CHAPTER 2

EXPERIMENTAL

2.1 MATERIALS

Acrylic acid (Merck), methacrylic acid (Merck), hydroquinone (BDH), 8-hydroxy quinoline (Fluka), benzoyl chloride (BDH), copper(II) acetate (Fluka), nickel(II) acetate (Fluka) were used as received.

2.2 PURIFICATION OF CHEMICALS

2.2.1 Acetone

Acetone was dried with anhydrous calcium sulphate, filtered and distilled. The fraction boiling at 57°C was collected (b.p 57°C) (Furniss et al 1994).

2.2.2 Chloroform

Chloroform (1000ml) was shaken several times with half of its volume of water, dried over anhydrous calcium chloride for 24 hrs and distilled. The portion boiling at 61°C was collected (b.p. 61°C) (Furniss et al 1994).

2.2.3 N,N-Dimethyl formamide

N,N-Dimethyl formamide (DMF) was purified by azeotropic distillation with benzene. 1000ml of DMF with 100ml of benzene azeotrope
which distilled between 70-75°C was collected. The residual DMF was shaken with powdered barium oxide, filtered, distilled under nitrogen atmosphere at reduced pressure and the fraction boiling at 76°C/39mm Hg was collected (b.p.76°C/39mm Hg) (Furniss et al 1994).

2.2.4 Ethanol

Rectified spirit (1000ml) was refluxed with calcium oxide for 6hrs, allowed to stand over-night and distilled. The fraction boiling at 80°C was collected (b.p.80°C) (Furniss et al 1994).

2.2.5 Methanol

Methanol (1000ml) was treated with magnesium metal and distilled. The fraction boiling at 65°C was collected (b.p. 65°C) (Furniss et al 1994).

2.2.6 Ethyl methyl ketone

Ethyl methyl ketone (EMK) (1000ml) was dried with anhydrous calcium sulphate, filtered and distilled. The fraction boiling at 80°C was collected (b.p. 80°C) (Furniss et al 1994).

2.2.7 Tetrahydrofuran

Tetrahydrofuran (THF) (1000ml) was dried with calcium sulphate and filtered. It was further treated with lithium aluminium hydride. The mixture was refluxed for 6hrs over a steam bath and distilled. The fraction boiling at 65°C was collected and stored over metallic sodium (b.p.65-66°C) (Furniss et al 1994).
2.2.8 Triethylamine

Triethylamine was distilled and the fraction boiling at 89°C was collected (b.p.89°C) (Furniss et al 1994).

2.2.9 Purification of p-aminophenol

p-aminophenol was recrystallised from distilled ethanol.

2.2.10 Purification of 8-hydroxy quinoline

Recrystallised from rectified spirit then with water.

2.2.11 Purification of initiator

Benzoyl peroxide (5g) was dissolved in 50ml chloroform and precipitated by adding 50ml methanol (Perrin and Amarigo1988).

2.3 PREPARATION OF 8-HYDROXY-5-AZOQUINOLINE HYDROXY BENZENE

8-hydroxyquinoline (4.35g 0.03M) was dissolved in conc.HCl (20ml) and kept below 5°C in a ice bath. p-aminophenol (3.27g, 0.03M) was dissolved in conc.HCl (20ml) by heating and the solution formed was cooled down quickly to a temperature below 5°C with vigorous stirring to obtain a suspension. To this suspension was added sodium nitrite (2.55g, 0.03M) in 20ml of water. After stirring at 0-5°C for 30 minutes a yellow solution was obtained. To this 8-hydroxyquinoline solution was added slowly while stirring. The mixture was then stirred for half an hour and then neutralized with saturated Na₂CO₃ solution. The product precipitated out from the solution and was collected by filtering (7g, yield 80%) of 8-hydroxy-5-
azoquinoline hydroxybenzene was obtained after recrystallising the crude product from ethanol (Mang et al 1996).

2.4 PREPARATION OF ACRYLOYL CHLORIDE

Acryloyl chloride was prepared according to the method of Stempel et al (1950). A mixture of acrylic acid (46g, 0.64mol), benzoyl chloride (178.8g, 1.28mol) and hydroquinone (0.5g) were taken in a 2L round bottom flask and distilled at a fairly rapid rate. The fraction boiling between 91-100°C was collected which is then redistilled and the fraction boiling between 73-75°C at 740mm Hg was collected, Yield 24 g (70%).

\[
\begin{array}{c}
\text{H}_2\text{C}=\text{CH} \quad + \quad \text{Cl}\text{O}\text{C-CH}=\text{CH}_2 \\
\text{HO} \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quan...
2.6 MONOMER SYNTHESIS

2.6.1 8-hydroxy-5-azoquinoline phenyl(meth)acrylate (8H5AQPA/8H5AQPMA)

The monomer 8-hydroxy-5-azoquinoline phenylacrylate (i) was prepared by reacting 8-hydroxy-5-azoquinoline hydroxybenzene (5.3g, 0.02M), triethyl amine (2.78ml, 0.02M), EMK (25ml) were taken in a three necked flask equipped with stirrer, thermometer and stoppered funnel and the contents were cooled to -5°C. Acryloyl chloride (5mmol) in EMK (25ml) was added drop wise with constant stirring at that temperature. The reaction mixture was gradually allowed to attain ambient temperature and stirring continued for another 2hrs. The quaternary ammonium salt formed was filtered. The filtrate was thoroughly washed with distilled water, dried over anhydrous sodium sulphate and the solvent evaporated in vacuo. Yield: 75%. By adopting similar procedure, the other monomer 8-hydroxy-5-azoquinoline phenyl methacrylate (ii) was prepared (yield 82%).

2.6.2 8-hydroxy-5-azoquinoline phenol-formaldehyde (8H5AQP-F)

A mixture of 8-hydroxy-5-azoquinoline hydroxy benzene (5mmol), 37% formalin solution (5mmol) and oxalic acid (0.2g, 3 wt%) taken in a reaction tube, sealed and placed in an oil bath at 100°C for 24 hrs. The tube was then cooled, dessealed and the water decanted. The solid remaining in the tube was dissolved in DMF. The resulting solution was added drop wise to 10% aqueous sodium chloride solution (500ml) with constant stirring. The product (iii) that separated was filtered, washed several times with distilled water and dried in vacuo (yield 81%).
2.6.3 8-hydroxy-5-azoquinoline phenyl(meth)acrylate-formaldehyde (8H5AQPA-F)/(8H5AQPMA-F)

8-Hydroxy-5-azoquinolinephenol-formaldehyde (8H5AQPF) (2.6g, 0.02M) in DMF, triethylamine (2.78ml, 0.02M), hydroquinone (0.5g) and DMF (25ml) were taken in a three necked flask equipped with a stirrer, thermometer and separating funnel and the contents were cooled to 0 to -5°C. Acryloyl chloride (1.8ml, 0.02M) was added drop wise with constant stirring at that temperature. The reaction mixture was then stirred for another two hrs at room temperature and the quaternary ammonium salt was filtered off. The filtrate was thoroughly washed with distilled water, dried over anhydrous sodium sulphate and the solvent was removed to get a solid (iv)(yield 82%).

The IR and $^1$H-NMR spectra were consistent with the assigned structure. By adopting similar procedure, the other macro monomer 8-hydroxy-5-azoquinoline phenylmethacrylate-formaldehyde (v) was prepared (yield 70%).

2.7 POLYMERISATION

The monomers i-v (except iii) were polymerised by free radical polymerization using benzoyl peroxide as initiator. A typical procedure for the polymerization of 8H5AQPA is described: 8-hydroxy-5-azoquinoline phenyl acrylate (3mmol) DMF (50ml) and benzoyl peroxide 0.5g were taken in a 100ml standard reaction tube and purged with nitrogen gas for 30min, closed and kept in a thermostat at 70°C for 8hrs and cooled. Excess of methanol was added to the content, the precipitated poly(8H5AQPA)(I) was filtered, washed with methanol and purified by dissolving in DMF and reprecipitating with methanol. The purified polymer was dried in vacuo at 50°C for constant weight. By adopting similar procedure, the other polymers poly(8-hydroxy5-azoquinoline phenyl mthacrylate(II), poly(8-hydroxy-5-
azoquinoline phenol formaldehyde(III), poly(8-hydroxy-5-azoquinoline phenyl acrylate formaldehyde(IV) and poly(8-hydroxy-5-azoquinoline phenyl methacrylate(V) were prepared.

2.8 PREPARATION OF POLYMER-METAL COMPLEXES IN DMF MEDIUM

Polymer-metal complexes were prepared at room temperature by solution technique. A typical procedure for the preparation of poly(8H5AQPA)-Cu(II) complex (Ia) is as follows. The polymer (6mmol of repeat unit) was dissolved in 30ml of DMF. An aqueous solution of Cu(II)/(Ni(II) acetate (0.62g) was added drop wise with constant stirring and the pH of the solution was adjusted to 7 with dilute ammonium hydroxide solution. The resulting mixture was digested on a water bath for 2hrs and kept overnight at room temperature. The precipitated polymer-metal complex of Cu(II) (Ia) was filtered, washed with hot distilled water followed by ethanol and dried at 60°C in vacuo. By adopting similar procedure, the other metal complexes (Ib, IIa, IIb, IIIa, IIIb, IVa, IVb, Va, Vb) were prepared.

2.9 CHARACTERISATION

2.9.1 Chemical Method

2.9.1.1 Estimation of metal content

1g of polymer-Cu(II) metal complex was decomposed in muffle furnace at 250°C for 2hrs. The decomposed product was washed with distilled water, the residue dissolved in concentrated sulphuric acid(10ml) and made up to 100ml in a standard measuring flask. 20ml of the made up solution was titrated against standard sodium thiosulfate iodometrically.

1g of polymer-Ni(II) metal complex was decomposed in muffle furnace at 250°C for 2hrs. The decomposed product was washed with
distilled water, the residue dissolved in concentrated sulphuric acid (10ml) and made up to 100ml in a standard measuring flask. 20 ml of the made up solution was complexed with standard DMG and estimated gravimetrically.

2.9.1.2 Solubility test

Solubility of the polymers was determined in various solvents viz. DMSO, DMF, THF, DMAc, methanol, acetone and chloroform. 2-3mg of substance was treated with 5ml of solvent and kept aside for 6hr with occasional shaking. If the polymer is insoluble in cold condition, the mixture was heated and cooled.

2.9.1.3 Viscosity

1% solutions of the polymer in dimethylformamide were prepared and filtered through glass filter to remove any dust particles. The dust free polymer solutions were taken in an Ubbelohde suspended level viscometer with a flow time of 160 seconds for dimethylformamide at room temperature. Flow times for the polymer solutions and solvent were recorded at the same temperature. Intrinsic viscosities $[\eta]$ for the polymer solutions were determined using the following set of expressions.

Relative viscosity $\eta_r = \frac{t_2}{t_1}$

where $t_1$ and $t_2$ are time of flow for solvent and polymer solution respectively.

Specific viscosity $\eta_{sp} = \eta_r - 1$

The intrinsic viscosity $[\eta]$ was calculated by plotting $\eta_{sp}$ versus C and extrapolating the straight line to zero concentration. The intercept obtained gives the value of $[\eta]$ for polymer.
2.9.2 Analytical method

2.9.2.1 Elemental analysis

Elemental analysis was carried out on a HERAEUS-CHNO-RAPID ANALYSER with sample weight of 3-5mg.

2.9.2.2 Gel permeation chromatography

The weight and number-average molecular weights ($\langle M_w \rangle$ and $\langle M_n \rangle$) of the polymers were determined on a gel permeation chromatography (Waters 501) equipped with a ultra gel column and refractive index (RI) detector. Tetrahydrofuran was used as a mobile phase in the column. The column was calibrated with standard polystyrene samples of molecular weight ranging from 1,00,000 to 5,000.

2.9.2.3 Infrared spectroscopy

IR spectra (KBr pellet) of the polymer and their respective metal complexes were recorded on a Bomem MB 104 FT-IR spectrophotometer.

2.9.2.4 $^1$H-NMR spectroscopy

$^1$H-NMR spectra of the polymers were recorded on a 400 MHz $^1$H-NMR spectrometer at room temperature in DMSO-d$_6$ using TMS as internal standard.

2.9.2.5 Differential Scanning Calorimetry

The glass transition temperature ($T_g$) of the polymers and their metal complexes were determined on a Mettler-TA3000 differential scanning calorimeter at a heating rate of 15°C/min with a sample weight of 5mg in air.
2.9.2.6 Thermogravimetric analysis

The thermogravimetric analysis of the polymers and polymer-metal complexes were carried out on a Mettler TA3000 thermogravimetric analyzer. 5 mg of sample was charged in the thermobalance of the analyzer and heated from ambient temperature to 800°C at a uniform rate of 10°C/min in nitrogen atmosphere.

2.9.2.7 Magnetic moment measurement

Magnetic moment studies of the polymer-metal complexes were conducted using Guoy method with sample weight of 2 mg and corrected for the diamagnetism of the component atom using Pascal’s constant.

\[ \mu_m = 2.83 \sqrt{X_m \times T} \]

2.9.2.8 Diffuse reflectance spectroscopy

Diffuse reflectance spectra of the polymer-metal complexes were recorded on a karl-zeiss VCU-28 spectrophotometer using MgO pellets.

2.9.2.9 X-ray diffraction

The X-ray diffraction experiments were performed on Phillips PW 1820 diffractometer with staton camera, using CuKα radiation of wavelength 1.542 Å.

2.9.2.10 Electrical conductivity measurements

The electrical conductivity measurements for polymer-metal complexes were carried out on a Keithley 640 electrometer, in the form of a pellet (thickness 2-3 mm, diameter 10 mm, length 2 mm). Silver paint was
applied on either side of the pellet to act as a supporting electrode and provide
good conducting contact between sample and electrode. The temperature of
the sample was measured using Chromel-Alumal thermocouple. The whole
assembly was kept inside a metal jacket and evacuated. The sample
temperature was controlled using a heating coil on the metal jacket. The
instrument was calibrated with a low conductivity standard sample to ensure
no tracking in the instrument.

2.10 APPLICATION STUDIES
2.10.1 Catalytic activity of polymer-metal complexes
2.10.1.1 Polymerisation initiation

Polymerisation initiation reaction was carried out in a 100 ml
standard polymerisation tube taking N-vinylpyrrolidone (3.5mmol), polymer-
metal complex (0.05mmol) (based on the metal) and EMK(10ml) and
deaerating the mixture, by passing nitrogen gas for half an hour. The
polymerization tube was sealed and kept in a thermostat for 8hr at 75°C.
Then the reaction mixture was poured into a beaker containing excess of
methanol. The precipitated polymer was filtered and washed with benzene.
The purified polymer was dried in vacuo at 60°C (Tsuchida and Nishide
1980).

2.10.1.2 Hydrolysis

Polymer metal-complex (0.05mmol based on the metal),
ethylacetate (10ml), distilled water(25ml) and methanol(15ml) were taken in a
100ml round bottomed flask and mixed well. The reaction mixture was kept
in a thermostat at 60°C and nitrogen was bubbled through the solution for
5hrs. The reaction mixture was filtered. Aliquot(1µl) was withdrawn and
analysed by gas chromatography (Angelici and Hopgood 1968).
2.10.2 Metal uptake studies of polymer in the presence of electrolytes

The polymer sample (25mg in 25ml of DMF) was added in an electrolytic solution (25ml) of sodium chloride of known concentrations. The pH of the solution was adjusted by using 0.1M HCl or 0.1M NH₃. The solution was stirred for 24h at room temperature. To this solution 10ml of 0.1M solution of metal ion Cu(II)/Ni(II) was added and the pH was adjusted to the required value. The mixture was again stirred at 25°C for 24hrs and filtered. The solid was washed and the Cu(II) ion content was determined iodimetrically and Ni(II) ion by gravimetrically. The amount of the metal ion uptake of the polymer was calculated from the difference between a blank experiment without the polymer and the reading in the actual experiments. The experiments were performed in the presence of sodium sulphate with Cu(II) and Ni(II) ions.

2.10.3 Effect of pH on metal-ion uptake

The optimum pH of the metal ion uptake was determined with a batch equilibration technique. Excess of metal ions Cu(II)/Ni(II)(10ml, 0.1M) were shaken with 25mg of the resin for 24hrs. The pH of the solution was adjusted before equilibration over a range of 1-10 with weak acid/base. The complex was filtered off, and the concentration of the Cu(II) ion remaining in the filtrate was determined by iodometrically and Ni(II) by gravimetrically.

2.10.4 Effect of contact time on metal-ion uptake

The saturation time was obtained by plotting percentage of metal uptake against contact time by keeping initial metal ion concentration fixed (2000µg per 10ml). The metal ions Cu(II)/Ni(II) were shaken with 25mg of the resin. The complexes were filtered off, and the concentration of the Cu(II)
ion remaining in the filtrate was determined by iodometrically and Ni(II) by gravimetrically.

2.10.5 Regenerative ability

The regenerative ability of polymer-metal complex was carried out as follows. Polymer-metal complex (1a)(1.0g) was taken in a boiling tube. To this hydrochloric acid (10ml, 7M) was added and set aside for 1hr. The blue colour solution thus formed was filtered and the polymer was washed with dilute HCl, distilled water and dried in vacuo at 50°C. The dried polymer was used again for complex formation. This revealed the good recyclability and stability of the polymer under acidic condition. This cycle was repeated several times to determine the reusability of the functionalised polymer (Kratz and Hendrick 1986).