Chapter 3

Materials and Methods

3.1 General

3.1.1 Reagents

Styrene and divinyl benzene (DVB) used were commercial products obtained from Merck, W Germany. Solvents were commercially available and were purified by literature procedures. The metal salts used were BDH grade and used as such. All the low molecular weight compounds used were commercially available and were purified by literature procedure. All the reagents and indicators were prepared by standard procedures.

3.1.2 Spectral methods

(a) Infrared spectra

The spectra were recorded on Shimadzu IR 470 spectrophotometer operating in the range 4000-400 cm\(^{-1}\). The samples were made as KBr pellets using well dried potassium bromide.

(b) Electronic spectra

The solid state electronic spectra were recorded on a Cary 2390 UV-VIS near IR spectrophotometer. Solution phase electronic spectra were recorded on a Shimadzu UV-VIS 160 spectrophotometer using spectroscopic grade solvents.
(c)  **ESR spectra**

ESR spectra of all the paramagnetic compounds were recorded on a Varian E-12 spectrometer. The measurements were carried out for solid samples at room temperature. In all the cases diphenyl picryl hydrazyl radical (DPPH) was used as external standard.

### 3.2 Preparative details

#### 3.2.1 Polymer supports

(a)  **2% DVB-crosslinked polystyrene**

The monomers (styrene and DVB) were washed with 1% sodium hydroxide solution (30 ml, 3 times) and with water (30 ml, 3 times) to remove the inhibitors. Polyvinyl alcohol (PVA) (0.3 g, MW-72000) was added to water (300 ml) at 80°C and stirred until dissolution. A mixture of styrene (10.2 g) and DVB (0.52 g) was dissolved in toluene (10 ml) and added to the PVA solution. Benzoyl peroxide (0.2 g) was added and the mixture was heated at 80°C with mechanical stirring for 8 h. The polymer was kept overnight, filtered, washed with hot water, methanol, chloroform, benzene and finally with acetone. The resin was dried in air oven at 70°C.

IR [KBr]: 1600 cm⁻¹ (C=C) 2900 cm⁻¹ (C-H).

(b)  **2% DVB-crosslinked chloromethyl polystyrene**

Polystyrene (3 g) was allowed to swell in dichloromethane (50 ml). Stannic chloride (7 g) was added to a well stirred mixture of polymer beads in dichloromethane containing chloromethyl methyl ether at 0°C. The temperature was allowed to rise to room temperature during a period of 1 h. The mixture was stirred for 55 h. The resin was collected by filtration and washed with dioxane-
water, dioxane-water-4N HCl, water, methanol and finally with dichloromethane. Drying in an air oven at 60°C afforded chloromethyl polystyrene.

IR (KBr): 700 cm\(^{-1}\) (-C-C)

(c) **Estimation of chlorine capacity**

The polymer (200 mg) was fused with pure anhydrous pyridine (3 ml) for 4 h at 100°C. It was quantitatively transferred into a conical flask using 50 per cent aqueous acetic acid (30 ml). Concentrated nitric acid (5 ml) was added to this followed by the slow addition of silver nitrate solution (0.1 N, 10 ml) with magnetic stirring. Distilled water (50 ml) was added to this followed by sufficient amount of toluene to form a layer over the water surface. The suspension was mixed well. The excess silver nitrate was back titrated with standard ammonium thiocyanate solution using ferric alum as the indicator.

3.2.2 **Preparation of polystyrene supported ligands**

(a) **Preparation of polystyrene supported amine**

Chloromethyl polystyrene (10 g, 2% DVB-crosslinked, 4.2 mmol Cl/g) was suspended in DMF (150 ml). Hexamethylene tetramine (11.2 g, 80 mmol) were added to this suspension and heated with stirring under reflux at 100°C in an oil bath for 8 h. The reaction mixture was filtered, washed with DMF, DMF-water (1:1), ethanol, ethanol-HCl (1:1) and water. It was then stirred with a solution of NaOH for 2 h, filtered washed several times with water and methanol, drained and dried in vacuum. A test sample of the mixture on heating with ninhydrin reagent (2 ml) gave a deep blue colour characteristic of amino groups. The unreacted chlorine was estimated by Volhard’s method.
(b) **Estimation of amino group**

The amino resin (100 mg) was stirred with 0.2 N HCl for 10 h. The resin was filtered and the filtrate together with washings were collected. Excess HCl was titrated against standard NaOH solution using phenolphthalein as indicator.

(c) **Preparation of Polystyrene Supported ethylene diamine**

Chloromethyl polystyrene (10 g) was suspended in dioxane (50 ml) for 3 h. A five-fold molar excess of ethylene diamine (14 ml) and pyridine (42 mmol 3.4 ml) was added. The mixture was heated with stirring under reflux at 100°C for 9 h. The reaction mixture was filtered, washed with water, dioxane and ethanol and dried in vacuum. Treatment with ninhydrin reagent showed deep blue colour indicating the presence of amino groups. The residual chlorine was estimated by Volhard’s method. Amino group was estimated by the method given in the previous section.

IR (KBr): 1570 cm\(^{-1}\) (N-H), 1170 cm\(^{-1}\) (C-N).

(d) **Preparation of polystyrene supported dithiocarbamate**

A mixture of aminomethyl polystyrene (5 g), sodium hydroxide (5 g in 50 ml water) and carbon disulphide (95 ml) was stirred for 6 h. When the mixture turned dark red, the resin was collected by filtration and washed several times with water, ethanol and methanol. Dried in vacuum.

IR (KBr): 1450 cm\(^{-1}\) (C-N), 1020 cm\(^{-1}\) (C-S).

(e) **Preparation of polymer-supported acetyl acetone**

Chloromethyl polystyrene (5 g) was swelled in THF. Acetyl acetone (10 ml) and diethyl amine (2.8 ml) were added and refluxed for 48 h. The resin was collected by filtration and washed several times with water and dichloromethane. Dried in vacuum. The residual chlorine was estimated by Volhard’s method.

IR (KBr): 1720 cm\(^{-1}\) (C=O), 1395 cm\(^{-1}\) (C-O).
(f) *Preparation of polystyrene supported-Schiff base*

A mixture of aminomethyl polystyrene (10 g) and salicylaldehyde (7 ml) in ethanol (200 ml) was refluxed at 90°C on a water bath for 4 h. It was then cooled and filtered. Washed successively with water, DMF, ethanol, chloroform and acetone. Dried in vacuum.

IR (KBr): 1630 cm\(^{-1}\) (C=N), 1150 cm\(^{-1}\) (C=O)

(g) *Preparation of polystyrene supported acid*

Chloromethyl polystyrene was first converted to the aldehyde resin which on oxidation yielded the acid resin.

(ii) *Preparation of Polystyrene supported aldehyde*

Chloromethyl polystyrene (10 g) was suspended in DMSO (300 ml). NaHCO\(_3\) (19 g) was added to it and the mixture was stirred at 140°C for 10 h. Resin was then filtered and washed several times with hot water and then with dioxane-water (1:1), dioxane, ethanol and dichloromethane. The resin was further purified by soxhlet extraction technique using benzene as the solvent. This was filtered and dried under vacuum.

IR (KBr): 1710 cm\(^{-1}\) (C=O)

(ii) *Oxidation of the polystyrene supported aldehyde*

To a mixture of conc H\(_2\)SO\(_4\) (5 ml), and conc CH\(_3\)COOH (300 ml), sodium dichromate was added till saturation. Aldehyde resin (20 g) was added to this mixture and heated at 70°C for 96 h. Filtered washed several times with water. Dried in vacuum.

IR (KBr): 1700 cm\(^{-1}\) (C=O), 3440 cm\(^{-1}\) (O-H)
(iii) *Estimation of acid group*

Polystyrene supported acid (300 mg) was added to a mixture of methanol (20 ml) and sodium hydroxide (20 ml). The mixture was kept for 30 h with occasional stirring. Excess NaOH was titrated against standard HCl using phenolphthalein as indicator.

(h) *Preparation of polystyrene supported azo dye*

Chloromethyl polystyrene (5 g) was added to azo dye (9 g) dissolved in dioxane (300 ml). Catalytic amount of ammonium fluoride was added to the mixture and refluxed at 120°C for 6 h. Resin was collected by filtration, washed several times with dioxane, water and ethanol. Dried in vacuum. The residual chlorine content was estimated by Volhard’s method.

IR (KBr): 1290 cm⁻¹ (C-N), 3470 cm⁻¹ (O-H).

3.2.3 *Complexation of polymeric ligands with metal ions: General procedure*

Polymeric ligands (a-g) were shaken with metal salt solution (0.1 M, 20 ml) for 6 h. The complexed resin was collected quantitatively. The uncomplexed metal ions in the filtrate were estimated by volumetric methods. From this the amount of metal complexed by the resin was found out. The complexation experiments were tried in the case of Cu, Zn, Ni, Co, Cd and Hg. The metal complexes were dried in vacuum.

(a) *Estimation of copper*

The copper solution (remaining after complexation) was made up to 250 ml in a standard flask. 20 ml of the solution was pipetted out into a conical flask.
NH\(_4\)OH solution was added drop by drop till a slight precipitate is formed. It was then dissolved in minimum amount of acetic acid. One or two drops of the acid was added in excess. 10 ml of 10% KI was then added to it and the liberated iodine titrated against standard sodium thiosulfate (0.2 M) solution using starch as indicator. At the endpoint blue colour changes to white.

(b) Estimation of nickel

The nickel salt solution (remaining after complexation) was made up to 250 ml. 10 ml of this solution was pipetted out into a conical flask. 5 ml NH\(_4\)Cl-NH\(_4\)OH buffer was added to keep pH 7, indicated by the yellow colour of the solution. It was then titrated against standard EDTA using murexide as indicator. Towards the end point pH was adjusted to 10 by adding NH\(_4\)OH. At the end point colour changed to violet.

(c) Estimation of cobalt

The cobalt solution (remaining after complexation) was made up to 250 ml. 10 ml of the solution was pipetted out into a conical flask. Standard EDTA solution (0.02 M, 20 ml) was added to it. 0.5 ml NH\(_4\)Cl-NH\(_4\)OH buffer was added and the excess EDTA was back titrated with standard ZnSO\(_4\) solution using Eriochrome black T indicator. At the end point colour changes from blue to violet.

(d) Estimation of cadmium

The cadmium solution (remaining after complexation) was made up to 250 ml. 10 ml of the solution was pipetted out into a conical flask. Hexamine salt (0.5 g) was added to adjust the pH. Titrated against standard EDTA using xylenol orange as indicator. At the end point colour changes from violet to yellow.
(e) **Estimation of zinc**

The zinc solution (remaining after complexation) was made up to 250 ml. 20 ml was pipetted out into a conical flask. 5 ml NH₄Cl-NH₄OH buffer was added and titrated against standard EDTA (0.2 M) using Eriochrome Black-T as indicator. At the end point colour changed from violet to blue.

(f) **Estimation of mercury**

The mercuric salt solution (remaining after complexation) was made up to 250 ml and 10 ml was pipetted out into a conical flask. 20 ml standard EDTA and (0.5 g) hexamine salt were added and titrated against standard ZnSO₄ solution using xylenol orange as indicator. At the end point colour changed from violet to yellow.

3.3 **Preparation of polymer supported mixed ligand complexes**

3.3.1 **Method 1**

This method involves the preparation of polymer supported mixed ligand complexes using polymer supported metal complexes (precursor complexes) and secondary ligands.

(a) **(Oxalato) (Polystyrene supported ethylene diamino) M(II) complex**

0.5 g potassium oxalate was dissolved in water. 1 g copper(II) or oxovanadyl(II) complex of P*NN (polystyrene supported ethylene diamine) was added to this solution, stirred for 6 h and filtered. Washed with water and dried.

(b) **(Phthalato) (Polystyrene supported ethylene diamino) M(II) complex**

Potassium phthalate (0.5 g) was dissolved in water. To this solution 1 g of the Cu(II) or VO(II) complex of P*NN was added and stirred for 6 h. Filtered and washed the polymer with water. Drained and dried.
(c)  \textit{(Acetato) (Polystyrene supported ethylene diamino) M(II) Complex}

To an aqueous solution of 1 g of sodium acetate, 1 g of the Cu(II) or VO(II) complex of P*NN was added. Stirred for 6 h. Filtered and washed the polymer with water. Drained and dried in vacuum.

(d)  \textit{Acetato (polystyrene supported dithiocarbamato) copper(II) complex}

To an aqueous solution of 1 g of sodium acetate, 1 g of the Cu(II) complex of P*SS (polystyrene supported dithiocarbamate) was added. Stirred for 6 h. Filtered and washed with water. Dried in vacuum.

3.3.2 \textit{Method 2: Preparation of polymer supported mixed ligand complexes using polymeric ligands and stable metal complexes}

(a)  \textit{Preparation of (acetyl acetonato) (polystyrene supported ethylene diamino) Cu(II) complex}

Polystyrene supported ethylene diamine (500 mg) was added to copper acetyl acetonate solution (1 g in 50 ml chloroform). Refluxed for 2 h. Resin was filtered washed with chloroform and dried.

(b)  \textit{Preparation of (Schiff base) (Polystyrene supported ethylene diamino) Cu(II) complex}

Polystyrene supported ethylene diamine (500 mg) was added to copper Schiff base solution (1.5 g in 50 ml methanol). Refluxed for 2 h. Resin was filtered washed with methanol and dried in vacuum.

(c)  \textit{Preparation of (acetato) (polystyrene supported acetyl acetonato) Cu(II) complex}

Poly styrene supported acetyl acetone (500 mg) was added to copper acetate solution (1 g in 50 ml methanol). Refluxed for 2 h. Resin was filtered and washed with methanol. Dried in vacuum.