CHAPTER III

EXPERIMENTAL

3.1 Materials

All reagents and solvents were of analytical grade quality. The solvents were obtained from Lab-Scan. *N,N*-dimethylformamide (DMF) was purified by distillation under reduced pressure over calcium hydride and stored over molecular sieves. Zinc (II) acetate dihydrate, nickel (II) acetate tetrahydrate, 2-hydroxy-3-methoxybenzaldehyde, triethylenetetramine, hexamethylene diisocyanate (HMDI), 4,4'-diphenylmethane diisocyanate (MDI), 4,4'-diaminodiphenylmethane (DAP), hexamethylenediamines (HMDA), 4,7,10-trioxa-1,13-tridecanediamine (TDA), *m*-xylylenediamine (XDA), bis(4-Hydroxyphenyl)propane (BPA), 1,6-hexanediol (HMDO), triethylene glycol (TEG), and polyethylene glycol (PEG, MW = 300) and dibutyltin dilaurate (DBTDL) were obtained from Fluka and Aldrich. All chemicals were used as received without further purification.

3.2 Measurements

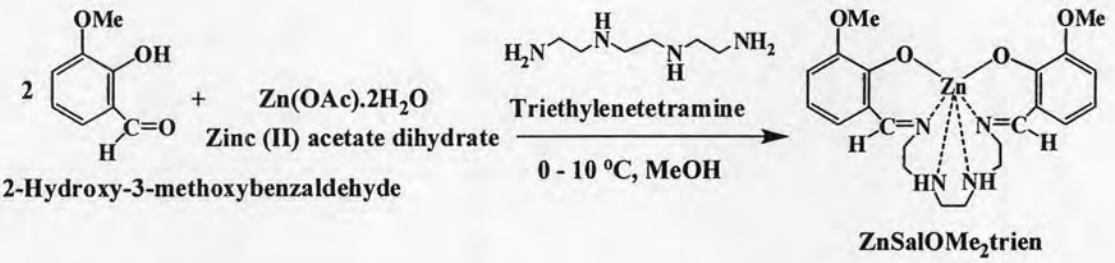
IR spectra of the samples were recorded on a Nicolet Impact 410 FTIR spectrophotometer at room temperature with potassium bromide (KBr) disk method. The samples were scanned over a range of 400-4000 cm^{-1} at a resolution of 16 cm^{-1} and the number of scan was 32. The measurement was controlled by Omnic Software. ^{1}H-NMR spectra were recorded in 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°C/min under air atmosphere. All samples were held in the analyzer at 120°C for 15 min and measured from temperature range 120°C to 1000°C. The result of thermal stability was reported in percentage weight loss of polymers. X-ray diffractometer (XRD) used in study was Bruker AXS Model D8 Discover with nickel filtered CuKα radiation (40kV, 40mA) at an angle of 2θ range from 5° to 40°. The scan speed was 0.02°/min and scan step was

0.3 sec/step. 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 dimethyl formamide (DMSO) by addition of samples to 1 mL of DMSO. Inherent viscosity (η_{inh}) of the polymers was determined at concentration of 0.5g/100 mL in DMSO at 40°C using a Cannon-Fenske viscometer according to ASTM D2270.

3.3 Synthetic procedures

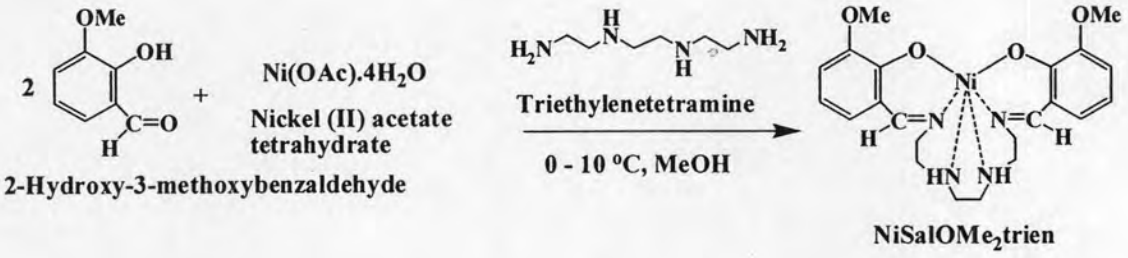
3.3.1 Synthesis of dimethoxysaltrien metal complexes ($MSalOMe_2trien$, M = Zn and Ni)

3.3.1.1 Synthesis of dimethoxysaltrien zinc complex ($ZnSalOMe_2trien$)



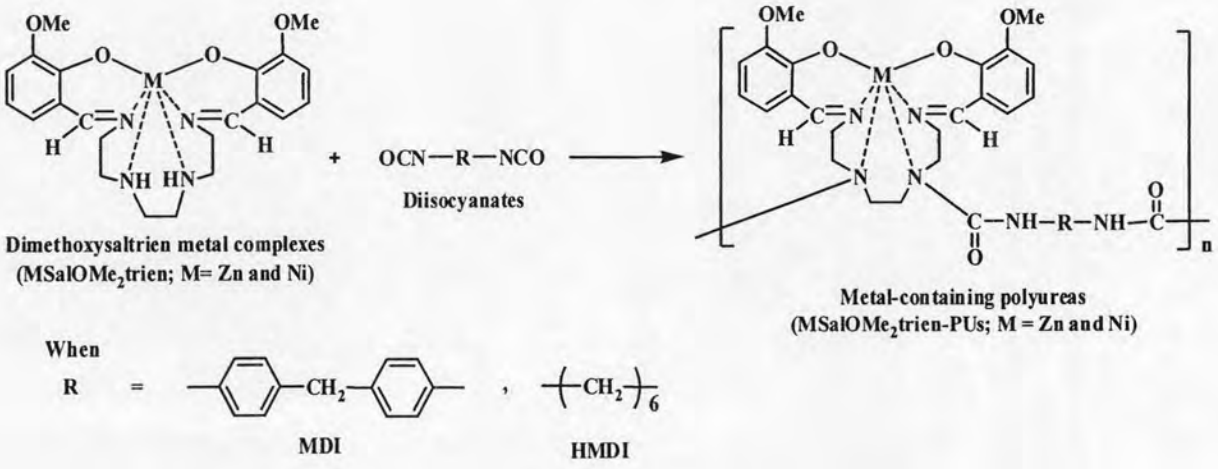
The preparation of $ZnSalOMe_2trien$ was performed according to the method reported in the literature [30]. A cool (0-10°C) methanol solution (10 mL) of triethylenetetramine (0.149 mL, 1.0 mmol) was added dropwise to a stirred cool methanol solution (15 mL) of 2-hydroxy-3-methoxybenzaldehyde (0.304 g, 2.0 mmol) and zinc (II) acetate dehydrate (0.220 g, 1.0 mmol). The solution turned yellow slowly and was stirred for 15 min at cool temperature. This stirring solution was neutralized by 2M sodium hydroxide solution (1.0 mL, 2.0 mmol) and stirred for 1 hour. The yellow crystals of $ZnSalOMe_2trien$ precipitated from the solution upon standing at room temperature for 10 hours. The yellow crystals were filtered and dried in vacuo to yield 0.3611 g (76%) of $ZnSalOMe_2trien$. IR (KBr, cm^{-1}); 3457 (NH), 3310, 2906, 2856, 1634 (C=N), 1597, 1535, 1474, 1445, 1402, 1337, 1217, 1109, 1079, 973,893, 854, 789, 741. ^{1}H-NMR (400 MHz, DMSO-d_6, ppm); δ 8.25 (2H, *s*, C**H**=N), 6.69 (2H, *dd*, Ar-**H**, J = 1.6, 8 Hz), 6.62 (2H, *dd*, Ar-**H**, J = 1.6, 8 Hz), 6.14 (2H, *t*, Ar-**H**, J = 7.6 Hz), 3.87-3.70 (2H, *m*, NC**H**$_2$), 3.59 (6H, *s*, OC**H**$_3$), 3.53-3.30 (2H, *m*, NC**H**$_2$), 3.22-2.99 (4H, *m*, HNC**H**$_2$), 2.84-2.74 (2H, *m*, HNC**H**$_2$), 2.40-2.28 (2H, *m*, HNC**H**$_2$).

3.3.1.2 Synthesis of dimethoxysaltrien nickel complex (NiSalOMe$_2$trien)



The experiment was performed according to the procedure described in experiment 3.3.1.1 employing nickel (II) acetate tetrahydrate (0.249 g, 1.0 mmol) instead of zinc (II) acetate dihydrate. The dark green crystals were filtered and dried in vacuo to yield 0.3020 g (64%): IR (KBr, cm^{-1}); 3438 (NH), 3302, 2904, 1633 (C=N), 1596, 1534, 1475, 1445, 1403, 1338, 1217, 1081, 977, 903, 856, 741.

3.3.2 Synthesis of metal-containing polyureas (MSalOMe$_2$trien-PUs) from the reaction between MSalOMe$_2$trien and diisocyanates



Polyureas were synthesized by polyaddition reaction between MSalOMe$_2$trien (M = Zn and Ni) and diisocyanate at the mole ratio of MSalOMe$_2$trien:diisocyanate = 1:1 according to the method reported in the literature [30] except DMF was used instead of CH_2Cl_2. MSalOMe$_2$trien (M = Zn and Ni) was dissolved in 15 mL of dried DMF in a 50 mL, two-necked round bottomed flask equipped with a nitrogen inlet. MDI in dried DMF (2 mL) was then added into the mixture. The polymerization was done at room temperature for 12 hours. Then, the polymer was filtered through suction

and washed with distilled CH_2Cl_2 several times and dried in vacuum. The composition of starting materials is shown in Table 3.1. Zinc- and nickel-containing polyureas were obtained as yellow and green powder, respectively. The yield obtained for the polymers was in the range 65-85%.

Table 3.1 Composition of starting materials in the preparation of $MSalOMe_2trien$-polyureas from $MSalOMe_2trien$ (M = Zn and Ni) and diisocyanates

Polymer codes	Weight of starting material (g)				Yield (%) from CH_2Cl_2 [30]	Yield (%) from DMF
	$ZnSalOMe_2trien$	$NiSalOMe_2trien$	MDI	HMDI		
$ZnSalOMe_2trien$-MDI	0.360 g (0.75 mmol)	-	0.188 g (0.75 mmol)	-	74	75
$ZnSalOMe_2trien$-HMDI	0.360 g (0.75 mmol)	-	-	0.121 mL (0.75 mmol)	75	85
$NiSalOMe_2trien$-MDI	-	0.354 g (0.75 mmol)	0.188 g (0.75 mmol)	-	70	70
$NiSalOMe_2trien$-HMDI	-	0.354 (1.13 mmol)	-	0.121 mL (0.75 mmol)	61	61

Polymers synthesized in CH_2Cl_2 [30]

$ZnSalOMe_2trien$-MDI: IR (KBr, cm^{-1}); 3310 (NH), 3039, 2982, 2906, 2823, 1630 (C=N), 1513, 1470, 1445, 1312, 1216, 1078, 972, 853, 741. ^1H NMR (400 MHz, DMSO-d_6, ppm); δ 8.25 (2H, *s*, C**H**=N), 7.32-7.36 (2H, *m*, Ar-**H**), 7.06-7.12 (2H, *m*, Ar-**H**), 6.81-6.87 (2H, *m*, Ar-**H**), 6.69 (2H, *d*, Ar-**H**, *J* = 7.6 Hz), 6.61 (2H, *d*, Ar-**H**, *J* = 7.2 Hz), 6.48-6.50 (2H, *m*, Ar-**H**), 6.14 (2H, *t*, Ar-**H**, *J* = 7.6 Hz), 3.84-3.72 (2H, *m*, NC$\mathbf{H}_2$), 3.59 (6H, *s*, OC$\mathbf{H}_3$), 3.49-3.40 (2H, *m*, NC$\mathbf{H}_2$), 3.18-3.03 (4H, *m*, HNC$\mathbf{H}_2$), 2.81-2.74 (2H, *m*, HNC$\mathbf{H}_2$), 2.39-2.31(2H, *m*, HNC$\mathbf{H}_2$).

$NiSalOMe_2trien$-MDI: IR (KBr, cm^{-1}); 3417 (NH), 2901, 1633 (C=N), 1601, 1544, 1512, 1442, 1411, 1311, 1219, 1079, 971, 740.

$ZnSalOMe_2trien$-HMDI: IR (KBr, cm^{-1}); 3312 (NH), 3044, 2928, 2856, 1632 (C=N), 1565, 1473, 1446, 1335, 1217, 1078, 972, 854, 741. ^1H NMR (400 MHz, DMSO-d_6, ppm); δ 8.25 (2H, *s*, C**H**=N), 6.69 (2H, *d*, Ar-**H**, *J* = 8.0 Hz), 6.61 (2H, *d*, Ar-**H**, *J* = 7.6 Hz), 6.13 (2H, *t*, Ar-**H**, *J* = 7.6 Hz), 5.80 (2H, *m*, N**H**), 3.85-3.73 (2H, *m*, NC$\mathbf{H}_2$), 3.59 (6H, *s*, OC$\mathbf{H}_3$), 3.55-3.40 (2H, *m*, NC$\mathbf{H}_2$), 3.20-3.05 (4H, *m*, HNC$\mathbf{H}_2$), 2.88-2.78 (2H, *m*, HNC$\mathbf{H}_2$), 2.45-2.35 (2H, *m*, HNC$\mathbf{H}_2$), 1.37 (4H, *br*, C$\mathbf{H}_2$), 1.24 (4H, *br*, C$\mathbf{H}_2$).

NiSalOMe$_2$trien-HMDI: IR (KBr, cm^{-1}); 3423 (NH), 2930, 2847, 1632 (C=N), 1564, 1473, 1442, 1337, 1216, 1079, 976, 853, 740, 643.

Polymers synthesized in DMF

ZnSalOMe$_2$trien-MDI: IR (KBr, cm^{-1}); 3416 (NH), 2922, 1632 (C=N), 1513, 1470, 1445, 1412, 1311, 1239, 1216. ^{1}H NMR (400 MHz, DMSO-d$_6$, ppm); δ 8.24 (2H, *s*, C**H**=N), 7.24-7.39 (2H, *m*, Ar-**H**), 7.02-7.11 (2H, *m*, Ar-**H**), 6.74-6.87 (2H, *m*, Ar-**H**), 6.71 (2H, *d*, Ar-**H**, *J* = 7.6 Hz), 6.60 (2H, *d*, Ar-**H**, *J* = 6.8 Hz), 6.41-6.51 (2H, *m*, Ar-**H**), 6.12 (2H, *t*, Ar-**H**, *J* = 7.6 Hz), 4.80 (2H, *m*, N**H**), 3.85-3.73 (2H, *m*, NC**H**$_2$), 3.67 (6H, *s*, OC**H**$_3$), 3.50-3.39 (2H, *m*, NC**H**$_2$), 3.17-3.02 (4H, *m*, HNC**H**$_2$), 2.80-2.74 (2H, *m*, HNC**H**$_2$), 2.41-2.30 (2H, *m*, HNC**H**$_2$).

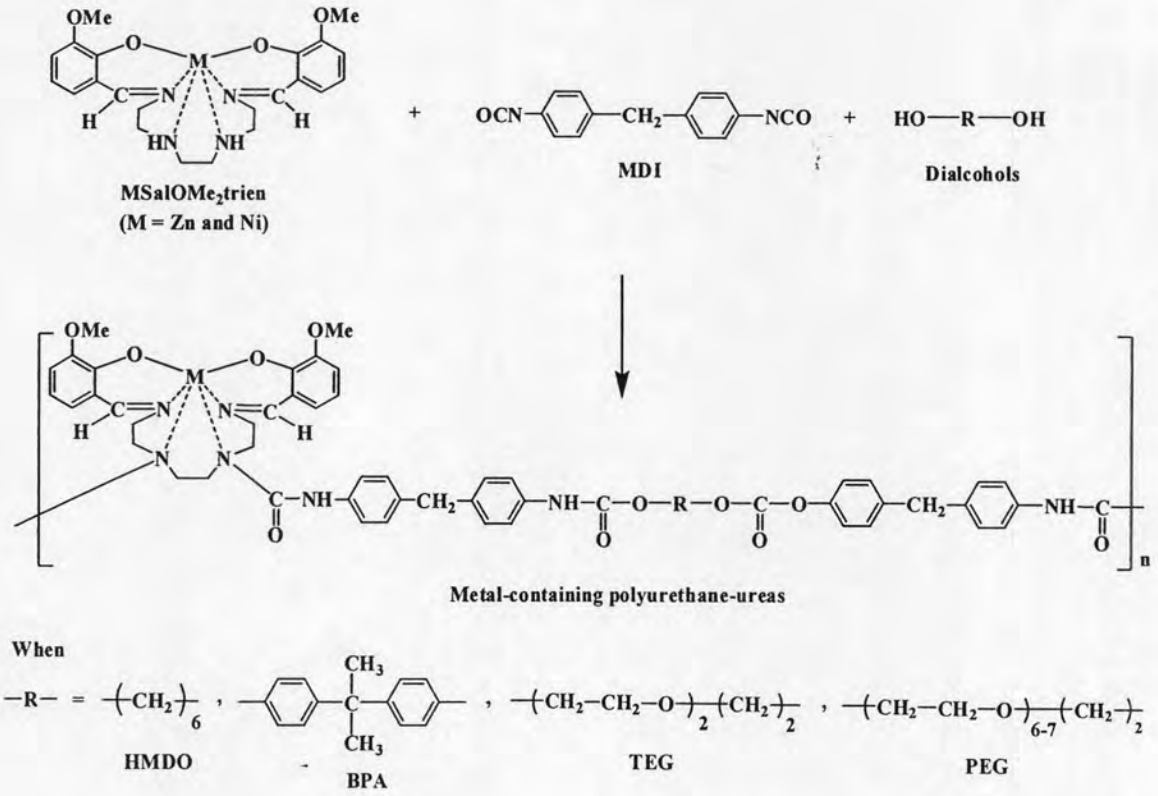
NiSalOMe$_2$trien-MDI: IR (KBr, cm^{-1}); 3388 (NH), 2909, 1634 (C=N), 1600, 1512, 1537, 1472, 1444, 1410, 1312, 1221, 1082, 975, 855, 741.

ZnSalOMe$_2$trien-HMDI: IR (KBr, cm^{-1}); 3334 (NH), 2930, 2856, 1632 (C=N), 1570, 1472, 1446, 1404, 1334, 1217, 1078, 972, 854, 740. ^{1}H NMR (400 MHz, DMSO-d$_6$, ppm); δ 8.20 (2H, *s*, C**H**=N), 6.67 (2H, *d*, Ar-**H**, *J* = 7.2 Hz), 6.60 (2H, *d*, Ar-**H**, *J* = 6.8 Hz), 6.12 (2H, *t*, Ar-**H**, *J* = 7.6 Hz), 5.76 (2H, *m*, N**H**), 3.86-3.71 (2H, *m*, NC**H**$_2$), 3.58 (6H, *s*, OC**H**$_3$), 3.52-3.40 (2H, *m*, NC**H**$_2$), 3.18-3.08 (4H, *m*, HNC**H**$_2$), 2.81-2.74 (2H, *m*, HNC**H**$_2$), 2.40-2.31 (2H, *m*, HNC**H**$_2$), 1.34 (4H, *br*, C**H**$_2$), 1.23 (4H, *br*, C**H**$_2$).

NiSalOMe$_2$trien-HMDI: IR (KBr, cm^{-1}); 331 (NH), 2931, 2856, 1628 (C=N), 1571, 1472; 1442, 1403, 1329, 1238, 1215, 1080, 973, 850, 738, 626.

3.3.3 Synthesis of metal-containing polyurethane-ureas (MSalOMe$_2$trien-PUUs) and metal-containing copolyureas (MSalOMe$_2$trien-coPUs)

3.3.3.1 Synthesis of metal-containing polyurethane-ureas (MSalOMe$_2$trien-PUUs) from the reaction between MSalOMe$_2$trien, MDI and dialcohols



Metal-containing polyurethane-ureas were synthesized by polyaddition reaction between MSalOMe$_2$trien (M = Zn and Ni), MDI and dialcohols. The mole ratio of MSalOMe$_2$trien:MDI:dialcohol employed was 1:2:1. Except for ZnSalOMe$_2$trien-MDI-PEG which two other mole ratios, 1.5:2:0.5 and 0.5:2:1.5, were employed. A typical procedure for the preparation of metal-containing polyurethane-ureas is as follows: MSalOMe$_2$trien and dialcohol were dissolved in 6 mL of dried DMF in a 50 mL, two-necked round bottomed flask equipped with a nitrogen inlet. MDI in dried DMF (2 mL) was then added into the mixture followed by addition of dibutyltin dilaurate (3-4 drops) as a catalyst. The polymerization was done at 90°C for 48 hours. The composition of starting materials is shown in Table 3.2. 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*. Zinc- and nickel-containing polyurethane-ureas were obtained as yellowish powder and dark-brown powder, respectively. The yield obtained for the polymers was in the range 69-92%.

Table 3.2 Composition of starting materials in the preparation of $MSalOMe_2trien$-PUUs from MDI

Polymer codes	Weight of starting material (g)				Yield (%)
	$ZnSalOMe_2trien$	$NiSalOMe_2trien$	MDI	Dialcohols	
$ZnSalOMe_2trien$-MDI-HMDO (1:2:1)	0.360 g (0.75 mmol)	-	0.376 g (1.50 mmol)	0.089 g (0.75 mmol)	87
$ZnSalOMe_2trien$-MDI-BPA (1:2:1)	0.360 g (0.75 mmol)	-	0.376 g (1.50 mmol)	0.172 g (0.75 mmol)	83
$ZnSalOMe_2trien$-MDI-TEG (1:2:1)	0.360 g (0.75 mmol)	-	0.376 g (1.50 mmol)	0.113 g (0.75 mmol)	69
$ZnSalOMe_2trien$-MDI-PEG (1.5: 2: 0.5)	0.539 (1.13 mmol)	-	0.376 g (1.50 mmol	0.113 g (0.38 mmol)	62
$ZnSalOMe_2trien$-MDI-PEG (1:2:1)	0.360 g (0.75 mmol)	-	0.376 g (1.50 mmol)	0.225 g (0.75 mmol)	75
$ZnSalOMe_2trien$-MDI-PEG (0.5: 2: 1.5)	0.180 g (0.376 mmol)	-	0.376 g (1.50 mmol	0.338 g (1.13 mmol)	54
$NiSalOMe_2trien$-MDI-HMDO (1:2:1)	-	0.354 g (0.75 mmol)	0.376 g (1.50 mmol)	0.089 g (0.75 mmol)	91
$NiSalOMe_2trien$-MDI-BPA (1:2:1)	-	0.354 g (0.75 mmol)	0.376 g (1.50 mmol)	0.172 g (0.75 mmol)	92
$NiSalOMe_2trien$-MDI-TEG (1:2:1)	-	0.354 g (0.75 mmol)	0.376 g (1.50 mmol)	0.113 g (0.75 mmol)	76
$NiSalOMe_2trien$-MDI-PEG (1:2:1)	-	0.354 g (0.75 mmol)	0.376 g (1.50 mmol)	0.225 g (0.75 mmol)	84

In the polymer codes, $ZnSalOMe_2trien$ and $NiSalOMe_2trien$ refer to metal complexes. MDI represented 4,4′-diphenylmethane diisocyanate. The last three digits refer to the mole ratios of the polymer compositions.

$ZnSalOMe_2trien$-MDI-HMDO (1:2:1): IR (KBr, cm^{-1}); 3352 (N–H), 2924 (C-H), 2853 (C-H), 1678 (C=O), 1610 (C=C), 1543 (N-H), 1513 (C=C), 1445 (C-H), 1413 (C-H), 1311 (C-O), 1237 (C-N), 1084 (C-O), 976, 819, 740 (C-H). ^{1}H NMR (400 MHz, DMSO-d_6, ppm); δ 8.95-8.20 (*m*, C**H**=N and OC=ON**H**), 7.51-7.43 (*m*, Ar-**H**), 7.39-7.28 (*m*, Ar-**H**), 7.18-7.02 (*m*, Ar-**H**), 6.92-6.73 (*m*, Ar-**H**), 6.52-6.41 (*m*, Ar-**H**), 4.94-4.71 (*m*, NC=ON**H**), 3.85-3.76 (*m*, Ar-C**H**$_2$-Ar), 3.76-3.46 (*m*, OC**H**$_2$ and OC**H**$_3$), 1.48-1.07 (*m*, C**H**$_2$).

ZnSalOMe$_2$trien-MDI-BPA (1:2:1): IR (KBr, cm^{-1}); 3378 (N–H), 2926 (C-H), 1678 (C=O), 1613 (C=C), 1544 (N-H), 1512 (C=C), 1446 (C-H), 1311 (C-O),1241 (C-N), 1082 (C-O), 832, 740 (C-H). ^{1}H NMR (400 MHz, DMSO-d$_6$, ppm); δ 9.15-9.02 (*brs*, OC=ON**H**), 8.94-7.89 (*m*, C**H**=N), 7.39-7.18 (*m*, Ar-**H**), 7.17-7.00 (*m*, Ar-**H**), 6.95 (*d*, *J* = 8.4 Hz, Ar-**H**), 6.93-6.73 (*m*, Ar-**H**), 6.61 (*d*, *J* = 8.4 Hz, Ar-**H**), 6.50-6.40 (*m*, Ar-**H**), 4.92-4.67 (*m*, NC=ON**H**), 3.86-3.48 (*m*, Ar-C**H**$_2$-Ar and OC**H**$_3$), 1.51 (*brs*, C**H**$_3$).

ZnSalOMe$_2$trien-MDI-TEG (1:2:1): IR (KBr, cm^{-1}); 3426 (N–H), 2924 (C-H), 2852 (C-H), 1677 (C=O), 1609 (C=C), 1543 (N-H), 1513 (C=C), 1445 (C-H), 1308 (C-O), 1241 (C-N), 1082 (C-O), 819, 740 (C-H). ^{1}H NMR (400 MHz, DMSO-d$_6$, ppm); δ 8.95-7.88 (*m*, C**H**=N and OC=ON**H**), 7.57-7.17 (*m*, Ar-**H**), 7.17-6.91 (*m*, Ar-**H**), 6.89-6.62 (*m*, Ar-**H**), 6.61-6.23 (*m*, Ar-**H**), 4.88-4.69 (*m*, NC=ON**H**), 3.96-3.36 (*m*, OC**H**$_2$, OC**H**$_3$, and Ar-C**H**$_2$-Ar).

ZnSalOMe$_2$trien-MDI-PEG (1.5:2:0.5): IR (KBr, cm^{-1}); 3353 (N–H), 2924 (C-H), 2852 (C-H), 1633 (C=N), 1601 (C=C), 1543 (N-H), 1512 (C=C), 1468 , 1445 (C-H), 1312 (C-O), 1238 (C-N), 1215, 1080 (C-O), 739 (C-H). ^{1}H NMR (400 MHz, DMSO-d$_6$, ppm); δ 8.98-8.17 (*m*, C**H**=N and OC=ON**H**), 7.40-7.18 (*m*, Ar-**H**), 7.17-6.93 (*m*, Ar-**H**), 6.92-6.74 (*m*, Ar-**H**), 6.68 (*d*, *J* = 6.8 Hz, Ar-**H**), 6.60 (*d*, *J* = 6.4 Hz, Ar-**H**), 6.52-6.41 (*m*, Ar-**H**), 6.12 (*t*, *J* = 7.6 Hz, Ar-**H**), 4.90-4.77 (*m*, NC=ON**H**), 3.93-3.53 (*m*, OC**H**$_2$, OC**H**$_3$, and Ar-C**H**$_2$-Ar).

ZnSalOMe$_2$trien-MDI-PEG (1:2:1): IR (KBr, cm^{-1}); 3426 (N–H), 2924 (C-H), 1678 (C=O), 1622 (C=C), 1543 (N-H), 1513 (C=C), 1446 (C-H), 1410, 1312 (C-O), 1240 (C-N), 1081 (C-O), 819, 741 (C-H). ^{1}H NMR (400 MHz, DMSO-d$_6$, ppm); δ 8.98-8.19 (*m*, C**H**=N and OC=ON**H**), 7.53-7.42 (*m*, Ar-**H**), 7.42-7.21 (*m*, Ar-**H**), 7.21-6.93 (*m*, Ar-**H**), 6.93-6.74 (*m*, Ar-**H**), 6.70 (*d*, *J* = 7.6 Hz, Ar-**H**), 6.60 (*d*, *J* = 7.2 Hz, Ar-**H**), 6.51-6.41 (*m*, Ar-**H**), 6.10 (*t*, *J* = 7.6 Hz, Ar-**H**), 4.98-4.72 (*m*, NC=ON**H**), 4.20-3.43 (*m*, OC**H**$_2$, OC**H**$_3$, and Ar-C**H**$_2$-Ar).

ZnSalOMe$_2$trien-MDI-PEG (0.5:2:1.5): 3348 (N–H), 2923 (C-H), 1676 (C=O), 1645 (C=N), 1600 (C=C), 1543 (N-H), 1512 (C=C), 1466, 1442 (C-H), 1411, 1310 (C-O), 1236 (C-N), 1079 (C-O), 817, 740 (C-H). ^{1}H NMR (400 MHz, DMSO-d$_6$, ppm); δ 8.97-8.13 (*m*, C**H**=N and OC=ON**H**), 7.42-7.20 (*m*, Ar-**H**), 7.19-6.92 (*m*, Ar-**H**), 6.91-6.75 (*m*, Ar-**H**), 6.55-6.31 (*m*, Ar-**H**), 4.92-4.72 (*m*, NC=ON**H**), 3.83-3.58 (*m*, OC**H**$_2$, OC**H**$_3$, and Ar-C**H**$_2$-Ar).

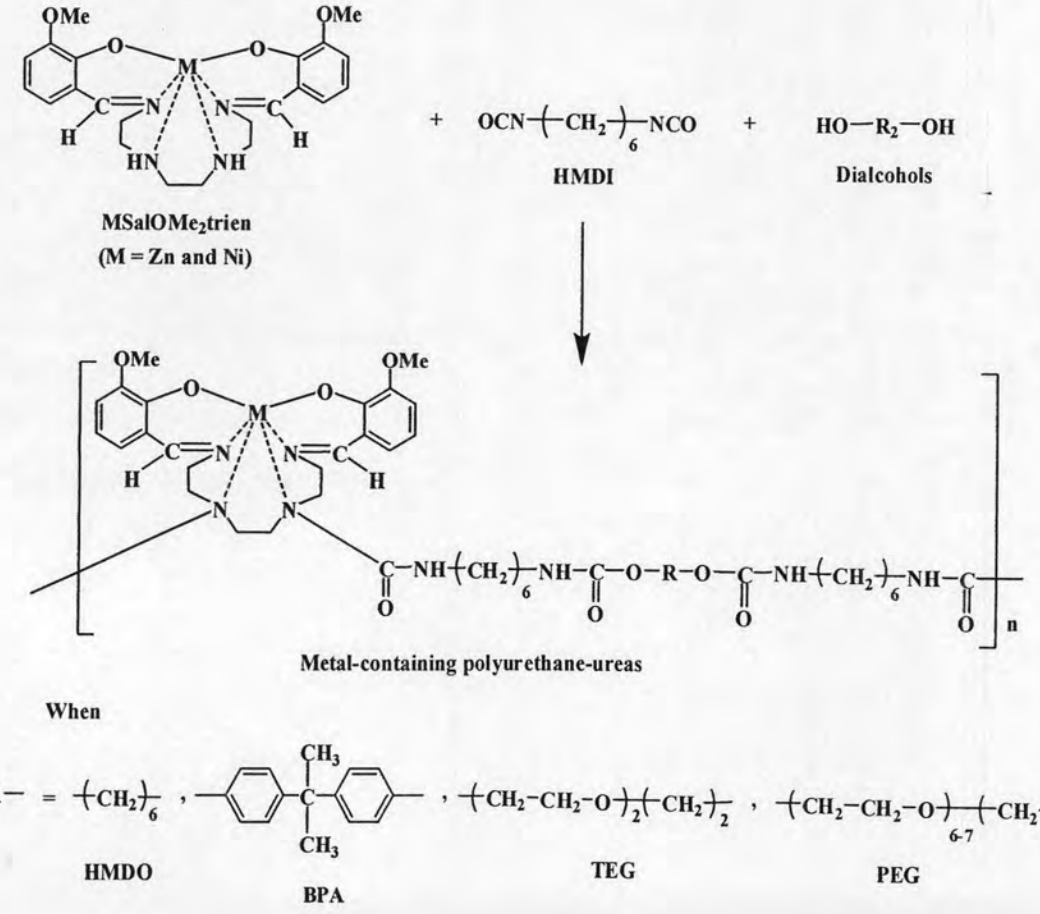
NiSalOMe$_2$trien-MDI-HMDO (1:2:1): IR (KBr, cm^{-1}); 3327 (N–H), 2925 (C-H), 1704 (C=O), 1631 (C=N), 1602 (C=C), 1535 (N-H), 1515 (C=C), 1470, 1444 (C-H), 1411, 1313 (C-O), 1226 (C-N), 1075 (C-O), 817, 744 (C-H).

NiSalOMe$_2$trien-MDI-BPA (1:2:1): IR (KBr, cm^{-1}); 3323 (N–H), 2924 (C-H), 1641 (C=N), 1600 (C=C), 1541 (N-H), 1512 (C=C), 1442 (C-H), 1411, 1311 (C-O), 1234 (C-N), 1075 (C-O), 835, 737 (C-H).

NiSalOMe$_2$trien-MDI-TEG (1:2:1): IR (KBr, cm^{-1}); 3420 (N–H), 2924 (C-H), 1665 (C=O), 1606 (C=C), 1540 (N-H), 1513 (C=C), 1461, 1445 (C-H), 1411, 1312 (C-O), 1235 (C-N), 1080 (C-O), 739 (C-H).

NiSalOMe$_2$trien-MDI-PEG (1:2:1): IR (KBr, cm^{-1}); 3304 (N-H), 2917 (C–H), 1707 (C=O), 1632 (C=N), 1600 (C=C), 1539 (N-H), 1514 (C=C), 1472, 1445 (C-H), 1411, 1311 (C-O), 1225 (C-N), 1080 (C-O), 741 (C-H).

3.3.3.2 Synthesis of metal-containing polyurethane-ureas (MSalOMe$_2$trien-PUUs) from the reaction between MSalOMe$_2$trien and HMDI and dialcohols



When

The experiment was performed according to procedure described in experiment 3.3.3.1 employing hexamethylene diisocyanate (HMDI) instead of MDI. The mole ratio of MSalOMe$_2$trien:HMDI:dialcohol employed was 1:2:1. The polymerization was done at 90°C for 48 hours. The composition of starting materials is shown in Table 3.3. Zinc- and nickel-containing polyurethane-ureas were obtained as orange-yellow powder and dark brown powder, respectively. The yield obtained for the polymers was in the range 54-92%.

Table 3.3 Composition of starting materials in the preparation of MSalOMe$_2$trien-PUUs from HMDI at the mole ratio of MSalOMe$_2$trien:HMDI:dialcohol = 1:2:1

Polymer codes	Weight of starting material (g)				Yield (%)
	ZnSalOMe$_2$trien	NiSalOMe$_2$trien	HMDI	Dialcohols	
ZnSalOMe$_2$trien-HMDI-HDO	0.360 g (0.75 mmol)	-	0.242 mL (1.50 mmol)	0.089 g (0.75 mmol)	70
ZnSalOMe$_2$trien-HMDI-BPA	0.360 g (0.75 mmol)	-	0.242 mL (1.50 mmol)	0.172 g (0.75 mmol)	88
ZnSalOMe$_2$trien-HMDI-TEG	0.360 g (0.75 mmol)	-	0.242 mL (1.50 mmol)	0.113 g (0.75 mmol)	75
ZnSalOMe$_2$trien-HMDI-PEG	0.360 g (0.75 mmol)	-	0.242 mL (1.50 mmol)	0.225 g (0.75 mmol)	54
NiSalOMe$_2$trien-HMDI-HDO	-	0.354 g (0.75 mmol)	0.242 mL (1.50 mmol)	0.089 g (0.75 mmol)	82
NiSalOMe$_2$trien-HMDI-BPA	-	0.354 g (0.75 mmol)	0.242 mL (1.50 mmol)	0.172 g (0.75 mmol)	92
NiSalOMe$_2$trien-HMDI-TEG	-	0.354 g (0.75 mmol)	0.242 mL (1.50 mmol)	0.113 g (0.75 mmol)	65
NiSalOMe$_2$trien-HMDI-PEG	-	0.354 g (0.75 mmol)	0.242 mL (1.50 mmol)	0.225 g (0.75 mmol)	56

ZnSalOMe$_2$trien-HMDI-HMDO: IR (KBr, cm^{-1}); 3348 (N–H), 2929 (C-H), 2857 (C-H), 1702 (C=O), 1628 (C=N), 1551 (N-H), 1450 (C-H), 1244 (C-N), 1217, 1080 (C-O), 740 (C-H). ^{1}H NMR (400 MHz, DMSO-d$_6$, ppm); δ 8.56-7.90 (*m*, C**H**=N), 7.18-6.94 (*brs*, OC=ON**H**), 6.93-5.88 (*m*, Ar-**H**), 5.81-5.64 (*brs*, NC=ON**H**), 3.98-3.83 (*m*, HNCO-OC**H**$_2$), 3.84-3.53 (*m*, OC**H**$_3$), 3.01-2.86 (*m*, HN-C**H**$_2$), 1.64-1.09 (*m*, C**H**$_2$).

ZnSalOMe$_2$trien-HMDI-BPA: IR (KBr, cm^{-1}); 3343 (N-H), 2929 (C-H), 2857 (C-H), 1628 (C=N), 1569 (N-H), 1512 (C=C), 1450 (C-H), 1244 (C-N), 1219, 1178, 1082

(C-O), 834, 740 (C-H). ^{1}H NMR (400 MHz, DMSO-d_6, ppm); δ 9.21-9.04 (*brs*, OC=ONH), 8.54-7.87 (*m*, CH=N), 6.95 (*d*, *J* = 7.9 Hz, Ar-H), 6.90-6.66 (*m*, Ar-H), 6.61 (*d*, *J* = 7.9 Hz, Ar-H), 6.52-5.95 (*m*, Ar-H), 5.81-5.63 (*brs*, NC=ONH), 3.93-3.50 (*m*, OCH_3), 3.08-2.83 (*m*, HN-CH_2), 1.50 (*s*, CH_3), 1.38-1.06 (*brs*, CH_2).

ZnSalOMe$_2$trien-HMDI-TEG: IR (KBr, cm^{-1}); 3353 (N–H), 2928 (C-H), 2856 (C-H), 1704 (C=O), 1627 (C=N), 1550 (N-H), 1449 (C-H), 1316 (C-O), 1243 (C-N), 1216, 1080 (C-O), 739 (C-H). ^{1}H NMR (400 MHz, DMSO-d_6, ppm); δ 8.56-7.90 (*m*, CH=N), 7.25-5.85 (*m*, Ar-H), 5.83-5.62 (*brs*, NC=ONH), 4.09-3.95 (*m*, OC=ONH), 3.82-3.44 (*m*, OCH_2 and OCH_3), 3.10-2.84 (*m*, HN-CH_2), 1.51-1.10 (*m*, CH_2).

ZnSalOMe$_2$trien-HMDI-PEG: IR (KBr, cm^{-1}); 3345 (N–H), 2928 (C-H), 2856 (C-H0, 1629 (C=N), 1563 (N-H), 1465 (C-H), 1450, 1319 (C-O), 1242 (C-N), 1217, 1082 (C-O), 740 (C-H). ^{1}H NMR (400 MHz, DMSO-d_6, ppm); δ 8.56-7.93 (*m*, CH=N), 7.24-5.89 (*m*, Ar-H), 5.81-5.66 (*brs*, NC=ONH), 4.14-3.86 (*m*, OC=ONH), 3.77-3.44 (*m*, OCH_2 and OCH_3), 3.08-2.79 (*m*, HN-CH_2), 1.51-1.09 (*m*, CH_2).

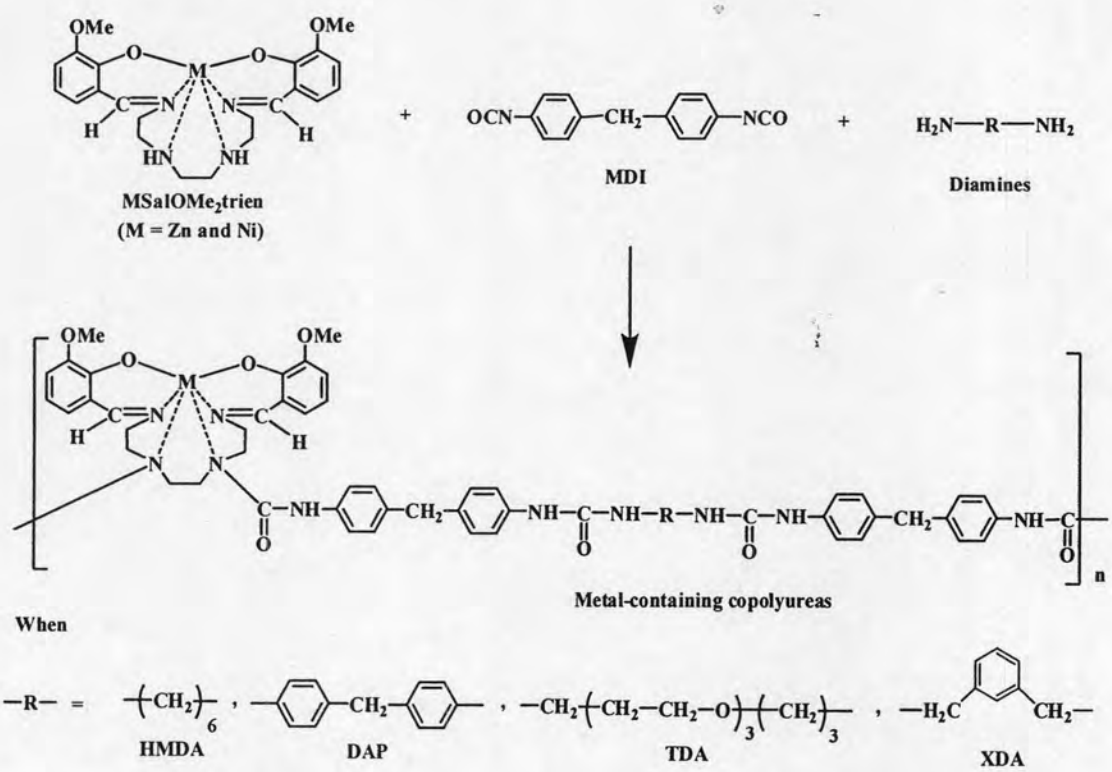
NiSalOMe$_2$trien-HMDI-HMDO: IR (KBr, cm^{-1}); 3333 (N–H), 2930 (C-H), 2857 (C-H), 1700 (C=O), 1633 (C=N), 1545 (N-H), 1450 (C-H), 1247 (C-N), 1142, 1079 (C-O), 738 (C-H).

NiSalOMe$_2$trien-HMDI-BPA: IR (KBr, cm^{-1}); 3362 (N–H), 2929 (C-H), 2858 (C-H), 1622 (C=N), 1562 (N-H), 1513 (C=C), 1451 (C-H), 1244 (C-N), 1176, 1082 (C-O), 834, 739 (C-H).

NiSalOMe$_2$trien-HMDI-TEG: IR (KBr, cm^{-1}); 3331 (N–H), 2930 (C-H), 2857 (C-H), 1706 (C=O), 1631 (C=N), 1547 (N-H), 1450 (C-H), 1248 (C-N), 1107 (C-O), 738 (C-H).

NiSalOMe$_2$trien-HMDI-PEG: IR (KBr, cm^{-1}); 3328 (N–H), 2929 (C-H), 2858 (C-H), 1703 (C=O), 1628 (C=N), 1571 (N-H), 1471 (C-H), 1444, 1331 (C-O), 1246 (C-N), 1086 (C-O), 740 (C-H).

3.3.3.3 Synthesis of metal-containing copolyureas (MSalOMe$_2$trien-coPUs) from the reaction between MSalOMe$_2$trien, MDI and diamines



Metal-containing copolyureas were synthesized by polyaddition reaction between MSalOMe$_2$trien (M = Zn and Ni), MDI and diamines. The mole ratio of MSalOMe$_2$trien:MDI:diamine employed was 1:2:1. A typical procedure for the preparation of metal-containing copolyureas is as follows: MSalOMe$_2$trien and diamine were dissolved in 8 mL of dried DMF in a 50 mL, two-necked round bottomed flask equipped with a nitrogen inlet. MDI in dried DMF (2 mL) was then added into the mixture followed by addition of dibutyltin dilaurate (3-4 drops) as a catalyst. The polymerization was done at 90°C for 48 hours. The composition of starting materials is shown in Table 3.4. 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*. Zinc- and nickel-containing copolyureas were obtained as brown powder and dark-brown powder, respectively. The yield obtained for the polymers was in the range 78-96%.

Table 3.4 Composition of starting materials in the preparation of MSalOMe$_2$trien-coPUs from MDI at the mole ratio of MSalOMe$_2$trien:MDI:diamine = 1:2:1

Polymer codes	Weight of starting material (g)				Yield (%)
	ZnSalOMe$_2$trien	NiSalOMe$_2$trien	MDI	Diamines	
ZnSalOMe$_2$trien-MDI-HMDA	0.360 g (0.75 mmol)	-	0.376 g (1.50 mmol)	0.087 g (0.75 mmol)	90
ZnSalOMe$_2$trien-MDI-DAP	0.360 g (0.75 mmol)	-	0.376 g (1.50 mmol)	0.149 g (0.75 mmol)	85
ZnSalOMe$_2$trien-MDI-XDA	0.360 g (0.75 mmol)	-	0.376 g (1.50 mmol)	0.102 g (0.75 mmol)	88
ZnSalOMe$_2$trien-MDI-TDA	0.360 g (0.75 mmol)	-	0.376 g (1.50 mmol)	0.166 g (0.75 mmol)	84
NiSalOMe$_2$trien-MDI-HMDA	-	0.354 g (0.75 mmol)	0.376 g (1.50 mmol)	0.087 g (0.75 mmol)	91
NiSalOMe$_2$trien-MDI-DAP	-	0.354 g (0.75 mmol)	0.376 g (1.50 mmol)	0.149 g (0.75 mmol)	96
NiSalOMe$_2$trien-MDI-XDA	-	0.354 g (0.75 mmol)	0.376 g (1.50 mmol)	0.102 g (0.75 mmol)	92
NiSalOMe$_2$trien-MDI-TDA	-	0.354 g (0.75 mmol)	0.376 g (1.50 mmol)	0.166 g (0.75 mmol)	78

ZnSalOMe$_2$trien-MDI-HMDA: IR (KBr, cm^{-1}); 3337 (N–H), 2931 (C-H), 1634 (C=N, C=O), 1604 (C=C), 1548 (N-H), 1513 (C=C), 1465 (C-H), 1411, 1310 (C-O), 1239 (C-N), 1085, 741 (C-H). ^{1}H NMR (400 MHz, DMSO-d$_6$, ppm); δ 8.59-8.19 (*brs*, HNC=ON**H**Ar and C**H**=N), 7.33-7.17 (*m*, Ar-**H**), 7.09-6.92 (*m*, Ar-**H**), 6.89-6.75 (*m*, Ar-**H**), 6.54-6.39 (*m*, Ar-**H**), 6.11-5.97 (*brs*, HNC=ON**H**CH$_2$), 4.93-4.68 (*brs*, NC=ON**H**), 3.79-3.54 (*m*, Ar-C**H**$_2$-Ar and OC**H**$_3$), 3.13-2.97 (*m*, HN-C**H**$_2$), 1.52-1.16 (*m*, C**H**$_2$).

ZnSalOMe$_2$trien-MDI-DAP: IR (KBr, cm^{-1}); 3366 (N–H), 3030 (C-H), 2928 (C-H), 1669 (C=O), 1639 (C=N), 1603 (C=C), 1512 (C=C), 1445 (C-H), 1412, 1311 (C-O), 1235 (C-N), 1082, 818, 741 (C-H). ^{1}H NMR (400 MHz, DMSO-d$_6$, ppm); δ 8.59-8.46 (*m*, HNC=ON**H**Ar), 7.41-7.24 (*m*, Ar-**H**), 7.21-6.99 (*m*, Ar-**H**), 6.90-6.77 (*m*, Ar-**H**), 6.54-6.39 (*m*, Ar-**H**), 4.98-4.72 (*brs*, NC=ON**H**), 4.09-3.40 (*m*, Ar-C**H**$_2$-Ar and OC**H**$_3$).

ZnSalOMe$_2$trien-MDI-XDA: IR (KBr, cm^{-1}); 3380 (N–H), 2924 (C-H), 1636 (C=N, C=O), 1602 (C=C), 1546 (N-H), 1514 (C=C), 1446 (C-H), 1410, 1311 (C-O), 1221 (C-N), 1082, 740 (C-H). ^{1}H NMR (400 MHz, DMSO-d$_6$, ppm); δ 8.57-8.35 (*brs*, HNC=ON**H**Ar), 8.29-8.14 (*m*, C**H**=N), 7.41-7.23 (*m*, Ar-**H**), 7.23-7.11 (*m*, Ar-**H**),

7.11-6.93 (*m*, Ar-**H**), 6.93-6.72 (*m*, Ar-**H**), 6.67 (*d*, *J* = 7.6 Hz, Ar-**H**), 6.63-6.52 (*m*, Ar-**H**), 6.51-6.42 (*m*, HNC=ONH$\mathbf{CH_2}$), 6.10 (*t*, *J* = 7.6 Hz, Ar-**H**), 4.93-4.73 (*m*, NC=ON**H**), 4.33-4.19 (*m*, Ar-C$\mathbf{H_2}$-NH), 3.94-3.50 (*m*, Ar-C$\mathbf{H_2}$-Ar and OC$\mathbf{H_3}$).

ZnSalOMe$_2$trien-MDI-TDA: IR (KBr, cm^{-1}); 3343 (N–H), 2869 (C-H), 1665 (C=O), 1630 (C=N), 1602 (C=C), 1546 (N-H), 1512 (C=C), 1444 (C-H), 1410, 1310 (C-O), 1236 (C-N), 1090 (C-O), 740 (C-H). ^{1}H NMR (400 MHz, DMSO-d$_6$, ppm); δ 8.83-7.99 (*brs*, C**H**=N and HNC=ON**H**Ar), 7.39-7.18 (*m*, Ar-**H**), 7.17-6.92 (*m*, Ar-**H**) 6.92-6.72 (*m*, Ar-**H**), 6.57-6.36 (*m*, Ar-**H**), 6.17-5.99 (*brs*, HNC=ON**H**CH$_2$), 4.90-4.75 (*brs*, NC=ON**H**), 3.85-3.56 (*m*, Ar-C$\mathbf{H_2}$-Ar and OC$\mathbf{H_2}$), 3.55-3.44 (*m*, OC$\mathbf{H_3}$), 3.20-2.95 (*m*, HN-C$\mathbf{H_2}$), 1.72-1.49 (*m*, C$\mathbf{H_2}$).

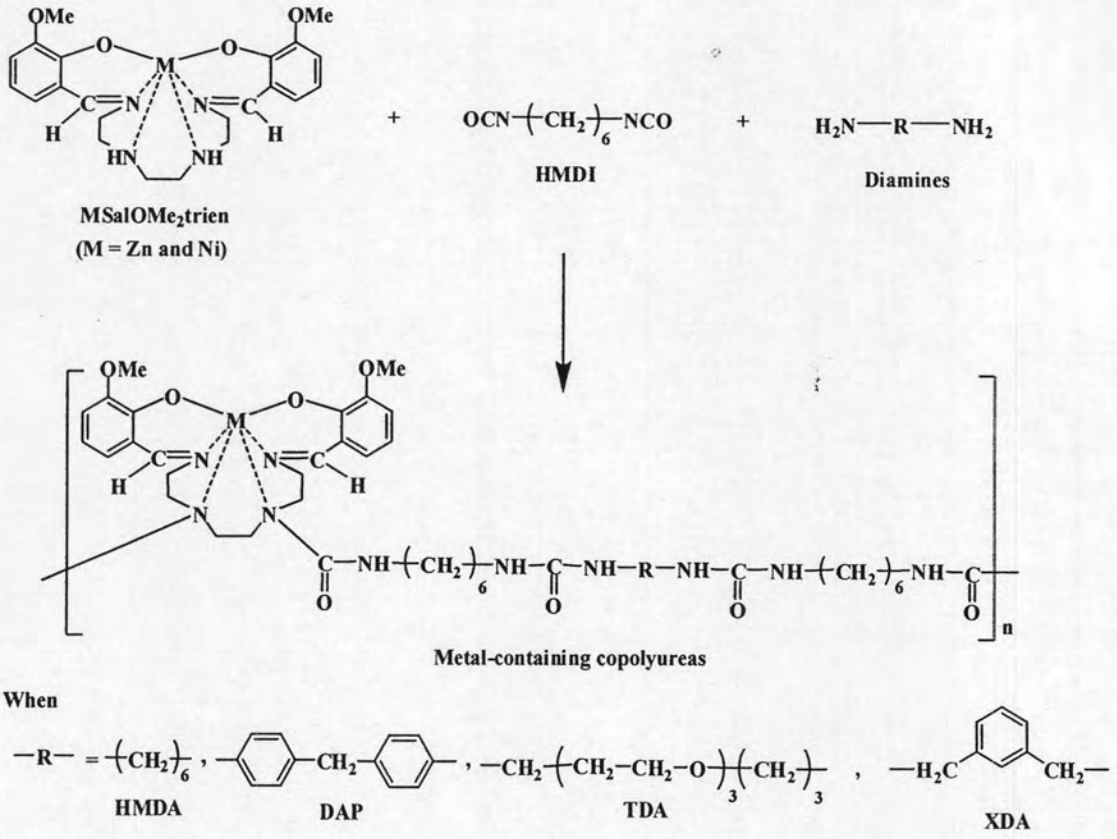
NiSalOMe$_2$trien-MDI-HMDA: IR (KBr, cm^{-1}); 3377 (N–H), 2927 (C-H), 2856 (C-H), 1639 (C=N, C=O), 1605 (C=C), 1546 (N-H), 1514 (C=C), 1465 (C-H), 1410, 1312 (C-O), 1238 (C-N), 1084 (C-O), 740 (C-H).

NiSalOMe$_2$trien-MDI-DAP: IR (KBr, cm^{-1}); 3313 (N–H), 3033 (C-H), 2923 (C-H), 1642 (C=N, C=O), 1600 (C=C), 1544 (N-H), 1513 (C=C), 1444 (C-H), 1411, 1310 (C-O), 1235 (C-N), 1083 (C-O), 817, 740 (C-H).

NiSalOMe$_2$trien-MDI-XDA: IR (KBr, cm^{-1}); 3382 (N–H), 2924 (C-H), 2856 (C-H), 1670 (C=O), 1639 (C=N), 1605 (C=C), 1544 (N-H), 1514 (C=C), 1465, 1444 (C-H), 1410, 1312 (C-O), 1237 (C-N), 1083 (C-O), 740 (C-H).

NiSalOMe$_2$trien-MDI-TDA: IR (KBr, cm^{-1}); 3365 (N–H), 2924 (C-H), 1661 (C=O), 1603 (C=N), 1545 (N-H), 1514 (C=C), 1461, 1445 (C-H), 1410, 1312 (C-O), 1237 (C-N), 1104 (C-O), 740 (C-H).

3.3.3.4 Synthesis of metal-containing copolyureas (MSalOMe$_2$trien-coPUs) from the reaction between MSalOMe$_2$trien, HMDI and diamines



When

The experiment was performed according to procedure described in experiment 3.3.3.3 employing hexamethylene diisocyanate (HMDI) instead of MDI. The mole ratio of MSalOMe$_2$trien:HMDI:diamine employed was 1:2:1. The composition of starting materials is shown in Table 3.5. Zinc- and nickel-containing copolyureas were obtained as yellow-orange powder and brown powder, respectively. The yield obtained for the polymers was in the range 48-96%.

Table 3.5 Composition of starting materials in the preparation of $MSalOMe_2trien$-coPUs from HMDI at the mole ratio of $MSalOMe_2trien$:HMDI:diamine = 1:2:1

Polymer codes	Weight of starting material (g)				Yield (%)
	$ZnSalOMe_2trien$	$NiSalOMe_2trien$	HMDI	Diamines	
$ZnSalOMe_2trien$-HMDI-HMDA	0.360 g (0.75 mmol)	-	0.242 mL (1.50 mmol)	0.087 g (0.75 mmol)	90
$ZnSalOMe_2trien$-HMDI-DAP	0.360 g (0.75 mmol)	-	0.242 mL (1.50 mmol)	0.149 g (0.75 mmol)	85
$ZnSalOMe_2trien$-HMDI-XDA	0.360 g (0.75 mmol)	-	0.242 mL (1.50 mmol)	0.102 g (0.75 mmol)	88
$ZnSalOMe_2trien$-HMDI-TDA	0.360 g (0.75 mmol)	-	0.242 mL (1.50 mmol)	0.166 g (0.75 mmol)	84
$NiSalOMe_2trien$-HMDI-HMDA	-	0.354 g (0.75 mmol)	0.242 mL (1.50 mmol)	0.087 g (0.75 mmol)	91
$NiSalOMe_2trien$-HMDI-DAP	-	0.354 g (0.75 mmol)	0.242 mL (1.50 mmol)	0.149 g (0.75 mmol)	96
$NiSalOMe_2trien$-HMDI-XDA	-	0.354 g (0.75 mmol)	0.242 mL (1.50 mmol)	0.102 g (0.75 mmol)	92
$NiSalOMe_2trien$-HMDI-TDA	-	0.354 g (0.75 mmol)	0.242 mL (1.50 mmol)	0.166 g (0.75 mmol)	78

$ZnSalOMe_2trien$-HMDI-HMDA: IR (KBr, cm^{-1}); 3400 (N–H), 2927 (C-H), 2856 (C-H), 1627 (C=N, C=O), 1573 (N-H), 1461 (C-H), 1248 (C-N), 1082 (C-O), 739 (C-H). ^1H NMR (400 MHz, DMSO-d_6, ppm); δ 8.62-7.84 (*brs*, C**H**=N), 7.15-6.15 (*m*, Ar-**H**), 6.10-5.95 (*brs*, HNC=ON**H**CH_2), 5.80-5.67 (*brs*, NC=ON**H**), 3.84-3.58 (*m*, O**C**H_3 and HN-**C**H_2), 1.51-0.70 (**C**H_2).

$ZnSalOMe_2trien$-HMDI-DAP: IR (KBr, cm^{-1}); 3417 (N–H), 2928 (C-H), 2857 (C-H), 1624 (C=N, C=O), 1574 (N-H), 1515 (C=C), 1448 (C-H), 1313 (C-O), 1243 (C-N), 1082 (C-O), 740 (C-H). ^1H NMR (400 MHz, DMSO-d_6, ppm); δ 8.97-8.38 (*brs*, HNC=ON**H**Ar), 8.26-8.19 (*m*, C**H**=N), 7.61-6.37 (*m*, Ar-**H**), 5.98-5.60 (*brs*, NC=ON**H**), 4.93-4.74 (*m*, HNC=ON**H**CH_2), 3.88-3.49 (*m*, O**C**H_3 and Ar-**C**H_2-Ar), 3.02-2.82 (*m*, HN-**C**H_2), 1.40-0.90 (*m*, **C**H_2).

$ZnSalOMe_2trien$-HMDI-XDA: IR (KBr, cm^{-1}); 3349 (N–H), 2928 (C-H), 2857 (C-H), 1629 (C=N, C=O), 1566 (N-H), 1452 (C-H), 1245 (C-N), 1219, 1083 (C-O), 740 (C-H). ^1H NMR (400 MHz, DMSO-d_6, ppm); δ 8.86-7.89 (*m*, C**H**=N), 7.54-6.15 (*m*, Ar-**H** and HNC=ON**H**CH_2), 5.99-5.85 (*brs*, HNC=ON**H**CH_2Ar), 5.81-5.68 (*brs*,

NC=ONH), 4.37-4.01 (*m*, Ar-CH_2), 3.85-3.54 (*m*, OCH_3), 3.09-2.84 (*m*, HN-CH_2), 1.60-0.70 (*m*, CH_2).

ZnSalOMe$_2$trien-HMDI-TDA: IR (KBr, cm^{-1}); 3351 (N–H), 2927 (C-H), 2857 (C-H), 1628 (C=N, C=O), 1566 (N-H), 1452 (C-H), 1244 (C-N), 1218, 1087 (C-O), 740 (C-H). ^{1}H NMR (400 MHz, DMSO-d_6, ppm); δ 8.62-7.85 (*m*, CH=N), 7.14-5.99 (*m*, Ar-H), 5.88-5.67 (*brs*, NC=ONHAr and NC=ONHCH_2), 3.67 (*brs*, OCH_3), 3.50-3.46 (*m*, OCH_2), 3.09-2.83 (*m*, HN-CH_2), 1.57-0.70 (*m*, CH_2).

NiSalOMe$_2$trien-HMDI-HMDA: IR (KBr, cm^{-1}); 3333 (N–H), 2929 (C-H), 2856 (C-H), 1623 (C=N, C=O), 1573 (N-H), 1462 (C-H), 1248 (C-N), 1082 (C-O), 738 (C-H).

NiSalOMe$_2$trien-HMDI-DAP: IR (KBr, cm^{-1}); 3407 (N–H), 2927 (C-H), 2856 (C-H), 1621 (C=N, C=O), 1551 (N-H), 1515 (C=C), 1463 (C-H), 1313 (C-O), 1243 (C-N), 1083 (C-O), 739 (C-H).

NiSalOMe$_2$trien-HMDI-XDA: IR (KBr, cm^{-1}); 3350 (N–H), 2927 (C-H), 2856 (C-H), 1628 (C=N,C=O), 1569 (N-H), 1445 (C-H), 1248 (C-N), 1082 (C-O), 738 (C-H).

NiSalOMe$_2$trien-HMDI-TDA: IR (KBr, cm^{-1}); 3340 (N–H), 2927 (C-H), 2856 (C-H), 1622 (C=N,C=O), 1451 (C-H), 1247 (C-N), 1089 (C-O), 739 (C-H).

3.3.4 Synthesis of reference polyurethanes and polyureas

The reference polyurethanes and polyureas were synthesized according to procedure described in experiment 3.3.3 but MSalOMe$_2$trien (M = Zn and Ni) was not used in the reaction. The mole ratio of diisocyanate:dialcohol or diamine employed was 1:1. The composition of starting materials is shown in Table 3.6. The reference polyurethanes and polyureas were obtained as white or yellow powder. The yield obtained for the polymers was in the range 38-97%.

Table 3.6 Composition of starting materials in the preparation of reference polyurethanes and polyureas at the mole ratio of diisocyanate:dialcohol or diamine employed was 1:1

Polymer codes	Weight. of Diisocyanates (g)	Weight of diamines (g)	Weight of dialcohols (g)	Yield (%)
MDI-HMDO	0.376 g (0.15 mmol)	-	0.178 g (0.15 mmol)	97
MDI-BPA	0.376 g (0.15 mmol)	-	0.344 g (0.15 mmol)	46
MDI-TEG	0.376 g (0.15 mmol)	-	0.226 g (0.15 mmol)	85
MDI-PEG	0.376 g (0.15 mmol)	-	0.450 g (0.15 mmol)	53
HMDI-HMDO	0.242 mL (0.15 mmol)	-	0.178 g (0.15 mmol)	38
HMDI-BPA	0.242 mL (0.15 mmol)	-	0.344 g (0.15 mmol)	58
HMDI-TEG	0.242 mL (0.15 mmol)	-	0.226 g (0.15 mmol)	40
HMDI-PEG	0.242 mL (0.15 mmol)	-	0.450 g (0.15 mmol)	37
MDI-HMDA	0.376 g (0.15 mmol)	0.174 g (0.15 mmol)	-	71
MDI-DAP	0.376 g (0.15 mmol)	0.298 g (0.15 mmol)	-	75
MDI-XDA	0.376 g (0.15 mmol)	0.204 g (0.15 mmol)	-	85
MDI-TDA	0.376 g (0.15 mmol)	0.332 g (0.15 mmol)	-	64
HMDI-HMDA	0.242 mL (0.15 mmol)	0.174 g (0.15 mmol)	-	64
HMDI-DAP	0.242 mL (0.15 mmol)	0.298 g (0.15 mmol)	-	53
HMDI-TDA	0.242 mL (0.15 mmol)	0.204 g (0.15 mmol)	-	96
HMDI-XDA	0.242 mL (0.15 mmol)	0.332 g (0.15 mmol)	-	74

Reference polyurethanes

MDI-HMDO: IR (KBr, cm^{-1}); 3323 (NH), 2930 (C-H), 2851 (C-H), 1706 (C=O), 1599 (C=C), 1528 (N-H)), 1412 (C-H), 1410, 1311 (C-O), 1228 (C-N), 1069 (C-O), 816, 769 (C-H), 508. ^{1}H-NMR (400 MHz, DMSO-d_6, ppm); δ 8.58-8.45 (*brs*, N**H**), 7.43-7.25 (*m*, Ar-**H**), 7.17-6.99 (*m*, Ar-**H**), 4.13-3.95 (*m*, C**H**$_2$O-CONH), 3.86-3.61 (*brs*, Ar-C**H**$_2$-Ar), 1.70-1.49 (*m*, C**H**$_2$), 1.49-1.12 (*m*, C**H**$_2$).

MDI-BPA: IR (KBr, cm^{-1}); 3308 (NH), 2910 (C-H), 2840 (C-H), 1645 (C=O), 1597 (C=C), 1545 (N-H), 1511 (C=C), 1410 (C-H), 1308 (C-O), 1234 (C-N), 1108 (C-O), 1011, 812 (C-H), 649, 508. ^{1}H-NMR (400 MHz, DMSO-d_6, ppm); δ 8.60-8.45 (*brs*,

NH), 7.41-7.24 (*m*, Ar-H), 7.18-6.99 (*m*, Ar-H), 6.90-6.77 (*m*, Ar-H), 6.53-6.41 (*m*, Ar-H), 3.87-3.61 (*brs*, Ar-CH_2-Ar), 1.57-1.17 (*brs*, CH_3).

MDI-TEG: IR (KBr, cm^{-1}); 3310 (NH), 3122 (C-H), 2923 (C-H), 1713 (C=O), 1647, 1601 (C=C), 1539 (N-H), 1459, 1411 (C-H), 1311 (C-O), 1231 (C-N), 1113, 1071, 818, 770 (C-H), 510. ^{1}H-NMR (400 MHz, DMSO-d_6, ppm); δ 9.75-7.57 (*m*, O=CNHAr), 8.54 (*s*, O=CNHCH_2), 7.56-7.25 (*m*, Ar-H), 7.23-6.95 (*m*, Ar-H), 4.27-4.04 (*brs*, CH_2O-CONH), 3.85-3.71 (*brs*, Ar-CH_2-Ar), 3.70-3.40 (*brs*, OCH_2).

MDI-PEG: IR (KBr, cm^{-1}); 3313 (NH), 3034, 2906, 1710 (C=O), 1645, 1599 (C=C), 1540 (N-H), 1509 (C=C), 1411 (C-H), 1309 (C-O), 1234 (C-N), 1108 (C-O), 815 (C-O), 642, 510. ^{1}H-NMR (400 MHz, DMSO-d_6, ppm); δ 8.62-8.43 (*brs*, O=CNHAr), 7.34 (*d*, J = 8.4 Hz, Ar-H), 7.10 (*d*, J = 8.0 Hz, Ar-H), 4.24-4.09 (*brs*, CH_2O-CONH), 3.84-3.73 (*brs*, Ar-CH_2-Ar), 3.72-3.38 (*m*, OCH_2).

HMDI-HMDO: IR (KBr, cm^{-1}); 3328 (N–H), 3057 (C-H), 2937 (C-H), 2861 (C-H), 1692 (C=O), 1538 (N-H), 1472 (C-H), 1341 (C-O), 1258 (C-N), 1140 (C-O), 1001, 778 (C-H). ^{1}H-NMR (400 MHz, DMSO-d_6, ppm); δ 7.19-6.91 (*brs*, NH), 4.08-3.75 (*brs*, CH_2O-CONH), 3.06-2.80 (*brs*, CH_2-NH), 1.66-0.91 (*m*, CH_2).

HMDI-BPA: IR (KBr, cm^{-1}); 3336 (N–H), 2966 (C-H), 2934 (C-H), 1713 (C=O), 1536 (N-H), 1500 (C=C), 1463 (C-H), 1258 (C-N), 1210, 1172 (C-O), 1015.

HMDI-TEG: IR (KBr, cm^{-1}); 3330 (N–H), 2932 (C-H), 2855 (C-H), 1691 (C=O), 1620, 1580, 1478, 1462, 1256 (C-N), 1119 (C-O), 626.

HMDI-PEG: IR (KBr, cm^{-1}); 3332 (N–H), 2933 (C-H), 2857 (C-H), 1694 (C=O), 1621, 1579, 1478, 1462, 1256 (C-N), 1110 (C-O), 627.

Reference polyureas

MDI-HMDA: IR (KBr, cm^{-1}); 3319 (NH), 2926 (C-H), 2855 (C-H), 1648 (C=O), 1598 (C=C), 1551 (N-H), 1513 (C=C), 1408 (C-H), 1309, 1236 (C-N), 1108, 1011, 816, 761, 652, 508. ^{1}H-NMR (400 MHz, DMSO-d_6, ppm); δ 8.42-8.24 (*m*, NH), 7.26 (*d*, J = 7.6 Hz, Ar-H), 7.01 (*d*, J = 8.0 Hz, Ar-H), 6.82 (*d*, J = 7.2 Hz, Ar-H), 6.46 (*d*, J = 8.0 Hz, Ar-H), 6.19-6.00 (*brs*, NH), 3.84-3.53 (*m*, Ar-CH_2-Ar), 3.13-2.95 (*m*, CH_2-NH), 1.55-1.11 (*m*, CH_2).

MDI-DAP: IR (KBr, cm^{-1}); 3308 (NH), 2918 (C-H), 2848 (C-H), 1644 (C=O), 1598 (C=C), 1545 (N-H), 1512 (C=C), 1410 (C-H), 1307, 1236 (C-N), 1112, 1018, 812,

649, 505. ^{1}H-NMR (400 MHz, DMSO-d_6, ppm); δ 8.53 (*s*, N**H**), 7.33 (*d*, *J* = 8.4 Hz, Ar-**H**), 7.09 (*d*, *J* = 8.0 Hz, Ar-**H**), 3.79 (*s*, Ar-C**H**$_2$-Ar).

MDI-XDA: IR (KBr, cm^{-1}); 3316 (N–H), 3029 (C-H), 2917 (C-H), 1653 (C=O), 1590 (C=C), 1546 (N-H), 1512 (C=C), 1409, 1308, 1229 (C-N). ^{1}H-NMR (400 MHz, DMSO-d_6, ppm); δ 8.64-8.38 (*m*, N**H**-Ar), 7.44-6.91 (*m*, Ar-**H**), 6.70-6.47 (*m*, N**H**-CH$_2$), 4.37-4.15 (*m*, NH-C**H**$_2$-Ar), 3.89-3.65 (*m*, Ar-C**H**$_2$-Ar).

MDI-TDA: IR (KBr, cm^{-1}); 3327 (N–H), 2865 (C-H), 1654 (C=O), 1598 (C=C), 1547 (N-H), 1509 (C=C), 1408, 1308 (C-O), 1232 (C-N), 1100, 815, 650. ^{1}H-NMR (400 MHz, DMSO-d_6, ppm); δ 8.43-8.22 (*brs*, N**H**-Ar), 7.39-7.14 (*brs*, Ar-**H**), 7.13-6.89 (*brs*, Ar-**H**), 6.17-5.96 (*brs*, N**H**-CH$_2$), 3.99-3.39 (*m*, Ar-C**H**$_2$-Ar and OC**H**$_2$), 3.20-2.97 (*brs*, C**H**$_2$-NH), 1.73-1.48 (*brs*, C**H**$_2$).

HMDI-HMDA: IR (KBr, cm^{-1}); 3352 (N–H), 2932 (C-H), 2855 (C-H), 1629 (C=O), 1573 (N-H), 1477, 1459, 1439, 1254 (C-N), 642.

HMDI-DAP: IR (KBr, cm^{-1}); 3330(N–H), 2928 (C-H), 2856 (C-H), 1646 (C=O), 1597 (C=C), 1550 (N-H), 1512 (C=C), 1408, 1308, 1234 (C-N).

HMDI-XDA: IR (KBr, cm^{-1}); 3343 (N–H), 2928 (C-H), 2858 (C-H), 1632 (C=O), 1567 (N-H), 1467, 1249 (C-N), 699, 649.

HMDI-TDA: IR (KBr, cm^{-1}); 3335 (N–H), 2931 (C-H), 2863 (C-H), 1625 (C=O), 1575 (N-H), 1478, 1354, 1256 (C-N), 1116, 644. ^{1}H-NMR (400 MHz, DMSO-d_6, ppm); δ 5.86-5.68 (*m*, N**H**), 3.57-3.43 (*m*, OC**H**$_2$), 3.10-2.87 (*m*, C**H**$_2$-NH), 1.66-1.49 (*m*, C**H**$_2$ of TDA), 1.41-1.15 (*m*, C**H**$_2$ of HMDI).