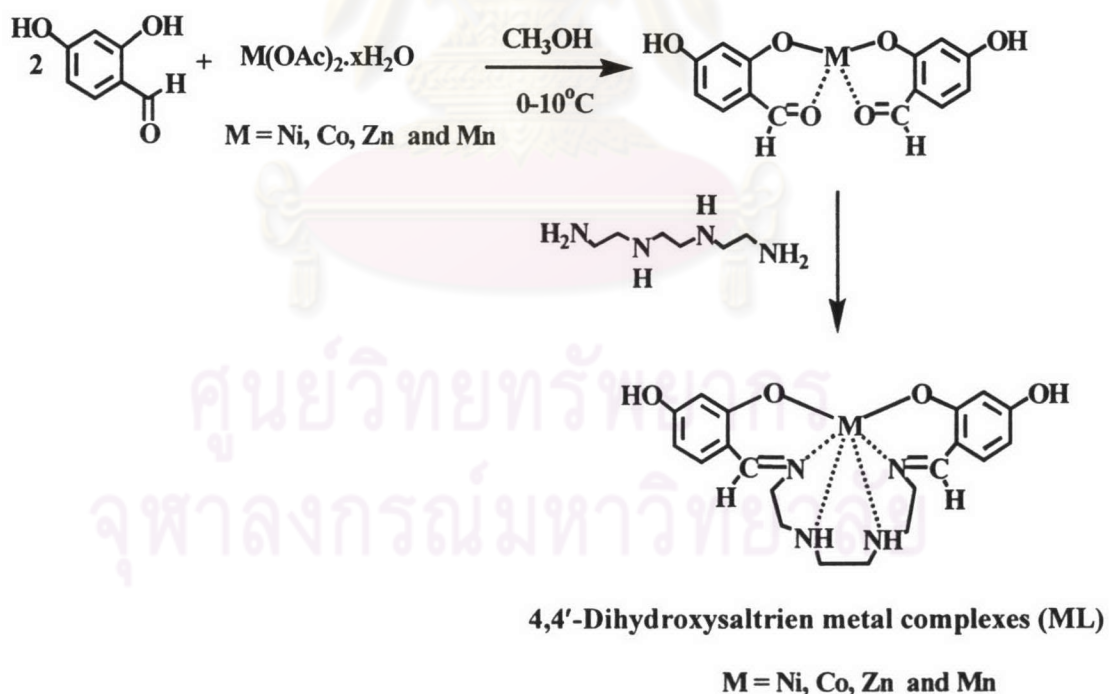


## CHAPTER III

### RESULTS AND DISCUSSIONS

It has been known that Schiff base ligands can be synthesized by condensation reactions of primary amines with carbonyl compounds. In this study, the hexadentate Schiff base ligand was synthesized from the reaction between 2,4-dihydroxybenzaldehyde and triethylenetetramine. The reaction involved an attack of amino group at the carbonyl carbon of aldehyde followed by loss of water to give the tetradentate Schiff base ligand. However, the Schiff base ligand decomposed when isolation from the mixture was attempted. Therefore, 4,4'-dihydroxysaltrien metal complexes were prepared by adding metal acetates to 2,4-dihydroxybenzaldehyde to form a template intermediate. Subsequently, the solution of triethylenetetramine was then added (Scheme 3.1).



**Scheme 3.1** Synthesis of 4,4'-dihydroxysaltrien metal complexes

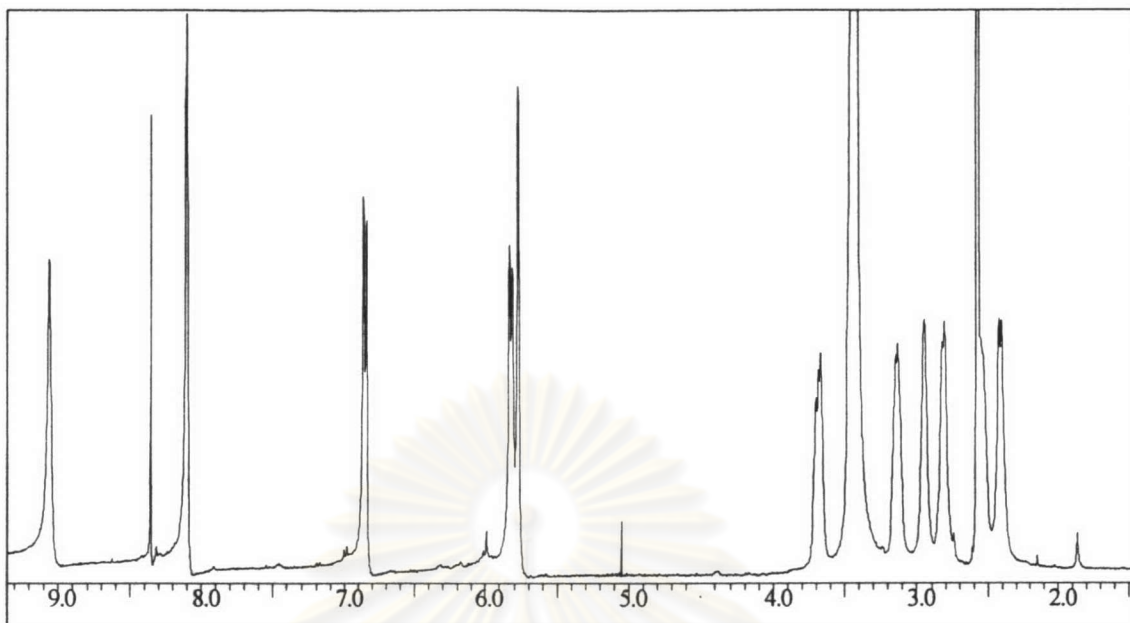
### 3.1 Synthesis of 4,4'-dihydroxysaltrien metal complexes (ML)

#### 3.1.1 4,4'-Dihydroxysaltrien zinc complex (ZnL)

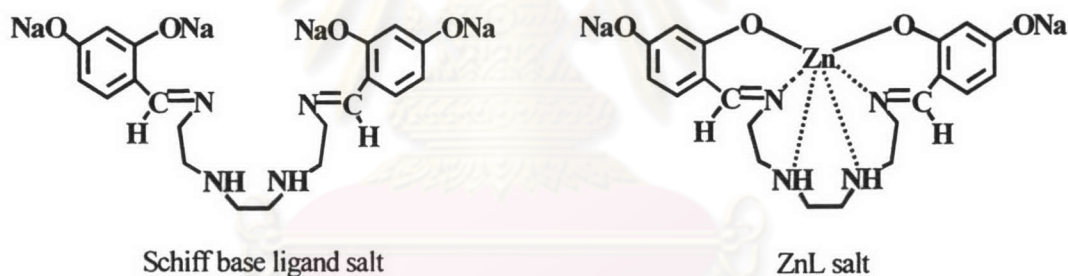
In the synthesis of ZnL, the mole ratio of 2,4-dihydroxybenzaldehyde:zinc acetate:triethylenetetramine was taken as 2:1:1. First, 2,4-dihydroxybenzaldehyde and metal acetate were mixed in methanol. Subsequently, the methanolic solution of triethylenetetramine was added dropwise to the above mixture and the reaction mixture was then neutralized by adding a sodium hydroxide solution. The pink solids were obtained immediately after adding sodium hydroxide. The mixture was filtered to remove the pink precipitate. The filtrate was allowed to stand at room temperature for 6 hours and the yellow crystals were obtained.

The solubility of pink solids and yellow crystals was investigated. At room temperature, the yellow crystals are soluble in dimethyl formamide and dimethyl sulfoxide but insoluble in *n*-hexane, tetrahydrofuran, water, methanol, chloroform, dichloromethane, toluene, acetone and ethyl acetate while the pink solids are insoluble in any solvents.

Figure 3.1 depicts the  $^1\text{H}$  NMR spectrum of yellow crystals.  $^1\text{H}$  NMR spectrum shows hydroxyl -OH protons at 9.06 ppm, imine -CH=N- protons at 8.10 ppm, and aromatic protons at 6.86-6.84 (2H), 5.83-5.81 (2H) and 5.77 (2H) ppm. The  $\text{CH}_2$  signals appear as 6 multiplets at 3.70-3.66 (2H), 3.14-3.13 (2H), 2.94 (2H), 2.81-2.80 (2H), 2.54-2.53 (2H) and 2.41-2.39 (2H). The  $^1\text{H}$  NMR spectrum of the pink solid is similar to that of yellow crystals but the hydroxyl (-OH) protons were absent (Figure A.1).  $^1\text{H}$  NMR data indicate that the yellow crystals are 4,4'-dihydroxysaltrien zinc complex (ZnL) and the pink solids are the mixture of hexadentate Schiff base ligand salt and salt of 4,4'-dihydroxysaltrien zinc complex (ZnL salt) as shown in Figure 3.2.

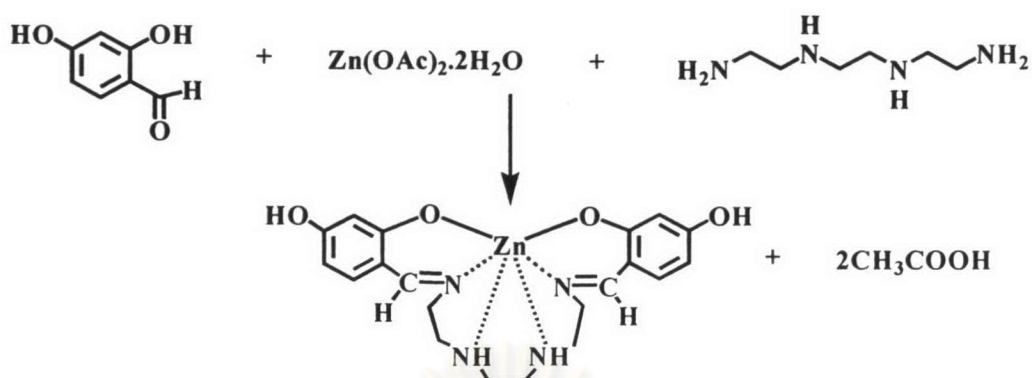


**Figure 3.1**  $^1\text{H}$  NMR spectrum of the yellow crystals

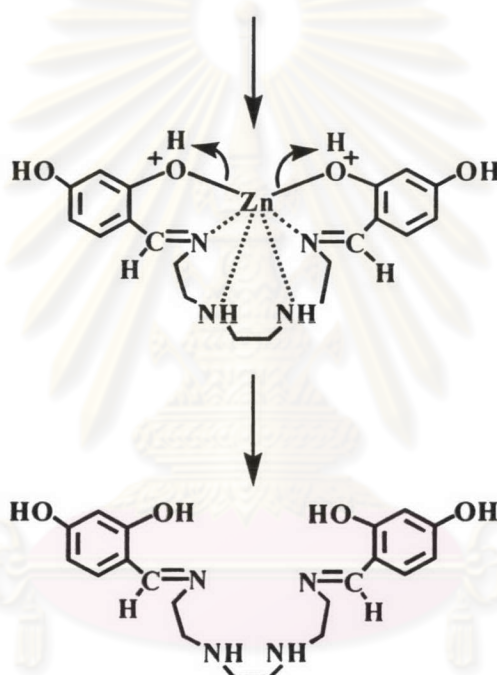


**Figure 3.2** Structure of ligand salt and ZnL salt

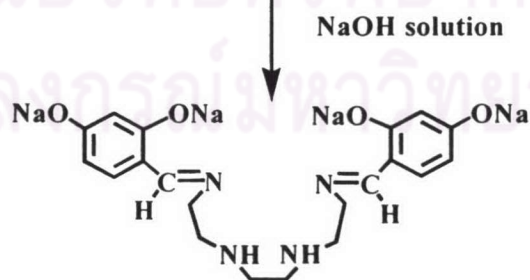
A possible route to the formation of Schiff base ligand salt is shown in Scheme 3.2. The formation of acetic acid as by-product caused protonation of phenolic oxygen of the complex to give Schiff base ligand. When sodium hydroxide solution was added to neutralize the reaction mixture, salt of Schiff base ligand was obtained and it could precipitate together with ZnL salt as pink solids.



4,4'-Dihydroxysaltrien metal complexes (ML)



Schiff base ligand



Schiff base ligand salt

**Scheme 3.2** Formation of Schiff base ligand salt



To increase the yield of ZnL, different bases were employed instead of sodium hydroxide. The composition of starting materials was also varied as shown in Table 3.1.

**Table 3.1** Composition of starting materials in the synthesis of ZnL

Mole ratio of 2,4-dihydroxybenzaldehyde: zinc acetate:triethylenetetramine	Base	Yield of ligand salt and ZnL salt (wt%) <sup>a</sup>	Yield of ZnL (%)
2:1:1	NaOH	16	13
2:1:1	NaHCO <sub>3</sub>	11	9
2:1:1	Na <sub>2</sub> CO <sub>3</sub>	14	- <sup>b</sup>
2:1:1	KOH	13	27
2:1:1	K <sub>2</sub> CO <sub>3</sub>	10	51
2:1:2	K <sub>2</sub> CO <sub>3</sub>	-	11

<sup>a</sup>yields based on the weight of starting materials

<sup>b</sup>the filtrate decomposed after it was allowed to stand at room temperature for 6 h.

The best yield of ZnL (51%) was obtained when using potassium carbonate as a base. The mole ratio of 2,4-dihydroxybenzaldehyde:zinc acetate:triethylenetetramine was changed to 2:1:2 since excess triethylenetetramine can neutralize acetic acid from the reaction (Scheme 3.1) and therefore prevent the formation of by products. It was found that using excess triethylenetetramine could avoid the formation of ligand salt and ZnL salt. However, ZnL was obtained in low yield (11%). Therefore, the suitable method for the synthesis of ZnL was done using 2,4-dihydroxybenzaldehyde:zinc acetate: triethylenetetramine at the mole ratio of 2:1:1 and employing potassium carbonate as a base.

ZnL was characterized by IR, <sup>1</sup>H NMR, elemental analysis and MALDI-TOF MS. <sup>1</sup>H NMR spectrum (Figure 3.1) supports that structure since it shows the imine (-CH=N-) protons at  $\delta$  8.10 ppm. IR spectrum (Figure A.2) shows -NH stretching at 3315 cm<sup>-1</sup>. The imine stretching is observed at 1629 cm<sup>-1</sup> and the bands at 990 and 841 cm<sup>-1</sup> correspond to absorption peak of 1,2,4-trisubstituted benzene bending. Elemental analysis data shows that the experimentally determined percentage values of carbon, hydrogen and nitrogen agreed with the formula C<sub>20</sub>H<sub>24</sub>N<sub>4</sub>O<sub>4</sub>Zn.3H<sub>2</sub>O of ZnL.

MALDI-TOF MS of ZnL (Figure A.3) was found as 450.1 which is the molecular ion of  $C_{20}H_{24}N_4O_4Zn$ .

### 3.1.2 4,4'-Dihydroxysaltrien nickel complex (NiL)

The mole ratio of starting materials in the synthesis of NiL is shown in Table 3.2. When the mole ratio of 2,4-dihydroxybenzaldehyde:nickel acetate:triethylenetetramine was 2:1:1 and sodium hydroxide was employed as a base, the mixture of ligand salt and NiL salt was obtained as pink solids in 14 % yield and NiL was not obtained. NiL was obtained as green crystals in low yield (24%), when potassium carbonate was used.

The mole ratio of 2,4-dihydroxybenzaldehyde:nickel acetate:triethylenetetramine was then taken as 2:1:2 to avoid the formation of ligand salt and NiL salt. The results show that the mixture of salts could be avoided in all bases. The highest yield of NiL was obtained when employing potassium carbonate as a base and the mole ratio of 2,4-dihydroxybenzaldehyde:nickel acetate:triethylenetetramine was 2:1:2.

**Table 3.2** Composition of starting materials in the synthesis of NiL

Mole ratio of 2,4-dihydroxybenzaldehyde: nickel acetate:triethylenetetramine	Base	Yield of ligand salt and NiL salt (wt%) <sup>a</sup>	Yield of NiL (%)
2:1:1	NaOH	14	- <sup>b</sup>
2:1:1	K <sub>2</sub> CO <sub>3</sub>	12	24
2:1:2	NaOH	-	57
2:1:2	NaHCO <sub>3</sub>	-	78
2:1:2	KOH	-	80
2:1:2	K <sub>2</sub> CO <sub>3</sub>	-	89

<sup>a</sup> yields based on the weight of starting materials.

<sup>b</sup> the filtrate decomposed after it was allowed to stand at room temperature for 6 h.

At room temperature, the ligand salt and NiL salt are insoluble in organic solvents. NiL is soluble in dimethyl formamide and dimethyl sulfoxide but insoluble in *n*-hexane, tetrahydrofuran, water, methanol, chloroform, dichloromethane, toluene, acetone and ethyl acetate.

NiL structure was confirmed using IR spectroscopy, elemental analysis and MALDI-TOF MS. The IR spectrum (Figure A.4) shows the important characteristic absorption bands as follows:  $3312\text{ cm}^{-1}$  (N-H stretching),  $1634\text{ cm}^{-1}$  (C=N stretching),  $1598\text{ cm}^{-1}$  (aromatic C=C stretching),  $1214\text{ cm}^{-1}$  (aromatic C-O stretching) and  $989$  and  $841\text{ cm}^{-1}$  (C-H bending of 1,2,4-trisubstituted benzene). Elemental analysis data agree with the formula  $\text{C}_{20}\text{H}_{24}\text{N}_4\text{O}_4\text{Ni}\cdot 3\text{H}_2\text{O}$ . MALDI-TOF MS of NiL (Figure A.5) was found as 443.5, which is the molecular ion of  $\text{C}_{20}\text{H}_{24}\text{N}_4\text{O}_4\text{Ni}$ .

### 3.1.3 4,4'-Dihydroxysaltrien cobalt complex (CoL)

CoL was synthesized using the same procedure as ZnL. Table 3.3 shows the composition of starting materials and bases employed in the synthesis. At the mole ratio of 2,4-dihydroxybenzaldehyde:cobalt acetate:triethylenetetramine of 2:1:1 with sodium hydroxide as a base, the mixture of ligand salt and CoL salt was obtained in high yield (28%) while CoL was obtained as dark brown solid in low yield (26%). When sodium hydrogen carbonate and potassium carbonate was employed, yield of CoL was comparable to that of the reaction employing sodium hydroxide. CoL was not obtained with sodium carbonate and potassium hydroxide.

To avoid the formation of salts, the mole ratio of 2,4-dihydroxybenzaldehyde:cobalt acetate:triethylenetetramine was changed to 2:1:2, it was found that both salts and CoL were not obtained.

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**Table 3.3** Composition of starting materials in the synthesis of CoL

Mole ratio of 2,4-dihydroxybenzaldehyde: cobalt acetate:triethylenetetramine	Base	Yield of ligand salt and CoL salt (wt%) <sup>a</sup>	Yield of the dark brown solid (CoL)
2:1:1	NaOH	28	26
2:1:1	NaHCO <sub>3</sub>	31	28
2:1:1	Na <sub>2</sub> CO <sub>3</sub>	28	- <sup>a</sup>
2:1:1	KOH	-	- <sup>b</sup>
2:1:1	K <sub>2</sub> CO <sub>3</sub>	32	31
2:1:2	K <sub>2</sub> CO <sub>3</sub>	-	- <sup>b</sup>

<sup>a</sup>yields based on the weight of starting materials.

<sup>b</sup>the filtrate decomposed after it was allowed to stand at room temperature for 6 h.

At room temperature, the ligand salt and CoL salt are insoluble in organic solvents. CoL is soluble in dimethyl formamide and dimethyl sulfoxide but insoluble in *n*-hexane, tetrahydrofuran, water, methanol, chloroform, dichloromethane, toluene, acetone and ethyl acetate.

CoL structure was confirmed by IR spectroscopy. The IR spectrum (Figure A.6) shows the important characteristic absorption bands as follows: 3374 cm<sup>-1</sup> (N-H stretching), 1611 cm<sup>-1</sup> (C=N stretching), 1577 cm<sup>-1</sup> (aromatic C=C stretching), 1226 cm<sup>-1</sup> (aromatic C-O stretching) and 983 and 847 cm<sup>-1</sup> (C-H bending of 1,2,4-trisubstituted benzene).

However, CoL decomposed when it was dried under reduced pressure. The color of CoL changed from dark brown to black. Therefore, CoL is unstable and it could not be used in the synthesis of metal-containing polymers.

#### 3.1.4 4,4'-Dihydroxysaltrien manganese complex (MnL)

Employing the previous synthesis method, the mole ratio of starting materials in the synthesis of MnL were varied as shown in Table 3.4. Similar results have also been obtained for the mole ratio of 2,4-dihydroxybenzaldehyde:manganese acetate:triethylenetetramine = 2:1:1. When sodium hydroxide was employed as a base, the mixture of ligand and MnL salts was obtained as brown solid in 25% yield and MnL precipitated as dark brown solid in low yield (27%).



When the base was changed to potassium carbonate, yield of MnL was 22% but MnL was not obtained with sodium hydrogen carbonate, sodium carbonate and potassium hydroxide.

In case of the mole ratio of 2,4-dihydroxybenzaldehyde:manganese acetate:triethylenetetramine = 2:1:2, MnL was obtained when the reaction mixture was not neutralized with base, MnL crystallized as brown crystals in high yield (81%) and this procedure was the most suitable synthesis procedure for MnL.

At room temperature, the ligand salt and MnL salt are insoluble in organic solvents while the MnL is soluble in dimethyl formamide and dimethyl sulfoxide but insoluble in *n*-hexane, tetrahydrofuran, water, methanol, chloroform, dichloromethane, toluene, acetone and ethyl acetate. However, MnL decomposed when it was dissolved in solvents. The color of MnL solution changed from dark brown to black and therefore MnL could not be used in the synthesis of metal-containing polymers.

**Table 3.4** Composition of starting materials in the synthesis of MnL

Mole ratio of 2,4-dihydroxybenzaldehyde: manganese acetate:triethylenetetramine	Base	Yield of ligand salt and MnL salt (wt%)	Yield of MnL (%)
2:1:1	NaOH	25	27
2:1:1	NaHCO <sub>3</sub>	17	- <sup>b</sup>
2:1:1	Na <sub>2</sub> CO <sub>3</sub>	8	- <sup>b</sup>
2:1:1	KOH	-	- <sup>b</sup>
2:1:1	K <sub>2</sub> CO <sub>3</sub>	23	22
2:1:2	K <sub>2</sub> CO <sub>3</sub>	-	- <sup>b</sup>
2:1:2	-	-	81

<sup>a</sup> yields based on the weight of starting materials.

<sup>b</sup> the filtrate decomposed after was allowed to stand at room temperature for 6 h.

The structure of MnL was confirmed by IR spectroscopy and elemental analysis. IR spectrum (Figure A.7) shows the important characteristic absorption bands as follows: 3374 cm<sup>-1</sup> (N-H stretching), 1611 cm<sup>-1</sup> (C=N stretching), 1577 cm<sup>-1</sup> (aromatic C=C stretching), 1226 cm<sup>-1</sup> (aromatic C-O stretching) and 990 and 847 cm<sup>-1</sup> (aromatic C-H bending). Elemental analysis data shows percentage values of C, H and N that agree with the formula C<sub>20</sub>H<sub>24</sub>N<sub>4</sub>O<sub>4</sub>Mn.H<sub>2</sub>O.

### 3.2 Synthesis of metal-containing polyurethane-ureas

#### 3.2.1 Investigation of the reaction between ZnL and prepolymer

DSC technique was employed in order to investigate the reactivity of ZnL complex with prepolymer. PB900 was chosen as the prepolymer. The suitable temperature of the polymerization reaction could be determined using DSC technique. DSC experiment was performed by heating a mixture of ZnL:PB900 at the mole ratio of 1:1 in a DSC cell using closed aluminum pan in air. The temperature range was 25-300 °C at a heating rate of 20 °C /min. DSC thermogram (Figure 3.3) shows both exothermic peak and endothermic peaks. The exothermic peak at 121 °C indicates that the polymerization reaction occurs. Therefore, the chosen reaction temperature for the synthesis of metal-containing polyurethane-ureas from the reaction between ZnL and prepolymer was 120 °C. The endothermic peaks were observed around 152 and 202 °C, followed by decomposition of the material.

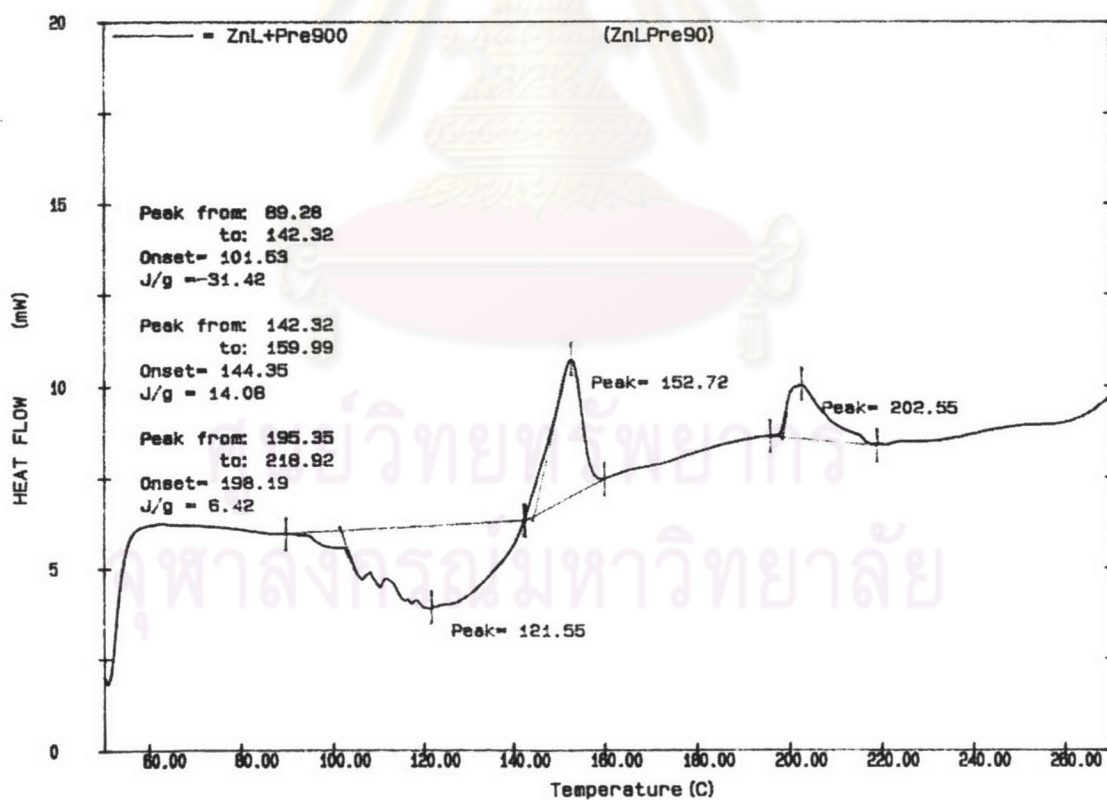


Figure 3.3 DSC thermogram of ZnL:PB900 mixture at the mole ratio of 1: 1

### 3.2.2 Synthesis of zinc-containing polyurethane-ureas from the reaction between ZnL and PB900

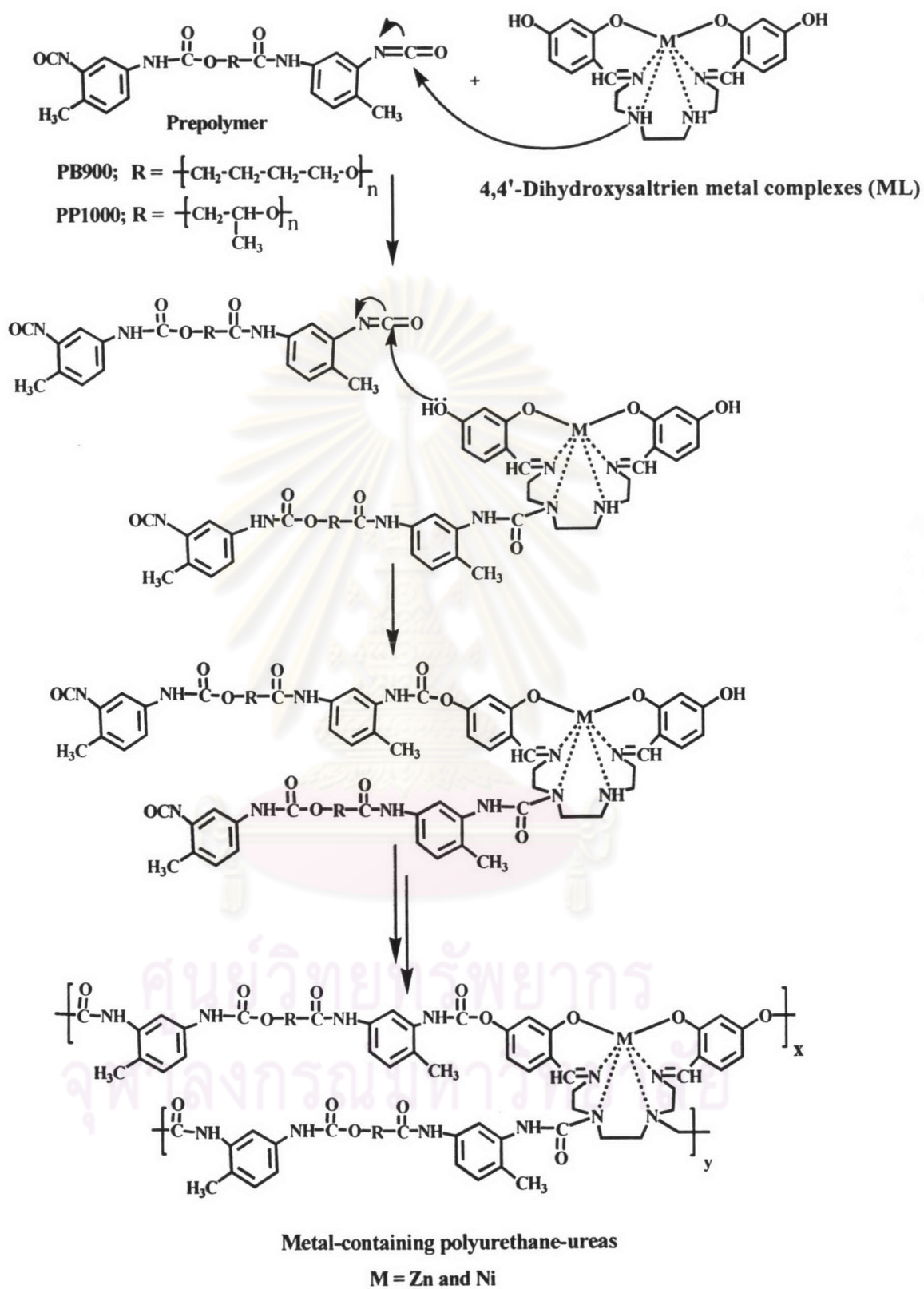
Having obtained the polymerization temperature from DSC experiment, isothermal polymerization reaction between ZnL and PB900 at different mole ratios was investigated using IR spectroscopy. Isothermal experiment was done by heating a mixture of ZnL:PB900 in different mole ratios at 120 °C in a hot air oven. The completeness of polymerization reaction was observed by the disappearance of isocyanate ( $-NCO$ ) peak of PB900 at  $2275\text{ cm}^{-1}$  in IR spectrum.

The possible polymerization mechanism is that the  $-NH-$  and  $-OH$  groups of ZnL undergo a reaction with isocyanate groups of PB900 to give metal-containing polyurethane-urea. When NiL and PP1000 were employed, the polymerization is proposed to be the same as in the case of ZnL and PB900. The general polymerization mechanism of ML with prepolymer is shown in Scheme 3.3.



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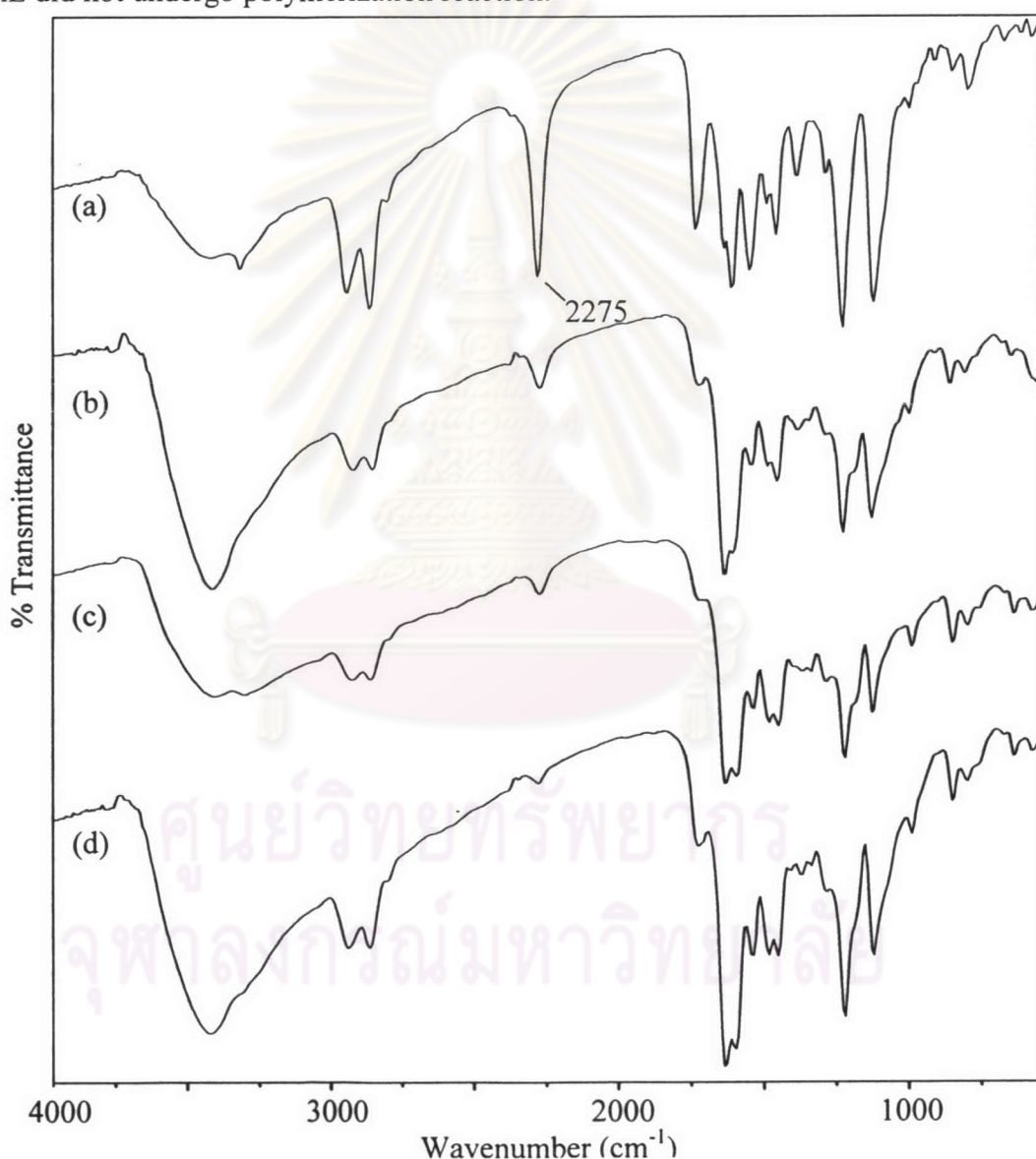




**Scheme 3.3** Possible mechanism of the reaction between metal complex and prepolymers

At the mole ratio of ZnL:PB900 = 1:1 (Figure 3.4), the  $\text{-NCO}$  peak ( $2275\text{ cm}^{-1}$ ) disappeared after the polymerization was done for 4 hours. However, the new peaks of  $\text{-C=O}$  stretching of urea  $\text{-NCON-}$  and urethane  $\text{-OCON-}$  groups in the polymer could not be identified since these peaks overlap with the  $\text{-C=O}$  peak of urethane linkage in PB900, which appears around  $1720\text{ cm}^{-1}$ .

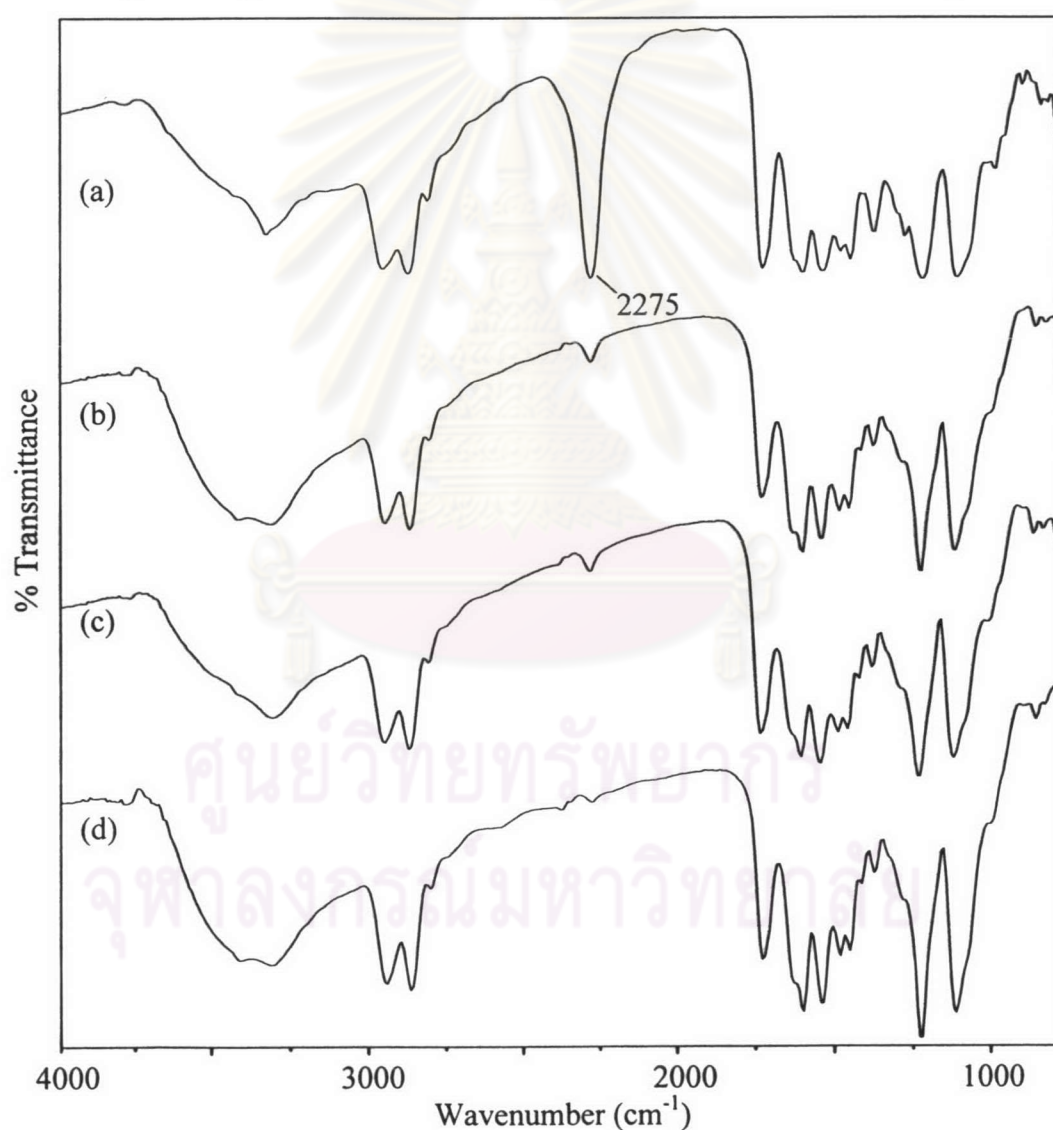
Although the polymerization was completed, the peak at  $1634\text{ cm}^{-1}$  was still observed. This peak is due to the  $\text{-C=N-}$  absorption in ZnL. This indicates that part of ZnL did not undergo polymerization reaction.



**Figure 3.4** IR spectra of a reaction mixture of ZnL:PB900 at the mole ratio of 1:1 when the reaction was done at  $120\text{ }^{\circ}\text{C}$ : (a) before heating; (b) after 1 h; (c) after 2 h; and (d) after 4 h

The isolation of metal-containing polyurethane-ureas was done by dissolving the product mixture in dimethyl sulfoxide and the resulting solution was then added to water to precipitate the polymer. By employing the mole ratio of ZnL:PB900 = 1:1, the polymer was obtained in 40 % yield.

The mole ratio of ZnL:PB900 was then changed to 1:2. The polymerization was carried out using the same method as described in the case of ZnL:PB900 at the mole ratio of 1:1. The IR spectra in Figure 3.5 shows that the polymerization was completed after 4 hours. The polymer was isolated using the same method as described previously. It was found that the polymer was obtained in 79 % yield.



**Figure 3.5** IR spectra of a reaction mixture of ZnL: PB900 at the mole ratio of 1: 2 when the reaction was done at 120 °C: (a) before heating; (b) after 1 h; (c) after 2 h and (d) after 4 h

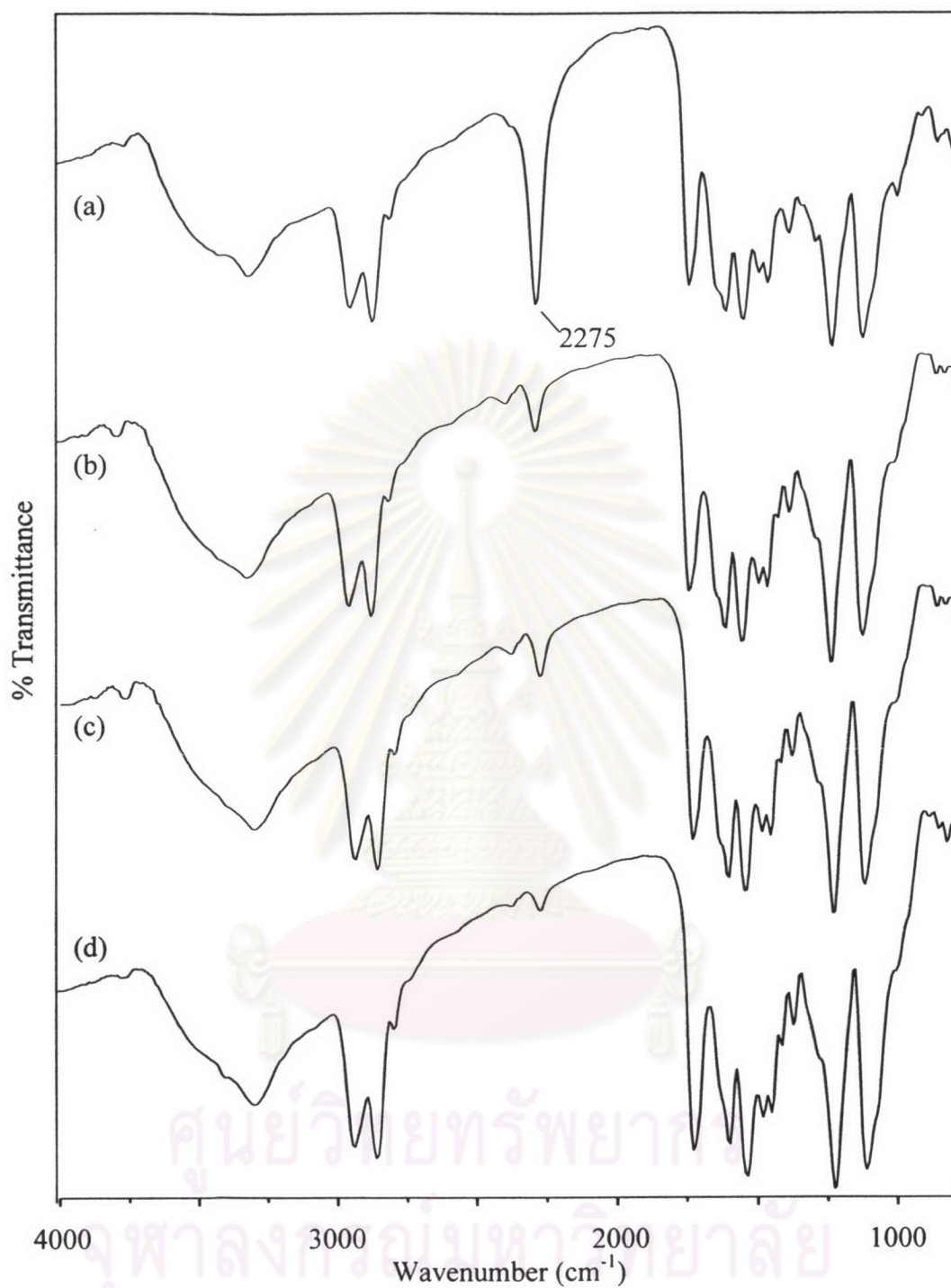


Employing the same method, the polymerization reaction of ZnL:PB900 was carried out at the mole ratio of 1:3 to investigate the possibility of the formation of crosslinked polymers.

Although polymerization was done for 8 hours, the –NCO peak of PB900 was still observed as shown in Figure 3.6. This indicates that part of PB900 did not undergo polymerization reaction. It has been known that a crosslinked polymer is not soluble in organic solvents such as dimethyl formamide and dimethyl sulfoxide. During the step of polymer isolation, it was found that the reaction mixture was soluble in dimethyl sulfoxide and polymer was then precipitated by the addition of water. This indicates that the reaction did not give crosslinked polymer. The control experiment showed that addition of water to a PB900 solution in dimethyl sulfoxide did not give precipitate. The polymer was obtained in 80 %yield.

The above data indicate that polymerization mechanism occurs as proposed in Scheme 3.3. –NH– and –OH groups of metal complex undergo a reaction with isocyanate group of prepolymer to give metal-containing polyurethane-ureas and crosslinking reaction does not occur.

All polyurethane-ureas obtained from the different mole ratio of ZnL:PB900 have the similar IR spectra. Therefore, the suitable mole ratio of ML:prepolymer for synthesis of metal-containing polyurethane-ureas is 1:2.

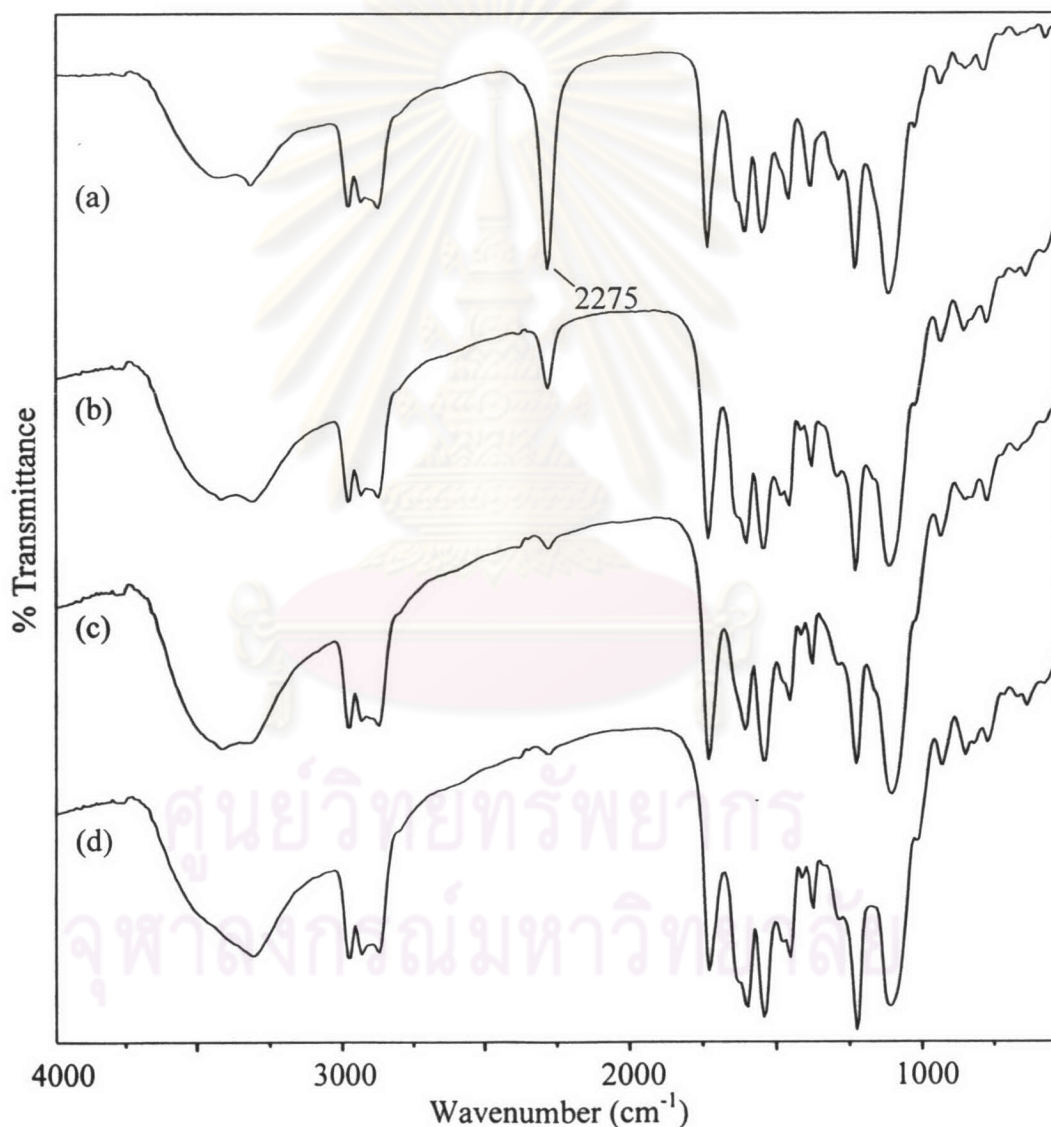


**Figure 3.6** IR spectra of a reaction mixture of ZnL:PB900 at the mole ratio of 1:3 when the reaction was done at 120 °C: (a) before heating; (b) after 3 h; (c) after 5 h and (d) after 8 h

### 3.2.3 Synthesis of zinc-containing polyurethane-ureas from the reaction between ZnL and PP1000

Zinc-containing polyurethane-ureas based on PP1000 was synthesized using the same method as described in the case of ZnL:PB900 at the mole ratio of 1:2

IR spectra (Figure 3.7) show that the polymerization was completed after 5 hours. The reaction mixture was soluble in dimethyl sulfoxide and the polymer was precipitated in water. The polymer was obtained in 82 % yield.



**Figure 3.7** IR spectra of a reaction mixture of ZnL:PP1000 at the mole ratio of 1:2 when the reaction was done at 120 °C: (a) before heating; (b) after 1 h; (c) after 3 and (d) after 5 h



### 3.2.4 Synthesis of nickel-containing polyurethane-ureas from the reaction between NiL and PB900

Nickel-containing polyurethane-ureas were carried out at the same method as described in the synthesis of polymer from ZnL and PB900. The polymers were prepared by varying the mole ratio of NiL:PB900 as 1:1, 1:2 and 1:3. The polymerization was done in a hot air oven at 120 °C.

At the mole ratio of NiL:PB900 = 1:1, the polymerization was completed after 3 hours. IR spectra (Figure A.8) show the imine peak at  $1634\text{ cm}^{-1}$ , which was similar to in case of ZnL. This indicates that the imine part of NiL did not undergo a reaction. The polymer was obtained in moderate yield (41%).

When the mole ratio of NiL:PB900 was changed to 1:2, the polymerization was completed after 2 hours (Figure A.9). The polymer was obtained in 76 % yield.

By the same method, the polymer was synthesized at the mole ratio of NiL:PB900 = 1:3 to investigate possibility of crosslinking reaction. When the reaction mixture was done after 8 hours, the isocyanate peak at  $2275\text{ cm}^{-1}$  was still observed (Figure A.10). This is a similar result to the case of ZnL:PB900 that part of PB900 did not undergo a reaction. The reaction mixture was soluble in dimethyl sulfoxide and was then precipitated by addition of water. This confirms that the crosslinking reaction does not occur. The polymer was obtained in 80 % yield.

From the obtained data indicates that the polymerization mechanism of NiL with prepolymer is  $\text{-NH-}$  and  $\text{-OH}$  groups of NiL undergo a reaction with isocyanate group in prepolymer as described in the case of zinc-containing polyurethane-ureas. The most suitable mole ratio of NiL:prepolymer in the synthesis of nickel-containing polyurethane-ureas is 1:2.

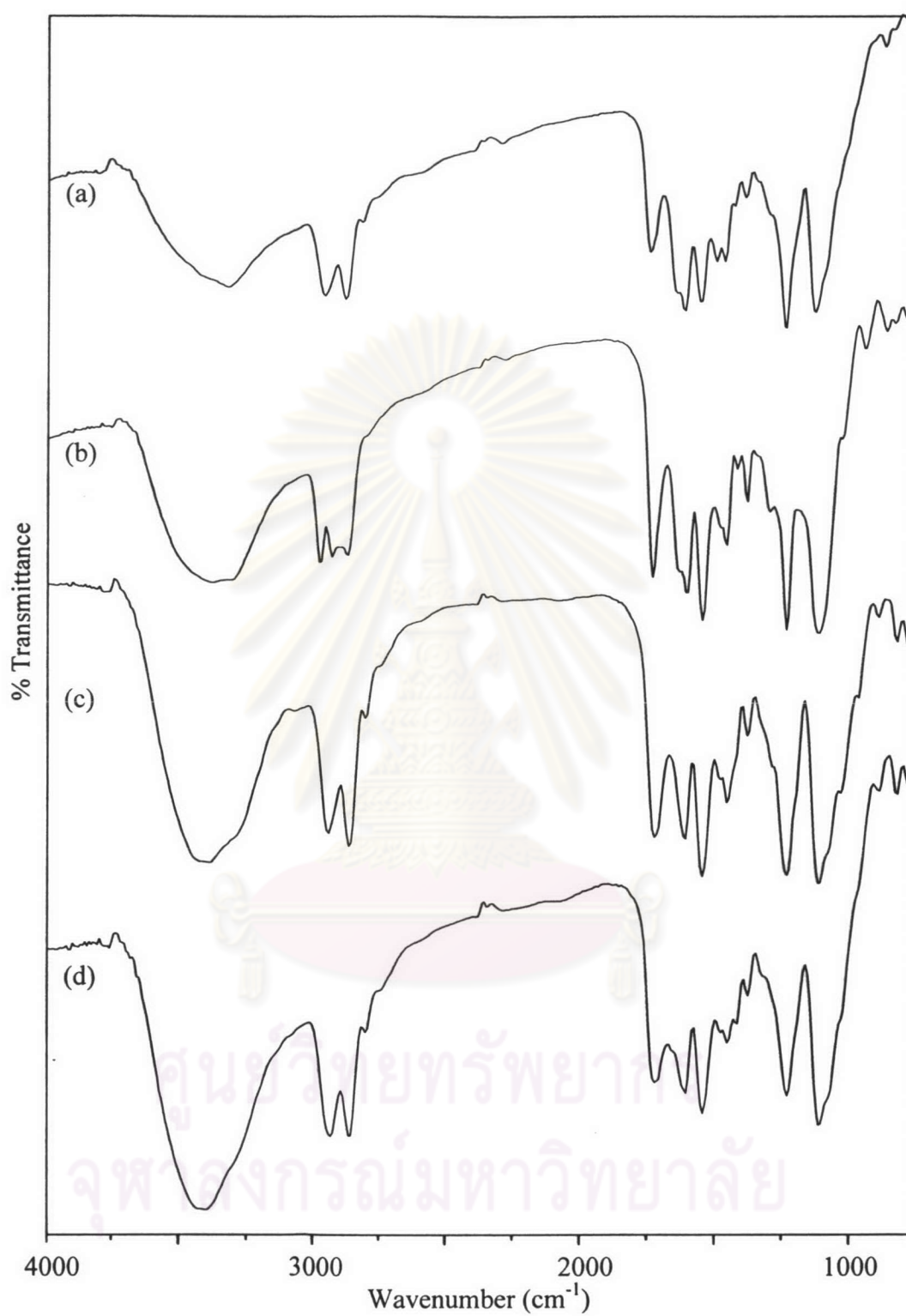
### 3.2.5 Synthesis of nickel-containing polyurethane-ureas from the reaction between NiL and PP1000

Employing the same method, nickel-containing polyurethane-ureas based on PP1000 was synthesized by the polymerization reaction between NiL:PP1000 at the mole ratio of 1:2. IR spectra (Figure A.11) show that the polymerization was completed after heating the reaction mixture for 4 hours. The polymer was obtained in 83 % yield.

### 3.2.6 Characterization of metal-containing polyurethane-ureas using Infrared spectroscopy

All obtained metal-containing polyurethane-ureas have similar IR spectra as shown in Figure 3.8. The N-H stretching shows a peak between  $3447\text{-}3304\text{ cm}^{-1}$ . The C-H stretching due to the methylene groups are observed between  $2974\text{-}2791\text{ cm}^{-1}$ . The carbonyl stretching of the urethane ( $-\text{OCON}-$ ) and urea ( $-\text{NCON}-$ ) groups show a peak at  $1726\text{-}1713\text{ cm}^{-1}$  and the peak at  $1634\text{-}1606\text{ cm}^{-1}$  is attributed to the C=N stretching. This confirms the presence of metal complex in the obtained polymer. The new carbonyl band of urea ( $-\text{NCON}-$ ) group overlaps with urethane carbonyl band of prepolymer.

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**Figure 3.8** IR spectra of metal-containing polyurethane-ureas: (a) Zn-PB; (b) Ni-PB; (c) Zn-PP and (d) Ni-PP



### 3.3 Synthesis of metal-containing copolyurethane-ureas

Polyurethane-ureas are a class of very important copolymer and are of commercial interest in many application. Nanjundan and coworkers[10-14] have studied the metal-containing polyurethane-ureas and they found that these polymers have good thermal stability. Therefore, the metal-containing copolyurethane-ureas are of our interest since the obtained polymers are expected to show good thermal stability.

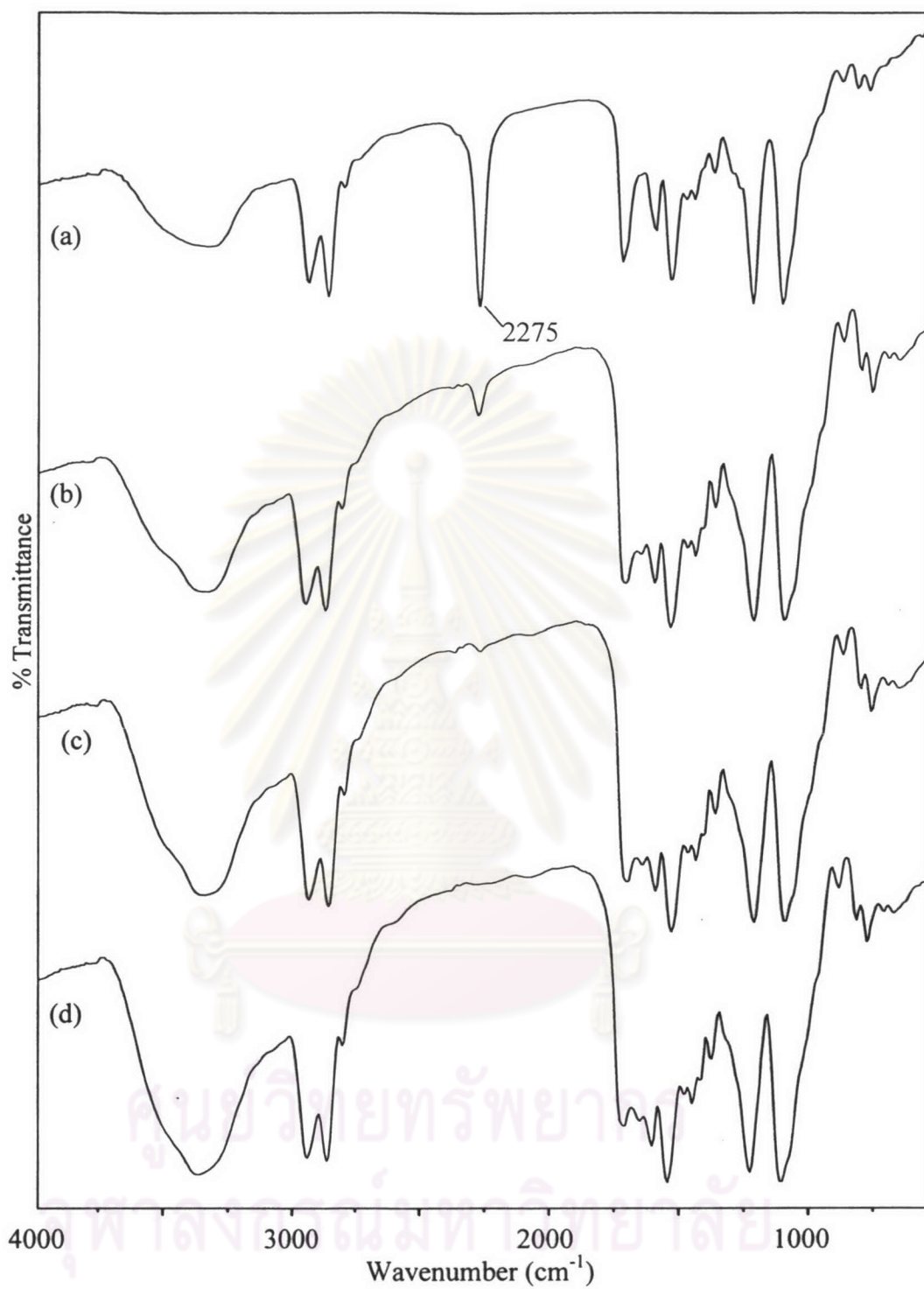
#### 3.3.1 Synthesis of metal-containing copolyurethane-ureas from ML, prepolymer and xylylenediamine

Copolyurethane-ureas were synthesized from the reaction between ML, prepolymer and xylylenediamine in the presence of xylylenediamine (Scheme 3.4). The  $-NH_2$  groups in xylylenediamine can undergo a reaction with  $-NCO$  groups in prepolymer to form urea linkages. Xylylenediamine was used as a chain-extender to yield copolymer with different wt% of metal complex in the polymer chain.

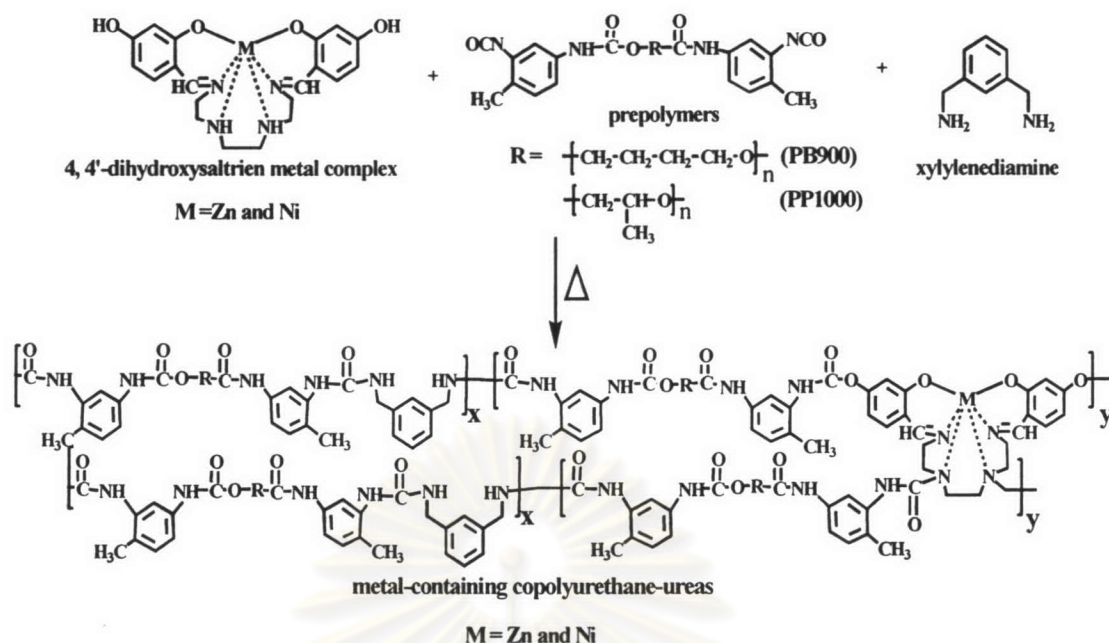
Polymerization reaction of prepolymer, ML and xylylenediamine in different mole ratios was investigated. The experiments were done at a constant temperature of 120 °C in a hot air oven. The completeness of reaction was confirmed by the disappearance of isocyanate ( $-NCO$ ) peak of prepolymer at  $2275\text{ cm}^{-1}$  in IR spectrum:

As an example, Figure 3.9 shows the IR spectrum of polymerization reaction between ZnL, PB900 and xylylenediamine at the mole ratio of 1:3:1 at different times. When the reaction mixture was heated for 1 hour, there was a presence of a new C=O stretching vibration of  $-NCON-$  group at  $1650\text{ cm}^{-1}$ . The completeness of the polymerization was supported by the absence of  $-NCO$  peak at  $2275\text{ cm}^{-1}$  after heating for 3 hours.

The polymerization mechanism is proposed that the  $-NH-$  and  $-OH$  group of metal complex and the  $-NH_2$  of xylylenediamine undergo a reaction with  $-NCO$  group of prepolymer. The repeating unit in copolyurethane-ureas is random.



**Figure 3.9** IR spectra of a reaction mixture of ZnL:PB900:xylylenediamine at a mole ratio of 1:3:1 when the reaction was done at 120 °C: (a) before heating; (b) after 1 h; (c) after 2 h and (d) after 3 h



**Scheme 3.4** Synthesis of metal-containing copolyurethane-ureas

Metal-containing copolyurethane-ureas were synthesized with different wt% of metal complex as shown in Table 3.5. The polymers without metal complex (PB-D-11 and PP-D-11) were synthesized from the reaction between xylylenediamine and prepolymer to study the effect of metal complex in the polymer chain. Yields of the obtained polymer were 56-85 %.

**Table 3.5** Wt% of metal complex and yield of the obtained polymer

Polymer code	Wt% of metal complex	Yield (%)
Zn-PB-D-153	9.2	65
Zn-PB-D-131	15.0	70
Zn-PB-D-371	18.9	73
Ni-PB-D-153	9.1	64
Ni-PB-D-131	14.9	65
Ni-PB-D-371	18.8	68
Zn-PP-D-131	13.8	85
Ni-PP-D-131	13.7	83
PB-D-11	0	56
PP-D-11	0	60

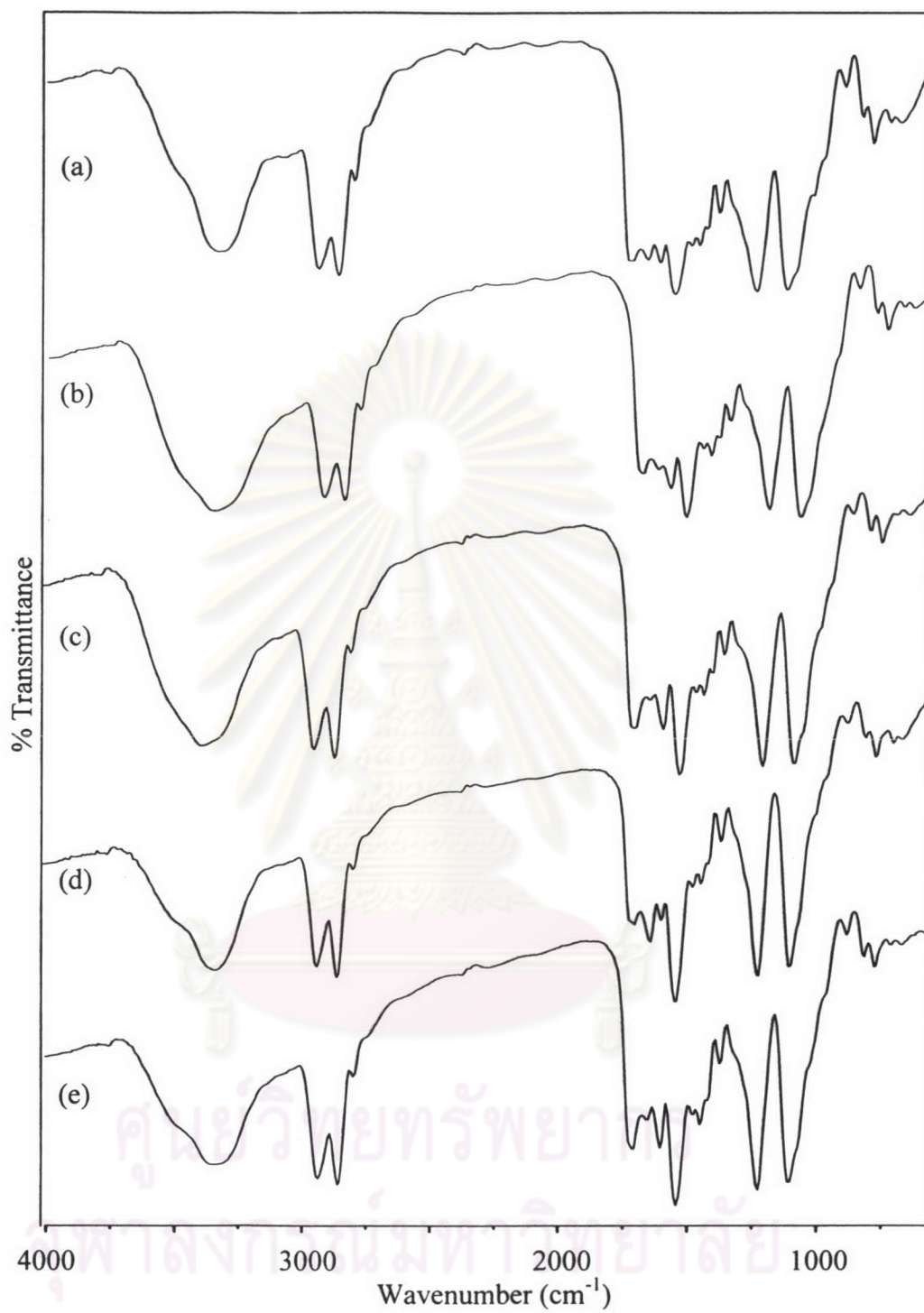


### 3.3.2 Characterization of metal-containing copolyurethane-ureas

#### 3.3.2.1 Infrared spectroscopy

IR spectra of the metal-containing copolyurethane-ureas based on ML, prepolymer and xylylenediamine are shown in Figure 3.10. All of the polymers have similar IR spectrum. The important characteristic absorption bands are as follows: 3363-3312  $\text{cm}^{-1}$  (N-H stretching), 2973-2796  $\text{cm}^{-1}$  (C-H stretching), 1727-1711  $\text{cm}^{-1}$  (urethane carbonyl), 1662-1638  $\text{cm}^{-1}$  (urea carbonyl), 1604-1599  $\text{cm}^{-1}$  (amine C=N and aromatic C=C stretching), 1547-1541  $\text{cm}^{-1}$  (N-H bending) and 1231-1224  $\text{cm}^{-1}$  (C-O stretching). There are two type of urea carbonyls in the polymer chain. The first one was obtained from the reaction between  $-\text{NH}_2$  of xylylendiamine and  $-\text{NCO}$  group of prepolymer and this urea carbonyl can be observed around 1650  $\text{cm}^{-1}$ . The second one was obtained from the reaction between  $-\text{NH}-$  group of metal complex and  $-\text{NCO}$  group of prepolymer, however, it cannot be observed because it overlaps with urethane carbonyl group of prepolymer, which results in a peak between 1727-1711  $\text{cm}^{-1}$ .

For example, the IR spectrum of Zn-PB-D-153 (Figure 3.10a) shows the medium peak of urea carbonyl around 1662-1638  $\text{cm}^{-1}$  and urethane carbonyl around 1727-1711  $\text{cm}^{-1}$ . Upon increasing wt% of metal complex in the polymer such as Zn-PB-D-131 and Zn-PB-D-371 (Figure 3.10b and 3.10c, respectively), the IR spectra show stronger urethane carbonyl absorption band and weaker urea carbonyl absorption.



**Figure 3.10** IR spectra of: (a) Zn-PB-D-153; (b) Zn-PB-D-131; (c) Zn-PB-D-371; (d) PB-D-11 and (e) PP-D-11

### 3.2.2.2 Solubility

Solubility of metal-containing polyurethane-ureas and copolyurethane-ureas was tested in various polar and non-polar solvents (Table 3.6).

At room temperature, all metal-containing polyurethane-ureas and copolyurethane-ureas were soluble in dimethyl formamide and dimethyl sulfoxide but insoluble in water, *n*-hexane, chloroform, dichloromethane, methanol, acetone, toluene and ethyl acetate. It was found that Zn-PB-12, Ni-PB-12, Zn-PP-12, Ni-PP-12, Ni-PB-D-153, Ni-PB-D-131, Ni-PB-D-371 and Ni-PP-D-131 were partial soluble in tetrahydrofuran.

**Table 3.6** Solubility of metal-containing polyurethane-ureas<sup>a</sup>

Polymer Code	THF	DMF	DMSO
Zn-PB-12	+	++	++
Ni-PB-12	+	++	++
Zn-PP-12	+	++	++
Ni-PP-12	+	++	++
Zn-PB-D-153	-	++	++
Zn-PB-D-131	-	++	++
Zn-PB-D-371	-	++	++
Ni-PB-D-153	+	++	++
Ni-PB-D-131	+	++	++
Ni-PB-D-371	+	++	++
Zn-PP-D-131	-	++	++
Ni-PP-D-131	+	++	++
PB-D-11	-	++	++
PP-D-11	-	++	++

-, Insoluble; +, Partial soluble; ++, Soluble

<sup>a</sup> 10 mg sample was dissolved in 2 ml of a solvent



### 3.2.2.3 Thermal stability

Thermal stability of metal-containing polyurethane-ureas was determined by weight loss measurement upon heating polymers in a hot air oven at 170 °C for 8 h. The weight loss data are shown in Table 3.7. The results indicate that nickel-containing polyurethane-ureas show less weight loss than zinc-containing polyurethane-ureas. Ni-PB-12 is the most thermally stable polymer since it shows the lowest weight loss.

**Table 3.7** Thermal stability of metal-containing polyurethane-ureas determined by weight loss measurement at 170 °C for 8 h

Polymer Code	Wt% loss after heating at 170 °C <sup>a</sup>					
	1 h	2 h	3 h	4 h	6 h	8 h
Zn-PB-12	2.3	5.9	8.6	10.7	13.2	16.2
Ni-PB-12	1.1	2.8	3.8	5.4	6.0	7.8
Zn-PP-12	4.8	7.0	8.5	10.6	13.2	15.6
Ni-PP-12	3.1	5.0	6.4	7.9	8.9	10.8

<sup>a</sup> the weight of sample used was 40-50 mg

Thermal stability of metal-containing copolyurethane-ureas was also determined using the same method as described above and the weight loss data are shown in Table 3.8. Thermal stability of metal-containing polyurethane-ureas and copolyurethane-ureas is compared to that of polyurethane-ureas without metal complex in the main chain (PB-D-11 and PP-D-11).

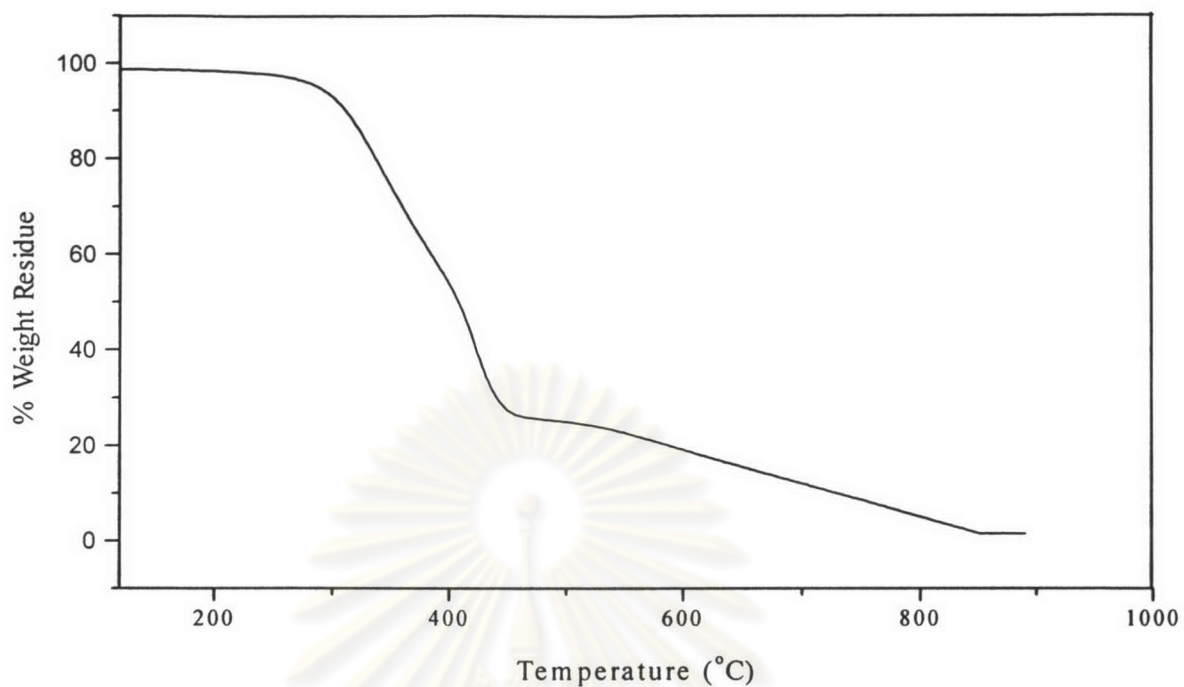
The data from Tables 3.7 and 3.8 indicate that the wt% loss decreases with increase wt% of ML in the polymers from 9% to 15%. However, wt% loss slightly increases with increase wt% of ML from 15% to 19% that may be due to the presence of lower degree of hydrogen bonding. The lowest weight loss was obtained when the amount of ML complex is 15 wt%. Among the metal-containing copolyurethane-ureas, the wt% loss of PB-based polymers is found to be lower than PP-based polymers. Also, nickel-containing copolyurethane-ureas show higher thermal stability than zinc-containing polymers.

**Table 3.8** Thermal stability of metal-containing copolyurethane-ureas determined by weight loss measurement at 170 °C for 8 h

Polymer Code	Wt%. of metal complex	Wt% loss after heating at 170 °C <sup>a</sup>					
		1 h	2 h	3 h	4 h	6 h	8 h
Zn-PB-D-153	9.2	2.6	5.1	6.2	6.8	7.7	10.2
Zn-PB-D-131	15.0	2.0	3.0	3.8	4.4	5.1	7.5
Zn-PB-D-371	18.9	3.0	4.5	5.8	6.6	7.7	9.2
Ni-PB-D-153	9.1	1.7	2.3	3.2	3.8	5.1	6.1
Ni-PB-D-131	14.9	1.1	1.4	2.0	2.6	3.5	4.1
Ni-PB-D-371	18.8	1.3	2.1	2.8	3.5	4.8	5.9
Zn-PP-D-131	13.8	4.4	6.8	8.4	9.7	11.4	13.1
Ni-PP-D-131	13.7	2.8	4.3	5.1	6.1	7.8	8.3
PB-D-11	0	18.6	24.2	26.8	28.4	29.6	30.4
PP-D-11	0	19.8	23.9	27.9	30.2	31.8	33.2

<sup>a</sup>the weight of sample used was 40-50 mg

TGA thermogram and weight loss data of Ni-PB-D-131 were investigated as shown in Figure 3.11 and Table 3.9. Ni-PB-D-131 was chosen because it showed the best thermal stability in isothermal TGA experiment. From the TGA thermogram, initial decomposition temperature (IDT) is found at 310 °C and polymer decomposes in two stages. The first stage may be considered a urethane-ureas scission followed by the formation of isocyanate and amine components. The second stage may correspond to the formation of ZnO and the residual weight at 800 °C corresponds to roughly the amount of ZnO formed. Scheme 3.5 shows possible mechanism of degradation.



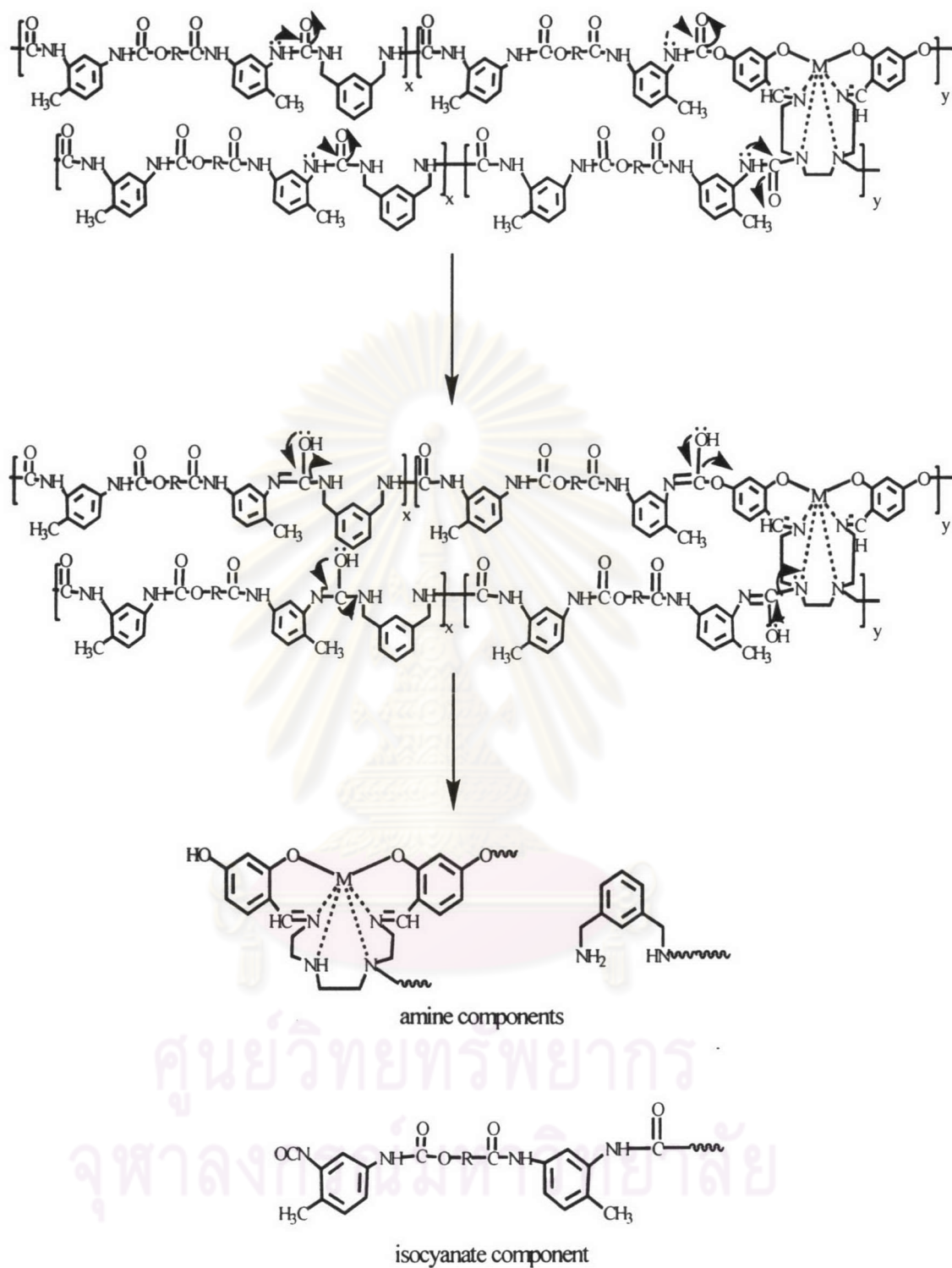
**Figure 3.11** TGA thermogram of Ni-PB-D-131

**Table 3.9** TGA data of Ni-PB-D-131

Polymer	IDTs (°C)	Temperature at wt. loss (°C)								Wt%. residue at 800 °C (%)
		10%	20%	30%	40%	50%	60%	70%	80%	
Ni-PB-D-131	310	310	336	358	382	406	422	440	588	5.1

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**Scheme 3.5** Proposed mechanism of degradation of metal-containing copolyurethane-ureas

Comparing the thermal stability of Ni-PB-D-131 to that of other metal-containing polymers report in the literature, metal-containing copoly(urethane-urea)s based on Nisal<sub>2</sub>trien which had been synthesized by Chantarasiri and coworkers[19]. Ni-PB-MDI-413 was prepared by the reaction between Nisal<sub>2</sub>trien, PB900 and diisocyanate (MDI) at the mole ratio of Nisal<sub>2</sub>trien: PB900: MDI as 4: 1: 3. TGA result showed IDT at 229 °C and the temperature of 50 wt% loss at 424 °C while those of Ni-PB-D-131 were found at 310 and 406 °C, respectively. Therefore, Ni-PB-D-131 shows better IDT than Ni-PB-MDI-413.



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