

## CHAPTER II

### EXPERIMENTAL

#### 2.1 Materials

All reagents and solvents were of analytical grade quality. The solvents were obtained as commercial grade and refluxed over calcium hydride ( $\text{CaH}_2$ ) before use. Methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) used in synthesis was kept in bottle filled with molecular sieve and distilled over  $\text{CaH}_2$  immediately before use. Zinc (II) acetate dihydrate, nickel (II) acetate tetrahydrate, salicylaldehyde, triethylenetetramine, were obtained from the Fluka Chemical Company. Toluene 2,4-diisocyanate terminated poly(propylene glycol) prepolymer, molecular weight 1000 and 2300 (PP 1000 and PP2300); toluene 2,4-diisocyanate terminated poly(1,4-butanediol) prepolymer, molecular weight 900 and 1600 (PB900 and PB1600), dibutyltin diraulate and 4,4'-methylenebis(phenyl isocyanate) (MDI) were obtained from the Aldrich Chemical Company. All chemicals were used without further purification.

#### 2.2 Analytical Procedures

The IR spectra were recorded on a Nicolet Impact 410 by the potassium bromide (KBr) method at room temperature.  $^1\text{H}$  NMR spectrum was recorded in  $\text{CDCl}_3$  solution on a Varian Mercury 400 MHz instrument. Chemical shifts are given in parts per million (ppm) downfield from tetramethylsilane as internal standard. The solubility of the polymers was tested in various polar and nonpolar solvents by 5 mg samples being added to 1 mL of solvent. Elemental analyses were carried out on Perkin Elmer Elemental Analyzer 2400 CHN. The thermal properties were examined using a Netzsch STA 409C thermal analyzer in air/nitrogen atmosphere with heating rate of  $20^\circ\text{Cmin}^{-1}$  in air atmosphere. The limiting oxygen index (LOI) data were carried out by an apparatus following ASTM D2863-70 and using a modified

procedure as described in the literatures.<sup>14</sup> The inherent viscosity of the polymer was determined in DMSO at 40°C with a Cannon-Fenske viscometer following ASTM D2270. The flow time of the DMSO solvent as well as the polymer solution (0.5 g/dL) was determined.

## 2.3 Synthesis Procedures

### 2.3.1 Preparation of hexadentate Schiff base zinc complex (ZnSal<sub>2</sub>trien)

The preparation of ZnSal<sub>2</sub>trien was performed according to the method reported in the literature.<sup>15</sup> A cool (0-10°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 zinc (II) acetate dihydrate (1.05 g, 4.84 mmol) in the methanol (15 mL). The mixture was stirred for 15 minutes then was neutralized by a 2 M sodium hydroxide solution (5 mL, 10 mmol) and stirred for 1 h. The yellow crystals of ZnSal<sub>2</sub>trien precipitated from the solution upon standing at room temperature for 10 hours. The yellow crystals were isolated by filtration and dried *in vacuo* for at least 24 hours (1.86 g, 93%). IR (KBr, cm<sup>-1</sup>); 3646 (NH), 3300, 3000, 2800, 1634 (C=N), 1600, 1448, 1200, 930, 870. <sup>1</sup>H NMR δ (200 MHz, CDCl<sub>3</sub>, ppm); 8.13 (2H, CH=N), 6.99-7.14 (4H, aromatic protons), 6.67-6.71 (2H, aromatic protons), 4.05-4.29 (2H, methylene protons), 3.21-3.48 (4H, methylene protons), 2.73-2.92 (2H, methylene protons), 2.35-2.61 (4H, methylene protons), <sup>13</sup>C NMR (ppm); 172, 168, 135, 133, 124, 119, 112, 56, 47, 43.

### 2.3.2 Preparation of hexadentate Schiff base nickel complex (NiSal<sub>2</sub>trien)

The preparation of NiSal<sub>2</sub>trien was performed according to the method reported in the literature.<sup>15</sup> A cool (0-10°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 (1.03g, 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 h. The brown crystal of NiSal<sub>2</sub>trien was

precipitated from the solution upon standing at room temperature for 10 hrs. The NiSal<sub>2</sub>trien crystal was isolated by filtration and dried *in vacuo* (0.532 g, 97%). IR (KBr, cm<sup>-1</sup>); 3634 (NH), 3448, 3278, 2900, 2866, 1642 (C=N), 1596, 1456, 1223, 953, 850.

### 2.3.3 Preparation of polyurethanes

#### 2.3.3.1 Preparation of zinc-containing polyurethane-urea from ZnSal<sub>2</sub>trien and PB900 (PB900-Zn-30)

ZnSal<sub>2</sub>trien (0.175 g, 0.419 mmol) was dissolved in dried methylene chloride (20 mL). The solution of ZnSal<sub>2</sub>trien was added to round bottom flask filled with PB900 (0.378 g, 0.420 mmol). Then dibutyltin diraulate 2-3 drops were added to the mixture as a catalyst. After refluxing under nitrogen gas for 8 hours at 40 °C, the mixture was poured into a large amount of methanol (250 mL) until the polymer precipitated from the mixture. The precipitated polymer was filtered and dried *in vacuo*. The polymer was obtained as yellow powder (0.3381 g, 61 %). IR (KBr, cm<sup>-1</sup>); 3400 (NH), 2924, 2858, 1720 (C=O), 1635 (C=N), 1536, 1456, 1230, 1113, 763. <sup>1</sup>H NMR δ (200 MHz, CDCl<sub>3</sub>, ppm, in 1 repeating unit of polymer); 8.6 (1H, urea proton), 8.4 (1H, urethane proton), 6.8-7.3 (14H, aromatic protons), 3.1-4.1 (4H, methyleneoxy protons), 1.8-2.2 (3H, methyl protons), 1.6 (4H, methylene protons). Analysis calc. for C<sub>66</sub>H<sub>94</sub>N<sub>8</sub>O<sub>14</sub>Zn; C 61.50; H 7.35; N 8.69. Found; C 61.51; H 7.38; N 8.36.

#### 2.3.3.2 Preparation of zinc-containing polyurethane-urea from ZnSal<sub>2</sub>trien and PB1600 (PB1600-Zn-20)

The experiment was performed according to the procedure described in 2.3.3.1 employing ZnSal<sub>2</sub>trien (0.150 g, 0.359 mmol) and PB1600 (0.575 g, 0.359 mmol). The precipitated polymer was filtered and dried *in vacuo*. The polymer was obtained as yellow powder (0.3650 g, 50 %). IR (KBr, cm<sup>-1</sup>); 3288 (NH), 2924, 2852, 1720 (C=O), 1635 (C=N), 1597, 1536, 1447, 1367, 1230, 1113, 814, 758. <sup>1</sup>H NMR δ

(200 MHz,  $\text{CDCl}_3$ , ppm, in 1 repeating unit of polymer); 8.6 (1H, urea proton), 8.4 (1H, urethane proton), 6.5-7.5 (14H, aromatic protons), 3.2-4.2 (4H, methyleneoxy protons), 1.8-2.4 (3H, methyl protons), 1.7 (4H, methylene protons). Analysis calc. for  $\text{C}_{106}\text{H}_{174}\text{N}_8\text{O}_{24}\text{Zn}$ ; C 63.34; H 8.73; N 5.57. Found; C 63.33; H 8.64; N 5.53.

### 2.3.3.3 Preparation of zinc-containing polyurethane-urea from $\text{ZnSal}_2\text{trien}$ and PP1000 (PP1000-Zn-30)

The experiment was performed according to the procedure described in 2.3.3.1 employing  $\text{ZnSal}_2\text{trien}$  (0.150 g, 0.359 mmol) and PP1000 (0.359 g, 0.359 mmol). The precipitated polymer was filtered and dried *in vacuo*. The polymer was obtained as yellow powder (0.3356 g, 66 %). IR (KBr,  $\text{cm}^{-1}$ ); 3293, 2970, 2924, 2863, 1729, 1635, 1536, 1449, 1378, 1291, 1224, 1106, 927, 763.  $^1\text{H}$  NMR  $\delta$  (200 MHz,  $\text{CDCl}_3$ , ppm, in 1 repeating unit of polymer); 8.56 (1H, urea proton), 8.43 (1H, urethane proton), 6.5-7.3 (14H, aromatic protons), 3.5-3.7 (2H, methyleneoxy protons), 3.3-3.5 (2H, methyleneoxy protons), 1.8-2.2 (3H, methyl protons), 1.1-1.3 (3H, methyl protons). Analysis calc. for  $\text{C}_{71}\text{H}_{104}\text{N}_8\text{O}_{18}\text{Zn}$ ; C 59.93; H 7.37; N 7.87. Found; C 59.93; H 7.38; N 7.87.

### 2.3.3.4 Preparation of zinc-containing polyurethane-urea from $\text{ZnSal}_2\text{trien}$ and PP2300 (PP2300-Zn-20)

The experiment was performed according to the procedure described in 2.3.3.1. employing  $\text{ZnSal}_2\text{trien}$  (0.150 g, 0.359 mmol) and PP2300 (0.826 g, 0.359 mmol). The precipitated polymer was filtered and dried *in vacuo*. The polymer was obtained as yellow elastomer (0.5135 g, 53 %). IR (KBr,  $\text{cm}^{-1}$ ); 3288, 2965, 1724, 1630, 1536, 1455, 1369, 1224, 922, 866, 763.  $^1\text{H}$  NMR  $\delta$  (200 MHz,  $\text{CDCl}_3$ , ppm, in 1 repeating unit of polymer); 8.56 (1H, urea proton), 8.43 (1H, urethane proton), 8-8.2 (1H, Schiff base proton) 6.4-7.4 (4H, aromatic protons), 3.5-3.7 (2H, methyleneoxy protons), 3.3-3.5 (2H, methyleneoxy protons), 1.8-2.2 (3H, methyl protons), 1.1-1.3 (3H, methyl protons). Analysis calc. for  $\text{C}_{137}\text{H}_{236}\text{N}_8\text{O}_{40}\text{Zn}$ ; C 60.93; H 8.81; N 4.15. Found; C 60.93; H 8.81; N 3.92.

### 2.3.3.5 Preparation of zinc-containing copolyurethanes-ureas from ZnSal<sub>2</sub>trien, prepolymers and MDI

The experiment was performed according to the procedure described in 2.3.3.1. 4,4-Methylenebis(phenyl isocyanate) was used at different wt % and dibutyltin diraulate was used as a catalyst. All starting materials were placed in round-bottom flask filled with dried methylene chloride (30 mL). The mixture was stirred to dissolve starting material and then 2 drops of dibutyltin diraulate were added. After refluxing under nitrogen gas for 8 hours, the mixture was poured into a large amount of methanol (250 mL) until the polymer precipitated from the mixture. The precipitated polymer was filtered and dried *in vacuo*. The polymer was obtained as yellow powder. The weight ratios of ZnSal<sub>2</sub>trien : Prepolymer : 4,4-methylenebis(phenyl isocyanate) were varied as shown in Table 2.1.

**Table 2.1** Composition of starting materials in the preparation of zinc-containing polyurethane-ureas and copolyurethane-ureas at various wt % of ZnSal<sub>2</sub>trien

Polymers	Wt % of ZnSal <sub>2</sub> trien in polymer	Wt. Of ZnSal <sub>2</sub> trien (g)	Wt. of pre polymer (g)	Wt. Of MDI (g)	Total wt. (g)	Yield (%)
PB900-Zn-30	30	0.1750	0.3780	-	0.5530	61
PB900-Zn-MDI-50	50	0.5426	0.3000	0.2417	1.0800	64
PB1600-Zn-20	20	0.1500	0.5749	-	0.7249	50
PB1600-Zn-MDI-30	30	0.2588	0.5300	0.0725	0.8613	50
PB1600-Zn-MDI-50	50	0.4830	0.2286	0.2536	0.9652	77
PP1000-Zn-30	30	0.1500	0.3590	-	0.5090	64
PP1000-Zn-MDI-50	50	0.4695	0.2500	0.2188	0.9383	57
PP2300-Zn-20	20	0.1500	0.8264	-	0.9764	52
PP2300-Zn-MDI-30	30	0.2953	0.5750	0.1144	0.9847	51
PP2300-Zn-MDI-50	50	0.5113	0.2300	0.2813	1.0200	74

### 2.3.3.6 Preparation of nickel-containing polyurethane-urea from NiSal<sub>2</sub>trien and PB900 (PB900-Ni-30)

NiSal<sub>2</sub>trien (0.150 g, 0.365 mmol) was dissolved in dried methylene chloride (20 mL). The solution of NiSal<sub>2</sub>trien was added to round bottom flask filled with PB900 (0.328 g, 0.365 mmol). Then dibutyltin diraulate (2-3 drops) was added to the mixture as a catalyst. After refluxing under nitrogen gas for 8 hours at temperature 40°C, solvent was removed from the mixture by rotary evaporator. The precipitated polymer was filtered and dried *in vacuo*. The polymer was obtained as brown elastomer (0.4712g, 98%). IR (KBr, cm<sup>-1</sup>); 3298, 2924, 2853, 1720, 1640, 1598, 1536, 1342, 1230, 1113, 758. Analysis calc. for C<sub>66</sub>H<sub>94</sub>N<sub>8</sub>O<sub>14</sub>Ni.3CH<sub>3</sub>OH; C 60.13; H 7.75; N 8.13. Found; C 60.14; H 9.21; N 8.07.

### 2.3.3.7 Preparation of nickel-containing polyurethane-urea from NiSal<sub>2</sub>trien and PB1600 (PB1600-Ni-20)

The experiment was performed according to the procedure described in 2.3.3.6 employing NiSal<sub>2</sub>trien (0.150 g, 0.365 mmol) and PB1600 (0.583 g, 0.365 mmol). The precipitated polymer was filtered and dried *in vacuo*. The polymer was obtained as brown elastomer (0.7076 g, 96 %). IR (KBr, cm<sup>-1</sup>); 3297, 2931, 2856, 1720, 1640, 1597, 1536, 1451, 1367, 1225, 1113, 885, 815, 756. Analysis calc. for C<sub>106</sub>H<sub>174</sub>N<sub>8</sub>O<sub>24</sub>Ni.3CH<sub>3</sub>OH; C 62.36; H 8.93; N 5.34. Found; C 62.57; H 8.96; N 5.39.

### 2.3.3.8 Preparation of nickel-containing polyurethane-urea from NiSal<sub>2</sub>trien and PP1000 (PP1000-Ni-30)

The experiment was performed according to the procedure described in 2.3.3.6 employing NiSal<sub>2</sub>trien (0.150 g, 0.365 mmol) and PP1000 (0.3282 g, 0.365 mmol). The precipitated polymer was filtered and dried *in vacuo*. The polymer was obtained as brown elastomer (0.5531 g, 97 %). IR (KBr, cm<sup>-1</sup>); 3293, 2970, 2924, 2858, 1720, 1635, 1598, 1541, 1455, 1373, 1291, 1230, 1112, 932, 820, 758. Analysis calc. for C<sub>71</sub>H<sub>104</sub>N<sub>8</sub>O<sub>18</sub>Ni.3CH<sub>3</sub>OH; C 62.36; H 8.93; N 5.34. Found; C 62.57; H 8.96; N 5.39.

### 2.3.3.9 Preparation of nickel-containing polyurethane-urea from NiSal<sub>2</sub>trien and PP2300 (PP2300-Ni-20)

The experiment was performed according to the procedure described in 2.3.3.6 employing NiSal<sub>2</sub>trien (0.150 g, 0.365 mmol) and PB2300 (0.8388 g, 0.365 mmol). The precipitated polymer was filtered and dried *in vacuo*. The polymer was obtained as brown elastomer (0.8915 g, 90%). IR (KBr, cm<sup>-1</sup>); 3297, 2922, 2865, 1724, 1635, 1597, 1536, 1451, 1376, 1343, 1296, 1230, 1108, 929, 864, 819, 758. Analysis calc. for C<sub>137</sub>H<sub>236</sub>N<sub>8</sub>O<sub>40</sub>Ni.3CH<sub>3</sub>OH; C 60.26; H 8.96; N 4.02. Found; C 60.28; H 9.07; N 4.02.

### 2.3.3.10 Preparation of nickel-containing copolyurethanes-ureas from NiSal<sub>2</sub>trien, prepolymers and MDI

The experiment was performed according to the procedure described in 2.3.3.6. MDI was used at different wt % and dibutyltin diraulate was used as a catalyst. All starting materials were placed in round-bottom flask filled with dried methylene chloride (30 mL). The mixture was stirred to dissolve starting material and then 2 drops of dibutyltin diraulate were added. After refluxing under nitrogen gas for 8 hours, the mixture was poured into a large amount of methanol (250 mL) until the polymer precipitated from the mixture. The precipitated polymer was filtered and dried *in vacuo*. The polymer was obtained as light green powder. The weight ratios of NiSal<sub>2</sub>trien : Prepolymer : MDI were varied as shown in Table 2.2.

**Table 2.2** Composition of starting materials in the preparation of nickel-containing polyurethane-ureas and copolyurethane-ureas at various wt % of NiSal<sub>2</sub>trien

Polymers	wt % of NiSal <sub>2</sub> trien in polymer	Wt. of NiSal <sub>2</sub> trien (g)	Wt. of pre polymer (g)	Wt. Of MDI (g)	Total wt. (g)	Yield (%)
PB900-Ni-30	30	0.1500	0.3282	-	0.4782	98
PB900-Ni-MDI-50	50	0.5553	0.3000	0.2542	1.1095	62
PB1600-Ni-20	20	0.1500	0.5835	-	0.7335	96
PB1600-Ni-MDI-30	30	0.3126	0.6400	0.0900	1.0426	52
PB1600-Ni-MDI-50	50	0.4936	0.2286	0.2643	0.9865	70
PP1000-Ni-30	30	0.1500	0.3647	-	0.5147	97
PP1000-Ni-MDI-50	50	0.4781	0.2500	0.2282	0.9563	42
PP2300-Ni-20	20	0.1500	0.8388	-	0.9888	90
PP2300-Ni-MDI-30	30	0.2982	0.5750	0.1188	0.9920	26
PP2300-Ni-MDI-50	50	0.5224	0.2300	0.2926	1.0450	70