

## CHAPTER II

### EXPERIMENTAL SECTION

**2.1 Materials.** All reagents and solvents were of analytical grade quality. Nickel (II) acetate tetrahydrate, zinc (II) acetate dihydrate, triethylenetetramine, salicylaldehyde and tetrabutylammonium hydroxide were obtained from the Fluka Chemical Company. Diglycidyl ether of bisphenol-A (DGEBA), D.E.R. 330 grade, with epoxy equivalent weight of 185, was also obtained from the Fluka Chemical Company. All chemicals were used without further purification.

**2.2 Analytical Procedures.** The IR spectra were recorded on a Nicolet Impact 410. NMR spectra were recorded in  $\text{CDCl}_3$  solution on an ACF 200 MHz Bruker instrument. Chemical shifts are given in parts per million (ppm) downfield from tetramethylsilane as an internal standard. X-ray spectroscopy was carried out using a Bruker Analytical SMART CCD X-Ray systems. Elemental analyses were carried out on a Perkin Elmer Elemental Analyzer 2400 CHN. FAB mass spectra were obtained on a Finnigan MAT 90 mass spectrometer using glycerol as a matrix. Thermal properties of epoxy polymers were measured on a Netzsch Dynamic Mechanical Analyzer (DMA 240), a Perkin Elmer Differential Scanning Calorimeter (DSC7) and a Netzsch Simultaneous Thermal Analyzer (STA 409 C).

### 2.3 Synthetic Procedures.

**2.3.1 Preparation of Schiff's Base Ligand (L).** The following methods were modified from those reported by Marvel<sup>22</sup> and Tongraung<sup>21</sup>. A cool (0-10 °C) methanolic solution (10 ml) of triethylenetetramine (0.84 ml, 5.65 mmol) was added dropwise to a solution of salicylaldehyde (1.38 g, 11.28 mmol) in methanol (15ml) at

0 °C. The mixture was stirred for 1 hour. The yellow powder formed was then isolated by filtration and dried under vacuum (1.71 g, 85% based on salicylaldehyde).  $^1\text{H}$  NMR  $\delta$  (ppm); 8.33 (2H, s, CH=N), 7.20-7.32 (4H, m, aromatic protons), 6.94 (2H, d,  $J=7.4$  Hz, aromatic protons), 6.86 (2H, t,  $J=7.4$ Hz, aromatic protons), 3.72 (4H, t,  $J=6.8$ Hz, methylene protons), 2.70 (4H, t,  $J=6.7$ Hz, methylene protons), 2.57 (4H, s, methylene protons).  $^{13}\text{C}$  NMR  $\delta$  (ppm); 168, 162, 132, 131, 118.5, 118, 117, 59, 58, 53. IR( $\text{cm}^{-1}$ ); 3462 (NH), 3200, 3000, 2800, 1639 (C=N), 1608, 1400, 1285, 990, 860. Analysis calc. for  $\text{C}_{20}\text{H}_{26}\text{N}_4\text{O}_2$ ; C 67.80; H 7.35; N 15.82. Found; C 67.50; H 6.48; N 13.30.

**2.3.1.1 Preparation of NiL complex.** A solution of nickel (II) acetate tetrahydrate (0.52 g, 2.44 mmol) in methanol (15 ml) was added dropwise to a solution of the ligand L (0.86 g, 2.43 mmol) in methanol (20 ml) at 0 °C over a period of 10 minutes. The mixture was neutralized with a 2 M NaOH solution (2.4 ml, 4.8 mmol) and stirred for 1 hour. The brown crystals of NiL precipitated from solution upon standing at room temperature for 10 hours (0.25 g, 29 % based on L).

**2.3.1.2 Preparation of ZnL complex.** The experiment was performed according to the procedure described in experiment 2.3.1.1 employing zinc (II) acetate dihydrate instead of nickel (II) acetate tetrahydrate. The yellow crystals of ZnL precipitated from the solution upon standing at room temperature for 10 hours (0.3 g, 30 % based on L).

**2.3.2. Preparation of NiL complex by a one-pot reaction.** A cool (0-10 °C) solution (10 ml) of triethylene tetramine (1 ml, 6.70 mmol) in methanol (10 ml) was added dropwise to a stirred cool solution of salicylaldehyde (1.18 g, 9.66 mmol) and nickel (II) acetate tetrahydrate (1.03 g, 4.84 mmol) in methanol (15 ml). The mixture

was neutralized by a 2 M sodium hydroxide solution (5 ml, 10 mmol) and stirred for another 1 hour. The brown crystals of NiL precipitated from the solution upon standing at room temperature for 7 hours (1.77 g, 89 % based on salicylaldehyde). The crystal was collected by filtration. m.p. 200 °C dec. IR( $\text{cm}^{-1}$ ); 3640 (NH), 3300, 3000, 2960, 2800, 1638 (C=N), 1601, 1448, 1250, 950, 850. m/z 411.3 ( $\text{M}^+ - 3\text{H}_2\text{O}$ ). UV ( $\lambda_{\text{max}}$ ); 386 nm. Analysis. calc. for  $\text{C}_{20}\text{H}_{24}\text{N}_4\text{O}_2\text{Ni} \cdot 3\text{H}_2\text{O}$ ; C 51.65; H 6.46; N 12.05. Found; C 52.05; H 6.21; N 12.19.

**2.3.3 Preparation of ZnL complex by a one-pot reaction.** The experiment was performed according to the procedure described in experiment 2.3.2 employing zinc (II) acetate dihydrate instead of nickel (II) acetate tetrahydrate. The yellow crystals of ZnL precipitated from the solution upon standing at room temperature for 7 hours (1.99 g, 99 % based on salicylaldehyde). m.p. 235 °C.  $^1\text{H}$  NMR  $\delta$  (ppm); 8.13 (2H, s, CH=N), 6.99-7.14 (4H, m, aromatic protons), 6.67-6.71 (2H, d,  $J=8.54$ , aromatic protons), 6.37-6.44 (2H, m, aromatic protons), 4.05-4.29 (2H, m, methylene protons), 3.21-3.48 (4H, m, methylene protons), 2.73-2.92 (2H, m, methylene protons), 2.35-2.61 (4H, m, methylene proton).  $^{13}\text{C}$   $\delta$  NMR(ppm); 172, 168, 135, 133, 124, 119, 112, 56, 47, 43. IR ( $\text{cm}^{-1}$ ); 3646 (NH), 3300, 3000, 2800, 1645 (C=N), 1600, 1448, 1200, 930, 870. m/z 417.3( $\text{M}^+ - \text{H}_2\text{O}$ ). UV ( $\lambda_{\text{max}}$ ) 366 nm. Analysis. calc. for  $\text{C}_{20}\text{H}_{24}\text{N}_4\text{O}_2\text{Zn} \cdot \text{H}_2\text{O}$ ; C 55.12; H 6.01; N 12.79. Found; C 54.65; H 6.59; N 12.79.

**2.3.4 Preparation of Nickel-containing epoxy polymer.** NiL was used as a crosslinking agent and tetrabutylammoniumhydroxide ( $\text{Bu}_4\text{NOH}$ ) was used as a catalyst. The equivalent weight ratios of NiL:DGEBA: $\text{Bu}_4\text{NOH}$  were varied as shown in Table 2.1.

**Table 2.1.** Composition of starting materials in the preparation of Ni-containing epoxy polymers.

Equivalent weight ratio of NiL:DGEBA:Bu <sub>4</sub> NOH	Weight of starting materials (g)		
	NiL	DGEBA	Bu <sub>4</sub> NOH
1 : 6 : 0	0.73	3.5	0
1 : 6 : 0.2	0.73	3.5	0.33
1 : 8 : 0.2	0.55	3.5	0.25
1 : 10 : 0.2	0.44	3.5	0.20
1 : 12 : 0.2	0.37	3.5	0.17
1 : 14 : 0.2	0.31	3.5	0.14

Dried NiL was added to hot degassed DGEBA. The mixture was heated and degassed under vacuum for 1 hour at 100 °C. Tetrabutylammonium hydroxide was then added. The mixture was stirred and degassed under vacuum for 1 hour, then heated at 100 °C and degassed under vacuum again. The degassed mixture was cast into a mold and cured at 140 °C for 4 hours. The polymer obtained was then characterized by IR spectroscopy. The glass transition temperature ( $T_g$ ) and thermal stability of the polymer were measured by DMA and STA, respectively. Mechanical testing of the polymers were performed according to the procedure described in ASTM D638 (tensile testing).

**2.3.5 Preparation of Zinc-containing epoxy polymer.** The experiment was performed according to the procedure described in experiment 2.3.4. ZnL was used as crosslinking agent and Bu<sub>4</sub>NOH was used as a catalyst. The equivalent weight ratios of ZnL:DGEBA:Bu<sub>4</sub>NOH were varied as shown in Table 2.2.

**Table 2.2.** Composition of starting materials in the preparation of Zn-containing epoxy polymers.

Equivalent weight ratio of ZnL:DGEBA:Bu <sub>4</sub> NOH	Weight of starting materials (g)		
	ZnL	DGEBA	Bu <sub>4</sub> NOH
1 : 6 : 0	0.69	3.5	0
1 : 6 : 0.2	0.69	3.5	0.33
1 : 8 : 0.2	0.51	3.5	0.25
1 : 10 : 0.2	0.41	3.5	0.20
1 : 12 : 0.2	0.34	3.5	0.17
1 : 14 : 0.2	0.29	3.5	0.13

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