

## **CHAPTER III**

### **EXPERIMENTAL**

#### **General**

##### **1 Instrumentation**

Infrared spectra were recorded on a Perkin Elmer 1706 Infrared Spectrophotometer.

Atomic absorption were analyzed on a Varian Model SpectrAA 300 Atomic Absorption Spectrophotometer.

The DSC and TGA chromatograms were recorded on a Netzsch DSC 200 and Perkin Elmer TGA 7, respectively.

Merck TLC plastic sheets (silica gel F254 precoated) was used for Thin Layer Chromatography experiments.

##### **2 Reagents and Raw Material**

Chemicals used in this work were obtained from various suppliers as shown in Table 3.1.

**Table 3.1** Source of chemicals.

Material	Grade of chemical	Company
D.E.R. 331 Epoxy Resin (E.E.W.=182-192)	-	Dow
2,4-Diamino-6-hydroxypyrimidine	AR	Aldrich
1,4-Dioxane	Reagent	Carlo Erba
Ethylacetate	AR	Carlo Erba
Dimethylformamide (DMF)	Reagent	Riedel
Dimethylsulfoxide (DMSO)	AR	Riedel
Methanol	AR	Baker
Nitric acid	AR	BDH
Cobalt(II)chloride hexahydrate	AR	Fluka
Copper(II)nitrate trihydrate	AR	Riedel
Lead(II)nitrate	AR	Riedel
Nickel(II)nitrate hexahydrate	AR	Riedel
Zincnitrate hexahydrate	AR	Fluka

### 3 Conditions for Instrumental Analysis

**3.1 Atomic Absorption Spectrophotometer (AA) were used to analyze concentration of different metal ions in solution. The conditions are shown as follows:**

Variables \ Elements	Lead (Pb <sup>2+</sup> )	Zinc (Zn <sup>2+</sup> )	Nickel (Ni <sup>2+</sup> )	Copper (Cu <sup>2+</sup> )	Cobalt(Co <sup>2+</sup> )
Instrument Mode	Absorbance	Absorbance	Absorbance	Absorbance	Absorbance
Calibration Mode	Concentration	Concentration	Concentration	Concentration	Concentration
Measurement Mode	Integration	Integration	Integration	Integration	Integration
Lamp Position	-	1	1	1	-
Lamp Current (mA)	-	5	4	4	-
Slit Width (nm)	0.5	1.0	0.2	0.2	0.2
Slit Height (nm)	Normal	Normal	Normal	Normal	Normal
Wavelength (nm)	283.3	213.9	232.0	327.4	240.7
Flame	Air-Acetylene	Air-Acetylene	Air-Acetylene	Air-Acetylene	Air-Acetylene
Sample Introduction	Manual	Manual	Manual	Manual	Manual
Delay Time (sec)	6	6	6	6	6
Time Constant (sec)	0.05	0.05	0.05	0.05	0.05
Measurement Time (sec)	2.0	2.0	2.0	2.0	2.0
Replicates	3	3	3	3	3
Background Correction	On	On	On	On	On
Air Flow (L/min)	13.5	13.5	13.5	13.5	13.5
Acetylene Flow (L/min)	2.00	2.00	2.00	2.00	2.00

### 3.2 Thermal Analysis

#### A. Differential Scanning Calorimetry (DSC)

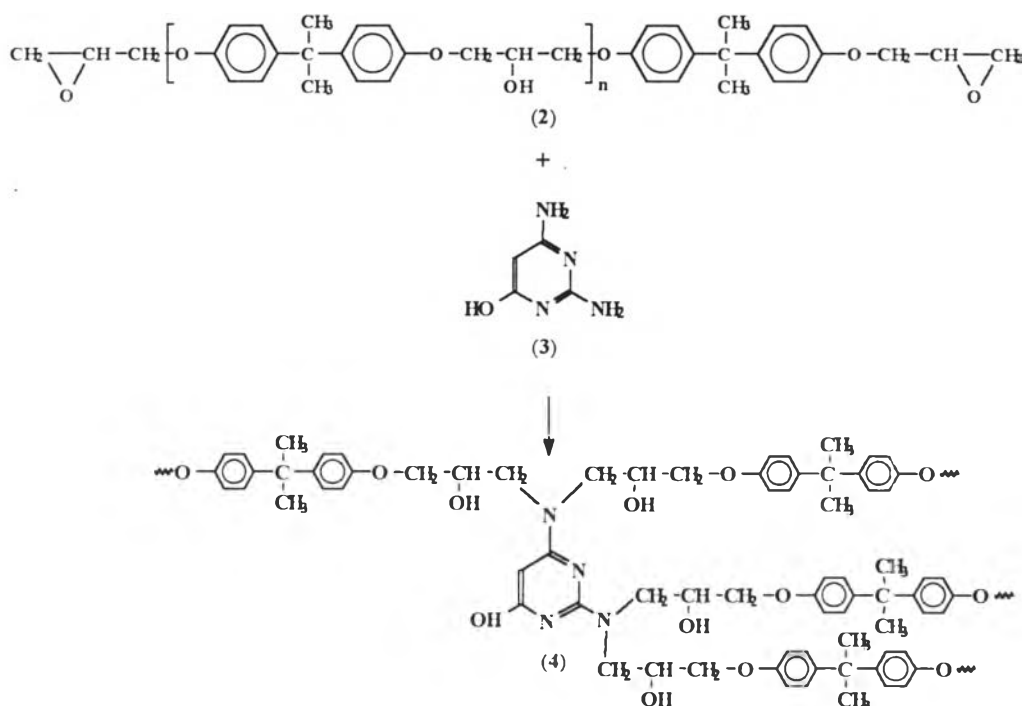
Sample	Sample container	Heating cycle	Temperature range (°C)	Heating rate (°C/min.)	Atmosphere
Uncured epoxy resin	closed Al pans with pierced lids	1	-100 - 210	20	nitrogen gas
		cool down	210 - -100	10	
		2	-100 - 210	20	
	closed Al pans without pierced lids	-	-80 - 350	10	nitrogen gas
Crosslinked resin	closed Al pans with pierced lids	1	-100 - 210	20	nitrogen gas
		cool down	210 - -100	10	
		2	-100 - 210	20	

#### B. Thermogravimetric Analysis (TGA)

Sample	Sample container	Temperature range (°C)	Heating rate (°C/min.)	Atmosphere
Crosslinked resin	closed Al pans with pierced lids	ambient - 600	20	nitrogen gas

## Experimental Procedures

### 1 Preparation of Crosslinked Resins (4) Derived from the Reaction of Bisphenol-A Epoxy Resin (2) with 2,4-Diamino-6-hydroxypyrimidine (3) Crosslinker



The diamine (3) and epoxy resin (2) were mixed at equivalent weight ratios (3:2) of 2:1, 2:1.25, 2:1.5, 2:1.75, 1:1, 3:1 and 4:1. The specified ratios of the two components were weighted accurately using electrical balance and mixed well in a beaker. The mixtures were subsequently heated up to 100°C for a few minutes. Then the mixtures were placed on a watch glass coating with silicone grease, and they were weighted accurately. Later the mixtures in the watch glass were heated up to 185°C and maintained to that temperature for 2 hours. Then the mixtures were cooled to room temperature. The obtained crosslinked resin was placed in a beaker containing 50 ml of dioxane. The resin

and the solvent were warmed up with continuous stirring in order to remove unreacted epoxy resin (2) from the crosslinked resin. The solution was subsequently filtered yielding the crosslinked resin, which was then repurify by rewashing with dioxane until the unreacted epoxy resin (2) was no more presented in the filtrate, which was tested using Thin Layer Chromatography (ethyl acetate as eluent). The crosslinked resin (4) was dried in an oven at 110°C for 1 hour to remove dioxane minor remaining in the resin, and reweighted accurately.

Weights of diamine (3) and epoxy resin (2) used at various equivalent weight ratios and yield (%) of each ratio were reported as shown in Table 3.2.

**Table 3.2** Weight of Bisphenol-A epoxy resin (2) and 2,4-diamino-6-hydroxypyrimidine (3) and yield (%) at various equivalent weight ratios of 3:2.

Equivalent weight ratio of 3:2	Weight of 3 (g) (MW.=126.12)	Weight of 2 (g) (E.E.W.=187)	Yield (%) of 4
2:1	1.26	3.88	69
2:1.25	1.26	4.73	63
2:1.5	1.26	5.78	50
2:1.75	1.26	6.74	49
1:1	1.26	7.50	42
3:1	1.89	3.80	92
4:1	2.53	3.79	97

The crosslinked resins were crushed into fine powder. Then it was passed through dry-sieved to obtain a particle size of 20 mesh.

The structure and the cure temperature of the products were determined using the Infrared Spectrophotometric (IR), Differential Scanning Calorimetric (DSC) and Thermogravimetric (TGA) methods.



## **2 Characterization of the Crosslinked Resins (4)**

### **2.1 Fourier-Transform Infrared Spectrophotometry (FTIR)**

Infrared spectra of sample (KBr) were obtained under dry air purge. The IR absorptions were appeared at the wavenumber of 1028, 1248, 1463, 1509, 1634, 2926, 2964, 3038 and 3390  $\text{cm}^{-1}$ .

### **2.2 Differential Scanning Calorimetry (DSC)**

The DSC measurements were carried out over a  $-100$  to  $210^{\circ}\text{C}$  temperature range in closed Al pans under nitrogen atmosphere with a heating rate of  $20^{\circ}\text{C}/\text{min}$ . The glass transition temperatures of the crosslinked resins (4) at the equivalent weight ratios (3:2) of 2:1, 2:1.5 and 1:1 were  $117.0$ ,  $112.7$  and  $114.9^{\circ}\text{C}$ , respectively.

### **2.3 Thermogravimetric Analysis (TGA)**

Thermogravimetric analysis was carried out under nitrogen atmosphere from ambient up to  $600^{\circ}\text{C}$  with a heating rate of  $20^{\circ}\text{C}/\text{min}$ .

### **3 Determination of Percent Weight Increase of the Crosslinked Resins (4) upon Swelling in Dioxane [8]**

The crosslinked resins with the equivalent weight ratios (3:2) of 2:1, 2:1.5, 1:1, 3:1 and 4:1 were used. The resins were weighted exactly to 0.5 g and placed in a 50 ml beaker containing 25 ml of 80% dioxane solution in water. The mixtures were allowed to stand for 2 hours. After swelling they were filtered through filter paper. The swollen resins were weighted within 15 minutes. The percent weight increase was calculated using the following equation:-

$$\% \text{ weight increase} = \frac{(\text{weight of the swollen resin} - \text{initial weight})}{\text{initial weight}} \times 100$$

### **4 Selective Chelation of the Crosslinked Resins (4)**

Preliminary studies of selective chelation of the crosslinked resins (4) were investigated. The various metal ions such as Co(II), Cu(II), Pb(II), Ni(II) and Zn(II) in water were used. The metal content of these solutions was measured by Atomic Absorption (AA) spectrophotometer using calibration method.

The chelation abilities in various solvents were also investigated. The solvents were 100% water, 40% dioxane solution in water, 80% dioxane solution in water, 80% DMF solution in water, 80% DMSO solution in water and 80% methanol solution in water (v/v).



### - Metal-uptaken Experiments

Exact weight of 0.5 g of the crosslinked resins (4) were placed in a 125 ml Erlenmeyer flask. 20 ml of 0.5 M metal stock solutions in water were added, and the flask was covered with paraffin film to prevent solvent evaporation. The mixture was shaken at room temperature for 3 hours. Then the solutions were filtered, and the crosslinked resin (4) were thoroughly washed with water. The metal stock solutions and the filtrates were diluted to appropriate concentration. The metal contents of these solutions were measured by AA spectrophotometer.

80% dioxane aqueous solution was used in comparison to chelating in water but now the copper solution was not used because the copper salt could not dissolve in that solution.

The chelation with metal ions in basic  $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$  buffer solutions could not be performed because the formation of precipitates from the reactions of Ni(II), Co(II), Cu(II) and Zn(II) with hydroxide and Pb(II) with chloride.

The crosslinked resins showed insignificantly on chelating capacities with those metal ions except for Pb(II). Therefore, the Pb(II) chelating of these resins was investigated more detailed.

## **5 Measurement of Chelating Capacity of Pb(II)**

### **5.1 Batch Method.**

Exact weight of 0.5 g of the resin at various equivalent weight ratios (3:2) were placed in a 125 ml Erlenmeyer flask containing 20 ml (1 mmol) of the Pb(II) stock solution in 80% dioxane aqueous solution. The flasks were covered with paraffin film and shaken for 3 hours at room temperature. After that the mixtures were filtered and washed well with 80% dioxane aqueous solution. The stock solution and the filtrate were diluted to appropriate concentrations, and the Pb(II) contents of these solutions were measured.

For the Pb(II) solution in 40% dioxane, 80% DMSO, 80% DMF and 80% methanol aqueous solutions were analogous to the 80% dioxane aqueous solution. For the three latter solutions, the crosslinked resins at the equivalent weight ratios 3:2 of 2:1.25 and 2:1.75 were not used.

### **5.2 Column Method.**

The resins with the equivalent weight ratios (3:2) of 2:1 and 1:1 were used. An exact weight of 2.5 g of the specified ratios were placed in a 50 ml beaker containing 40 ml of dioxane, and let stand for 2 hours to allow dioxane permeating through the resins to yield swollen resin. Then they were packed into a glass column ( $\phi$  1x40 cm). Resin height was about 90 mm. Then 20 ml of 0.05 M stock Pb(II) solution in 80% dioxane aqueous solution was passed through the column at a flow rate of 0.5 ml/min. Three equal portions of 60 ml 80% dioxane aqueous solution were passed through the column to elute non-adsorbed Pb(II) ions. Pb(II) ions adsorbed on the column were eluted by

passing 1 M nitric acid in 80% dioxane solution through the loaded resin with three equal portions of 45 ml. After elution, the resin was washed again with 80% dioxane aqueous solution till the neutralized filtrate was obtained testing using pH paper.

The adsorption and elution of Pb(II) ion in 80% dioxane aqueous solution was repeated by the same procedure. The stock solution and the filtrates were diluted to appropriate concentration, and the Pb(II) contents of these solutions were each measured. The amount of Pb(II) ions adsorbed on the resin was calculated by the change in the Pb(II) concentration.

### **5.3 Determination of the Maximum Pb(II) Chelating Capacity.**

The resin prepared from the equivalent weight ratio (3:2) of 1:1 was used for the investigation. Exact weight of 0.5 g of the resin was placed in 125 ml erlenmeyer flask. 20 ml of Pb(II) solution in 80% dioxane aqueous solution with various Pb(II) concentrations (0.005, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.08, 0.10 M) were added. The mixtures were allowed to stand for 3 hours with stirring at room temperature. The amount of Pb(II) remaining in the solution was determined using AAS, and the amount of Pb(II) chelated on the resin was calculated from the changes of the Pb(II) concentration in solutions.

### **5.4 Determination of Pb(II) Chelation Rate**

Exact weight of 0.5 g of the resin prepared from the equivalent weight ratio (3:2) of 2:1 was added into 20 ml of 0.05 M Pb(II) solution and stirred at room temperature. The Pb(II) concentration in the supernatant at time intervals of 10, 20, 30, 40, 50, 60, 80, 100, 120, 150, 190 minutes was

measured using AAS. The amount of Pb(II) chelated on the resin was calculated from the changes of the Pb(II) concentration in the solutions.

#### **6 Investigation of Using the Crosslinked Resin (4) for Pb(II) Chelation in Waste Water Obtained from Battery Factory**

The method used was developed in this laboratory in order to determine amount of Pb(II) presented in waste water from battery factory.

Waste water was filtered and neutralized with NaOH pellets. The sample was then diluted with dioxane to the concentration of 50% v/v. 20 ml of the solution was added into the 125 ml erlenmeyer flask containing exact weight of 0.5 g of the crosslinked resin prepared from the equivalent weight ratio (3:2) of 2:1. The mixture was allowed to stand for 3 hours. Subsequently, the solution was filtered and diluted to the volume of 50 ml. The Pb(II) contents in the waste water and the sample were determined using AAS. The adsorbed mole was calculated by the difference in Pb(II) contents of the stock solution from the sample.