CHAPTER II

EXPERIMENTAL METHODS

2.1 Chemicals

Diphenylamine, DPA was procured from Qualigens, India. Aniline, ANI and substituted anilines namely o-Toluidine, OT and o-Chloroaniline, OCA were purchased from Fluka, USA and they were used as such. Potassium Peroxydisulphate (E-merck GR), special grade Dimethyl formamide, DMF, potassium ferricyanide (AR) and acetone were used as such without any further purification. The other chemicals namely sodium hydroxide, sodium dithionite, sodium anthraquinone β-sulphonate and lead acetate used were of purest quality available, mostly BDH, Analar products. Analar sulphuric acid from BDH, India was used in this study for preparing the background electrolyte solution. All solutions were prepared from doubly distilled water.

2.2 Instrumentation

The electrochemical studies were made using BAS 100 A - Electrochemical Analyser with a Houston digital plotter. This instrument is designed to carry out 38 electrochemical analytical techniques. Each technique can be easily and readily accessed using the display monitor, the key-board and a few simple commands. After selecting the desired technique, requests are made for the values of other essential potential cell/output control functions, which are then duly entered through the key-board control. In essence, BAS-100 A is a user-friendly system requiring very few operational instructions to generate data.
Cell arrangement

Pulse Potentiostatic Method, PPMS and cyclic voltammetry techniques were employed for the electropolymerization of monomers and characterization of the deposited polymers respectively by using three-electrode cell assembly. The platinum disk electrode with $2.545 \times 10^{-2}$ cm$^2$ geometric area of cross section was used as working electrode and platinum foil as the counter electrode and Ag/AgCl electrode saturated with 3M sodium chloride gel filling solution served as reference.

The cell stand has provisions to purge and blanket the sample solutions with an inert gas. Purging is done mainly to remove oxygen by bubbling nitrogen gas through the solution before starting the polymerization. The blanketing function is to maintain an inert atmosphere above the sample preventing any traces of oxygen or air components from re-entering the sample solution that might interfere with the process. Electropolymerization was performed under unstirred condition.

The cell stand has an in-built magnetic stirrer and the stirring functions could be controlled. The cell stand is provided with a glass cell vial of 16 ml capacity in which the test solution can be placed for investigation. Using the provision of a small o-ring in the cell stand, the electrode height within the cell can be adjusted.

Electrode pre-treatment

A freshly polished and cleaned platinum electrode surface contains surface functions that show quasi-reversible redox behaviour. To get reproducible results, great care should be taken during the electrode pre-treatment. The objective of polishing the electrode is to remove the products of the redox reaction or
physical adsorption that accumulate during certain experiments and to achieve ultraclean surface.

The platinum disc electrode was polished according to the procedure outlined below: It was washed with doubly distilled water to remove the soluble impurities and then rinsed with methanol to flush away the encrusted material on the surface. It was wiped well with fine grade surgical cotton. The dry electrode was well polished on a polishing pad applying an even pressure and using a smooth ‘figure 8’ motion for a few minutes. The polished electrode was rinsed well with doubly distilled water and then wiped with cotton to ensure the complete removal of any powdery material from the electrode surface.

The effectiveness of this electrode pre-treatment could be verified by recording the cyclic voltammograms of Ferricyanide system and especially by measuring the peak separation, \( \Delta E_p = E_{p^c} - E_{p^a} \).

From earlier studies [148], it has been established that the polished and cleaned electrode when potentiodynamically scanned between -0.5V and 1.3V in the medium for 30 minutes at a slow scan rate of 40 mV/s would give reproducible cyclic voltammogram of ferricyanide system with \( \Delta E_p \) value quite close to 60 mV. The electrode pre-treatment procedure adopted in the present investigation was checked for this reproducible behaviour and hence followed to activate the electrode throughout the study.

**Purification of nitrogen gas**

The dry nitrogen gas used was purified from traces of oxygen by passing the gas through the columns of Fieser's solution [149]. Fieser's solution was prepared by dissolving sodium dithionite (15g) in a warm solution of sodium...
hydroxide (20%) followed by the addition of sodium anthraquinone-β-sulphonate (2g) with vigorous stirring. A blood-red coloured solution was obtained. The columns of Fieser's solution were covered with black paper in order to avoid any light-induced reactions in the Fieser's solution. The solution was renewed as and when the colour changed from red. The nitrogen gas, after passing through the Fieser's solution was further purified by removing the traces of sulphide and sulphur-dioxide by passing it through a glass columns containing saturated lead acetate solution. The nitrogen gas was finally sent through a column containing distilled water which could trap any water-soluble gas and impurities.

2.3 Synthesis of homopolymers

Poly(diphenylamine), PDPA, Polyaniline, PANI, Poly(o-toluidine) POT and Poly(o-Chloroaniline) POCA were synthesized by electrochemical and chemical methods.

2.3.1 Electrochemical homopolymerization by PPSM

Homopolymers mentioned above were electrochemically deposited using the pulse potentiostatic method [52,53] by applying pulses through the following programme. \( E_c \) and \( E_a \) are the lower and upper limits for the cathodic and anodic region and \( t_c \) and \( t_a \) are the static pulse duration at the cathodic and anodic limits. Thus periodic pulses were applied for the total experimental time, \( t_{\text{exp}} \).

Using the three-electrode cell assembly, electropolymerization of monomer in sulphuric acid aqueous solution was performed on platinum working electrode by applying specific cathodic \( (E_c) \) and anodic \( (E_a) \) potential pulses with cathodic time interval, \( t_c \) and anodic time interval, \( t_a \) vs. Ag/AgCl for the total experimental
time. Schematic representation of the pulse potentiostatic programme used for the electrochemical polymerization of polymeric films is outlined below:

![Schematic diagram of pulse potentiostatic programme](image)

Electrochemical homopolymerization was carried out using the three electrode cell assembly in a single compartment reaction cell of 16ml capacity in nitrogen atmosphere. The homopolymer films were deposited electrochemically on the platinum electrode from sulphuric acid aqueous solution of the monomer. After electropolymerization by PPSM/cyclic voltammetry technique (63,89,150), the polymer film coated electrode was transferred into an another electrochemical cell and was cycled between specific potentials in monomer free background electrolyte. The Cyclic voltammogram, CV of the stabilised film was recorded after obtaining a stable CV pattern with minimal changes in peak potential and peak current values.

2.3.2 Chemical homopolymerization

The homopolymers were also synthesised chemically in a manner analogous to the synthesis of PANI [151] using potassium peroxydisulphate, PDS
as the oxidant. A typical procedure is given here for the chemical synthesis of PDPA.

A solution of DPA (25 mM) prepared by dissolving 0.845g of DPA in 200 ml of 4M sulphuric acid was cooled below 273 K using freezing mixture. A pre-cooled solution of PDS (30 mM) containing 0.7g in 80 ml of 4M sulphuric acid was then added drop wise to the monomer solution with constant stirring over a period of 20 minutes. The solution was further stirred for about an hour in the freezing mixture. A bright emerald green product was found to be precipitated. The precipitate was filtered through a sintered-glass crucible and washed with 4M sulphuric acid continuously till the filtrate was colourless. The acid-doped PDPA was dried under vacuum for 48 hrs at room temperature.

2.3.3 Potentiostatic bulk electropolymerization

In the present study the homopolymers were also synthesised by potentiostatic method[90] in a manner analogues to the synthesis of PDPA. A split-cell with the anodic and cathodic compartments separated by a sintered-glass disc of fine porosity was employed. The monomer solution of DPA (25 mM) in 4M H₂SO₄ was taken in the anodic compartment into which a platinum foil working electrode was introduced. Adequate quantity of 4M H₂SO₄ was taken in the cathodic compartment fitted with a platinum wire auxiliary electrode and Ag/AgCl reference electrode.

The electric current for the electrochemical reaction was provided by a constant current-voltage power supply. A potentiostat fabricated at Central Electrochemical Research Institute (CECRI), Karaikudi, India was used for the electrochemical synthesis. Current densities varying from 10μA.cm⁻² to 10 mA.cm⁻² are sufficient to initiate the polymerization process. Using a constant potential of 0.8V, the polymerization was conducted for one hour.
The green coloured PDPA obtained in large quantities was removed from the anodic compartment and filtered through a Buchner funnel. It was then washed continuously with 4M sulphuric acid till the filtrate was colourless. It was dried under dynamic vacuum at room temperature for 48 hours.

2.4 Electrochemical behaviour of homopolymer films

The electrochemically and chemically synthesised homopolymers, PDPA, PANI, POT and POCA were characterized by cyclic voltammetry [63,89,91,152].

2.4.1 Electrochemically deposited homopolymer films

Electrochemical characterization of homopolymer films were performed adopting the following procedure: The polymer film was deposited onto the platinum electrode surface during the pulse potential method between 0.0V and 0.8V vs. Ag/AgCl reference electrode for a fixed monomer concentration for 1000 pulse number. The polymer-coated electrode was then washed repeatedly with the monomer free background electrolyte and a green coloured deposit was seen on the electrode surface.

CV of the stabilised homopolymer films

The polymer-film coated electrode was placed in a monomer-free electrolyte and equilibrated by repeatedly cycling in their corresponding potentials till a constant pattern of cyclic voltammogram, CV without any appreciable change in the peak potential or peak current values were obtained. The CVs of the stabilized film were then recorded using the same potential range.
2.4.2 Chemically/electrochemically (bulk) synthesized homopolymer films

The electrochemical behaviour of the chemically synthesized PDPA and PANI samples were also studied. MacDiarmid et al. [65] performed the cyclic voltammetric studies for chemically synthesized PANI by any one of the following two methods:

i) Platinum mesh method

The polymer was ground to a fine powder and approximately 1mg was impregnated with glass filter (1cm²) by a spatula. The filter paper was then shaken to remove any excess of PANI powder and was placed on platinum mesh which was folded so as to encase the filter paper on both sides.

ii) Film formation method

The finely ground PANI powder was suspended in acetone or chloroform and a few drops of the suspension evenly poured onto a platinum foil (1cm²) electrode and allowed to dry in air.

Both methods were observed to yield identical cyclic voltammograms. However, the CV studies of chemically prepared PANI required a pre-conditioning in order to obtain reproducible CVs. This may involve complete permeation of the electrode into the polymer powder particles. MacDiarmid [65] in his studies cycled the polymer powder deposited platinum electrodes at least 10-20 times in 1M hydrochloric acid between -0.2 V and 0.4 V vs. SCE.

In the present study, film formation method was employed. A sample of chemically synthesized PDPA/PANI was suspended in acetone. A few drops of the suspension was transferred onto a platinum disc electrode and allowed to
dry in air so as to cast a thin polymer film. Atleast three to four castings were made to have adequate electro active material on the electrode.

The PDPA/PANI coated electrode was then placed in the background electrolyte and pre-conditioned by cycling between appropriate potentials to achieve a constant characteristic CV pattern of the polymer sample. Pre-conditioning normally required the potential scanning atleast for 10 cycles. The CV of the pre-conditioned electrode was then recorded under experimental conditions as maintained for the characterizing the electrochemically synthesied film.

2.5 Synthesis of copolymers

In the present investigation, copolymers of DPA and ANI with other monomers like OT and OCA were synthesised by electrochemical and chemical methods.

2.5.1 Electrochemical copolymerization by PPSM

Copolymers of DPA and ANI namely, poly(DPA-co-ANI), poly(DPA-co-OT), poly(DPA-co-OCA), poly(ANI-co-OT) and poly(ANI-co-OCA) were electrochemically synthesized by PPSM method and the typical procedure is outlined below:

The electrochemical copolymerization was performed in a single-compartment reaction cell of 16 ml capacity fitted with platinum disc working electrode, platinum wire auxiliary electrode and Ag/AgCl reference electrode. The copolymer films were deposited electrochemically on the platinum electrode from the mixture of monomers, DPA and ANI in aqueous sulphuric acid solution.
Similar experiments were conducted using various feed-ratio of DPA/ANI and CVs of the stabilised copolymer films were also recorded.

Electrochemical synthesis of the copolymers of DPA with ANI, OT and OCA and ANI with OT and OCA were performed under identical conditions as stated above. After electropolymerization, the copolymer film coated electrode was transferred into another electrochemical cell and was cycled between specific potentials in background electrolyte. The cyclic voltammograms of the stabilised films were recorded after obtaining a stable CV pattern with minimal changes in peak potential and peak current values.

2.5.2 Chemical copolymerization

Copolymers of DPA with ANI, OT and OCA and ANI with OT and OCA were prepared by the oxidation of monomers with the appropriate co-monomers in fixed feed ratio using PDS as the oxidant in acidic aqueous medium. A typical procedure for the preparation of poly(DPA-co-OCA) is given below:

A mixture containing DPA and OCA (in the feed ratio of 1:1) was prepared by dissolving 0.825gm of DPA (25mM) and 0.638gm of OCA (25mM) in 200 ml of 4M sulphuric acid. It was cooled well below 273K using freezing mixture. A pre-cooled solution of PDS (60mM) containing 1.4 g in 80ml of 4M Sulphuric acid was then added dropwise to the mixture with stirring over a period of 20 minutes. The solution was further stirred for about an hour in the freezing mixture.

The resulting green precipitate was filtered through a sintered-glass crucible and was washed well with 4M sulphuric acid till the filtrate was
colourless. The acid doped copolymer was then dried under dynamic vacuum for 48 hours at room temperature.

Experiments were conducted in a similar manner under appropriate conditions using the other comonomers and the samples were collected.

2.5.3 Potentiostatic bulk electropolymerization

In the present investigation, the copolymers of DPA with ANI, OT and OCA and aniline with OT and OCA were also synthesised by potentiostatic method [90].

A split-cell with anodic and cathodic compartments separated by a sintered glass disc of fine porosity was employed. The solution containing a mixture of monomer and the co-monomer in the feed ratio of 0.5 : 0.5 was taken in the anodic compartment which was filtered with the platinum foil working electrode. Enough volume of background electrolyte was poured into the cathodic compartment and the platinum wire auxiliary electrode and Ag/AgCl reference electrode were introduced. A potentiostat was used for providing a constant voltage power supply and applying the appropriate potentials, the bulk electropolymerization was carried out.

The green coloured copolymer samples obtained in voluminous quantities was removed from the anodic compartment and filtered through a Buchner funnel. The precipitate was washed well with monomer free background electrolyte till the filtrate became colourless. It was then dried under dynamic vacuum at room temperature for 48 hours. All copolymer samples prepared by this method were collected for further characterization.
2.6 Electrochemical behaviour of copolymer films

The electrochemically and chemically prepared copolymers samples of DPA and ANI were characterized by cyclic voltammetry \[63,89,91,152\]

2.6.1 Electrochemically deposited copolymer films

The procedure adopted to study the electrochemical characteristics of copolymer films systematically was outlined below: The copolymer film was deposited on the platinum electrode surface by PPSM technique between the specific potential pulses at a constant scan rate from solutions containing DPA or ANI with co-monomers in various feed ratio. The film growth was carried out in nitrogen atmosphere. The copolymer coated electrodes was repeatedly washed with background electrolyte.

CV of the stabilised copolymer films

The copolymer-coated electrode was then placed in a monomer-free electrolyte and equilibrated by repetitive cycling between appropriate potentials till a constant CV pattern without any appreciable change in the peak potential or peak current values was obtained. Equilibration was achieved within a few cycles of potential scanning which is indicative of the stable nature of the film. The CV of the stabilised copolymer film was then recorded.

2.6.2 Chemically/electrochemically synthesized copolymer films

The electrochemical behaviour of the chemically synthesized copolymer samples were also studied, making use of film formation method \[65\]. A thin-film of copolymer was cast on the platinum working electrodes by evaporating a suspension of the copolymer in acetone spread on the electrode.
The copolymer-coated electrode was then placed in corresponding aqueous sulphuric acid and preconditioned to achieve a constant characteristic CV pattern of the copolymer sample. Pre-conditioning normally required the potential scanning at least for 10 cycles. The CV of the pre-conditioned electrode was then recorded under experimental conditions as maintained for the characterization of electrochemically synthesized copolymer films.

2.7 Other characterizations of the homopolymers and copolymers of DPA and ANI

The homopolymers as well as copolymers of DPA and ANI were also characterized through different approaches such as measurement of conductivity, FTIR spectroscopy and UV-Visible spectroscopy. The effect of pH was studied for both PDPA and PANI homopolymers.

2.7.1 Electrochemical characterization of homopolymer films in various acidity conditions

In the present investigation, attempt was made to study the electrochemical characteristics of homopolymer films deposited by PPSM under varying acidity conditions. For this purpose the PDPA/PANI film was deposited on the platinum electrode surface electrochemically using a solution of DPA/ANI in aqueous acid medium for 1000 pulse number in the corresponding potential pulse ranges. The polymer-coated electrode was stabilised as detailed in section 2.4.1.

As the effect of pH on the electroactivity of PDPA/PANI film was studied in the pH ranges of -1.85 to +0.4, a series of solutions were prepared with sulphuric acid of concentrations varying from 4M to 0.5M. The pH values
given here for solution more acidic than pH = 1.0 are Hammett acidity functions, 
$H_0$, which reflects the proton donating ability of highly acidic solutions more accurately than pH [153].

The stabilised polymer-coated electrode was transferred to a buffer solution of known pH ($H_0 = -1.85$) and the CV was recorded for the same potential range at a constant scan rate. Similarly, CVs were recorded for the polymer-coated electrode in other buffer solutions (with $H_0 = -1.85$, -0.84, -0.26, +0.13 and +0.4) under identical conditions.

### 2.7.2 Conductivity measurements

The electrical conductivity of homopolymers and copolymers were determined by using Four-probe method[135]. This method involves using a special probe head which contains four equally spaced spring-loaded electrodes. A sample is placed on the platform of the Four probe resistivity set-up and the probe head is lowered onto the sample until the four pins make good contact with the sample. The constant current source is used to pass a steady current through the two outermost probes and the voltage-drop across the inner two probes is measured at room temperature.

The conductivities of chemically synthesized homopolymers and copolymer samples of DPA and ANI were determined using Four probe resistivity set-up (Concord Instruments, India). The samples were pressed into pellets using bench-type hydraulic press by applying a pressure of three tonnes. Under room temperature conditions, the output voltages (mV) were recorded for current values ranging from 1.0 to 10 mA. The average thickness of the sample, $d$ was 0.05 cm.
From the values of current, I and voltage, V, the resistivity, R and hence the conductivity, \( \sigma \) of the sample can be calculated using the following equation,

\[
R = \frac{\rho}{\sigma} = \frac{1}{\sigma} \times \frac{2\pi S}{F(d/s)} \times \frac{V}{I}
\]

where S is the average distance between the pins, usually 0.1cm, F(d/s) is the correction factor for the thickness d of the sample used, I is the probe current and V is the output voltage. The appropriate correction factor, F(d/s) for film thickness is determined using the calibration curve given in the instruction manual of the instrument.

2.7.3 FTIR spectroscopy

FTIR spectra of the chemically synthesized homopolymers and copolymers of DPA and ANI were recorded using Bruker IFS 66V FT-IR spectrophotometer in the region 500 cm\(^{-1}\) to 4000 cm\(^{-1}\) using KBr pellets.

2.7.4 UV-Visible spectroscopy

UV-Visible spectra of chemically prepared homopolymers and co-polymers of DPA and ANI were recorded in DMF solvent, (solution concentration is 0.05 mg/ml) using Shimadzu UV-Visible spectrophotometer-2401 PC Model.