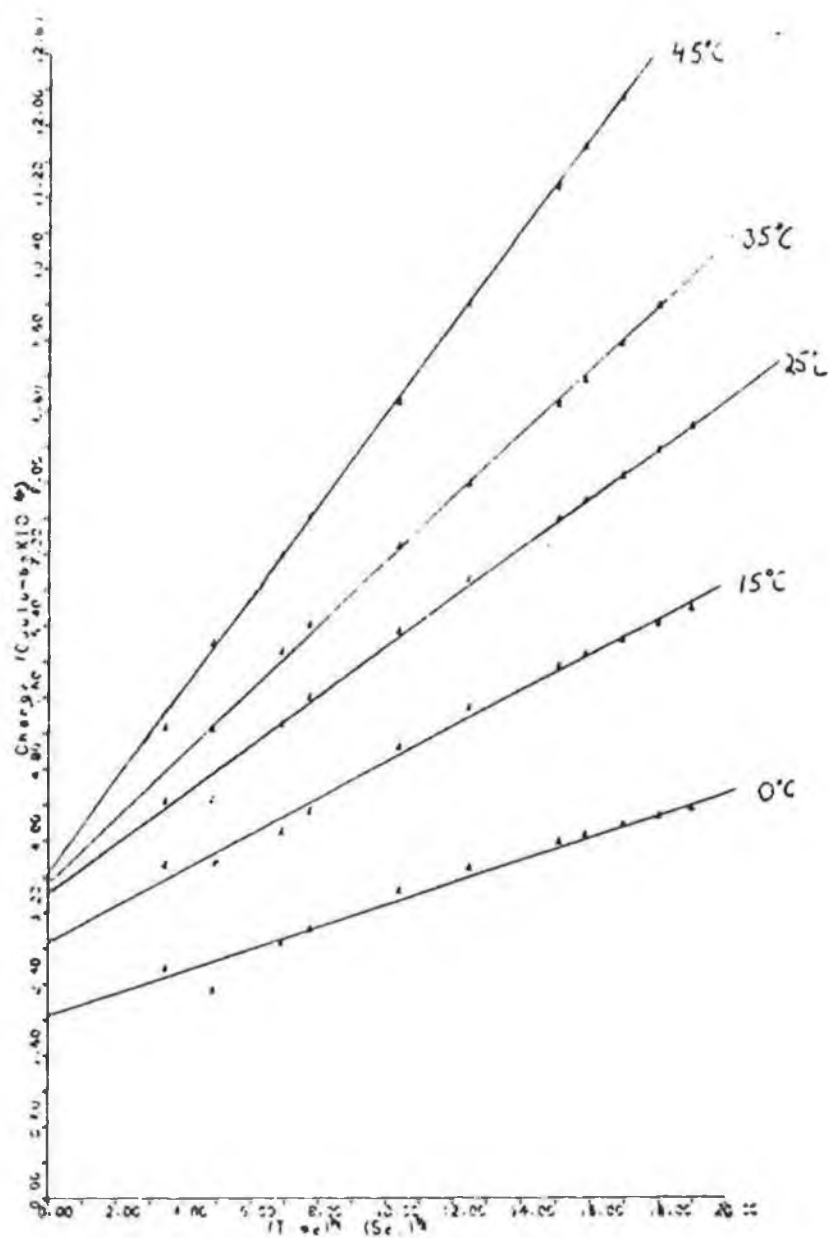


Figure 10: Chronocoulometric (Charge) vs. $(\text{time})^{1/2}$ plots at different temperatures for the Ru(bpy)₂-poly-4(5)VIm metallopolymer GR1.

Temperature (°C)	$C_T D_{app}^{1/2} \times 10^{-10}$
0	2.5
15	4.4
25	5.9
35	7.5
45	10.68

TABLE 5: Table showing the variation of $C_T D_{app}$ with temperature for a $Ru(bpy)_2$ -poly-4(5)-Vim metallopolymer (GR1).

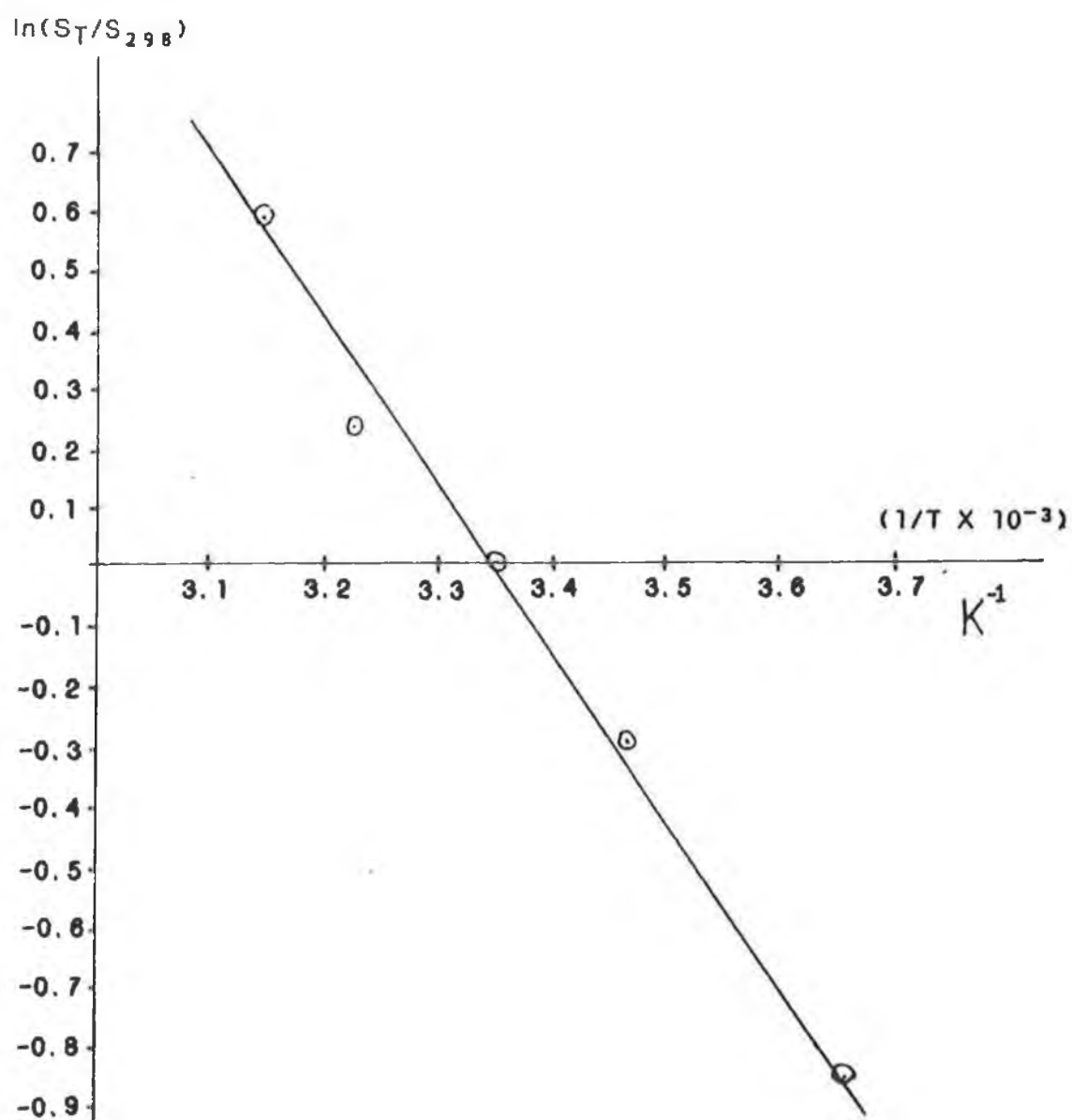


Figure 11: Plot of $\ln(S_T/S_{298})$ vs. $1/T$ for the $\text{Ru}(\text{bpy})_2$ -poly 4(5)Vlm metallopolymer GR1.

These chronocoulometry experiments have shown that diluting the vinylpyridine polymer with methacrylate units has increased the difficulty of charge transport through the metallopolymer film. Measurements of E_a have indicated that for copolymers with increasing amounts of methylmethacrylate, movement of the polymer chains becomes more important for charge transport. It has been found¹⁶ for polyvinylpyridine containing electrostatically bound $Ru^{III}(edta)$ that ion movement within the layer is sufficient for charge transport. It is possible that an increase in methylmethacrylate increases the inter site distances and thus makes movement of the polymer backbone necessary for inter site communication. Hence anything which physically increases the inter site distances increases the energy of activation for charge transport. Using the same technique for the measurement of E_a , it was found that movement of the polymer chain is also important for charge transport in the poly 4(5)VIm metallopolymer- GR1. This is possibly because of the crosslinks in this polymer formed by the bis-substituted species which would make ion movement within the layer more difficult.

5.3 Rotating Disc Electrode Studies

The feasibility of the use of a particular modified electrode in electro-catalytic processes can be comprehensively analysed by hydrodynamic methods and in particular by rotating disc electrode experiments. Using rotating disc electrodes, the effect of changing the polymer backbone chain of the vinylpyridine-methylmethacrylate copolymers on the effectiveness of the electro-catalytic reactions was investigated. The properties of the vinylimidazole metallopolymer in the mediation of the oxidation of Fe^{II} were also studied. A broad discussion of the theory of hydrodynamic methods is given in section 2.2.2.

5.3.1 $\text{Ru}(\text{bpy})_2$ -Poly-4VP-MMA Metallopolymers.

An example of current-potential curves for the oxidation of Fe^{II} at a glassy carbon electrode coated with polymer PM2R1 is shown in figure 12. As in the case of the homopolymer^{9, 18, 19}, the oxidation of the Fe^{II} is mediated at potentials where the species Ru^{III} is produced. Since the formal potential of $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}/[\text{Fe}(\text{H}_2\text{O})_6]^{+}$ is around +0.3V with respect to SCE at a bare carbon electrode electrode it can be seen from figure 12 that with a modified electrode no peak is observed at this potential and it can be assumed therefore that only negligible amounts of Fe^{II} are able to diffuse to the bare electrode surface. Since even though the process is kinetically slow, some current would be seen if any $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ reached the electrode surface. Cyclic voltammograms taken before and after these experiments indicate that only between 5 and 10% of metallopolymer coating is lost during the experiment. The limiting current is dependent on a number of factors including rotation rate, temperature, number of $[\text{Ru}(\text{bpy})_2]^{2+}$ sites in the film and the concentration of Fe^{II} ions in solution. In the studies undertaken an attempt was made to ensure the

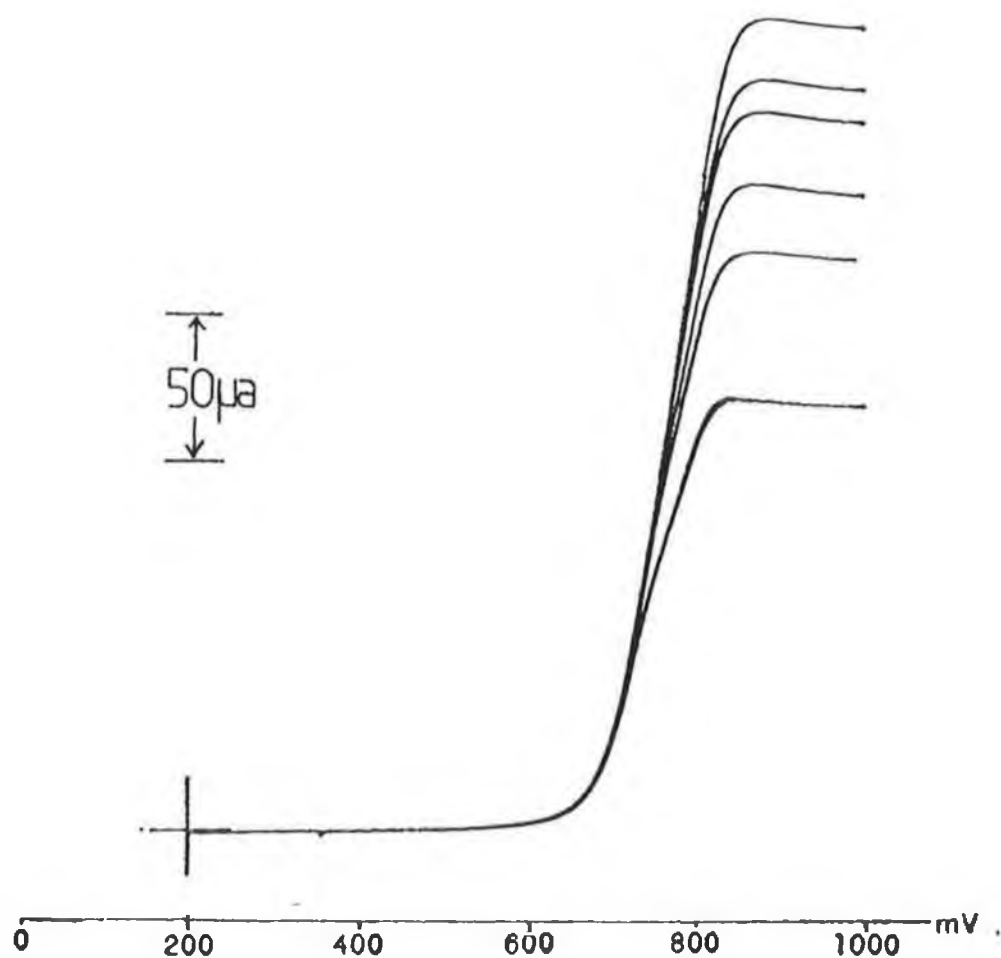


Figure 12: Current-Potential curves at different rotation rates for the oxidation of the species $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ at a glassy carbon electrode coated with metallopolymer PM1R1. (substrate concentration: 2.14×10^{-4} moles of $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ in $0.9\text{M Na}_2\text{SO}_4/0.1\text{M H}_2\text{SO}_4$)

latter factors were kept constant between polymers. In particular, the same quantity of electroactive material was applied to the disc for each metallopolymer and the concentration of Fe^{II} was kept constant in all studies.

These current-potential curves can be conveniently analysed by Koutecky-Levich plots of $1/i(\text{lim})$ against $1/\omega^{1/2}$. Where ω is the rotation rate and i_{lim} is the limiting current. An example of such a plot for PM4R5 is shown in figure 13. It can be seen from this figure that a straight line is obtained indicating that the following equation holds:

$$\frac{1}{i} = \frac{1}{i_a} + \frac{1}{i_f} \quad (5)$$

Where i_f is the film current which can be obtained from the intercept and reflects the competition between the cross-exchange reaction and diffusion of substrate through the film and the Levich current i_a is proportional to $(\omega)^{1/2}$. The nature of the process follows the S or SR case as detailed by Saveant et. al.¹¹ where:

- (a) no second wave is observed
- (b) A plot of $1/i_{\text{lim}}$ versus $1/\omega^{1/2}$ is linear
- (c) The slope is inversely proportional to the substrate concentration.

In the S case, the film current is completely supplied by the cross-exchange reaction (i_k) and the film current is therefore:

$$i_f = i_k \quad (6)$$

In the SR case, the film current is composed of the cross-exchange current (i_k) due to redox reactions between the substrate and the Ru

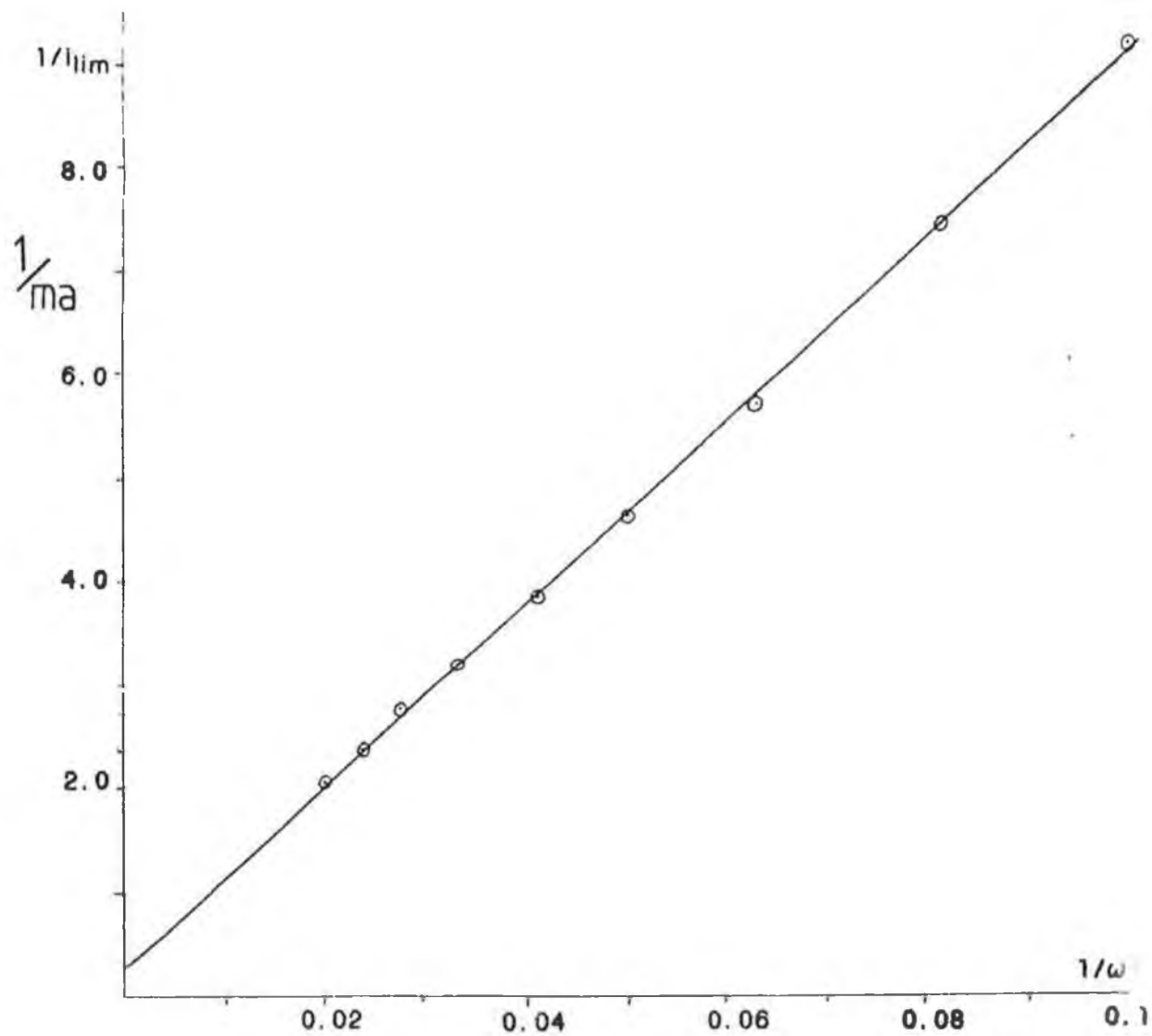


Figure 13: Koutecky-Levich plot of $1/i_{lim}$ against $1/\omega^{1/2}$ for the metallopolymer PM4R5.

couple near the surface of the polymer film and the substrate current (i_s) due to diffusion of the substrate through the polymer film:

$$i_f = (i_k i_s)^{1/2} \quad (7)$$

However the cross-exchange reaction component of current is usually much faster than diffusion of the substrate through the coating and hence i_k is much greater than i_s and from figure 12 it can be seen that little substrate reaches the electrode. Values for the film currents of the metallopolymer studied are given in table 6. As expected from the activation energies obtained earlier, an increase in the film current is observed as the amount of vinylpyridine in the copolymer backbone is increased. This phenomenon may be explained by the fact that the acidic environment in which the experiments were carried out protonates the vinylpyridine groups, leading to repulsions between neighbouring pyridine units. The amount of repulsion increases as the amount of vinylpyridine in the copolymer increases, leading to a more porous polymer structure. This would allow easier penetration of the substrate Fe^{II} ions into the polymer film which would increase i_k and i_s and hence the film current. Also the vinylpyridine part of the copolymer is more soluble in aqueous solutions than the methylmethacrylate and thus more vinylpyridine in the polymer would make reaction with the substrate and the metal sites easier because of better swelling of the film in the aqueous electrolyte. This would lead to a faster mediation process and a subsequent increase in current. However the increase in positive charge attained by the protonated vinylpyridines would be expected to repel the positively charged substrate $[Fe(H_2O)_6]^{2+}$, but this effect seems to be insignificant compared to the others mentioned above.

The variation of the current-potential curves with temperature were studied

Polymer	4-Vinylpyridine/Methyl Methacrylate Ratio	Film Current I_f
PM1R1	1 : 4	0.38
PM2R1	1 : 1	0.54
PM3R1	2 : 1	2.33
PM4R5	4 : 1	4.0
GR1	—	3.63

TABLE 6: Values for the film currents of the $\text{Ru}(\text{bpy})_2$ containing metallopolymer (background electrolyte concentration is: $1 \times 10^{-4} \text{M}$ $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$, $\Gamma_{\text{Ru}} = 2.26 \times 10^{-8} \text{ moles/cm}^2$, electrode is glassy carbon.)

and it was found that the limiting current increases with increased temperature. This is to be expected as the rate of diffusion of the substrate and the mixed valence interactions of the bound reactant would be increased with an increase in temperature. Hence the cross exchange reaction follows an Arrhenius type behaviour in common with other mediating layers¹⁵. Koutecky-Levich plots of the metallopolymers (fig. 14) show that as the temperature increases, the intercepts tend towards zero indicating that the process becomes kinetically easier, since as the intercept tends to zero, the film current tends to infinity. When the intercept passes through zero it indicates that the kinetics of the process are too fast to be monitored under these particular conditions²⁰. At this point the electron transfer process is no longer kinetically limited by the cross-exchange reaction at the electrode surface and the current is then limited by the diffusion of substrate to the electrode (i.e. the Levich current i_a).

5.3.2 $\text{Ru}(\text{bpy})_3$ -Poly-4(5)VIm metallopolymers.

Figure 15 shows current-potential curves for metallopolymer GR1 (which is based on poly-4(5)-vinylimidazole at different rotation rates in $2 \times 10^{-3} \text{M}$ $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$). It can be seen that oxidation of the Fe^{II} takes place at potentials between 450 and 550mV where Ru^{III} is formed indicating that the oxidation is mediated by the attached redox couple at the polymer surface. Oxidation of Fe^{II} at the bare electrode cannot be observed from these I-E curves which suggests that i_s is negligible. The film current for this polymer compared to those for the vinylpyridine-methylmethacrylate metallopolymers is given in table 6. The film current is in the same region as the copolymers but near the high end, indicating that mediation of the Fe^{II} is relatively kinetically easy. The 4(5)-VIm polymer is more soluble in

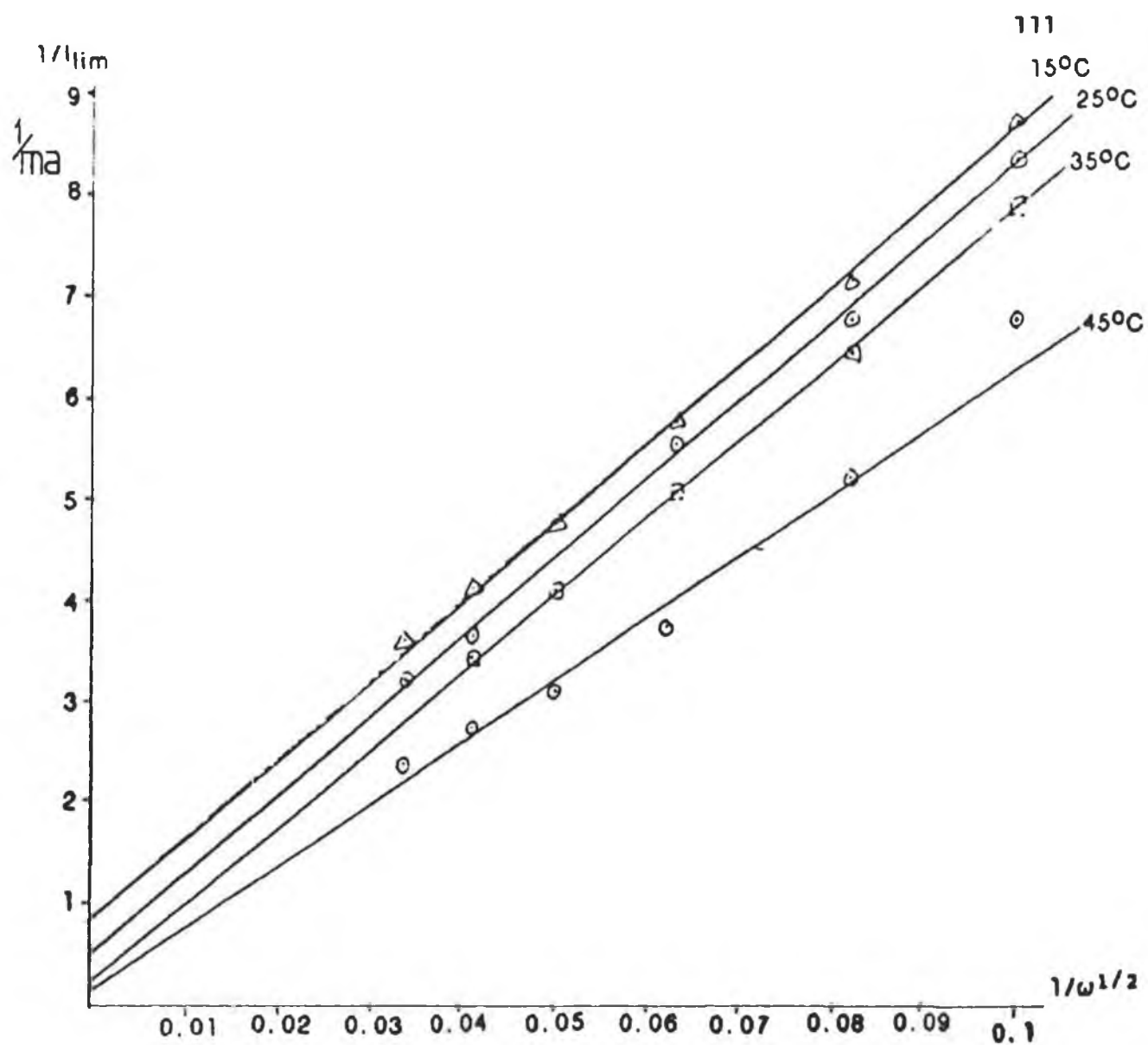


Figure 14: Koutecky-Levich plots of metallopolymer PM3R1 at different temperatures (conditions as stated in fig. 12)

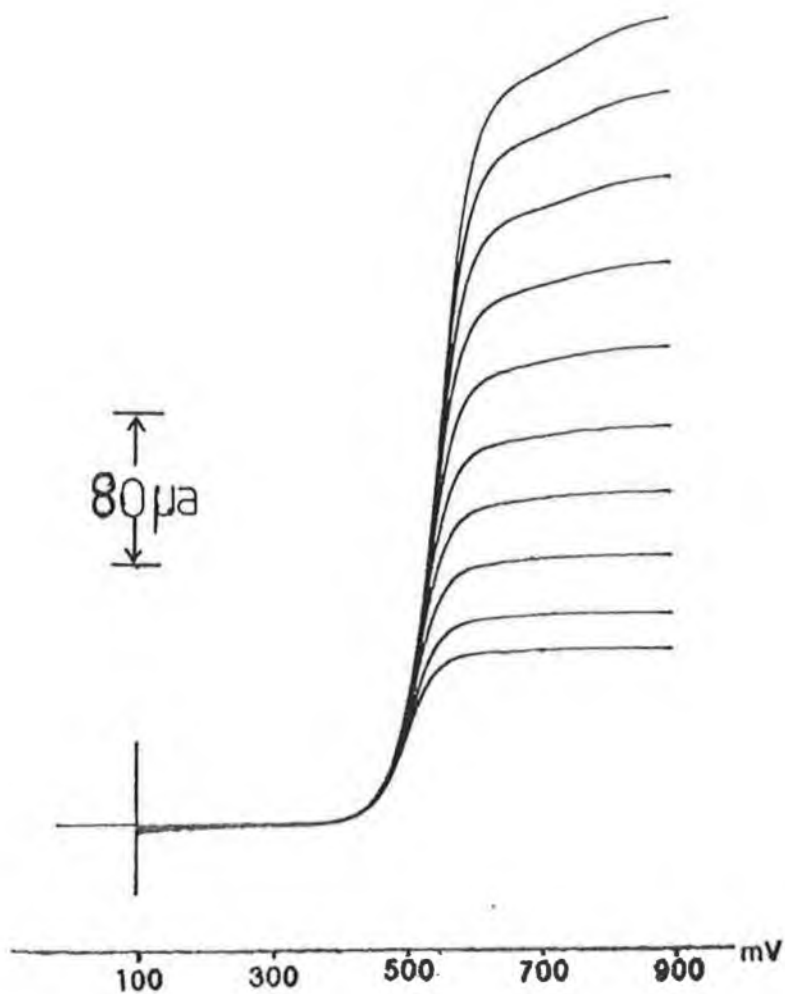


Figure 15: Current-Potential curves at different rotation rates for the oxidation of the species $[\text{Fe}(\text{H}_2\text{O})_6]^3+$ by the metallopolymer GR1. (substrate concentration: $1.14 \times 10^{-4}\text{M}$ of substrate in the same electrolyte as stated in figure 12)

aqueous solutions than the copolymers of PVP-MMA and would therefore swell up more in the electrolyte thus allowing reaction of the substrate with the Ru sites easier and more substrate to penetrate near the surface. Experiments carried out over a range of temperatures show that the limiting current of this metallopolymer increases with increasing temperature.

The effect of diluting the vinylpyridine polymer backbone with methylmethacrylate on electrocatalytic reactions involving the substrate $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ is to make mediation more difficult. The result for the PVIm metallopolymer is in agreement with the range of activation energies obtained for charge propagation in the copolymers. When charge propagation is hindered, automatically the mediating properties of the layers will be affected aswell.

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CHAPTER 6

PHOTOCHEMICAL STUDIES OF MODEL COMPOUNDS AND METALLOPOLYMERS

6.1 Photochemical Studies of Mononuclear Model Compounds

The photochemical behaviour of some $[\text{Ru}(\text{bpy})_2\text{XY}]^{n+}$ complexes have been studied^{1, 2, 3} with much interest in recent years. Both photoinduced ligand exchange reactions and cis-trans rearrangements have been observed. Clear et. al.³ have reported the photosolvation of $[\text{Ru}(\text{bpy})_2(\text{PVP})\text{Cl}]^+$ in methanol. The species $[\text{Ru}(\text{bpy})_2(\text{PVP})(\text{Solvent})]^{2+}$ is produced upon photolysis which, if chloride anions are present is further photoanated to form $[\text{Ru}(\text{bpy})_2\text{Cl}(\text{Solvent})]^+$. The model compounds reported in this work were photolysed to provide information on the photochemical processes observed for the metallopolymer. 10^{-4}M solutions of the mononuclear model compounds were subjected to photolysis by high intensity visible light in three different solvents: acetonitrile, methanol and acetone. The photochemical behaviour of the compounds was followed using UV/Vis spectroscopy (see experimental chapter for details).

6.1.1 Photolysis in Acetone

Upon photolysis, the absorbance spectrum of the solution of the model compound $[\text{Ru}(\text{bpy})_2(4\text{MIm})\text{Cl}]\text{PF}_6$ in acetone (fig. 1) shows a shift of the lowest MLCT band from 525 nm to 505 nm with a large reduction in the extinction coefficient from 7400 to 4100 $\text{M}^{-1}\text{dm}^3\text{cm}^{-1}$. A uv/vis spectrum of the solution after 3 hours indicated that the photolysis had been completed after 20 minutes.

A series of spectra taken during the photolysis of the bis-substituted model compound $[\text{Ru}(\text{bpy})_2(4\text{MIm})_2](\text{PF}_6)_2$ shows (fig. 2) a decrease in the lowest MLCT absorption peak at 495 nm with a concurrent increase in a peak at 475 nm, giving rise to an isosbestic point at 483 nm. An isosbestic point suggests that there is only one equilibrium over the range of conditions investigated⁴; that is that there are no important side

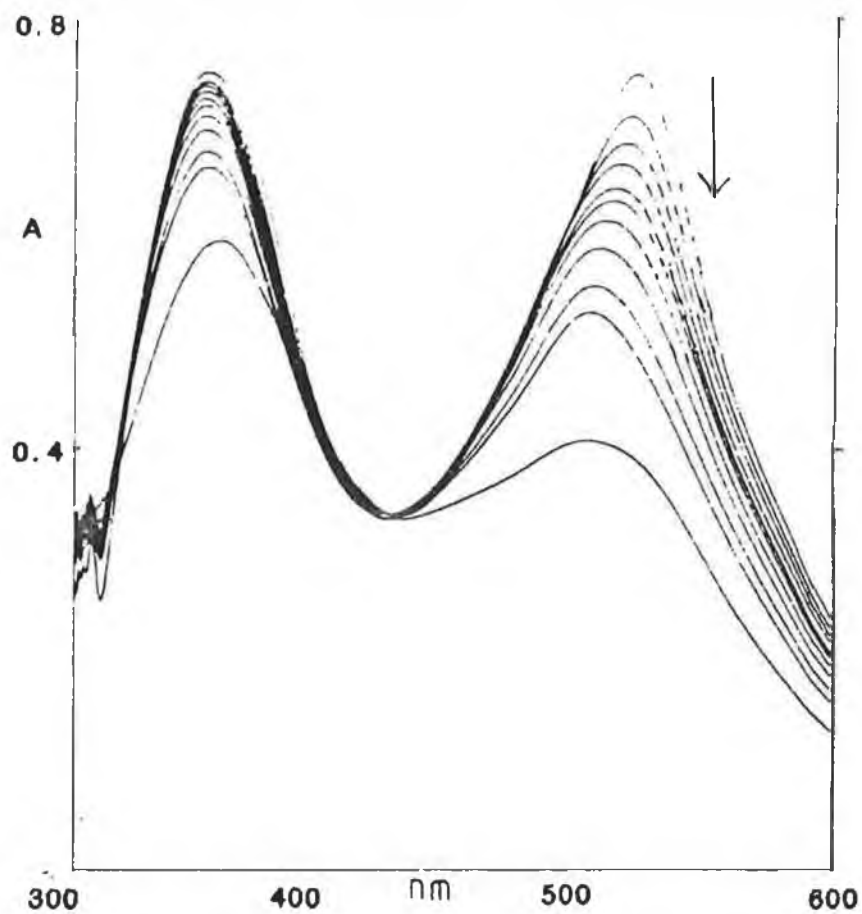


Fig. 1: UV/Vis absorption spectrum showing the photolysis of $[\text{Ru}(\text{bpy})_2(4\text{MIm})\text{Cl}] \text{PF}_6$ in acetone.

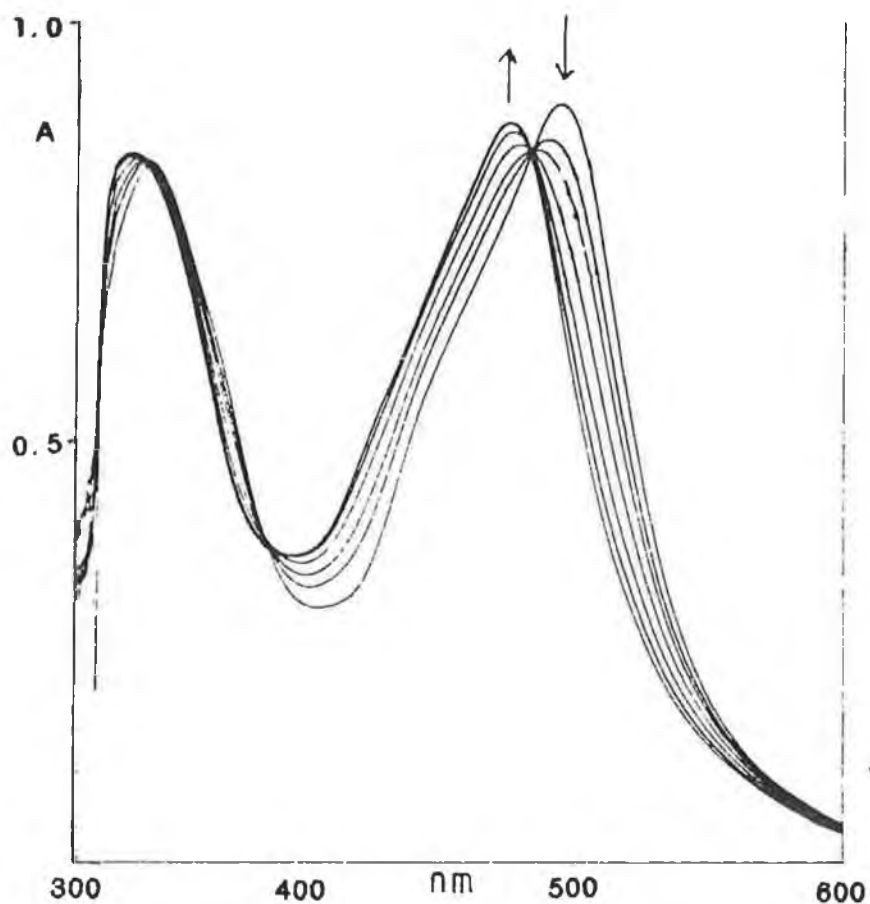


Fig. 2 : UV/Vis absorption spectrum showing the photolysis of $[\text{Ru}(\text{bpy})_2(4\text{MIm})_2] (\text{PF}_6)_2$ in acetone.

reactions. This photolysis reaction was completed within 45 minutes since a spectrum of the solution 3 hours later showed no change.

If in the first model compound the chloride ligand is being replaced by solvent molecules (i. e. the species $[\text{Ru}(\text{bpy})_2(4\text{MIm})(\text{Acetone})]^{2+}$ is produced), then the product of the photolysis of the chloro compound would be the first substitution product of the photolysis of the bis substituted compound. However it can be seen from figures 1 and 2 that the photolysis of the bis substituted compound does not produce an MLCT band equivalent to the MLCT band obtained for the photolysis product of the chloro compound. Moreover a substitution of the chloride ligand for the chloro compound would require a change in the overall charge of the complex. i. e. :



which would not be thermodynamically favourable in non-polar organic solvents. Hence from the above experiments it appears that replacement of the 4MIm ligand by solvent molecules is taking place and photolysis is therefore proceeding differently than the corresponding pyridine compounds³ in methanol. Since initially, photosubstitution of the chloride ligand does not take place.

The photolysis product of the chloro compound ($[\text{Ru}(\text{bpy})_2(\text{acetone})\text{Cl}]^+$) has a similar uv/vis absorption spectrum to that obtained⁵ for the complex $[\text{Ru}(\text{bpy})_2(\text{MeOH})\text{Cl}]^+$ which has it's MLCT peaks at 351 nm and 505 nm. The photolysis spectrum of the bis model compound (fig. 2) did not produce any changes in the uv/vis spectrum after 45 minutes indicating that only one of the 4MIm ligands was replaced and the spectrum produces only one isosbestic point at the lower MLCT band. This seems to suggest

that in acetone it is more difficult to substitute the second imidazole ligand and the photolysis product of the bis imidazole model compound is $[\text{Ru}(\text{bpy})_2(4\text{MIm})(\text{Acetone})]^{2+}$.

6.1.2 Photolysis in Acetonitrile

The model compounds readily undergo photochemical reaction in acetonitrile (CH_3CN). The lowest MLCT peak of the chloro model compound at 520 nm decreased whilst a peak at 480 nm simultaneously increased (fig. 3) and an isobestic point formed at 493 nm which shifted slightly after 8 minutes. There was little change in the spectrum after 15 minutes and none after 60 minutes. Jones and Cole-Hamilton have reported⁶ the MLCT bands for the compound $[\text{Ru}(\text{bpy})_2(\text{CH}_3\text{CN})\text{Cl}]^+$ in acetonitrile as being 342 nm and 476 nm which corresponds well with those reported above for the photolysis product of the chloro model compound. This evidence suggests that for the chloro compound, displacement of the 4MIm ligand by an acetonitrile molecule is taking place.

The photolysis of the bis model compound produced a spectrum where the lowest MLCT band at 490 nm decreased while a peak at 455 nm simultaneously increased creating an isosbestic point at 465 nm (fig. 4). The photolysis was carried out for 60 minutes but there was little change after 15 minutes and a further spectrum after 3 hours indicated no change. Assuming that as with the mono compound, the 4MIm ligands are being replaced then the formation of the one isosbestic point and the observed shifts suggest that only one 4MIm ligand is being replaced to give the following photolysis product: $[\text{Ru}(\text{bpy})_2(4\text{MIm})(\text{CH}_3\text{CN})]^{2+}$. The formation of the bis acetonitrile complex ($[\text{Ru}(\text{bpy})_2(\text{CH}_3\text{CN})_2]^{2+}$) which has¹ its lowest MLCT band at 426 nm was not observed with the reaction times studied.

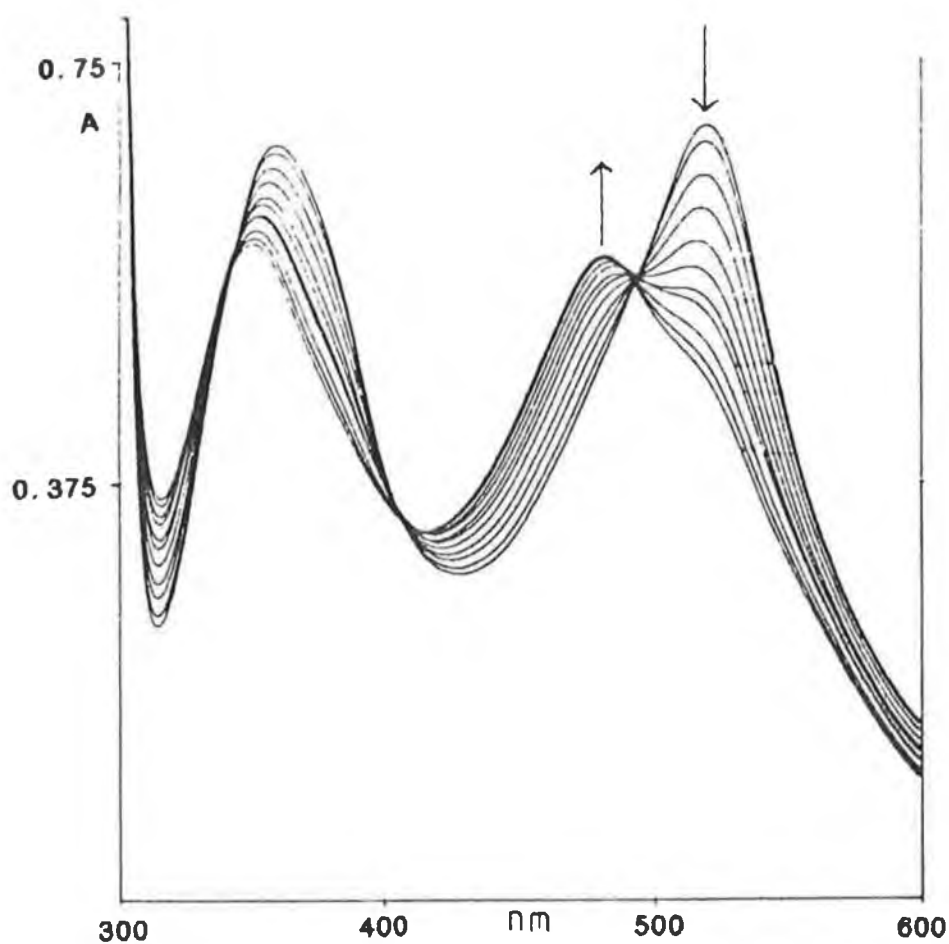


Fig. 3 : UV/Vis absorption spectrum showing the photolysis of $[\text{Ru}(\text{bpy})_2(4\text{MIm})\text{Cl}]\text{PF}_6$ in acetonitrile.

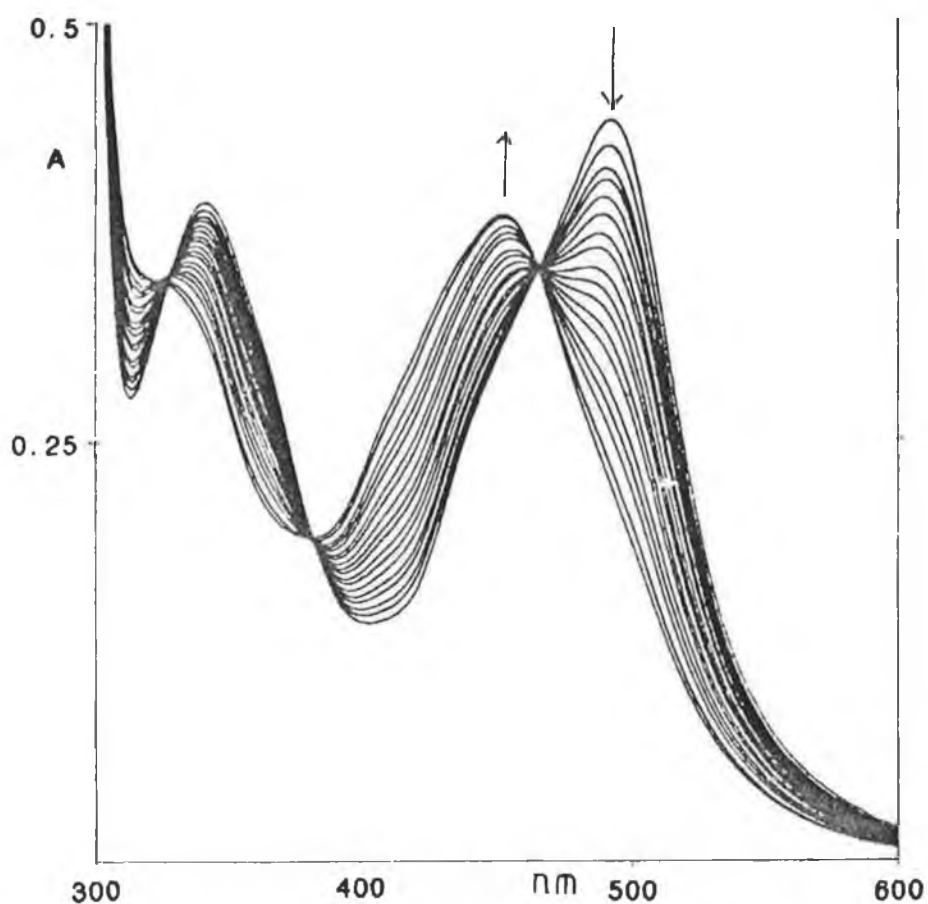


Fig. 4 : UV/Vis absorption spectrum showing the photolysis of $[\text{Ru}(\text{bov})_2(4\text{MIm})_2](\text{PF}_6)_2$ in acetonitrile.

The rate of substitution of the 4MIm ligands which takes place for both compounds within 15 minutes is much faster in acetonitrile than in methanol or acetone.

6.1.3 Photolysis in Methanol

The chloro model compound undergoes a photochemical reaction in methanol which is indicated by the uv/vis spectra in figure 5 which show the lowest MLCT peak shifting from 508 nm to 485 nm without forming an isosbestic point. The complex $[\text{Ru}(\text{bpy})_2(\text{MeOH})\text{Cl}]^+$ is not being formed, since its lowest MLCT peak is at⁵ 505 nm and since no isosbestic points are present, it is difficult to determine the photochemical process. However the spectra indicates that displacement of either the 4MIm ligand or the chloride ligand by methanol or water molecules is taking place and possibly substitution of the both ligands at the same time occurs to give the species $[\text{Ru}(\text{bpy})_2(\text{Solvent})_2]^{2+}$. It is interesting to note that $[\text{Ru}(\text{bpy})_2(\text{OH}_2)_2]^{2+}$ has^{5,7} its lowest MLCT band at 484 nm which corresponds with that obtained for the photolysis product in figure 5.

Upon photolysis of the bis imidazole model compound (fig. 6) the MLCT absorption peak at 495 nm shifts to a higher energy at 475 nm, suggesting the formation of $[\text{Ru}(\text{bpy})_2(4\text{MIm})(\text{MeOH})]^{2+}$. It should be noted that this absorption maximum is the same as that obtained for the photolysis of the same compound in acetone and also corresponds to that obtained⁵ for the species $[\text{Ru}(\text{bpy})_2(\text{PVP})(\text{MeOH})]^{2+}$. The formation of the aquo species $[\text{Ru}(\text{bpy})_2(4\text{MIm})(\text{OH}_2)]^{2+}$ is unlikely as its lowest MLCT band has been reported in this work at 492 nm. The photolysis is apparently complete within 60 minutes, but the rate of substitution is quicker than in acetone but slower than in acetonitrile.

On the basis of these experiments it would appear that the 4MIm ligands

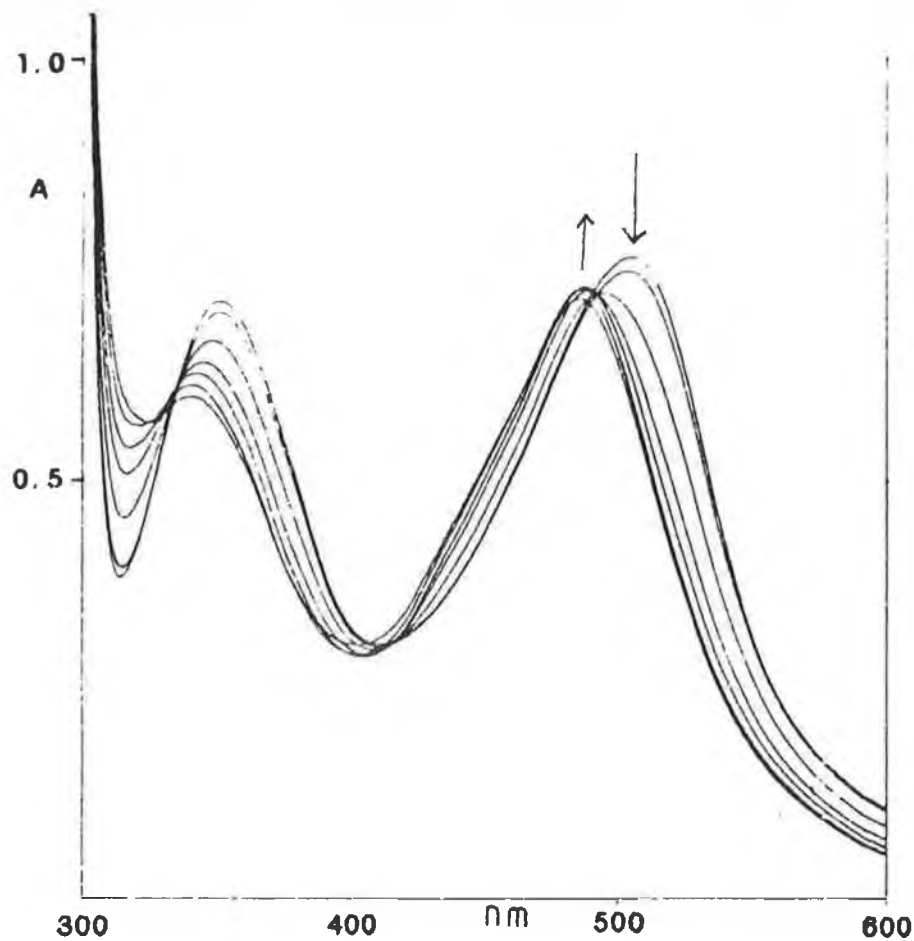


Fig. 5 : UV/Vis absorption spectrum showing the photolysis of $[\text{Ru}(\text{bpy})_2(4\text{MIm})\text{Cl}] \text{PF}_6$ in Methanol.

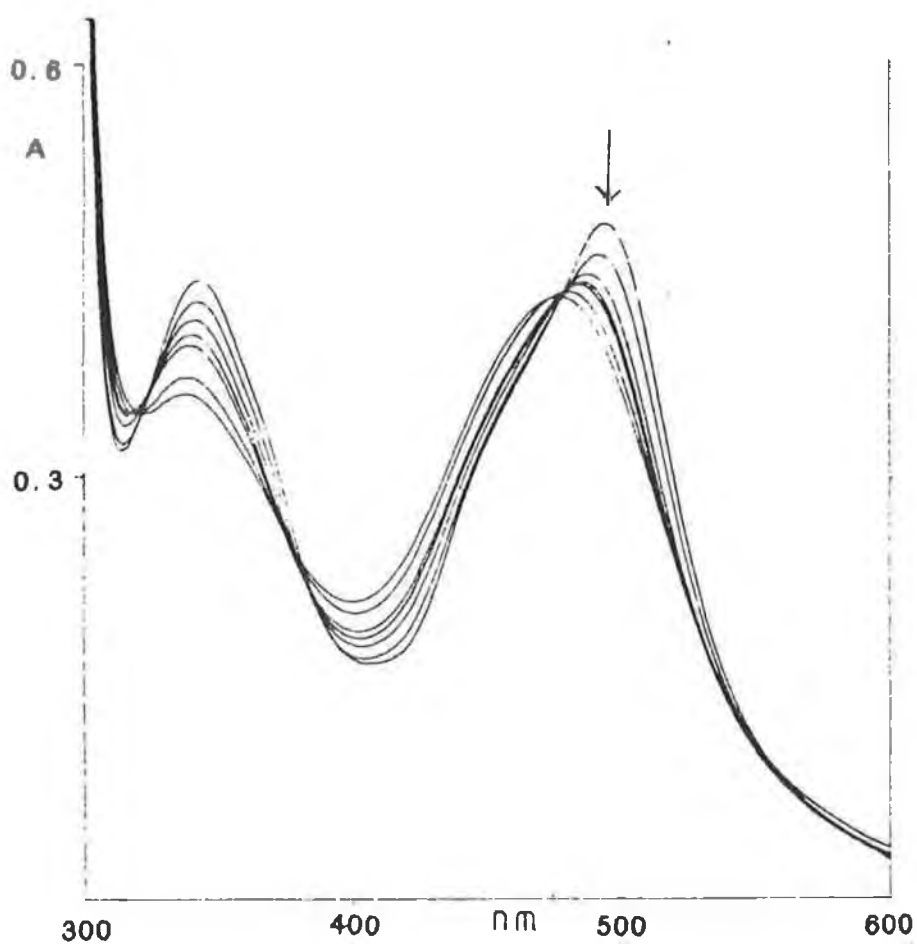


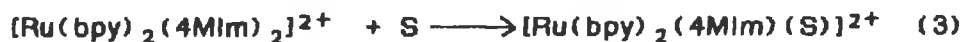
Fig. 6 : UV/Vis absorption spectrum showing the photolysis of $[\text{Ru}(\text{bpy})_2(4\text{MIm})_2]^+ (\text{PF}_6)_2$ in Methanol.

are labile, and that these ligands are being replaced by solvent molecules upon photolysis. The expected reaction sequence would be:

For the chloro model compound:

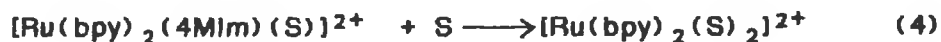


and for the bis imidazole model compound:



where S is a solvent molecule

For the reaction times studied the substitution of both 4MIm ligands by the solvent molecules was not observed:



From the above photolysis studies it can be seen that replacement of the 4MIm ligand is relatively easy for solvent molecules which can form coordinate bonds with the metal. It also appears that the chloride ligand remains with the complex in non-polar solvents but in methanol both the chloride and the 4VIm ligands come off. The ability of solvent molecules studied to replace 4MIm seems to be dependent on their ability to form ligands with transition metals with the sequence determined from the photolysis reaction times as being:



6.2 Photolysis of $\text{Ru}(\text{bpy})_2$ -Metallopolymers, both in solution and in thin films.

6.2.1 Photolysis of $\text{Ru}(\text{bpy})_2$ -poly 4(5)-VIm in Methanol.

Spectra taken during photolysis of the $\text{Ru}(\text{bpy})_2$ -containing poly-4(5)-vinylimidazole metallopolymer BR1 in methanol show that the lowest MLCT peak shifts from 495 nm to 475 nm. If ligand replacement is taking place with the model compounds by photolysis, then it should also happen with the polymeric ligands of the metallopolymers. The work carried out on the model compounds suggests that although one ligand of a bis species can be substituted, the remaining ligand is more difficult to replace. From these results it is also expected that upon photolysis the polymeric ligand of the chloro species will be replaced by solvent and that the result would be detachment of the complex from the polymer chain.

Since BR1 has been shown to contain more bis than chloro species, (see experimental chapter) the photochemical behaviour would be expected to be as observed for $[\text{Ru}(\text{bpy})_2(4\text{MIm})_2](\text{PF}_6)_2$ in methanol. A comparison of the spectra of BR1 (fig. 7) with those of the model compound (fig. 6) shows similar behaviour. Both spectra show a shift from 495nm to a higher energy at 475nm and this shift to a higher energy for the metallopolymer suggests the formation of $[\text{Ru}(\text{bpy})_2\text{PVIm}(\text{MeOH})]^{2+}$ as for the 4MIm model compound in reaction (3). Photolysis of the vinylimidazole metallopolymer BR1 in a 1M H_2SO_4 solution shows a slight change in the positions of the MLCT bands from 512 nm to 505 nm, and a decreased extinction coefficient for the photolysis product. Photolysis of similar $\text{Ru}(\text{bpy})_2$ containing metallopolymers in 1M H_2SO_4 have produced^{1,9} the aquo compound, and as the MLCT bands for the bis and aquo species of the poly-4VIm metallopolymers are very close to one another, a photolysis

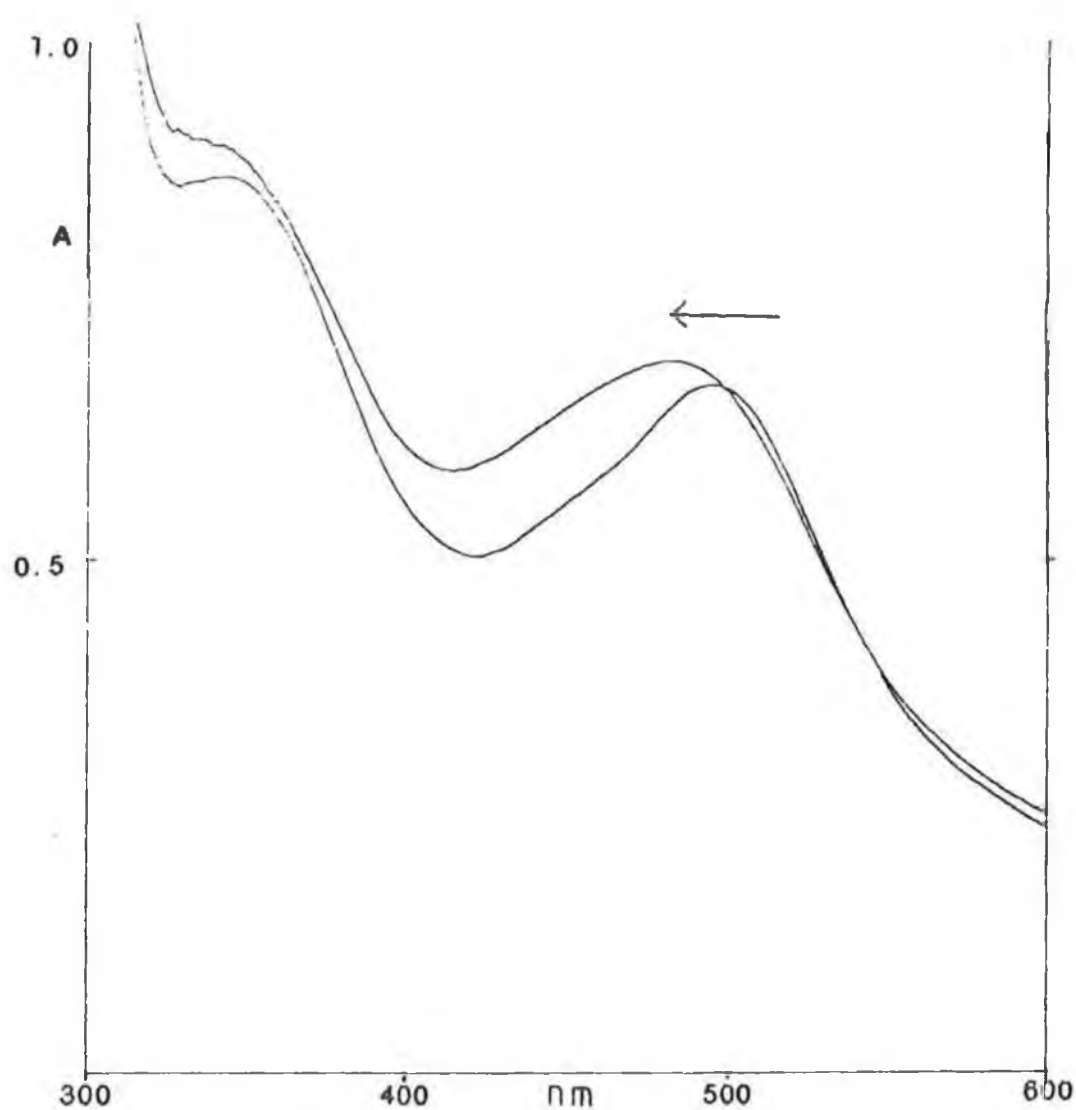


Fig. 7 : UV/Vis absorption spectrum showing the photolysis of Metallopolymer BR1 ($[\text{Ru}(\text{bpy})_2(\text{PVIm})_2]^{2+}$) in methanol.

of the bis to the aquo species would not be seen by uv/vis spectroscopy.

6.2.2 Photolysis at Electrodes Modified with $\text{Ru}(\text{bpy})_2$ -poly-4(5)-VIm.

Photolysis of surface bound N-vinylimidazole metallopolymer in 1M HClO_4 has been reported and the formation of an aquo complex suggested⁹. A set of Cyclic Voltammograms taken during the photolysis of the metallopolymer AR1 in 1M HClO_4 shows (fig. 8) a similar series to those obtained for N-vinylimidazole⁹. Within 4 minutes there is substitution of the chloride ligand of the $[\text{Ru}(\text{bpy})_2(\text{PVIm})\text{Cl}]^+$ complex species (and a corresponding decrease in it's peak at 0.51V) to give a species with an $E_{1/2}$ at +0.62V (vs SCE). The position of this peak is in between +0.51V and +0.69V (the $E_{1/2}$ for the mono and bis species respectively); which suggests that this peak could be due to the aquo complex $([\text{Ru}(\text{bpy})_2(\text{PVIm})(\text{OH}_2)]^{2+})$. The formation of isosbestic points shows that the perchlorate anion does not cause the polymer film to dissolve from the electrode surface. The ClO_4^- anion has been shown to be superior to the sulphate and chloride anions in replacing anion sites in polymer layers¹⁰.

The photolysis of this metallopolymer in 1M H_2SO_4 (fig. 9) proceeds over a period of 140 minutes and hence is much slower than photolysis in 1M HClO_4 . The $E_{1/2}$ at +0.57V shifts down to +0.53V and a shift of the redox wave from +0.76V to +0.74V is also observed. The presence of the wave at +0.74V possibly corresponds to the formation of the aquo complex since it lies some 15–20mV more negative than that obtained for the bis species. It has been shown in the literature^{1,3} that the photolysis of a number of $[\text{Ru}(\text{bpy})_2\text{L}_2]^{2+}$ complexes (including where L = pyrazole) in 1M H_2SO_4 proceeds as follows:

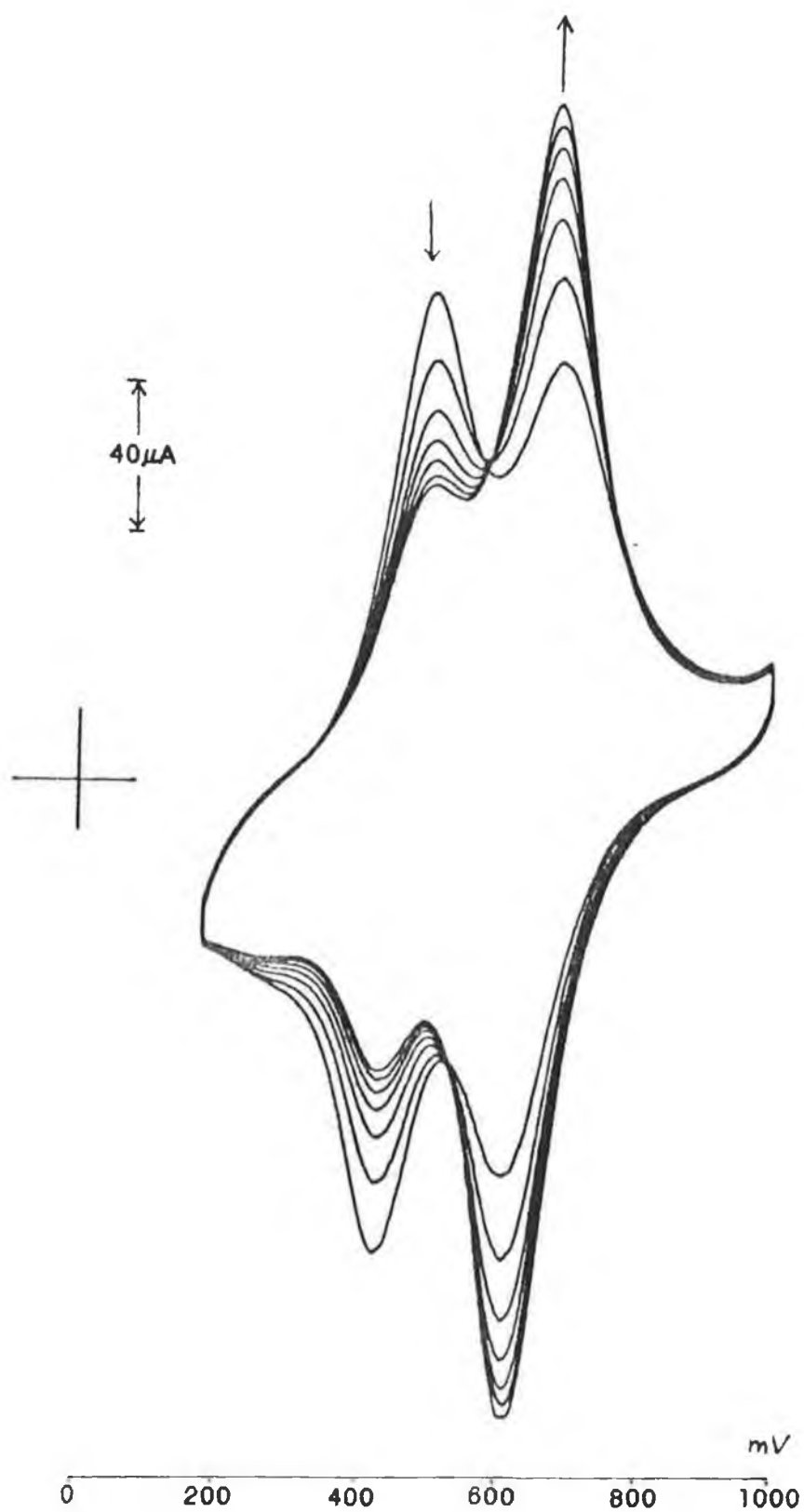


Fig. 8 : Cyclic Voltammogram showing the photolysis at the electrode of metallopolymer AR1 ($[\text{Ru}(\text{bpy})_2(\text{PVIm})_2]^{2+}$) in 1M HClO_4 .

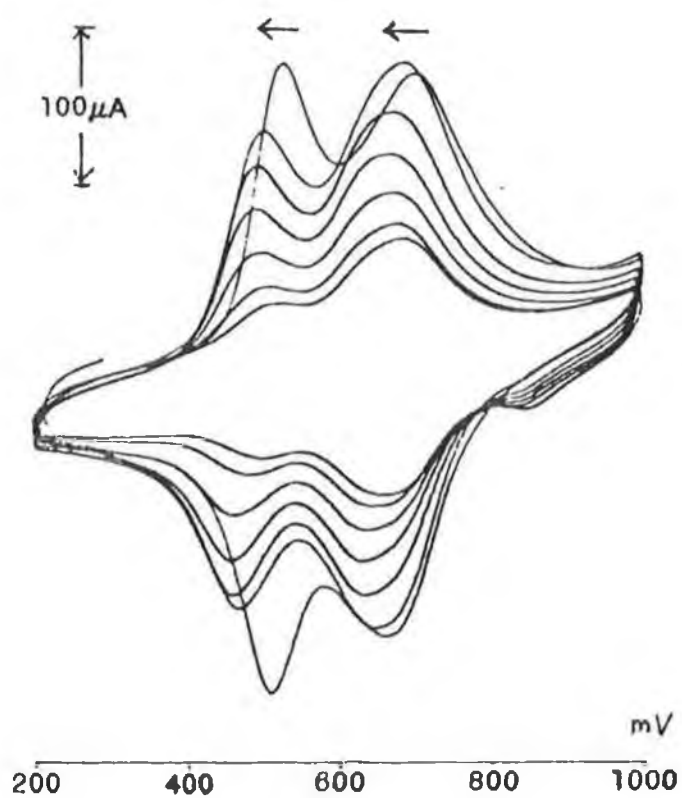


Fig. 9 : Cyclic Voltammogram showing the photolysis at the electrode of metallopolymer AR1 ($[\text{Ru}(\text{bpy})_2(\text{PVIm})_2]^{2+}$) in 1M H_2SO_4 .



Clear et. al.³ reported the photolysis of $[\text{Ru}(\text{bpy})_2(\text{PVP})\text{Cl}]$ in 0.1M H_2SO_4 and observed the formation of $[\text{Ru}(\text{bpy})_2(\text{PVP})(\text{OH}_2)]^{2+}$ and no loss of ruthenium from the polymer backbone. The photolysis of surface bound $[\text{Ru}(\text{bpy})_2(\text{NVIm})\text{Cl}]^{2+}$ in H_2SO_4 media has recently been reported¹¹ by Geraty et. al., who proposed the formation of a photochemically induced sulphate species with $E_{1/2}$ at 0.51V vs. SCE. Hence there is strong evidence to suggest that fig. 9 shows the formation of the aquo complex $[\text{Ru}(\text{bpy})_2(\text{PVIm})(\text{OH}_2)]^{+2}$ with $E_{1/2}$ at +0.74V and the sulphate complex $[\text{Ru}(\text{bpy})_2(\text{PVIm})(\text{SO}_4)]^+$ with $E_{1/2}$ at +0.53V. The photolysis of the metallopolymer AR1 in 1M HCl shows (fig. 10) a rapid dissolution of the polymer film from the electrode surface as shown by the decreasing signal over 15 minutes.

6.2.3 Photolysis of $\text{Ru}(\text{bpy})_2$ - Poly 4VP-MMA

Photolysis studies of electrodes modified with poly 4-vinylpyridine containing $\text{Ru}(\text{bpy})_2$ centres have been reported in the literature⁸. It is expected that the metallopolymers based on copolymers of 4-vinylpyridine and methylmethacrylate will not differ significantly.

Figure 11 shows the CV recorded during the photolysis of one of the copolymers containing $\text{Ru}(\text{bpy})_2$ centres in 1M H_2SO_4 . It can be seen that the metallopolymer with an initial single peak at +0.69V (vs SCE) undergoes a complicated photolytic reaction to give 3 species with reversible peaks at +0.625V, +0.682V and +0.820V as well as a peak indicating the formation of an irreversible species at +0.900V. The reversible peak at 0.820V is probably indicative of the aquo species $[\text{Ru}(\text{bpy})_2(\text{PVP})(\text{OH}_2)]^{2+}$ and the sulphate complex $[\text{Ru}(\text{bpy})_2(\text{PVP})-$

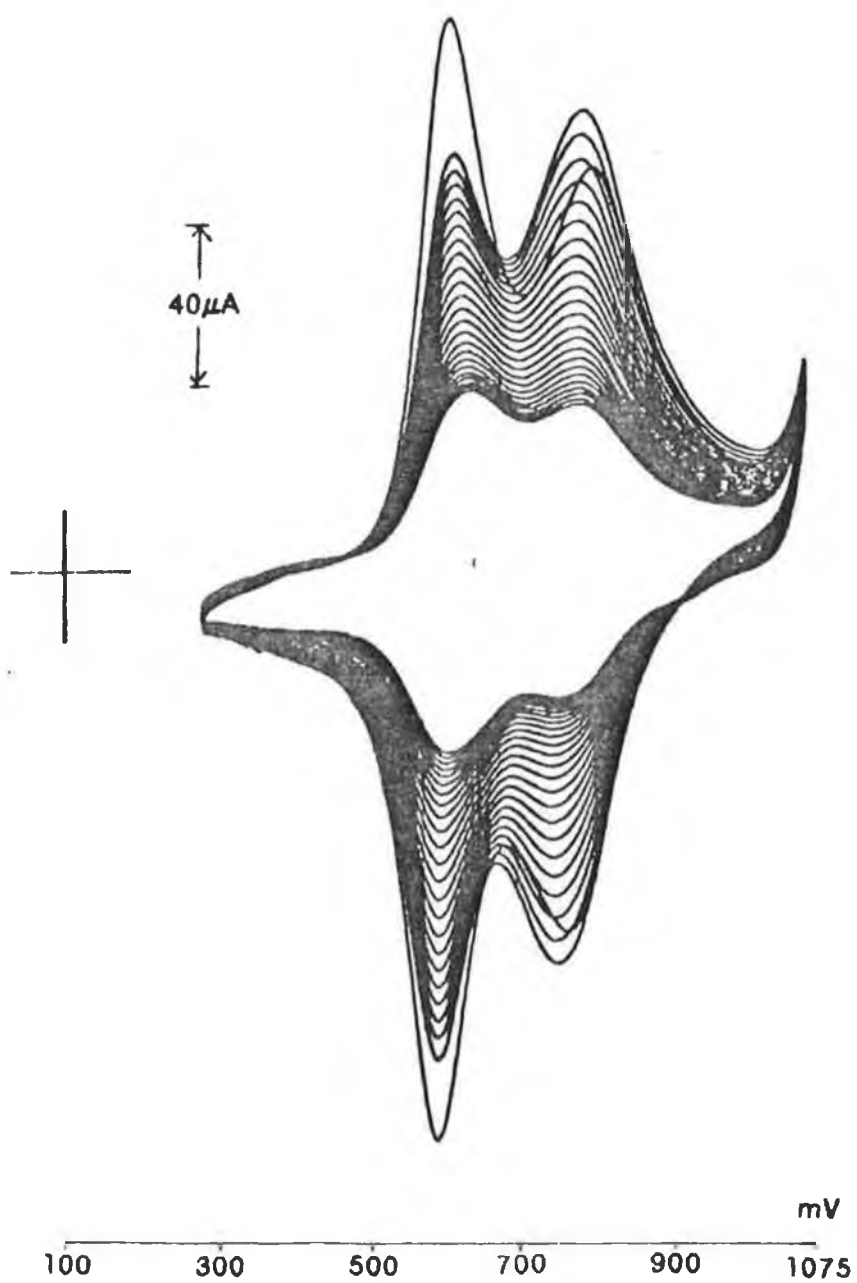


Fig. 10 : Cyclic Voltammogram showing the photolysis at the electrode of metallopolymer AR1 ($[\text{Ru}(\text{bpy})_2(\text{PVIm})_2]^{2+}$) in 1M HCl.

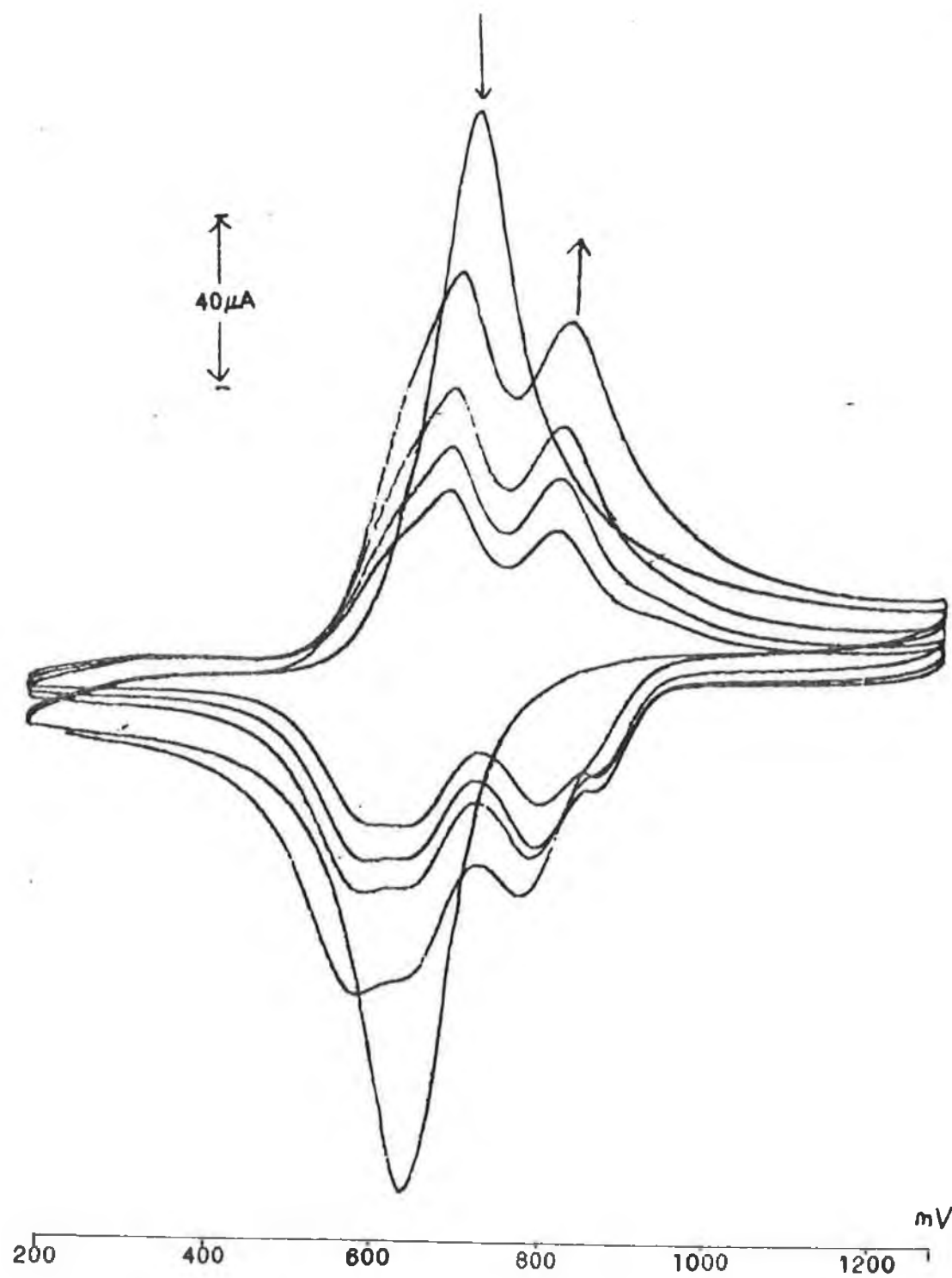


Fig. 11 : Cyclic Voltammogram showing the photolysis at the electrode of metallopolymer PM2R1 ($\text{[Ru(bpy)}_2\text{(PVP-MMA)Cl]}^+$) in 1M H_2SO_4 .

$[\text{Ru}(\text{bpy})_2(\text{PVP})(\text{SO}_4)]$ is also formed and has a peak at 0.625V. The peak at +0.9V could be due to the $\text{Ru}^{\text{III/IV}}$ redox couple observed before for the homopolymer poly 4-vinylpyridine $\text{Ru}(\text{bpy})_2$ compound¹².

The results obtained for the photolysis of the metallopolymer both in solution and as thin films are similar to those reported for other $\text{Ru}(\text{bpy})_2$ based metallopolymer systems^{11, 12}. However, because of the increased lability of the imidazole polymer and loss of polymer film from electrode surfaces, less clear results were obtained. It is worthwhile pointing out that in thin films, sulphate complexes are formed upon photolysis in H_2SO_4 , and this is not observed in solution.

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CHAPTER 7

CONCLUDING REMARKS

A range of 18 copolymers (PVP-MMA) with different 4-vinylpyridine : methylmethacrylate ratios have been synthesised and from these materials a range of polymer bound $\text{Ru}(\text{bpy})_2$ complexes were prepared. It was hoped that a study of these metallopolymers would provide information on how the polymer backbone and the reaction conditions for the formation of the metallopolymer would affect their physical and chemical properties of the metallopolymers formed. The polymer of 4(5)-vinylimidazole was prepared in a seven-step synthesis and reacted with $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ under different reaction conditions.

Spectroscopic analysis using UV/Vis and emission techniques shows that for the 4VP-MMA metallopolymers, at least two species were formed. The species $[\text{Ru}(\text{bpy})_2(\text{PVP})\text{Cl}]^+$ and $[\text{Ru}(\text{bpy})_2(\text{PVP})_2]^{2+}$ were identified¹ (where PVP stands for any of the PVP-MMA copolymers) by both UV/Vis and emission spectroscopy. However the presence of the aquo species: $[\text{Ru}(\text{bpy})_2(\text{PVP})(\text{H}_2\text{O})]^{2+}$ was not observed by spectroscopy. UV/Vis spectral studies on the poly-4(5)VIm metallopolymers shows the formation of at least two species: $[\text{Ru}(\text{bpy})_2(\text{PVIm})\text{Cl}]^+$ and $[\text{Ru}(\text{bpy})_2(\text{PVIm})_2]^{2+}$.

Formation of the bis substituted species is much easier and proceeds more quickly than for the homopolymer of 4-vinylpyridine². This was attributed to the fact that imidazole is a σ electron donor and pyridine is a π electron acceptor so that the incoming poly 4(5)-vinylimidazole ligand does not compete for electron density with the bipyridyl π acceptor ligands. To identify the different species contained in the $\text{Ru}(\text{bpy})_2$ - containing poly-4(5)VIm and to obtain an indication of the properties of the different species in isolation, a number of model compounds were prepared. The ligand used for these model compounds was 4(5)-methylimidazole which would be expected to mimic closely the properties of the polymer. The aquo species $[\text{Ru}(\text{bpy})_2(\text{PVIm})(\text{H}_2\text{O})]^{2+}$ does not show any fluorescence

and the model compounds suggest that the emission spectra of the metallopolymer are mostly due to the bis substituted species $[\text{Ru}(\text{bpy})_2(\text{PVIm})_2]^{2+}$. The model compounds suggest that the chloro species should have its emission λ_{max} at 685nm, but at room temperature is too close to that of the bis species (at 645nm) for a resolved peak. Measurements at low temperatures might clarify the situation.

The PVP-MMA metallopolymer were coated onto graphite electrode surfaces and the cyclic voltammetry experiments show that the nature of the polymer bound metal complex obtained from the reaction between $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ and the copolymers of 4-vinylpyridine and methylmethacrylate depend strongly on the reaction conditions. An increase in the water content of the reaction mixture and of the amount of methylmethacrylate in the polymer backbone and also a decrease in Ru to vinylpyridine units was found by cyclic voltammetry to increase the amount of bis substituted species formed. The aquo species $[\text{Ru}(\text{bpy})_2(\text{PVP})-(\text{H}_2\text{O})]^{2+}$ (which has an $E_{1/2}$ at 0.82V vs SCE) was not observed by cyclic voltammetry in these metallopolymer. The formation of two species for the copolymers is different from the results obtained² under the same reaction conditions with the homopolymer 4-vinylpyridine, where only the species $[\text{Ru}(\text{bpy})_2(\text{PVP})\text{Cl}]^+$ was obtained and agrees with results obtained in the literature¹. The presence of the bis species is detected by cyclic voltammetry in 6 of the metallopolymer whereas emission spectroscopy at room temperature shows its presence in 13 of the metallopolymer. This indicates that the $[\text{Ru}(\text{bpy})_2(\text{PVP})_2]^{2+}$ site is a more intense emitting species than the chloro species and for this reason emission spectroscopy is a more useful technique than cyclic voltammetry for the detection of the bis substituted species while electrochemical methods are more useful to

determine product ratios. For the polymer bound complex obtained from the reaction between $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ and poly 4(5)-vinylimidazole, evidence for the formation of at least two species is obtained, which is similar to results obtained by Geraty³ for poly N-vinylimidazole. The cyclic voltammograms obtained for the model compounds suggests that the peak at 0.635V (vs SCE in TEAP/ CH_3CN) corresponds to the species $[\text{Ru}(\text{bpy})_2(\text{PVIm})\text{Cl}]^+$. The second peak observed could be due to either the aquo or bis substituted species or both, since the half wave potentials of these two species are very close (at 0.92V and 0.94V vs SCE respectively) and would not be resolved in the cyclic voltammograms. It has been shown by spectroscopic methods that the chloro and bis substituted species are present in the poly 4(5)VIm metallopolymer. The presence of the aquo complex has not been conclusively proven either by spectroscopy or cyclic voltammetry, as it has similar uv/vis and electrochemical properties to the bis substituted species and does not emit.

Chronocoulometry was used to obtain an indication of the ease of charge transport across a film of metallopolymer attached to a glassy carbon electrode. It was found for the metallopolymer of PVP-MMA studied by chronocoulometry that an increase in the amount of methylmethacrylate in the polymer backbone increases the difficulty of charge transport through the metallopolymer film. The values obtained for the activation energy for charge transport (E_a), suggest that for copolymers with increasing amounts of methylmethacrylate, movement of the polymer chains to bring the attached electroactive complexes nearer and so facilitate electron hopping between metal sites becomes important for charge transport. For polyvinylpyridine containing electrostatically bound $\text{Ru}(\text{edta})^{3+}$, ion

movement within the layer has been suggested⁴ as the rate determining step. It is possible that an increase in methylmethacrylate increases the inter site distances and thus makes movement of the polymer backbone necessary for inter site communication. Measurement of E_a for a poly 4(5)VIm metallopolymer indicated that some movement of the polymer chain is required for charge transport. In general the activation energies obtained are higher than expected for ion movement to be the rate determining step. The metallopolymer studied contained approximately 10% bis substituted species which forms inter-chain bonds and thus might further reduce the mobility of the polymer segments and contribute to the difficulty of charge transport.

Electrodes modified with PVP-MMA and 4(5)VIm metallopolymers were used for the oxidation of Fe^{II} and it was found that oxidation of this substrate is mediated by the polymer coating. Diluting the vinylpyridine polymer backbone with methylmethacrylate results in a less efficient mediation of the oxidation of the substrate $[Fe(H_2O)_6]^{2+}$. This is probably due to decreased repulsion in acidic electrolytes between neighbouring polymer units because of an increase in the neutral monomer methylmethacrylate. This leads to decreased mobility of the substrate within the surface of the polymer layer. Mediation by 4(5)VIm metallopolymers is kinetically easier than for the copolymers probably because the 4(5)VIm polymer is more soluble in aqueous electrolytes.

Photolysis studies on the model compounds in acetone and acetonitrile show that the 4-methylimidazole (4MIm) ligand of the chloro compound is being photosubstituted by solvent molecules and also that only one of the 4MIm ligands in the bis substituted compound is being replaced. In methanol it appears that both the 4MIm and chloride ligands are replaced

simultaneously by solvent molecules. The bis substituted compound behaves differently since it appears that one of the 4MIm ligands is replaced by a methanol molecule. The results obtained for the photolysis of the metallopolymers both in solution and as thin films are similar to those reported for other $\text{Ru}(\text{bpy})_2$ based metallopolymer systems^{5, 2}.

However, because of the increased lability of the imidazole polymer and loss of polymer film from electrode surfaces, less clear results were obtained. It is worthwhile pointing out that in thin films, sulphate complexes are formed upon photolysis in H_2SO_4 , and this is not observed in solution.

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