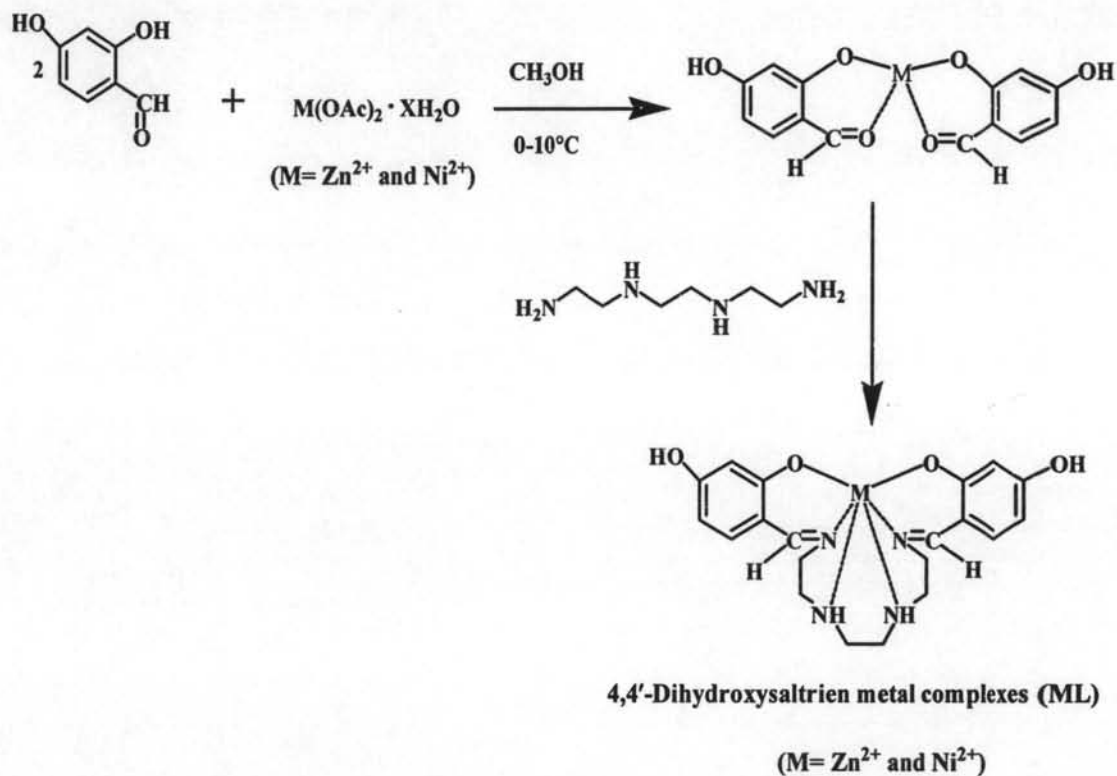


CHAPTER IV

RESULTS AND DISCUSSION

4.1 Synthesis of 4,4'- dihydroxysaltrien metal complexes (ML)

4,4'-Dihydroxysaltrien metal complexes (ML, where $M = \text{Zn}^{2+}$ and Ni^{2+}) were synthesized following the synthetic route as described in the literature [28]. The reaction between 2,4-dihydroxybenzaldehyde and metal (II) acetate in methanol formed a template intermediate. Subsequently, the solution of triethylenetetramine was then added to obtain 4,4'- dihydroxysaltrien metal complexes (ML) as shown in Scheme 4.1.



Scheme 4.1 Synthesis of 4,4'- dihydroxysaltrien metal complexes (ML)

The metal complexes were soluble in dimethyl formamide and dimethyl sulphoxide but insoluble in hexane, tetrahydrofuran, water, methanol, chloroform, dichloromethane, acetonitrile and toluene.

4.1.1 Characterization of 4,4'- dihydroxysaltrien metal complexes (ML)

The obtained metal complexes were characterized by IR spectroscopy. The data agreed with those reported in the literature [28].

IR spectra of ZnL exhibited absorption bands of NH stretching at 3313 cm^{-1} , C=N stretching at 1630 cm^{-1} , aromatic C=C stretching at 1546 cm^{-1} and aromatic C-O stretching at 1217 cm^{-1} . The bands at 986 and 842 cm^{-1} correspond to the characteristic absorption peak of aromatic bending of 1,2,4-trisubstituted benzene.

IR spectra of NiL exhibited absorption bands of NH stretching at 3314 cm^{-1} , C=N stretching at 1634 cm^{-1} , aromatic C=C stretching at 1558 cm^{-1} and aromatic C-O stretching at 1215 cm^{-1} . The bands at 984 and 840 cm^{-1} correspond to the characteristic absorption peak of aromatic bending of 1,2,4-trisubstituted benzene.

^1H NMR and ^{13}C NMR data of ZnL also supported its structure as shown in Table 4.1 and Appendix [A.1-A.2].

Table 4.1 ^1H NMR and ^{13}C NMR data of ZnL

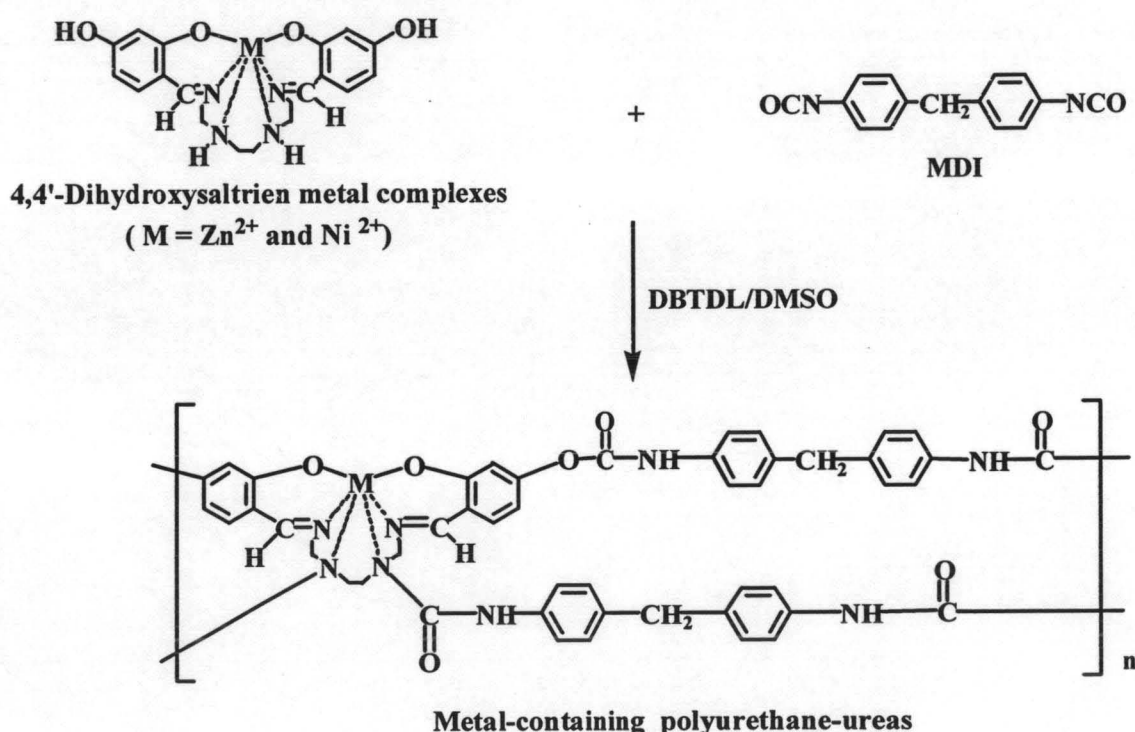
^1H NMR signals				^{13}C NMR signals		
-CH=N	Ar-H	-OH	-CH ₂	-CH=N	Ar-H	-CH ₂
8.10	6.85 (d, 2H) 5.82 (d, 2H) 5.77 (s, 2H)	9.06 (s, 2H)	3.70-3.66 (m, 2H) 3.14-3.13 (m, 2H) 2.94 (s, 2H) 2.80 (d, 2H) 2.54-2.53 (m, 2H) 2.40 (d, 2H)	165.8	173.6, 161.5 136.2, 113.6 106.4, 101.2	54.4, 45.7, 43.4

4.2 Synthesis of metal-containing polyurethane-ureas (ML-PUUs)

4.2.1 Synthesis of ML-PUUs from the reaction between ML and MDI

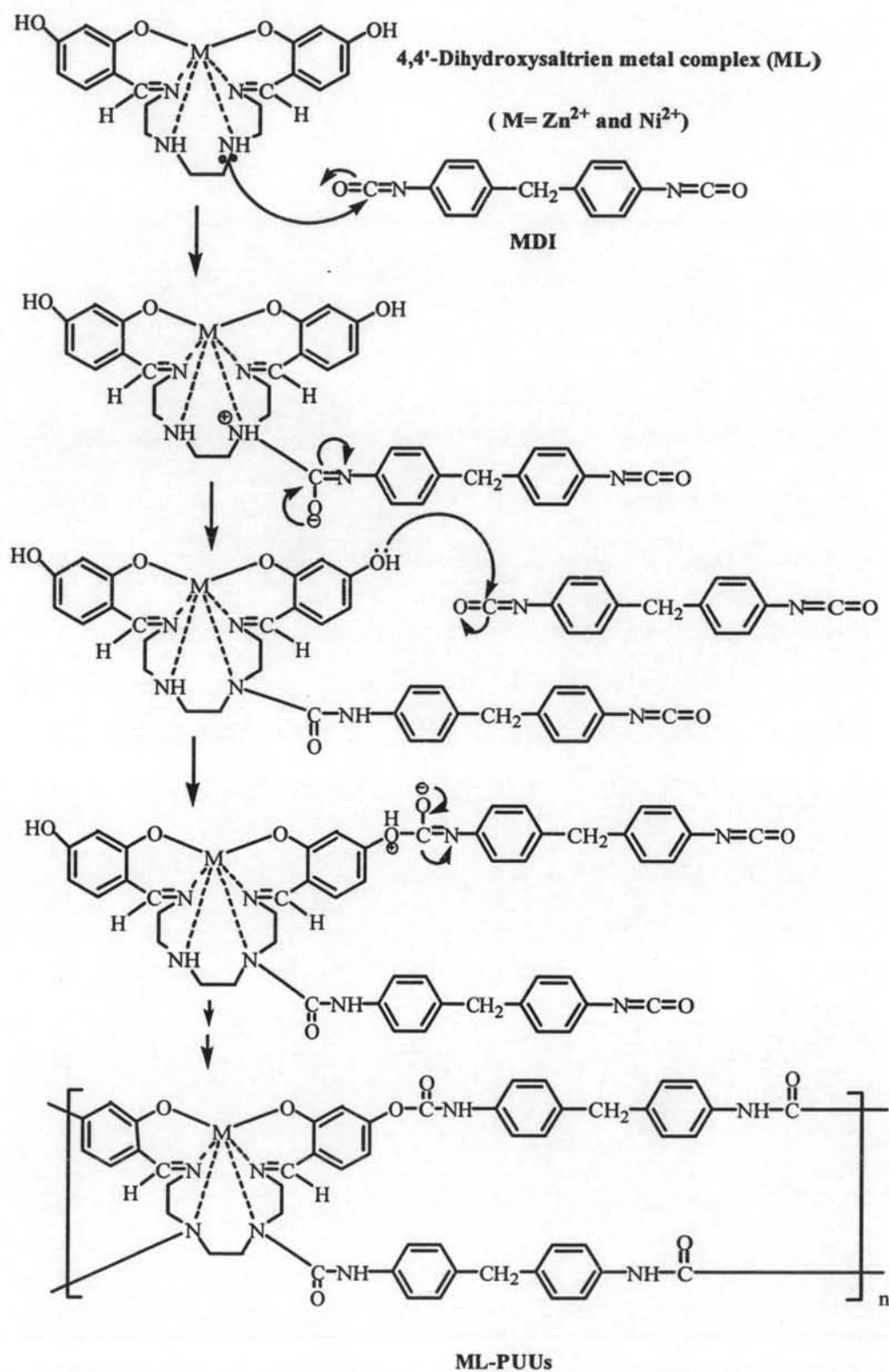
Polyurethane-ureas were synthesized by polyaddition reaction of ML and MDI. MDI was chosen as diisocyanate in the synthesis since TGA data of the MDI-based polyurethane-ureas indicated that these polymers were the most thermally stable polymers when compared to the polymers obtained from other diisocyanates [29].

Metal containing polyurethane-ureas were synthesized from the reaction between ML (where $M = \text{Zn}^{2+}$ and Ni^{2+}) and MDI as described in the literature [29] (Scheme 4.2). The reaction was carried out at the mole ratio of ML:MDI as 1:2 in dried DMSO at 80-90 °C for 24 and 96 hours with DBTDL as a catalyst. The yield of zinc and nickel-containing polyurethane-ureas were 96% and 87%, respectively. Zinc and nickel-containing polyurethane-ureas were obtained as red-orange and red-brown powder, respectively. Metal containing polyurethane-ureas were synthesized at different reaction times as 24 and 96 hours to study the influence of reaction times on the properties of the ML-PUUs.



Scheme 4.2 Synthesis of metal-containing polyurethane-ureas (ML-PUUs) from the reaction between ML and MDI

The possible polymerization mechanism is that the amino and hydroxyl groups in ML undergo reaction with isocyanate groups in MDI to give urea and urethane linkages, respectively (Scheme 4.3).



Scheme 4.3 Possible mechanism of the reaction between ML and MDI.

4.2.2 Characterization of metal-containing polyurethane-ureas (ML-PUUs)

4.2.2.1 IR spectroscopy of ML-PUUs

IR spectra of zinc- and nickel-containing polyurethane-ureas are shown in Figures 4.1 and 4.2, respectively. All polymers showed N-H stretching signals of urea and urethane groups appeared between $3322\text{--}3341\text{ cm}^{-1}$. The C-H stretching signals appeared between $2848\text{--}2923\text{ cm}^{-1}$ and the carbonyl (C=O) stretching of urethane and urea appeared as a shoulder around $1685\text{--}1700\text{ cm}^{-1}$ and peak of urethane linkage overlapped with the urea linkage peak. The imine (C=N) absorption band was observed around $1600\text{--}1603\text{ cm}^{-1}$.

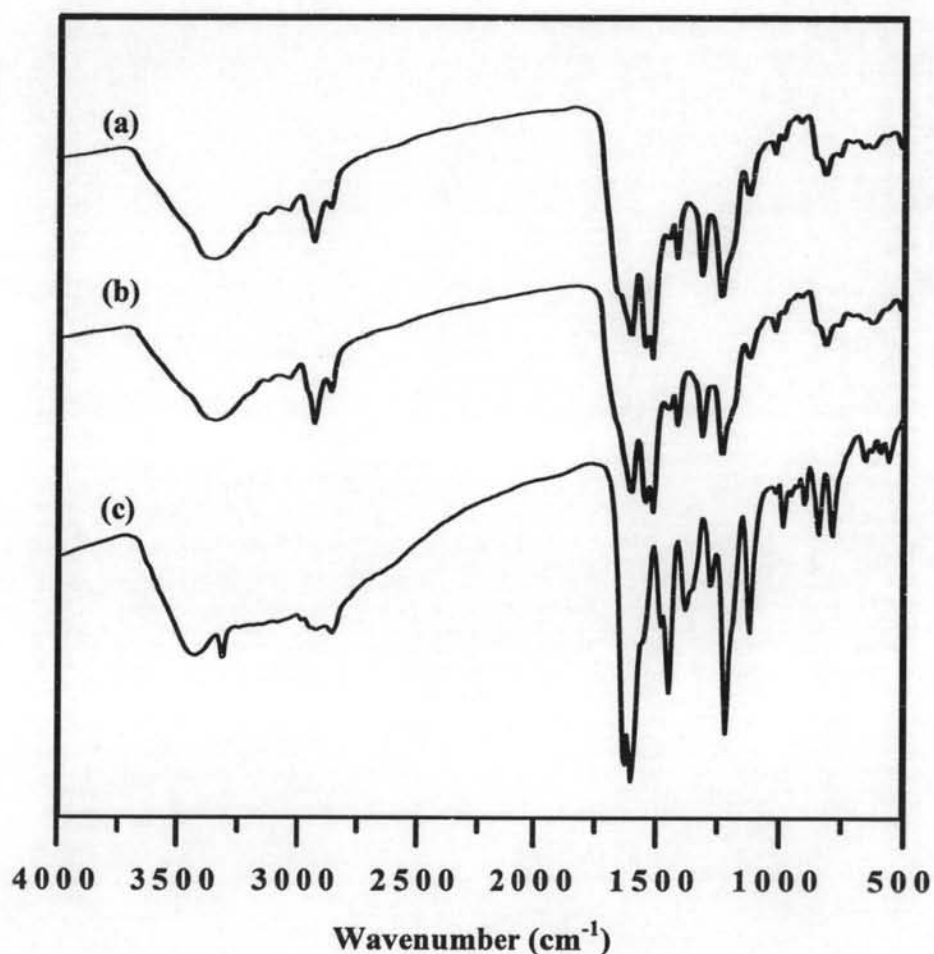


Figure 4.1 IR spectra of (a) ZnL-MDI (24hr); (b) ZnL-MDI (96hr); (c) ZnL

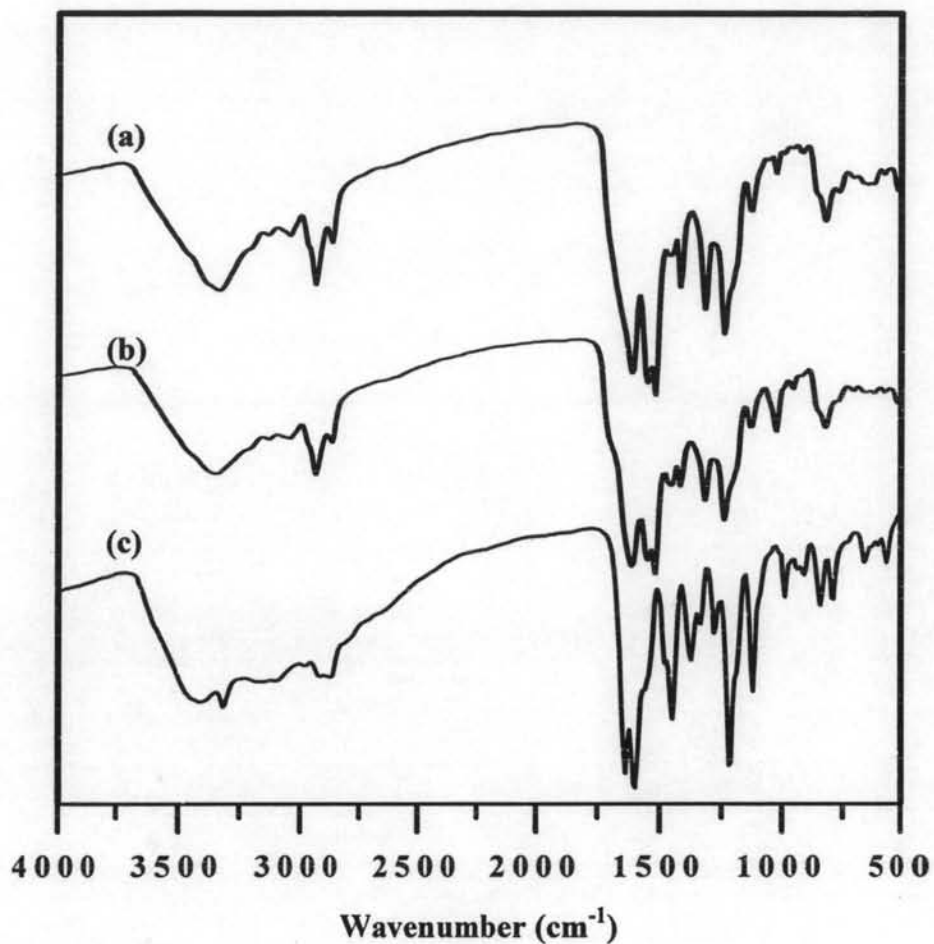


Figure 4.2 IR spectra of (a) NiL-MDI (24hr); (b) NiL-MDI (96hr); (c) NiL

It was found that both zinc- and nickel- containing polyurethane-ureas showed similar IR spectra.

4.2.2.2 Solubility

Solubility of metal containing polyurethane-ureas was tested in various polar and non-polar solvents. All metal-containing polyurethane-ureas obtained from different polymerization times exhibited the same solubility. These polymers were soluble in polar solvents such as DMF and DMSO but insoluble in hexane, toluene, CH₃CN, H₂O, CH₂Cl₂, CHCl₃, MeOH and THF.

4.2.2.3 Inherent viscosity

Inherent viscosity of all polymers was measured at 40 °C in DMSO as described in Appendix [B-1]. The viscosity data of metal-containing polyurethane-ureas are given in Table 4.2.

Table 4.2 Inherent viscosity of metal-containing polyurethane-ureas

Polymers	η_{inh} (dL/g) ^a
ZnL-MDI (24 hr)	0.1628
ZnL-MDI (96 hr)	0.1648
NiL-MDI (24 hr)	0.1188
NiL-MDI (96 hr)	0.1566

^a determined at a concentration 0.5 g/ 100 mL in DMSO at 40 °C

The inherent viscosity of metal containing polyurethane-ureas was found to be in the range of 0.1188-0.1648 dL/g. Zinc-containing polyurethane-ureas (96 hr) showed the same viscosity as zinc-containing polyurethane-ureas (24 hr). Nickel-containing polyurethane-ureas (96 hr) exhibited higher viscosity than nickel-containing polyurethane-ureas (24 hr). Zinc-containing polyurethane-ureas showed higher viscosity than nickel-containing polyurethane-ureas.

4.2.2.4 Thermogravimetric analysis

TGA thermogram and weight loss data of zinc-containing polyurethane-ureas obtained from different polymerization times are presented in Figure 4.3 and Table 4.3, respectively.

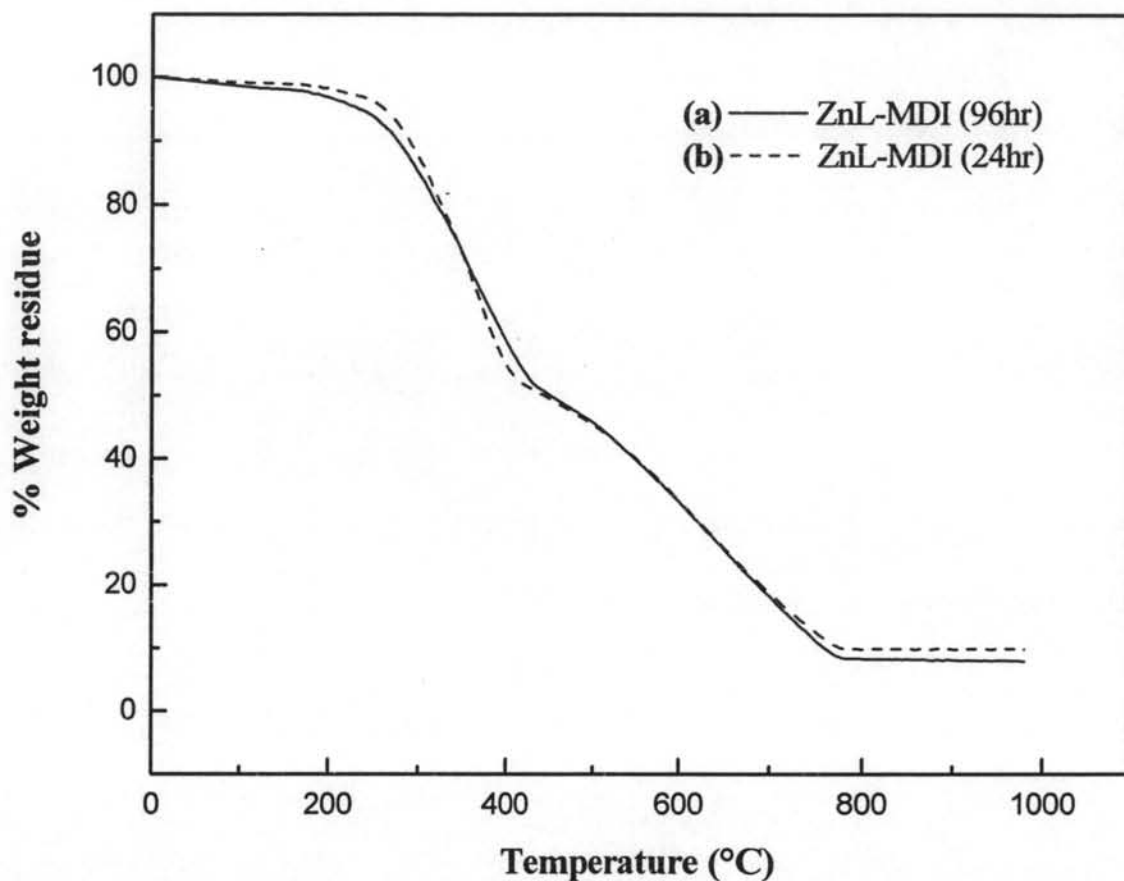


Figure 4.3 TGA thermogram of (a) ZnL-MDI (96 hr); (b) ZnL-MDI (24 hr)

Table 4.3 TGA data of zinc-containing polyurethane-ureas

Polymer	IDT (°C)	Weight loss (%) at different temperature (°C)						
		300	400	500	600	700	800	900
ZnL-MDI (96 hr)	241	15	41	54	67	82	92	92
ZnL-MDI (24 hr)	248	13	45	55	67	81	90	90

Figure 4.4 and Table 4.4 show TGA curves and weight loss data of nickel-containing polyurethane-ureas obtained from different polymerization times.

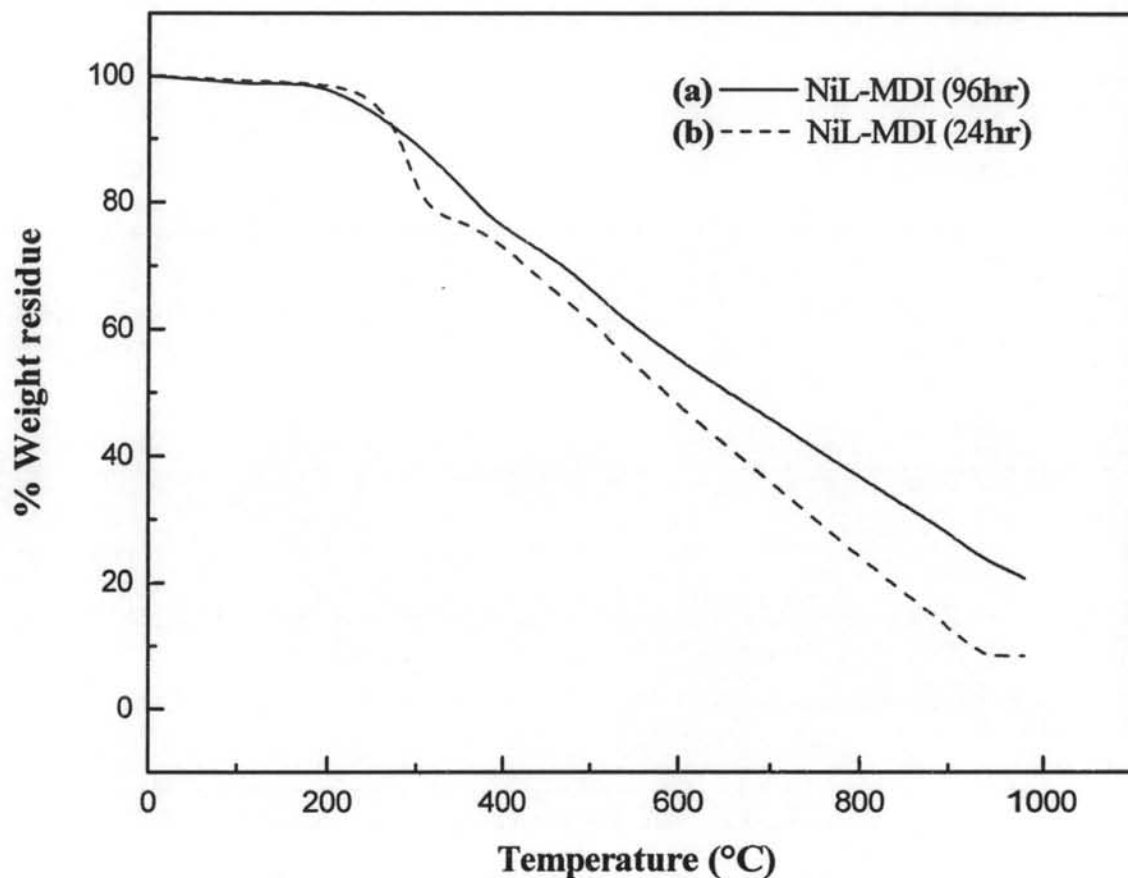


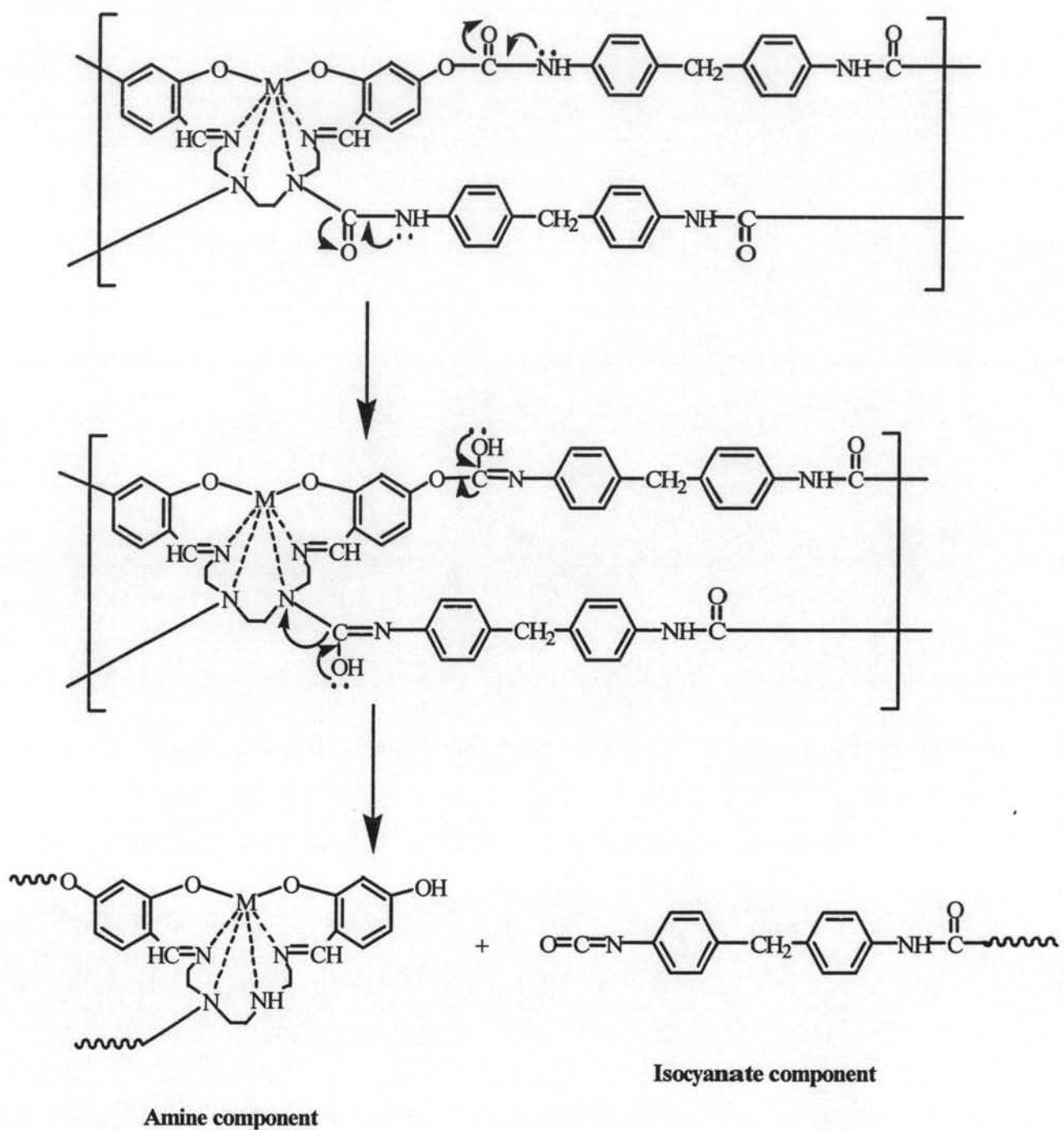
Figure 4.4 TGA thermogram of (a) NiL-MDI (96 hr); (b) NiL-MDI (24 hr)

Table 4.4 TGA data of nickel-containing polyurethane-ureas

Polymer	IDT (°C)	Weight loss (%) at different temperature (°C)						
		300	400	500	600	700	800	900
NiL-MDI (96 hr)	228	11	24	34	45	54	63	72
NiL-MDI (24 hr)	248	17	27	39	52	64	76	87

From TGA thermograms, initial decomposition temperature (IDT) of metal-containing polymers was found to be in the range of 228-248 °C. The residual weight at 600 °C were in the range of 33-55%. Zinc-containing polyurethane-ureas (96 hr) showed the same residual weight at 600 °C as zinc-containing polyurethane-ureas (24 hr). Nickel-containing polyurethane-ureas (96 hr) showed higher thermal stability than nickel-containing polyurethane-ureas (24 hr). The above TGA results indicated that ZnL had higher reactivity towards MDI than NiL since the reaction between ZnL and MDI was completed after 24 hr while the reaction between NiL and MDI took 96 hr to complete. Therefore, the polymerization time of 96 hr is a suitable condition to obtain metal-containing polyurethane-ureas.

Possible mechanism of degradation proceeded *via* urethane-urea scission to give isocyanate and imine component (Scheme 4.4).



Scheme 4.4 Proposed mechanism of degradation of metal-containing polyurethane-ureas

4.2.2.5 Flame retardancy

The flammability behavior of metal-containing polyurethane-ureas was investigated by measuring the limiting oxygen index value (LOI). LOI is the minimum concentration of oxygen, expressed as volume percent, in a mixture of oxygen and nitrogen that will support flaming combustion of a material. LOI measurement was carried out as described in appendix [B-2].

All polymers having a LOI greater than 21 do not burn in atmosphere since the oxygen content in atmosphere is 21%. LOI of ZnL-MDI and NiL-MDI were 22.6 and 22.3, respectively.

4.2.2.6 ^1H NMR spectroscopy

From the previous work reported by Krisiri [28], ^1H NMR spectra of zinc-containing polyurethane-ureas (ZnL-MDI) in $\text{DMSO-}d_6$ and its characteristic signals are presented in Figure 4.5 and Table 4.5, respectively.

^1H NMR spectra of ZnL-MDI showed the characteristic imine $-\text{CH}=\text{N}-$ protons at 8.56 ppm, and aromatic protons of ZnL at 7.25, 6.81, 6.47 ppm. The aromatic protons of MDI showed signals at 7.33-7.29 and 7.09-7.03 ppm. The methylene protons of ZnL in the aliphatic region of 2.4-3.7 could not be clearly observed due to the overlapping with large peaks of H_2O in $\text{DMSO-}d_6$. Therefore, the chemical shift that could be clearly observed is mainly in the aromatic region.

The comparison between the chemical shift of ZnL-MDI and ZnL in $\text{DMSO-}d_6$ are shown in Table 4.5.

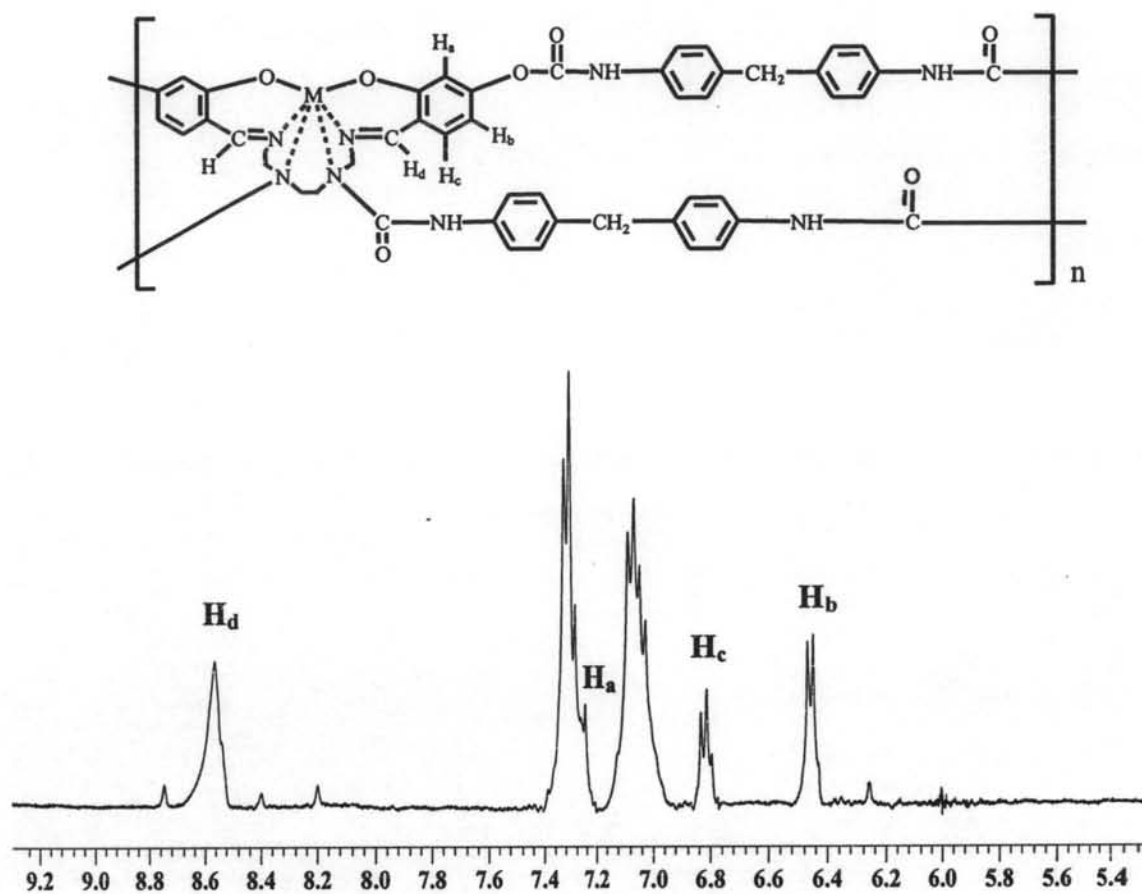


Figure 4.5 ^1H NMR spectrum of ZnL-MDI in $\text{DMSO-}d_6$

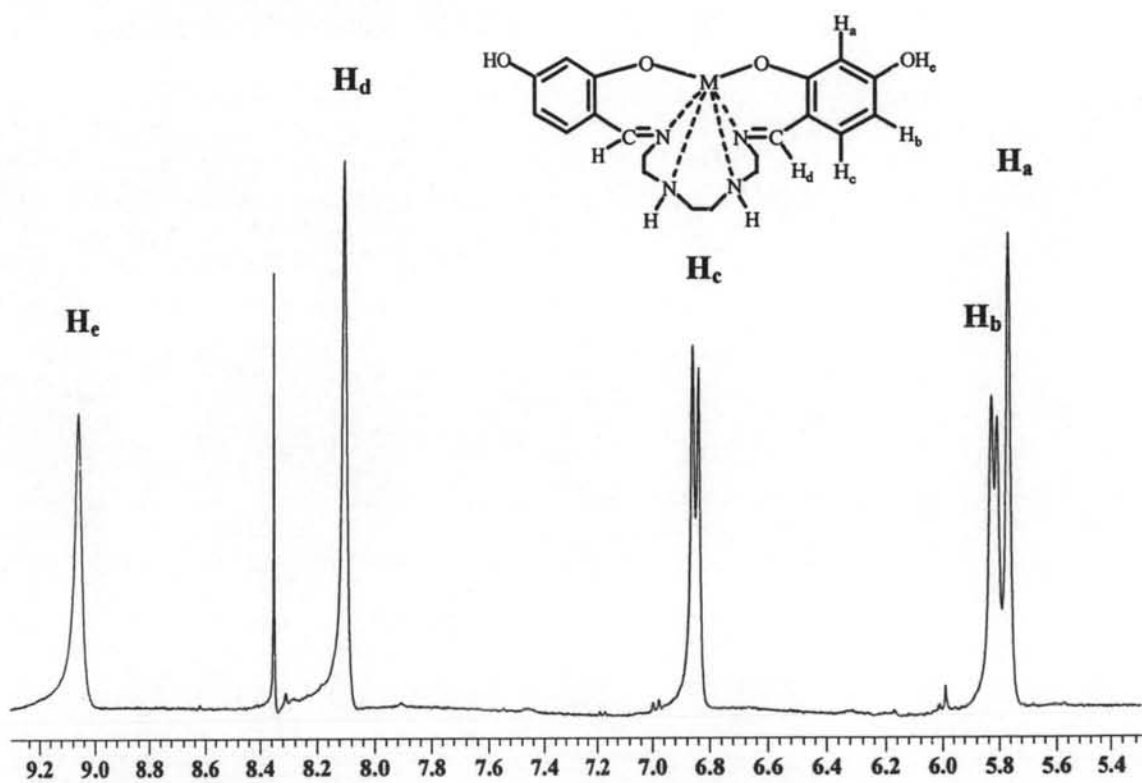


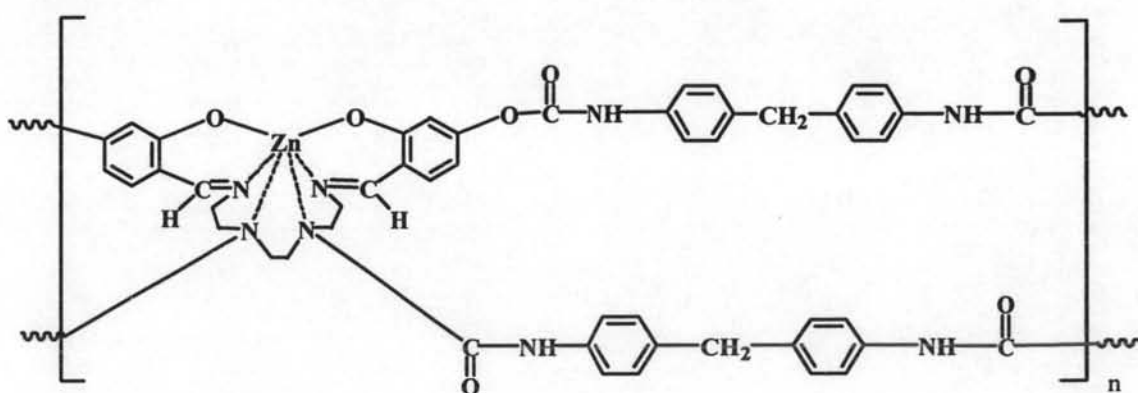
Figure 4.6 ^1H NMR spectrum of ZnL in $\text{DMSO-}d_6 + \text{CDCl}_3$

Table 4.5 Chemical shift of ZnL and ZnL-MDI

Polymers	Chemical shift (ppm)				
	H _a	H _b	H _c	H _d	H _e
ZnL	5.78	5.83	6.87	8.10	9.06
ZnL-MDI	7.25	6.47	6.81	8.56	-

From ^1H NMR spectrum, chemical shifts of ZnL and ZnL-MDI were found that they appeared at different positions. The aromatic protons of the ZnL itself (H_a, H_b, H_c) showed resonance signals at 5.78-6.87 ppm, while these protons in ZnL-MDI showed the resonance signals at 6.47-7.25 ppm due to the electron withdrawing effect of the carbonyl carbon of urethane group. This effect was obvious in the resonance signal of H_a in ZnL and ZnL-MDI, which shifted from 5.78 to 7.25 ppm, respectively. The signal of CH=N in both ZnL and ZnL-MDI also shifted slightly from 8.10 to 8.56 ppm, respectively.

Therefore, the above data from ^1H NMR supported the structure of ZnL-MDI, which was a linear chain polymer, as shown in Figure 4.7. However, there was another possible structure of ZnL-MDI, which was a crosslinked polymer, as shown in Figure 4.8.

**Figure 4.7** Possible linear chain structure of ZnL-MDI

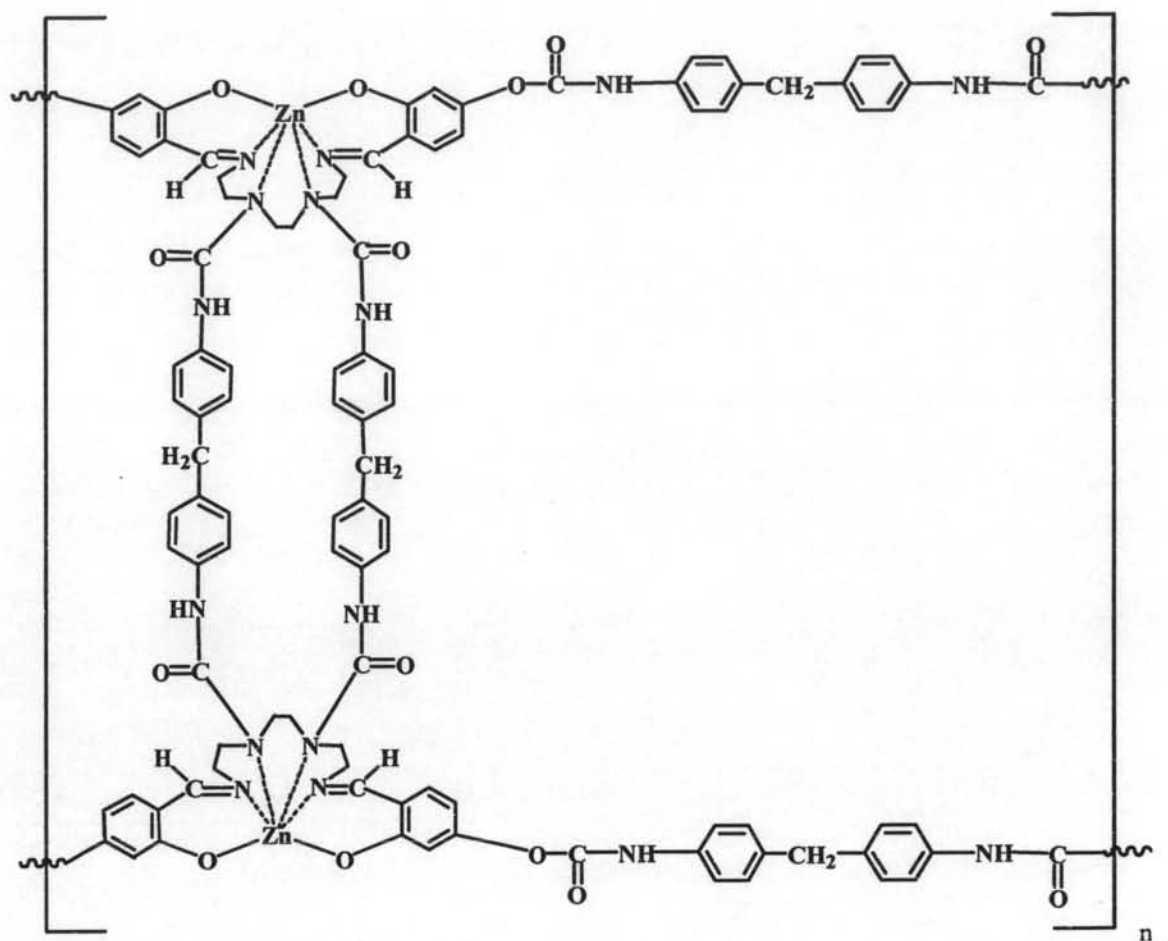


Figure 4.8 Possible crosslinked structure of ZnL-MDI

From the solubility study, it was found that ZnL-MDI was soluble in both DMF and DMSO. Therefore, this result indicated that the possible structure of ZnL-MDI should be linear rather than crosslinked.

4.2.2.7 X-ray diffraction

The X-ray diffraction patterns of ZnL-MDI and NiL-MDI are presented in Figure 4.9. The X-ray diffraction patterns revealed that the ZnL-MDI and NiL-MDI were amorphous in nature.

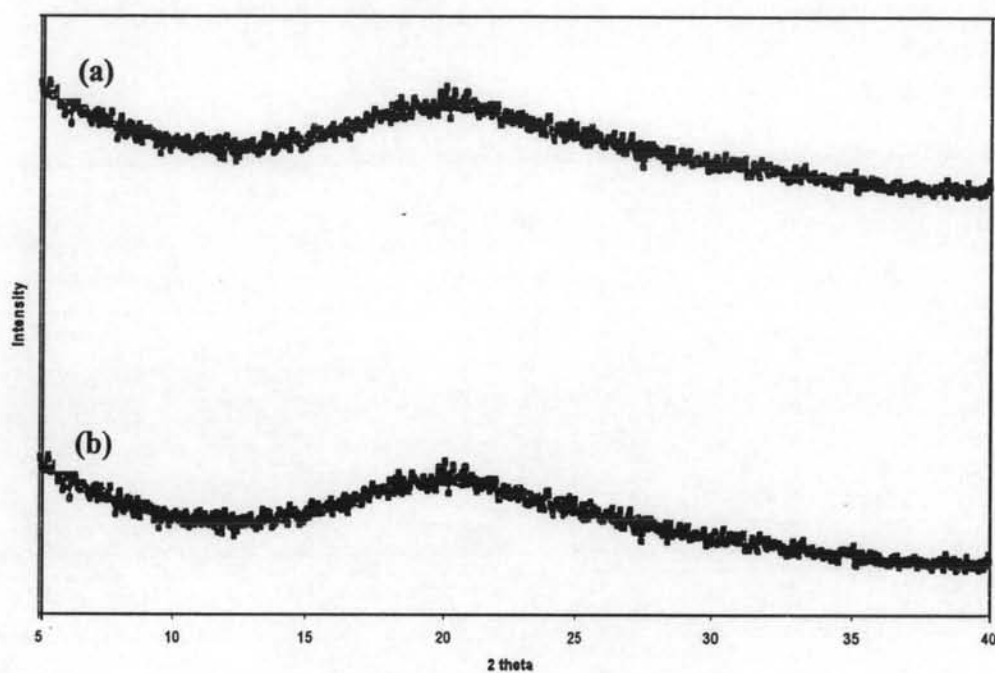
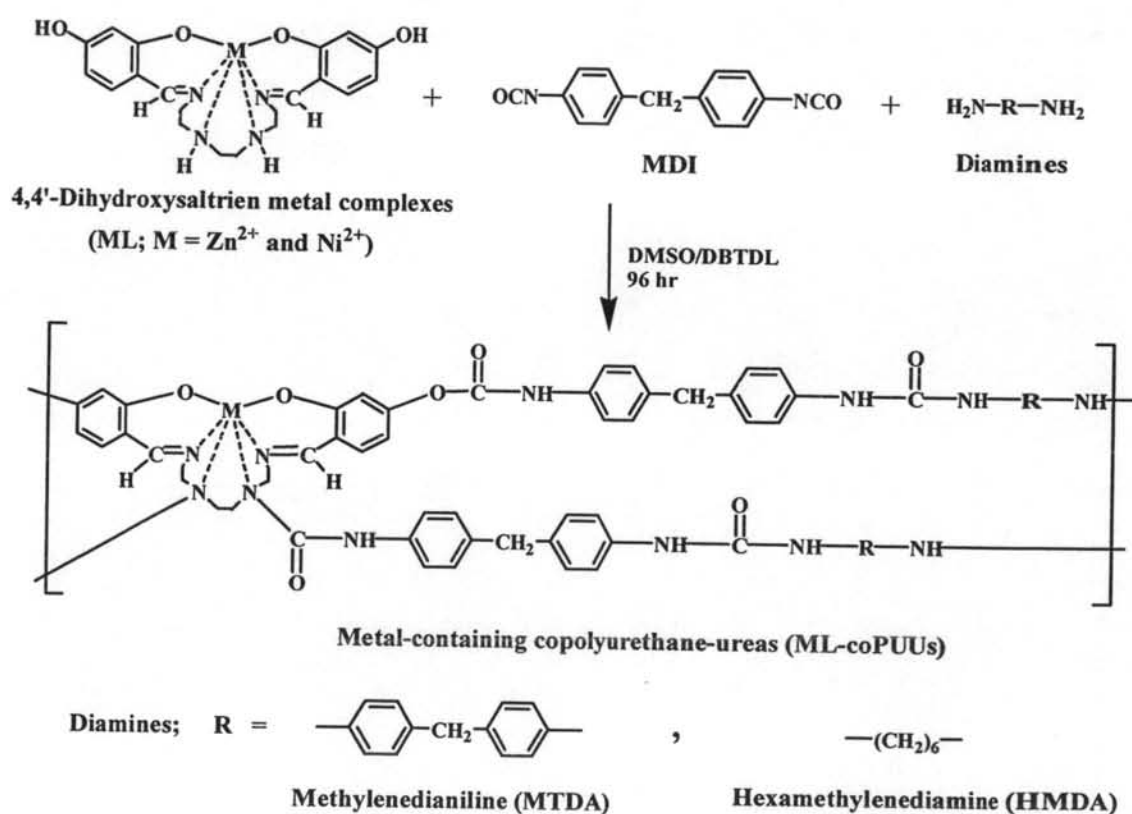


Figure 4.9 XRD patterns of (a) ZnL-MDI; (b) NiL-MDI

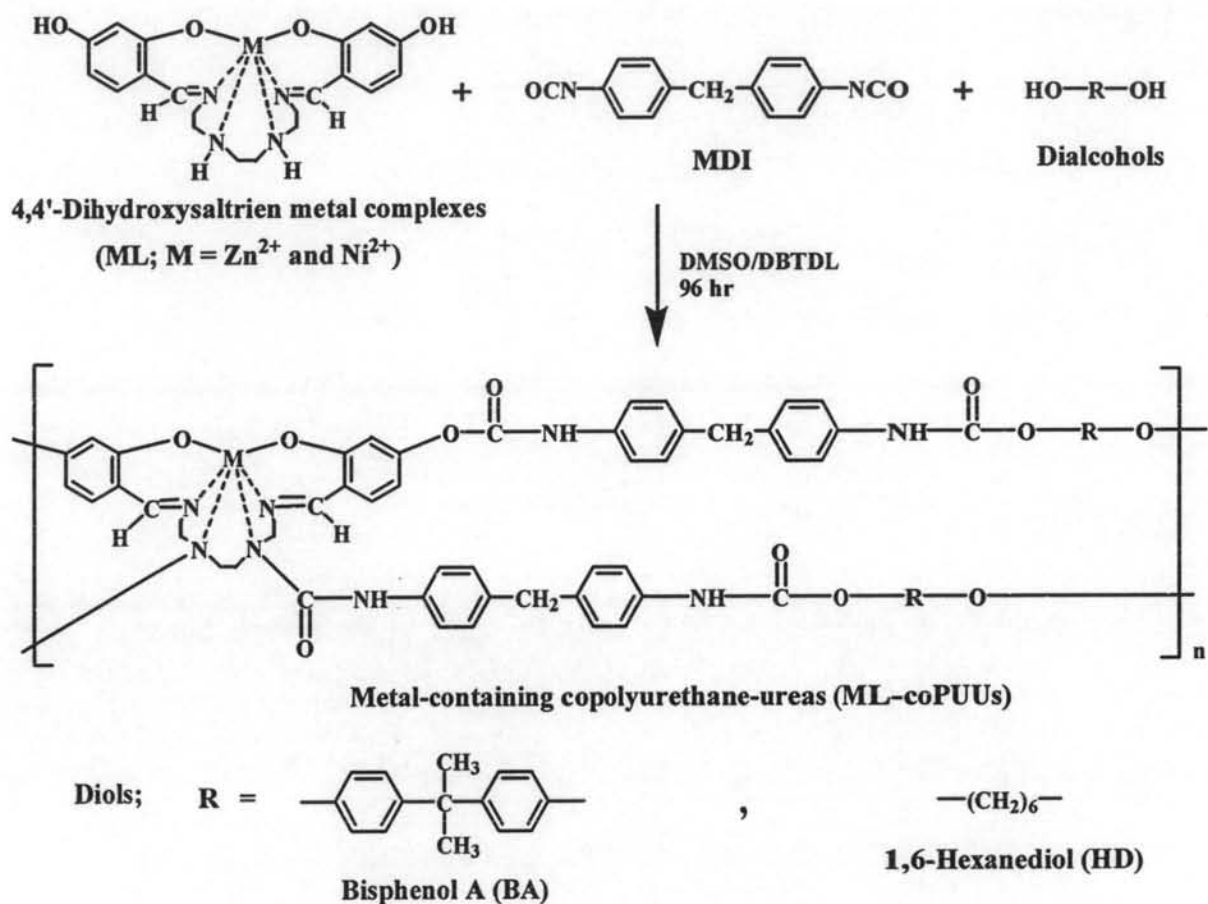
4.3 Synthesis of metal-containing copolyurethane-ureas (ML-coPUUs) from the reaction between ML, MDI and diamines or dialcohols

Synthesis of copolyurethane-ureas containing nickel and zinc 4,4'-dihydroxy saltrien complexes in the presence of diamines or dialcohols were done by the reaction between ML with MDI and diamines or dialcohols as shown in Schemes 4.5 and 4.6, respectively. The blank polyurethane-ureas without metal complexes were also prepared by the reaction of MDI with diamines or dialcohols.

The purpose of this work was to increase the urea or urethane linkages into the polymer structure by addition of diamines or dialcohols during the polymerization. The blank polyurethane-ureas were synthesized to study the influence of metal complexes on the thermal property of polymers. It was expected that these copolyurethane-ureas based on diamines would show good thermal stability because of higher urea linkage in the polymer which resulted in more hydrogen bonding whereas the copolyurethane-ureas based on dialcohols would show good solubility due to more urethane linkage in the polymer.



Scheme 4.5 Synthesis of ML-coPUUs from the reaction between ML, MDI and diamines



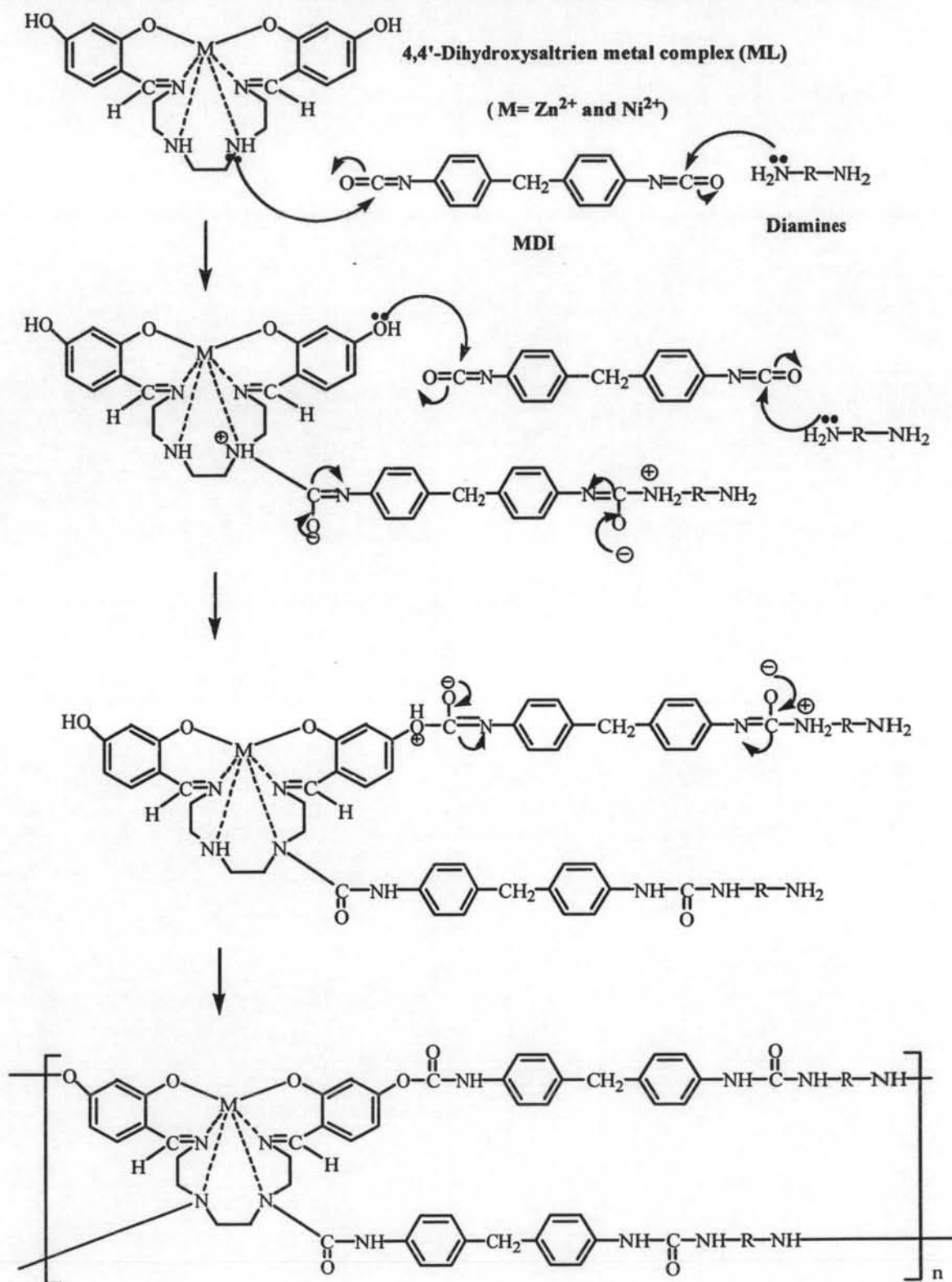
Scheme 4.6 Synthesis of ML-coPUUs from the reaction between ML, MDI and dialcohols

Metal-containing copolyurethane-ureas were synthesized from different compositions by taking the molar ratio of ML:MDI:diamines or dialcohols as 0.5:3:1.5, 1.0:3:1.0, 1.5:3:0.5 to study the influence of diamines or dialcohols content on properties of the polymers. The external appearance of polymers from varying the mole ratio of starting materials is shown in Table 4.6. The yields of copolyurethane-ureas and blank polyurethane-ureas were found to be in the ranges 57-87% and 45-77%, respectively (Table 4.6).

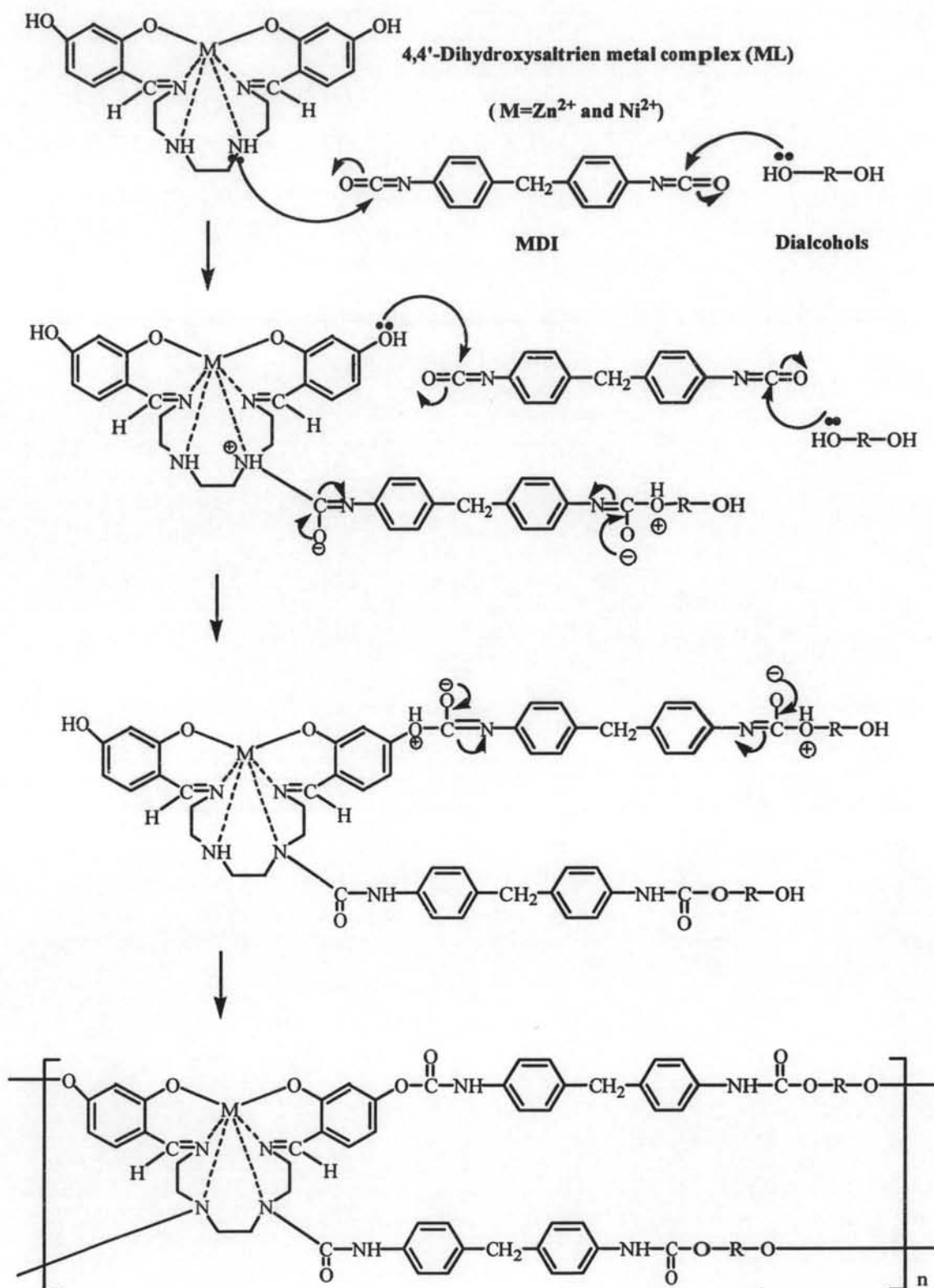
Table 4.6 Synthesis data of polymers

Polymers	Yield (%)	External appearance
MDI-MTDA (1:1)	77	Yellowish white powder
MDI-HMDA (1:1)	73	Yellowish white powder
MDI-BA (1:1)	45	Yellowish white powder
MDI-HD (1:1)	76	Yellowish white powder
ZnL-MDI-MTDA (0.5:3:1.5)	69	Light yellow powder
ZnL-MDI-MTDA (1.0:3:1.0)	67	Yellow powder
ZnL-MDI-MTDA (1.5:3:0.5)	86	Orange yellow powder
ZnL-MDI-HMDA (0.5:3:1.5)	80	Brown yellow powder
ZnL-MDI-HMDA (1.0:3:1.0)	57	Yellow powder
ZnL-MDI-HMDA (1.5:3:0.5)	79	Orange yellow powder
ZnL-MDI-BA (0.5:3:1.5)	70	Light yellow powder
ZnL-MDI-BA (1.0:3:1.0)	69	Orange yellow powder
ZnL-MDI-BA (1.5:3:0.5)	65	Yellow powder
ZnL-MDI-HD (0.5:3:1.5)	80	Yellow powder
ZnL-MDI-HD (1.0:3:1.0)	77	Yellowish orange powder
ZnL-MDI-HD (1.5:3:0.5)	87	Orange yellow powder
NiL-MDI-MTDA (0.5:3:1.5)	68	Yellowish brown powder
NiL-MDI-MTDA (1.0:3:1.0)	65	Dark brown powder
NiL-MDI-MTDA (1.5:3:0.5)	66	Brown powder
NiL-MDI-HMDA (0.5:3:1.5)	74	Yellow brown powder
NiL-MDI-HMDA (1.0:3:1.0)	72	Yellow brown powder
NiL-MDI-HMDA (1.5:3:0.5)	70	Red brown powder
NiL-MDI-BA (0.5:3:1.5)	60	Yellow brown powder
NiL-MDI-BA (1.0:3:1.0)	57	Red brown powder
NiL-MDI-BA (1.5:3:0.5)	82	Red brown powder
NiL-MDI-HD (0.5:3:1.5)	63	Brown powder
NiL-MDI-HD (1.0:3:1.0)	59	Red brown powder
NiL-MDI-HD (1.5:3:0.5)	69	Red brown powder

The possible polymerization mechanism is proposed that the NH and OH of metal complexes and NH_2 of diamines or OH of dialcohols undergo a reaction with isocyanate group in MDI to give urea and urethane linkages (Schemes 4.7 and 4.8).



Scheme 4.7 Possible mechanism of the reaction between ML, MDI and diamines



Scheme 4.8 Possible mechanism of the reaction between ML, MDI and dialcohols

4.3.1 Characterization of metal-containing copolyurethane-ureas (ML-coPUUs)

4.3.1.1 IR spectroscopy

IR spectra of the metal-containing copolyurethane-ureas are shown in Figures 4.10-4.18.

4.3.1.1.1 ML-MDI-MTDA copolymers

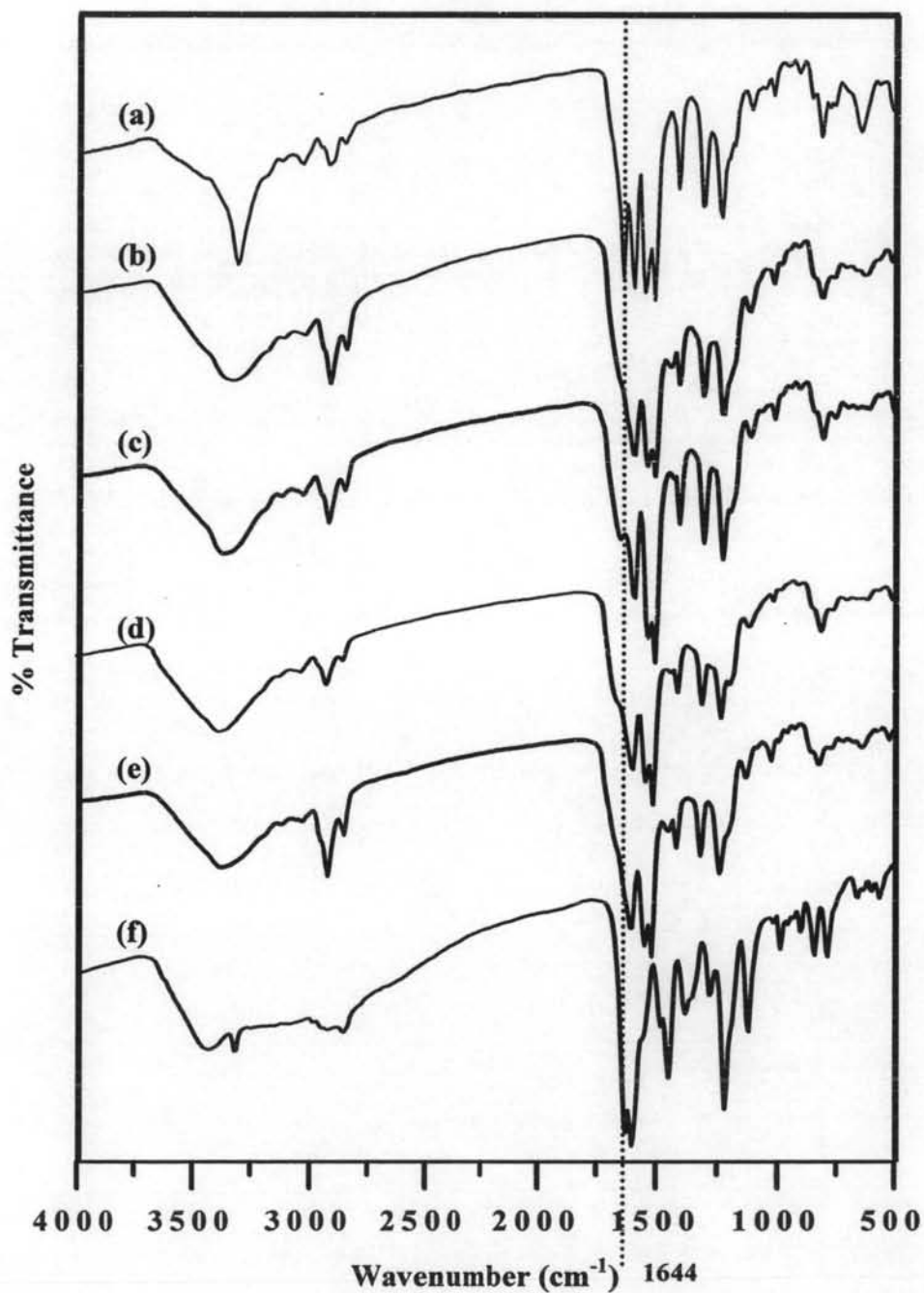


Figure 4.10 IR spectra of (a) MDI-MTDA (1:1); (b) ZnL-MDI (1:2); (c) ZnL-MDI-MTDA (0.5:3:1.5); (d) ZnL-MDI-MTDA (1.0:3:1.0); (e) ZnL-MDI-MTDA (1.5:3:0.5); (f) ZnL

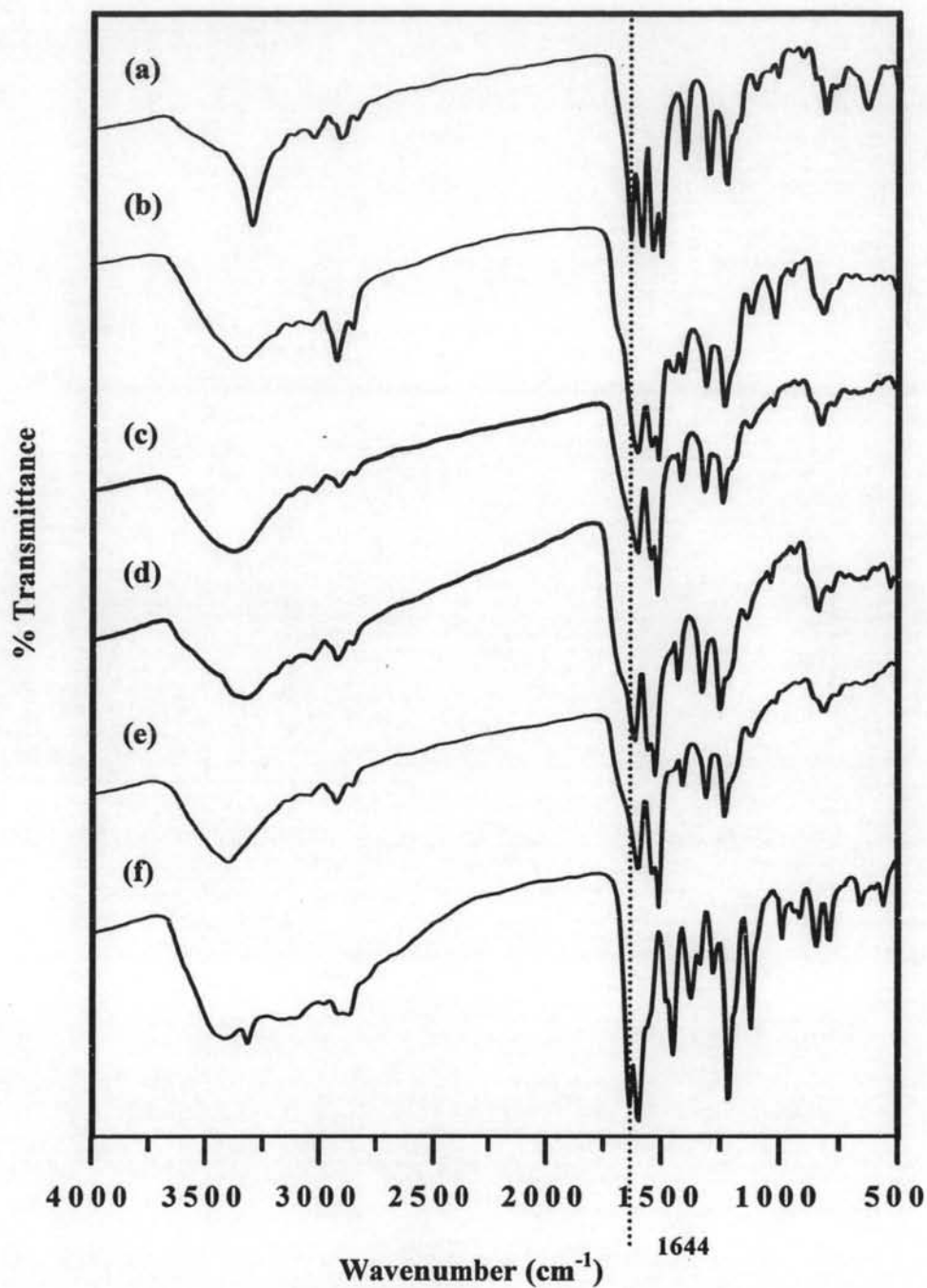
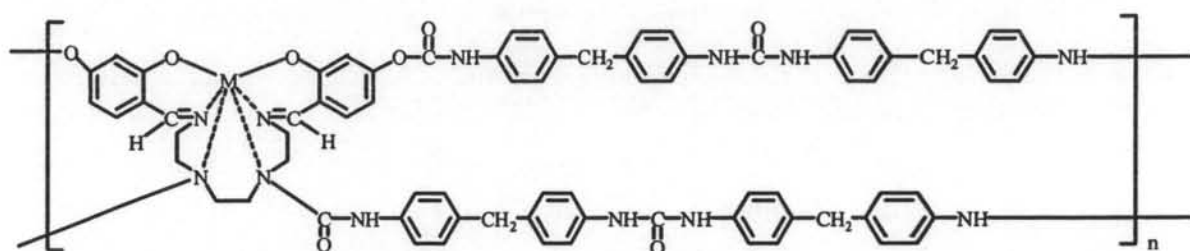


Figure 4.11 IR spectra of (a) MDI-MTDA (1:1); (b) NiL-MDI (1:2); (c) NiL-MDI-MTDA (0.5:3:1.5); (d) NiL-MDI-MTDA (1.0:3:1.0); (e) NiL-MDI-MTDA (1.5:3:0.5); (f) NiL



From Figures 4.10 (a) and 4.11 (a), the blank polyurea showed N-H band of urea group at 3308 cm^{-1} . The C-H stretching signals appeared at 2918 and 2848 cm^{-1} . The carbonyl (C=O) of urea linkage (-NCON-) showed a strong sharp peak at 1644 cm^{-1} . The aromatic C=C stretching absorption band was observed around $1598\text{-}1512\text{ cm}^{-1}$. All metal-containing copolyurethane-ureas had similar IR spectra as shown in Figure 4.10 (c-e) and 4.11 (c-e). The important characteristic absorption bands are as follows: $3394\text{-}3368\text{ cm}^{-1}$ (N-H stretching), $2923\text{-}2848\text{ cm}^{-1}$ (C-H stretching), $1710\text{-}1644\text{ cm}^{-1}$ (C=O of urethane and urea), 1600 cm^{-1} (imine C=N) and $1540\text{-}1512\text{ cm}^{-1}$ (aromatic C=C stretching). Normally, the carbonyl of aromatic urea is found in the region $1680\text{-}1630\text{ cm}^{-1}$. The urea carbonyl of MDI-MTDA showed a strong sharp peak at 1644 cm^{-1} . The carbonyl of urethane and urea in ML-MDI appeared as a shoulder around $1700\text{-}1685\text{ cm}^{-1}$. For comparison between MDI-MTDA and ML-MDI-MTDA, the result showed that the carbonyl of ML-MDI-MTDA was observed as a shoulder around $1710\text{-}1644\text{ cm}^{-1}$, which included carbonyl absorption of ML-MDI and MDI-MTDA.

4.3.1.1.2 ML-MDI-HMDA copolymers

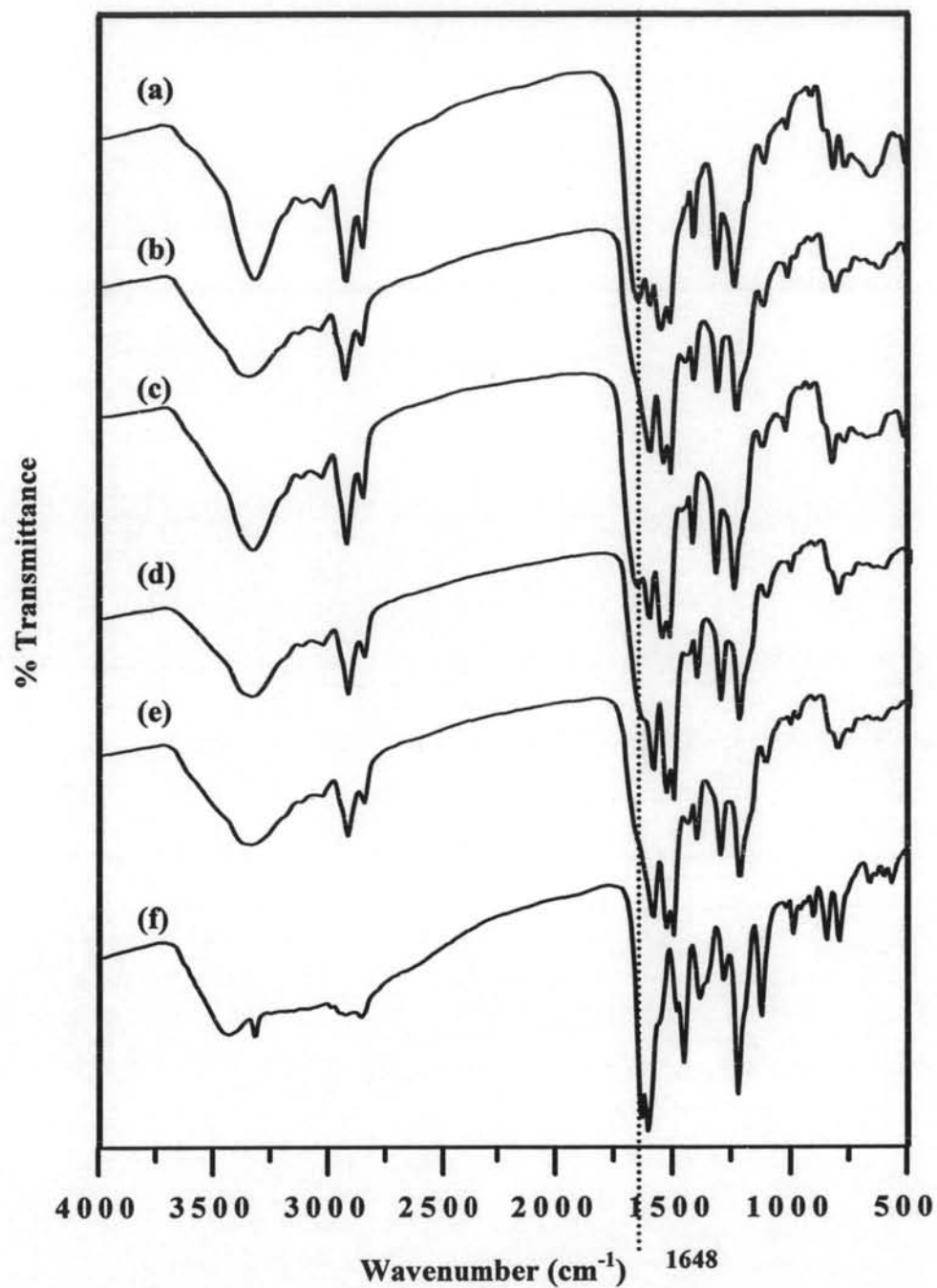


Figure 4.12 IR spectra of (a) MDI-HMDA (1:1); (b) ZnL-MDI (1:2); (c) ZnL-MDI-HMDA (0.5:3:1.5); (d) ZnL-MDI-HMDA (1.0:3:1.0); (e) ZnL-MDI-HMDA (1.5:3:0.5); (f) ZnL

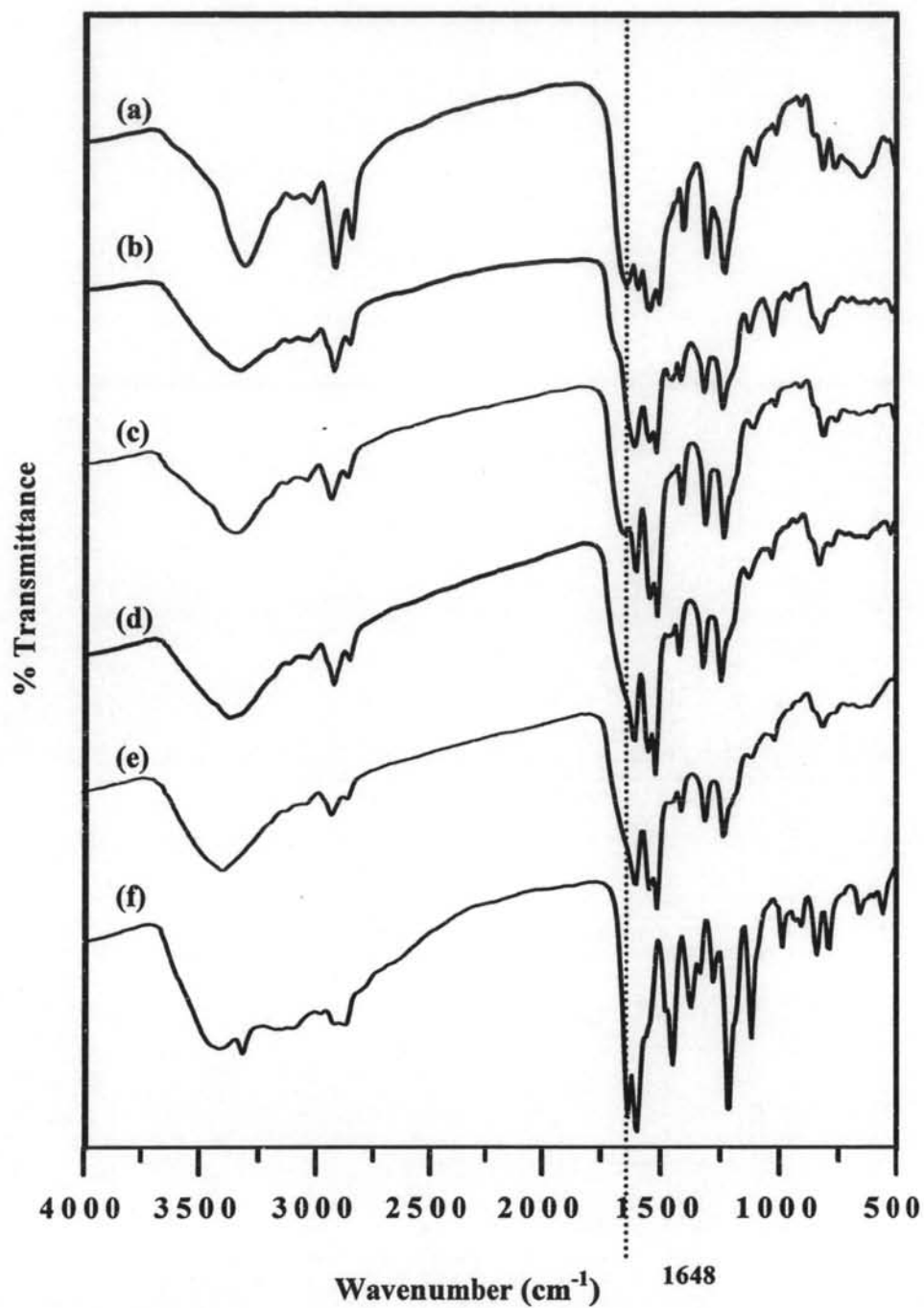
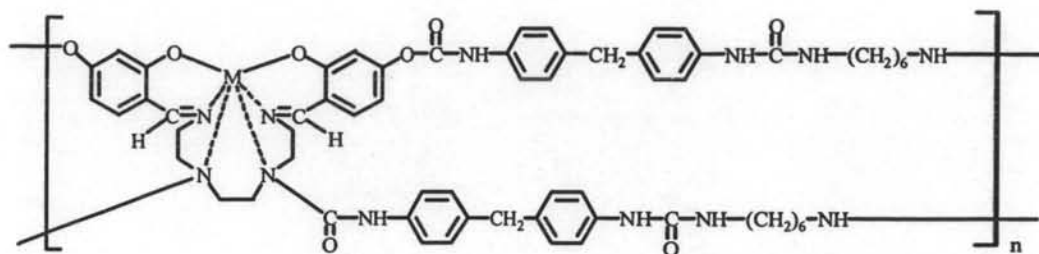


Figure 4.13 IR spectra of (a) MDI-HMDA (1:1); (b) NiL-MDI (1:2); (c) NiL-MDI-HMDA (0.5:3:1.5); (d) NiL-MDI-HMDA (1.0:3:1.0); (e) NiL-MDI-HMDA (1.5:3:0.5); (f) NiL



From Figures 4.12 (a) and 4.13 (a), the blank polyurea showed N-H band of urea group at 3319 cm^{-1} . The C-H stretching signals appeared at 2926 and 2855 cm^{-1} . The carbonyl (C=O) of urea linkage (-NCON-) appeared at 1648 cm^{-1} . The aromatic C=C stretching absorption band was observed around 1598 - 1513 cm^{-1} . All metal-containing copolyurethane-ureas had similar IR spectra as shown in Figure 4.12 (c-e) and 4.13 (c-e). The important characteristic absorption bands are as follows: 3394 - 3330 cm^{-1} (N-H stretching), 2926 - 2855 cm^{-1} (C-H stretching), 1718 - 1648 cm^{-1} (C=O of urethane and urea), 1600 cm^{-1} (imine C=N) and 1544 - 1509 cm^{-1} (aromatic C=C stretching). Normally, the carbonyl of aliphatic urea is found in the region 1720 - 1640 cm^{-1} . The urea carbonyl of MDI-HMDA appeared at 1648 cm^{-1} . The carbonyl of urethane and urea in ML-MDI appeared as a shoulder around 1700 - 1685 cm^{-1} . For comparison between MDI-HMDA and ML-MDI-HMDA, the result showed that the carbonyl of ML-MDI-HMDA was observed as a shoulder around 1718 - 1648 cm^{-1} , which included carbonyl absorption of ML-MDI and MDI-HMDA.

4.3.1.1.3 ML-MDI-BA copolymers

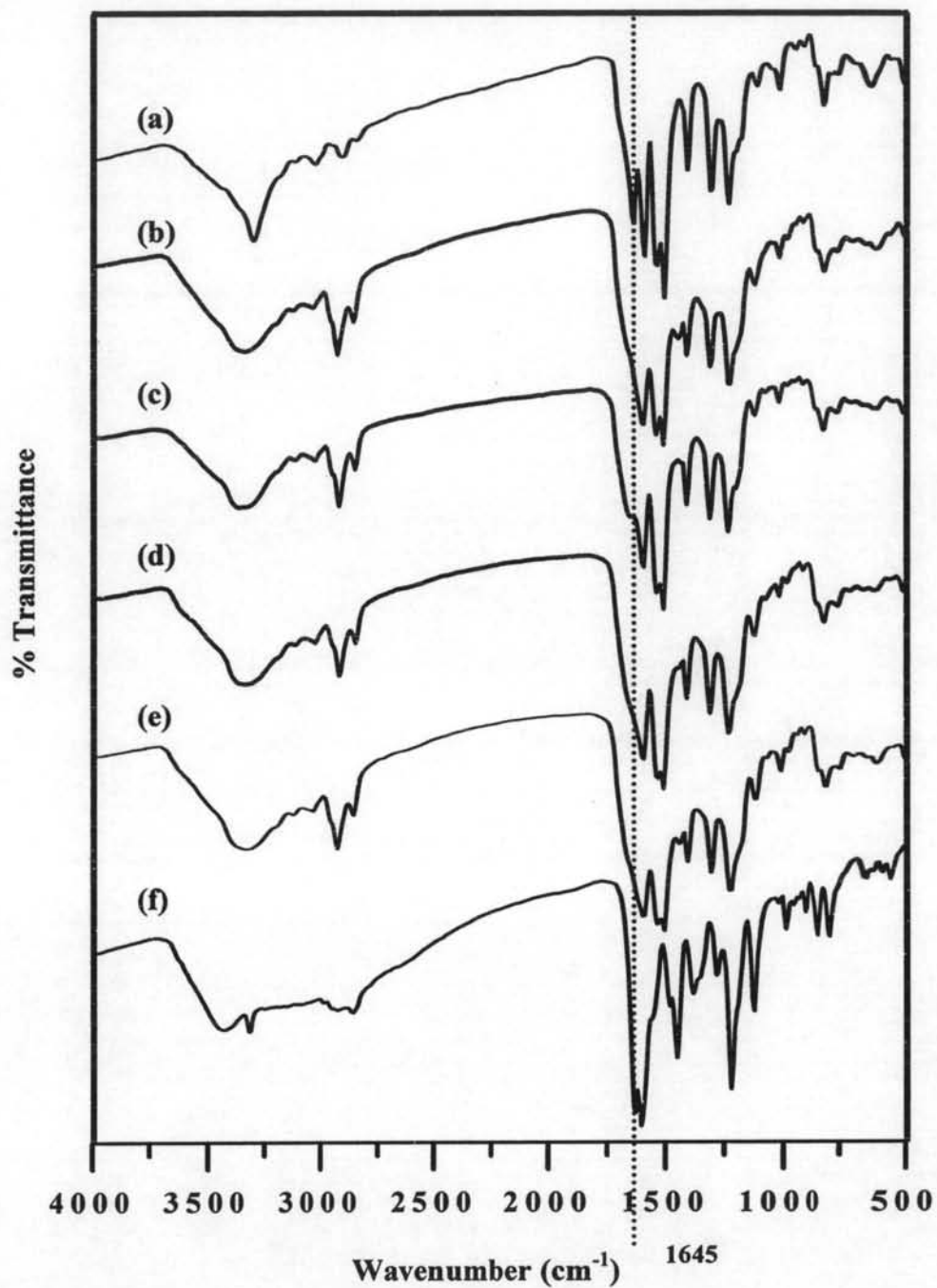


Figure 4.14 IR spectra of (a) MDI-BA (1:1); (b) ZnL-MDI (1:2); (c) ZnL-MDI-BA (0.5:3:1.5); (d) ZnL-MDI-BA (1.0:3:1.0); (e) ZnL-MDI-BA (1.5:3:0.5); (f) ZnL

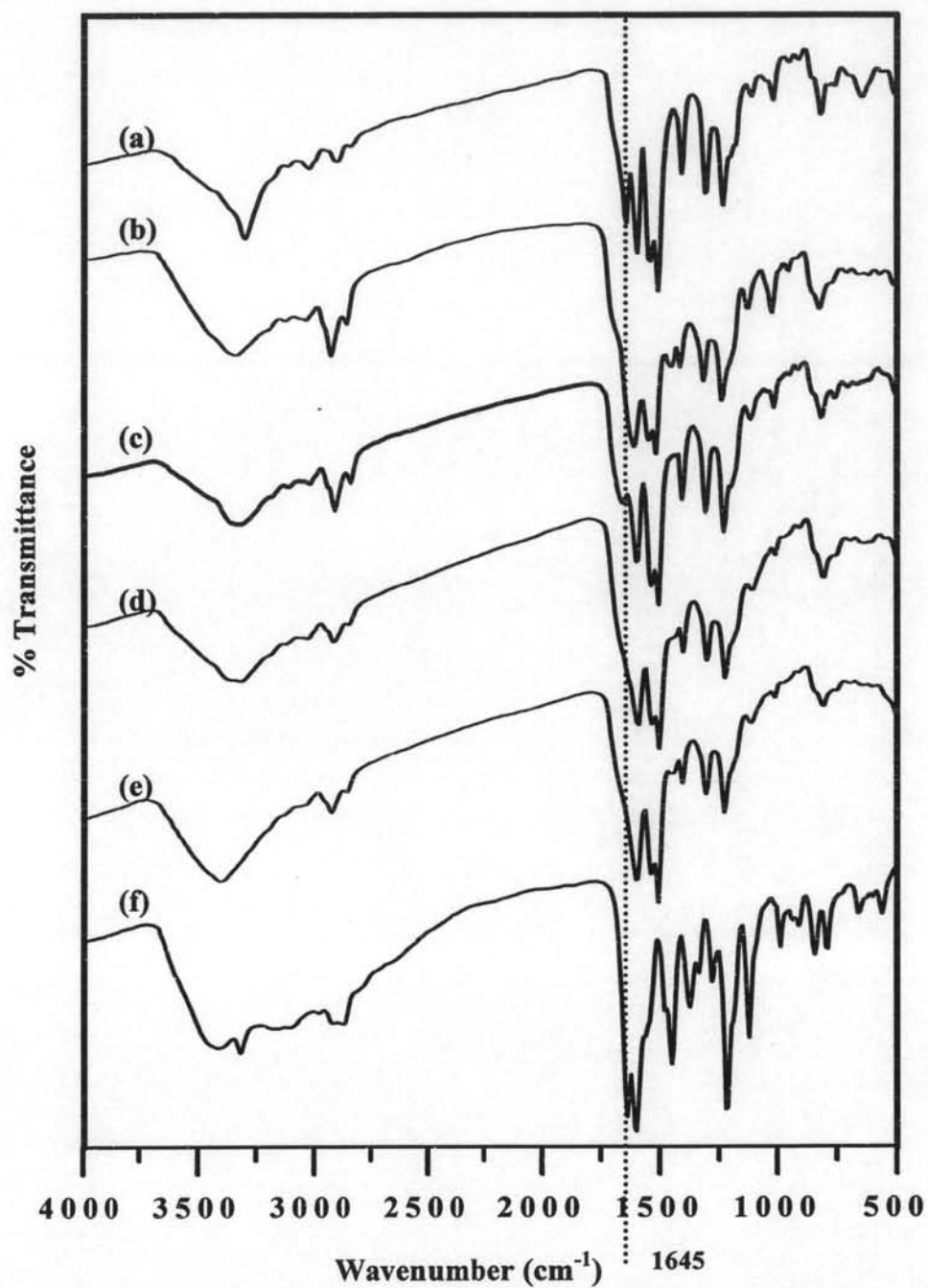


Figure 4.15 IR spectra of (a) MDI-BA (1:1); (b) NiL-MDI (1:2); (c) NiL-MDI-BA (0.5:3:1.5); (d) NiL-MDI-BA (1.0:3:1.0); (e) NiL-MDI-BA (1.5:3:0.5); (f) NiL

4.3.1.1.4 ML-MDI-HD copolymers

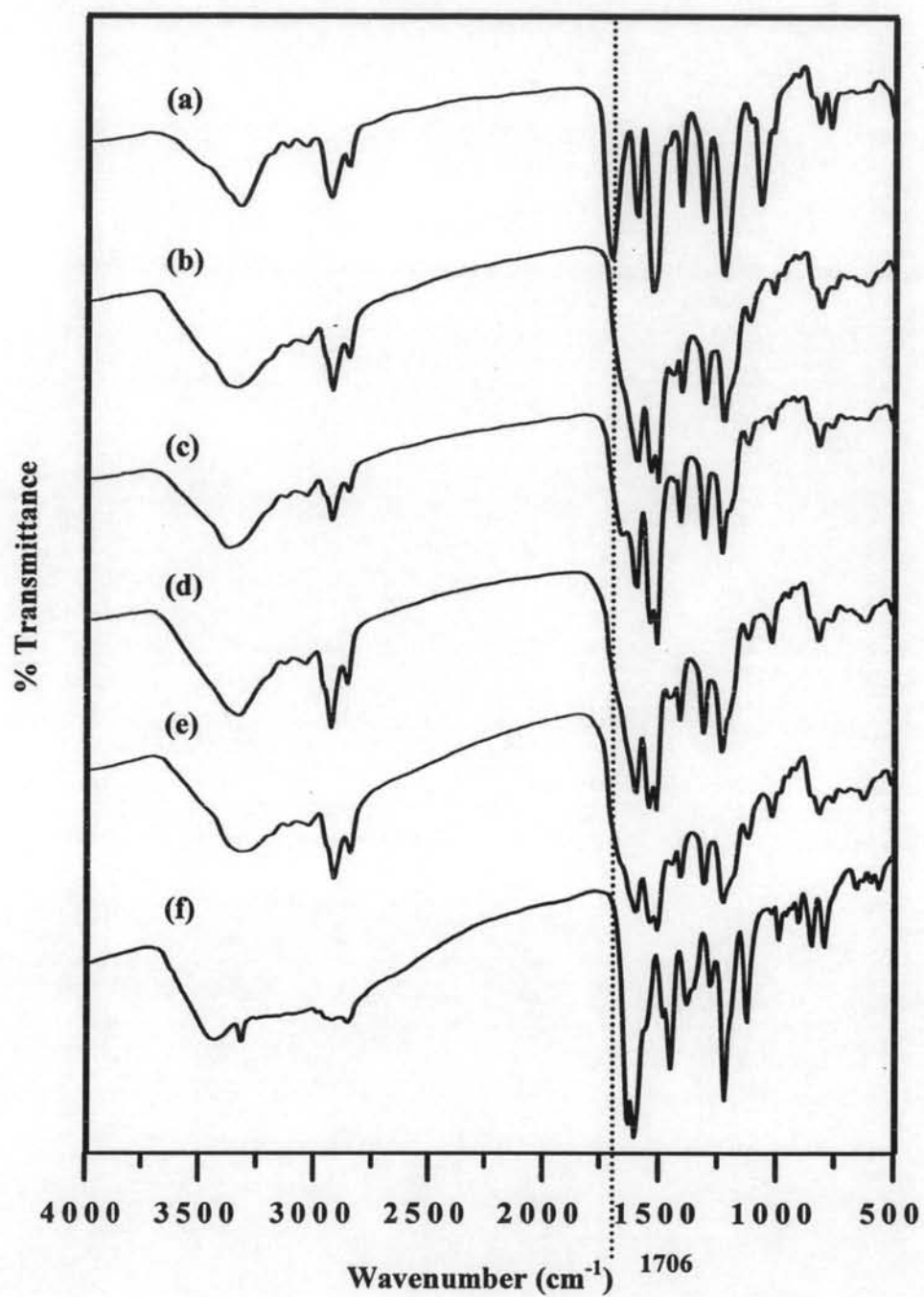


Figure 4.16 IR spectra of (a) MDI-HD (1:1); (b) ZnL-MDI (1:2); (c) ZnL-MDI-HD (0.5:3:1.5); (d) ZnL-MDI-HD (1.0:3:1.0); (e) ZnL-MDI-HD (1.5:3:0.5); (f) ZnL

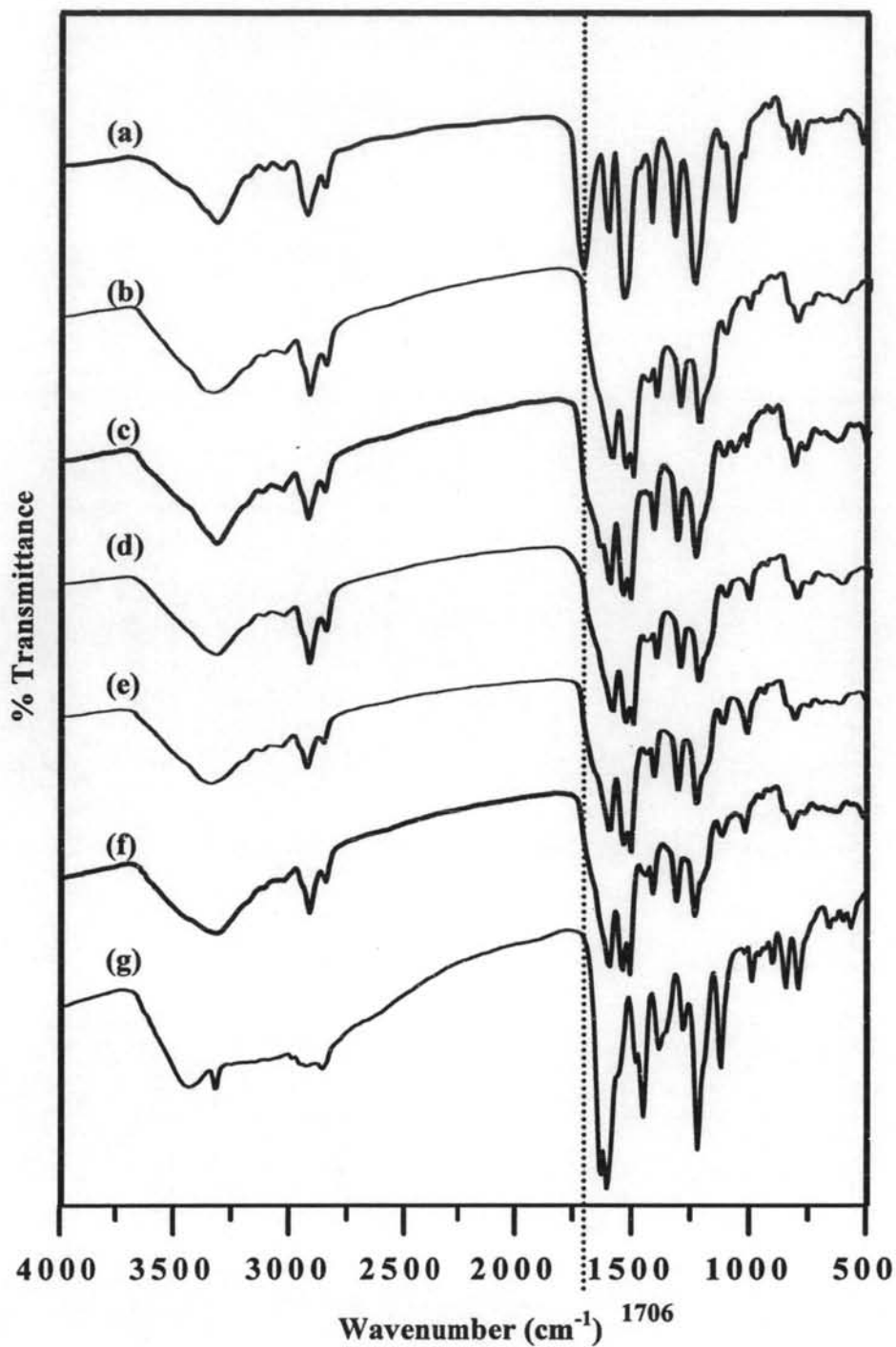


Figure 4.17 IR spectra of (a) MDI-HD (1:1); (b) ZnL-MDI (1:2); (c) ZnL-MDI-HD (0.5:3:2.0); (d) ZnL-MDI-HD (1.0:3:1.0, 1step); (e) ZnL-MDI-HD (1.0:3:1.0, 2step); (f) ZnL-MDI-HD (1.25:3:0.5); (g) ZnL

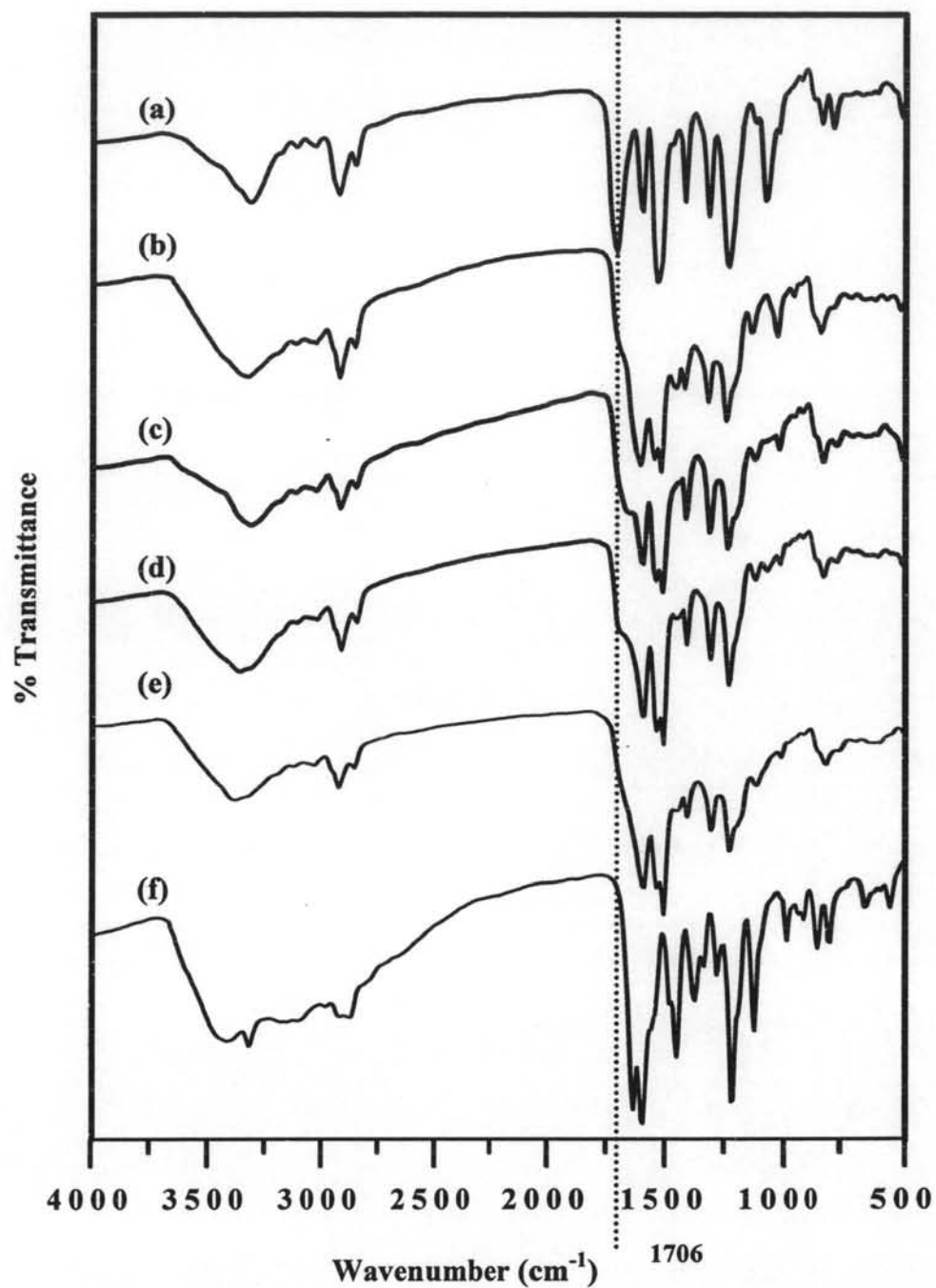
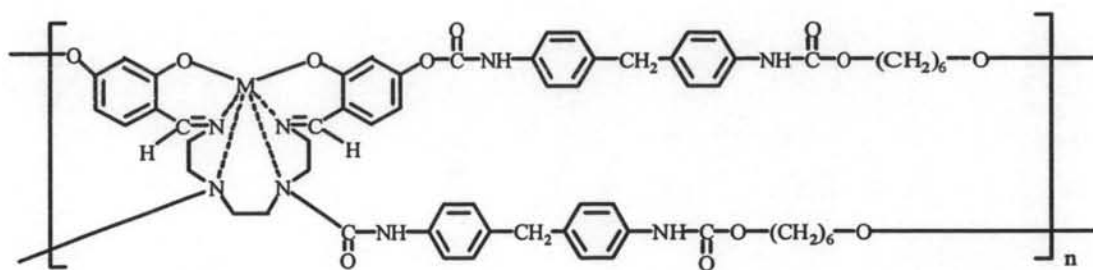


Figure 4.18 IR spectra of (a) MDI-HD (1:1); (b) NiL-MDI (1:2); (c) NiL-MDI-HD (0.5:3:1.5); (d) NiL-MDI-HD (1.0:3:1.0); (e) NiL-MDI-HD (1.5:3:0.5); (f) NiL



From Figures 4.16 (a) 4.17 (a) and 4.18 (a), the blank polyurethane showed NH band of urethane group at 3323 cm^{-1} . The C-H stretching signals appeared at 2930 and 2851 cm^{-1} . The carbonyl (C=O) of urethane linkage (-NCOO-) appeared at 1706 cm^{-1} . The aromatic C=C stretching absorption band was observed around $1599\text{-}1528\text{ cm}^{-1}$. All metal-containing copolyurethane-ureas had similar IR spectra as shown in Figure 4.16 (c-e), 4.17 (c-f) and 4.18 (c-e). The important characteristic absorption bands are as follows: $3350\text{-}3315\text{ cm}^{-1}$ (N-H stretching), $2925\text{-}2848\text{ cm}^{-1}$ (C-H stretching), $1720\text{-}1670\text{ cm}^{-1}$ (C=O of urethane and urea), $1601\text{-}1600\text{ cm}^{-1}$ (imine C=N) and $1544\text{-}1509\text{ cm}^{-1}$ (aromatic C=C stretching). Normally, the carbonyl of aliphatic urethane is found in the region $1780\text{-}1660\text{ cm}^{-1}$. The urethane carbonyl of MDI-HD appeared at 1706 cm^{-1} . The carbonyl of urethane and urea in ML-MDI appeared as a shoulder around $1700\text{-}1685\text{ cm}^{-1}$. For comparison between MDI-HD and ML-MDI-HD, the result showed that the carbonyl of ML-MDI-HD was observed as a shoulder around $1720\text{-}1670\text{ cm}^{-1}$, which included carbonyl absorption of ML-MDI and MDI-HD.

4.3.1.2 NMR spectroscopy

^1H NMR spectra of zinc-containing copolyurethane-ureas was recorded in $\text{DMSO-}d_6$. Their spectra are presented in Figures 4.19-4.22 and Appendix [A.3-A.15].

4.3.1.2.1 ZnL-MDI-MTDA copolymers

^1H NMR spectra of zinc-containing copolyurethane-ureas based on MTDA are shown in Figure 4.19. ^1H NMR spectrum of MTDA showed signals at δ 6.98-6.99 (Ar-H), 6.62-6.64 (Ar-H), 3.80 (CH_2) and 3.52 (NH_2). For MDI-MTDA, the spectrum showed signal for N-H proton of urea group around δ 8.47-8.49. The aromatic protons of MDI were observed at δ 7.28-7.32 and 7.03-7.09 whereas aromatic protons of MTDA were found at δ 6.81-6.83 and 6.44-6.46. The peaks around δ 3.65-3.78 were due to the protons in methyl $\text{Ph-CH}_2\text{-Ph}$ group. In ZnL-MDI-MTDA, the spectrum showed signals for the inter and intramolecular hydrogen bond N-H protons at δ 8.54 and other non-hydrogen bonded N-H proton at δ 5.92. The aromatic protons of MDI showed signals at δ 7.28-7.33 and 7.03-7.09 whereas aromatic protons of ZnL and MTDA appeared at δ 7.26, 6.81-6.83 and 6.44-6.46. The peaks around δ 3.65-3.78 were due to the protons in $\text{Ph-CH}_2\text{-Ph}$ group.

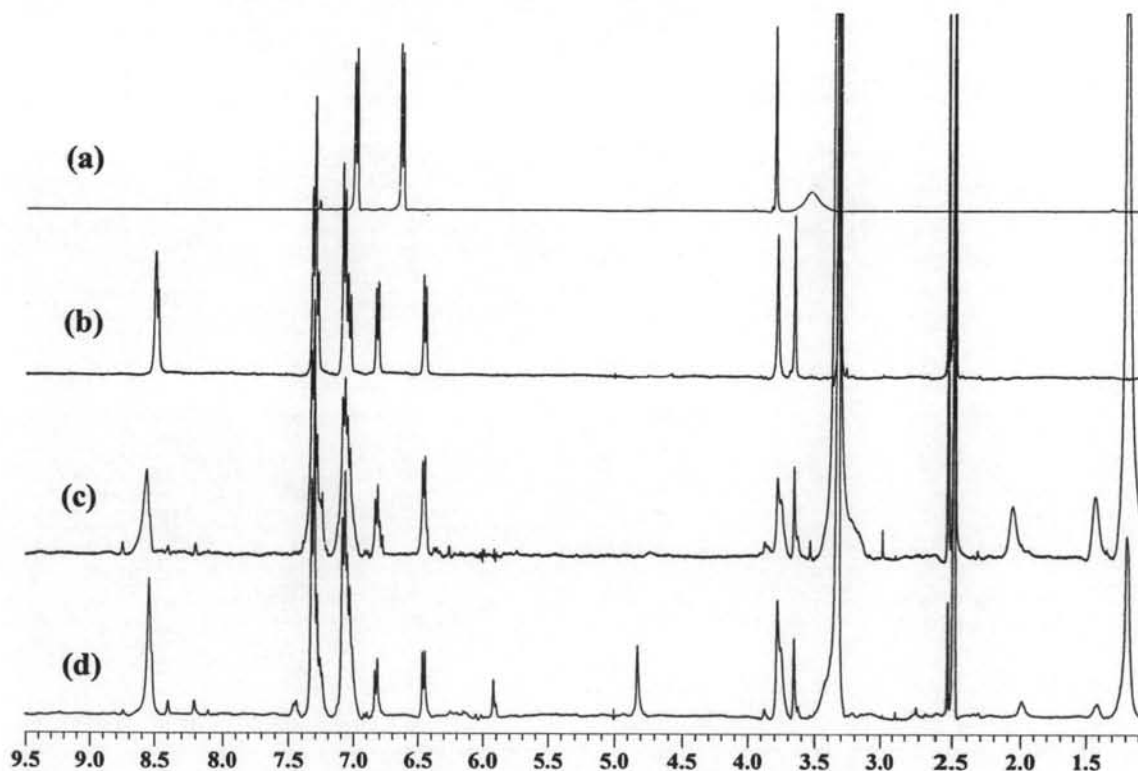


Figure 4.19 ^1H NMR spectra of (a) MTDA; (b) MDI-MTDA (1:1); (c) ZnL-MDI (1:2); (d) ZnL-MDI-MTDA (1:3:1)

4.3.1.2.2 ZnL-MDI-HMDA copolymers

^1H NMR spectra of zinc-containing copolyurethane-ureas based on HMDA are shown in Figure 4.20. ^1H NMR spectrum of HMDA showed signals at δ 2.58-2.62 (N-CH₂), 1.15-1.36 (CH₂). For MDI-HMDA, the spectrum showed peaks around δ 8.28 due to the urea N-H proton attached to the aromatic. The aromatic protons appeared peak around δ 7.23-7.32 and 6.98-7.06. The peaks at δ 6.05 were due to the urea NH proton attached to CH₂. The signals around δ 3.71-3.77 were due to the protons in Ph-CH₂-Ph group. The methylene groups attached to N-H showed signals around δ 3.02-3.03. The other methylene groups were observed between δ 1.21-1.38. In ZnL-MDI-HMDA, the spectrum showed signals for the inter and intramolecular hydrogen bond N-H protons at δ 8.53 and 8.26 and other non-hydrogen bonded N-H proton at δ 6.03. The aromatic protons of MDI showed signals between δ 7.24-7.33 and 7.00-7.09 whereas aromatic protons of ZnL appeared at δ 7.26, 6.82 and 6.45. The signals around δ 3.62-3.78 were due to the protons in Ph-CH₂-Ph group. The methylene groups attached to -NH showed signals around δ 3.02-3.04. The other methylene groups were observed between δ 1.20-1.39.

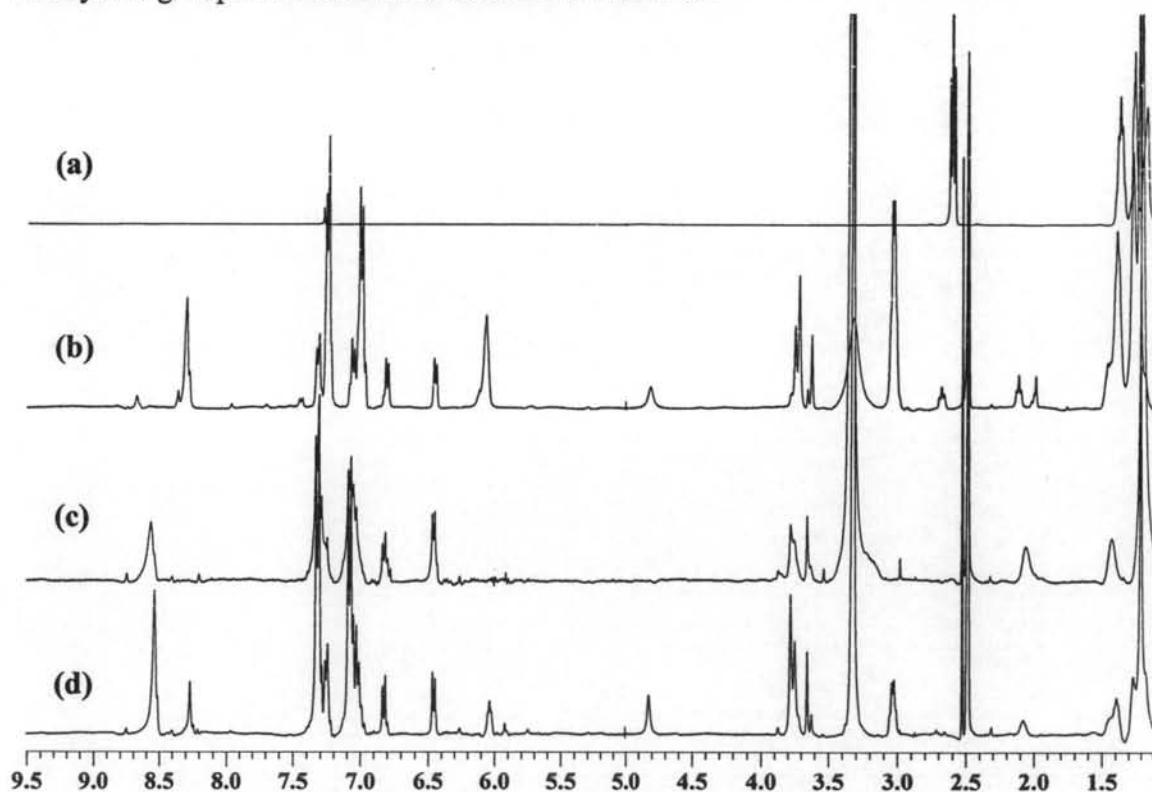


Figure 4.20 ^1H NMR spectra of (a) HMDA; (b) MDI-HMDA (1:1); (c) ZnL-MDI (1:2); (d) ZnL-MDI-HMDA (1:3:1)

4.3.1.2.3 ZnL-MDI-BA copolymers

^1H NMR spectra of zinc-containing copolyurethane-ureas based on BA are shown in Figure 4.21. ^1H NMR spectrum of BA showed signals at δ 6.94-6.96 (Ar-H), 6.60-6.62 (Ar-H), 1.52 (CH_3). For MDI-BA, the spectrum showed signals for N-H proton of the urethane group around δ 8.53. The aromatic protons of MDI were observed at δ 7.33-7.35 and 7.09-7.11 whereas aromatic protons of BA were found at δ 6.83-6.85 and 6.47-6.48. The peaks around δ 3.67-3.80 were due to the proton in Ph- CH_2 -Ph group. In ZnL-MDI-BA, the spectrum showed signal for inter and intra molecular hydrogen bonded NH protons at δ 8.56. The aromatic protons of MDI showed signal between δ 7.30-7.35 and 7.05-7.11 whereas aromatic protons of ZnL and BA appeared at δ 7.26, 6.83-6.85 and 6.46-6.48. The peaks around δ 3.68-3.80 were due to the protons in Ph- CH_2 -Ph group.

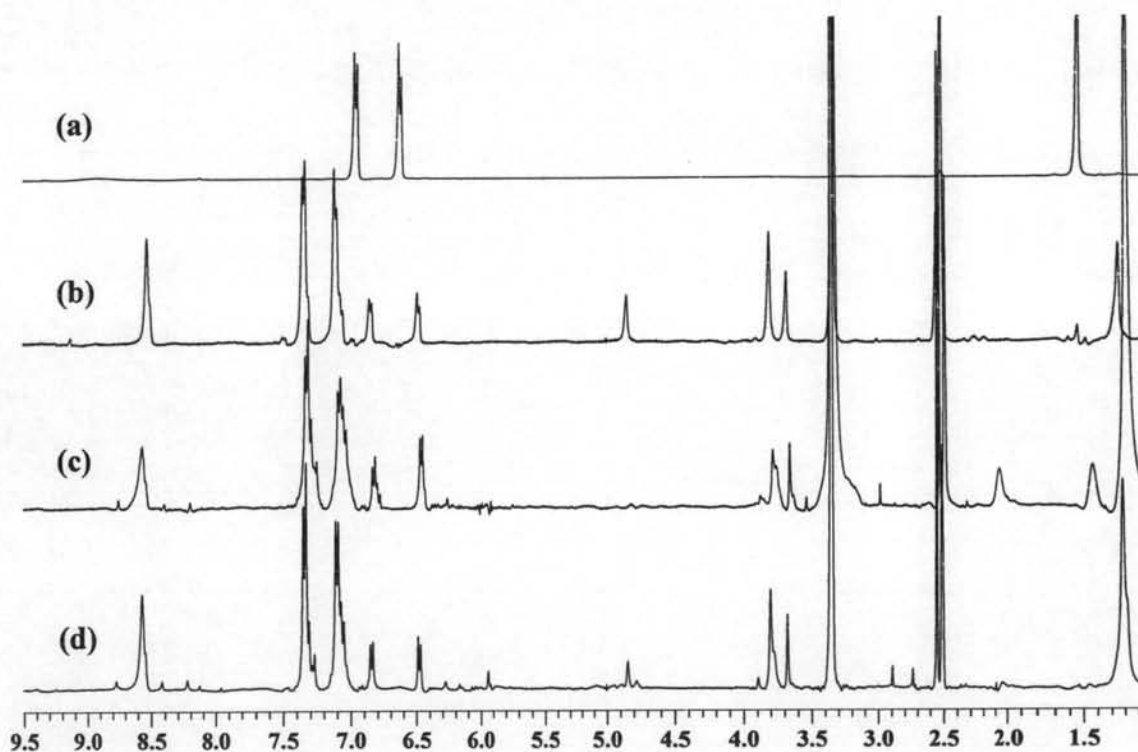


Figure 4.21 ^1H NMR spectra of (a) BA; (b) MDI-BA (1:1); (c) ZnL-MDI (1:2); (d) ZnL-MDI-BA (1:3:1)

4.3.1.2.4 ZnL-MDI-HD copolymers

^1H NMR spectra of zinc-containing copolyurethane-ureas based on HD are shown in Figure 4.22. ^1H NMR spectrum of HD showed signals at δ 3.61-3.65 (O-CH₂), 1.39-2.18 (CH₂). For MDI-HD, the urethane N-H proton showed peak around 8.50 and 9.47. The aromatic protons showed peak around δ 7.32-7.33 and 7.05-7.07. The methyleneoxy group attached to -CONH showed signal at δ 4.03. The signals at δ 3.80 were due to the protons in Ph-CH₂-Ph group. The other methylene groups were observed between δ 1.16-1.59. In ZnL-MDI-HD, the spectrum showed signals at 8.54 ppm for the N-H proton of urethane-urea groups. The aromatic protons of MDI showed signal between δ 7.28-7.33 and 7.03-7.09 whereas aromatic protons of ZnL appeared at δ 7.25, 6.82 and 6.45. The signal around δ 3.65-3.78 was due to the protons in Ph-CH₂-Ph groups. The other methylene groups were observed between δ 1.16-1.44.

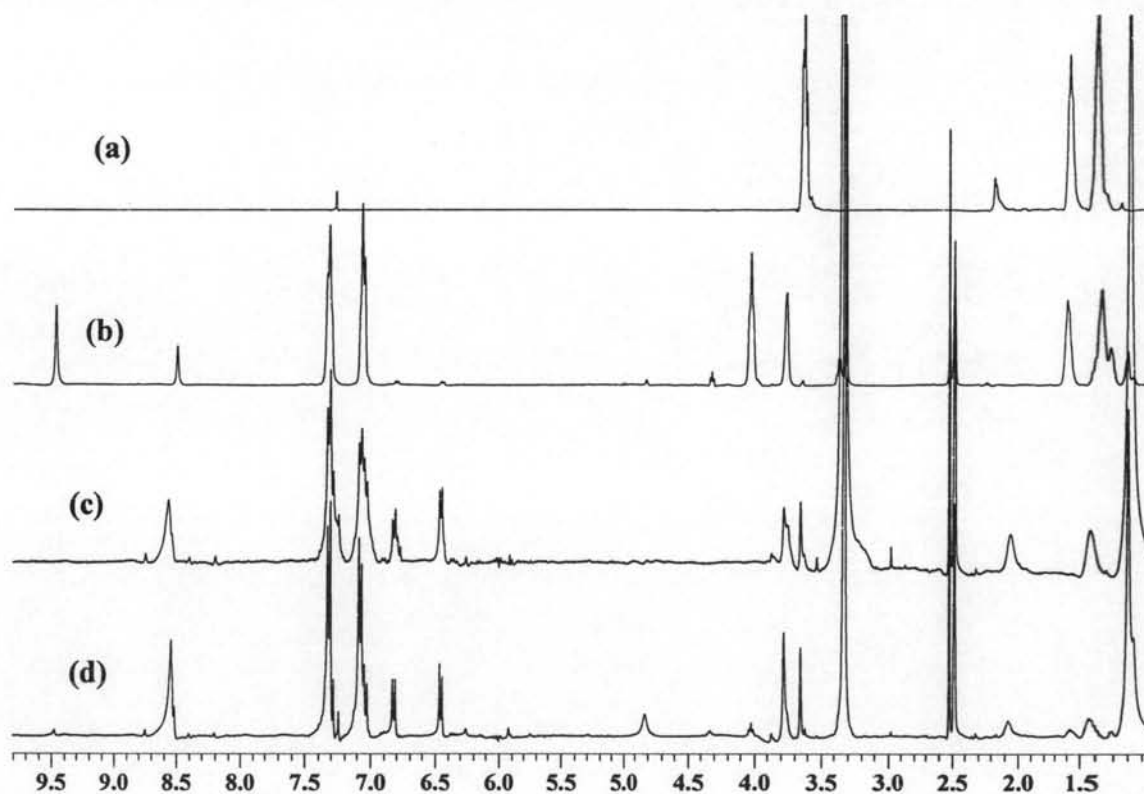


Figure 4.22 ^1H NMR spectra of (a) HD; (b) MDI-HD (1:1); (c) ZnL-MDI (1:2); (d) ZnL-MDI-HD (1:3:1).

4.3.1.3 Solubility

The solubility of metal-containing polymers was tested in various polar and nonpolar solvents (Table 4.7). Solubility test shows that these metal-containing polymers were insoluble in hexane, toluene, CH₃CN, H₂O, CH₂Cl₂, CHCl₃, MeOH and THF. They were soluble in polar solvents such as DMF and DMSO.

Table 4.7 Solubility of metal-containing polymers^a

Polymers	Hexane	Toluene	CH ₃ CN	H ₂ O	CH ₂ Cl ₂	CHCl ₃	MeOH	THF	DMF	DMSO
ZnL-MDI (1:2)	-	-	-	-	-	-	-	-	++	++
NiL-MDI (1:2)	-	-	-	-	-	-	-	-	+	++
MDI-MTDA (1:1)	-	-	-	-	-	-	-	-	+/-	+
MDI-HMDA (1:1)	-	-	-	-	-	-	-	-	+	++
MDI-BA (1:1)	-	-	-	-	-	-	-	-	+/-	+
MDI-HD (1:1)	-	-	-	-	-	-	-	-	++	++
ZnL-MDI-MTDA (0.5:3:1.5)	-	-	-	-	-	-	-	-	++	++
ZnL-MDI-MTDA (1.0:3:1.0)	-	-	-	-	-	-	-	-	++	++
ZnL-MDI-MTDA (1.5:3:0.5)	-	-	-	-	-	-	-	-	++	++
ZnL-MDI-HMDA (0.5:3:1.5)	-	-	-	-	-	-	-	-	++	++
ZnL-MDI-HMDA (1.0:3:1.0)	-	-	-	-	-	-	-	-	++	++
ZnL-MDI-HMDA (1.5:3:0.5)	-	-	-	-	-	-	-	-	++	++
ZnL-MDI-BA (0.5:3:1.5)	-	-	-	-	-	-	-	-	++	++
ZnL-MDI-BA (1.0:3:1.0)	-	-	-	-	-	-	-	-	++	++
ZnL-MDI-BA (1.5:3:0.5)	-	-	-	-	-	-	-	-	++	++
ZnL-MDI-HD (0.5:3:1.5)	-	-	-	-	-	-	-	-	++	++
ZnL-MDI-HD (1.0:3:1.0)	-	-	-	-	-	-	-	-	++	++
ZnL-MDI-HD (1.5:3:0.5)	-	-	-	-	-	-	-	-	++	++

(-) Insoluble; (+/-) Partial soluble; (+) Soluble; (++) Good soluble

^a 10 mg sample was dissolved in 2 ml of a solvent

Table 4.7 (continued)

Polymers	Hexane	Toluene	CH ₃ CN	H ₂ O	CH ₂ Cl ₂	CHCl ₃	MeOH	THF	DMF	DMSO
NiL-MDI-MTDA (0.5:3:1.5)	-	-	-	-	-	-	-	-	+	++
NiL-MDI-MTDA (1.0:3:1.0)	-	-	-	-	-	-	-	-	+	++
NiL-MDI-MTDA (1.5:3:0.5)	-	-	-	-	-	-	-	-	+	++
NiL-MDI-HMDA (0.5:3:1.5)	-	-	-	-	-	-	-	-	++	++
NiL-MDI-HMDA (1.0:3:1.0)	-	-	-	-	-	-	-	-	++	++
NiL-MDI-HMDA (1.5:3:0.5)	-	-	-	-	-	-	-	-	+	++
NiL-MDI-BA (0.5:3:1.5)	-	-	-	-	-	-	-	-	+	++
NiL-MDI-BA (1.0:3:1.0)	-	-	-	-	-	-	-	-	+	++
NiL-MDI-BA (1.5:3:0.5)	-	-	-	-	-	-	-	-	+	++
NiL-MDI-HD (0.5:3:1.5)	-	-	-	-	-	-	-	-	++	++
NiL-MDI-HD (1.0:3:1.0)	-	-	-	-	-	-	-	-	++	++
NiL-MDI-HD (1.5:3:0.5)	-	-	-	-	-	-	-	-	+	++

(-) Insoluble; (+-) Partial soluble; (+) Soluble; (++) Good soluble

^a 10 mg sample was dissolved in 2 ml of a solvent

The maximum amount of each polymer that was able to dissolve in 1 mL of DMSO was determined as shown in Table 4.8.

Table 4.8 The maximum solubility of metal-containing polymers

Polymers	Maximum solubility (mg)/ DMSO 1 (mL)
ZnL-MDI (1:2)	92
MDI-MTDA (1:1)	5
MDI-HMDA (1:1)	30
MDI-BA (1:1)	5
MDI-HD (1:1)	90
ZnL-MDI-MTDA (0.5:3:1.5)	103
ZnL-MDI-MTDA (1.0:3:1.0)	75
ZnL-MDI-MTDA (1.5:3:0.5)	62
ZnL-MDI-HMDA (0.5:3:1.5)	125
ZnL-MDI-HMDA (1.0:3:1.0)	88
ZnL-MDI-HMDA (1.5:3:0.5)	84
ZnL-MDI-BA (0.5:3:1.5)	148
ZnL-MDI-BA (1.0:3:1.0)	132
ZnL-MDI-BA (1.5:3:0.5)	130
ZnL-MDI-HD (0.5:3:1.5)	238
ZnL-MDI-HD (1.0:3:1.0)	229
ZnL-MDI-HD (1.5:3:0.5)	222

Table 4.8 (continued)

Polymers	Maximum solubility (mg)/ DMSO 1 (mL)
NiL-MDI (1:2)	56
MDI-MTDA (1:1)	5
MDI-HMDA (1:1)	30
MDI-BA (1:1)	5
MDI-HD(1:1)	90
NiL-MDI-MTDA (0.5:3:1.5)	45
NiL-MDI-MTDA (1.0:3:1.0)	37
NiL-MDI-MTDA (1.5:3:0.5)	27
NiL-MDI-HMDA (0.5:3:1.5)	47
NiL-MDI-HMDA (1.0:3:1.0)	40
NiL-MDI-HMDA (1.5:3:0.5)	28
NiL-MDI-BA (0.5:3:1.5)	68
NiL-MDI-BA (1.0:3:1.0)	54
NiL-MDI-BA (1.5:3:0.5)	50
NiL-MDI-HD (0.5:3:1.5)	140
NiL-MDI-HD (1.0:3:1.0)	125
NiL-MDI-HD (1.5:3:0.5)	116

The data from Table 4.8 showed that zinc-containing copolymers showed higher solubility than nickel-containing copolymers. The solubility of metal-containing copolymers increased with increasing amount of diamines or dialcohols in the copolymers. The copolymers based on dialcohol exhibited higher solubility than diamine-based copolymers. This might be due to higher urethane linkage in the dialcohol-based copolymers. The copolymers based on aliphatic diamines exhibited higher solubility than aromatic diamine-based copolymers. The aliphatic dialcohols-based copolymers showed higher solubility than the copolymers based on aromatic dialcohols might be due to the higher flexibility of the aliphatic part. The poor solubility of MDI-MTDA and MDI-BA because these polymers have more crosslinked structures.

4.3.1.4 Inherent viscosity

The inherent viscosity of metal-containing copolyurethane-ureas was measured at 40 °C in DMSO. The viscosity data are shown in Table 4.9.

Table 4.9 Inherent viscosity of metal-containing copolyurethane-ureas

Polymers	η_{inh} (dL/g) ^a
ZnL-MDI (1:2)	0.1648
MDI-MTDA (1:1)	0.0940
MDI-HMDA (1:1)	0.1000
MDI-BA (1:1)	0.1156
MDI-HD (1:1)	0.1390
ZnL-MDI-MTDA (0.5:3:1.5)	0.1361
ZnL-MDI-MTDA (1.0:3:1.0)	0.1409
ZnL-MDI-MTDA (1.5:3:0.5)	0.1184
ZnL-MDI-HMDA (0.5:3:1.5)	0.1012
ZnL-MDI-HMDA (1.0:3:1.0)	0.1012
ZnL-MDI-HMDA (1.5:3:0.5)	0.1275
ZnL-MDI-BA (0.5:3:1.5)	0.1565
ZnL-MDI-BA (1.0:3:1.0)	0.1465
ZnL-MDI-BA (1.5:3:0.5)	0.1390
ZnL-MDI-HD (0.5:3:1.5)	0.1539
ZnL-MDI-HD (1.0:3:1.0)	0.1688
ZnL-MDI-HD (1.5:3:0.5)	0.1625

^a determined at a concentration 0.5 g/ 100 mL in DMSO 40 °C

Table 4.9 (Continued)

Polymers	η_{inh} (dL/g) ^a
NiL-MDI (1:2)	0.1566
MDI-MTDA (1:1)	0.0940
MDI-HMDA (1:1)	0.1000
MDI-BA (1:1)	0.1156
MDI-HD (1:1)	0.1390
NiL-MDI-MTDA (0.5:3:1.5)	0.1150
NiL-MDI-MTDA (1.0:3:1.0)	0.1145
NiL-MDI-MTDA (1.5:3:0.5)	0.0980
NiL-MDI-HMDA (0.5:3:1.5)	0.1390
NiL-MDI-HMDA (1.0:3:1.0)	0.1545
NiL-MDI-HMDA (1.5:3:0.5)	0.1130
NiL-MDI-BA (0.5:3:1.5)	0.1700
NiL-MDI-BA (1.0:3:1.0)	0.1390
NiL-MDI-BA (1.5:3:0.5)	0.1110
NiL-MDI-HD (0.5:3:1.5)	0.1513
NiL-MDI-HD (1.0:3:1.0)	0.1654
NiL-MDI-HD (1.5:3:0.5)	0.1540

^a determined at a concentration 0.5 g/ 100 mL in DMSO 40 °C

The data showed that the inherent viscosity of the metal-containing copolyurethane-ureas was found to be in the range between 0.0940-0.1700 dl/g. The viscosity of metal-containing copolyurethane-ureas was higher than blank polyurethane-ureas without metal complexes in both Zn and Ni series. This indicated that metal complexes did not dissociate from the polymer in solvent.

4.3.1.5 X-ray diffraction

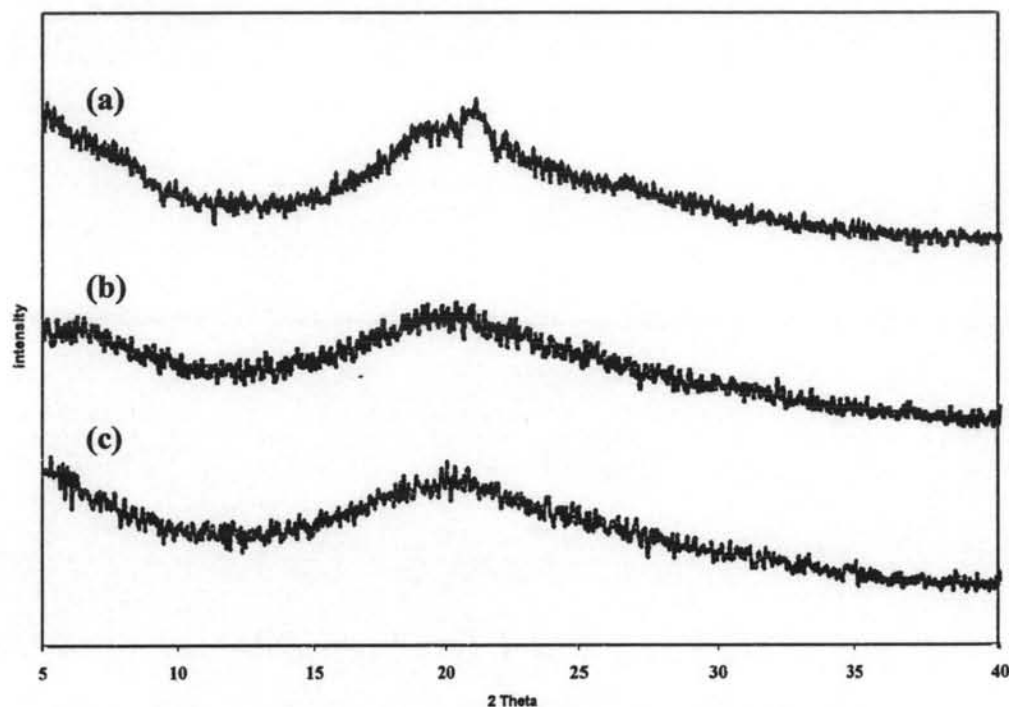


Figure 4.23 XRD patterns of (a) ZnL-MDI-HD (1.0:3:1.0); (b) ZnL-MDI; (c) NiL-MDI

Fig 4.23 shows the XRD patterns of metal-containing polyurethane-ureas and metal-containing copolyurethane-urea. The XRD pattern of metal-containing copolyurethane-urea was similar to those of metal-containing polyurethane-ureas. The polymers did not show any sharp peak so they were considered to be amorphous in nature. The amorphous of polymers is supported by the solubility test of polymers which showed that the metal-containing polymers were soluble in DMF and DMSO.

4.3.1.6 Thermogravimetric analysis

4.3.1.6.1 ZnL-MDI- MTDA copolymers

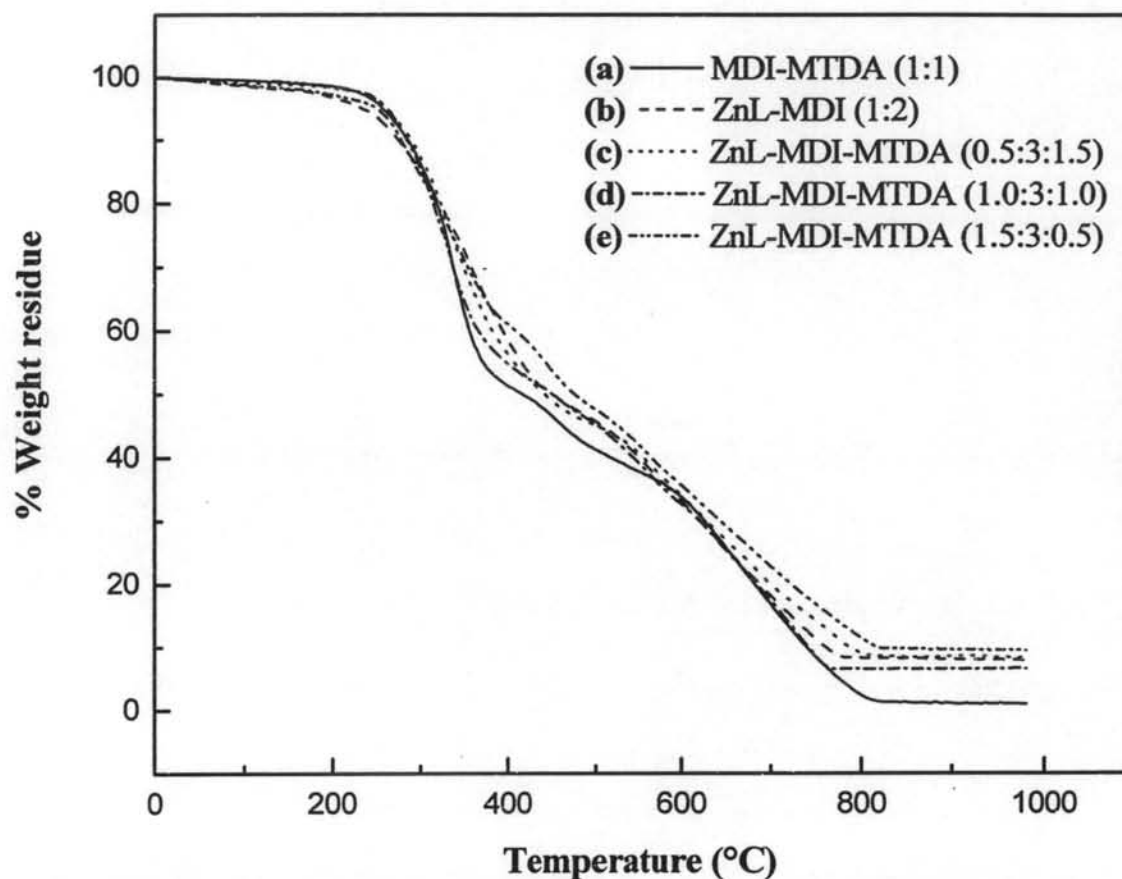


Figure 4.24 TGA thermogram of (a) MDI-MTDA; (b) ZnL-MDI (1:2); (c) ZnL-MDI-MTDA (0.5:3:1.5); (d) ZnL-MDI-MTDA (1.0:3:1.0); (e) ZnL-MDI-MTDA (1.5:3:0.5)

Table 4.10 TGA data of zinc-containing copolyurethane-ureas based on MTDA

Polymer	IDT (°C)	Weight loss (%) at different temperature (°C)						
		300	400	500	600	700	800	900
MDI-MTDA (1:1)	270	14	49	59	66	83	98	99
ZnL-MDI (1:2)	241	15	41	54	67	82	92	92
ZnL-MDI-MTDA (0.5:3:1.5)	275	13	44	55	66	80	91	91
ZnL-MDI-MTDA (1.0:3:1.0)	272	15	45	55	67	83	93	93
ZnL-MDI-MTDA (1.5:3:0.5)	253	16	39	52	64	77	89	90

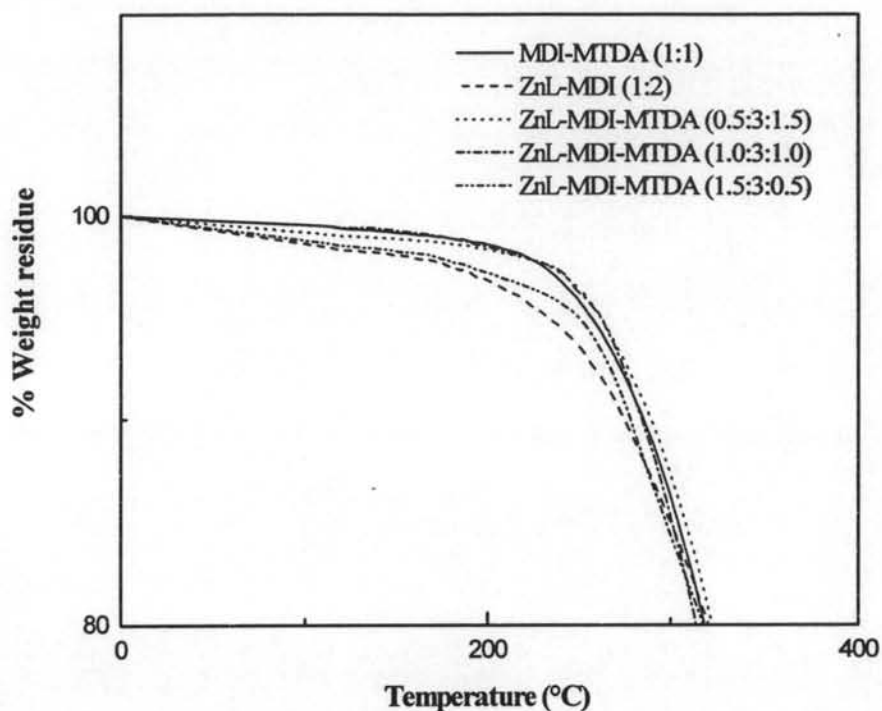


Figure 4.25 The IDT of zinc-containing copolyurethane-ureas based on MTDA

TGA results of ZnL-MDI-MTDA copolymers (Figure 4.24 and Table 4.10) showed that the amount of MTDA in zinc-containing copolyurethane-ureas did not effect on the percentage of weight loss at 600 °C when compared to ZnL-MDI. Initial decomposition temperature (IDT) of the copolymers (Figure 4.25) was found to be in the range 253-275 °C. For comparison, zinc-containing polyurethane-ureas without MTDA were synthesis from ZnL and MDI. It was found that the IDT of ZnL-MDI-MTDA was higher than that of ZnL-MDI. The IDT of ZnL-MDI-MTDA increased with increasing amount of MTDA in the copolymers.

4.3.1.6.2 NiL-MDI-MTDA copolymers

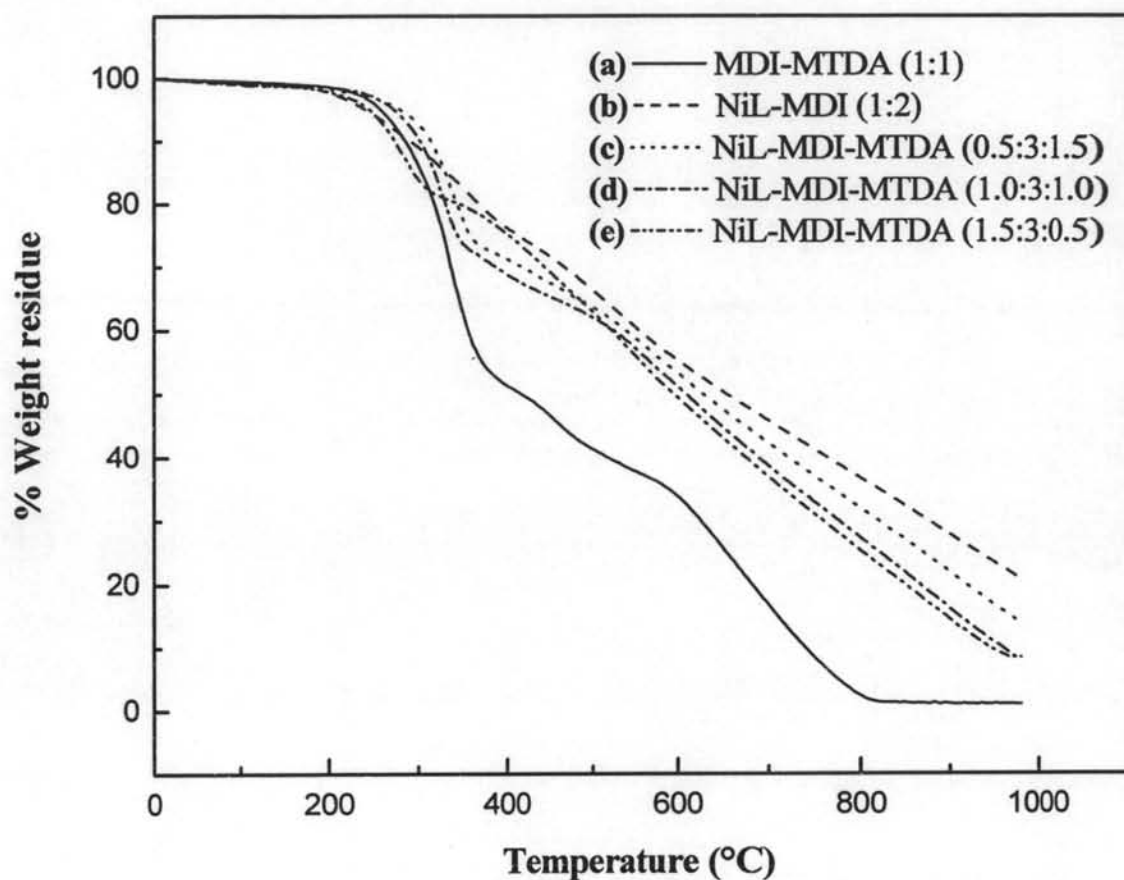


Figure 4.26 TGA thermogram of (a) MDI-MTDA; (b) NiL-MDI (1:2); (c) NiL-MDI-MTDA (0.5:3:1.5); (d) NiL-MDI-MTDA (1.0:3:1.0); (e) NiL-MDI-MTDA (1.5:3:0.5)

Table 4.11 TGA data of nickel-containing copolyurethane-ureas based on MTDA

Polymer	IDT (°C)	Weight loss (%) at different temperature (°C)						
		300	400	500	600	700	800	900
MDI-MTDA (1:1)	270	14	49	59	66	83	98	99
NiL-MDI (1:2)	228	11	24	34	45	54	63	72
NiL-MDI-MTDA (0.5:3:1.5)	301	7	29	36	47	58	68	78
NiL-MDI-MTDA (1.0:3:1.0)	289	9	31	38	49	61	73	84
NiL-MDI-MTDA (1.5:3:0.5)	246	16	25	37	51	63	75	86

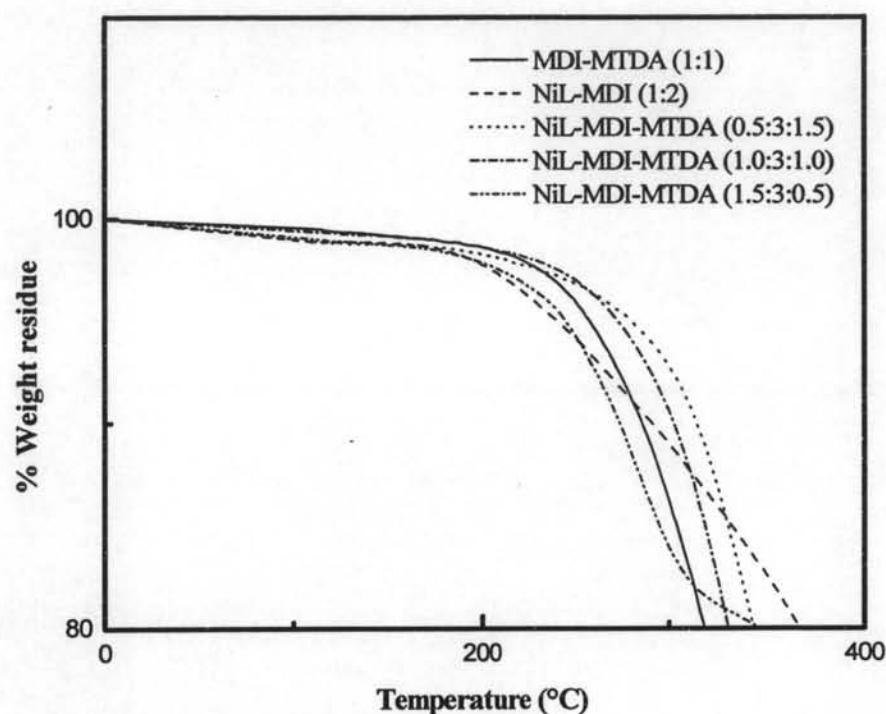


Figure 4.27 The IDT of nickel-containing copolyurethane-ureas based on MTDA

TGA results of NiL-MDI-MTDA copolymers (Figure 4.26 and Table 4.11) showed that the amount of MTDA in nickel-containing copolyurethane-ureas did not effect on the percentage of weight loss at 600 °C when compared to NiL-MDI. Initial decomposition temperature (IDT) of NiL-MDI-MTDA (Figure 4.27) was found to be in the range 246-301 °C. For comparison, nickel-containing polyurethanes-ureas without MTDA were synthesized from NiL-MDI. It was found that the IDT of NiL-MDI-MTDA was higher than that of NiL-MDI. The IDT of NiL-MDI-MTDA was found to be increased with increase in MTDA content.

4.3.1.6.3 ZnL-MDI-HMDA copolymers

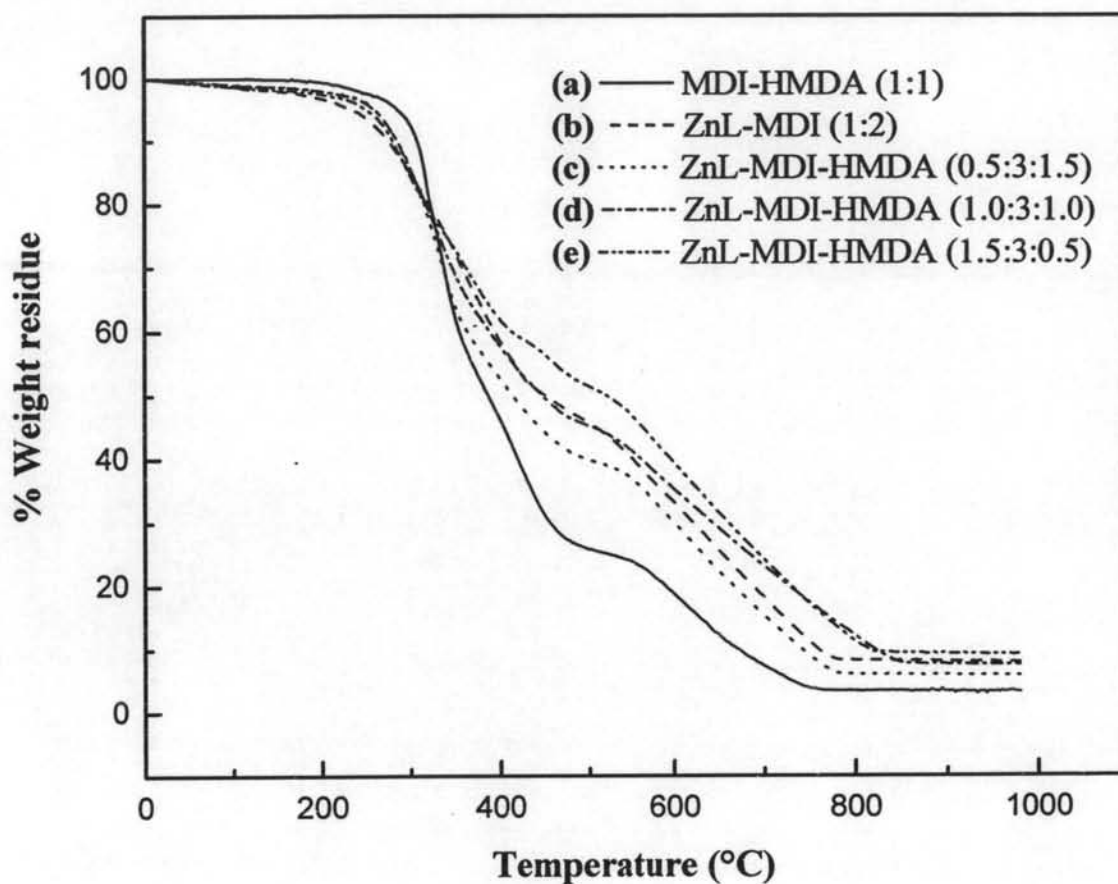


Figure 4.28 TGA thermogram of (a) MDI-HMDA; (b) Zn-MDI (1:2); (c) ZnL-MDI-HMDA (0.5:3:1.5); (d) ZnL-MDI-HMDA (1.0:3:1.0); (e) ZnL-MDI-HMDA (1.5:3:0.5)

Table 4.12 TGA data of zinc-containing copolyurethane-ureas based on HMDA

Polymer	IDT (°C)	Weight loss (%) at different temperature (°C)						
		300	400	500	600	700	800	900
MDI-HMDA (1:1)	303	7	54	74	81	93	97	97
ZnL-MDI (1:2)	241	15	41	54	67	82	92	92
ZnL-MDI-HMDA (0.5:3:1.5)	263	14	47	60	70	85	94	94
ZnL-MDI-HMDA (1.0:3:1.0)	261	14	42	55	65	77	88	92
ZnL-MDI-HMDA (1.5:3:0.5)	258	15	38	49	61	76	89	91

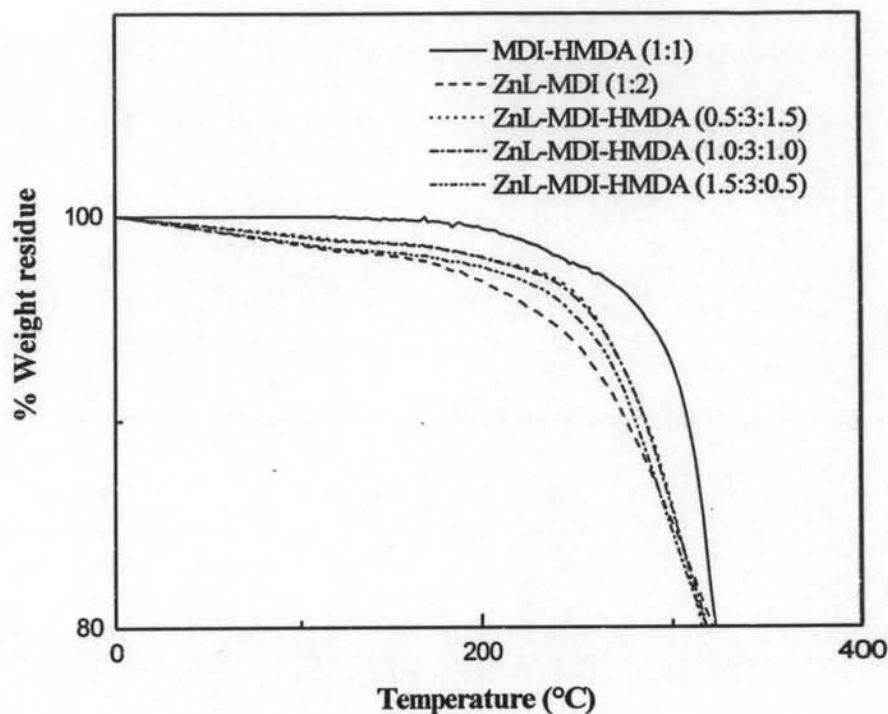


Figure 4.29 The IDT of zinc-containing copolyurethane-ureas based on HMDA

TGA curves and data of ZnL-MDI-HMDA are given in Figure 4.28 and Table 4.12. The amounts of HMDA in zinc-containing copolyurethane-ureas have small effect on the percentage of weight loss at 600 °C when compared to ZnL-MDI. The TGA result of these polymers showed that with increasing HMDA content, the percentage of weight loss at 600 °C increased. The IDT of the copolymers (Figure 4.29) was found to be in the range 258-263 °C. Comparing to the polyurethane-ureas obtained from ZnL and MDI, the ZnL-MDI-HMDA showed an increased in IDT when the amount of HMDA in the ZnL-MDI-HMDA was increased.

4.3.1.6.4 NiL-MDI-HMDA copolymers

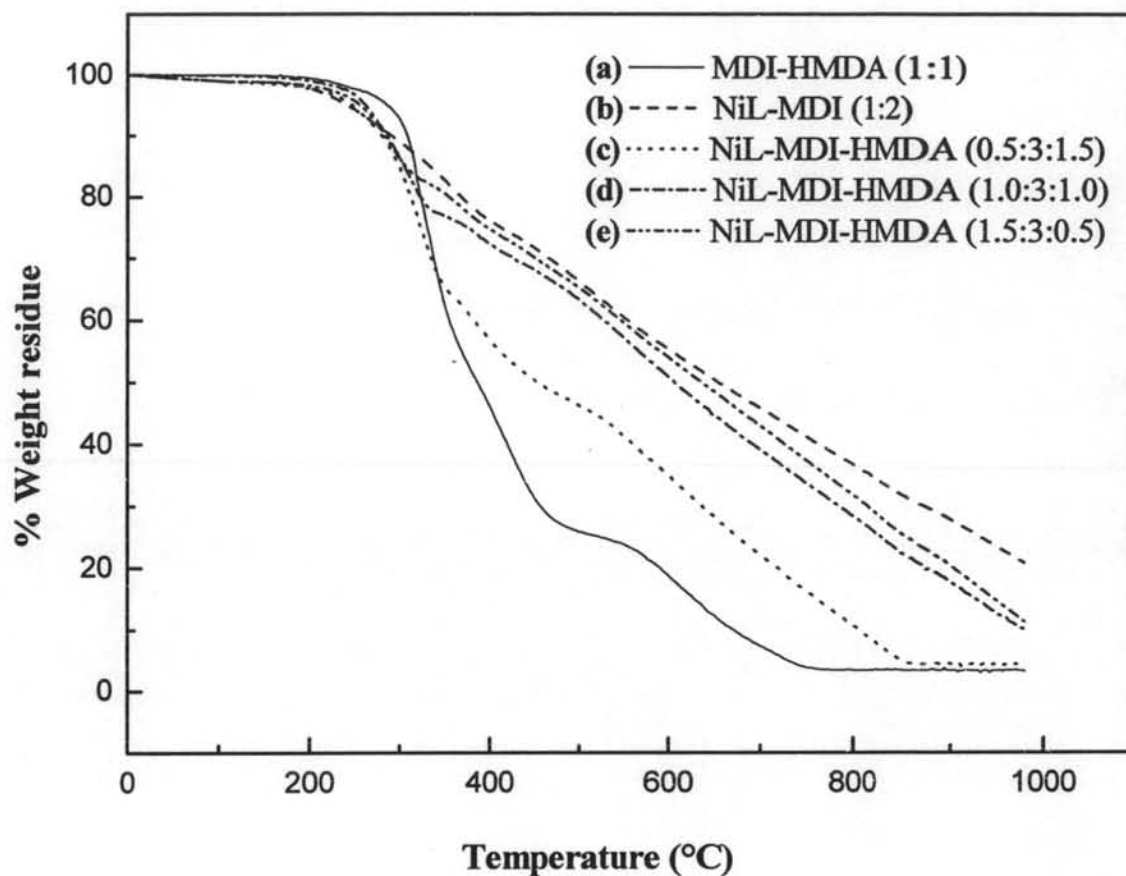


Figure 4.30 TGA thermogram of (a) MDI-HMDA; (b) NiL-MDI (1:2); (c) NiL-MDI-HMDA (0.5:3:1.5); (d) NiL-MDI-HMDA (1.0:3:1.0); (e) NiL-MDI-HMDA (1.5:3:0.5)

Table 4.13 TGA data of nickel-containing copolyurethane-ureas based on HMDA

Polymer	IDT (°C)	Weight loss (%) at different temperature (°C)						
		300	400	500	600	700	800	900
MDI-HMDA (1:1)	303	7	54	74	81	93	97	97
NiL-MDI (1:2)	228	11	24	34	45	54	63	72
NiL-MDI-HMDA (0.5:3:1.5)	240	15	43	54	65	78	89	96
NiL-MDI-HMDA (1.0:3:1.0)	252	14	28	37	49	61	72	82
NiL-MDI-HMDA (1.5:3:0.5)	248	14	25	35	46	57	68	80

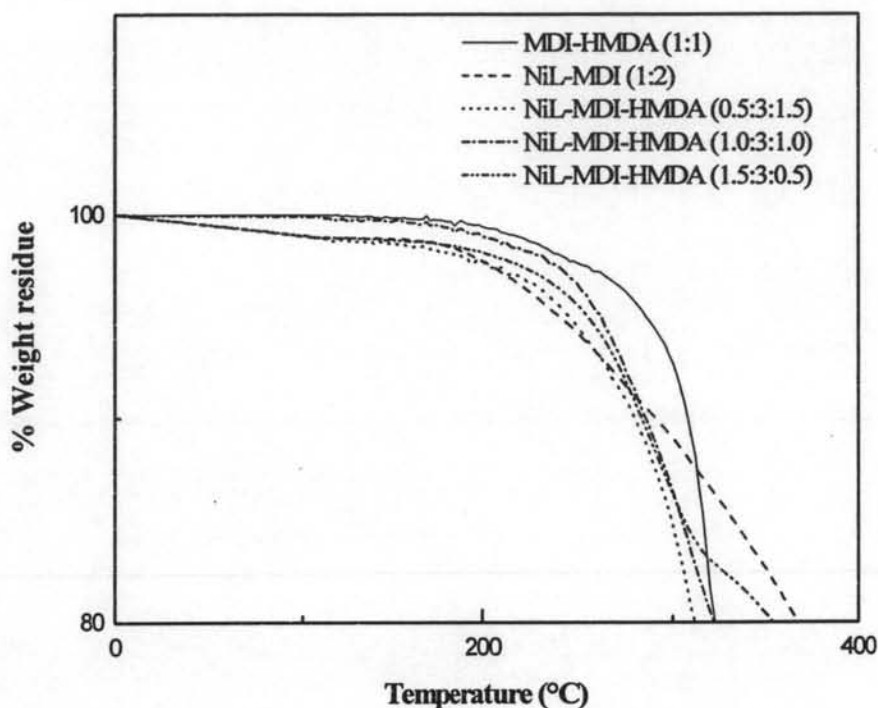


Figure 4.31 The IDT of nickel-containing copolyurethane-ureas based on HMDA

From TGA result (Figure 4.30 and Table 4.13, respectively) showed that the NiL-MDI-HMDA (0.5:3:1.5) had the lowest char yield of 35% at 600 °C, which was lower than that NiL-MDI. The percentage of weight loss at 600 °C of these polymers increased with increasing amount of HMDA in the copolymers. IDT of NiL-MDI-HMDA (Figure 4.31) was found to be in the range 240-252 °C. For comparison, the nickel-containing polyurethane-ureas without HMDA was synthesized from NiL and MDI. It was found that the IDT of NiL-MDI-HMDA was higher than those of NiL-MDI.

4.3.1.6.5 ZnL-MDI-BA copolymers

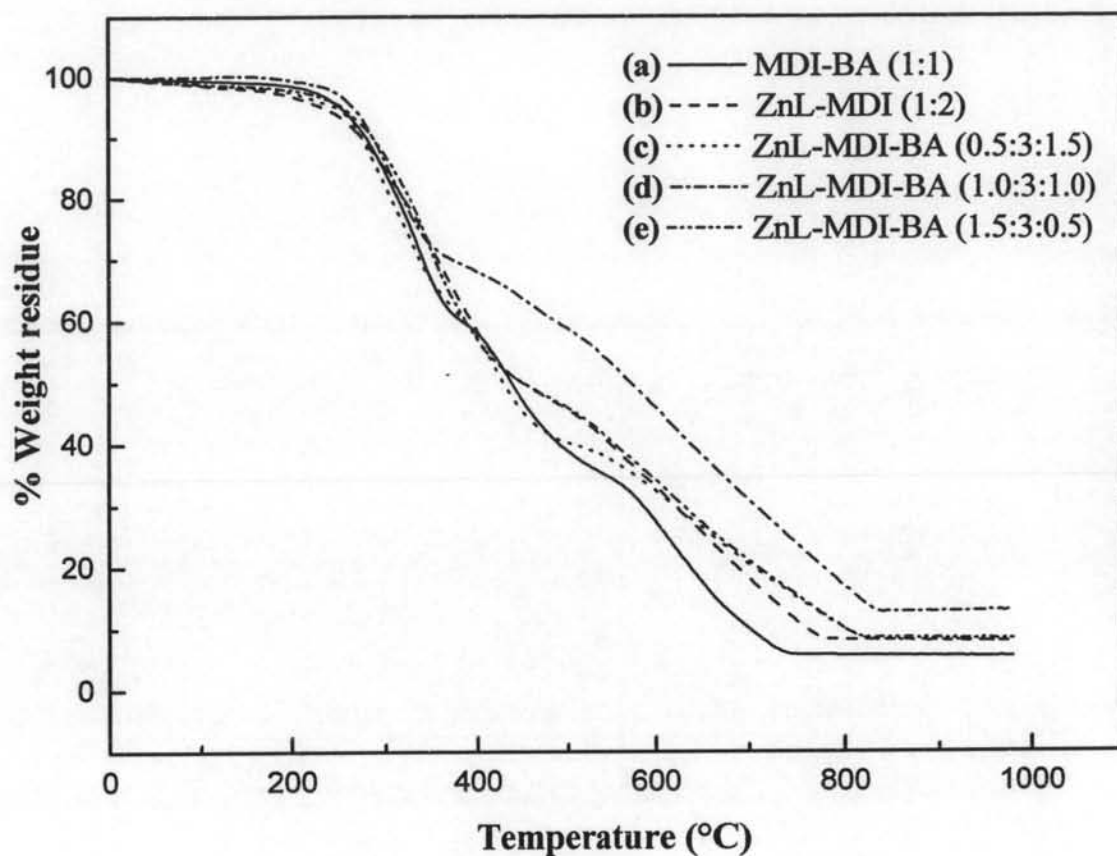


Figure 4.32 TGA thermogram of (a) MDI-BA; (b) ZnL-MDI (1:2); (c) ZnL-MDI-BA (0.5:3:1.5); (d) ZnL-MDI-BA (1.0:3:1.0); (e) ZnL-MDI-BA (1.5:3:0.5)

Table 4.14 TGA data of zinc-containing copolyurethane-ureas based on BA

Polymer	IDT (°C)	Weight loss (%) at different temperature (°C)						
		300	400	500	600	700	800	900
MDI-BA (1:1)	262	15	42	61	72	90	94	94
ZnL-MDI (1:2)	241	15	41	54	67	82	92	92
ZnL-MDI-BA (0.5:3:1.5)	257	18	43	60	68	80	90	90
ZnL-MDI-BA (1.0:3:1.0)	258	14	32	41	54	69	83	87
ZnL-MDI-BA (1.5:3:0.5)	263	13	43	54	66	79	90	91

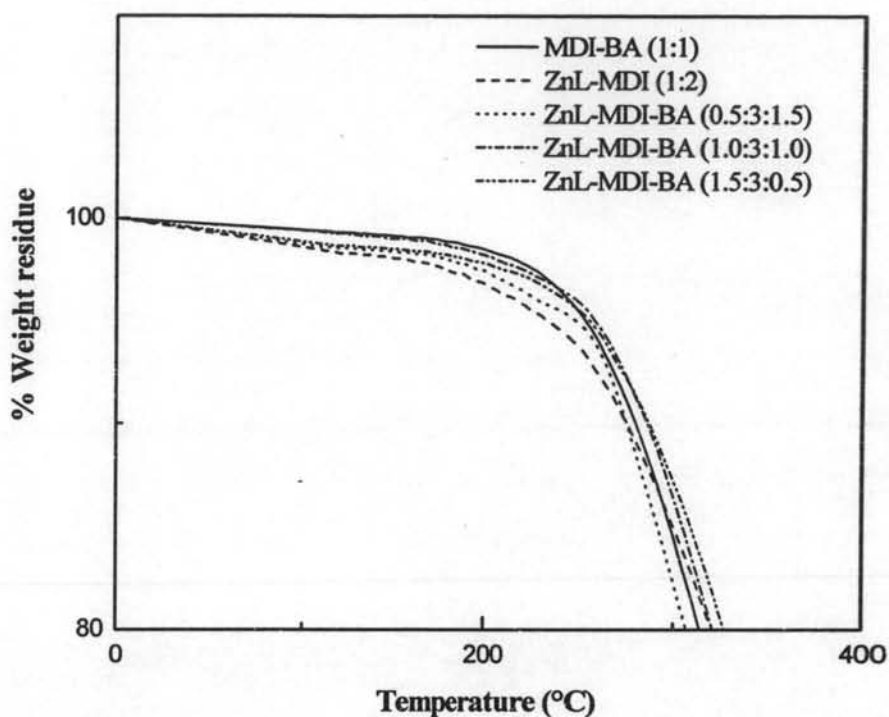


Figure 4.33 The IDT of zinc-containing copolyurethane-ureas based on BA

TGA results of ZnL-MDI-BA were presented in Figure 4.32 and Table 4.14, respectively. The char yield at 600 °C of ZnL-MDI-BA (1.0:3:1.0) was 46%, which was higher than that of ZnL-MDI. The IDT of ZnL-MDI-BA (Figure 4.33) was found to be in the range 257-263 °C. For comparison, the zinc-containing polyurethane-ureas without BA were synthesized from ZnL and MDI. It was found that the IDT of ZnL-MDI-BA was higher than that of ZnL-MDI. The ZnL-MDI-BA showed an increased in IDT when the amount of zinc in the ZnL-MDI-BA was increased.

4.3.1.6.6 NiL-MDI-BA copolymers

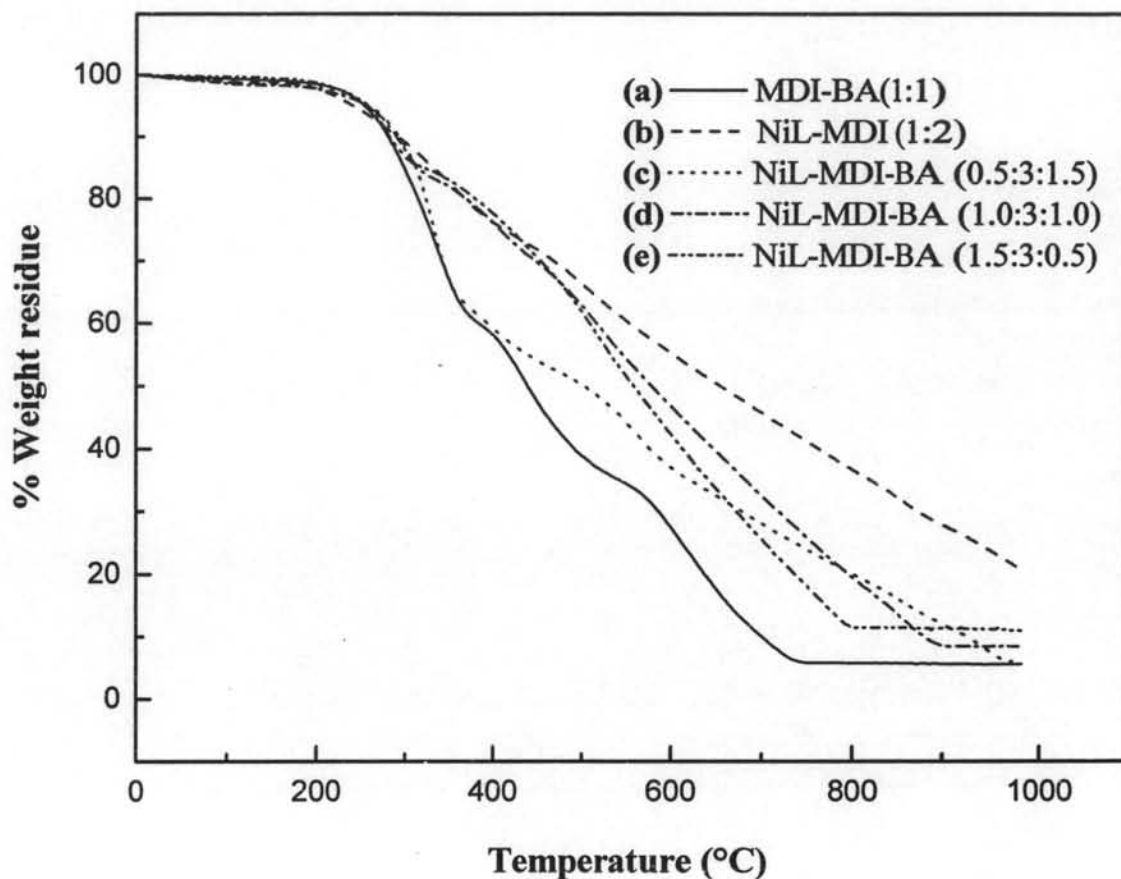


Figure 4.34 TGA thermogram of (a) MDI-BA; (b) NiL-MDI (1:2); (c) NiL-MDI-BA (0.5:3:1.5); (d) NiL-MDI-BA (1.0:3:1.0); (e) NiL-MDI-BA (1.5:3:0.5)

Table 4.15 TGA data of nickel-containing copolyurethane-ureas based on BA

Polymer	IDT (°C)	Weight loss (%) at different temperature (°C)						
		300	400	500	600	700	800	900
MDI-BA (1:1)	262	15	42	61	72	90	94	94
NiL-MDI (1:2)	228	11	24	34	45	54	63	72
NiL-MDI-BA (0.5:3:1.5)	268	12	41	50	63	72	80	88
NiL-MDI-BA (1.0:3:1.0)	262	12	24	37	53	67	81	92
NiL-MDI-BA (1.5:3:0.5)	253	13	22	38	58	74	87	87

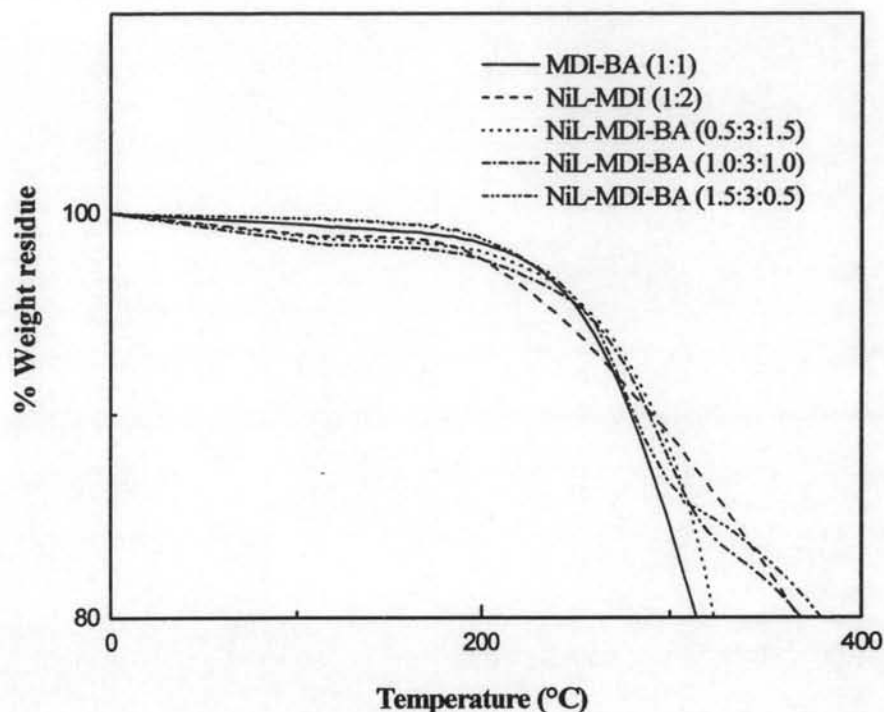


Figure 4.35 The IDT of nickel-containing copolyurethane-ureas based on BA

TGA curves and data of nickel-containing copolyurethane-ureas based on BA are given in Figure 4.34 and Table 4.15, respectively. TGA result indicated that the char yield at 600 °C of NiL-MDI-BA decreased by introducing BA into the polymers. In comparison between NiL-MDI-BA at different molar ratios, the result showed that the NiL-MDI-BA (1.0:3:1.0) had the highest char yield at 600 °C. IDT of NiL-MDI-BA (Figure 4.35) was found to be in the range 253-268 °C. For comparison, the nickel-containing polyurethane-ureas without BA were synthesized from NiL and MDI. It was found that the IDT of NiL-MDI-BA was higher than those of NiL-MDI. The IDT of NiL-MDI-BA increased with increasing amount of BA in the copolymers.

4.3.1.6.7 ZnL-MDI-HD copolymers

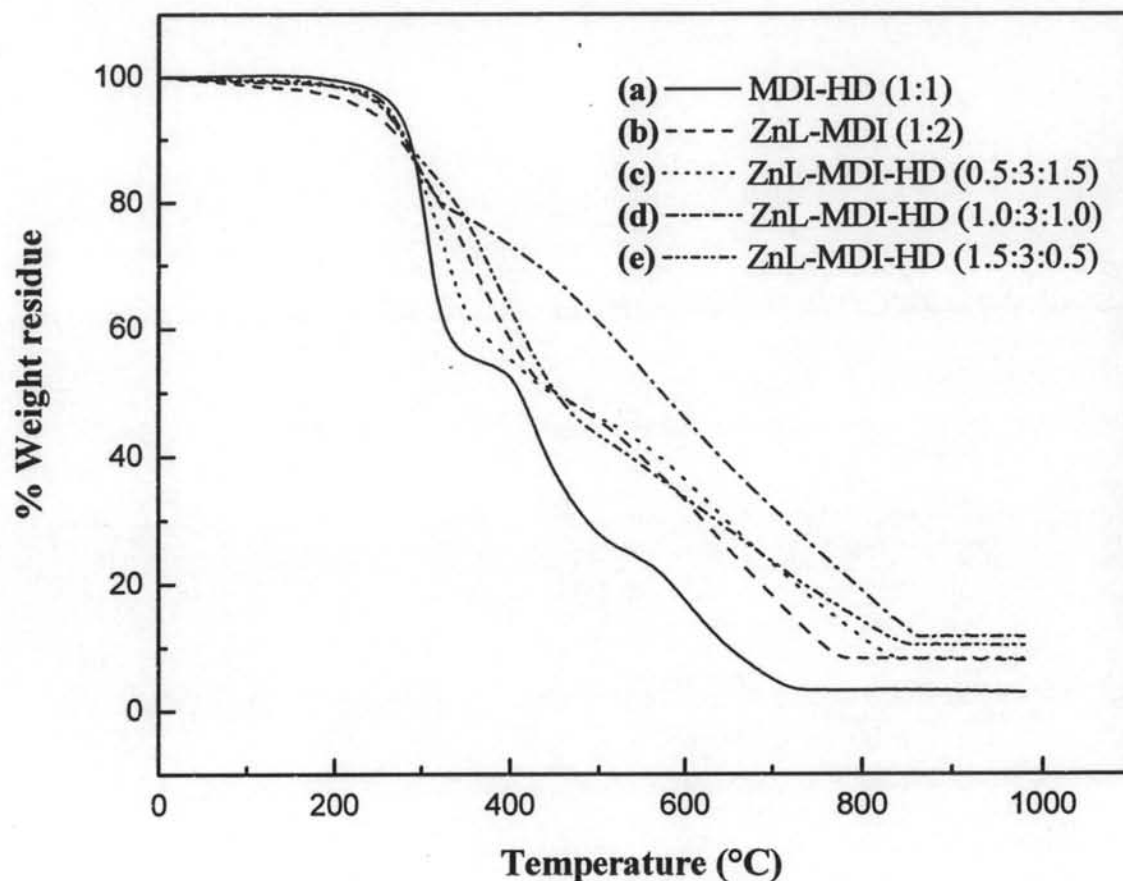


Figure 4.36 TGA thermogram of (a) MDI-HD; (b) ZnL-MDI (1:2); (c) ZnL-MDI-HD (0.5:3:1.5); (d) ZnL-MDI-HD (1.0:3:1.0); (e) ZnL-MDI-HD (1.5:3:0.5)

Table 4.16 TGA data of zinc-containing copolyurethane-ureas based on HD

Polymer	IDT (°C)	Weight loss (%) at different temperature (°C)						
		300	400	500	600	700	800	900
MDI-HD (1:1)	279	19	48	72	82	95	97	97
ZnL-MDI (1:2)	241	15	41	54	67	82	92	92
ZnL-MDI-HD (0.5:3:1.5)	255	16	45	54	64	77	88	92
ZnL-MDI-HD (1.0:3:1.0)	256	15	27	39	54	68	81	88
ZnL-MDI-HD (1.5:3:0.5)	255	13	37	57	66	76	86	90

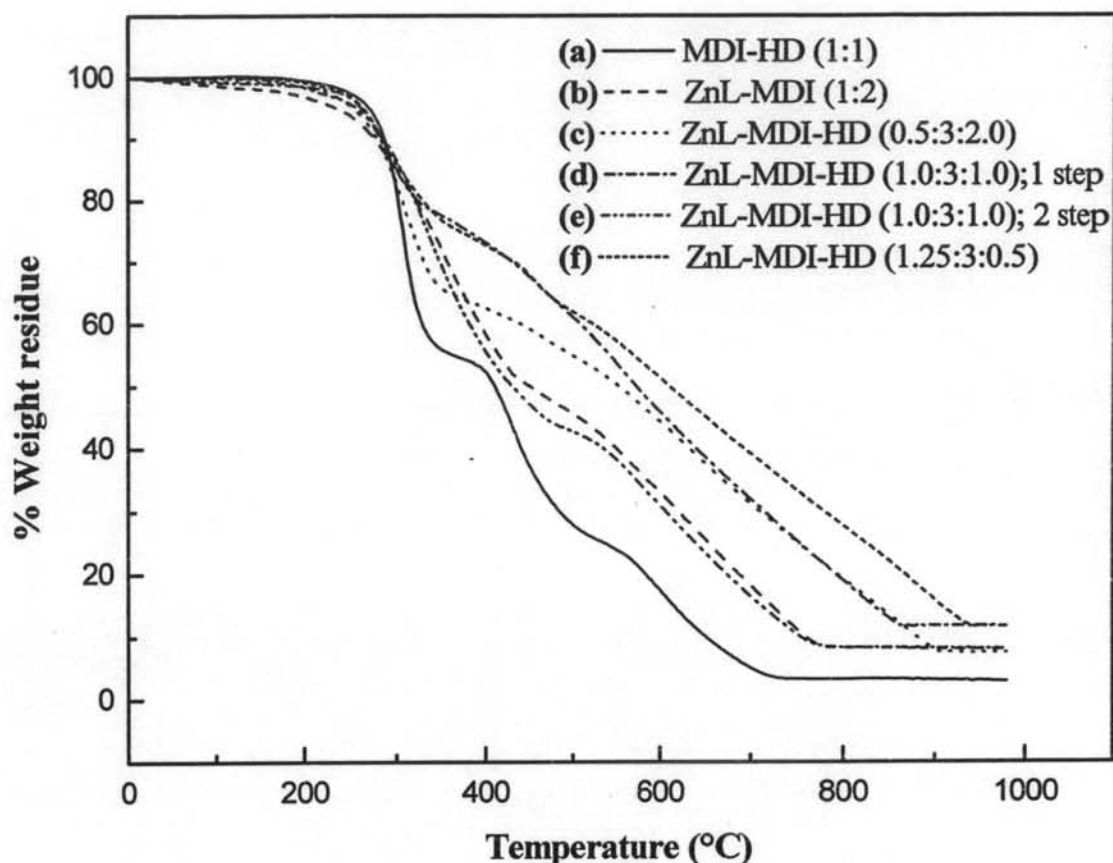


Figure 4.37 TGA thermogram of (a) MDI-HD; (b) ZnL-MDI (1:2); (c) ZnL-MDI-HD (0.5:3:2.0); (d) ZnL-MDI-HD (1.0:3:1.0), 1 step; (e) ZnL-MDI-HD (1.0:3:1.0), 2 step; (f) ZnL-MDI-HD (1.25:3:0.5)

Table 4.17 TGA data of zinc-containing copolyurethane-ureas based on HD

Polymer	IDT (°C)	Weight loss (%) at different temperature (°C)						
		300	400	500	600	700	800	900
MDI-HD (1:1)	279	19	48	72	82	95	97	97
ZnL-MDI (1:2)	241	15	41	54	67	82	92	92
ZnL-MDI-HD (0.5:3:2.0)	258	17	37	45	56	69	81	92
ZnL-MDI-HD (1.0:3:1.0); 1 step	256	15	27	39	54	68	81	88
ZnL-MDI-HD (1.0:3:1.0); 2 step	260	14	44	57	69	84	92	92
ZnL-MDI-HD (1.25:3:0.5)	255	14	27	38	49	61	72	84

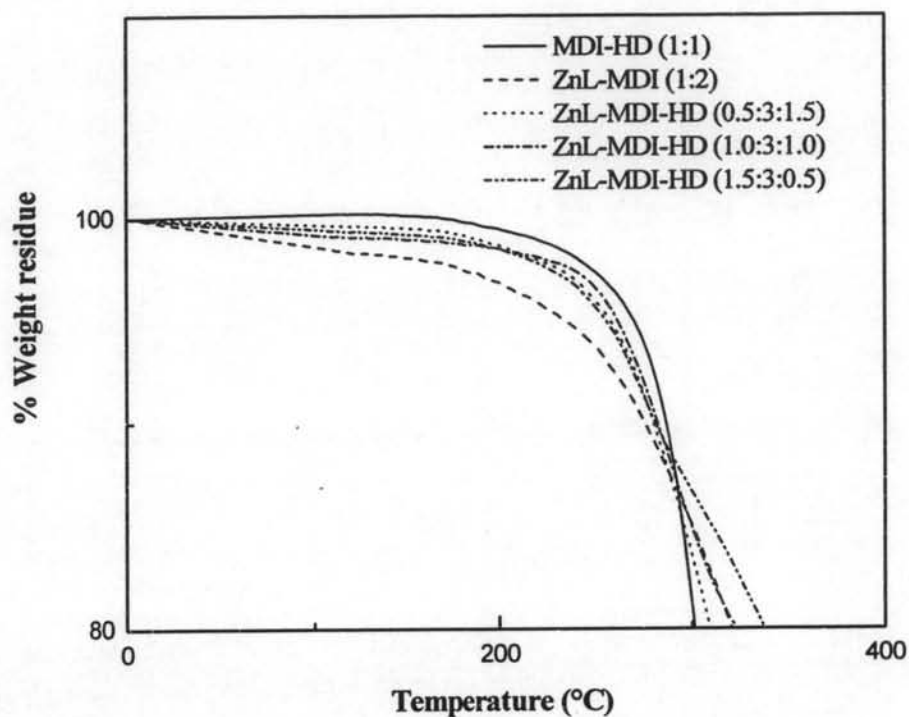


Figure 4.38 The IDT of zinc-containing copolyurethane-ureas based on HD

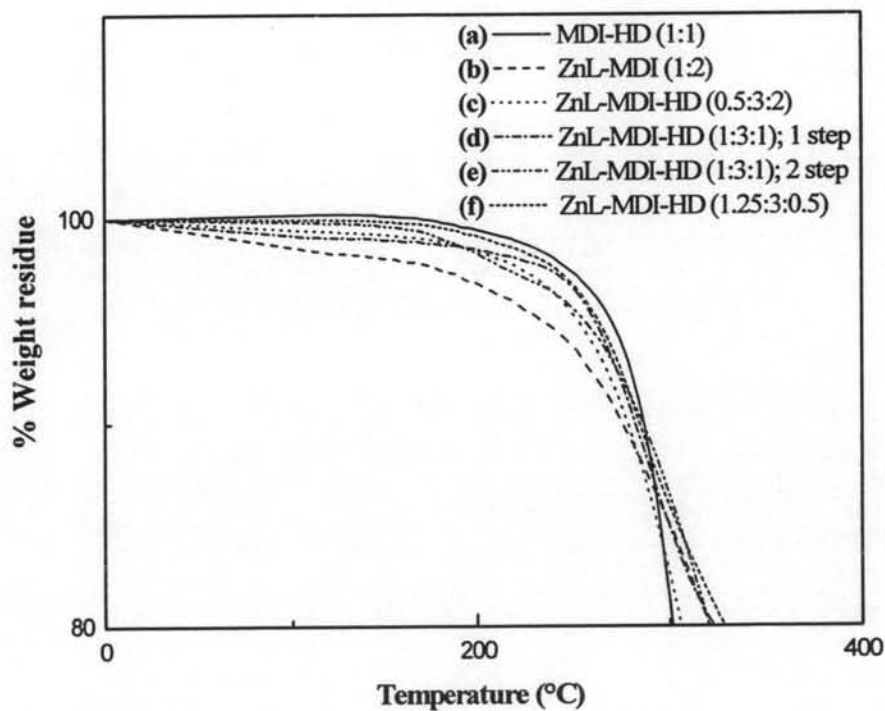


Figure 4.39 The IDT of zinc-containing copolyurethane-ureas based on HD

TGA curve and data of zinc-containing copolyurethane-ureas based on HD are shown in Figure 4.36 and Table 4.16, respectively. The TGA data of zinc-containing copolyurethane-ureas based on HD followed the same trend as described in the case of zinc-containing copolyurethane-ureas based on BA. The char yield at 600 °C of ZnL-MDI-HD (1.0:3:1.0) was 46%, which was higher than that of ZnL-MDI. TGA curve of ZnL-MDI-HD (1.0:3:1.0) synthesized by one step process show better thermal stability than ZnL-MDI-HD (1.0:3:1.0) synthesized by a two step process (Figure 4.37 and Table 4.17). TGA data of ZnL-MDI-HD (1.0:3:1.0) synthesized by one step process showed good thermal stability. ZnL-MDI-HD were synthesized from different compositions by taking the molar ratio of ZnL-MDI-HD as 0.5:3:2.0 and 1.25:3:0.5. It was found that ZnL-MDI-HD at the molar ratio of 0.5:3:2.0 and 1.25:3:0.5 showed the same thermal stability as ZnL-MDI-HD (1.0:3:1.0). The IDT of ZnL-MDI-HD (Figure 4.38-4.39) was found to be in the range 255-260 °C. For comparison, the zinc-containing polyurethane-ureas without HD were synthesized from ZnL and MDI. It was found that the IDT of ZnL-MDI-HD was higher than that of ZnL-MDI. The amounts of HD in ZnL-MDI-HD have small effect on the IDT of the copolymers.

4.3.1.6.8 NiL-MDI-HD copolymers

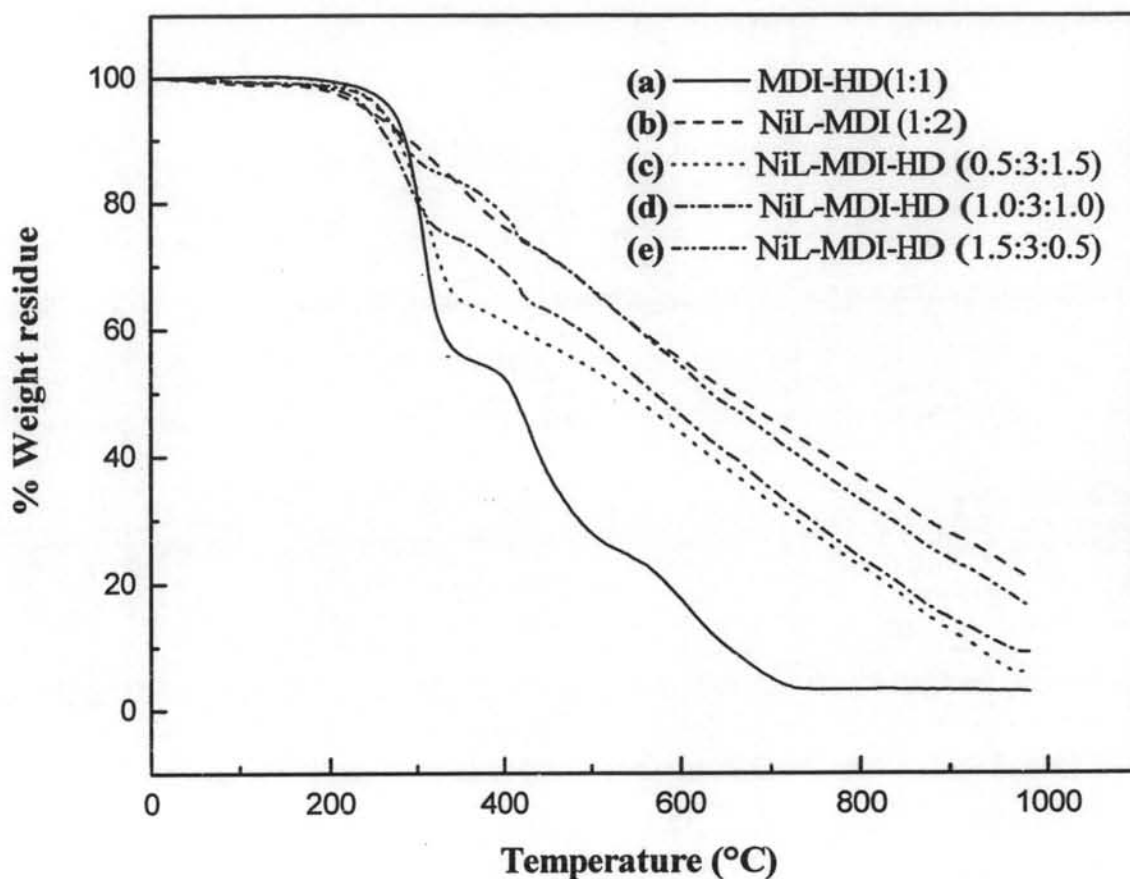


Figure 4.40 TGA thermogram of (a) MDI-HD; (b) NiL-MDI (1:2); (c) NiL-MDI-HD (0.5:3:1.5); (d) NiL-MDI-HD (1.0:3:1.0); (e) NiL-MDI-HD (1.5:3:0.5)

Table 4.18 TGA data of nickel-containing copolyurethane-ureas based on HD

Polymer	IDT (°C)	Weight loss (%) at different temperature (°C)						
		300	400	500	600	700	800	900
MDI-HD (1:1)	279	19	48	72	82	95	97	97
NiL-MDI (1:2)	228	11	24	34	45	54	63	72
NiL-MDI-HD (0.5:3:1.5)	248	18	39	46	56	67	77	88
NiL-MDI-HD (1.0:3:1.0)	232	20	31	41	53	65	76	86
NiL-MDI-HD (1.5:3:0.5)	240	13	22	34	46	57	67	76

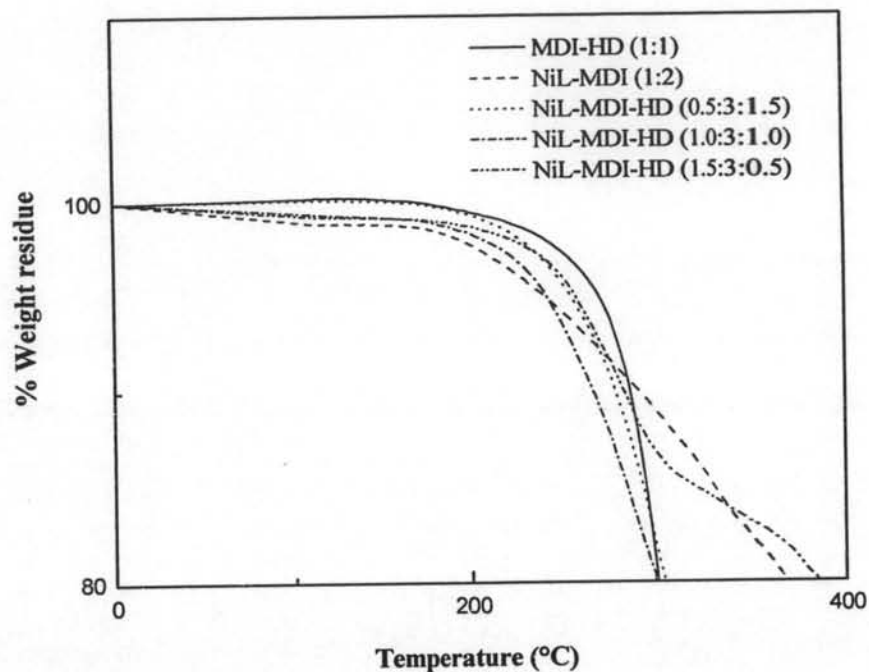


Figure 4.41 The IDT of nickel-containing copolyurethane-ureas based on HD

TGA curves and data of nickel-containing copolyurethane-ureas based on HD are given in Figure 4.40 and Table 4.18, respectively. TGA of nickel-containing copolyurethane-ureas based on HD followed the same trend as described in the case of nickel-containing copolyurethane-ureas based on BA that the percentage of weight loss at 600 °C of NiL-MDI-HD was increased by introducing HD into the polymers. IDT of NiL-MDI-HD (Figure 4.41) was found to be in the range 232-248 °C. For comparison, nickel-containing polyurethane-ureas without HD was synthesized from NiL and MDI. It was found that the IDT increased with increasing amount of HD in the copolymers. The presence of diamines and dialcohols in the nickel-containing copolyurethane-ureas did not help increasing the thermal stability. It was possibly because NiL-MDI already had good thermal stability.

From TGA thermograms, the blank copolyurethane-ureas showed slightly higher IDT than metal-containing copolyurethane-ureas, but their rates of decomposition were higher than that of the metal-containing copolyurethane-ureas. This may be due to the fact that the metal catalyses the first stage decomposition and retards the further stages of decompositions, which is similar to Nanjundan's work [23].

4.3.1.7 Differential scanning calorimetry

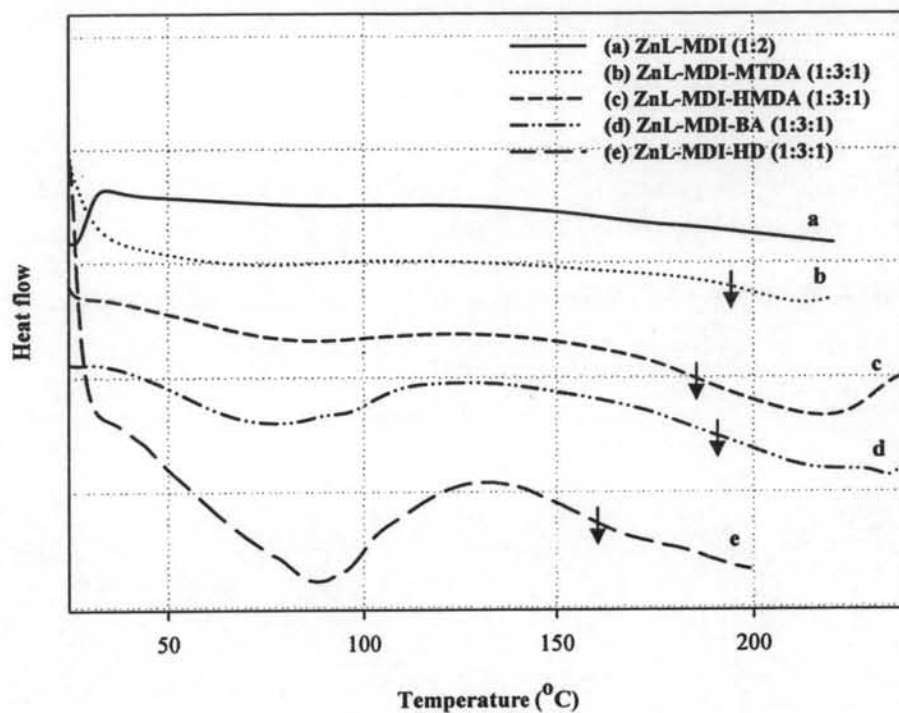


Figure 4.42 DSC curve of zinc-containing copolyurethane-ureas

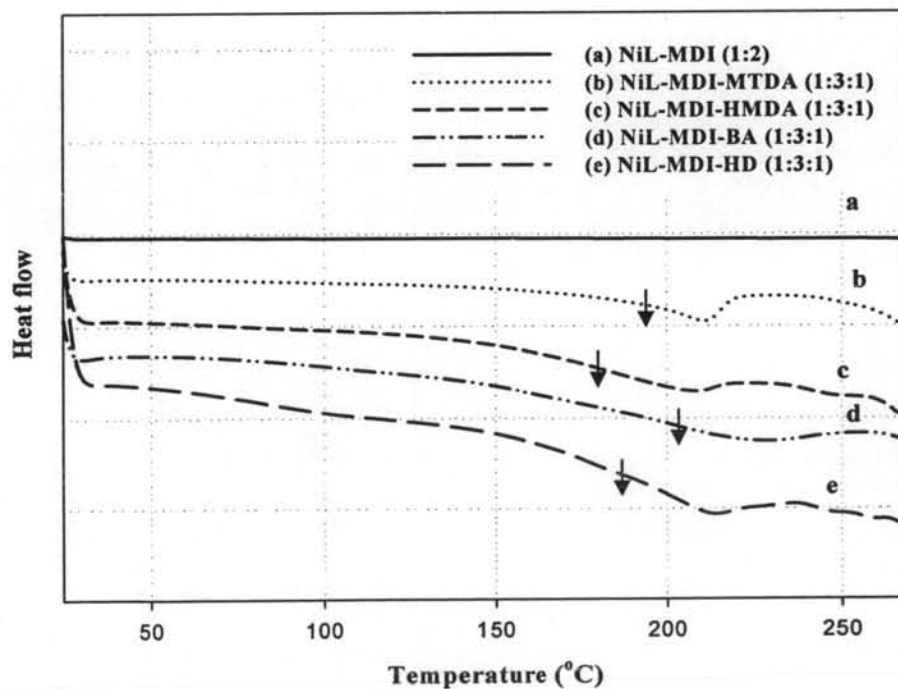


Figure 4.43 DSC curve of nickel-containing copolyurethane-ureas

Table 4.19 T_g of metal-containing copolyurethane-ureas

Polymers	T_g (°C)
ZnL-MDI (1:2)	-
ZnL-MDI-MTDA (1:3:1)	197
ZnL-MDI-HMDA (1:3:1)	187
ZnL-MDI-BA (1:3:1)	192
ZnL-MDI-HD (1:3:1)	161
NiL-MDI (1:2)	-
NiL-MDI-MTDA (1:3:1)	194
NiL-MDI-HMDA (1:3:1)	184
NiL-MDI-BA (1:3:1)	200
NiL-MDI-HD (1:3:1)	188

Glass transition temperature (T_g) were determined at the middle of the transition in the heat capacity taken from the heating DSC traces. All the samples were second scanned from room temperature to 250 °C. The T_g of polymers is indicated by arrows as in Figures 4.42-4.43. Table 4.19 showed the T_g values of polymers. A single glass transition temperature was observed by DSC due to homogeneous phase. The T_g of ZnL-MDI (1:2) and NiL-MDI (1:2) could not be clearly observed.

4.3.1.8 Flame retardancy

Flame retardant properties of copolyurethane-ureas were compared from their limiting oxygen index (LOI) values as shown in Table 4.20.

Table 4.20 LOI data of metal-containing copolyurethane-ureas

Polymers	LOI
NiL-MDI (1:2)	22.3
ZnL-MDI (1:2)	22.6
ZnL-MDI-MTDA (0.5:3:1.5)	23.6
ZnL-MDI-MTDA (1.0:3:1.0)	23.3
ZnL-MDI-MTDA (1.5:3:0.5)	22.8
ZnL-MDI-HMDA (0.5:3:1.5)	23.4
ZnL-MDI-HMDA (1.0:3:1.0)	23.1
ZnL-MDI-HMDA (1.5:3:0.5)	22.8
ZnL-MDI-BA (0.5:3:1.5)	23.1
ZnL-MDI-BA (1.0:3:1.0)	22.2
ZnL-MDI-BA (1.5:3:0.5)	22.8
ZnL-MDI-HD (0.5:3:1.5)	22.7
ZnL-MDI-HD (1.0:3:1.0)	22.5
ZnL-MDI-HD (1.5:3:0.5)	22.4
NiL-MDI-MTDA(0.5:3:1.5)	23.5
NiL-MDI-MTDA (1.0:3:1.0)	23.4
NiL-MDI-MTDA (1.5:3:0.5)	22.2
NiL-MDI-HMDA (0.5:3:1.5)	22.2
NiL-MDI-HMDA (1.0:3:1.0)	22.6
NiL-MDI-HMDA (1.5:3:0.5)	22.1
NiL-MDI-BA (0.5:3:1.5)	22.2
NiL-MDI-BA (1.0:3:1.0)	22.5
NiL-MDI-BA (1.5:3:0.5)	22.1
NiL-MDI-HD (0.5:3:1.5)	21.8
NiL-MDI-HD (1.0:3:1.0)	21.6
NiL-MDI-HD (1.5:3:0.5)	22.2

All metal-containing copolyurethane-ureas showed the same LOI value. The metal-containing copolyurethane-ureas based on MTDA showed slightly higher flame retardancy than those derived from HMDA because of the presence of aromatic rings in the main chain of polymers. The LOI values of copolyurethane-ureas based on dialcohols followed the same trend as described in the case of diamines-base copolyurethane-ureas.