

CHAPTER II

EXPERIMENTAL

2.1 Materials

All reagents and solvents were of analytical grade quality. The solvents were obtained from Baker Chemical Company. Methylene chloride (CH_2Cl_2) was refluxed over calcium hydride (CaH_2) and distilled immediately before use. Zinc (II) acetate dihydrate, salicylaldehyde, triethylenetetramine, hexyl isocyanate, phenyl isocyanate, hexamethylene diisocyanate, 2,4-toluene 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 by the potassium bromide (KBr) method. NMR spectra were recorded in CDCl_3 solution on an ACF 200 MHz Bruker instrument. Chemical shifts are given in parts per million (ppm) downfield from tetra methylsilane as internal standard. Elemental analyses were carried out on Perkin Elmer Elemental Analyzer 2400 CHN. X-ray crystallography was carried out using a Bruker Analytical SMART CCD X-ray systems. The experimental parameters are shown in Appendix B. The thermal properties were examined using a Netzsch differential scanning calorimeter (DSC 200). All the samples were heated in DSC cell using a closed aluminium pan under dry nitrogen atmosphere with the heating rate of $10^\circ\text{C}/\text{min}$. Thermogravimetric measurements

were performed on a Netzsch thermogravimetric analyzer (STA 409C) at the heating rate of $10^{\circ}\text{C}/\text{min}$ under air/nitrogen(30/20) atmosphere. Liquid crystalline properties were observed by an Olympus polarizing optical microscope equipped with a Mettler hot stage. All the samples were placed between glass slides and heated to the isotropic melt.

2.3 Synthetic Procedures

2.3.1 Preparation of metallomesogen: the liquid crystalline hexadentate Schiff base zinc complex (ZnL_1)

The preparation of ZnL_1 was carried out according to the method reported in the literature [18]. A cool ($0\text{-}10^{\circ}\text{C}$) 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 zinc (II) acetate dihydrate (1.05 g, 4.84 mmol) in methanol (15 ml). The mixture was neutralized by a 2M sodium hydroxide solution (5 ml, 10 mmol) and stirred for 1 hour. The yellow crystals of ZnL_1 precipitated from the solution upon standing at room temperature for 10 hours. The yellow crystal was isolated by filtration and dried in vacuo (1.86 g, 93%): mp 220°C (observed by polarizing optical microscope). IR (KBr, cm^{-1}); 3646 (NH), 3300, 3000, 2800, 1634(C=N), 1600, 1448, 1200, 930, 870. ^1H NMR δ (200 MHz, CDCl_3 , ppm); 8.13 (2H, $\text{CH}=\text{N}$), 6.99-7.14 (4H, aromatic protons), 6.67-6.71 (2H, aromatic protons), 6.37-6.44 (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). ^{13}C NMR δ (CDCl_3 , ppm); 172, 168(C=N), 135, 133, 133, 124, 119, 112, 56, 47, 43.

2.3.2 Preparation of ZnL₁ derivatives

2.3.2.1 Preparation of ZnL₂ from the reaction between ZnL₁ and hexyl isocyanate

Hexyl isocyanate (0.153 ml, 1.05 mmol) was added dropwise to the solution of ZnL₁ (0.200 g, 0.48 mmol) in dried methylene chloride (15 ml). The mixture was stirred at room temperature. The progress of the reaction was followed by using IR spectroscopy. After stirring for 5 hours, the solution was evaporated under a reduced pressure to give ZnL₂ as a yellow powder. The residue was washed with hexane and then maintained in vacuo for 48 hours to remove traces of solvent. The yield was 0.271 g (84%): mp 120°C (observed by polarizing optical microscope). IR (cm⁻¹); 3350 (NH), 2950, 2920, 2850, 1726(C=O), 1634(C=N), 1600, 1506, 1467, 1372(CH₃), 1200, 1040, 758. ¹H NMR δ (200 MHz, CDCl₃, ppm); 8.13 (2H, CH=N), 6.99-7.14 (4H, aromatic protons), 6.67-6.71 (2H, aromatic protons), 6.37-6.44 (2H, aromatic protons), 4.05-4.29 (2H, methylene protons), 3.21-3.48 (2H, methylene protons), 3.19-3.05(4H, methylene protons), 2.73-2.92 (2H, methylene proton), 2.35-2.61 (2H, methylene protons) and 1.20-1.88 (20H, (CH₂)₅), 0.77-0.93 (6H, CH₃). ¹³C NMR δ (CDCl₃, ppm); 172, 168 (C=N), 159 (C=O), 135, 133, 123, 119, 112, 56, 47, 43, 39, 32, 30, 27, 22, 14 (CH₃). Elemental Analysis: Calcd for C₃₄H₅₀N₆O₄Zn (672.20): C 60.75; H 7.50; N 12.50. Found: C 60.50; H 7.65; N 12.45.

2.3.2.2 Preparation of ZnL₃ from the reaction between ZnL₁ and phenyl isocyanate

The experiment was performed according to the procedure described in experiment 2.3.2.1 employing phenyl isocyanate (0.100 ml, 0.91 mmol) instead of hexyl isocyanate. ZnL₃ was obtained as dark yellow powder with the yield of 0.270 g (90%) precipitated from methylene chloride: mp 145°C (observed by polarizing

optical microscope). IR (cm^{-1}); 3350 (NH), 3000, 2850, 1705 (C=O), 1634(C=N), 1600, 1580 (aromatic C=C), 1490, 1450, 1200, 1040, 758, 692. ^1H NMR δ (200 MHz, CDCl_3 , ppm); 8.13 (2H, $\text{CH}=\text{N}$), 7.22-7.60 (4H, aromatic protons), 6.83-7.21 (6H, aromatic protons), 6.61-6.81 (4H, aromatic protons), 6.31-6.44 (2H, aromatic protons), 3.50-4.29 (4H, methylene protons), 2.73-2.92 (2H, methylene proton) and 1.51-1.75 (8H, methylene protons). ^{13}C NMR δ (CDCl_3 , ppm); 172, 171, 170, 169, 168, 159, 138, 135, 134, 133, 132, 130, 129, 127, 124, 123, 119, 118.9, 118.7, 118, 117, 115, 113.8, 113.6, 112, 56, 55.9, 55, 52, 46, 45.6, 45, 44, 43. Elemental Analysis: Calcd for $\text{C}_{34}\text{H}_{34}\text{N}_6\text{O}_4\text{Zn}$ (656.06): C 62.25; H 5.22; N 12.81. Found: C 62.25; H 5.38; N 12.82.

2.3.3 Preparation of polyurethanes

2.3.3.1 Preparation of PU_1ZnL_1 from the reaction between ZnL_1 and hexamethylene diisocyanate

Hexamethylene diisocyanate (HDI) (0.105 ml, 0.65 mmol) was added dropwise to the stirred solution of ZnL_1 (0.300 g, 0.72 mmol) in dried methylene chloride (20 ml) at room temperature. After stirring for 30 minutes, PU_1ZnL_1 precipitated from the solution as yellow powder. To ensure the complete reaction, the mixture was stirred for another 5 hours. The progress of the reaction was followed by using IR spectroscopy. The precipitated product was filtered and dried in vacuo to yield 0.40 g (74%) of PU_1ZnL_1 : mp 170°C (observed by polarizing optical microscope). IR (KBr, cm^{-1}); 3300 (NH), 2980, 2850, 1726 (C=O), 1634 (C=N) 1600, 1490, 1467, 1200, 1040, 930, 758, 697.

2.3.3.2 Preparation of PU_2ZnL_1 from the reaction between ZnL_1 , hexamethylene diisocyanate and 1,6-hexanediol

1,6-Hexanediol (0.125 g, 1.00 mmol) was dissolved in 15 ml of dried CH_2Cl_2 in two-necked round-bottom flask fitted with a reflux condenser, magnetic stirrer, thermometer and additional funnel charged with HDI and dried CH_2Cl_2 . Nitrogen was kept flowing through the system continuously. HDI (0.250 g, 1.50 mmol) was added dropwise to the solution at 40°C . After 5 hours, a solution of ZnL_1 (0.417 g, 1.00 mmol) dissolved in 10 ml of dried CH_2Cl_2 was added to the solution. PU_2ZnL_1 precipitated after 30 minutes as yellow powder. The solution was kept stirring for another 10 hours to ensure the complete reaction. The progress of the reaction was followed by using IR spectroscopy. The precipitated product was filtered and dried in vacuo to yield 0.580 g (66%) of PU_2ZnL_1 : mp 170°C (observed by polarizing optical microscope). IR (KBr, cm^{-1}); 3300 (NH), 2920, 2880, 1705 (C=O), 1634 (C=N), 1540, 1506, 1480, 1460, 1200, 1040, 758.

2.3.3.3 Preparation of PU_3ZnL_1 from the reaction between ZnL_1 and 2,4-toluene diisocyanate

The experiment was performed according to the procedure described in experiment 2.3.3.1 employing 2,4-toluene diisocyanate (TDI) (0.0685 ml, 0.48 mmol) instead of HDI. PU_3ZnL_1 precipitated after stirring for 45 minutes as light yellow powder. The precipitated product was filtered and dried in vacuo to yield 0.40 g (73%): mp 224°C . IR (KBr, cm^{-1}); 3300 (NH), 3000, 2850, 1705 (C=O), 1634 (C=N), 1600, 1580 (NH-Ar), 1490, 1467, 1450, 1372 (CH_3), 1200, 1040, 758, 692.

2.3.3.4 Preparation of PU_4ZnL_1 from the reaction between ZnL_1 , 2,4-toluene diisocyanate and 1,6-hexanediol

The experiment was performed according to the procedure described in experiment 2.3.3.2 employing TDI (0.310 g, 1.50 mmol) instead of HDI. PU_4ZnL_1 precipitated after stirring for 45 minutes as light yellow powder. The precipitated product was filtered and dried in vacuo to yield 61%: mp 244°C. IR (KBr, cm^{-1}); 3300 (NH), 2920, 2880, 1726 (C=O), 1634(C=N), 1580 (NH-Ar), 1540, 1506, 1480, 1460, 1372 (CH_2), 1200, 1040, 758, 692.

