

## CHAPTER II

### EXPERIMENTAL

#### 2.1 Materials

All reagents and solvents were of analytical grade quality. Methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) was refluxed over calcium hydride ( $\text{CaH}_2$ ) and distilled immediately before use. Nickel (II) acetate tetrahydrate, salicylaldehyde, triethylenetetramine, hexyl isocyanate, hexamethylene diisocyanate and 1,6-hexanediol were 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 IR spectrometer using the potassium bromide (KBr) method. The thermal properties were examined using a Netzsch DSC 200 differential scanning calorimeter. All the samples were heated in DSC cell using a closed aluminium pan under dry nitrogen atmosphere with the heating rate of  $10\text{ }^\circ\text{C}/\text{min}$ . Elemental analyses were carried out on Perkin Elmer 2400 CHN Elemental Analyzer. Thermogravimetric measurements were performed on a Netzsch STA 409C thermogravimetric analyzer at the heating rate of  $10\text{ }^\circ\text{C}/\text{min}$  in air atmosphere. Liquid crystalline properties were observed by Olympus SC35 polarizing optical microscope equipped with a Mettler FP5 heating stage.

#### 2.3 Synthetic procedures

##### 2.3.1 Preparation of hexadentate Schiff base nickel complex ( $\text{NiL}_1$ )

A cool ( $0\text{-}10\text{ }^\circ\text{C}$ ) solution of triethylenetetramine (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, 4.84 mmol) in methanol (20 mL). The mixture was neutralized by a 2M sodium hydroxide solution (5 mL, 10 mmol) and stirred for 1 hour. The brown crystal of NiL<sub>1</sub> was precipitated from the solution upon standing at room temperature for 10 hours. The NiL<sub>1</sub> crystal was isolated by filtration and dried in vacuum (0.532 g, 97%)

IR (KBr, cm<sup>-1</sup>); 3634 (NH), 3448, 3278, 2900, 2866, 1642 (C=N), 1596, 1456, 1223, 953, 850.

### 2.3.2 Preparation of NiL<sub>1</sub> derivative (NiL<sub>2</sub>) from the reaction between NiL<sub>1</sub> and hexyl isocyanate

Hexyl isocyanate (0.228 mL, 1.57 mmol) was added dropwise to the solution of NiL<sub>1</sub> (0.309 g, 0.75 mmol) in dried methylenechloride (30 mL). The mixture was stirred and refluxed under N<sub>2</sub> atmosphere. The progress of the reaction was followed by using IR spectroscopy. After stirring for 12 hours, the solution was allowed to stand at room temperature for 18 hours and the brown powder of NiL<sub>2</sub> was precipitated and filtered. The yield was 0.498 g (90%) mp. 236 °C, followed by decomposition at the material (observed by DSC)

IR (KBr, cm<sup>-1</sup>); 3300 (NH), 2930, 2843, 1726 (C=O), 1649 (C=N), 1572, 1549, 1447, 1258, 1188, 897, 749, 652. Analysis calc. for C<sub>34</sub>H<sub>50</sub>N<sub>6</sub>O<sub>4</sub>Ni.H<sub>2</sub>O; C 59.75; H 7.67; N 12.30. Found; C 59.54; H 7.67; N 12.47.

### 2.3.3 Preparation of nickel containing polyurea (PU<sub>1</sub>NiL<sub>1</sub>) from the reaction between NiL<sub>1</sub> and hexamethylene diisocyanate

Hexamethylene diisocyanate (HDI) (0.242 mL, 1.5 mmol) was added dropwise to the solution of NiL<sub>1</sub> (0.678 g, 1.65 mmol) in dried methylene chloride (30 mL). The mixture was stirred and refluxed under N<sub>2</sub> atmosphere. The progress of reaction was followed by using IR spectroscopy. The optimum condition was obtained from heating a reaction mixture and stirred for 12 hours. The mixture was then allowed to stand at room temperature for 18 hours. The brown powder of PU<sub>1</sub>NiL<sub>1</sub> was precipitated and filtered. The yield was 0.609 g. (72%)

IR (KBr,  $\text{cm}^{-1}$ ); 3332 (NH), 2924, 2866, 1721, (C=O), 1640 (C=N), 1578, 1538, 1457, 1398 ( $\text{CH}_3$ ), 1223, 1095, 763. Analysis calc. for  $\text{C}_{36}\text{H}_{50}\text{N}_8\text{O}_6\text{Ni}\cdot\text{H}_2\text{O}$ ; C 56.37; H 6.84; N 14.62. Found; C 56.49; H 6.84; N 14.62.

### 2.3.4 Preparation of nickel containing polyurethane ( $\text{PU}_2\text{NiL}_1$ ) from the reaction between $\text{NiL}_1$ , hexamethylene diisocyanate and 1,6-hexanediol

Hexamethylene diisocyanate (0.267 mL, 1.65 mmol) was added dropwise to the solution of 1,6-hexane diol (0.177 g, 1.5 mmol) in dried methylene chloride (30 mL) to synthesized prepolymer. The mixture was refluxed under  $\text{N}_2$  and stirred for 8 hours. The extent of the reaction was checked by the titration of unreacted NCO groups by the known method. The reaction was stopped when one-half of the NCO groups were consumed. After stirring for 8 hours  $\text{NiL}_1$  (0.308 g, 1.5 mmol) was added to prepolymer and stirred at a reflux temperature. The progress of the reaction was followed by using IR spectroscopy. After stirring at reflux temperature for 18 hours, the optimum yield of  $\text{PU}_2\text{NiL}_1$  was obtained. The solution was then allowed to stand at room temperature for 18 hours and the brown powder of  $\text{PU}_2\text{NiL}_1$  was precipitated and filtered. The yield was 0.574 g (62%)

IR (KBr,  $\text{cm}^{-1}$ ); 3320 (NH), 2924, 2866, 1716 (C=O), 1640 (C=N), 1541, 1461, 1339 ( $\text{CH}_3$ ), 1211, 1001, 782. Analysis calc. for  $\text{C}_{64}\text{H}_{102}\text{N}_{12}\text{O}_{14}\text{Ni}$ ; C 58.13; H 7.78; N 12.71. Found; C 58.16; H 7.78; N 12.47.

ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย