

CHAPTER II

EXPERIMENTAL

2.1 Materials

All reagents and solvents were of analytical grade quality. The solvents were obtained from Labscan Asia Co,Ltd. Manganese (II) acetate tetrahydrate, nickel (II) acetate tetrahydrate, cobalt (II) acetate tetrahydrate, 2,4-dihydroxybenzaldehyde, 1,2-diaminocyclohexane, pentaethylenediamine, tolylene 2,4-diisocyanate terminated poly(propylene glycol) prepolymer MW1000 (PP), tolylene 2,4-diisocyanate terminated poly(1,4-butanediol) prepolymer MW 900 (PB), *m*-xylylenediamine and dibutyltin dilaurate were obtained from Fluka and Aldrich. All chemicals were used without further purification.

2.2 Analytical Procedures

The IR spectra were recorded on Nicolet Impact 410 FTIR spectrometer at room temperature by the potassium bromide (KBr) method. Elemental analyses were carried out using Perkin-Elmer 2400 CHN Analyzer. Matrix-assisted laser desorption ionization-time of flight (MALDI-TOF) mass spectra were obtained on a Bruker Biflex mass spectrometer by using α -cyanocinnamic acid as the matrix. The percent weight loss of polymers was analyzed by heating samples (50 - 60 mg) in a hot air oven at 170°C for 8 hours. Thermogravimetric analysis was examined using a Netzsch STA 409C thermogravimetric analyzer in 1 : 1 air/nitrogen atmosphere with the heating rate 20°C/min. Solubility of polymers was tested in various polar and non-polar solvents by 10 mg samples being added to 2 ml of solvent and kept overnight.

2.3 Synthetic Procedure

2.3.1 Preparation of 4,4'-dihydroxysalpentaen metal complexes (MnL_1)

2.3.1.1 Preparation of 4,4'-dihydroxysalpentaen manganese complex (MnL_1)

A cool (0 - 10°C) solution of pentaethylenhexamine (0.24 ml, 1 mmol) in methanol (10 ml) was added dropwise to a stirred cool solution of 2,4-dihydroxybenzaldehyde (0.276 g, 2 mmol) and manganese (II) acetate tetrahydrate (0.245 g, 1 mmol) in methanol (10 ml) and the mixture was stirred for 10 minutes. The mixture was neutralized by addition of 2M potassium hydroxide solution (1 ml, 2 mmol) and stirred for another 30 minutes. The solution was allowed to stand at room temperature for 3 hours. The brown powder of MnL_1 precipitated and was then isolated by filtration and dried *in vacuo*. The yield of MnL_1 was 0.343 g (65%). IR (KBr, cm^{-1}); 3392, 1576, 1480, 1361, 1230, 1186, 1124, 980, 852.

2.3.1.2 Preparation of 4,4'-dihydroxysalpentaen cobalt complex (CoL_1)

A cool (0 - 10°C) solution of pentaethylenhexamine (0.24 ml, 1 mmol) in methanol (10 ml) was added dropwise to a stirred cool solution of 2,4-dihydroxybenzaldehyde (0.276 g, 2 mmol) and manganese (II) acetate tetrahydrate (0.249 g, 1 mmol) in methanol (10 ml) and the mixture was stirred for 10 minutes. The mixture was neutralized by addition of 2M potassium carbonate solution (1 ml, 1 mmol) and stirred for another 30 minutes. The solution was allowed to stand at room temperature for 3 hours. The brown powder of CoL_1 precipitated and was then isolated by filtration and dried *in vacuo*. The yield of CoL_1 was 0.212 g (40%). IR (KBr, cm^{-1}); 3415, 1587, 1481, 1364, 1232, 1126, 842.

2.3.2 Preparation of 4,4'-dihydroxysalicyclohexane metal complexes (ML₂)

2.3.2.1 Preparation of 4,4'-dihydroxysalicyclohexane manganese complex (MnL₂)

A cool (0 - 10°C) solution of 1,2-diaminocyclohexane (0.13 ml, 1.07 mmol) in methanol (10 ml) was added dropwise to a stirred cool solution of 2,4-dihydroxybenzaldehyde (0.295 g, 2.14 mmol) and manganese (II) acetate tetrahydrate (0.262 g, 1.07 mmol) in methanol (15 ml) and the mixture was stirred for 15 minutes. The mixture was neutralized by addition of 2M sodium hydroxide solution (1.1 ml, 2.14 mmol) and stirred for another 1 hour. The brown powder of MnL₂ salt precipitated and was then isolated by filtration. The filtrate solution was allowed to stand at room temperature for 24 hours and the dark brown crystal of MnL₂ was then precipitate. The MnL₂ crystal was isolated by filtration and dried *in vacuo* (0.167 g, 34%). IR (KBr, cm⁻¹) 3411, 2932, 2855, 1579, 1483, 1358, 1299, 1254, 1233, 1186, 1126; MALDI-TOF MS (m/z); 358.2, 378.8, 391.1, 406.5 (C₂₀H₂₀MnN₂O₄), 429.4, 461.5; Anal. calcd. for C₂₀H₂₀MnN₂O₄·1.5H₂O: C 55.50; H 5.52; N 6.88, found C 55.30; H 5.34; N 6.45.

2.3.2.2 Preparation of 4,4'-dihydroxysalicyclohexane nickel complex (NiL₂)

A cool (0 - 10°C) solution of 1,2-diaminocyclohexane (0.52 ml, 4.28 mmol) in methanol (10 ml) was added dropwise to a stirred cool solution of 2,4-dihydroxybenzaldehyde (0.295 g, 2.14 mmol) and nickel (II) acetate tetrahydrate (0.266 g, 1.07 mmol) in methanol (15 ml) and the mixture was stirred for 15 minutes. The mixture was neutralized by addition of 2M sodium hydroxide solution (1.1 ml, 2.14 mmol) and stirred for another 1 hour. The dark orange crystal of NiL₂ precipitated from solution upon standing at room temperature overnight (20 hours). The NiL₂ crystal was isolated by filtration and dried *in vacuo* (0.419 g, 85%). IR (KBr, cm⁻¹) 3406, 3157, 2932, 1611,

1549, 1452, 1355, 1228, 1189, 1127; MALDI-TOF MS (m/z); 410.8 ($C_{20}H_{20}NiN_2O_4$), 433.9 ($C_{20}H_{19}NiN_2O_4Na$), 449.1; Anal. calcd. for $C_{20}H_{19}N_2NiO_4Na \cdot CH_3OH$: C 54.23; H 4.98; N 6.02, found C 54.70; H 5.68; N 6.07.

2.3.3 Preparation of metal-containing polyurethanes

2.3.3.1 Preparation of metal-containing polyurethane from MnL_2 and PB (Mn-PB)

Tolylene 2,4-diisocyanate terminated poly(1,4-butanediol) prepolymer (PB) (0.180 g, 0.20 mmol) was mixed with dibutyltin dilaurate (DBTDL) (0.051 g, 0.08 mmol) as a catalyst in a watch glass. MnL_2 (0.087 g, 0.20 mmol) was added and the mixture was stirred well to become homogeneous. This mixture was heated in a hot air oven at $90^\circ C$ for 17 hours. After the reaction was completed, the polymer was purified by dissolving in DMSO and a mixture of methanol and water was added to precipitate the polymer. The product was filtered, washed several times with methanol and dried *in vacuo*. The polymer was obtained as brown elastomer (0.214 g, 80%). IR (KBr, cm^{-1}); 3388, 2928, 2858, 1721, 1606, 1544, 1450, 1373, 1228, 1109, 883, 811, 770.

2.3.3.2 Preparation of metal-containing polyurethane from MnL_2 and PP (Mn-PP)

The experiment was performed according to the procedure described in 2.3.3.1 employing tolylene 2,4-diisocyanate terminated poly(propylene glycol) prepolymer (PP) (0.200 g, 0.20 mmol) and MnL_2 (0.087 g, 0.20 mmol) as starting materials and dibutyltin dilaurate (0.051 g, 0.08 mmol) as a catalyst. The precipitated polymer was filtered and dried *in vacuo*. The polymer was

obtained as brown elastomer (0.144 g, 50%). IR (KBr, cm^{-1}); 3338, 2926, 2859, 1724, 1545, 1452, 1414, 1376, 1229, 1104, 934, 816, 764.

2.3.3.3 Preparation of metal-containing polyurethane from NiL_2 and PB (Ni-PB)

The experiment was performed according to the procedure described in 2.3.3.1 employing PB (0.180 g, 0.20 mmol) and NiL_2 (0.092 g, 0.20 mmol) as starting materials and dibutyltin dilaurate (0.051 g, 0.08 mmol) as a catalyst. The precipitated polymer was filtered and dried *in vacuo*. The polymer was obtained as orange elastomer (0.122 g, 45%). IR (KBr, cm^{-1}); 3381, 2932, 2859, 1704, 1612, 1542, 1449, 1362, 1229, 1125, 1001, 875, 847.

2.3.3.4 Preparation of metal-containing polyurethane from NiL_2 and PP (Ni-PP)

The experiment was performed according to the procedure described in 2.3.3.1 employing PP (0.200 g, 0.20 mmol) and NiL_2 (0.092 g, 0.20 mmol) as starting materials and dibutyltin dilaurate (0.051 g, 0.08 mmol) as a catalyst. The precipitated polymer was filtered and dried *in vacuo*. The polymer was obtained as orange elastomer (0.172 g, 59%). IR (KBr, cm^{-1}); 3445, 2925, 2858, 1721, 1613, 1547, 1456, 1375, 1231, 1092, 1011, 929, 837.

2.3.4 Preparation of metal-containing polyurethane-ureas

2.3.4.1 Preparation of metal-containing polyurethane-urea from MnL_2 , PB and *m*-xylylenediamine (Mn-PB-X)

Toluene 2,4-diisocyanate terminated poly(1,4-butanediol) prepolymer (PB) (0.250 g, 0.28 mmol) was mixed with dibutyltin dilaurate (DBTDL) (0.071 g, 0.11 mmol) as catalyst in a watch glass. MnL_2 (0.061 g, 0.14 mmol)

was added and the mixture was stirred well to become homogeneous. Then *m*-xylylenediamine (0.019 g, 0.14 mmol) was added and the reaction mixture was mixed thoroughly. This mixture was heated in a hot air oven at 90°C for 17 hours. After the reaction was completed, the polymer was purified by dissolving in DMSO and a mixture of methanol and water was added to precipitate the polymer. The product was filtered, washed several times with methanol and dried *in vacuo*. The polymer was obtained as brown elastomer (0.182 g, 55%). IR (KBr, cm⁻¹); 3343, 2929, 2857, 1721, 1658, 1602, 1542, 1448, 1415, 1372, 1226, 1109, 872, 811, 770.

2.3.4.2 Preparation of metal-containing polyurethane-urea from MnL₂, PP and *m*-xylylenediamine (Mn-PP-X)

The experiment was performed according to the procedure described in 2.3.4.1 employing tolylene 2,4-diisocyanate terminated poly(propylene glycol) prepolymers (PP) (0.264 g, 0.26 mmol), MnL₂ (0.056 g, 0.13 mmol) and *m*-xylylenediamine (0.019 g, 0.13 mmol) as starting materials and dibutyltin dilaurate (0.064 g, 0.10 mmol) as a catalyst. The precipitated polymer was filtered and dried *in vacuo*. The polymer was obtained as brown elastomer (0.197 g, 58%). IR (KBr, cm⁻¹); 3338, 2971, 2927, 1720, 1653, 1545, 1452, 1376, 1230, 1102, 867, 811, 765.

2.3.4.3 Preparation of metal-containing polyurethane-urea from NiL₂, PB and *m*-xylylenediamine (Ni-PB-X)

The experiment was performed according to the procedure described in 2.3.4.1 employing PB (0.250 g, 0.28 mmol), NiL₂ (0.065 g, 0.14 mmol) and *m*-xylylenediamine (0.019 g, 0.14 mmol) as starting materials and dibutyltin dilaurate (0.071 g, 0.11 mmol) as a catalyst. After the reaction was completed, the polymer was purified by dissolving in DMSO and cold water (0 - 10°C) was added to precipitate the polymer. The precipitated polymer was filtered

and dried *in vacuo*. The polymer was obtained as orange elastomer (0.160 g, 48 %). IR (KBr, cm^{-1}); 3311, 2929, 2857, 1725, 1645, 1607, 1542, 1452, 1372, 1227, 1111, 872, 771.

2.3.4.4 Preparation of metal-containing polyurethane-urea from NiL_2 , PP and *m*-xylylenediamine (Ni-PP-X)

The experiment was performed according to the procedure described in 2.3.4.1 employing PP (0.264 g, 0.26 mmol), NiL_2 (0.060 g, 0.13 mmol) and *m*-xylylenediamine (0.018 g, 0.13 mmol) as starting materials and dibutyltin dilaurate (0.064 g, 0.10 mmol) as a catalyst. The precipitated polymer was filtered and dried *in vacuo*. The polymer was obtained as orange elastomer (0.174 g, 51%). IR (KBr, cm^{-1}); 3318, 2925, 2859, 1720, 1607, 1552, 1453, 1376, 1231, 1099, 930, 767.

2.3.5 Preparation of polyurea without metal complex in the main chain

2.3.5.1 Preparation of polyurea without metal complex in the main chain from PB and *m*-xylylenediamine (PB-X)

Tolylene 2,4-diisocyanate terminated poly(1,4-butanediol) prepolymers (PB) (0.180 g, 0.20 mmol) was mixed with dibutyltin dilaurate (0.051 g, 0.08 mmol) as a catalyst in a watch glass. The *m*-xylylenediamine (0.027 g, 0.20 mmol) was added and the mixture was stirred well to become homogeneous. This mixture was heated in a hot air oven at 90°C for 17 hours. After the reaction was completed, the polymer was purified by dissolving in DMSO and a mixture of methanol and water was added to precipitate the polymer. The product was filtered, washed several times with methanol and dried *in vacuo*. The polymer was obtained as white elastomer (0.190 g, 92%). IR (KBr, cm^{-1}); 3318, 2930, 2858, 1724, 1639, 1599, 1554, 1372, 1230, 1108, 1006, 878, 816, 770.

2.3.5.2 Preparation of polyurea without metal complex in the main chain from PP and *m*-xylylenediamine (PP-X)

The experiment was performed according to the procedure described in 2.3.5.1 employing PP (0.200 g, 0.20 mmol) and *m*-xylylenediamine (0.027 g, 0.20 mmol) as starting materials and dibutyltin dilaurate (0.051 g, 0.08 mmol) as a catalyst. The precipitated polymer was filtered and dried *in vacuo*. The polymer was obtained as white elastomer (0.188 g, 83%). IR (KBr, cm^{-1}); 3321, 2971, 2926, 2867, 1724, 1645, 1599, 1547, 1472, 1451, 1375, 1230, 1098, 929, 872, 811, 770.

