CHAPTER II

EXPERIMENTAL

2.1 Materials

All reagents and solvents were of analytical grade quality. The solvents were obtained from Baker. *N*, *N*′-Dimethylformamide (DMF) was dried over calcium hydride (CaH_2) and distilled under reduced pressure. Methylene chloride (CH_2Cl_2) was refluxed over calcium hydride (CaH_2) and distilled immediately before use. Zinc (II) acetate dihydrate, Nickel (II) acetate tetrahydrate, salicylaldehyde, triethylenetetramine, hexamethylene diisocyanate (HMDI), 2,4-toluene diisocyanate (TDI), 4,4′-methylene*bis*(phenyl isocyanate) (MDI), poly(tetramethylene oxide) (PTMO) and dibutyltin dilaurate (DBTDL) were obtained from the Fluka and Sigma-Aldrich . All chemicals were used without further purification.

2.2 Analytical procedures

The IR spectra of the samples were recorded on a Nicolet Impact 410 by the potassium bromide (KBr) method. Elemental analyses were carried out on a Perkin Elmer 2400 CHN Elemental Analyzer. Liquid crystalline property was observed by an Olympus SC 35 polarizing optical microscope equipped with a Mettler FP5 heating stage. Thermogravimetric analysis examined using a Netzsch STA 409C thermogravimetric analyzer in 1:1 air/nitrogen atmosphere with the heating rate 20°C/min. The limiting oxygen index (LOI) data was obtained on an apparatus produced in accordance with standard ASTM D2863-70 and measurement was made using a modified procedure.[16] The inherent viscosity of the polymer was determined in DMSO at 40°C with a Cannon-Fenske viscometer following ASTM D2270. The

flow time for the solvent as well as the polymer solution (0.5 g/dl) was determined. The solubility of the polymers was tested in various polar and nonpolar solvents by 5 mg samples being added to 1 ml of solvent and kept overnight.

2.3 Synthetic procedures

2.3.1 Preparation of hexadentate Schiff base metal complexes ($Msal_2trien$)

2.3.1.1 Preparation of hexadentate Schiff base zinc complex ($Znsal_2trien$)

The preparation of $Znsal_2trien$ was carried out according to the method in the literature.[17] A mixture of salicylaldehyde (1.18 g, 9.66 mmol) and zinc (II) acetate dihydrate (1.05 g, 4.84 mmol) in methanol (15 ml) was prepared and then cooled to 0°C. A methanolic solution (10 ml) of triethylenetetramine (1 ml, 6.70 mmol) was added dropwise over a period of 20 minutes. This mixture was stirred for 10 minutes and neutralized by adding a solution of 2 N sodium hydroxide (1.67 ml) and stirred at 0°C for 30 minutes. Upon standing at room temperature for 10 hours, $Znsal_2trien$ crystallized from solution and was subsequently isolated by filtration and was dried under vacuum. The zinc complex was obtained as a yellow crystal (1.86 g, 93%): mp 220°C. 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, C<u>H</u>=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 δ NMR ($CDCl_3$, ppm); 172, 168 (<u>C</u>=N), 135, 133, 133, 124, 119, 112, 56, 47, 43.

2.3.1.2 Preparation of hexadentate Schiff base nickel complex ($Nisal_2trien$)

The experiment was performed according to the procedure described in experiment 2.3.1.1 employing nickel (II) acetate tetrahydrate (1.03 g, 4.84 mmol) instead of zinc (II) acetate dihydrate. The brown crystal of $Nisal_2trien$ precipitated from the solution upon standing at room temperature for 48 hours (0.532 g, 97%): IR (KBr, cm^{-1}); 3634, (NH), 3448, 3278, 2900, 2866, 1642, (C=N), 1596, 1456, 1223, 953, 850.

2.3.2 Preparation of metal-containing polyureas

2.3.2.1 Preparation of metal-containing polyurea from $Znsal_2trien$ and MDI

The solution of $Znsal_2trien$ (0.417 g, 1 mmol) in dried methylene chloride (20 ml) were added to the solution of MDI (0.250 g, 1 mmol) in dried methylene chloride (20 ml). The reaction mixture was refluxed with stirring under nitrogen atmosphere and heat at 40°C for 6 hours. The progress of the reaction was followed by IR spectroscopy. The product was precipitated by pouring the reaction mixture into methanol. The precipitated polymer was filtered off and dried under vacuum. The polymer was obtained as yellow powder (0.480 g, 72%): IR (KBr, cm^{-1}); 3305 (NH), 2914, 2850, 1700 (C=O), 1633 (C=N) 1533, 1465, 1410, 1237, 1064, 758. Elemental Analysis: Calcd for $C_{37}H_{48}N_6O_4Zn$ (698); C 63.65; H 5.77; N 12.04. Found: C 63.34; H 5.88; N 12.12.

2.3.2.2 Preparation of metal-containing polyurea from $Znsal_2trien$ and TDI

The experiment was performed according to the procedure described in experiment 2.3.2.1 employing TDI (0.174 g, 1 mmol) instead of MDI. The reaction mixture was stirred at 40°C for 8 hours. The product was obtained as yellow powder (0.437 g, 74%): IR (KBr, cm^{-1}) 3312 (NH), 2917, 2864, 1711 (C=O), 1634 (C=N) 1533, 1463, 1404, 1227, 759.

2.3.2.3 Preparation of metal-containing polyurea from $Znsal_2trien$ and HMDI

The experiment was performed according to the procedure described in experiment 2.3.2.1 employing HMDI (0.168 g, 1 mmol) instead of MDI. The reaction mixture was stirred at 40°C for 8 hours. The product was obtained as yellow powder (0.422 g, 72%): IR (KBr, cm^{-1}); 3322 (NH), 2924, 2855, 1721 (C=O), 1635 (C=N) 1535, 1448, 1400, 1256, 758.

2.3.2.4 Preparation of metal-containing polyurea from $Nisal_2trien$ and MDI

The experiment was performed according to the procedure described in experiment 2.3.2.1 employing $Nisal_2trien$ (0.411 g, 1 mmol) instead of $Znsal_2trien$. The reaction mixture was stirred at 40°C for 8 hours. The product was obtained as brown powder (0.463 g, 70%): IR (KBr, cm^{-1}) 3300 (NH), 2906, 2827, 1700 (C=O), 1654 (C=N) 1599, 1511, 1408, 1230, 759. Elemental Analysis: Calcd for $C_{37}H_{48}N_6O_4Ni$ (677); C 63.46; H 5.33; N 12.69. Found: C 61.32; H 5.96; N 12.87.

2.3.3 Preparation of metal-containing polyurethane-ureas

2.3.3.1 Preparation of metal-containing polyurethane-ureas from PTMO, MDI and $Znsal_2trien$

The experiment was performed according to the procedure described in the literature.[18] Into 50 ml equipped with a magnetic stirrer, a reflux condenser, thermometer and nitrogen inlet were added PTMO, MDI and DMF (10 ml). The reaction mixture was stirred for 30 minutes at 80°C under nitrogen atmosphere. To this solution, two drops of DBTDL as the catalyst was added. A solution of $Znsal_2trien$ and DMF (10 ml) were added, and the reaction mixture was stirred for 4 hours at 80°C. The product was precipitated by pouring the reaction mixture into methanol. The precipitated polymer was filtered off and dried in vacuum. The polymers were obtained as yellow powder: IR (KBr, cm^{-1}); 3309 (NH), 2935, 2856, 1706 (C=O), 1634 (C=N) 1600, 1539, 1232, 758. The mole ratio of PTMO: MDI: $Znsal_2trien$ were varied as shown in Table 2.1.

Table 2.1 Composition of starting materials in the preparation of metal-containing polyurethane-ureas from PTMO, MDI and $Znsal_2trien$.

Code	Molecular weight of PTMO	Mole ratio of PTMO : MDI : $Znsal_2trien$	Wt % of Metal complex in polymer	Weight of PTMO (g)	Weight of MDI (g)	Weight of $Znsal_2trien$ (g)	Weight of Product (g)	Yield (%)
P6MZn-30	650	1 : 2 : 1	27	0.163	0.125	0.104	0.247	63
P6MZn-40	650	1 : 3 : 2	37	0.163	0.188	0.209	0.386	69
P6MZn-50	650	1 : 5 : 4	47	0.163	0.313	0.417	0.607	68
P6MZn-60	650	1 : 10 : 9	54	0.163	0.626	0.939	1.001	58
P1MZn-20	1400	1 : 2 : 1	18	0.350	0.125	0.104	0.435	75
P1MZn-30	1400	1 : 3 : 2	28	0.350	0.188	0.209	0.552	74
P1MZn-40	1400	1 : 5 : 4	39	0.350	0.313	0.417	0.659	61
P1MZn-50	1400	1 : 10 : 9	49	0.350	0.626	0.939	1.321	69
P2MZn-20	2000	1 : 2 : 1	14	0.500	0.125	0.104	0.569	78
P2MZn-30	2000	1 : 3 : 2	23	0.500	0.188	0.209	0.672	75
P2MZn-40	2000	1 : 5 : 4	34	0.500	0.313	0.417	0.763	62
P2MZn-50	2000	1 : 10 : 9	45	0.500	0.626	0.939	1.115	54

2.3.3.2 Preparation of metal-containing polyurethane-ureas from PTMO, MDI and $Nisal_2trien$

The experiment was performed according to the procedure described in experiment 2.3.3.1 employing $Nisal_2trien$ instead of $Znsal_2trien$. The products were obtained as brown powder: IR (KBr, cm^{-1}); 3309 (NH), 2935, 2856, 1706 (C=O), 1643 (C=N) 1598, 1543, 1231, 757. The mole ratio of PTMO: MDI: $Nisal_2trien$ were varied as shown in Table 2.2.

Table 2.2 Composition of starting materials in the preparation of metal-containing polyurethane-ureas from PTMO, MDI and $Nisal_2trien$.

Code	Molecular weight of PTMO	Mole ratio PTMO : MDI : $Nisal_2trien$	Wt % of Metal complex in polymer	Weight of PTMO (g)	Weight of MDI (g)	Weight of $Nisal_2trien$ (g)	Weight of Product (g)	Yield (%)
P6MNi-30	650	1 : 2 : 1	26	0.163	0.125	0.103	0.285	73
P6MNi-40	650	1 : 3 : 2	37	0.163	0.188	0.206	0.411	74
P6MNi-50	650	1 : 5 : 4	46	0.163	0.313	0.411	0.550	62
P6MNi-60	650	1 : 10 : 9	54	0.163	0.626	0.925	0.925	54
P1MNi-20	1400	1 : 2 : 1	18	0.350	0.125	0.103	0.451	78
P1MNi-30	1400	1 : 3 : 2	28	0.350	0.188	0.206	0.476	64
P1MNi-40	1400	1 : 5 : 4	38	0.350	0.313	0.411	0.580	54
P1MNi-50	1400	1 : 10 : 9	49	0.350	0.626	0.925	1.121	59
P2MNi-20	2000	1 : 2 : 1	14	0.500	0.125	0.103	0.524	72
P2MNi-30	2000	1 : 3 : 2	23	0.500	0.188	0.206	0.608	68
P2MNi-40	2000	1 : 5 : 4	34	0.500	0.313	0.411	0.783	64
P2MNi-50	2000	1 : 10 : 9	45	0.500	0.626	0.925	1.169	57

2.3.3.3 Preparation of polyurethanes from PTMO and MDI

Into 50 ml flask equipped with a magnetic stirrer, a reflux condenser, thermometer and nitrogen inlet were added PTMO (Mw 650, 0.163 g), MDI (0.626 g) and DMF (10 ml). To this solution, two drops of DBTDL as the catalyst was added. The reaction mixture was stirred for 6 hours at 80°C under nitrogen atmosphere. The product was precipitated by pouring the reaction into methanol. The precipitated polymer was filtered off and dried in vacuum. The polymers were obtained as white powder (0.237 g, 30%): IR (KBr, cm^{-1}); 3316 (NH), 2945, 2851, 1724 (C=O), 1644 (C=N) 1607, 1527, 1214, 770.