CHAPTER II

EXPERIMENTAL

2.1 Materials

All reagents and solvents were of analytical grade quality. The solvents were obtained from Lab-Scan. The reagents were obtained from Fluka, Aldrich, Merck and Riedel-deHaën. Manganese (II) acetate tetrahydrate, cobalt (II) acetate tetrahydrate, zinc (II) acetate dihydrate, copper (II) acetate monohydrate, tetraethylenepentamine, 1,2-diaminocyclohexane (a mixture of *cis-* and *tran-* isomers), tolylene 2,4-diisocyanate terminated poly(1,4-butanediol) prepolymer MW 900 (PB900), tolylene 2,4-diisocyanate terminated poly(propylene glycol) prepolymer MW 1000 (PP1000), *m*-xylylenediamine and dibutyltin dilaurate (DBTDL) were used without further purification.

2.2 Analytical procedures

IR spectra of the metal complexes and polymers were recorded on a Nicolet Impact 410 FTIR spectrophotometer at room temperature with the KBr disk method. The ^{1}H NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 solution on a Varian Mercury-400 BB instrument using the proton residual as internal reference. Elemental analysis was carried out using a Perkin-Elmer 2400 CHN Analyzer. Matrix-assisted laser desorption ionization-time of flight (MALDI-TOF) mass spectra were obtained on a Bruker Bifex mass spectrometer using α-cyanocinnamic acid as a matrix. Thermogravimetric analysis (TGA) was carried out in a Netsch STA 409C thermogravimetric analyzer at the heating rate of 20°C/min under air/nitrogen (50/50) atmosphere. The polymerization reaction was studied using a Perkin-Elmer DSC 7 differential scanning calorimeter and all samples were heated in DSC cell using a closed aluminium pan under air with the heating rate of 20°C/min. The solubility of

metal complexes and polymers was investigated in various polar and nonpolar solvents by dissolving 10 mg of the samples in 2 ml of solvents and kept overnight.

2.3 Synthetic procedures

2.3.1 Synthesis of 4,4′-dihydroxysaltetraen manganese complex (MnL_1)

A mixture of 2,4-dihydroxybenzaldehyde (0.287 g, 2.08 mmol) and manganese (II) acetate tetrahydrate (0.255 g, 1.04 mmol) in methanol (20 ml) was prepared and then cooled to 0°C. A cooled methanolic solution (10 ml) of tetraethylenepentamine (0.2 ml, 1.04 mmol) was added dropwise to the mixture over a period of 15 minutes. This mixture was stirred for 15 minutes and neutralized by adding a solution of different bases (2M NaOH, 2M $NaHCO_3$, 1M Na_2CO_3, 2M KOH and 1M K_2CO_3) (1.04 ml). The mixture was stirred at 0°C for 30 minutes. Upon standing at room temperature for 2 hours, the brown powder of MnL_1 precipitated from the reaction mixture. The manganese complex was isolated by filtration and dried under vacuum. The yield of MnL_1 obtained from using 2M KOH as a base was 0.46 g (92%): IR (KBr, cm^{-1}); 3420, 3239, 2947, 2886, 1581 (C=N), 1481, 1364, 1232, 1126, 986, 847. Elemental analysis: Calcd for $C_{22}H_{28}MnN_5O_4K$; C 50.76; H 5.42; N 13.45. Found: C 50.31; H 4.82; N 10.61.

2.3.2 Synthesis of 4,4′-dihydroxysaltetraen cobalt complex (CoL_1)

The procedure for the synthesis of cobalt complex was performed according to the same method described in experiment 2.3.1 using cobalt (II) acetate tetrahydrate (0.259 g, 1.04 mmol) instead of manganese (II) acetate tetrahydrate. CoL_1 precipitated as grey powder. The yield of CoL_1 obtained from using 2M KOH as a base was 0.17 g (34%): IR (KBr, cm^{-1}); 3420, 3239, 2947, 2889, 1597 (C=N), 1481, 1368, 1232, 1126, 986, 847. Elemental analysis: Calcd for $C_{22}H_{28}CoN_5O_4K.CH_3OH$; C 49.63; H 5.80; 12.58. Found: C 48.99; H 5.71; N 11.39.

2.3.3 Synthesis of 4,4′-dihydroxysalcyclohexane zinc complex (ZnL_2)

2.3.3.1 Preparation of 4,4′-dihydroxysalcyclohexane ligand (L_2)

The preparation of 4,4′-dihydroxysalcyclohexane ligand (L_2) was carried out according to the method reported in the literature.[20] In a 100 ml round-bottomed flask, 2.46 mmol (0.340 g) of 2,4-dihydroxybenzaldehyde and 30 ml of methanol were placed and then cooled to 0°C. A cooled methanolic solution (10 ml) of 1,2-diaminocyclohexane (0.15 ml, 1.23 mmol) was added dropwise to the mixture over a period of 15 minutes. The color of the mixture gradually changed to yellow and was stirred for another 15 minutes. It was difficult to isolate the obtained ligand as a solid because it decomposed when dried. Therefore, the yellow solution of ligand was used further for the synthesis of zinc complex (ZnL_2).

2.3.3.2 Synthesis of the zinc complex (ZnL_2)

A cooled methanolic solution (20 ml) of zinc (II) acetate dihydrate (0.270 g, 1.23 mmol) was added dropwise to the stirred cooled methanolic solution (40 ml) of the ligand (1.23 mmol). This mixture was stirred for 30 minutes and neutralized by adding a solution of 2M NaOH (1.23 ml, 2.46 mmol). The mixture was stirred at 0°C for 1 hour, the orange powder then precipitated from the mixture. The orange powder was removed by filtration and the filtrate was allowed to stand at room temperature for 3 days. The light yellow crystals of ZnL_2 precipitated and was subsequently isolated by filtration and dried under vacuum. The yield was 0.21 g (40%): IR (KBr, cm^{-1}); 3460, 3188, 2932, 2862, 1606 (C=N), 1551, 1447, 1359, 1220, 1134, 992, 848. ^1H NMR δ (400 MHz, $CDCl_3$ + DMSO-d_6, ppm); 9.20 (2H, *s*, OH), 8.09 (2H, *s*, CH=N), 6.90 (2H, *d*, aromatic protons, J = 7.9 Hz), 6.08 (2H, *s*, aromatic protons), 5.94 (2H, *q*, aromatic protons, J = 7.8 Hz), 3.01-3.12 (2H, *m*, cyclohexane protons), 2.30-2.45 (2H, *m*, cyclohexane protons), 1.84-2.03 (2H, *m*, cyclohexane protons), 1.19-1.46 (4H, *m*, cyclohexane protons). MALDI-TOF MS (m/z); 419, 441. Elemental analysis: Calcd for $C_{20}H_{20}ZnN_2O_4.H_2O$ (436); C 55.12; H 5.09; N 6.43. Found: C 54.83; H 4.82; N 6.66.

2.3.4 Synthesis of 4,4′-dihydroxysalcyclohexane copper complex (CuL_2)

A mixture of 2,4-dihydroxybenzaldehyde (0.340 g, 2.46 mmol) and copper (II) acetate monohydrate (0.246 g, 1.23 mmol) in methanol (30 ml) was prepared and then cooled to 0°C. A cooled methanolic solution (10 ml) of 1,2-diaminocyclohexane was added dropwise to the mixture over a period of 15 minutes. The amount of 1,2-diaminocyclohexane employed were 1.23 mmol (0.15 ml), 2.46 mmol (0.30 ml), 3.69 mmol (0.45 ml) and 4.92 mmol (0.60 ml). The reaction mixture was stirred for 15 minutes and neutralized by adding a solution of 2M NaOH (1.23 ml, 2.46 mmol). The mixture was then stirred at 0°C for 30 minutes. Upon standing at room temperature overnight, CuL_2 precipitated and was subsequently isolated by filtration and dried under vacuum. CuL_2 was obtained as purple crystals. The yield of CuL_2 obtained from using 4.92 mmol (0.60 ml) of 1,2-diaminocyclohexane was 0.45 g (88%): IR (KBr, cm^{-1}); 3424, 3192, 2932, 2862, 1615 (C=N), 1544, 1450, 1355, 1225, 1128, 989, 846. MALDI-TOF MS (m/z); 440, 418, 435, 440, 456. Elemental analysis: Calcd for $C_{20}H_{19}CuN_2O_4Na$ (438); C 54.85; H 4.37; N 6.40. Found: C 54.74; H 5.24; N 6.44.

2.3.5 Investigation of polymerization reaction between 4,4′-dihydroxysalcyclohexane metal complexes and prepolymer

2.3.5.1 Differential scanning calorimetry (DSC)

A mixture of tolylene 2,4-diisocyanate terminated poly(1,4-butanediol) prepolymer, MW 900 (PB900) (0.135 g, 0.15 mmol) and ZnL_2 (0.063 g, 0.15 mmol) was mixed well to become homogeneous then using differential scanning calorimetry (DSC) to obtain the polymerization temperature.

2.3.5.2 IR spectroscopy

2.3.5.2.1 Polymerization reaction between ZnL_2 and prepolymer

Into a watch glass covered by aluminum foil containing 0.270 g (0.30 mmol) PB900 was added 0.125 g (0.30 mmol) of ZnL_2. The mixture was mixed well to become homogeneous and heated at 120°C in an oven. The polymerization reaction was followed by using IR spectroscopy. After the reaction was completed, the polymer was purified by dissolving in DMSO. A mixture of methanol and water was then added to this solution to precipitate the polymer. The precipitated polymer was filtered and dried in vacuum.

2.3.5.2.2 Polymerization reaction between CuL_2 and prepolymer

The experiment was performed according to the same procedure described in experiment 2.3.5.2.1 using 0.125 g (0.30 mmol) of CuL_2 instead of ZnL_2.

2.3.6 Synthesis of polyurethanes containing 4,4′-dihydroxysalcyclohexane metal complexes

2.3.6.1 Synthesis of zinc-containing polyurethane from the reaction between ZnL_2 and PB900 (Zn-PB900)

Into a watch glass covered by aluminum foil containing 0.270 g (0.30 mmol) of PB900 was added 0.125 g (0.30 mmol) of ZnL_2 followed by two drops of dibutyltin dilaurate (DBTDL). The mixture was mixed well to become homogeneous and heated at 120°C in an oven for 15 hours. After the reaction was completed, the polyurethane was purified by dissolving in DMSO. A mixture of methanol and water was then added to this solution to precipitate the polymer. The precipitated polymer was filtered and dried in vacuum. The polyurethane was obtained as yellow elastomer. The yield was 0.22 g (56%): IR (KBr, cm^{-1}); 3301 (NH), 2927, 2856, 1726 (C=O), 1602 (C=N), 1599, 1542, 1446, 1367, 1223, 1108, 994, 850, 765.

2.3.6.2 Synthesis of copper-containing polyurethane from the reaction between CuL_2 and PB900 (Cu-PB900)

The experiment was performed according to the same procedure described in experiment 2.3.6.1 using 0.125 g (0.30 mmol) of CuL_2 instead of ZnL_2. The polyurethane was obtained as dark purple elastomer. The yield was 0.30 g (76%): IR (KBr, cm^{-1}); 3289 (NH), 2928, 2857, 1720 (C=O), 1615 (C=N), 1540, 1448, 1359, 1225, 1118, 992, 846, 759.

2.3.6.3 Synthesis of zinc-containing polyurethane from the reaction between ZnL_2 and PP1000 (Zn-PP1000)

The experiment was performed according to the same procedure described in experiment 2.3.6.1 using 0.300 g (0.30 mmol) of tolylene 2,4-diisocyanate terminated poly(propylene glycol) prepolymer, MW 1000 (PP1000) instead of PB900. The polyurethane was obtained as yellow elastomer. The yield was 0.25 g (59%): IR (KBr, cm^{-1}); 3301 (NH), 2972, 2929, 2862, 1718 (C=O), 1602 (C=N), 1541, 1448, 1374, 1225, 1096, 934, 848, 765.

2.3.6.4 Synthesis of copper-containing polyurethane from the reaction between CuL_2 and PP1000 (Cu-PP1000)

The experiment was performed according to the same procedure described in experiment 2.3.6.1 using 0.125 g (0.30 mmol) of CuL_2 instead of ZnL_2 and 0.300 g (0.30 mmol) of PP1000 instead of PB900. The polyurethane was obtained as dark purple elastomer. The yield was 0.35 g (82%): IR (KBr, cm^{-1}); 3289 (NH), 2967, 2926, 2863, 1725 (C=O), 1615 (C=N), 1542, 1450, 1373, 1226, 1112, 931, 844, 759.

2.3.7 Synthesis of polyurethane-ureas without metal in the main chain

2.3.7.1 Synthesis of polyurethane-urea from the reaction between *m*-xylylenediamine and PB900 (Xy-PB900)

The experiment was performed according to the same procedure described in experiment 2.3.6.1 using 0.041 g (0.30 mmol) of *m*-xylylenediamine instead of ZnL_2. The polyurethane-urea was obtained as white elastomer. The yield was 0.28 g (90%): IR (KBr, cm^{-1}); 3319 (NH), 2930, 2857, 1728 (C=O of -NCOO-), 1639 (C=O of -NCON-), 1553, 1476, 1445, 1370, 1229, 1109, 878, 770, 668.

2.3.7.2 Synthesis of polyurethane-urea from the reaction between *m*-xylylenediamine and PB1000 (Xy-PP1000)

The experiment was performed according to the same procedure described in experiment 2.3.6.1 using 0.041 g (0.30 mmol) of *m*-xylylenediamine instead of ZnL_2 and 0.300 g (0.30 mmol) of PP1000 instead of PB900. The polyurethane-urea was obtained as white elastomer. The yield was 0.32 g (94%): IR (KBr, cm^{-1}); 3319 (NH), 2971, 2926, 2867, 1728 (C=O of -NCOO-), 1645 (C=O of -NCON-), 1547, 1451, 1375, 1230, 1097, 930, 770, 663.

2.3.8 Synthesis of polyurethane-ureas containing 4,4′-dihydroxysalcyclohexane metal complexes

2.3.8.1 Synthesis of zinc-containing polyurethane-urea from the reaction between ZnL_2, *m*-xylylenediamine and PB900 (Zn-Xy-PB900)

Into a watch glass covered by aluminum foil containing 0.270 g (0.30 mmol) of PB900 was added 0.063 g (0.15 mmol) of ZnL_2 and 0.020 g (0.15 mmol) of *m*-xylylenediamine followed by two drops of dibutyltin dilaurate (DBTDL). The mixture was mixed well to become homogeneous and heated at 120°C in an oven for 15 hours. After the reaction was completed, the polyurethane-urea was purified by

dissolving in DMSO. A mixture of methanol and water was then added to this solution to precipitate the polymer. The precipitated polymer was filtered and dried in vacuum. The polyurethane-urea was obtained as yellow elastomer. The yield was 0.21 g (59%): IR (KBr, cm^{-1}); 3323 (NH), 2924, 2856, 1722 (C=O of -NCOO-), 1639 (C=O of -NCON-), 1602 (C=N), 1543, 1451, 1371, 1226, 1104, 882, 769, 672.

2.3.8.2 Synthesis of copper-containing polyurethane-urea from the reaction between CuL_2, *m*-xylylenediamine and PB900 (Cu-Xy-PB900)

The experiment was performed according to the same procedure described in experiment 2.3.7.1 using 0.062 g (0.15 mmol) of CuL_2 instead of ZnL_2. The polyurethane-urea was obtained as purple elastomer. The yield was 0.29 g (82%): IR (KBr, cm^{-1}); 3311 (NH), 2929, 2857, 1725 (C=O of -NCOO-), 1645 (C=O of -NCON-), 1607 (C=N), 1544, 1449, 1369, 1226, 1110, 998, 882, 771, 671.

2.3.8.3 Synthesis of zinc-containing polyurethane-urea from the reaction between ZnL_2, *m*-xylylenediamine and PP1000 (Zn-Xy-PP1000)

The experiment was performed according to the same procedure described in experiment 2.3.7.1 using 0.300 g (0.30 mmol) of PP1000 instead of PB900. The polyurethane-urea was obtained as yellow elastomer. The yield was 0.26 g (68%): IR (KBr, cm^{-1}); 3323 (NH), 2971, 2923, 2859, 1725 (C=O of -NCOO-), 1639 (C=O of -NCON-), 1602 (C=N), 1543, 1457, 1376, 1228, 1100, 928, 866, 769, 663.

2.3.8.4 Synthesis of copper-containing polyurethane-urea from the reaction between CuL_2, *m*-xylylenediamine and PP1000 (Cu-Xy-PP1000)

The experiment was performed according to the same procedure described in experiment 2.3.7.1 using 0.062 g (0.15 mmol) of CuL_2 instead of ZnL_2 and 0.300 g (0.30 mmol) of PP1000 instead of PB900. The polyurethane-urea was obtained as

purple elastomer. The yield was 0.34 g (89%): IR (KBr, cm^{-1}); 3311 (NH), 2967, 2926, 2864, 1724 (C=O of -NCOO-), 1607 (C=N), 1543, 1451, 1374, 1227, 1105, 931, 812, 771, 664.