CHAPTER II

EXPERIMENTAL

2.1 Materials. All reagents and solvents were of analytical grade quality. The solvents were obtained from Baker Chemical Company. Sodium hydroxide, cobalt(II)acetate tetrahydrate, nickel(II)acetate tetrahydrate, 1,3-diaminopropane and 2,4-dihydroxybenzaldehyde were obtained from Fluka Chemical Company. Copper(II) acetate monohydrate was obtained from Riedel-Deltaen Chemical Company. Diglycidyl ether of bisphenol A (DGEBA), D.E.R. 331 grade, with epoxy equivalent weight of 182-192 was obtained from Dow Chemical Company. All chemicals were used without further purification.

2.2 Analytical Procedures. The IR spectra were recorded on a Nicolet Impact 410. Elemental analyses were carried out on a Perkin Elmer Elemental Analyzer 2400 CHN. The thermal propertry of epoxy polymers were measured on a Netzch Differential Scaning Calorimeter (DSC 200), Dynamic Mechanical Analyser (DMA 240), and Thermalgravimetry Analyzer (TGA). All thermal measurements were carried out at the Scientific and Technological Research Equipment Center of Chulalongkorn University.

2.3 Synthetic Procedures. The preparations of 1,3-bis-(2,4-dihydroxybenzaldiimine)-propane the **Co-1** complex, the **Ni-1** complex, the **Cu-1** complex were previously reported.[20,22]

2.3.1 Preparation of 1,3-bis-(2,4-dihydroxybenzaldiimine)-propane (1).

The following methods were emulated from those reported by A. Bottcher and C.S. Marvel, et. al[20,22] with slight modification. A methanolic solution (10 ml) of 1,3-diaminopropane 0.5 ml (10.64 mmol) was added dropwise into a stirred cool (0-10°C) methanolic solution (100 ml) of 2,4-dihydroxybenzaldehyde (2.94 g, 21.28 mmol). The mixture gradually turned yellow and was stirred for another 15 minutes. The desired ligand (1) was difficult to isolate as a solid because it would decompose when dried. Therefore, the yellow solution was used directly for the preparation of metal complexes.

2.3.2 Preparation of the Cu-1 Complex. A solution (40 ml) of copper(II) acetate (2.13 g, 10.64 mmol) was added dropwise by an addition funnel into a stirred cool methanolic solution (110 ml) of the ligand (1) (10.64 mmol). The mixture was neutralized by a 2M sodium hydroxide solution (10.64 ml, 21.28 mmol). The green powder then precipitated and subsequently isolated by filtration and dried (3.87 g, 87%)

Anal. Calcd. for ($C_{17}H_{16}N_2O_4Cu \cdot 2H_2O$); C, 49.57; H,4.89; N, 6.80; Cu, 15.43 Found; C, 48.74; H, 4.63; N, 6.34; Cu, 15.84%

2.3.3 Preparation of the Ni-1 Complex. A solution (40 ml) of nickel(II) acetate (2.68 g, 10.78 mmol) was added dropwise by addition funnel into a stirred cool methanolic solution (110 ml) of ligand (1) (10.78 mmol). The mixture was neutralized by a 2M sodium hydroxide solution (10.78 ml, 21.56 mmol). The brown greenish powder then precipitated and the mixture was stirred for another 15 minutes. The supernatant solution was then isolated. Crystal of Ni-1 was precipitated from the solution in 4 days (3.95 g, 90%).

Anal. Calcd. for ($C_{17}H_{16}N_2O_4Ni \cdot 2H_2O$); C, 50.16; H, 4.95; N, 6.88; Ni, 14.42 Found; C, 50.19; H, 4.80; N, 6.65; Ni, 13.45%

2.3.4 Preparation of the Co-1 Complex. A methanolic solution (40 ml) of cobalt(II)acetate (2.68 g, 10.78 mmol) was added dropwise by addition funnel into a stirred cool methanolic solution (80 ml) of the ligand (1) (10.78 mmol). The mixture was neutralized by a 2M sodium hydroxide solution (10.78 ml, 21.56 mmol). The brown powder then precipitated and the mixture was stirred for another 15 minutes. The brown precipitates were subsequently isolated by fitration and dried (3.73 g, 85%).

Anal. Calcd. for ($C_{17}H_{16}N_2O_4Co \cdot 4H_2O$); C, 46.06; H, 5.25; N, 6.55; Co, 13.29 Found; C, 46.75; H, 5.46; N, 6.32; Co, 12.09%

2.3.5 Preparation of Cobalt-Containing Epoxy Polymer. Into each of four 50 ml round bottom flasks containing 0.40 g (0.98 mmol), 0.60 g (1.47 mmol), 1.20 g (2.94 mmol) and 1.43 g (3.52 mmol) of dried **Co-1** was added a hot degassed DGEBA (2 g, 5.88 mmol). The mixture was heated at 120 °C and stirred to become homogeneous. Then, it was degassed under vacuum. The degassed mixture was put into a metal mold and heated at 200 °C for 5 h. The polymer obtained was then characterized by IR spectoscopy. The glass transition temperature (T_g) and thermal stability of the polymer were measured by DMA and TGA, respectively.

2.3.6 Preparation of Nickel-Containing Epoxy Polymer. Into each of five 50 ml round bottom flasks containing 0.40 g (0.98 mmol), 0.60 g (1.47 mmol), 1.20 g (2.94 mmol) and 1.43 g (3.52 mmol), and 2.39 g (5.88 mmol) of dried **Ni-1** was added a hot degassed DGEBA (2 g, 5.88 mmol). The mixture was heated at 120 °C and stirred to become homogeneous. Then, it was degassed under vacuum. The degassed mixture was put into a metal mold and heated at 240 °C for 3 h. 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 TGA, respectively.

2.3.7 Preparation of Copper-Containing Epoxy Polymer. Into each of four 50 ml round bottom flasks containing 0.40 g (0.98 mmol), 0.61 g (1.47 mmol), 1.21 g (2.94 mmol) and 1.43 g (3.52 mmol) of dried **Cu-1** was added a hot degassed DGEBA (2 g, 5.88 mmol). The mixture was heated at 120 °C and stirred to become homogeneous. Then, it was degassed under vacuum. The degassed mixture was put into a metal mold and heated at 200 °C for 3 h. 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 TGA, respectively.