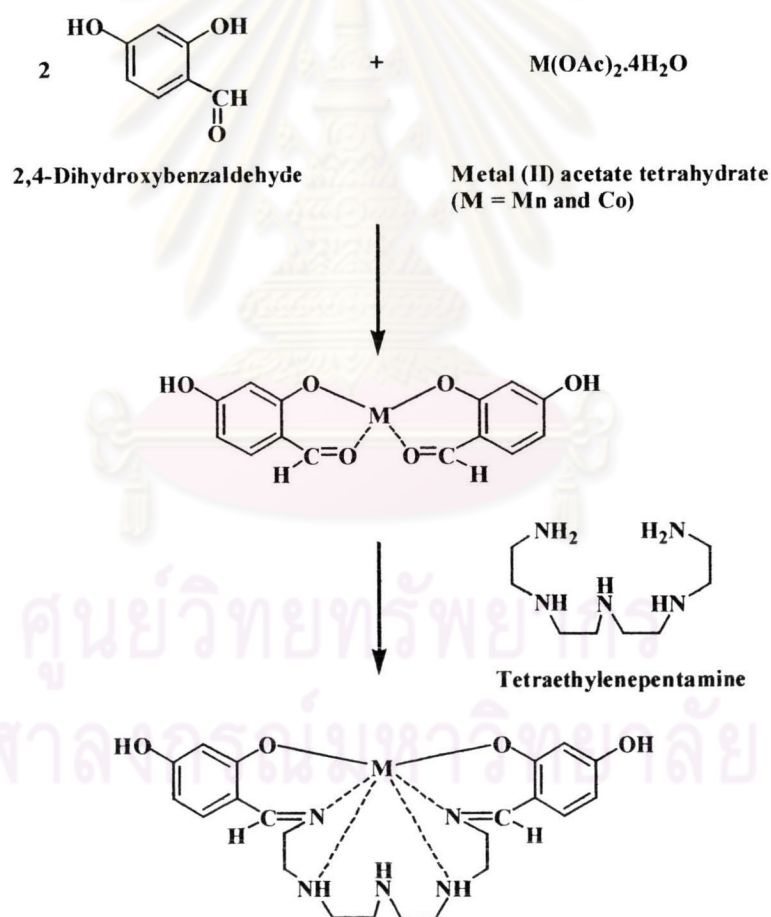


CHAPTER III

RESULTS AND DISCUSSION

3.1 Synthesis of 4,4'-dihydroxysaltetraen metal complexes (ML_1)

4,4'-Dihydroxysaltetraen metal complexes (ML_1) were synthesized by the reaction between 2,4-dihydroxybenzaldehyde and metal acetate tetrahydrate (where $M = Mn$ and Co) in methanol to form a template intermediate. Then, tetraethylenepentamine was added to obtain ML_1 (Scheme 3.1).



Scheme 3.1 Synthesis of 4,4'-dihydroxysaltetraen metal complexes (ML_1)

The reaction was neutralized by adding a solution of different bases. The brown powder of MnL_1 and the gray powder of CoL_1 precipitated immediately. After the powder of ML_1 was isolated, the filtrate was kept upon standing at room temperature, however it was decomposed. The solubility of ML_1 was tested in DMF and DMSO. The results from the solubility testing are shown in Table 3.1.

Table 3.1 Solubility of metal complexes (ML_1) using various bases^a

Metal complexes	Bases	Solvents	
		DMF	DMSO
MnL_1	2M NaOH	-	-
	2M NaHCO ₃	-	-
	1M Na ₂ CO ₃	-	-
	2M KOH	-	±
	1M K ₂ CO ₃	-	-
CoL_1	2M NaOH	-	-
	2M NaHCO ₃	-	-
	1M Na ₂ CO ₃	-	-
	2M KOH	-	±
	1M K ₂ CO ₃	-	-

-, Insoluble; ±, partial soluble

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

From the results of solubility testing, the metal complexes obtained from using 2M KOH as a base were further characterized.

3.2 Characterization of ML_1

The obtained metal complexes were characterized by IR spectroscopy and elemental analysis. Figure 3.1 shows IR spectra of MnL_1 and CoL_1 . IR spectrum of MnL_1 in Figure 3.1(a) exhibits an absorption band of OH stretching at 3420 cm^{-1} , NH stretching at 3239 cm^{-1} and C=N stretching at 1581 cm^{-1} . The bands at 986 and 847 cm^{-1} correspond to the characteristic absorption peak of aromatic bending of 1,2,4-trisubstituted benzene.

IR spectrum of CoL_1 in Figure 3.1(b) exhibits an absorption band of OH stretching at 3420 cm^{-1} , NH stretching at 3239 cm^{-1} and C=N stretching at 1597 cm^{-1} . The bands at 986 and 847 cm^{-1} correspond to the characteristic absorption peak of aromatic bending of 1,2,4-trisubstituted benzene.

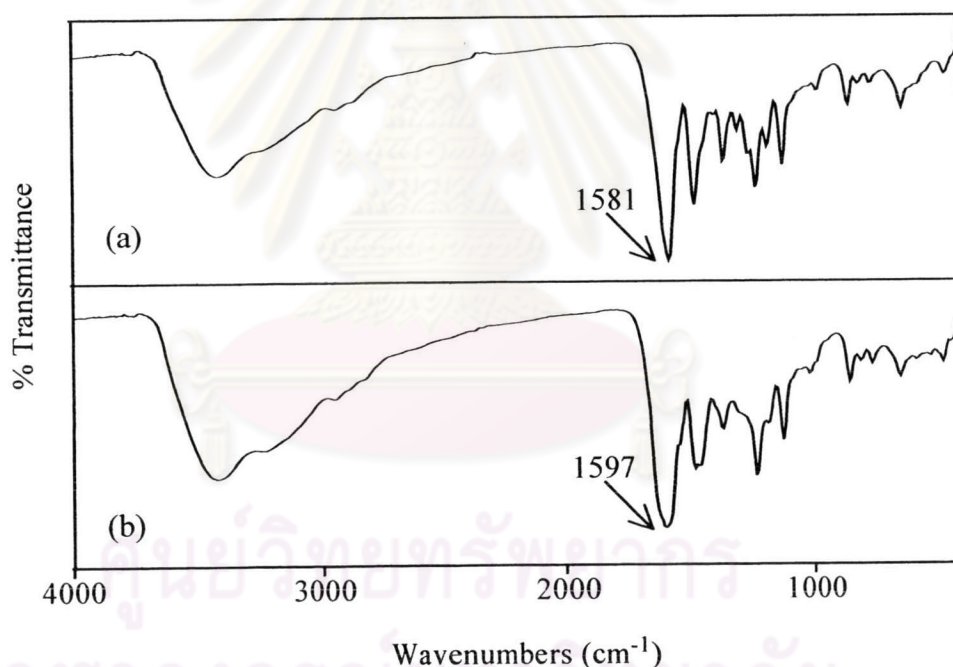


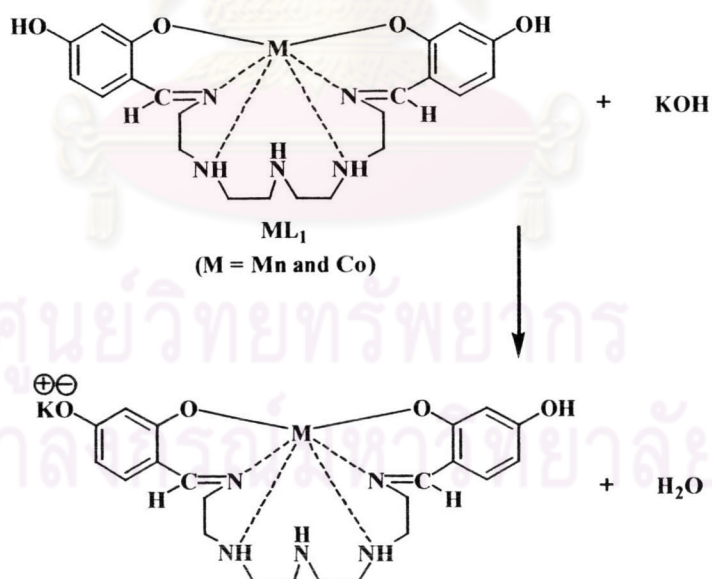
Figure 3.1 IR spectra of (a) MnL_1 (b) CoL_1

Elemental analysis data of metal complexes is shown in Table 3.2. The results from elemental analysis data suggest that the possible molecular formula of MnL_1 and CoL_1 be $C_{22}H_{28}MnN_5O_4K$ and $C_{22}H_{28}CoN_5O_4K \cdot CH_3OH$, respectively, which might occurred from the reaction between KOH and ML_1 (Scheme 3.2). Since the

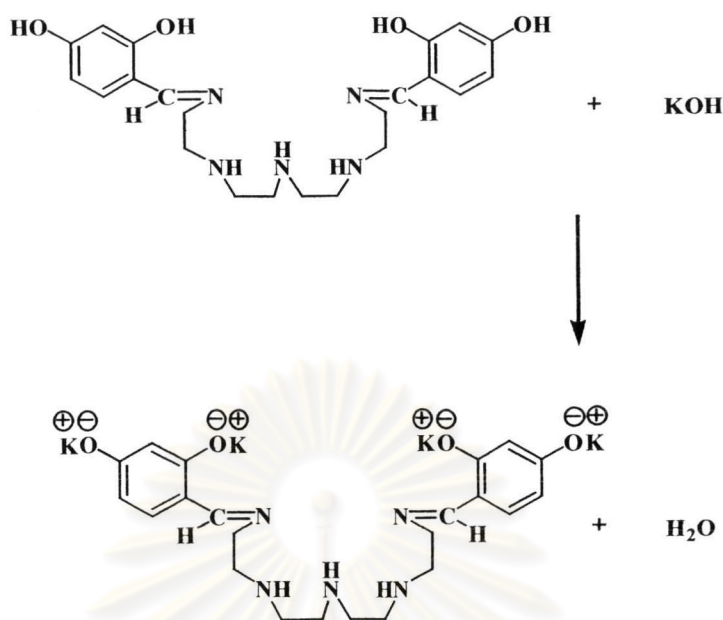
percentage values of carbon, hydrogen and nitrogen were lower than the calculated values, the obtained products might be a mixture of ML_1 and ligand salt occurred from the reaction between OH groups of the ligand which did not form metal complex and KOH as shown in Scheme 3.3. Purification of ML_1 was unsuccessful because it decomposed during the process.

Table 3.2 Elemental analysis data of ML_1

Metal complexes (ML_1)	Possible molecular formula	% C found (calcd.)	% H found (calcd.)	% N found (calcd.)
MnL ₁	C ₂₂ H ₂₈ MnN ₅ O ₄ K	50.31 (50.76)	4.82 (5.42)	10.61 (13.45)
CoL ₁	C ₂₂ H ₂₈ CoN ₅ O ₄ K·CH ₃ OH	48.99 (49.63)	5.71 (5.80)	11.39 (12.58)



Scheme 3.2 Possible reaction between ML_1 and KOH



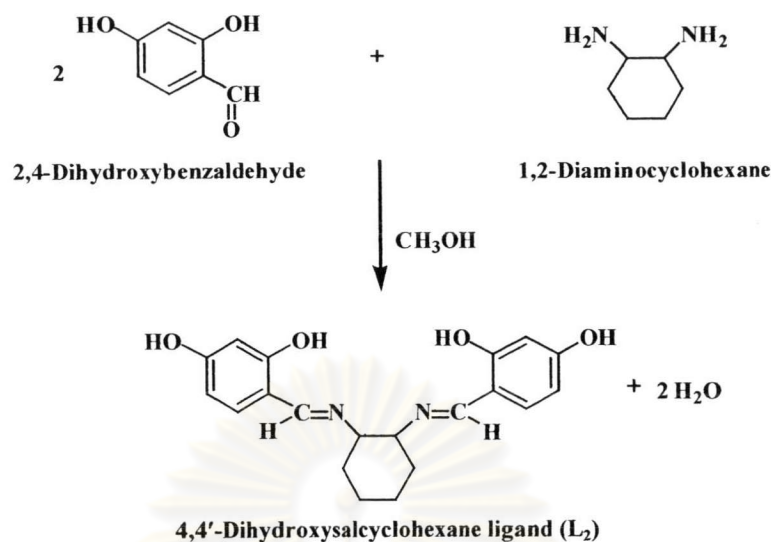
Scheme 3.3 Possible reaction between ligand and KOH

After several attempts, the synthesis of ML_1 was accomplished. Therefore 4,4'-dihydroxysalicyclohexane metal complexes (ML_2 , where $M = Zn$ and Cu) were the next target molecules.

3.3 Synthesis of 4,4'-dihydroxysalicyclohexane metal complexes (ML_2)

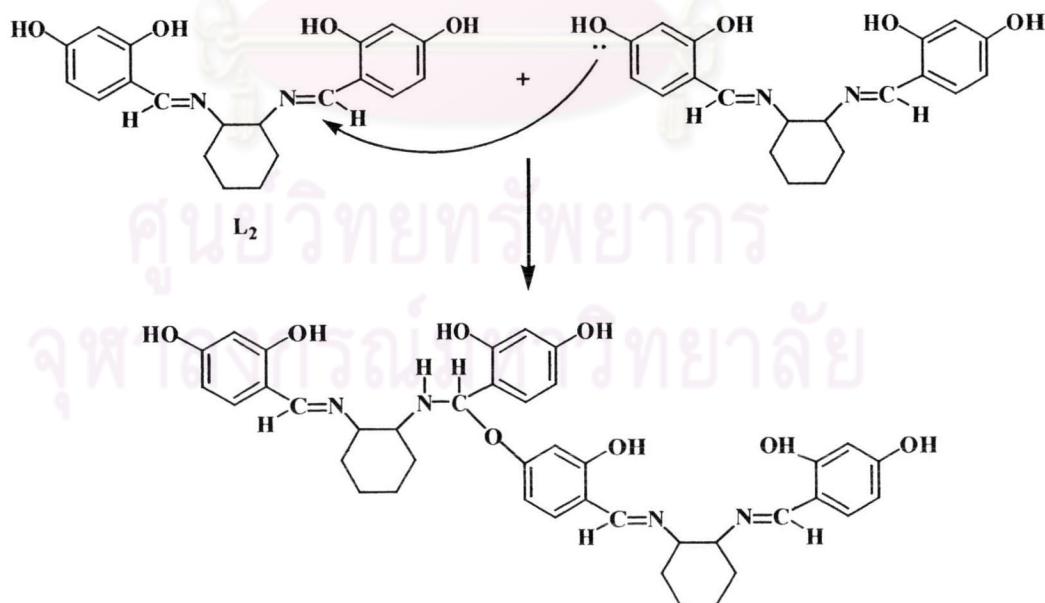
3.3.1 Preparation of 4,4'-dihydroxysalicyclohexane ligand (L_2)

4,4'-Dihydroxysalicyclohexane ligand was prepared by using a similar method described in the literature.²⁰ Starting from 2,4-dihydroxybenzaldehyde and 1,2-diaminocyclohexane, lone pair of electrons on the nitrogen of amine attacked carbonyl carbon of the aldehyde followed by loss of water, giving 4,4'-dihydroxysalicyclohexane ligand (L_2) (Scheme 3.4).



Scheme 3.4 Preparation of 4,4'-dihydroxysalicycyclohexane ligand (L_2)

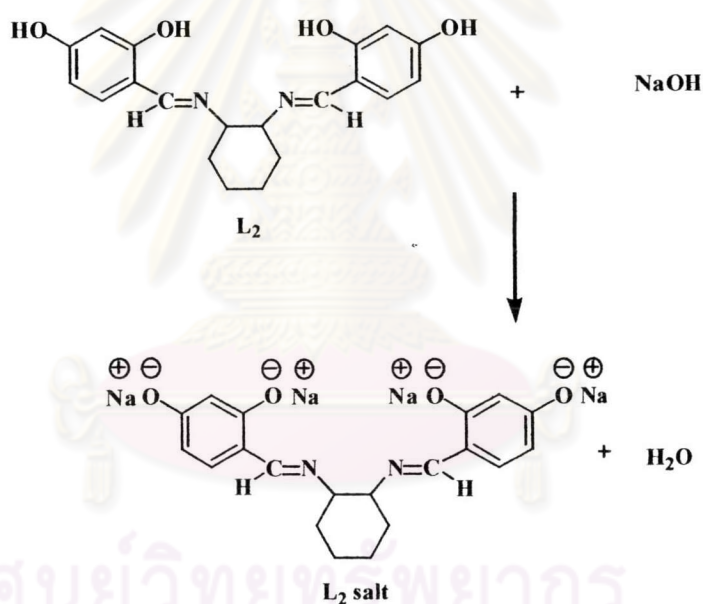
The ligand L_2 was stable in methanolic solution but unstable when the solvent was removed. When the solution of L_2 was evaporated to dryness, L_2 decomposed to a viscous product.²⁰ The decomposition might be due to the reaction between phenolic and imine groups as shown in Scheme 3.5. Therefore, the ligand L_2 had to be kept in methanolic solution and used immediately in the next steps without purification.



Scheme 3.5 Possible decomposition reaction of L_2

3.3.2 Synthesis of 4,4'-dihydroxysalicyclohexane zinc complex (ZnL_2)

4,4'-Dihydroxysalicyclohexane zinc complex (ZnL_2) was synthesized by addition of zinc (II) acetate dihydrate into the methanolic solution of the ligand L_2 . After neutralization of the reaction mixture by 2M NaOH, the orange powder then precipitated immediately. The orange powder might be L_2 sodium salt which came from the reaction between OH group of L_2 and NaOH as shown in Scheme 3.6. This L_2 salt was insoluble in DMF and DMSO. IR spectrum of L_2 salt (Figure 3.2) exhibits an absorption band of C=N stretching at 1590 cm^{-1} . After isolation of the orange powder by filtration, the filtrate was kept at room temperature for 3 days to obtain light yellow crystals of ZnL_2 . The synthesis of ZnL_2 is shown in Scheme 3.7.



Scheme 3.6 Possible reaction between L_2 and NaOH to give L_2 salt

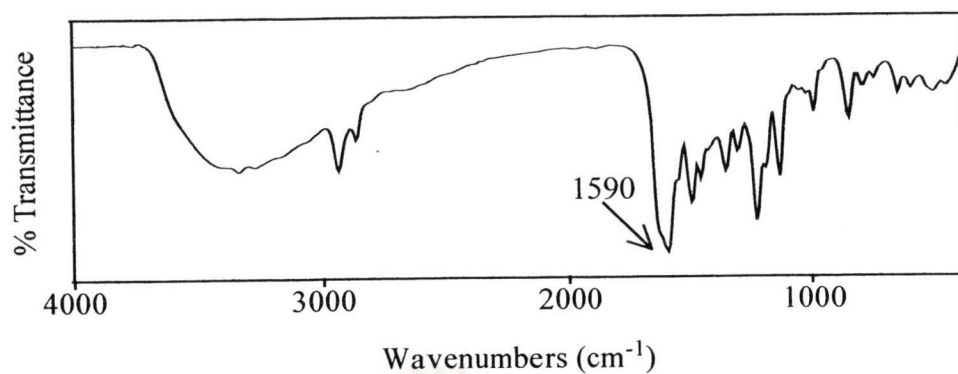
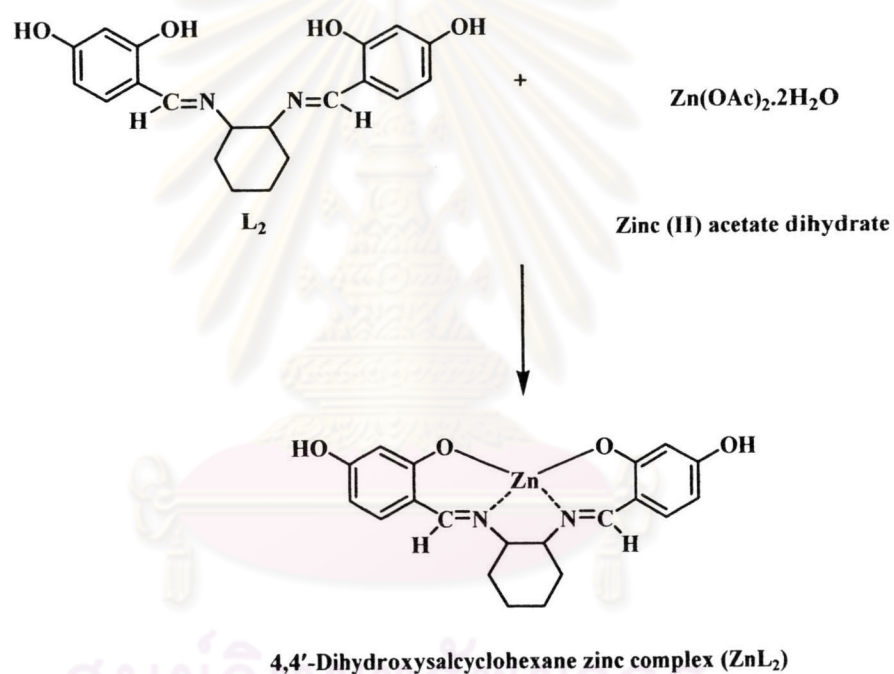


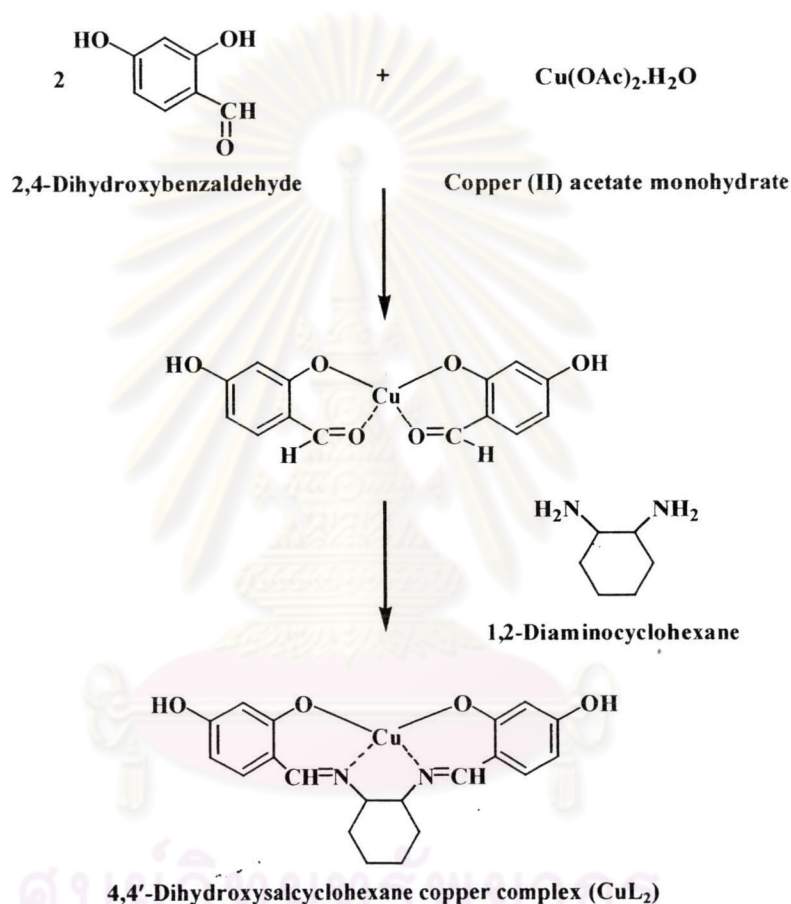
Figure 3.2 IR spectrum of L₂ salt



Scheme 3.7 Synthesis of 4,4'-dihydroxysalicyclohexane zinc complex (ZnL₂)

3.3.3 Synthesis of 4,4'-dihydroxysalicyclohexane copper complex (CuL_2)

4,4'-Dihydroxysalicyclohexane copper complex (CuL_2) was synthesized by the reaction between 2,4-dihydroxybenzaldehyde and copper (II) acetate monohydrate in methanol to form a template intermediate. Then, 1,2-diaminocyclohexane was added to give CuL_2 (Scheme 3.8).



Scheme 3.8 Synthesis of 4,4'-dihydroxysalicyclohexane copper complex (CuL_2)

The synthesis of CuL_2 was done by varying the mole ratio of 2,4-dihydroxybenzaldehyde:copper (II) acetate monohydrate:1,2-diaminocyclohexane as 2:1:1, 2:1:2, 2:1:3 and 2:1:4. The synthesis data of CuL_2 obtained from varying the mole ratio of starting materials are shown in Table 3.3. From these results, the mole ratio of 2,4-dihydroxybenzaldehyde:copper (II) acetate monohydrate:1,2-diaminocyclohexane as 2:1:4 was chosen for the synthesis CuL_2 .

Table 3.3 Synthesis data of CuL₂

Mole ratio of 2,4-dihydroxybenzaldehyde:copper (II) acetate monohydrate:1,2-diaminocyclohexane	Appearance of CuL ₂	Yield of CuL ₂ (%)
2:1:1	purple powder	23
2:1:2	purple powder	35
2:1:3	purple powder	61
2:1:4	purple crystals	88

3.4 Characterization of ZnL₂

The structure of ZnL₂ was confirmed by IR spectroscopy, ¹H NMR spectroscopy, elemental analysis and mass spectrometry. IR spectrum of ZnL₂ (Figure 3.3) exhibits an absorption band of OH stretching at 3460 cm⁻¹ and C=N stretching at 1606 cm⁻¹. The bands at 992 and 848 cm⁻¹ correspond to the characteristic absorption peak of aromatic bending of 1,2,4-trisubstituted benzene.

Elemental analysis data of ZnL₂ is shown in Table 3.4. The result from elemental analysis data shows that the possible molecular formula of ZnL₂ is C₂₀H₂₀ZnN₂O₄.H₂O and the experimentally determined percentage values of carbon, hydrogen and nitrogen are within the calculated values.

¹H NMR spectroscopy and MALDI-TOF MS were also used to confirm molecular formula of ZnL₂. ¹H NMR spectrum (Figure 3.4) of ZnL₂ shows the OH protons at δ 9.20 and the imine CH=N protons at δ 8.09. The signals at δ 6.90, 6.08 and 5.94 are due to the aromatic protons. The signals between δ 3.01-3.12, 2.30-2.45, 1.84-2.03 and 1.19-1.46 are due to the cyclohexane protons. MALDI-TOF MS data (Table 3.5 and Appendix) shows that the obtained zinc complex is a mixture of ZnL₂ (C₂₀H₂₀ZnN₂O₄) and ZnL₂ salt (C₂₀H₁₉ZnN₂O₄Na). C₂₀H₁₉ZnN₂O₄Na might come from the reaction between NaOH in the solution and ZnL₂ (Scheme 3.9).

This result does not have an effect on the preparation of metal-containing polymers since both ZnL_2 and ZnL_2 salt can react with isocyanate-terminated prepolymers in the synthesis of zinc-containing polyurethanes.

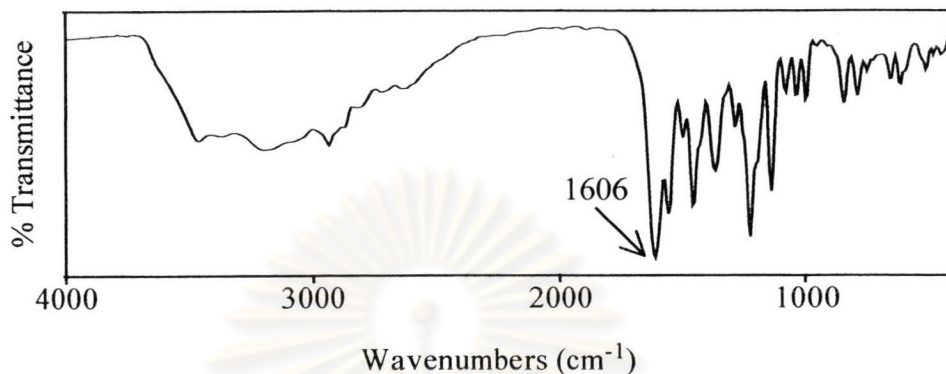


Figure 3.3 IR spectrum of ZnL_2

Table 3.4 Elemental analysis data of ZnL_2

Possible molecular formula	% C found (cald.)	% H found (cald.)	% N found (cald.)
$C_{20}H_{20}ZnN_2O_4 \cdot H_2O$	54.83 (55.12)	4.82 (5.09)	6.66 (6.43)

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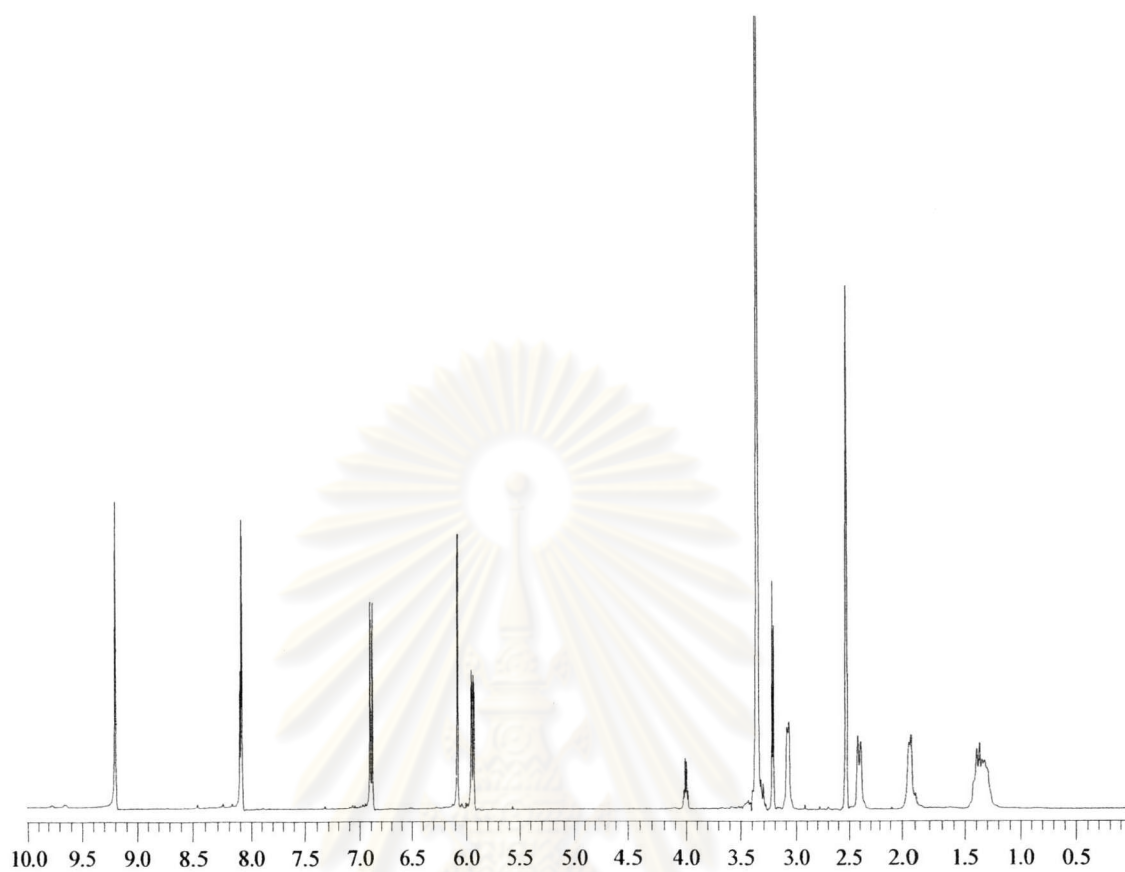
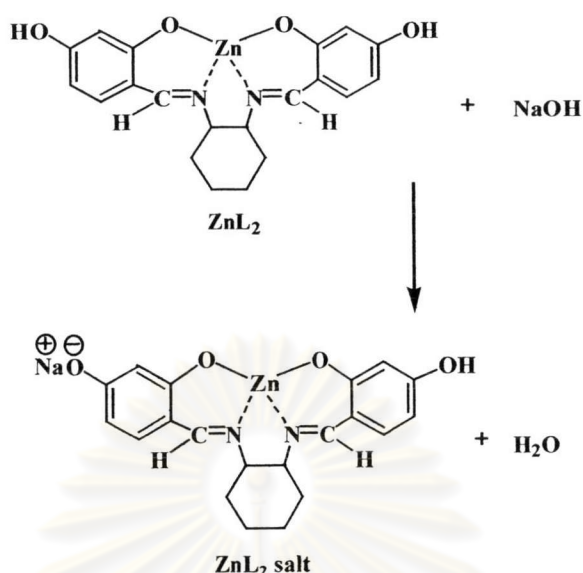


Figure 3.4 ^1H NMR spectrum of ZnL_2

Table 3.5 MALDI-TOF MS data of ZnL_2

m/z	Formula
419	$\text{C}_{20}\text{H}_{20}\text{ZnN}_2\text{O}_4$
441	$\text{C}_{20}\text{H}_{19}\text{ZnN}_2\text{O}_4\text{Na}$



Scheme 3.9 Possible reaction between ZnL_2 and $NaOH$ to give ZnL_2 salt

3.5 Characterization of CuL_2

The structure of CuL_2 was confirmed by IR spectroscopy, elemental analysis and mass spectrometry. IR spectrum of CuL_2 (Figure 3.5) exhibits an absorption band of OH stretching at 3424 cm^{-1} and C=N stretching at 1615 cm^{-1} . The bands at 989 and 846 cm^{-1} correspond to the characteristic absorption peak of aromatic bending of 1,2,4-trisubstituted benzene.

Elemental analysis data of CuL_2 is shown in Table 3.6. The result from elemental analysis data suggests that the possible molecular formula of CuL_2 should be $C_{20}H_{19}CuN_2O_4Na$ but the percentage value of hydrogen was higher than the calculated value. This might be because the obtained products are the mixture of $C_{20}H_{19}CuN_2O_4Na$ and $C_{20}H_{20}CuN_2O_4$. This result does not have an effect in the next polymerization step since CuL_2 and CuL_2 salt can react with isocyanate-terminated prepolymers in the synthesis of copper-containing polyurethanes.

MALDI-TOF MS was also used to confirm molecular formula of CuL_2 . MALDI-TOF MS data (Table 3.7 and Appendix) shows that the obtained copper complex is a mixture of CuL_2 ($\text{C}_{20}\text{H}_{20}\text{CuN}_2\text{O}_4$) and CuL_2 salt ($\text{C}_{20}\text{H}_{19}\text{CuN}_2\text{O}_4\text{Na}$). $\text{C}_{20}\text{H}_{19}\text{CuN}_2\text{O}_4\text{Na}$ was obtained from the reaction between NaOH in the solution and CuL_2 (Scheme 3.10).

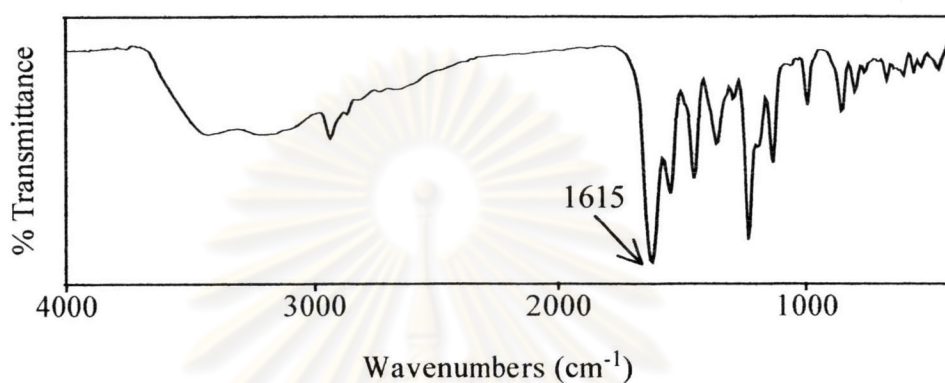


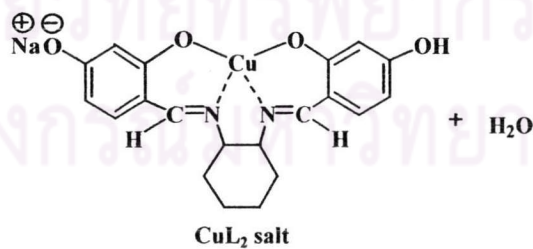
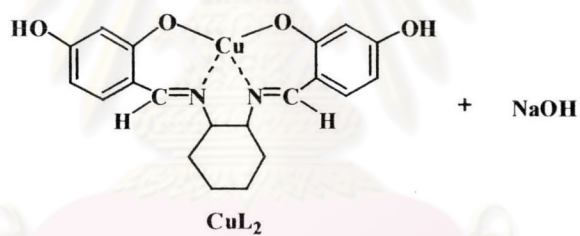
Figure 3.5 IR spectrum of CuL_2

Table 3.6 Elemental analysis data of CuL_2

Possible molecular formula	% C found (cald.)	% H found (cald.)	% N found (cald.)
$\text{C}_{20}\text{H}_{19}\text{CuN}_2\text{O}_4\text{Na}$	54.74 (54.85)	5.24 (4.37)	6.44 (6.40)

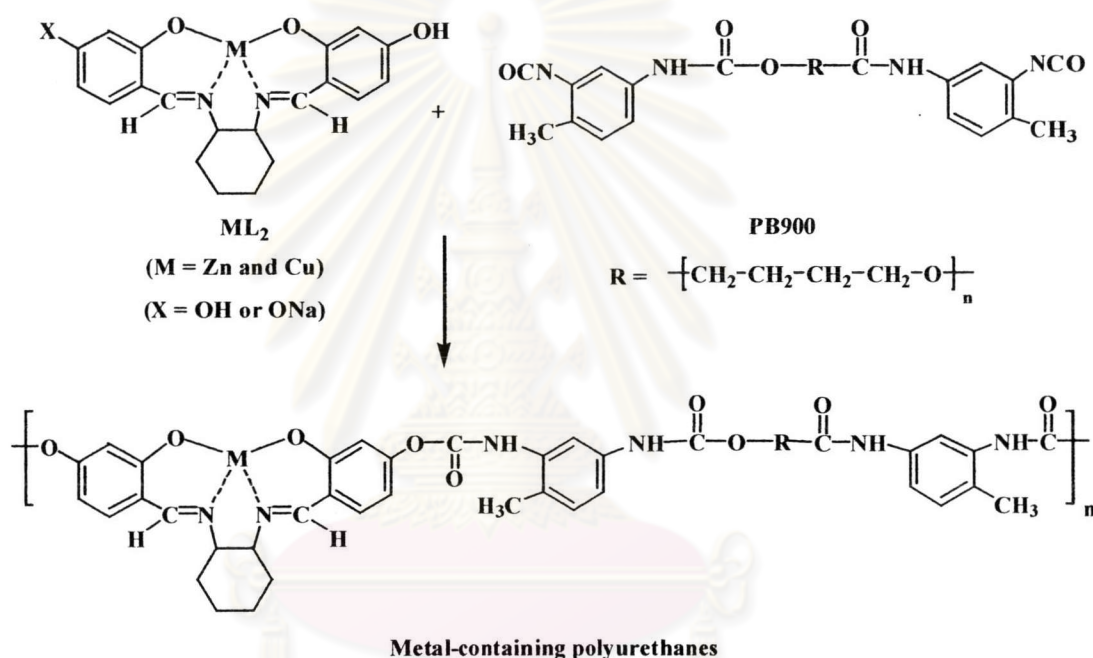
Table 3.7 MALDI-TOF MS data of CuL_2

m/z	Formula
418	$\text{C}_{20}\text{H}_{20}\text{CuN}_2\text{O}_4$
435	$\text{C}_{20}\text{H}_{20}\text{CuN}_2\text{O}_4 \cdot \text{H}_2\text{O}$
440	$\text{C}_{20}\text{H}_{19}\text{CuN}_2\text{O}_4\text{Na}$
456	$\text{C}_{20}\text{H}_{19}\text{CuN}_2\text{O}_4\text{Na} \cdot \text{H}_2\text{O}$

**Scheme 3.10** Possible reaction between CuL_2 and NaOH to give CuL_2 salt

3.6 Investigation of polymerization reaction between 4,4'-dihydroxysalicyclohexane metal complexes and prepolymers

The next step was to investigate the polymerization reaction between 4,4'-dihydroxysalicyclohexane metal complexes (ML_2) and tolylene 2,4-diisocyanate terminated poly(1,4-butanediol) prepolymer, MW 900 (PB900) by using differential scanning calorimetry (DSC) and IR spectroscopy. The reaction between ML_2 and PB900 is shown in Scheme 3.11.



Scheme 3.11 The polymerization reaction between ML_2 and PB900

3.6.1 Differential scanning calorimetry (DSC)

DSC thermogram of the mixture between ZnL_2 and PB900 at the mole ratio of 1:1 is shown in Figure 3.6. The thermogram shows exothermic peak between 70-156°C with the peak maxima around 117°C. This result suggests that the polymerization reaction between ZnL_2 and PB900 occurs at this temperature range. Therefore, the temperature at 120°C was chosen for the synthesis of polyurethanes containing 4,4'-dihydroxysalicyclohexane metal complexes.

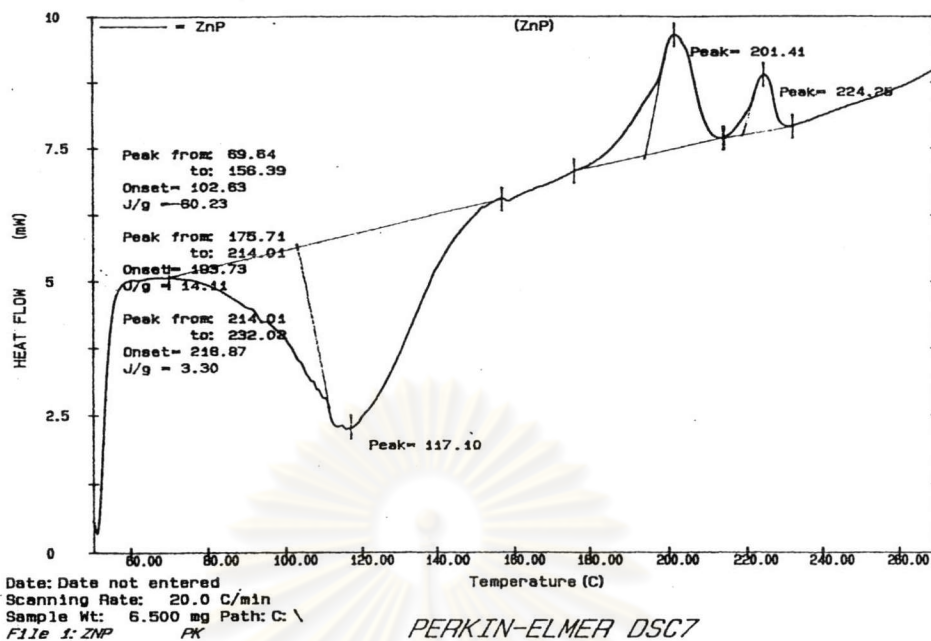


Figure 3.6 DSC thermogram of ZnL₂ : PB900 mixture at the mole ratio of 1 : 1

3.6.2 IR spectroscopy

Having obtained the polymerization temperature from DSC, IR spectroscopy was used to investigate the polymerization reaction between ML₂ and PB900 at the mole ratio of 1:1 at 120°C. The progress of the reaction was followed by the disappearance of the strong N=C=O absorption band of isocyanate group in PB900 at 2275 cm⁻¹. If the polymerization was completed, the IR absorption band at 2275 cm⁻¹ should disappear.

Figure 3.7 shows IR spectrum of the polymerization reaction between ZnL₂ and PB900 which was obtained by KBr method. It was found that the reaction was completed within 3 hours. After the reaction was completed, the zinc-containing polyurethane was purified by dissolving the crude product in DMSO. Then, a mixture of methanol and water was added in this solution to precipitate the polymer. The yellow polyurethane elastomer was obtained and dried in vacuum.

IR spectrum of zinc-containing polyurethane (Figure 3.8) shows the carbonyl (C=O) stretching of urethane linkage (-NCOO-) at 1726 cm⁻¹ and the imine (C=N) absorption band appears at 1602 cm⁻¹.

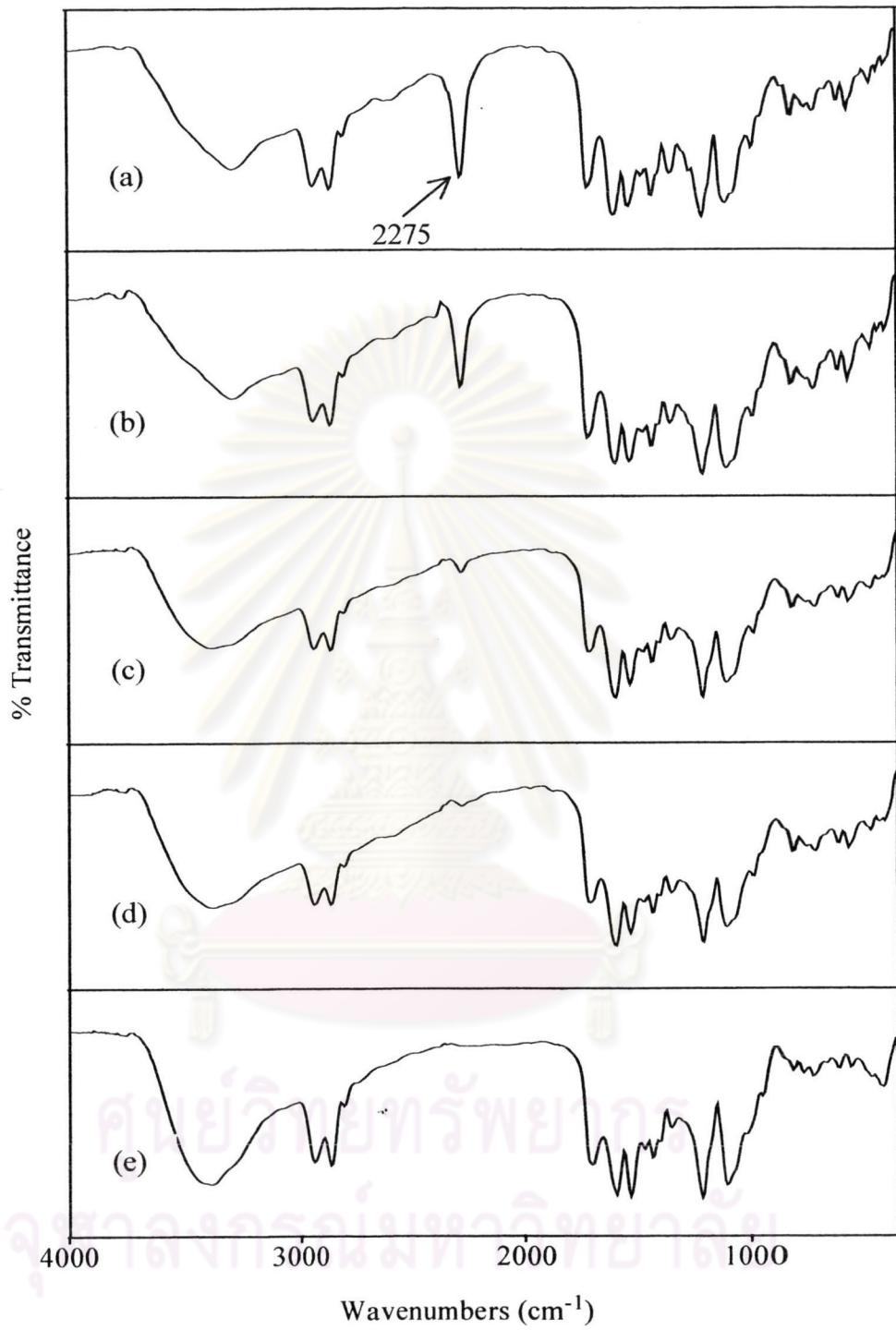


Figure 3.7 IR spectra of the polymerization reaction between ZnL_2 and PB900
(a) before heating (b) after heating 30 min (c) after 1 h (d) after 2 h
(e) after 3 h

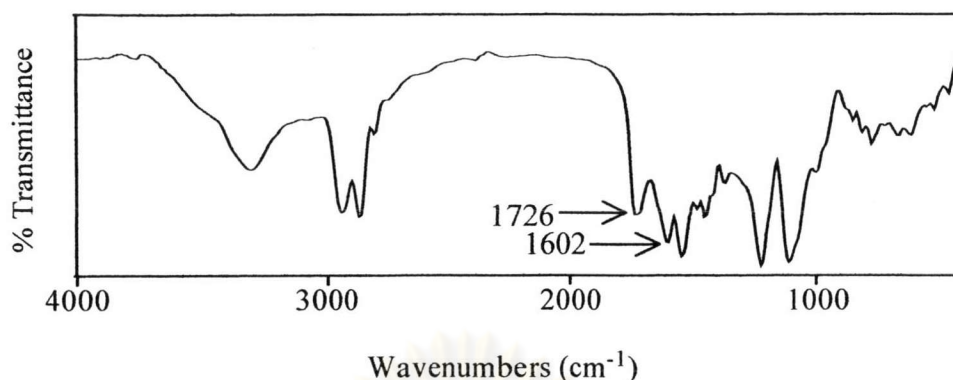


Figure 3.8 IR spectrum of zinc-containing polyurethane obtained from ZnL_2 and PB900

Figure 3.9 shows IR spectrum of the polymerization reaction between CuL_2 and PB900 which was obtained by KBr method. It was observed that the $N=C=O$ peak of PB900 at 2275 cm^{-1} disappeared within 5 hours. After the crude product was purified and dried in vacuum, the obtained product was purple powder like CuL_2 . This product was characterized by using IR spectroscopy and compared with IR spectrum of CuL_2 . It was found that the obtained product was CuL_2 and therefore the polymerization reaction between CuL_2 and PB900 did not occur. The disappearance of isocyanate peak at 2275 cm^{-1} might be due to the reaction between PB900 and moisture in air and the product is soluble in methanol during purification. To prove this, IR spectra of PB900 after heating at 120°C are shown in Figure 3.10. The strong $N=C=O$ absorption band of isocyanate group in PB900 at 2275 cm^{-1} upon heating disappeared to give white elastomer which was soluble in methanol. The results indicated that moisture in air can also react with isocyanate groups of PB900 but ZnL_2 had better reactivity than moisture while CuL_2 had lower reactivity than moisture. Hence, it can be concluded that ZnL_2 had better reactivity than CuL_2 .

From this result, dibutyltin dilaurate (DBTDL) was then used as a catalyst for the polymerization between CuL_2 and PB900. The reaction time was 15 hours to be sure that the polymerization was completed.

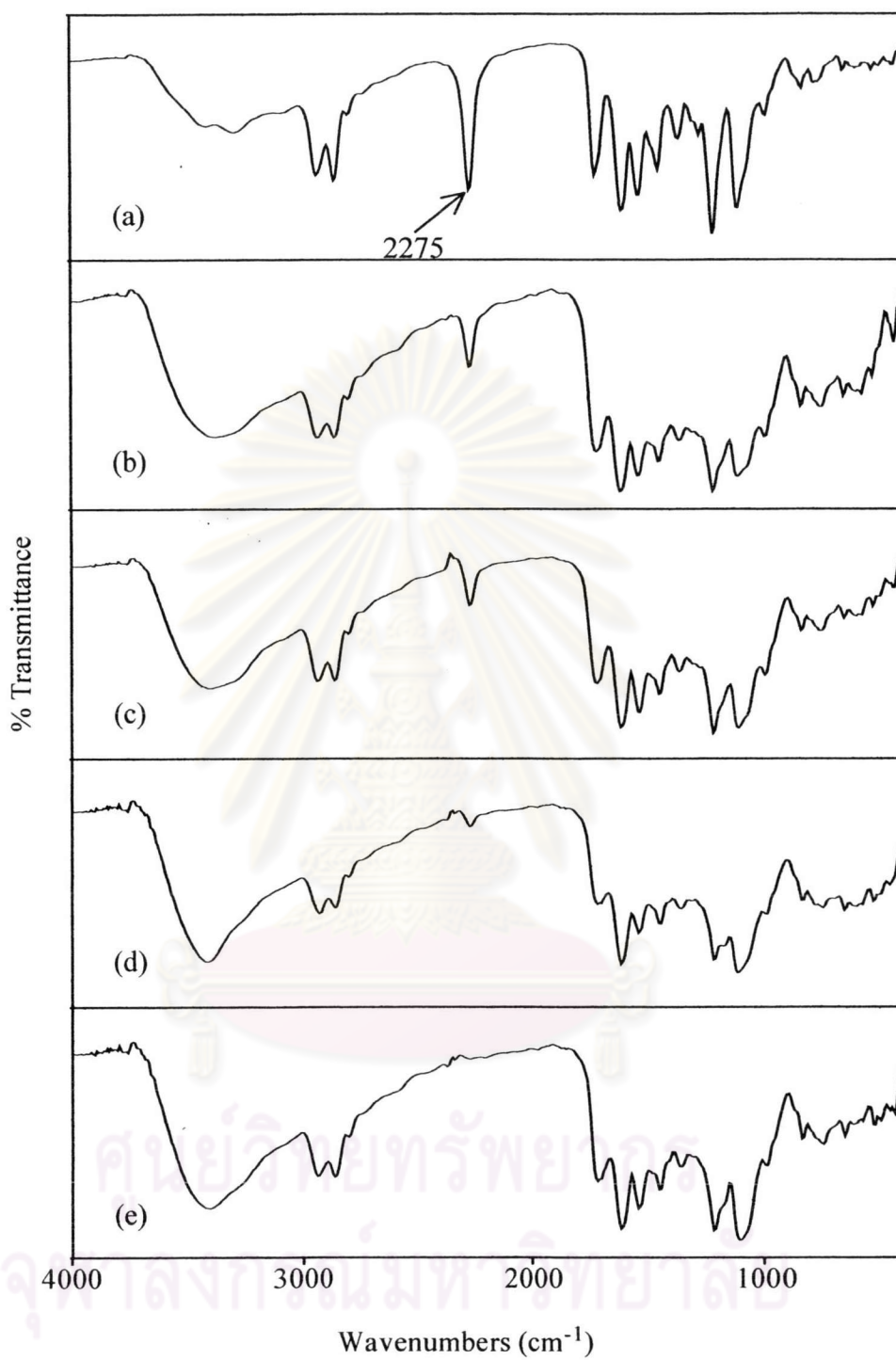


Figure 3.9 IR spectra of the polymerization reaction between CuL₂ and PB900 (a) before heating (b) after heating 30 min (c) after 1 h (d) after 3 h (e) after 5 h

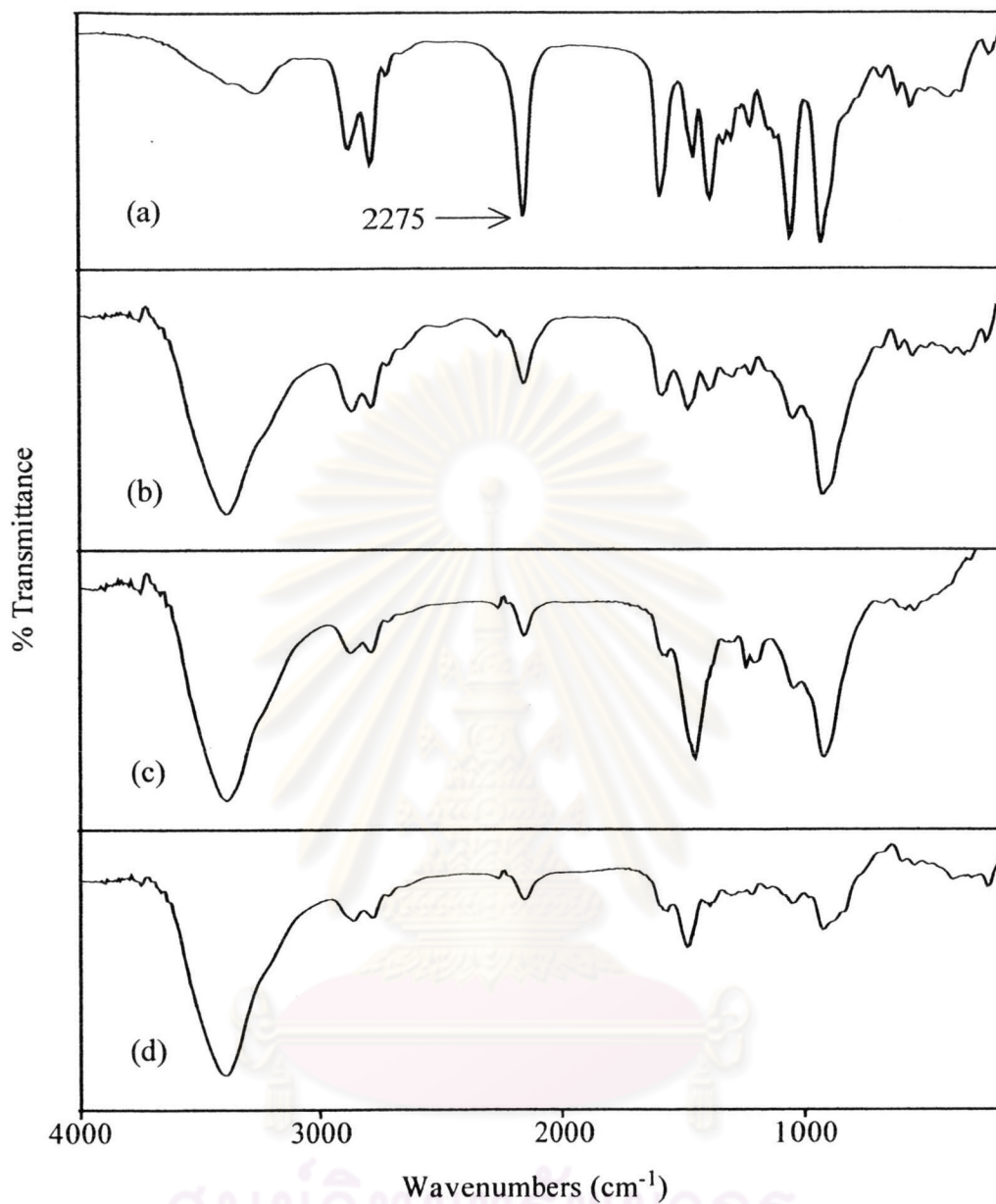


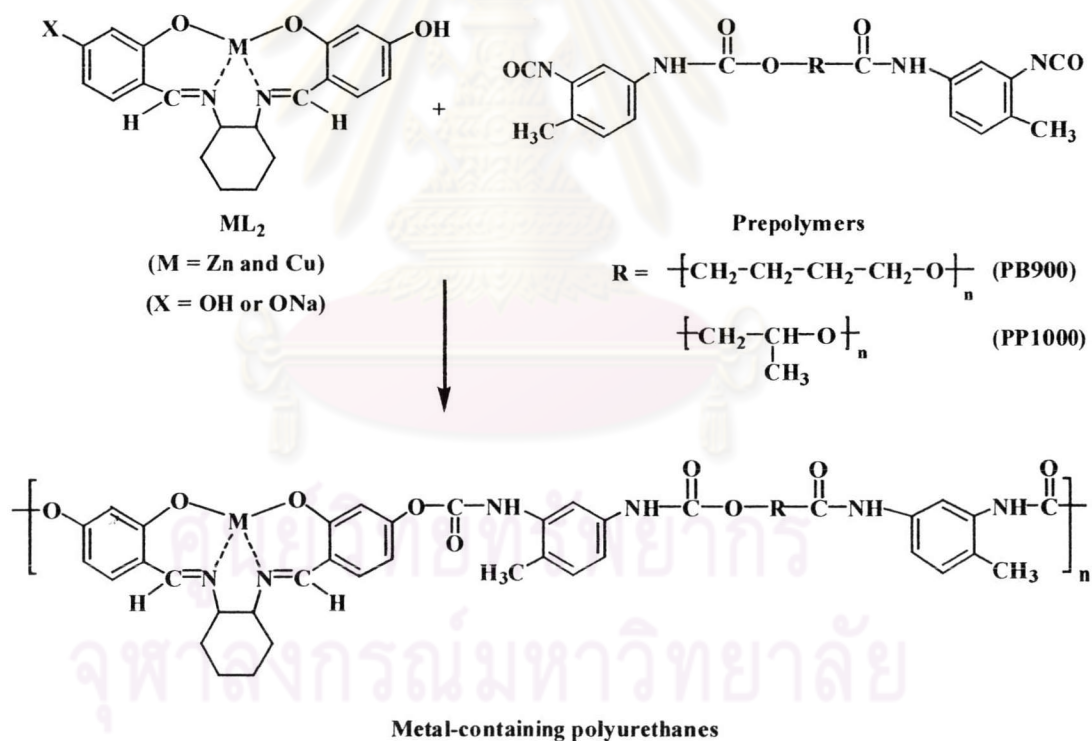
Figure 3.10 IR spectra of PB900

(a) before heating (b) after heating 30 min (c) after 1 h (d) after 3 h

Since the structure of PP1000 is similar to PB900, the polymerization condition between ML_2 and PP1000 employed was the same as that between ML_2 and PB900.

3.7 Synthesis of polyurethanes containing 4,4'-dihydroxysalicyclohexane metal complexes

Polyurethanes containing 4,4'-dihydroxysalicyclohexane metal complexes were synthesized from the reaction between 4,4'-dihydroxysalicyclohexane metal complexes (ML_2) and different prepolymers at the mole ratio of 1:1 at 120°C for 15 hours as shown in Scheme 3.12. The products from ZnL_2 with PB900 and PP1000 are coded as Zn-PB900 and Zn-PP1000, respectively and the products from CuL_2 with PB900 and PP1000 are coded as Cu-PB900 and Cu-PP1000, respectively. After the reaction was completed, the polyurethane was purified by dissolving in DMSO. Then, a mixture of methanol and water was added in this solution to precipitate the polyurethane and the polymer was then dried in vacuum.



Scheme 3.12 Synthesis of polyurethanes containing 4,4'-dihydroxysalicyclohexane metal complexes

3.8 Characterization of polyurethanes containing 4,4'-dihydroxycyclohexane metal complexes

All polyurethanes were characterized using IR spectroscopy and the IR spectra of these polyurethanes are shown in Figure 3.11.

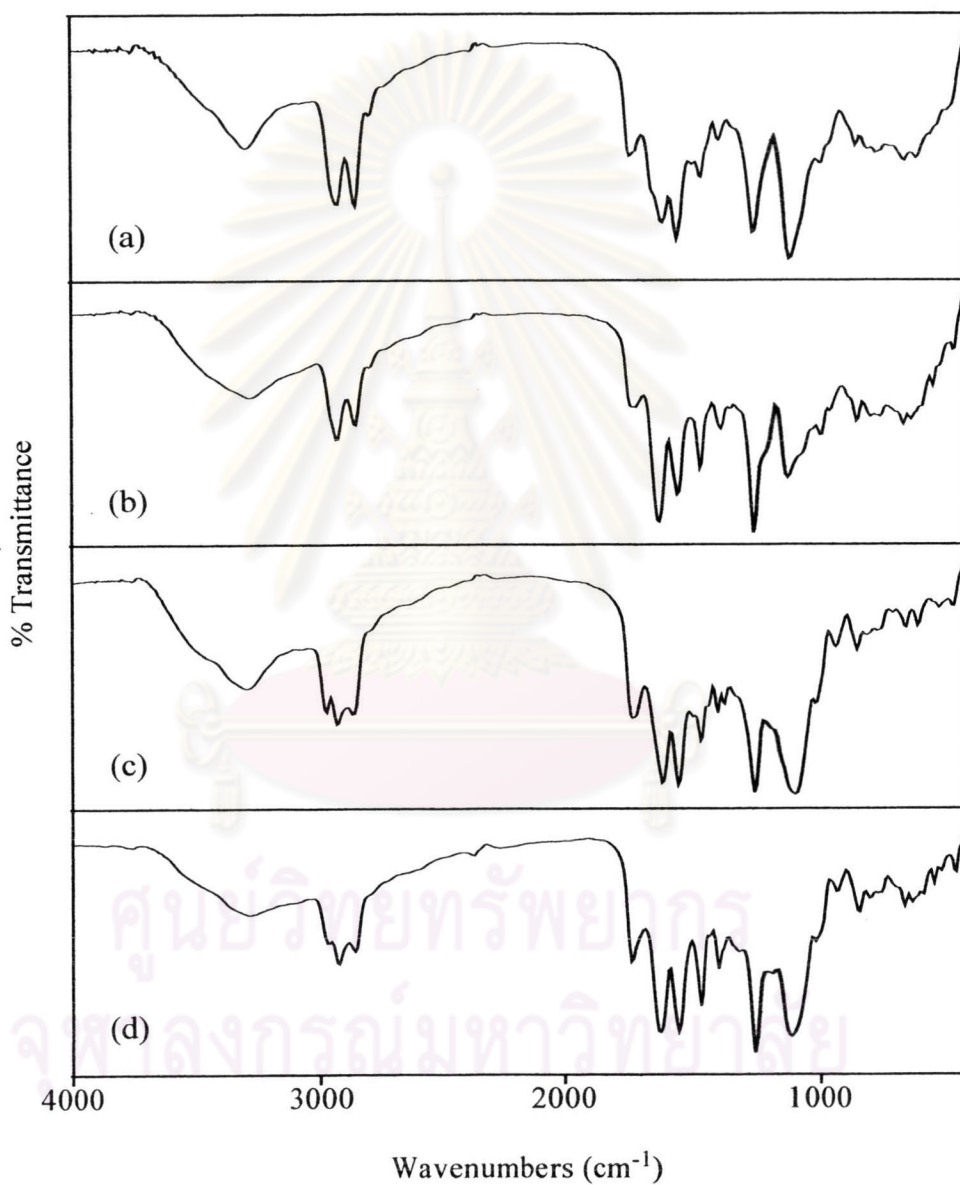


Figure 3.11 IR spectra of (a) Zn-PB900 (b) Cu-PB900 (c) Zn-PP1000 (d) Cu-PP1000

IR spectrum of Zn-PB900 [Figure 3.11(a)] shows the NH stretching of urethane linkage at 3301 cm^{-1} and the aliphatic CH stretching at 2927 and 2856 cm^{-1} . The carbonyl (C=O) stretching of urethane linkage (-NCOO-) appears at 1726 cm^{-1} . The imine (C=N) absorption band appears at 1602 cm^{-1} and benzene CH bending appears at 765 cm^{-1} .

IR spectrum of Cu-PB900 [Figure 3.11(b)] is similar to that of Zn-PB900. The spectrum shows the NH stretching of urethane linkage at 3289 cm^{-1} and the aliphatic CH stretching at 2928 and 2857 cm^{-1} . The carbonyl (C=O) stretching of urethane linkage (-NCOO-) appears at 1720 cm^{-1} . The imine (C=N) absorption band appears at 1615 cm^{-1} and benzene CH bending appears at 759 cm^{-1} .

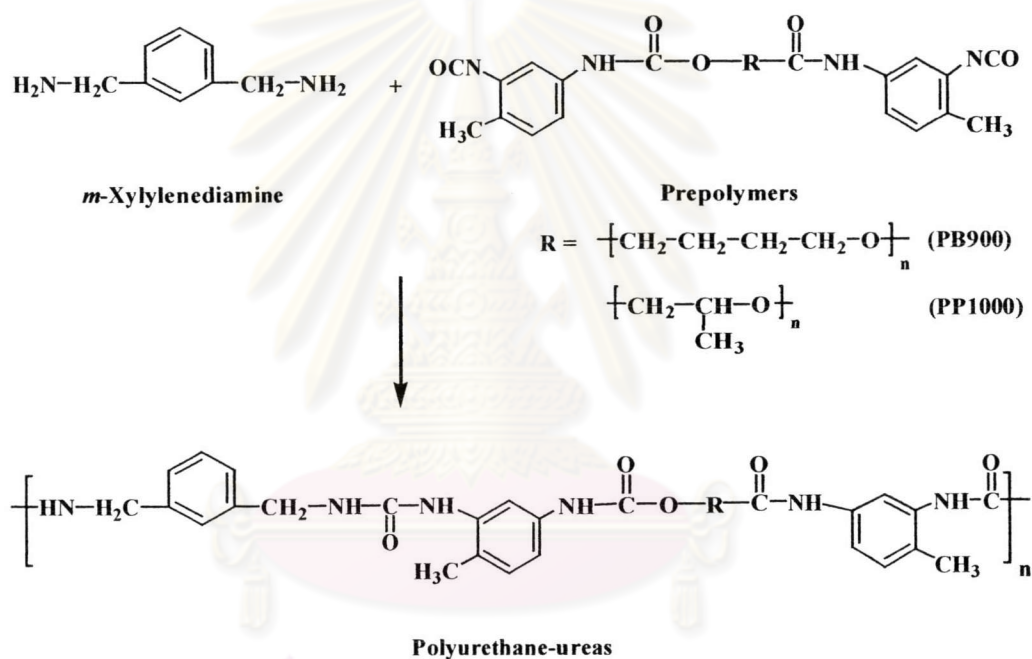
IR spectrum of Zn-PP1000 [Figure 3.11(c)] shows the NH stretching of urethane linkage at 3301 cm^{-1} and the aliphatic CH stretching at 2972 , 2929 and 2862 cm^{-1} . The carbonyl (C=O) stretching of urethane linkage (-NCOO-) appears at 1718 cm^{-1} . The imine (C=N) absorption band appears at 1602 cm^{-1} and benzene CH bending appears at 765 cm^{-1} .

IR spectrum of Cu-PP1000 [Figure 3.11(d)] is similar to that of Zn-PP1000. The spectrum shows the NH stretching of urethane linkage at 3289 cm^{-1} and the aliphatic CH stretching at 2967 , 2926 and 2863 cm^{-1} . The carbonyl (C=O) stretching of urethane linkage (-NCOO-) appears at 1725 cm^{-1} . The imine (C=N) absorption band appears at 1615 cm^{-1} and benzene CH bending appears at 759 cm^{-1} .

To study the effect of metal complexes in the polymer chain, two types of polyurethane-ureas were synthesized. The metal-containing polyurethane-ureas were synthesized from the reaction between ML_2 , prepolymers and *m*-xylylenediamine. Polyurethane-ureas without metal in the main chain were synthesized from the reaction between prepolymers and *m*-xylylenediamine.

3.9 Synthesis of polyurethane-ureas without metal in the main chain

Polyurethane-ureas without metal in the main chain were synthesized from the reaction between *m*-xylylenediamine and different prepolymers at the mole ratio of 1:1 as shown in Scheme 3.13. The polymers obtained from *m*-xylylenediamine with PB900 and PP1000 are coded as Xy-PB900 and Xy-PP1000, respectively. After the reaction was completed, the polyurethane-urea was purified by dissolving in DMSO. Then, the mixture of methanol and water was added in this solution to precipitate the polyurethane-urea.



Scheme 3.13 Synthesis of polyurethane-ureas without metal in the main chain

3.10 Characterization of polyurethane-ureas without metal in the main chain

Both polyurethane-ureas without metal in the main chain were characterized using IR spectroscopy and IR spectra of these polyurethane-ureas are shown in Figure 3.12.

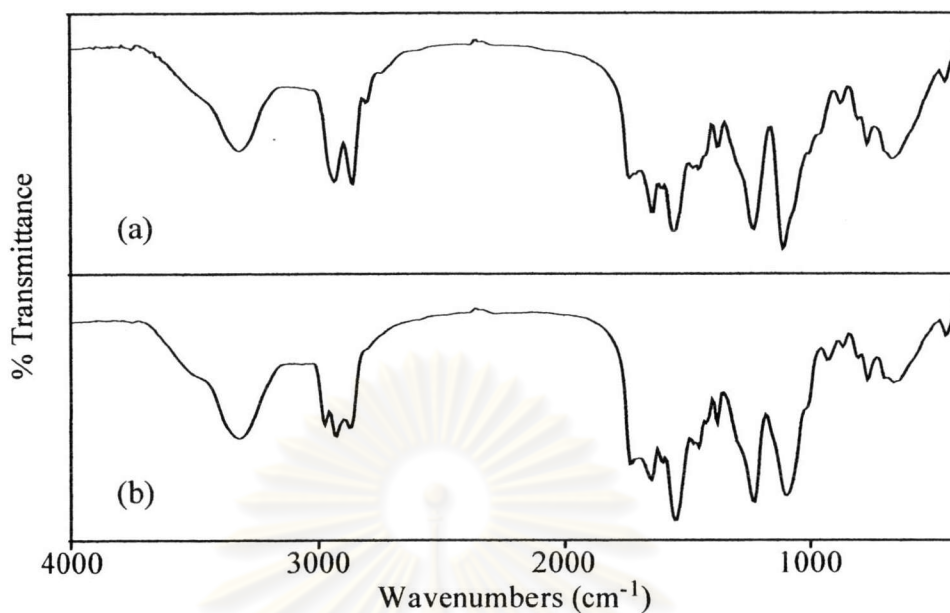


Figure 3.12 IR spectra of (a) Xy-PB900 (b) Xy-PP1000

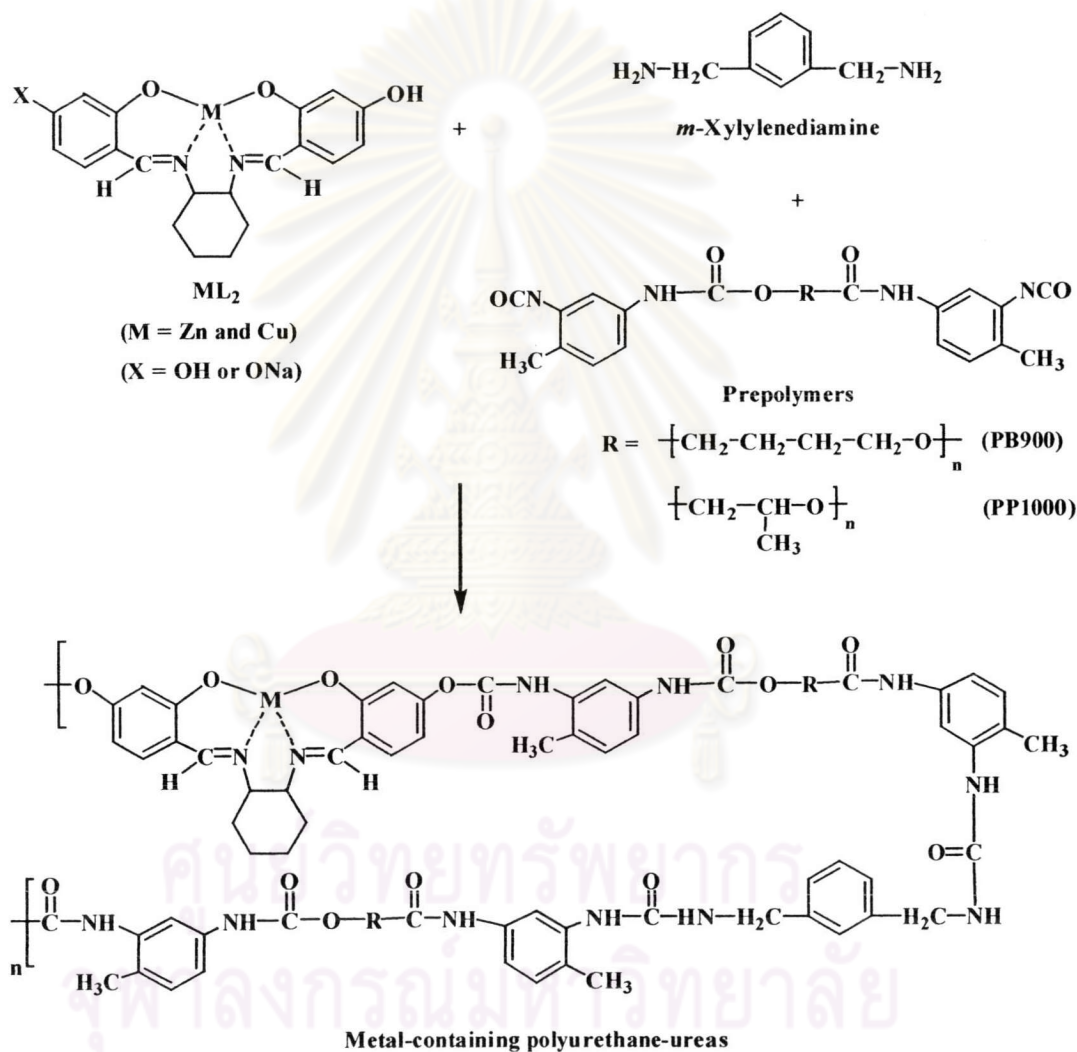
The IR spectrum of Xy-PB900 [Figure 3.12(a)] shows the NH stretching at 3319 cm^{-1} and the aliphatic CH stretching at 2930 and 2857 cm^{-1} . The carbonyl (C=O) stretching of urethane linkage (-NCOO-) and urea linkage (-NCON-) appears at 1728 and 1639 cm^{-1} , respectively. The benzene CH bending appears at 770 cm^{-1} .

The IR spectrum of Xy-PP1000 [Figure 3.12(b)] is similar to that of Xy-PB900. The spectrum shows the NH stretching at 3319 cm^{-1} and the aliphatic CH stretching at 2971 , 2926 and 2867 cm^{-1} . The carbonyl (C=O) stretching of urethane linkage (-NCOO-) and urea linkage (-NCON-) appears at 1728 and 1645 cm^{-1} , respectively. The benzene CH bending appears at 770 cm^{-1} .

3.11 Synthesis of polyurethane-ureas containing 4,4'-dihydroxysalicyclohexane metal complexes

Polyurethane-ureas containing 4,4'-dihydroxysalicyclohexane metal complexes were synthesized from the reaction between *m*-xylylenediamine, 4,4'-dihydroxysalicyclohexane metal complexes (ML_2) and different prepolymers at the mole ratio of 0.5:0.5:1 as shown in Scheme 3.14. The polymers obtained from

m-xylylenediamine, ZnL_2 or CuL_2 and PB900 are coded as Zn-Xy-PB900 and Cu-Xy-PB900, respectively and the polymers obtained from *m*-xylylenediamine, ZnL_2 or CuL_2 and PP1000 are coded as Zn-Xy-PP1000 and Cu-Xy-PP1000, respectively. After the reaction was completed, the polyurethane-urea was purified by dissolving in DMSO. Then, the mixture of methanol and water was added to this solution to precipitate the polyurethane-urea.



Scheme 3.14 Synthesis of polyurethane-ureas containing 4,4'-dihydroxycyclohexane metal complexes

3.12 Characterization of polyurethane-ureas containing 4,4'-dihydroxysalicyclohexane metal complexes

All polyurethane-ureas containing 4,4'-dihydroxysalicyclohexane metal complexes were characterized using IR spectroscopy and IR spectra of these polyurethane-ureas are shown in Figure 3.13.

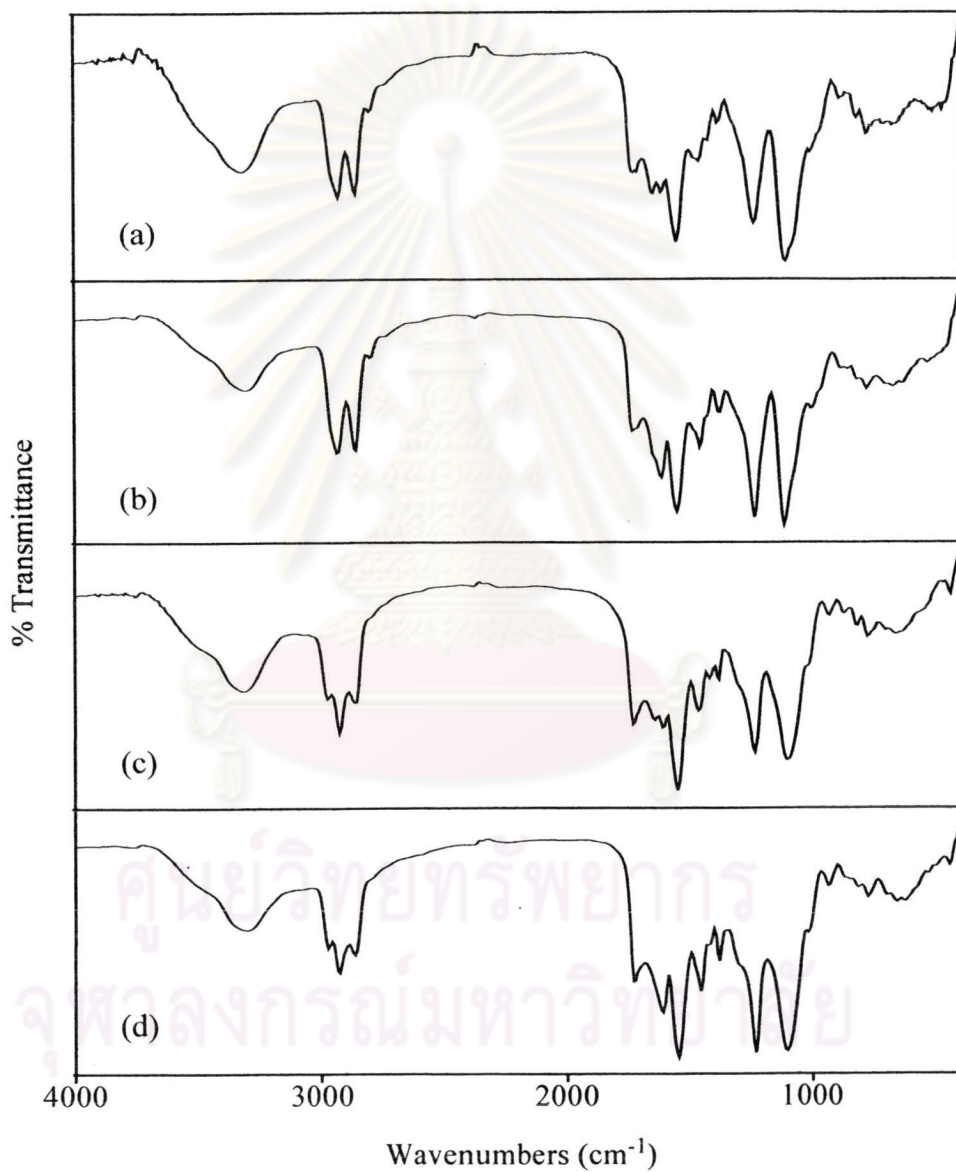


Figure 3.13 IR spectra of (a) Zn-Xy-PB900 (b) Cu-Xy-PB900 (c) Zn-Xy-PP1000 (d) Cu-Xy-PP1000

IR spectrum of Zn-Xy-PB900 [Figure 3.13(a)] shows the NH stretching at 3323 cm^{-1} and the aliphatic CH stretching at 2924 and 2856 cm^{-1} . The carbonyl (C=O) stretching of urethane linkage (-NCOO-) and urea linkage (-NCON-) appears at 1722 and 1639 cm^{-1} , respectively. The imine (C=N) absorption band appears at 1602 cm^{-1} and benzene CH bending appears at 769 cm^{-1} .

IR spectrum of Cu-Xy-PB900 [Figure 3.13(b)] is similar to that of Zn-Xy-PB900. The spectrum shows the NH stretching at 3311 cm^{-1} and the aliphatic CH stretching at 2929 and 2857 cm^{-1} . The carbonyl (C=O) stretching of urethane linkage (-NCOO-) appears at 1725 cm^{-1} and urea linkage (-NCON-) appears as a shoulder at 1645 cm^{-1} due to the overlapping with imine (C=N) absorption band. The imine (C=N) absorption band appears at 1607 cm^{-1} and benzene CH bending appears at 771 cm^{-1} .

IR spectrum of Zn-Xy-PP1000 [Figure 3.13(c)] shows the NH stretching at 3323 cm^{-1} and the aliphatic CH stretching at 2971 , 2923 and 2859 cm^{-1} . The carbonyl (C=O) stretching of urethane linkage (-NCOO-) and urea linkage (-NCON-) appears at 1725 and 1639 cm^{-1} , respectively. The imine (C=N) absorption band appears at 1602 cm^{-1} and benzene CH bending appears at 769 cm^{-1} .

IR spectrum of Cu-Xy-PP1000 [Figure 3.13(d)] is similar to that of Zn-Xy-PP1000. The spectrum shows the NH stretching at 3311 cm^{-1} and the aliphatic CH stretching at 2967 , 2926 and 2864 cm^{-1} . The carbonyl (C=O) stretching of urethane linkage (-NCOO-) appears at 1724 cm^{-1} but urea linkage (-NCON-) is not observed since it overlaps with the imine (C=N) absorption band that results in a broad absorption band. The imine (C=N) absorption band appears at 1607 cm^{-1} and benzene CH bending appears at 771 cm^{-1} .

3.13 Solubility

Solubility of polyurethanes containing 4,4'-dihydroxysalicyclohexane metal complexes, polyurethane-ureas containing 4,4'-dihydroxysalicyclohexane metal complexes and polyurethane-ureas without metal in the main chain was tested in various polar and nonpolar solvents.

Table 3.8 Solubility of all synthesized polymers^a

Polymers	Hexane	Toluene	Diethyl ether	CH ₂ Cl ₂	CHCl ₃	THF	CH ₃ OH	DMF	DMSO	H ₂ O
Zn-PB900	-	-	-	±	±	±	±	+	+	-
Cu-PB900	-	-	-	±	±	±	±	+	+	-
Zn-PP1000	-	-	-	±	±	±	±	+	+	-
Cu-PP1000	-	-	-	±	±	±	±	+	+	-
Zn-Xy-PB900	-	-	-	±	±	±	±	+	+	-
Cu-Xy-PB900	-	-	-	±	±	±	±	+	+	-
Zn-Xy-PP1000	-	-	-	±	±	±	±	+	+	-
Cu-Xy-PP1000	-	-	-	±	±	±	±	+	+	-
Xy-PB900	-	-	-	-	±	±	±	+	+	-
Xy-PP1000	-	-	-	-	±	±	±	+	+	-

-, Insoluble; ±, partial soluble; + soluble

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

From the results of solubility testing, all polymers are not soluble in hexane, toluene, diethyl ether and H₂O but soluble in DMF and DMSO. Most polymers are partial soluble in CH₂Cl₂, CHCl₃, CH₃OH and THF except Xy-PB900 and Xy-PP1000 which are not soluble in CH₂Cl₂.

These results indicated that the solubility of all polymers are better than that reported in the literature¹⁹ which might be due to the introduction of soft segment of PB or PP prepolymers into the polymer structure.

3.14 Thermal analysis

Before investigating the thermal property, all polymers were heated at 120°C for 2 hours in an oven to remove moisture. In the next step, the polymers were heated at 170°C for 1, 3 and 6 hours in the oven and their weight loss were obtained.

Table 3.9 shows the weight loss of all polymers after heating at 170°C for 1, 3 and 6 hours. Xy-PB900 shows higher thermal stability than Xy-PP1000 and therefore this result suggests that the polymers obtained from PB900 is more thermally stable than those obtained from PP1000 which might be due to the structure of PP1000 is more steric than PB900 and therefore difficult to form a closed chain packing. Comparing between the polymers obtained from different metal complexes, Cu-PB900 shows higher thermal stability than Zn-PB900 and Cu-PP1000 shows higher thermal stability than Zn-PP1000. Therefore, it can be concluded that the polymers having copper complex in the main chain is more thermally stable than those having zinc complex in the main chain because the presence of odd electrons in the outermost orbital enhances the metallic bond of CuL_2 . Furthermore, metal-containing polymers show higher thermal stability than polymers without metal in the main chain and the polymers having higher amount of metal complexes in the main chain show higher thermal stability.

Cu-PB900 shows the highest thermal stability and therefore this polymer was chosen for TGA experiment. TGA curve of Cu-PB900 is shown in Figure 3.14. The initial decomposition temperature (IDT) of Cu-PB900 is 263°C while another metal-containing polyurethanes and polyurethane-ureas reported in the literature⁴⁻⁷ show the IDTs in the range between 178-272°C. The residual weight at 800°C of Cu-PB900 is 9.4% corresponded to copper oxide and char formed at this temperature while another metal-containing polyurethanes and polyurethane-ureas reported in the literature⁵⁻⁷ have the residual weight at 800°C between 2.6-9.5%. Possible mechanism of

degradation proceeded via urethane scission to give isocyanate and hydroxyl components (Scheme 3.15).

Table 3.9 Weight loss of the polymers at 170°C

Polymers	% Weight of ML ₂ in polymer	% Weight loss		
		1 h	3 h	6 h
Zn-PB900	32	6.1	12.7	16.1
Cu-PB900	32	5.4	7.7	9.1
Zn-PP1000	29	9.4	16.5	20.4
Cu-PP1000	29	8.1	12.7	16.6
Zn-Xy-PB900	18	6.8	14.4	19.0
Cu-Xy-PB900	18	5.9	8.7	11.7
Zn-Xy-PP1000	16	9.9	18.0	21.7
Cu-Xy-PP1000	16	8.7	14.6	18.4
Xy-PB900	0	13.0	20.1	24.7
Xy-PP1000	0	15.1	25.0	28.5

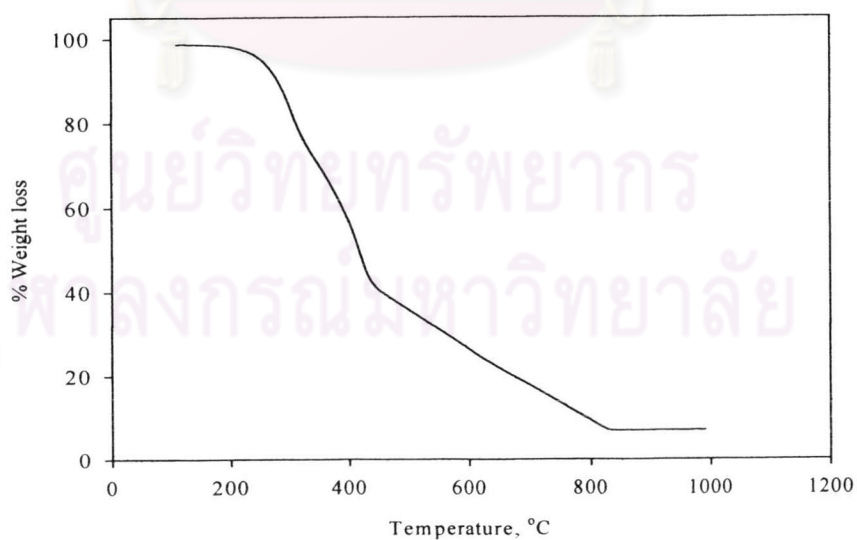
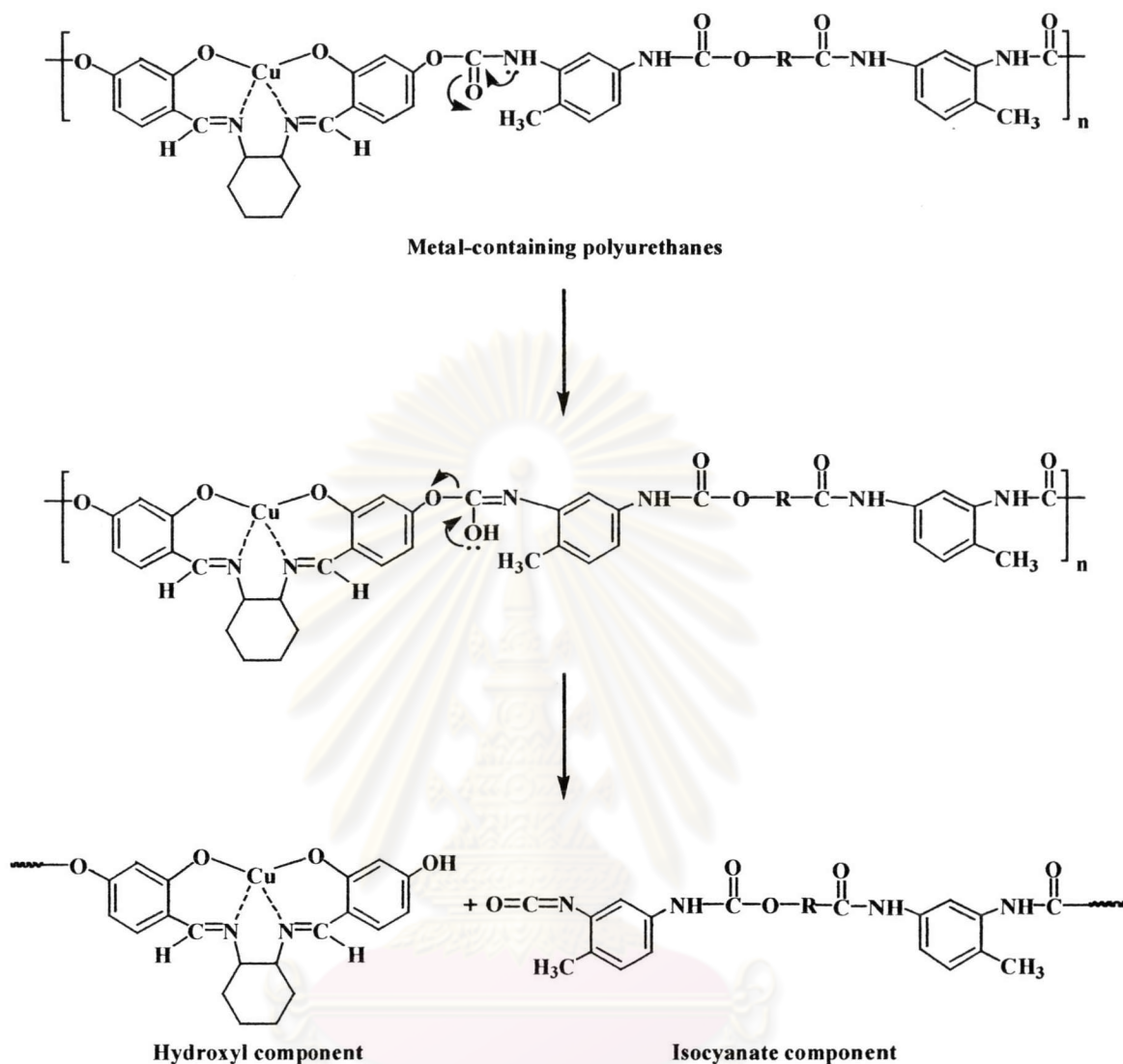


Figure 3.14 TGA curve of Cu-PB900



Scheme 3.15 Initial thermal degradation of Cu-PB900

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