Chapter 2

General Experimental

2.1 Introduction

General details of the materials and experimental procedures employed in this thesis are described in this Chapter. Included are brief explanations of the theoretical and practical aspects of each technique. Specific details of particular procedures will be given in the Experimental section of the relevant Chapters.

2.2 Materials

2.2.1 Monomers and Polymers

Aniline and pyrrole were purchased from Aldrich and Merck, respectively. Both were purified by distillation and stored under nitrogen at -18°C in a freezer prior to use. Poly(2-methoxyaniline-5-sulfonic acid) (PMAS) (M_w = 18067, M_n = 5700 and polydispersity = 3.16), synthesized at 5°C and purified by a cross flow dialysis[1], was kindly provided by Fatemeh Masdarolomoor in our laboratories. Poly-L-lysine hydrochloride (PLL) (MW 30,000-70,000 Da) was purchased from Sigma-Aldrich and used as received.

2.2.2 Reagents

(1*S*)-(+)-and (1*R*)-(-)-10-camphorsulfonic acid (HCSA) were purchased in the highest grade available from Aldrich and used as supplied. Ajax Chemicals supplied all aqueous acids and aqueous ammonia. The sources of other chemicals and reagents used in this thesis, such as ammonium persulfate oxidizing agent, hydrazine hydrate reducing agent, acids and bases, prochiral sulfides and alcohols, are detailed in the Chapters where they are employed.

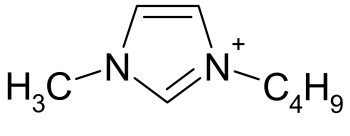
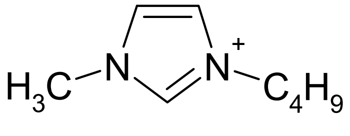
2.2.3 Solvents

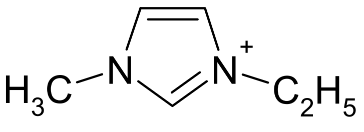
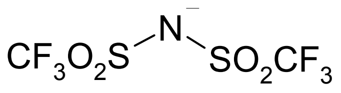
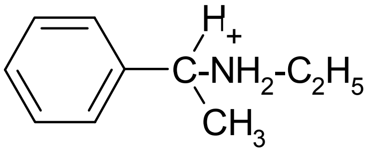
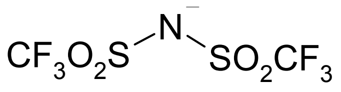
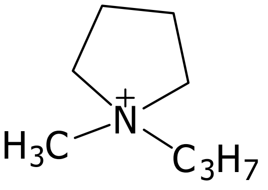
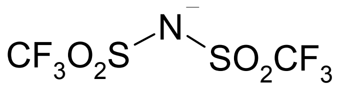
Acetonitrile, chloroform, methanol, diethylether, ethylacetate and hexane were supplied by Ajax Chemicals. NMP was purchased from Aldrich. All solvents were used as received.

2.2.4 Ionic Liquids

The ionic liquids, 1-butyl-3-methylimidazolium hexafluorophosphate (BMI-PF_6),[2] 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMI-TFSI),[2] 1-methyl-1-propylpyrrolidinium bis(trifluoromethanesulfonyl)imide (P_{13}-TFSI)[3] and the chiral (+)- or (-)- and (±)-α-methylbenzylethylamine bis(trifluoromethanesulfonyl)imide (MBEA-TFSI) were synthesized in-house following previously described methods[4]. 1-Butyl-3-methylimidazolium tetrafluoroborate (BMI-BF_4) was purchased from Solvent Innovation. All ionic liquids were deoxygened by purging with nitrogen gas for at least 30 min prior to use. The structures of the ionic liquids are shown in Table 2.1.

Table 2.1 Structures of the ionic liquids used in this thesis.

Ionic liquids	**Cation**	**Anion**
BMI-BF_4		BF_4^-
BMI-PF_6		PF_6^-

EMI-TFSI		 $CF_3O_2S-N^{-}-SO_2CF_3$
(+)-, (-)-, or (±)- MBEA-TFSI	 (+)- (-)- or (±)-	 $CF_3O_2S-N^{-}-SO_2CF_3$
P13-TFSI		 $CF_3O_2S-N^{-}-SO_2CF_3$

2.2.5 Electrodes

Various electrodes were used as working, auxiliary and reference electrodes. Working electrodes included: platinum (Pt) disc (surface area 0.014 cm^2) purchased from Bioanalytical Systems Inc. (BAS), Pt plate (5 cm x 5 cm) obtained from Goodfellow Ltd., glassy carbon (GC) disc (surface area 0.07 cm^2), GC plate (2 cm x 4 cm) purchased from BAS, and indium-tin-oxide (ITO)-coated glass (resistivity 8-12 Ω) obtained from Delta Technologies Ltd.

The platinum and glassy carbon electrodes were polished with alpha alumina (LECO®, 0.3 μm) slurries, thoroughly washed with Milli-Q water and scrubbed with Kim-wipe paper before using.

ITO-coated glass was sputter coated with platinum using a magnetron sputter coater SC100MS (Dynavac Engineering, AU), to assist the adherence of uniform polyaniline films on the surface. The ITO-coated glasses were cut (1 cm x 3 cm) and placed in the chamber of the sputter coater, with the conductive side to be coated facing a platinum target. Plasma of platinum ions was generated under a pressure of 2 x 10^{-6} bar of argon by applying a current of 30 mA. The sputter-coating was usually allowed to proceed for 5 seconds.

To investigate the effect of the Pt coating on ITO-coated glass, UV-visible transmittance, electrical conductivity and AFM of the ITO-coated glasses were measured before and after sputter-coating with platinum for 0, 5, 10 and 15 sec. The surface morphology and roughness were shown by AFM not to vary significantly among these samples. The surface conductivity of the samples increased with sputter-coating time; whereas the % transmittance of the ITO-Pt-coated glasses decreased as shown in Figure 2.1. However, for 5 sec sputter-coating, the % transmittance is only slightly less (between 350 and 550 nm) than that of untreated ITO-coated glass.

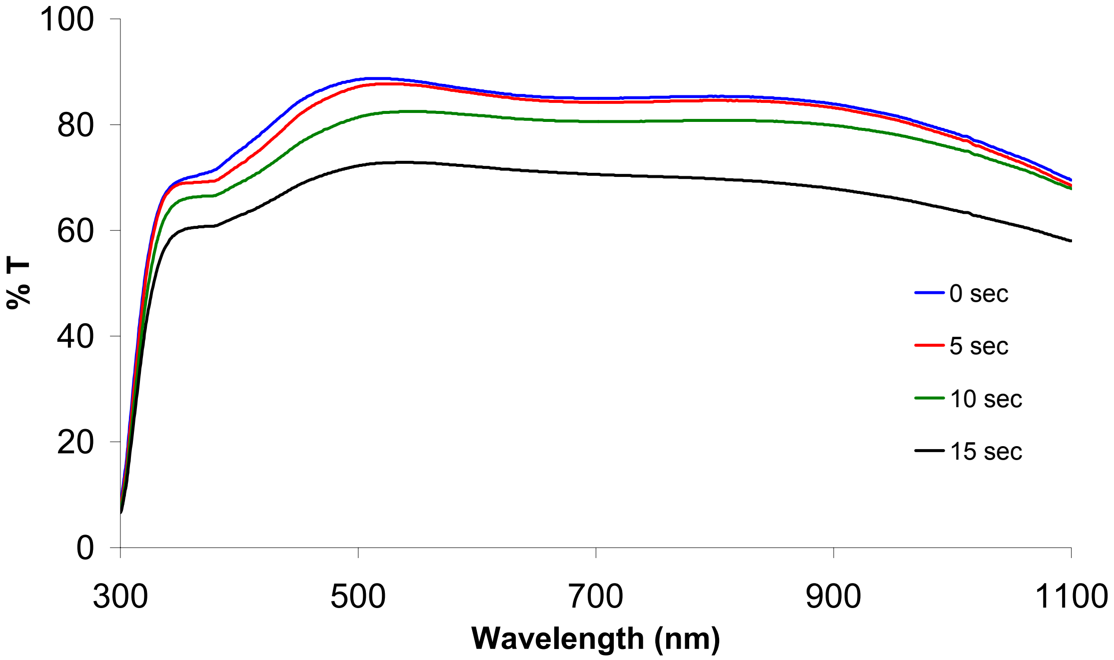


Figure 2.1 UV-visible transmittance of ITO-coated glass before and after sputter-coating with platinum by applying a current of 30 mA for various periods of time (0, 5, 10, and 15 sec).

Auxiliary electrodes used included reticulated vitreous carbon (RVC) (surface area 65 cm^2/cm^3) obtained from ERG Materials and Aerospace Corporation, Oakland, CA, USA, as well as platinum and stainless steel mesh.

Ag/AgCl $_{(3M\ NaCl\ (aq))}$ or Ag/Ag^+ (0.1 M TBAP in CH_3CN) reference electrodes were used for experiments in aqueous solution and organic solvents, respectively; while for the experiments in ionic liquids, Ag/AgCl $_{(EMI\text{-}TFSI)}$ or silver wire were used as reference electrode or quasi-electrode, respectively.

2.3 Techniques used for Preparation of Polyanilines

2.3.1 Electrochemical Polymerization

Electrochemical polymerization of aniline was normally carried out using a three-electrode electrochemical cell such as that shown in Figure 2.2.

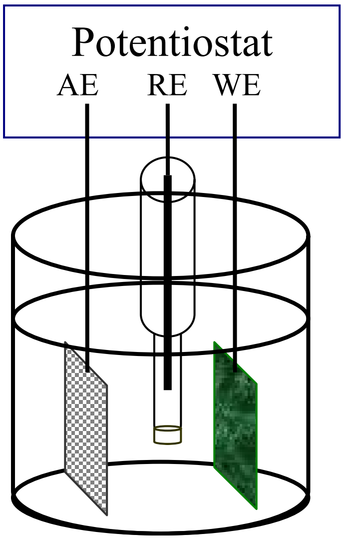


Figure 2.2 A three-electrode electrochemical cell.

The material and size of the working electrode (WE) on which the polyaniline film was formed depended on the further use planned. For example, ITO-coated glass was used for subsequent characterization of the polyaniline by UV-visible or circular dichroism spectroscopy. A Pt-disc or GC-disc electrode was normally used for electrochemical characterization of the polymer during or after growth. A large size Pt or GC plate was used for the preparation of large amounts of polyaniline.

Auxiliary electrodes (AE) were usually made of platinum, stainless steel mesh, or RVC, because they have a large surface area so that they do not limit the passage of current. A Ag/AgCl electrode in conjunction with a 3.0 M NaCl salt bridge was used as reference electrode (RE) in aqueous solution; while for synthesis in ionic liquids, Ag/AgCl with a EMI-TFSI salt bridge was usually employed.

The aqueous solutions used for electrodeposition of optically active PAn.(+)-HCSA emeraldine salt typically contained 0.2 M aniline monomer and 1.0 M (1*S*)-(+)-10-camphorsulfonic acid[5] chiral dopant, and were purged with nitrogen gas. Unless otherwise stated, the polymerizations were performed at room temperature (18-25°C).

Both potentiostatic and potentiodynamic polymerization were used. In the potentiostatic method, the PAn.(+)-HCSA emeraldine salt films were formed by applying a constant potential of +0.8 V when using a GC working electrode and +0.9 V when employing an ITO-Pt-coated glass electrode, due to the different resistivity of the two electrodes. By controlling the total charge passed during polymerization it is possible to control the film thickness or the amount of polymer formed/deposited. The constant potential was applied to the working electrode using a BAS CV-27, which also recorded the charge passed.

To produce polyaniline films suitable for spectroscopic characterization, a deposition charge of 120 mC/cm^2 was usually used for deposition onto ITO coated glass, while a charge of 50-70 mC/cm^2 was generally used for electrodeposition onto GC electrodes to give films for electrochemical characterization. The thin polyaniline films were washed with methanol to remove monomer, oligomers and excess dopant acid trapped on the films before further use.

Potentiodynamic polymerization of aniline in the presence of acid dopant was achieved by applying a potential sweep between -0.2 V and 1.0 V, -0.2 V and 1.1 V, or -0.2 V and 1.2 V at a specified scan rate (e.g. 50 mV/s) to the working electrode for 10-20 cycles, using a BAS CV-27 and a Mac Lab/ 2e (AD Instruments) with E.Chem software. The polymer films were usually washed with methanol to remove oligomer, excess monomer and unincorporated HCSA.

2.3.2 Chemical Polymerization

The polyaniline hydrochloride (PAn.HCl) emeraldine salt was synthesized by the oxidative polymerization of 1.0 mL of aniline in 100 mL of 1.0 M HCl, using 2.5 g of ammonium persulfate ($(NH_4)_2S_2O_8$) (APS) oxidant dissolved in 25 mL of 1.0 M HCl. The APS solution was added drop-wise using a burette. The reaction mixture was magnetically stirred in an ice bath to control the reaction temperature between 0-2°C. After two hrs, the PAn.HCl precipitate was collected by vacuum filtration and then washed with 100 mL of 1.0 M HCl and methanol until the filtrate was colourless.

2.3.3 De-doping/Re-doping of Polyanilines

De-doping

Powders or films of the emeraldine salts (ES) (e.g. PAn.HCl or PAn.(+)-HCSA) were converted to their emeraldine base (EB) form by stirring the powder or soaking the film in 50-100 mL of 1.0 M ammonium hydroxide for 30-60 min. The green colour of ES immediately turned to the blue of EB.

Re-doping

Powders or films of the EB were re-doped to the ES form (e.g. PAn.HCl or PAn.(+)-HCSA) by stirring the EB powder or soaking the EB film in 50-100 mL of 1.0 M HCl or 1.0 M (+)-HCSA for 30-60 min. The blue colour of EB returned to the green of ES.

2.4 Polymer Characterization Techniques

2.4.1 Ultraviolet-Visible-Near Infrared Spectroscopy

UV-visible-NIR spectroscopy is a very useful technique for probing the molecular and conformational structures of conducting polymers. Absorption of light in the UV-visible region causes electronic transitions between the valence and conduction bands. The particular absorption bands observed are indicative of the nature of the polymers, including the charge carriers and the polymer chain conformations. The absorption spectra of conducting polymers are also a function of their oxidation states. Absorption in near-infrared (NIR) region provides further information on the molecular conformations of conducting polymers.

Routine absorption spectra of thin polymer films electrodeposited on ITO-coated glass or evaporatively cast onto ordinary glass were measured using a Shimadzu UV-1601 spectrophotometer (300-1100 nm) or a Shimadzu MultiSpec-1501 with Hyper UV 1.50 software. A Cary 500 spectrophotometer (Variant) was used to record spectra over the extended region 300 to 2500 nm. The absorption spectra (250 to 1100 nm) of solutions were measured in 1 cm path length quartz cells.

2.4.2 Circular Dichroism (CD) Spectroscopy

Circular dichroism (CD) spectroscopy is one of the most powerful techniques for studying the optical activity and conformation of chiral molecules, particularly for optically active macromolecules such as proteins and chiral synthetic polymers. This technique involves measuring the difference in molar absorption coefficient/ molar absorptivity ($\Delta\varepsilon$) of left- and right-handed circularly polarized light by a chiral molecule, as shown in Equation (2.1).

$$\Delta\varepsilon = \varepsilon_L - \varepsilon_R \tag{2.1}$$

When $\Delta\varepsilon$ is positive, the CD band is called a positive circular dichroism Cotton effect. In contrast, if $\Delta\varepsilon$ is negative, the CD band is called a negative circular dichroism Cotton effect. When two (or more) chromophores of the same type are present nearby in the same molecule, bisignate or split CD bands may be observed because the energy level of the excited state is split. The bisignate CD bands are opposite in sign.

The CD bands of an optically active compound appear at the same wavelengths as the absorption bands in its UV-visible spectrum. For example, an aqueous solution of (+)-10-camphorsulfonic acid exhibits absorption maxima at 190 nm and 286 nm, while its corresponding CD spectrum shows a negative CD band at 192.5 nm and a positive band at 290.5 nm.[6]

The CD spectra of thin polyaniline films or dilute polymer solutions/dispersions were measured using a Jobin Yvon Dichrograph 6. Visible region (300-800 nm) was usually used when the polymer films were deposited/cast onto ITO-coated glass/glass, while CD spectra in UV-visible region could be recorded for aqueous solutions/dispersions using a 1 cm path length quartz cell. The CD spectrometer was calibrated using a 1 g/L aqueous solution of (+)-10-camphorsulfonic acid.

2.4.3 UV-visible and Circular Dichroism Spectroelectrochemistry

Spectroelectrochemistry combines the techniques of electrochemistry and spectroscopy. In a specially desired electrochemical cell, absorption spectra or circular dichroism spectra of polymer films deposited/coated on transparent ITO-coated glass can be monitored *in situ* as the films are oxidized or reduced by the application of a fixed potential. The electrochemical cell used for *in situ* UV-visible/CD spectroelectro chemistry in this thesis is shown in Figure 2.3.

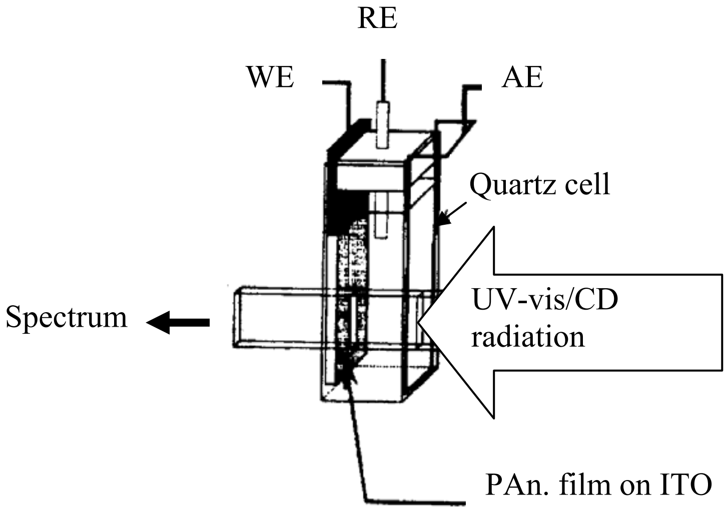


Figure 2.3 A three-electrode electrochemical cell for *in situ* UV-vis/CD spectroelectrochemical measurements.

2.4.4 Raman Spectroscopy

Raman spectroscopy typically provides qualitative information on the chemical structure of samples. The Raman spectrum is obtained by irradiating the sample with laser light of a certain frequency (or excitation radiation) and analysis of the scattered radiation caused by the Stokes shift. The difference in frequency of the incident and scattered radiation corresponds to the vibrational frequencies of the sample.

For polymer characterization, the simplest application of Raman spectroscopy is to look for the presence of specific vibrations of particular chemical groups that can be used to identify/confirm the kind of polymer. Moreover, absorption of the incident radiation by water and many other electrolytes is minimal. It is possible, therefore, to obtain the Raman spectrum for a sample while it is in solution or immersed in an electrolyte.

Raman spectra of polymer films or powders were measured using a Jobin Yvon Horiba Raman spectrometer connected to a CCD detector. The laser beam (He-Ne laser), with 632.8 nm exciting radiation, was focused on the sample by a x 100 lens. The laser was calibrated with SnO_2. Baseline correction and smooth were incorporated in the spectra using LabSpec software.

2.4.5 Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM)

SEM and AFM are generally used for investigating the surface morphology and micro/nanostructure of conducting polymers as grown. They can also be used to observe the morphology changes in a polymer after reaction with other chemicals or following thermal treatment.

The SEM images of polyaniline films electrodeposited onto ITO-Pt-coated glass were assessed with a Leica Cambridge 440 scanning electron microscope located in the Materials Engineering Department at the University of Wollongong. Prior to measurements, the polymer films were washed with methanol and coated with a very thin layer of gold to improve resolution.

Atomic force micrographs of polyaniline films electrodeposited on ITO-Pt-coated glass were obtained using the Atomic Force Microscope located in the Materials Engineering

Department at the University of Wollongong. The two-and three-dimensional images of 50 μm^2 sections of the films were obtained using the contact mode. A commercially available gold tip was used.

2.4.6 Cyclic Voltammetry (CV)

Cyclic voltammetry (CV) is one of the most common electrochemical techniques. It provides useful information on the electrochemical behaviour of compounds including conducting polymers, as well as on the mechanisms of polymer growth. In a general sense, CV involves scanning the potential between a potential more negative than the reduction potential to a potential higher than the oxidation potential of the compound under investigation, and plotting the current response at the working electrode as a function of the applied potential. The resulting current-potential plot is called the cyclic voltammogram. Cyclic voltammetry provides a rapid method for determination the potentials at which redox reactions take place.

In this thesis, cyclic voltammetry was used to study the redox properties of the conducting polymers after growth and during potentiodynamic polymerization, as well as to determine the redox potentials of monomers and prochiral substrates. In addition, it was used to determine the potential at which irreversible over-oxidation/degradation of the polymers occurs and to establish the useful potential windows of ionic liquids. A typical cyclic voltammogram for a reversible process is shown in Figure 2.4. The electrochemical cell and instrumentation used in these experiments are previously described in section 2.3.1.

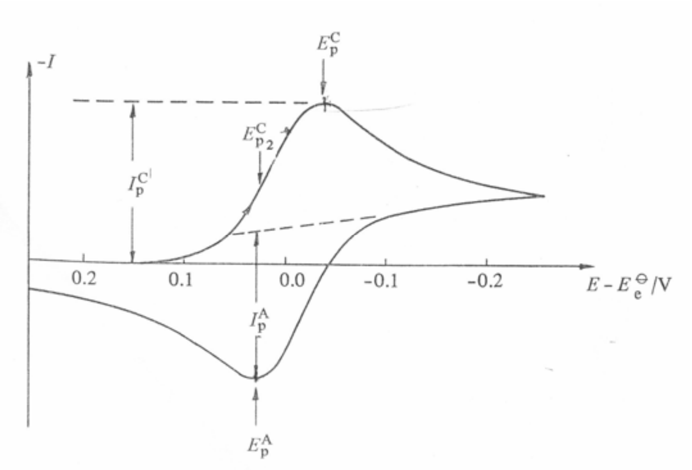


Figure 2.4 A typical cyclic voltammogram for a reversible process.

2.4.7 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is extensively used for determining the weight changes of a sample upon heat treatment. This change results from physical or chemical transformations of the sample. The TGA profile is normally a plot of the weight change as a function of temperature or time. For the thermal analysis of polyaniline, TGA is widely used to determine the amount of solvent/water incorporated in the polymer, the onset temperature for the loss or decomposition of dopant acid, and the decomposition of the polymer backbone.

Thermogravimetric analyses of the polymer powders, accurately weighed (*ca.* 8-10 mg) in alumina crucibles were conducted using a Setaram DTA/TGA 92B instrument located in the Institute for Superconducting and Electronic Materials (University of Wollongong). The temperature range between 50° and 700°C was used, with a heating rate of 10°C/min, under a nitrogen flow of 15 mL/min. The TGA of an ionic liquid sample was conducted using a STA 1500 (Rheometric Scientific) located at Monash University, in air or a nitrogen flow (20 mL/min) between 25°C and 450°C at a heating rate of 10°C/min. Accurately weighed samples (*ca*. 20-25 mg) were analyzed.

2.4.8 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is used to determine the amount of heat that is involved as a sample undergoes an exothermic or endothermic transition when the sample is heated at a controlled heating rate. It provides information on the thermal properties of the samples as they undergo physical and chemical transformations during thermal treatment. This technique is usually complementary to thermogravimetric analysis of the samples. From DSC results, information on physical changes (evaporation of solvents/moisture content, the glass transition temperature, melting temperature) and chemical changes (cross-linking, degradation/decomposition) can be obtained.

DSC profiles of polyaniline were obtained using a DSC Q100 (TA Instruments). Accurately weighed powder samples were placed in a sealed medium-pressure DSC aluminium pan. The analysis conditions were programmed by equilibrating samples at 105°C for 10 min to eliminate trace water and then cooling down to 40°C at a cooling rate of 20°C/min. The first scan was automatically started by heating at a temperature ramp of 10°C/min from 40°C to 200-350°C. The temperature was cooled down to 40°C at a cooling rate of 20°C/min before starting the second scan using the same conditions as the first run. All measurements were carried out under a nitrogen atmosphere at a flow rate of 50 mL/min.

DSC curves of ionic liquids were obtained using a DSC Q100 (TA Instruments) in a nitrogen flow (50 mL/min) between -80° and 200°C at a heating rate of 10°C/min for the first scan, and then cooling down to -80°C at a rate of 10° C/min before conducting the second scan under the same condition. Accurately weighed samples were loaded into aluminium pans and sealed with medium pressure in an atmosphere of nitrogen.

Glass transition temperature (T_g), crystallization point (T_c) and melting point (T_m) were obtained from the DSC profile.

2.4.9 Electrical Conductivity

The electrical conductivity of conducting polymers is generally measured using a four-point probe. This involves using four tip electrodes about 1 mm apart in a straight line, as shown in Figure 2.5.

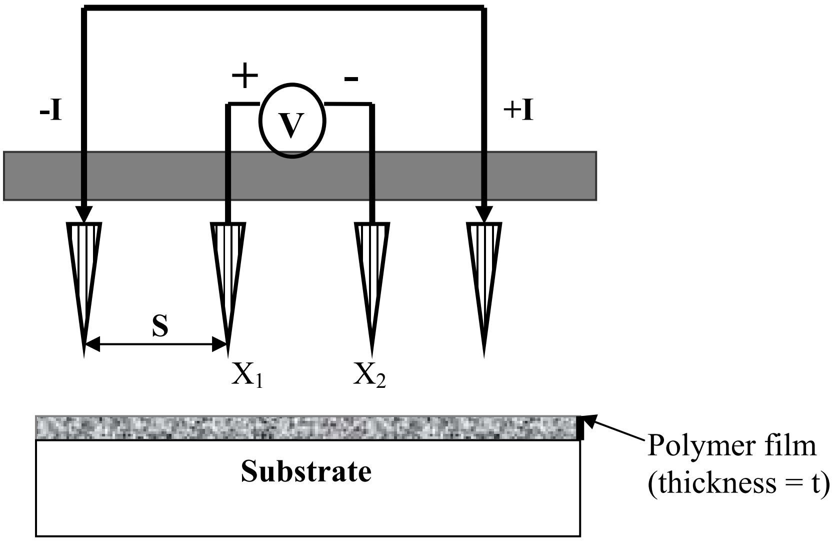


Figure 2.5 Four-point probe configuration.

The probe head can be raised and lowered from a stage. A constant current is applied through the two outermost probes and a voltage measurement is made across the two inner probes that are at distances X_1 and X_2. For a film of thickness t<<s (t = film thickness, s = distance between the inner and outer probes), the sheet resistance (ρ) for thin wafers and films is defined as follows:

$$\rho = \pi t/\ln 2\ (V/I)$$

$$Rs = \rho/t = 4.532\ (V/I)$$

where V is the voltage expressed in volts and I is current expressed in amperes. The conductivity of the sample can then be calculated from the reciprocal of resistivity.

The conductivity of a polymer film of the complex between PMAS and PLL cast onto a glass slide was measured using a Jandel four-point probe head Model RM2 (Jandel Engineering Ltd.). Thickness of the films was measured with a Mutiutoyo Digital micrometer (0.001 mm).

2.4.10 Polarimetry

In polarimetry, the specific rotation [α] of a substance is defined by Equation (2.2).

$$[\alpha] = \alpha / l \,.\, c \tag{2.2}$$

where α is the rotation of the plane of polarization expressed in degrees; l is the length of the cell expressed in decimeters; and c is the concentration of the substance expressed in g/cm^3 of solution. The specific rotation of the substance also depends on the solvent employed, the temperature, and the wavelength of the polarized light. Therefore, specific rotations are usually reported in the form $[\alpha]_\lambda^T$, with the concentration and the solvent used given alongside. Generally, a wavelength of 589 nm (sodium D-line) is used.

Optical rotations of samples in this thesis were measured with a Jasco DIP-370 Digital polarimeter in analytical reagent grade solvents, using a 10 cm path length cell.

2.5 References

1. F. Masdarolomoor, P.C. Innis, S.A. Ashraf, and G.G. Walace. *Purification and Characterization of Poly(2-methoxy aniline-5-sulfonic acid)* in *The International Conference on the Science and Technology of Synthetic Metals*. 2004. Wollongong, Australia.
2. J. Sun, M. Forsyth, and D.R. MacFarlane, *J. Phys. Chem. B.* **102** (1998): 8858.
3. D.R. MacFarlane, P. Meakin, J. Sun, N. Amini, and M. Forsyth, *J. Phys. Chem. B.* **103** (1999).
4. S.A. Ashraf, Y. Pornputtkul, A.L.P. Kane-Maguire, and G.G. Wallace, *(to be submitted).*
5. V. Aboutanos, L.A.P. Kane-Maguire, and G.G. Wallace, *Synth. Met.* **114** (2000): 313.
6. D.F. Gerald, *Circular Dichroism and The Conformational Analysis of Biomolecules*. (1996) New York and London: Plenum Press.