

CHAPTER III

EXPERIMENTAL

3.1 Materials

All reagents and solvents were of analytical grade quality. The solvents were obtained from Lab-Scan. Dimethylsulphoxide (DMSO) was purified by distillation under reduced pressure over calcium hydride and stored over molecular sieves. Zinc (II) acetate dihydrate, nickel (II) acetate tetrahydrate, 2,4-dihydroxybenzaldehyde, triethylenetetramine, 4,4'-methylenebis(phenyl isocyanate) (MDI), methylene dianiline (MTDA), hexamethylenediamines (HMDA), bisphenol A (BA) and 1,6-hexanediol (HD) and dibutyltin dilaurate (DBTDL) were obtained from Fluka and Aldrich. All chemicals were used as received without any purification.

3.2 Measurements

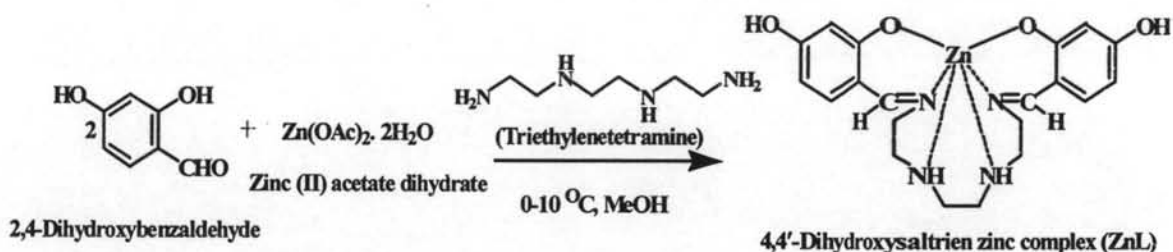
IR spectra of the samples were recorded on a Nicolet Impact 410 FTIR spectrophotometer at room temperature with potassium bromide (KBr) disk method. The samples were scanned over a range of 500-4000 cm^{-1} at a resolution of 16 cm^{-1} and the number of scan was 32. The measurement was controlled by Omnic Software. $^1\text{H-NMR}$ spectra were recorded in CDCl_3 and $\text{DMSO-}d_6$ on a Varian Mercury-400 BB instrument. Chemical shifts are given in parts per million (ppm) using the proton residual as internal reference. Thermogravimetric analysis (TGA) was examined using a Netzsch STA 409C thermogravimetric analyzer at heating rate 20 $^\circ\text{C}/\text{min}$ under air/nitrogen (50/50) atmosphere. All samples were held in the analyzer at 120 $^\circ\text{C}$ for 15 min and measured from temperature range 20 $^\circ\text{C}$ to 1000 $^\circ\text{C}$. The result of thermal stability was reported in percentage weight loss of polymers. Differential scanning calorimetric (DSC) analysis was carried out using a Netzsch DSC 204 F₁ phonic differential scanning calorimeter at heating rate of 10 $^\circ\text{C}/\text{min}$ under nitrogen atmosphere. Glass transition temperatures (T_g) were read at the middle of the transition in the heat capacity taken from the heating DSC traces. A sample was scanned from room temperature to 250 $^\circ\text{C}$. All the samples were heated in DSC cell

using a closed aluminum pan. X-ray diffractometer (XRD) used in study was Bruker model D8 Discover with nickel filtered $\text{CuK}\alpha$ radiation (40kV, 40mA) at an angle of 2θ range from 5 to 40° . The scan speed was $1.2^\circ/\text{min}$ and scan step was 0.02° . Solubility of polymer was tested in various polar and nonpolar solvents by placing 10 mg of samples to 2 mL of a solvent. Maximum solubility of polymers was tested in DMSO by addition of samples to 1 mL of DMSO. Inherent viscosity (η_{inh}) of the polymers was determined at concentration of $0.5\text{g}/100\text{ mL}$ in DMSO at 40°C using a Cannon-Fenske viscometer according to ASTM D2270. Limiting oxygen index (LOI) values were obtained on an apparatus following ASTM-D2863-70 and using a modified procedure as described in the literature [30].

3.3 Synthetic procedures

3.3.1 Synthesis of hexadentate Schiff base metal complexes (ML)

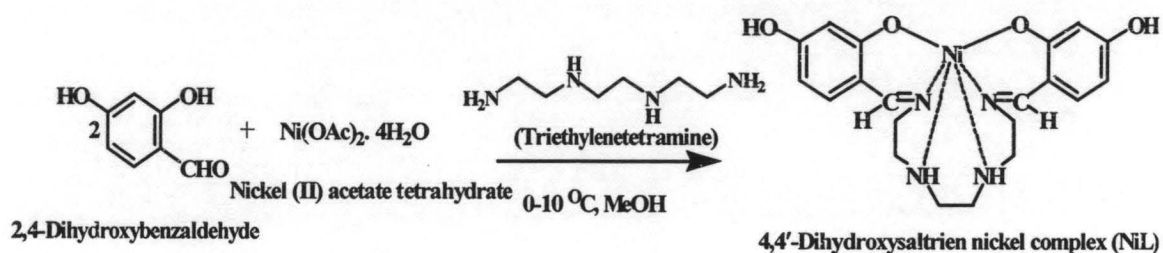
3.3.1.1 Synthesis of 4,4'-dihydroxysaltrien zinc complex (ZnL)



The preparation of ZnL was performed according to the method reported in the literature [28]. The mixture of 2,4-dihydroxybenzaldehyde (0.309 g, 2.22 mmol) and zinc (II) acetate dihydrate (0.244 g, 1.11 mmol) was stirred in methanol (25 mL) and then cooled to 0°C for 10 minutes. A cool 0°C solution of triethylenetetramine (0.165 mL, 1.11 mmol) in methanol (10 mL) was added dropwise to a mixture over a period of 5 minutes. This mixture was stirred for 10 minutes and neutralized by adding a solution of 1 N potassium carbonate (1.11 mL, 1.11 mmol) and stirred at 0°C for 30 minutes. The pink powder which precipitated immediately when adding solution of potassium carbonate was isolated by filtration. The yellow solution of

filtrate was allowed to stand at room temperature for 4 to 6 hours. ZnL was crystallized from yellow solution and subsequently isolated by filtration and dried under vacuum to remove solvent. The yield of ZnL was obtained as a yellow crystal (0.18 g, 36%): IR (KBr, cm^{-1}); 3313 (NH), 2856, 1630 (C=N), 1602, 1449, 1379, 1278, 1217, 1120, 986, 902, 842, 788, 660, 630, 563. $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6 + \text{CDCl}_3$, ppm); δ 9.06 (s, 2H, OH), 8.10 (s, 2H, CH=N), 6.85 (d, 2H, ArH, $J = 8.18$ Hz), 5.82 (d, 2H, ArH, $J = 7.78$ Hz), 5.77 (s, 2H, ArH), 3.70-3.66 (t, 2H, CH_2 , $J = 13.03$ Hz), 3.14-3.13 (m, 2H, CH_2), 2.94 (s, 2H, CH_2), 2.80 (d, 2H CH_2 , $J = 6.48$ Hz), 2.54-2.53 (m, 2H, CH_2), 2.40 (d, 2H, CH_2 , $J = 6.88$ Hz). $^{13}\text{C-NMR}$ (500 MHz, $\text{DMSO-}d_6$, ppm); δ 173.56, 165.78 (CH=N), 161.54, 136.17, 113.63, 106.44, 101.17, 54.42, 45.74, 43.40.

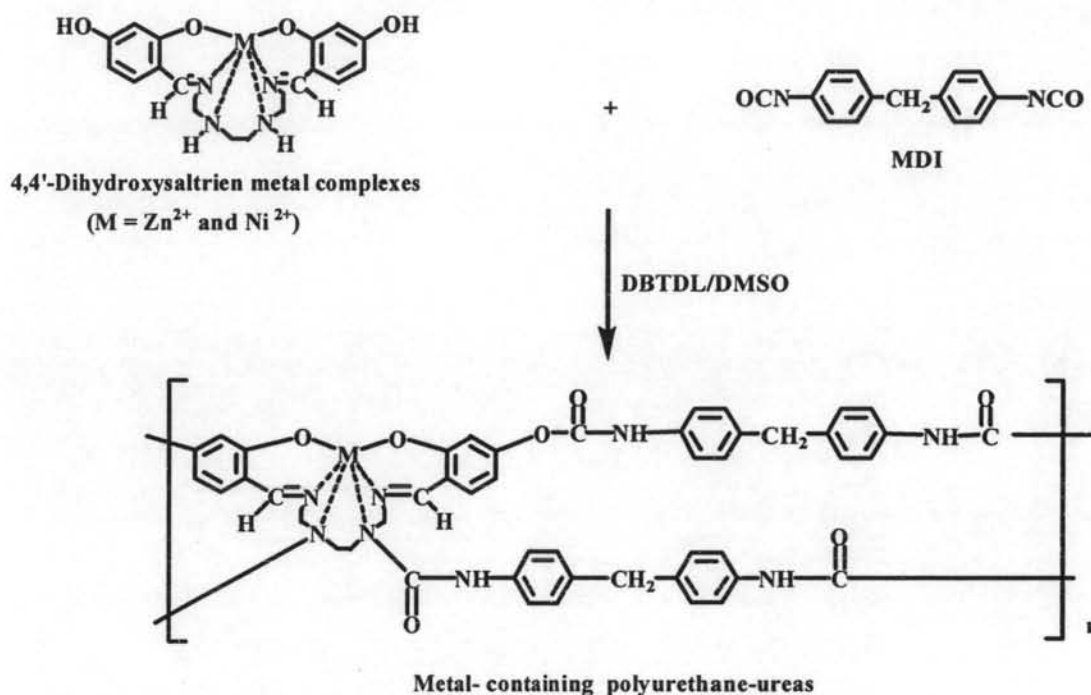
3.3.1.2 Synthesis of 4,4'-dihydroxysaltrien nickel complex (NiL)



The experiment was performed according to the procedure described in experiment 3.3.1.1 employing nickel (II) acetate tetrahydrate (0.281 g, 1.128 mmol) instead of zinc (II) acetate dihydrate. The green crystal of nickel complex (NiL) was filtered and dried *in vacuum* (0.35 g, 70%): IR (KBr, cm^{-1}); 3314(NH), 2860, 1634 (C=N), 1601, 1450, 1374, 1330, 1272, 1215, 1119, 984, 937, 905, 840, 789, 657, and 563.

3.3.2 Synthesis of metal-containing polyurethane-ureas (ML-PUUs) and copolyurethane-ureas (ML-coPUUs)

3.3.2.1 Synthesis of metal-containing polyurethane-ureas from the reaction between ML and MDI



Polyurethane-ureas were synthesized by polyaddition reaction between ML; ($M = \text{Zn}^{2+}$ and Ni^{2+}) and MDI. A typical procedure for the preparation of ML-PUUs is as follows: ML was dissolved in 1 mL of dried DMSO in a 50 mL, two-necked round bottomed flask equipped with a nitrogen inlet. Then, MDI was dissolved in DMSO (2 mL) and added to the ML solution. Dibutyltin dilaurate (DBTDL) (0.30 mL, 0.50 mmol) was as a catalyst and the reaction was maintained at 90 °C for 24 and 96 hours. The composition of starting material in the preparation of ML-PUUs is shown in Table 3.1. The polymer was precipitated by pouring the reaction mixture into distilled water. Then, the polymer was filtered through suction and washed with distilled methanol several times and dried *in vacuum*. The polymer was obtained as red-orange powder (ZnL-PUU) or red-brown powder (NiL-PUU). The yield obtained for the polymer was in the range 62-97%.

Table3.1 Composition of starting materials in the preparation of ML-PUUs

Polymer codes	Wt. of ZnL (g)	Wt. of NiL (g)	Wt. of MDI (g)	Reaction Time (hr)	Yield (%)
ZnL-MDI (1:2)	0.1410	-	0.1558	24	72
ZnL-MDI (1:2)	0.1410	-	0.1556	96	96
NiL-MDI (1:2)	-	0.1430	0.1616	24	62
NiL-MDI (1:2)	-	0.1430	0.1610	96	87

In the polymer codes, ZnL and NiL refers to metal complexes. MDI represents 4,4'-methylenebis(phenyl isocyanate). The last two digits refer to the mole ratios of the polymer compositions.

ZnL-MDI (1:2), 24 hr: IR (KBr, cm^{-1}); 3341 (NH), 2923, 2848, 1692 (C=O), 1600 (C=N), 1512, 1450, 1411, 1309, 1230, 1120, 1011, 980, 909, 813, 751, 623, 512.

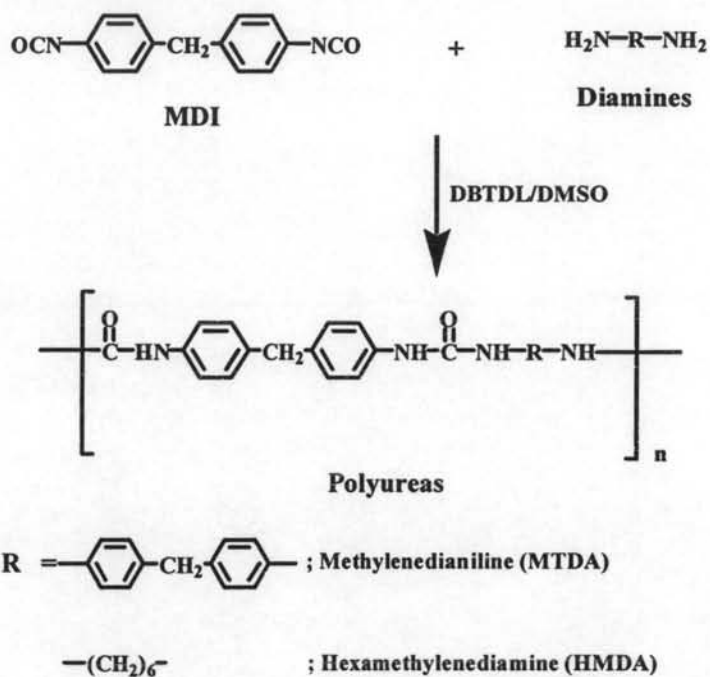
ZnL-MDI (1:2), 96 hr: IR (KBr, cm^{-1}); 3334 (NH), 2922, 2854, 1700 (C=O), 1600 (C=N), 1512, 1446, 1410, 1309, 1230, 1123, 1019, 983, 909, 815, 753, 625, 512.

$^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$ + CDCl_3 , ppm); δ 8.56 (CH=N), 7.33-7.29 (Ar-H), 7.25 (Ar-H), 7.09-7.03 (Ar-H), 6.81 (Ar-H), 6.47 (Ar-H).

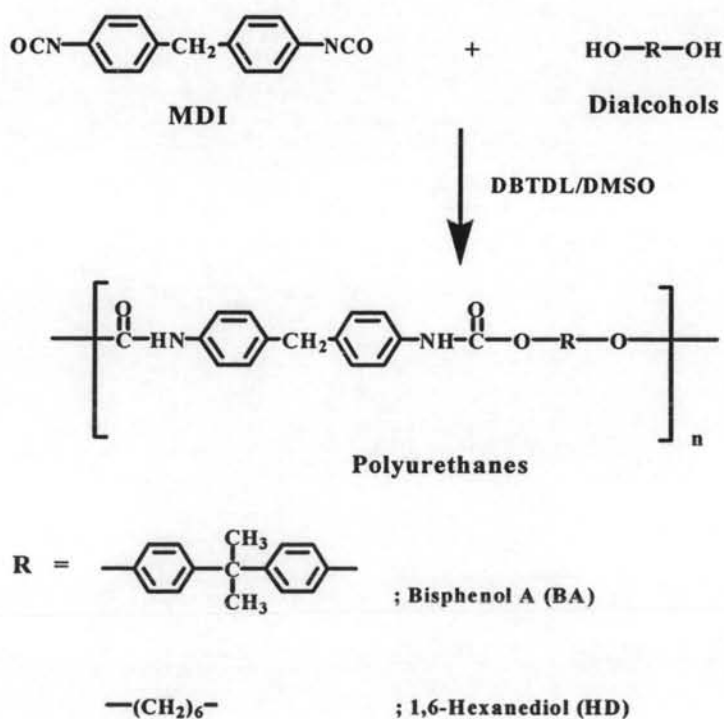
NiL-MDI (1:2), 24 hr: IR (KBr, cm^{-1}); 3322 (NH), 2923, 2848, 1699 (C=O), 1603 (C=N), 1542, 1513, 1450, 1410, 1310, 1232, 1116, 1017, 950, 813, 758, 505.

NiL-MDI (1:2), 96 hr: IR (KBr, cm^{-1}); 3333 (NH), 2922, 2848, 1699 (C=O), 1603 (C=N), 1542, 1512, 1449, 1410, 1310, 1232, 1127, 1015, 952, 824, 761, 512.

3.3.2.2 Synthesis of polyureas from the reaction between MDI and diamines



3.3.2.3 Synthesis of polyurethanes from the reaction between MDI and dialcohols



MDI and diamines or dialcohols was dissolved in DMSO (3 mL). Dibutyltin dilaurate (DBTDL) (0.30 mL, 0.50 mmole) was added as a catalyst and the reaction was carried out under nitrogen atmosphere at 90 °C for 96 hours. The polymer was precipitated by pouring the reaction mixture into distilled water. Then, the polymer was filtered through suction and washed with distilled methanol several times. The resulted powder was dried *in vacuum*. The polymers were obtained as yellowish white powder. The compositions of starting materials in the preparation of polymers are shown in Table 3.2. The yield obtained for the polymer was in the range 45-77 %.

Table3.2 Composition of starting materials in the preparation of polyureas and polyurethanes

Polymer codes	Wt. of MDI (g)	Wt. of diamine (g)	Wt. of dialcohols (g)	Yield (%)
MDI-MTDA (1:1)	0.1731	0.1377	-	77
MDI-HMDA(1:1)	0.2110	0.0978	-	73
MDI-BA (1:1)	0.2521	-	0.2282	45
MDI-HD (1:1)	0.3530	-	0.1663	76

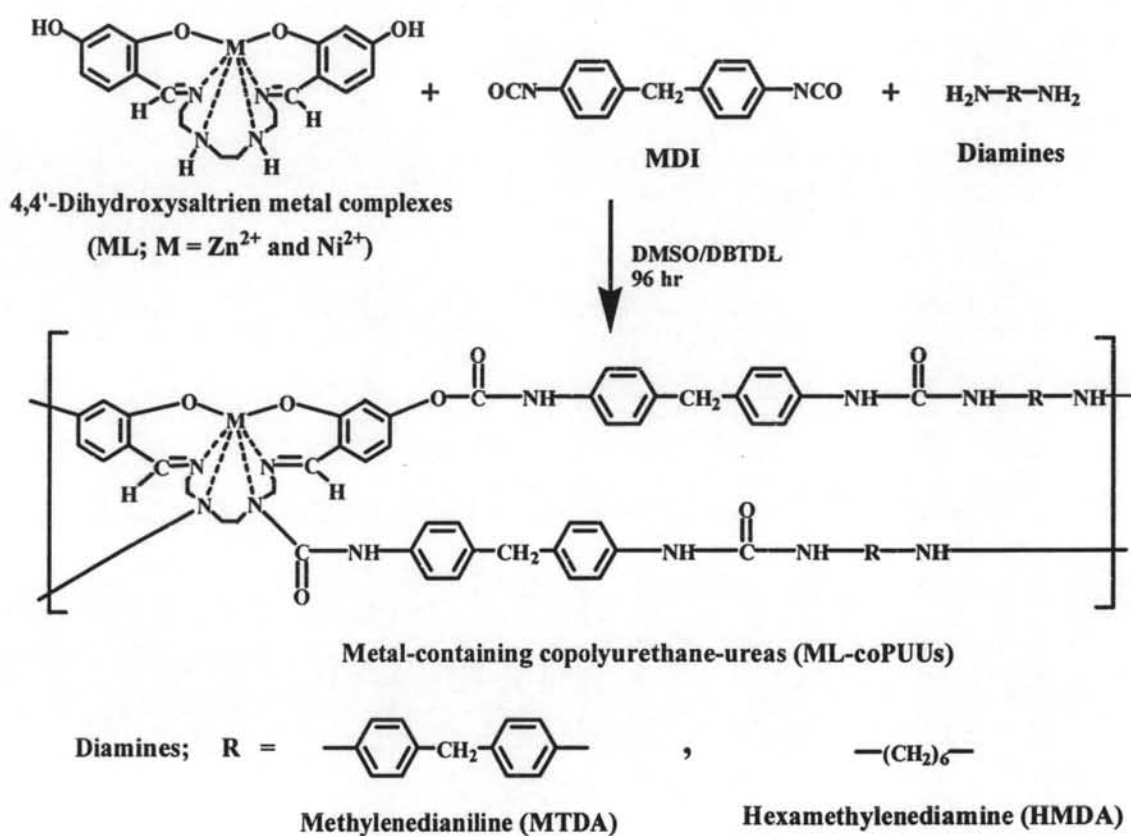
MDI-MTDA (1:1): IR (KBr, cm^{-1}); 3308 (NH), 2918, 2848, 1644 (C=O), 1598, 1545, 1512, 1410, 1307, 1236, 1112, 1018, 812, 649, 505. $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$, ppm); δ 8.47-8.49 (NH), 7.28-7.32 (Ar-H), 7.03-7.09 (Ar-H), 6.81-6.83 (Ar-H), 6.44-6.46 (Ar-H), 3.65-3.78 (Ph- CH_2 -Ph).

MDI-HMDA (1:1): IR (KBr, cm^{-1}); 3319 (NH), 2926, 2855, 1648 (C=O), 1598, 1551, 1513, 1408, 1309, 1236, 1108, 1011, 816, 761, 652, 508. $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$, ppm); δ 8.28 (NH), 7.23-7.32 (Ar-H), 6.98-7.06 (Ar-H), 6.05 (NH), 3.71-3.77 (Ph- CH_2 -Ph), 3.02-3.03 (CH_2 -NH).

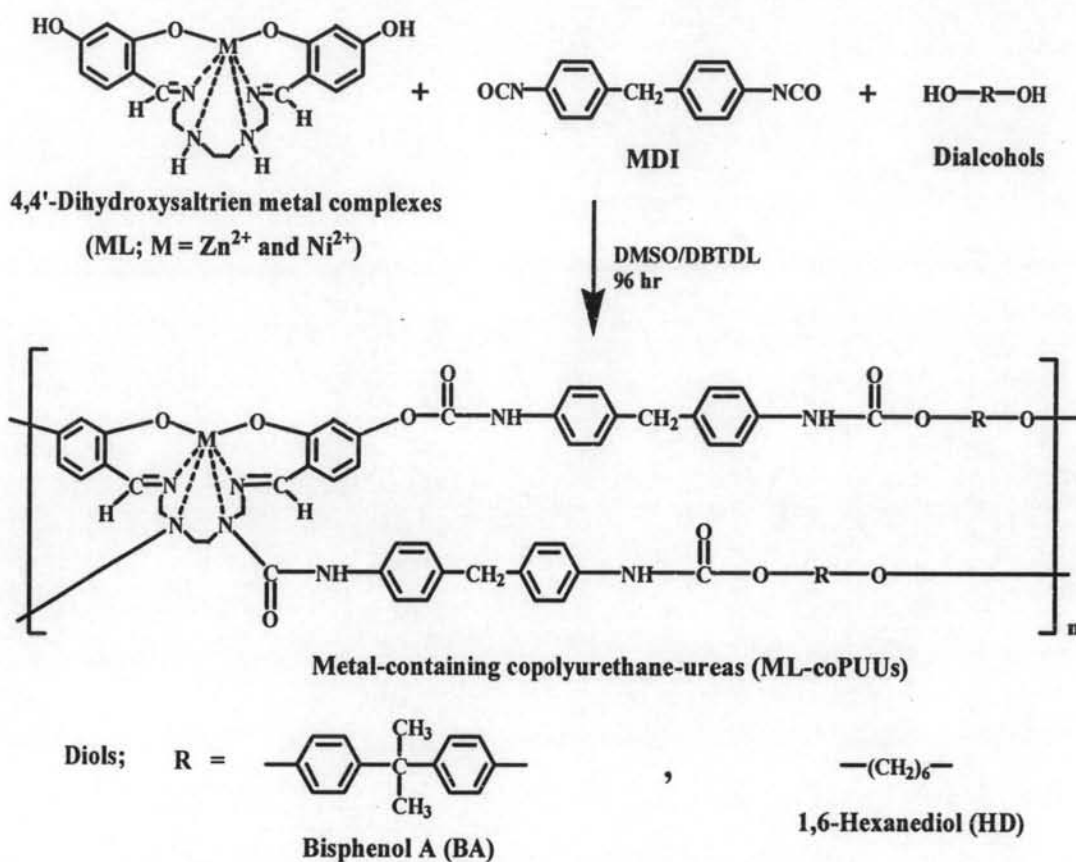
MDI-BA (1:1): IR (KBr, cm^{-1}); 3308 (NH), 2910, 2840, 1645 (C=O), 1597, 1545, 1511, 1410, 1308, 1234, 1108, 1011, 812, 649, 508. $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$, ppm); δ 8.53 (NH), 7.33-7.35 (Ar-H), 7.09-7.11 (Ar-H), 6.83-6.85 (Ar-H), 6.47-6.48 (Ar-H), 3.67-3.80 (Ph- CH_2 -Ph).

MDI-HD (1:1): IR (KBr, cm^{-1}); 3323 (NH), 2930, 2851, 1706 (C=O), 1599, 1528, 1412, 1410, 1311, 1228, 1069, 816, 769, 508. $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$, ppm); δ 9.47 (NH), δ 8.50 (NH), 7.32-7.33 (Ar-H), 7.05-7.07 (Ar-H), 4.03 ($\text{CH}_2\text{O-CONH}$), 3.80 (Ph- CH_2 -Ph).

3.3.2.4 Synthesis of metal-containing copolyurethane-ureas (ML-coPUUs) from ML, MDI and diamines



3.3.2.5 Synthesis of metal-containing copolyurethane-ureas (ML-coPUUs) from ML, MDI and dialcohols



The experiment was performed according to the procedure described in experiment 3.3.2.1. ML and MDI were dissolved in DMSO (7 mL) in a 50 mL two-necked round bottom flask under nitrogen atmosphere. After ML and MDI were mixed as the homogeneous solution, diamine or dialcohol in DMSO (1 mL) was added to the mixture rapidly with dibutyltin dilaurate (DBTDL) (0.30 mL, 0.50 mmole) as a catalyst at 90 °C for 96 hours. The polymer was precipitated by pouring the reaction mixture into distilled water. Then, the polymer was filtered through suction and washed with distilled methanol several times. The resulted powder was dried *in vacuum*. The composition of starting material in the preparation and yield of ML-coPUUs are shown in Table 3.3.

The polymerization of ML-coPUUs by a two-step process was performed according to the same procedure but the mixture of ML and MDI in dried DMSO was stirred for 48 hours. Then, diamine or diol in DMSO (1 mL) was added to the mixture. This mixture was stirred for 48 hours. The polymer was precipitated by pouring the reaction mixture into distilled water. Then, the polymer was filtered through suction and washed with distilled methanol several times and dried *in vacuum*.

Table 3.3 Composition of starting materials in the preparation of ML-coPUUs

Polymer codes	Weights of composition (g)				Yield (%)
	ZnL	MDI	Diamine	Dialcohol	
ZnL-MDI-MTDA (0.5:3.0:1.5)	0.1089	0.3583	0.1427	-	69
ZnL-MDI-MTDA (1.0:3.0:1.0)	0.1966	0.3269	0.0875	-	67
ZnL-MDI-MTDA (1.5:3.0:0.5)	0.2706	0.3018	0.0435	-	86
ZnL-MDI-HMDA (0.5:3.0:1.5)	0.1183	0.3960	0.0933	-	80
ZnL-MDI-HMDA (1.0:3.0:1.0)	0.2064	0.3414	0.0533	-	57
ZnL-MDI-HMDA (1.5:3.0:0.5)	0.2768	0.3101	0.0251	-	79
ZnL-MDI-BA (0.5:3.0:1.5)	0.1066	0.3494	-	0.1592	70
ZnL-MDI-BA (1.0:3.0:1.0)	0.1914	0.3188	-	0.0987	69
ZnL-MDI-BA (1.5:3.0:0.5)	0.2710	0.3020	-	0.0474	65
ZnL-MDI-HD (0.5:3.0:1.5)	0.1186	0.3958	-	0.0942	80
ZnL-MDI-HD (0.5:3.0:2.0)	0.1124	0.3759	-	0.1189	55
ZnL-MDI-HD (1.0:3.0:1.0); 1 step	0.2092	0.3490	-	0.0561	77
ZnL-MDI-HD (1.0:3.0:1.0); 2 step	0.2092	0.3488	-	0.0558	84
ZnL-MDI-HD(1.25:3.0:0.5)	0.2466	0.3287	-	0.0261	75
ZnL-MDI-HD (1.5:3.0:0.5)	0.2775	0.3088	-	0.0243	87

Polymer codes	Weights of composition (g)				Yield (%)
	ZnL	MDI	Diamine	Dialcohol	
NiL-MDI-MTDA(0.5:3.0:1.5)	0.1051	0.3571	0.1414	-	68
NiL-MDI-MTDA (1.0:3.0:1.0)	0.1948	0.3274	0.900	-	65
NiL-MDI-MTDA (1.5:3.0:0.5)	0.2700	0.3031	0.0401	-	66
NiL-MDI-HMDA (0.5:3.0:1.5)	0.1184	0.3943	0.0927	-	74
NiL-MDI-HMDA (1.0:3.0:1.0)	0.2010	0.3412	0.0570	-	72
NiL-MDI-HMDA (1.5:3.0:0.5)	0.2713	0.3062	0.0250	-	70
NiL-MDI-BA (0.5:3.0:1.5)	0.1038	0.3506	-	0.1591	60
NiL-MDI-BA (1.0:3.0:1.0)	0.1895	0.3167	-	0.0975	57
NiL-MDI-BA (1.5:3.0:0.5)	0.2670	0.3061	-	0.0458	82
NiL-MDI-HD (0.5:3.0:1.5)	0.1177	0.3949	-	0.0936	63
NiL-MDI-HD (1.0:3.0:1.0)	0.2067	0.3460	-	0.0556	59
NiL-MDI-HD (1.5:3.0:0.5)	0.2746	0.3075	-	0.0246	69

ZnL-MDI-MTDA (0.5:3:1.5): IR (KBr, cm^{-1}); 3368 (NH), 2922, 2851, 1707(C=O), 1600 (C=N), 1540, 1512, 1411, 1310, 1232, 1112, 1014, 812, 758, 508.

ZnL-MDI-MTDA (1.0:3:1.0): IR (KBr, cm^{-1}); 3376 (NH), 2922, 2851, 1708 (C=O), 1600 (C=N), 1542, 1512, 1411, 1310, 1233, 1116, 1014, 816, 763, 508. $^1\text{H-NMR}$ (400 MHz, DMSO- d_6 , ppm); δ 8.54 (NH), 5.92 (NH), 7.28-7.33 (Ar-H), 7.26 (Ar-H), 7.03-7.09 (Ar-H), 6.81-6.83 (Ar-H), 6.44-6.46 (Ar-H), 3.65-3.78 (Ph- CH_2 -Ph).

ZnL-MDI-MTDA (1.5:3:0.5): IR (KBr, cm^{-1}); 3377 (NH), 2923, 2852, 1710 (C=O), 1600 (C=N), 1542, 1513, 1411, 1310, 1231, 1123, 1014, 815, 760, 508.

ZnL-MDI-HMDA (0.5:3:1.5): IR (KBr, cm^{-1}); 3330 (NH), 2924, 2855, 1718 (C=O), 1600 (C=N), 1544, 1513, 1410, 1310, 1233, 1112, 1011, 816, 765, 508.

ZnL-MDI-HMDA (1.0:3:1.0): IR (KBr, cm^{-1}); 3337 (NH), 2923, 2854, 1716 (C=O), 1600 (C=N), 1543, 1513, 1410, 1309, 1232, 1123, 1018, 812, 760, 508. $^1\text{H-NMR}$ (400 MHz, DMSO- d_6 , ppm); δ 8.53 (NH), 8.26 (NH), 6.03 (NH), 7.24-7.33 (Ar-H), 7.26 (Ar-H), 7.00-7.09 (Ar-H), 6.82 (Ar-H), 6.45 (Ar-H), 3.62-3.78 (Ph- CH_2 -Ph), 3.02-3.04 (CH_2 -NH).

ZnL-MDI-HMDA (1.5:3:0.5): IR (KBr, cm^{-1}); 3340 (NH), 2923, 2855, 1718 (C=O), 1600 (C=N), 1542, 1512, 1410, 1309, 1230, 1116, 1014, 810, 761, 508.

ZnL-MDI-BA (0.5:3:1.5): IR (KBr, cm^{-1}); 3357 (NH), 2923, 2851, 1717 (C=O), 1600 (C=N), 1544, 1513, 1411, 1310, 1233, 1116, 1018, 816, 758, 508.

ZnL-MDI-BA (1.0:3:1.0): IR (KBr, cm^{-1}); 3342 (NH), 2921, 2851, 1720 (C=O), 1600 (C=N), 1544, 1513, 1411, 1309, 1231, 1116, 1014, 816, 754, 506. $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$, ppm); δ 8.56 (NH), 7.30-7.35 (Ar-H), 7.26 (Ar-H), 7.05-7.11 (Ar-H), 6.83-6.85 (Ar-H), 6.46-6.48 (Ar-H), 3.68-3.80 (Ph- CH_2 -Ph).

ZnL-MDI-BA (1.5:3:0.5): IR (KBr, cm^{-1}); 3329 (NH), 2923, 2851, 1716 (C=O), 1601 (C=N), 1543, 1513, 1411, 1310, 1230, 1116, 1018, 816, 758, 508.

ZnL-MDI-HD (0.5:3:1.5): IR (KBr, cm^{-1}); 3320 (NH), 2923, 2854, 1716 (C=O), 1600 (C=N), 1542, 1513, 1411, 1309, 1232, 1116, 1014, 820, 760, 633, 512.

ZnL-MDI-HD (0.5:3:2.0): IR (KBr, cm^{-1}); 3315 (NH), 2922, 2851, 1720 (C=O), 1600 (C=N), 1543, 1513, 1410, 1309, 1232, 1120, 1011, 816, 765, 625, 505.

ZnL-MDI-HD (1.0:3:1.0), 1step : IR (KBr, cm^{-1}); 3321 (NH), 2922, 2851, 1718 (C=O), 1600 (C=N), 1543, 1512, 1410, 1309, 1231, 1116, 1011, 816, 758, 629, 508. $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$, ppm); δ 8.54 (NH), 7.28-7.33 (Ar-H), 7.25 (Ar-H), 7.03-7.09 (Ar-H), 6.82 (Ar-H), 6.45 (Ar-H), 3.65-3.78 (Ph- CH_2 -Ph).

ZnL-MDI-HD (1.0:3:1.0), 2 step: IR (KBr, cm^{-1}); 3336 (NH), 2923, 2851, 1700 (C=O), 1601 (C=N), 1541, 1512, 1411, 1310, 1231, 1120, 1014, 812, 758, 629, 508.

ZnL-MDI-HD (1.25:3:0.5): IR (KBr, cm^{-1}); 3324 (NH), 2923, 2854, 1704 (C=O), 1600 (C=N), 1544, 1512, 1410, 1310, 1232, 1120, 1018, 816, 758, 628, 512.

ZnL-MDI-HD (1.5:3:0.5): IR (KBr, cm^{-1}); 3326 (NH), 2921, 2852, 1716 (C=O), 1601 (C=N), 1536, 1511, 1409, 1308, 1227, 1119, 1018, 816, 629, 508.

NiL-MDI-MTDA (0.5:3:1.5): IR (KBr, cm^{-1}); 3381 (NH), 2920, 2848, 1702 (C=O), 1600 (C=N), 1541, 1512, 1410, 1309, 1232, 1112, 1011, 812, 758, 512.

NiL-MDI-MTDA (1.0:3:1.0): IR (KBr, cm^{-1}); 3369 (NH), 2918, 2851, 1694 (C=O), 1600 (C=N), 1536, 1510, 1409, 1308, 1231, 1116, 1014, 812, 758, 508.

NiL-MDI-MTDA (1.5:3:0.5): IR (KBr, cm^{-1}); 3394 (NH), 2923, 2851, 1698 (C=O), 1600 (C=N), 1540, 1512, 1410, 1310, 1232, 1123, 1018, 812, 758, 512.

NiL-MDI-HMDA (0.5:3:1.5): IR (KBr, cm^{-1}); 3337 (NH), 2923, 2844, 1710 (C=O), 1600 (C=N), 1542, 1517, 1410, 1309, 1232, 1112, 1018, 808, 760, 508.

NiL-MDI-HMDA (1.0:3:1.0): IR (KBr, cm^{-1}); 3336 (NH), 2923, 2851, 1710 (C=O), 1600 (C=N), 1542, 1515, 1410, 1309, 1232, 1116, 1014, 808, 761, 512.

NiL-MDI-HMDA (1.5:3:0.5): IR (KBr, cm^{-1}); 3360 (NH), 2922, 2851, 1718 (C=O), 1600 (C=N), 1541, 1509, 1410, 1309, 1231, 1116, 1011, 812, 754, 508.

NiL-MDI-BA (0.5:3:1.5): IR (KBr, cm^{-1}); 3337 (NH), 2923, 2859, 1716 (C=O), 1601 (C=N), 1541, 1512, 1410, 1310, 1232, 1120, 1018, 820, 758, 512.

NiL-MDI-BA (1.0:3:1.0): IR (KBr, cm^{-1}); 3330(NH), 2921, 2859, 1720 (C=O), 1600 (C=N), 1548, 1512, 1410, 1309, 1232, 1112, 1014, 812, 765, 508.

NiL-MDI-BA (1.5:3:0.5): IR (KBr, cm^{-1}); 3350 (NH), 2923, 2858, 1718 (C=O), 1601 (C=N), 1541, 1512, 1411, 1310, 1232, 1120, 1018, 824, 758, 512.

NiL-MDI-HD (0.5:3:1.5): IR (KBr, cm^{-1}); 3319 (NH), 2921, 2848, 1702 (C=O), 1600 (C=N), 1541, 1511, 1410, 1309, 1231, 1120, 1014, 812, 758, 637, 512.

NiL-MDI-HD (1.0:3:1.0): IR (KBr, cm^{-1}); 3342 (NH), 2924, 2848, 1710 (C=O), 1601 (C=N), 1540, 1509, 1411, 1310, 1232, 1116, 1014, 816, 758, 641, 512.

NiL-MDI-HD (1.5:3:0.5): IR (KBr, cm^{-1}); 3350 (NH), 2925, 2848, 1708 (C=O), 1600 (C=N), 1540, 1512, 1410, 1309, 1231, 1116, 1011, 810, 758, 640, 512.