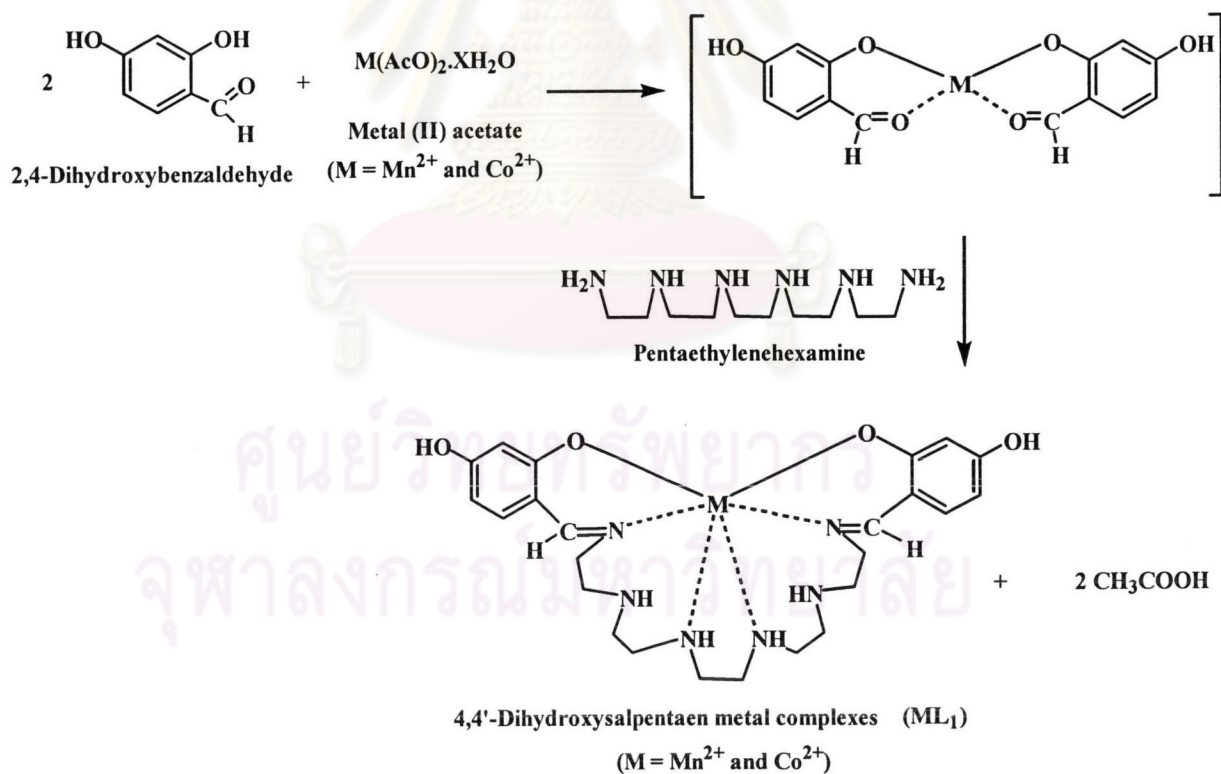


CHAPTER III

RESULTS AND DISCUSSION

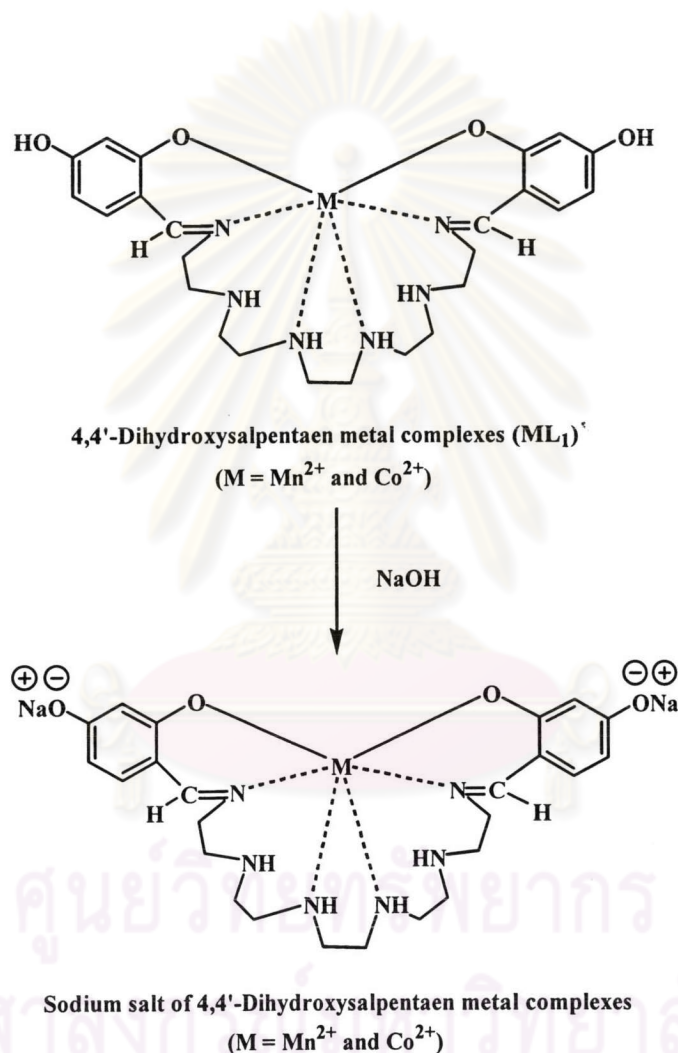
3.1 Synthesis of 4,4'-dihydroxysalpentaen metal complexes (ML_1)

4,4'-Dihydroxysalpentaen metal complexes were synthesized from 2,4-dihydroxybenzaldehyde, metal (II) acetate (where $M = Mn^{2+}$ and Co^{2+}) and pentaethylenhexamine. The reaction between 2,4-dihydroxybenzaldehyde and metal (II) acetate in methanol formed a template intermediate. Subsequently, the solution of pentaethylenhexamine was then added to obtain 4,4'-dihydroxysalpentaen metal complexes (Scheme 3.1).



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

After addition of pentaethylenhexamine, the reaction mixture was neutralized by NaOH solution. The obtained complexes were not soluble in any organic solvents including DMF and DMSO. This might be because NaOH formed sodium salt of these complexes instead of neutralization with acetic acid in the mixture (Scheme 3.2). Therefore, the possible products were sodium salts of 4,4'-dihydroxysalpentaen metal complexes.



Scheme 3.2 Possible reaction between 4,4'-dihydroxysalpentaen metal complexes and NaOH

The other bases, Na_2CO_3 , KOH and K_2CO_3 , were used instead of NaOH to improve the solubility of these metal complexes. It was expected that these bases would undergo neutralization with acetic acid and would not form sodium or potassium salts with the metal complexes. Therefore, the major products should be the metal complexes which should be soluble in DMF and DMSO. Table 3.1 shows the solubility of metal complexes obtained from neutralization with various bases.

Table 3.1 Solubility of ML_1 obtained from using various bases^a

Metal complexes	Bases	Solvents			
		DMF	DMF/80°C	DMSO	DMSO/80°C
MnL_1	NaOH	-	-	-	+
	NaHCO_3	-	-	+	+
	KOH	+	+	+	++
	K_2CO_3	-	+	+	+
CoL_1	NaOH	-	-	-	-
	NaHCO_3	-	-	-	+
	KOH	-	+	+	+
	K_2CO_3	-	+	+	++

-, insoluble; +, partial soluble; ++, soluble

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

From Table 3.1, the bases chosen for the synthesis of MnL_1 and CoL_1 were KOH and K_2CO_3 , respectively.

3.1.1 Characterization of 4,4'-dihydroxypentaen metal complexes

The obtained complexes were characterized by IR and elemental analysis. The IR spectra of MnL_1 and CoL_1 are shown in Figure 3.1.

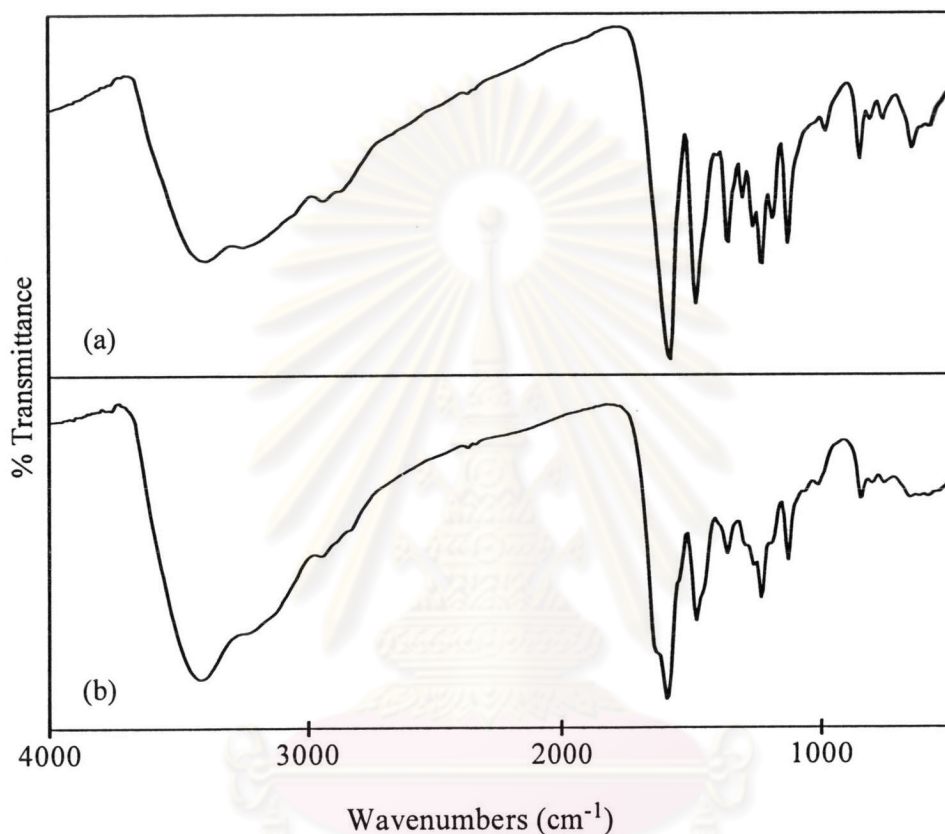


Figure 3.1 IR spectra of (a) MnL_1 (b) CoL_1

IR spectrum of MnL_1 in Figure 3.1 (a) exhibits an absorption band of OH stretching at 3392 cm^{-1} and NH stretching at 3240 cm^{-1} . The C=N peak overlaps with aromatic C=C stretching at 1576 cm^{-1} . The bands at 981 and 852 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 3415 cm^{-1} and NH stretching at 3230 cm^{-1} . The C=N peak at 1632 cm^{-1} appears as a shoulder with aromatic C=C stretching at 1587 cm^{-1} . The bands at 1006

and 842 cm^{-1} correspond to the characteristic absorption peak of aromatic bending of 1,2,4-trisubstituted benzene.

Elemental analysis data of both MnL_1 and CoL_1 do not agree with the calculated values as shown in Table 3.2. This result suggests that the obtained product is the mixture of ML_1 and potassium salt of ML_1 which occurs through the same reaction as in the case of ML_1 sodium salt (Scheme 3.2).

Table 3.2 Elemental analysis data of ML_1

Metal complexes	%C found (cald.)	%H found (cald.)	%N found (cald.)
MnL_1	50.45 (54.85)	5.31 (6.52)	15.63 (15.99)
CoL_1	47.51 (54.44)	3.86 (6.47)	12.41 (15.87)

Since ML_1 could not be obtained in good purity, the new tetradentate Schiff base metal complexes, 4,4'-dihydroxysalicyclohexane metal complexes (ML_2), were chosen for this research.

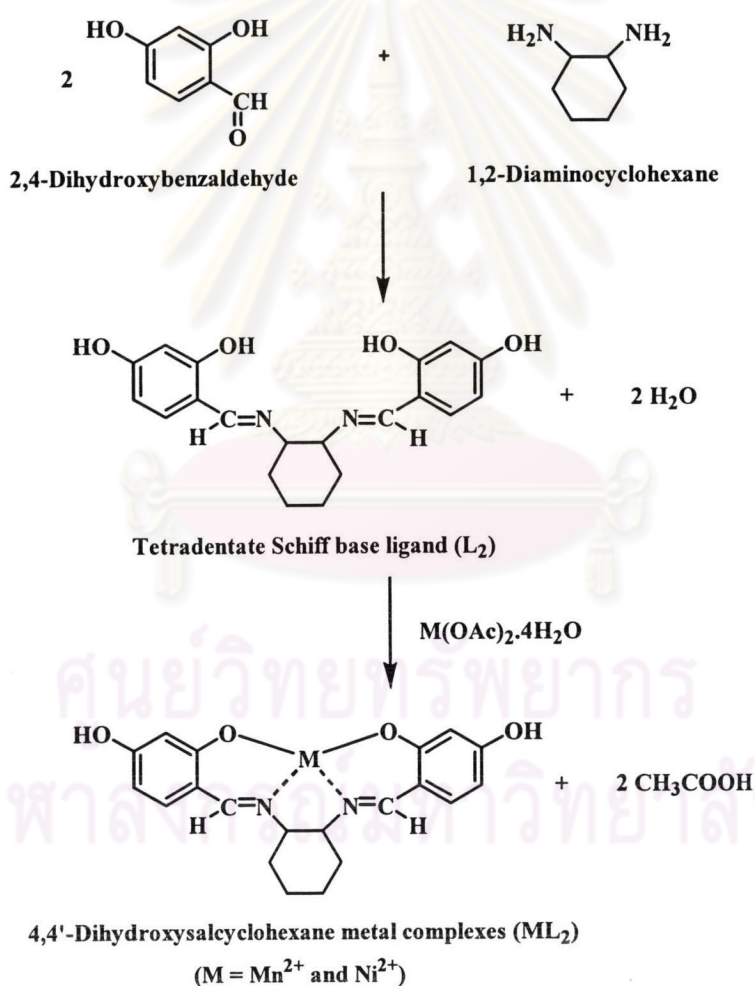
3.2 Synthesis of 4,4'-dihydroxysalicyclohexane metal complexes (ML_2)

3.2.1 Synthesis of 4,4'-dihydroxysalicyclohexane manganese complex (MnL_2)

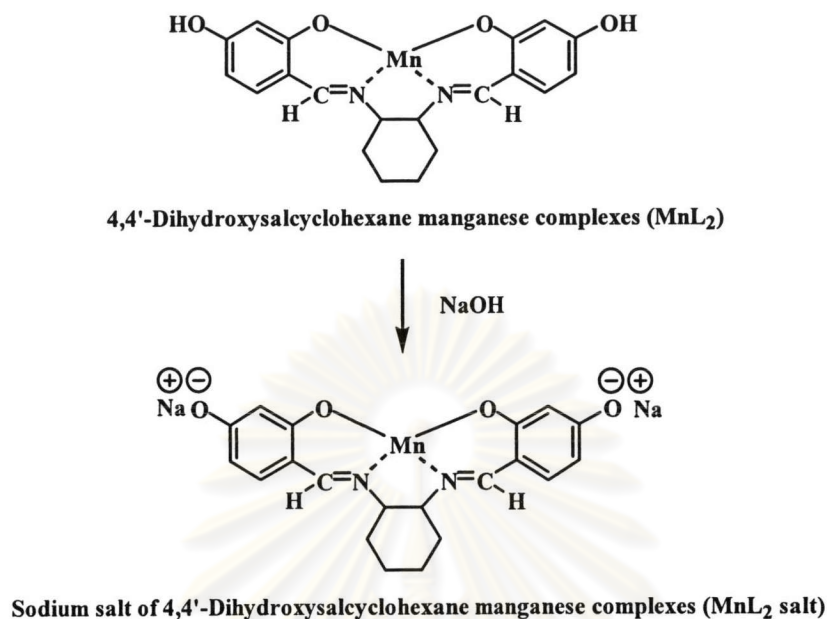
4,4'-Dihydroxysalicyclohexane manganese complex (MnL_2) was synthesized using two methods as follows:

The first method was a two step reaction (Scheme 3.3). The ligand L_2 was prepared from the reaction between 2,4-dihydroxybenzaldehyde and 1,2-diaminocyclohexane. The lone pair electron on the nitrogen of amine undergoes reaction with carbonyl carbon of aldehyde followed by the loss of water to give Schiff base ligand (L_2). The ligand L_2 was kept in methanolic solution and used in the

synthesis of MnL_2 without purification. MnL_2 was synthesized by addition of manganese (II) acetate tetrahydrate into the methanolic solution of the ligand L_2 . The ratio of 2,4-dihydroxybenzaldehyde : manganese acetate : 1,2-diaminocyclohexane employed was 2 : 1 : 1. After neutralization of the reaction mixture with NaOH, the brown powder precipitated immediately from the reaction mixture. This brown powder might occur from the reaction between MnL_2 and NaOH to yield MnL_2 salt as shown in Scheme 3.4. This MnL_2 salt was removed by filtration. Then, the filtrate was kept at room temperature overnight to obtain dark brown powder of MnL_2 . The yield of MnL_2 was 34%.



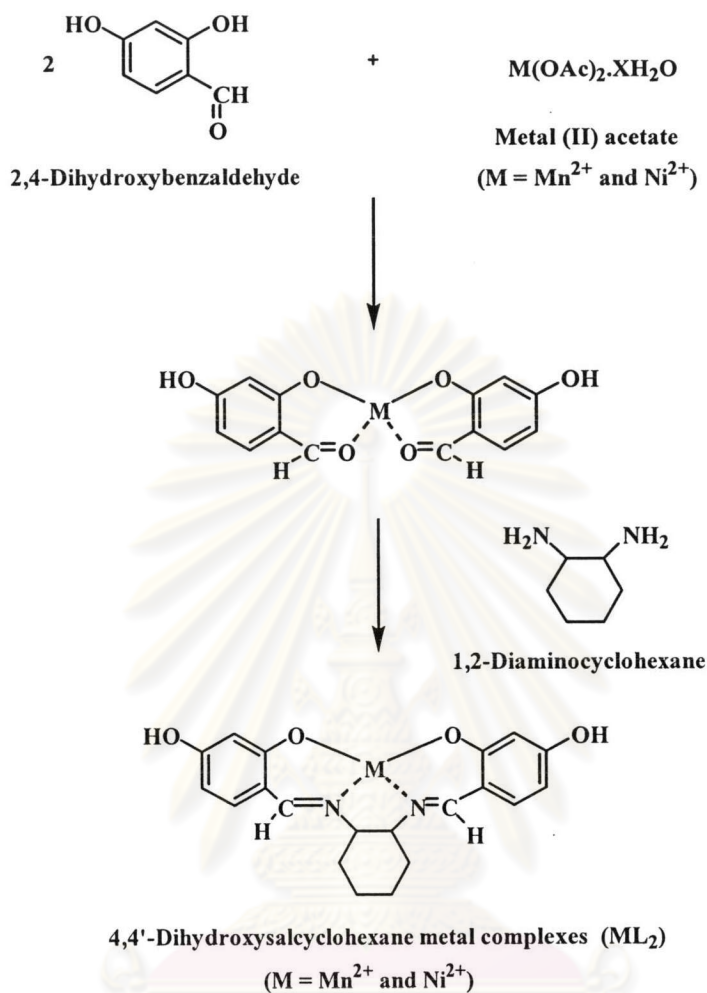
Scheme 3.3 Preparation of 4,4'-dihydroxysalicyclohexane metal complexes (ML_2) by two step reaction



Scheme 3.4 Possible reaction between MnL_2 and NaOH to yield MnL_2 salt

The second method in the preparation of MnL_2 was a one step reaction²¹. First, 2,4-dihydroxybenzaldehyde and manganese (II) acetate was mixed to form a template intermediate. 1,2-Diaminocyclohexane was then added to obtain MnL_2 as shown in Scheme 3.5.

The ratio of 2,4-dihydroxybenzaldehyde : metal acetate : 1,2-diaminocyclohexane employed was 2 : 1 : 1. After adding sodium hydroxide to neutralize the reaction mixture, the brown powder precipitated immediately and it was removed by filtration. This might be because NaOH formed sodium salt of MnL_2 instead of neutralization with acetic acid (Scheme 3.4). The filtrate was allowed to stand at room temperature for 24 hours and dark brown crystals of MnL_2 were obtained. The yield of MnL_2 was 49%.



Scheme 3.5 Preparation of ML_2 by one step reaction

From these results, the one step reaction and the mole ratio of 2,4-dihydroxybenzaldehyde : manganese (II) acetate tetrahydrate : 1,2-diaminocyclohexane as 2 : 1 : 1 was chosen for the synthesis of MnL_2 .

3.2.2 Synthesis of 4,4'-dihydroxysalicyclohexane nickel complex (NiL₂)

4,4'-Dihydroxysalicyclohexane nickel complex was also synthesized using two methods as in the case of MnL₂. The first method was a two step reaction. The ligand L₂ was prepared from the reaction between 2,4-dihydroxybenzaldehyde and 1,2-diaminocyclohexane (Scheme 3.3). The ligand L₂ was kept in methanolic solution and used in the synthesis of NiL₂ without purification.

In the next step, nickel (II) acetate tetrahydrate was added into the methanolic solution of the ligand L₂ to form NiL₂. The ratio of 2,4-dihydroxybenzaldehyde : nickel (II) acetate : 1,2-diaminocyclohexane employed was 2 : 1 : 1. After neutralization of the reaction mixture with NaOH, the orange powder precipitated immediately from the reaction mixture and this might be the sodium salt of NiL₂. This orange powder was then isolated by filtration. The filtrate was kept standing at room temperature overnight to obtain dark orange powder of NiL₂.

The second method was a one step reaction as described in the synthesis of MnL₂. 2,4-Dihydroxybenzaldehyde and nickel (II) acetate was mixed to form a template intermediate. 1,2-Diaminocyclohexane was then added to obtain NiL₂ (Scheme 3.5). This reaction was done by varying the amount of starting materials. The mole ratios of 2,4-dihydroxybenzaldehyde : nickel acetate : 1,2-diaminocyclohexane were varied from 2 : 1 : 1, 2 : 1 : 2, 2 : 1 : 3 and 2 : 1 : 4. The results are shown in Table 3.3.

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Table 3.3 Synthesis results of NiL₂ using a one step reaction

Mole ratio of 2,4-dihydroxybenzaldehyde : nickel (II) acetate tetrahydrate : 1,2-diaminocyclohexane	Results
2 : 1 : 1	<ul style="list-style-type: none"> • Orange powder precipitated immediately after addition of NaOH • Green powder precipitated after standing at room temperature overnight
2 : 1 : 2	<ul style="list-style-type: none"> • Nothing precipitated after addition of NaOH • Brown green powder precipitated after standing at room temperature overnight
2 : 1 : 3	<ul style="list-style-type: none"> • Nothing precipitated after addition of NaOH • No precipitation after standing at room temperature for 3 nights
2 : 1 : 4	<ul style="list-style-type: none"> • Nothing precipitated after addition of NaOH • Dark orange crystals of NiL₂ were obtained after the solution was kept at room temperature for 20 hours

From these results, the one step reaction and the mole ratio of 2,4-dihydroxybenzaldehyde : nickel (II) acetate tetrahydrate : 1,2-diaminocyclohexane as 2 : 1 : 4 was chosen for synthesis NiL₂. The yield of NiL₂ was 85%.

3.2.3 Characterization of 4,4'-dihydroxysalicyclohexane metal complexes

The metal complexes were characterized by IR, elemental analysis and MALDI-TOF MS. IR spectra of MnL_2 and NiL_2 are shown in Figure 3.2.

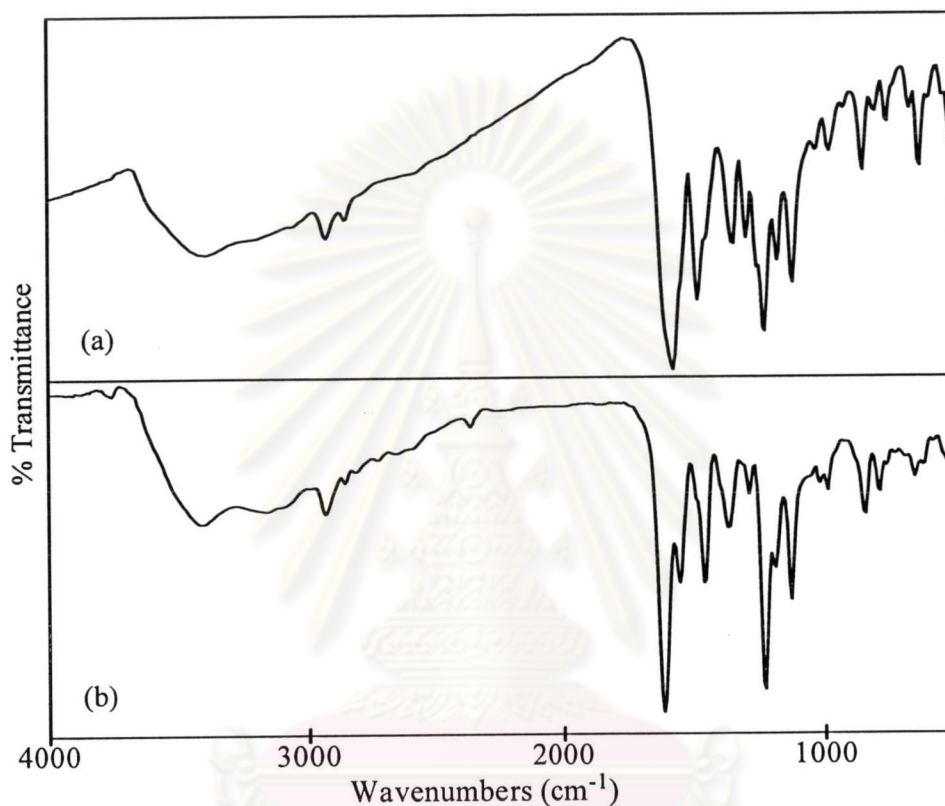


Figure 3.2 IR spectra of (a) MnL_2 (b) NiL_2

IR spectrum of MnL_2 in Figure 3.2 (a) exhibits an absorption band of OH stretching at 3387 cm^{-1} . The C=N peak appears as a shoulder due to overlapping with aromatic C=C stretching at 1575 cm^{-1} . The bands at 975 and 857 cm^{-1} correspond to the characteristic absorption peak of aromatic bending of 1,2,4-trisubstituted benzene.

IR spectrum of NiL_2 in Figure 3.2 (b) exhibits an absorption band of OH stretching and aromatic C=C stretching peaks at 3407 and 1550 cm^{-1} , respectively. The important band of C=N appears at 1611 cm^{-1} . The bands at 990 and 846 cm^{-1}

correspond to the characteristic absorption peak of aromatic bending of 1,2,4-trisubstituted benzene.

The metal complexes were characterized using MALDI-TOF MS. Figures 3.3 and 3.4 show MS spectra of MnL_2 and NiL_2 , respectively.

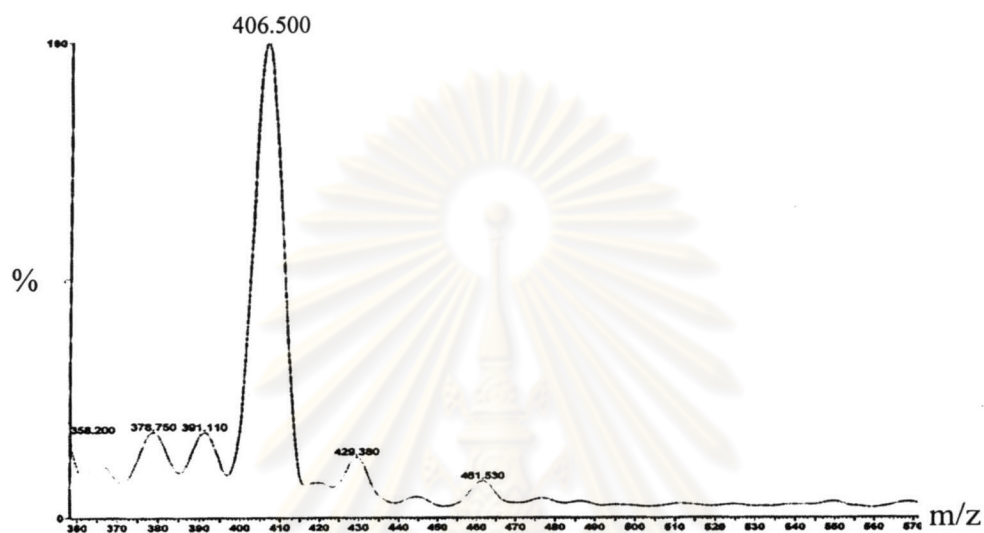


Figure 3.3 MS spectrum of MnL_2

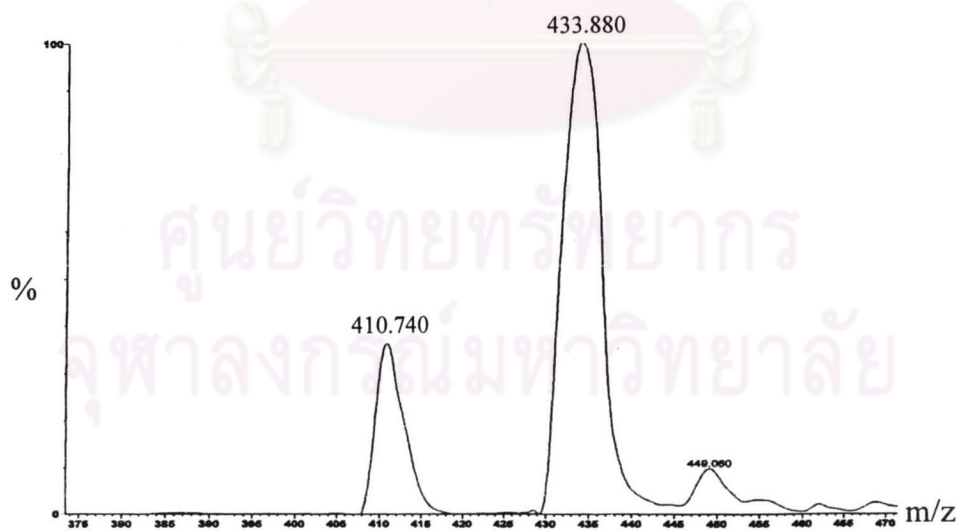


Figure 3.4 MS spectrum of NiL_2

The MS spectrum of MnL_2 shows peaks at 385.2, 378.8, 391.1, 406.5, 429.4 and 461.5. The highest peak occurs at 406.5 which is $C_{20}H_{20}MnN_2O_4$.

The MS spectrum of NiL_2 shows peaks at 410.7, 433.9 and 449.1. The highest peak occurs at 433.9 which is $C_{20}H_{19}NiN_2O_4Na$. The second peak appears at 410.7 which is $C_{20}H_{20}NiN_2O_4$.

From MALDI-TOF MS, the main structures of MnL_2 and NiL_2 are $C_{20}H_{20}MnN_2O_4$ and $C_{20}H_{19}N_2NiO_4Na$ (Figure 3.5), respectively.

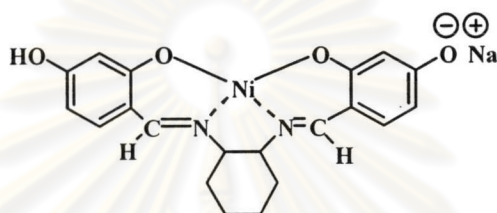


Figure 3.5 The main structure of NiL_2

Elemental analysis data of the metal complexes are shown in Table 3.4. It indicates that the metal complexes contain water and methanol in their molecules. Analytical data show that the experimentally determined percentage values of carbon, hydrogen and nitrogen are within the calculated values.

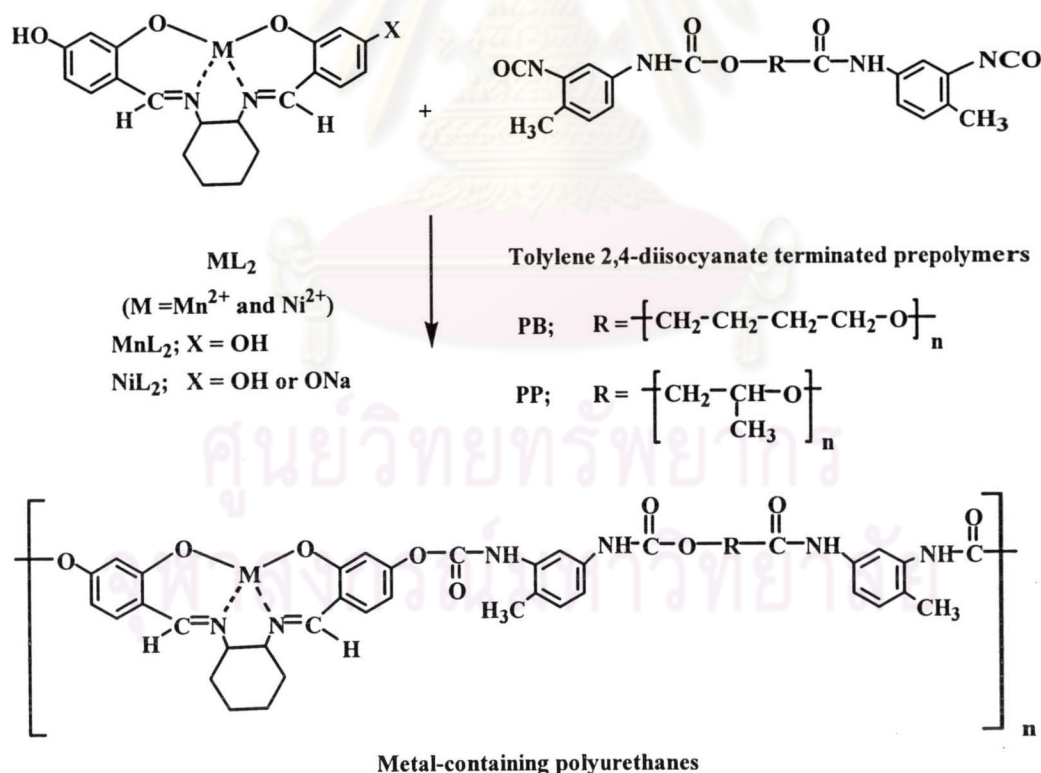
Table 3.4 Elemental analysis data of ML_2

Metal complexes	Formula	Analytical data found (calculated) (%)			Molecular weight
		C	H	N	
MnL_2	$C_{20}H_{20}MnN_2O_4 \cdot 1.5H_2O$	55.30 (55.50)	5.34 (5.52)	6.45 (6.88)	434.34
NiL_2	$C_{20}H_{19}N_2NiO_4Na \cdot CH_3OH$	54.70 (54.23)	5.68 (4.98)	6.07 (6.02)	465.10

NiL₂ has good solubility in both DMF and DMSO. MnL₂ also has good solubility in DMSO and has partial solubility in DMF. Both of them are not soluble in methanol.

3.3 Synthesis of metal-containing polyurethanes

Metal-containing polyurethanes were synthesized by the reaction of ML₂ with prepolymers. The prepolymers employed were tolylene 2,4-diisocyanate terminated poly(1,4-butanediol) that has a molecular weight 900 (PB) and tolylene 2,4-diisocyanate terminated poly(propylene glycol) that has a molecular weight 1000 (PP). The metal complexes have two phenolic groups which are able to react with isocyanate groups of prepolymers. This reaction was done at the mole ratio of prepolymers : ML₂ = 1 : 1. Scheme 3.6 shows the synthesis of metal-containing polyurethanes.



Scheme 3.6 Synthesis of metal-containing polyurethanes

3.3.1 Synthesis of manganese-containing polyurethanes from MnL_2 and prepolymers

3.3.1.1 Synthesis of Mn-PB from the reaction between MnL_2 and PB

IR spectroscopy was used to investigate the polymerization reaction between MnL_2 and PB to give the polymer Mn-PB. The reaction progress could be observed by disappearance of NCO absorption band in the prepolymers at 2275 cm^{-1} . Since the polymerization between diisocyanates and diols is normally done at the temperature range $80 - 120^\circ\text{C}$ [5-8, 12-16], therefore the polymerization temperature for MnL_2 and PB was chosen at 120°C without use of catalyst.

The NCO peak at 2275 cm^{-1} disappeared after heating for 2 hours (Figure 3.6) which suggested that the reaction was completed. The reaction time was taken for 24 hours to ensure the completeness of the reaction. Mn-PB was dissolved in DMSO, precipitated by addition of a mixture of methanol and water and dried *in vacuo* for 24 hours. IR spectrum of Mn-PB (Figure 3.7) shows the NH stretching at 3388 cm^{-1} and the aliphatic CH stretching at 2928 and 2858 cm^{-1} . The carbonyl (C=O) stretching of urethane linkage (-NCOO-) appears at 1721 cm^{-1} . The imine (C=N) absorption band appears at 1606 cm^{-1} . The aromatic C=C peak appears at 1544 cm^{-1} . The yield of Mn-PB was 20 %. Therefore, the catalyst was used to obtain higher yield of Mn-PB.

Dibutyltin dilaurate was then employed as a catalyst and the polymerization temperature used was 90°C . In this reaction condition, the reaction progress could not be followed since the polymer was tough and therefore could not be ground for the preparation of IR sample. The reaction mixture was heated for 17 hours to complete the polymerization reaction. The polymer was then purified by dissolving in DMSO and a mixture of methanol and water was added to precipitate the polymer. The polymer was filtered, washed several times with methanol and dried *in vacuo* for 24 hours. The yield of Mn-PB obtained by use of the catalyst was 80%. IR spectrum of Mn-PB obtained by the use of a catalyst is the same as that obtained without catalyst (Figure 3.7).

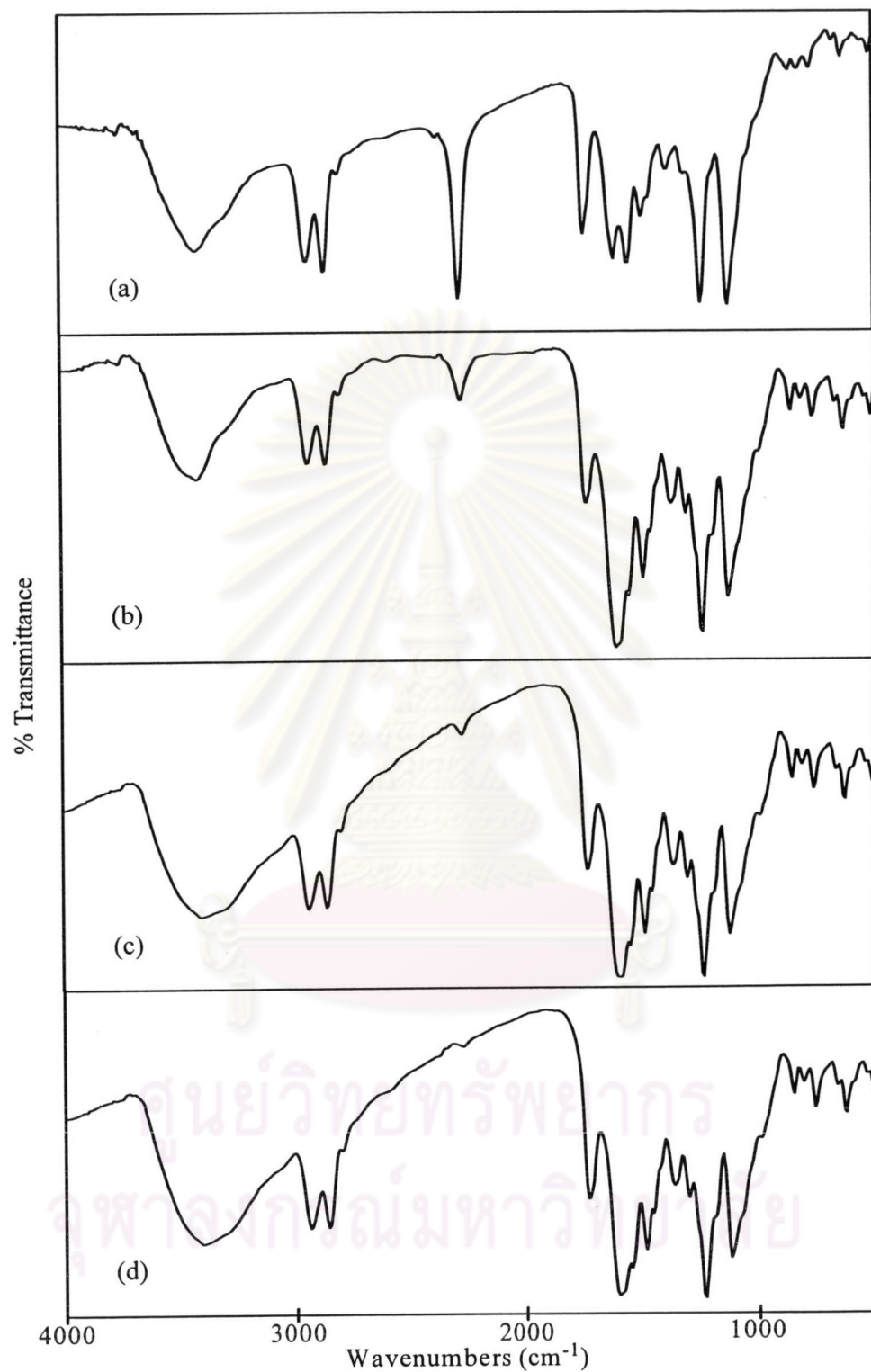


Figure 3.6 The progress of the reaction between MnL_2 and PB without using catalyst
(a) before heating (b) after heating at $120^\circ C$ for 30 min (c) after 1 h
(d) after 2 h

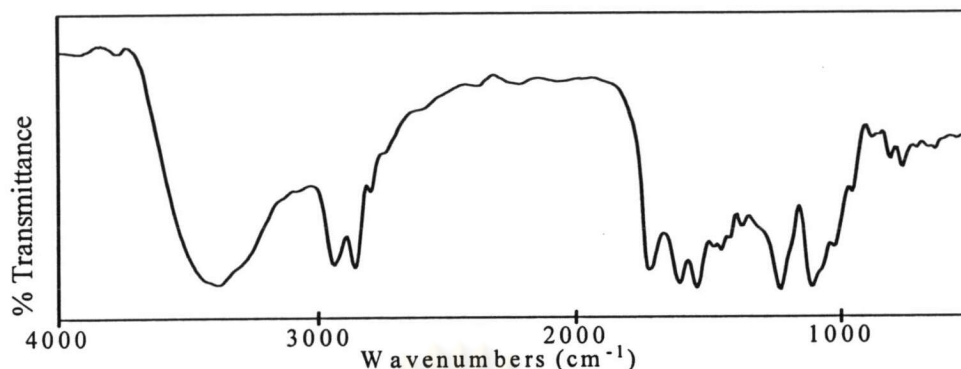


Figure 3.7 IR spectrum of Mn-PB obtained from the reaction between MnL_2 and PB without use of catalyst

3.3.1.2 Synthesis of Mn-PP from the reaction between MnL_2 and PP

Mn-PP was prepared using the same procedure as Mn-PB and dibutyltin dilaurate was employed as a catalyst. The yield of Mn-PP was 50%.

IR spectrum of Mn-PP (Figure 3.8) shows the NH stretching at 3338 cm^{-1} and the aliphatic CH stretching at 2926 and 2859 cm^{-1} . The carbonyl (C=O) stretching of urethane linkage (-NCOO-) appears at 1724 cm^{-1} . The imine absorption appears as a shoulder due to the overlapping with aromatic C=C peak. The aromatic (C=N) peak appears at 1545 cm^{-1} .

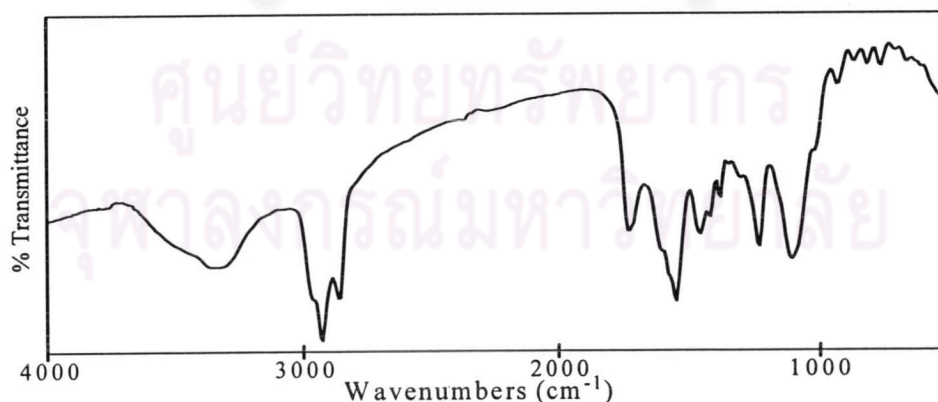


Figure 3.8 IR Spectrum of Mn-PP obtained from the reaction between MnL_2 and PP in the presence of catalyst

3.3.2 Synthesis of nickel-containing polyurethanes from NiL₂ and prepolymers

3.3.2.1 Synthesis of Ni-PB from the reaction between NiL₂ and PB

The polymerization temperature was chosen at 120°C and the catalyst was not used. The reaction progress was followed using IR spectroscopy. The completeness of the reaction could be observed by disappearance of NCO absorption band in prepolymers at 2275 cm⁻¹. From Figure 3.9, the NCO peak at 2275 cm⁻¹ disappeared after heating at 120°C for 6 hours.

After heating the reaction mixture for 24 hours, the crude product was dissolved in DMSO and the product was precipitated by addition of a mixture of methanol and water. The appearance of received products separated in 2 parts, dark orange powder and white elastomer. The white elastomer could not dissolve in DMSO and this result suggested that the white elastomer was a crosslinked polymer. The dark orange powder was NiL₂ and the white elastomer occurred from the reaction between PB and moisture in air to give a crosslinked polymer (Scheme 3.7)[1]. Their IR spectra (Figures 3.10 and 3.11) confirmed these results. Therefore, addition of a catalyst to the reaction between NiL₂ and PB was needed.

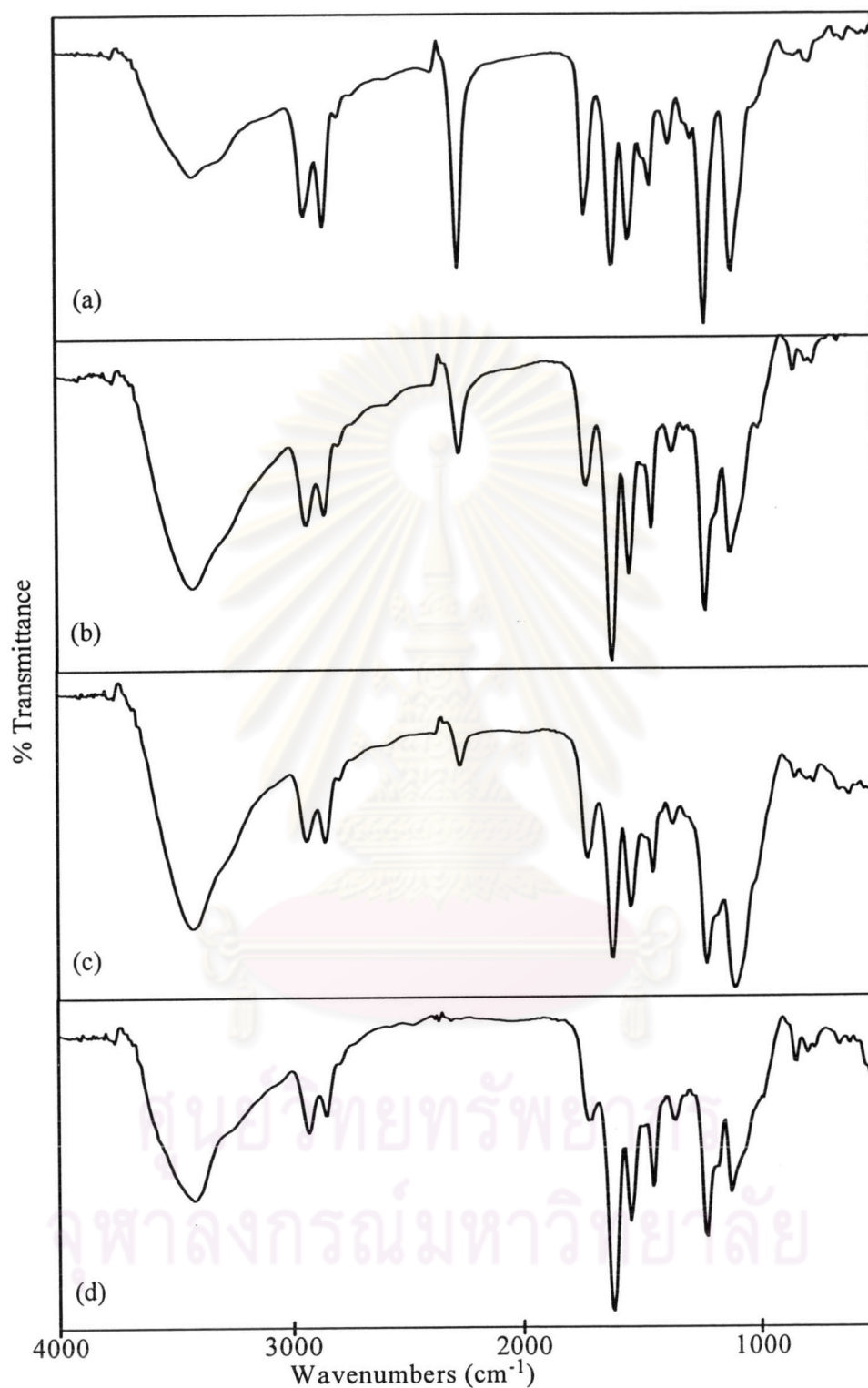


Figure 3.9 The progress of the reaction between NiL_2 and PB without using catalyst (a) before heating (b) after heating at 120°C for 1 h (c) after 3 h (d) after 6 h

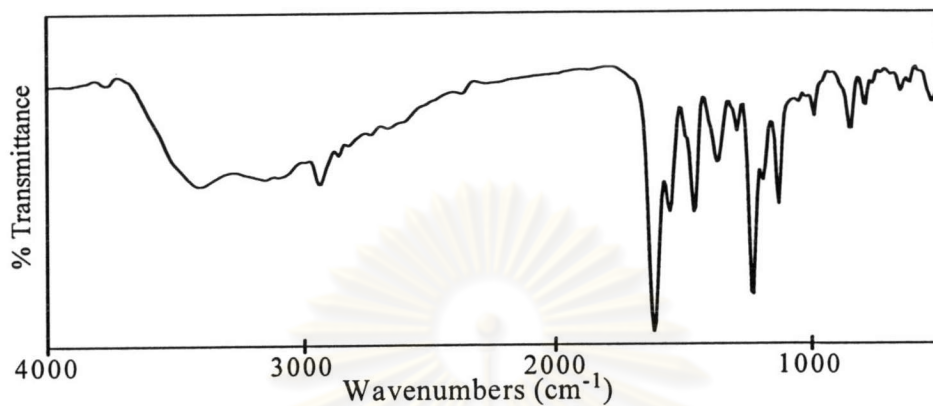


Figure 3.10 IR spectrum of dark orange powder of NiL₂ obtained from the reaction between NiL₂ and PB

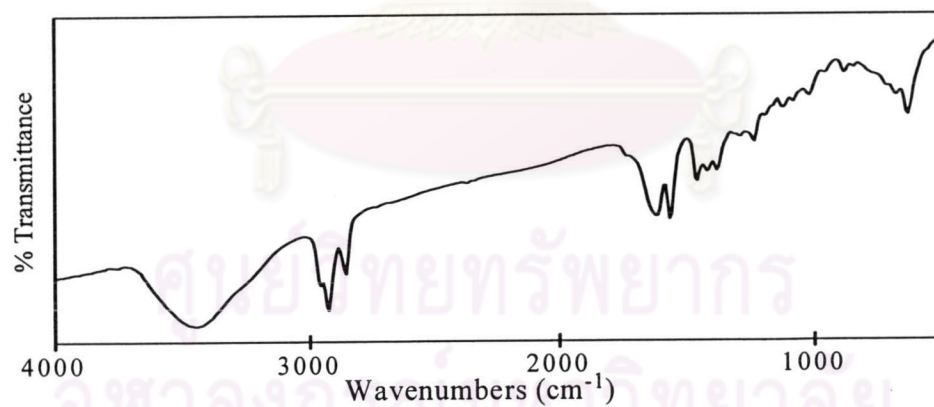
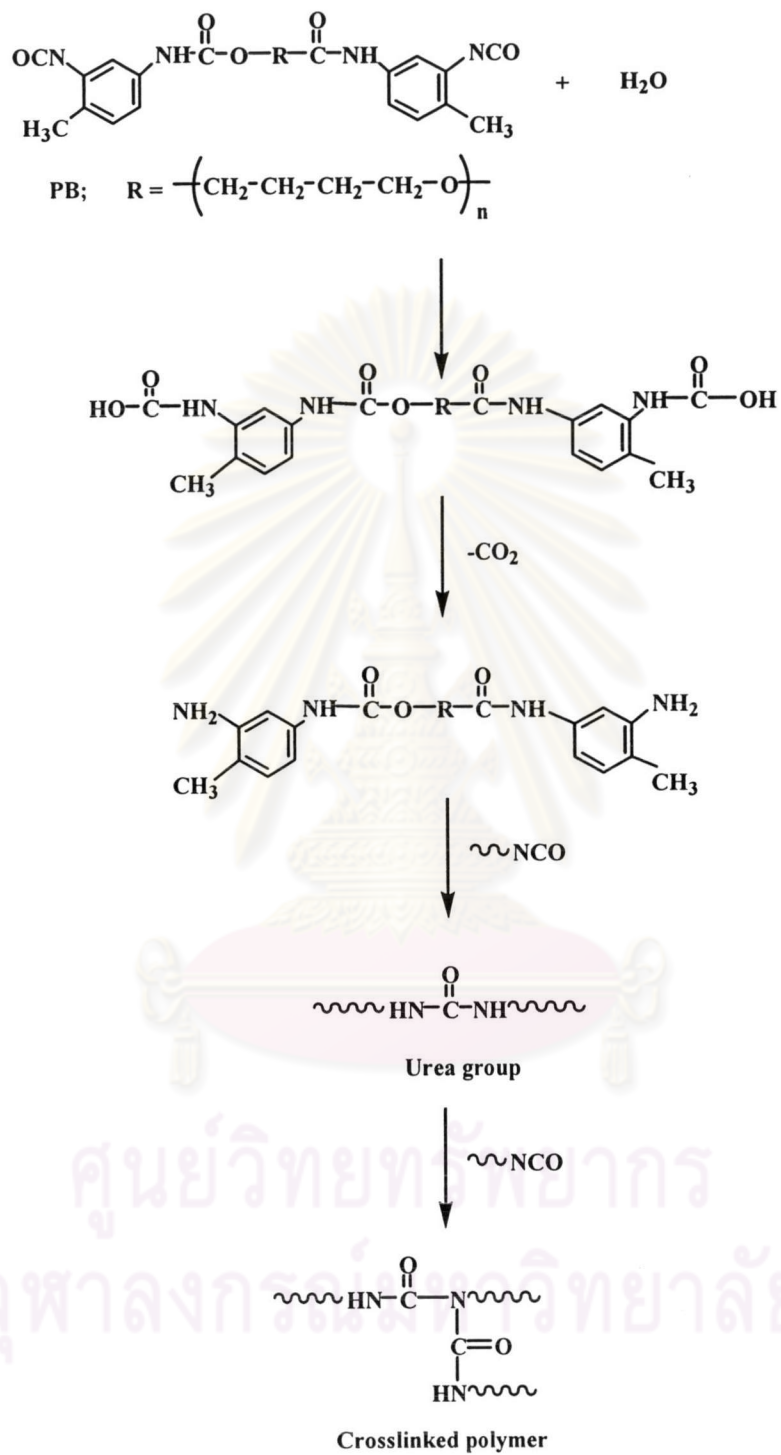


Figure 3.11 IR spectrum of a crosslinked polymer resulting from the reaction between PB and moisture in air



Scheme 3.7 Reaction between PB and moisture in air[1]

Dibutyltin dilaurate was then employed as a catalyst and the polymerization temperature used was 90°C. In this reaction condition, the reaction progress could not be followed since the polymer was tough and therefore could not be ground for the preparation of IR sample. The reaction mixture was heated for 17 hours to complete the polymerization reaction. The polymer was then purified by dissolving in DMSO and a mixture of methanol and water was added to precipitate the polymer. The polymer was filtered, washed several times with methanol and dried *in vacuo* for 24 hours. The yield of Ni-PB obtained was 45%.

The IR spectrum of Ni-PB (Figure 3.12) shows the NH stretching at 3371 cm^{-1} and the aliphatic CH stretching at 2932 and 2859 cm^{-1} . The carbonyl (C=O) stretching of urethane linkage (-NCOO-) appears at 1715 cm^{-1} . The imine (C=N) absorption band appears at 1612 cm^{-1} . The aromatic C=C peak appears at 1542 cm^{-1} .

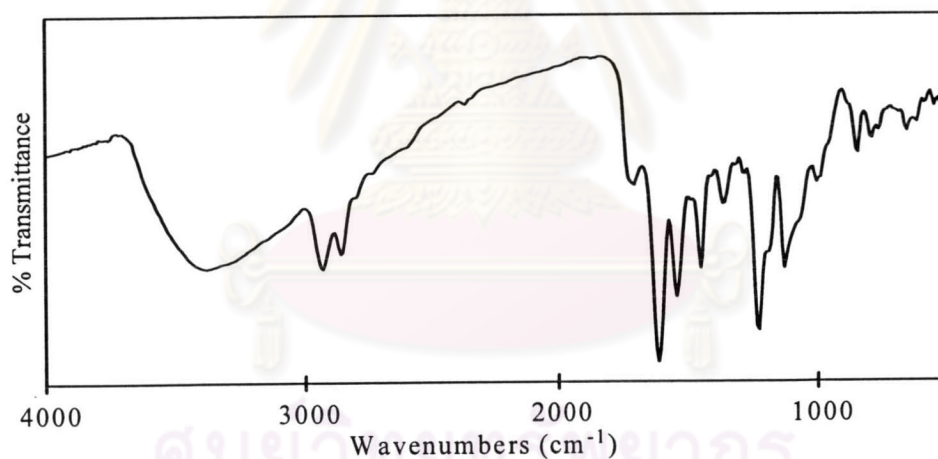


Figure 3.12 IR spectrum of Ni-PB obtained from the reaction between NiL_2 and PB in the presence of catalyst

3.3.2.2 Synthesis of Ni-PP from the reaction between NiL₂ and PP

Ni-PP was prepared using the same procedure as Ni-PB and dibutyltin dilaurate was employed as a catalyst. The yield of Ni-PP was 59%.

The IR spectrum of Ni-PP (Figure 3.13) shows the NH stretching at 3345 cm⁻¹ and the aliphatic CH stretching at 2925 and 2858 cm⁻¹. The carbonyl (C=O) stretching of urethane linkage (-NCOO-) appears at 1721 cm⁻¹. The imine (C=N) absorption band appears at 1613 cm⁻¹. The aromatic C=C peak appears at 1547 cm⁻¹.

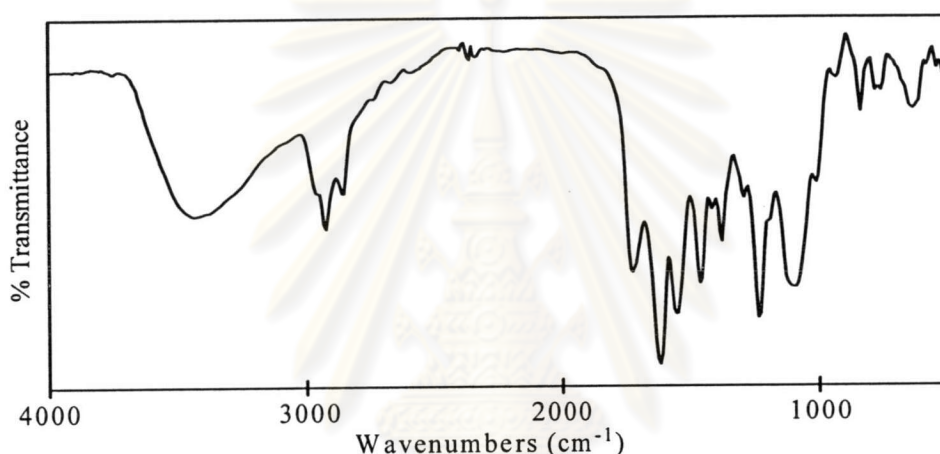
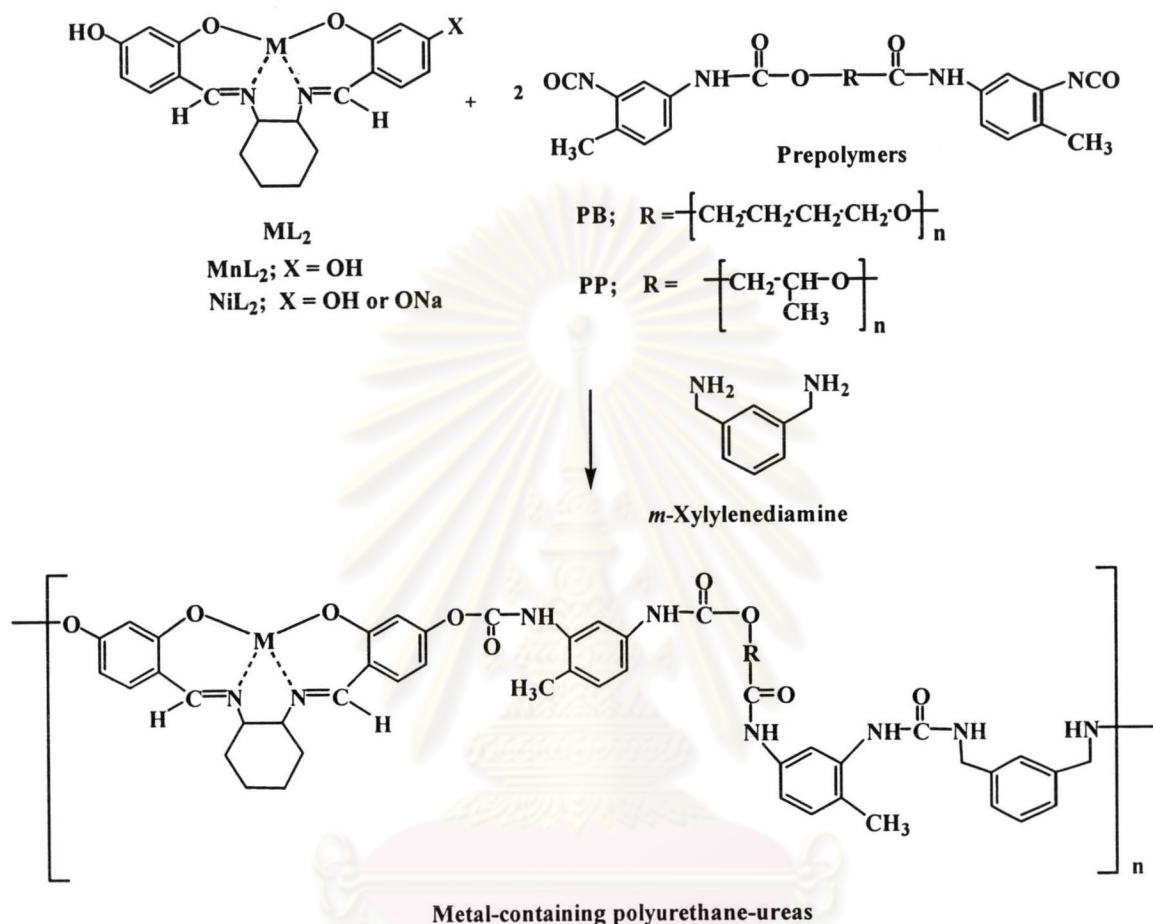


Figure 3.13 IR spectrum of Ni-PP obtained from the reaction between NiL₂ and PP in the presence of catalyst

3.4 Synthesis of metal-containing polyurethanes-ureas

Metal-containing polyurethane-ureas were synthesized from ML₂, *m*-xylylenediamine and PB or PP prepolymers (Scheme 3.8). These polymers were synthesized to compare their thermal properties with those of metal-containing polyurethanes which have different amount of metal complexes in the main chain. The % weight of ML₂ in the polymer was shown in Table 3.5. Polyurethane-ureas were prepared at the mole ratio of ML₂ : *m*-xylylenediamine : prepolymers = 0.5 : 0.5 : 1.

Dibutyltin dilaurate was added in these reactions as a catalyst. The polymerization was done in a hot air oven at 90°C for 17 hours.



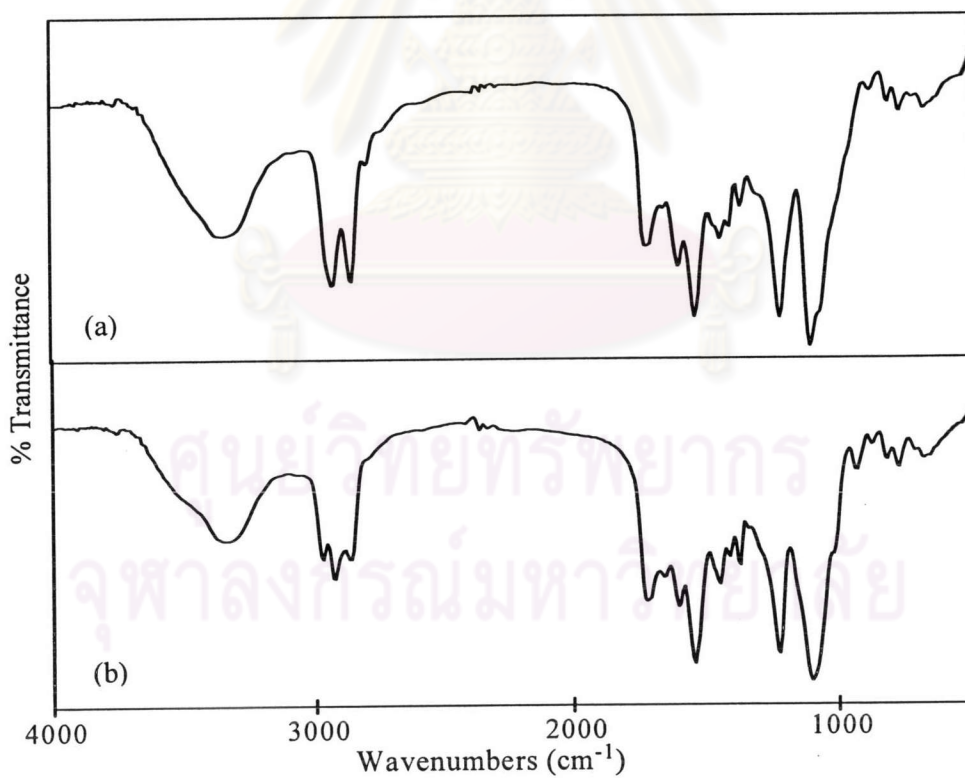
Scheme 3.8 Synthesis of metal-containing polyurethane-ureas

The polymers were purified by dissolving in DMSO and precipitated in a mixture of methanol and water. In the case of Ni-PB-X, the polymer was precipitated in cool water. The product was filtered, washed several times with methanol and dried *in vacuo* for 24 hours.

The manganese-containing polymers were brown elastomers and nickel-containing polymers were dark orange elastomers. The yields obtained for Mn-PB-X, Mn-PP-X, Ni-PB-X and Ni-PP-X were 55%, 58%, 48% and 51%, respectively. Their IR spectra are shown in Figures 3.14 - 3.15.

Table 3.5 Percent weight of ML_2 in polymers

Polymer codes	% Weight of ML_2 in polymers
Mn-PB	33
Mn-PB-X	18
Mn-PP	30
Mn-PP-X	17
Ni-PB	34
Ni-PB-X	19
Ni-PP	32
Ni-PP-X	18

**Figure 3.14** IR Spectra of manganese-containing polyurethane-ureas (a) Mn-PB-X
(b) Mn-PP-X

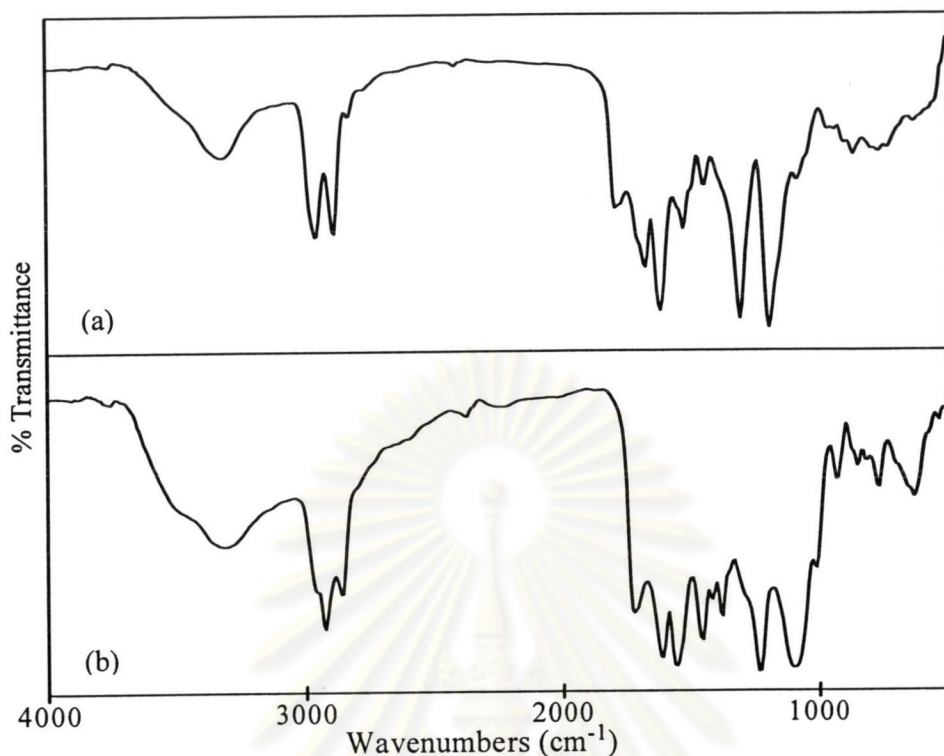


Figure 3.15 IR Spectra of nickel-containing polyurethane-ureas (a) Ni-PB-X
(b) Ni-PP-X

IR spectrum of Mn-PB-X in Figure 3.14 (a) shows the NH stretching at 3343 cm^{-1} and the aliphatic CH stretching at 2929 and 2857 cm^{-1} . The carbonyl (C=O) stretching of urethane linkage (-NCOO-) and urea linkage (-NCON-) appear at 1721 and 1658 cm^{-1} , respectively. The imine (C=N) absorption band appears at 1602 cm^{-1} .

IR spectrum of Mn-PP-X in Figure 3.14 (b) shows the NH stretching at 3338 cm^{-1} and the aliphatic CH stretching at 2971 and 2927 cm^{-1} . The carbonyl (C=O) stretching of urethane linkage (-NCOO-) and urea linkage (-NCON-) appear at 1720 and 1653 cm^{-1} , respectively. The imine (C=N) absorption band appears at 1603 cm^{-1} .

IR spectrum of Ni-PB-X in Figure 3.15 (a) 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 due to the overlapping with imine (C=N) absorption band. The imine (C=N) absorption band appears at 1607 cm^{-1} .

Dibutyltin dilaurate was used as a catalyst in these reactions. The polymer was dissolved in DMSO and precipitated in a mixture of methanol and water and dried *in vacuo* before characterization. The yield of PB-X and PP-X were 92% and 83%, respectively. Figures 3.16 (a) and 3.16 (b) show IR spectra of PB-X and PP-X, respectively.

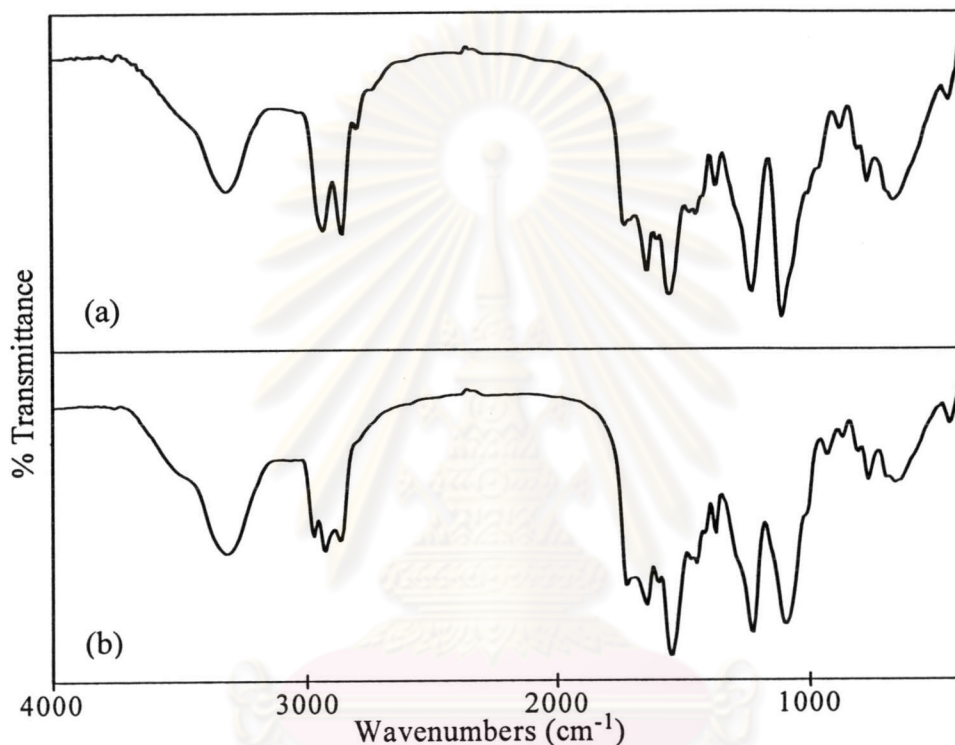


Figure 3.16 Spectra of polyureas without metal complexes in the main chain
(a) PB-X (b) PP-X

IR spectrum of PB-X in Figure 3.16 (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.

IR spectrum of PP-X in Figure 3.16 (b) shows similar spectrum to that of PB-X. The spectrum shows the NH stretching at 3319 cm^{-1} and the aliphatic CH stretching at

2971, 2926 and 2867 cm^{-1} . The carbonyl ($\text{C}=\text{O}$) stretching of urethane linkage ($-\text{NCOO}-$) and urea linkage ($-\text{NCON}-$) appears at 1728 and 1645 cm^{-1} , respectively.

3.6 Solubility of metal-containing polyurethanes, polyurethane-ureas and polyureas

The solubility of metal-containing polymers was tested in various polar and non-polar solvents. All metal-containing polyurethanes, polyurethane-ureas and polyureas without metal complexes in the main chain are soluble in DMF and DMSO. Manganese-containing polymers are less soluble than nickel-containing polymers. The solubility of metal-containing polymers is shown in Table 3.6.

Table 3.6 Solubility of metal-containing polymers^a

Polymer codes	Solvents									
	Hexane	Toluene	Diethyl ether	CHCl_3	THF	CH_2Cl_2	CH_3OH	DMF	DMSO	H_2O
Mn-PB	-	-	-	+	+	-	-	++	++	-
Mn-PB-X	-	-	-	+	+	-	-	+	++	-
Mn-PP	-	-	-	+	+	+	-	+	++	-
Mn-PP-X	-	-	-	+	+	+	-	+	++	-
Ni-PB	-	-	-	+	+	+	-	+	++	-
Ni-PB-X	-	-	-	+	+	+	-	++	++	-
Ni-PP	-	-	-	+	+	+	-	++	++	-
Ni-PP-X	-	-	-	+	+	+	-	++	++	-
PB-X	-	-	-	+	+	-	-	++	++	-
PP-X	-	-	-	+	+	-	-	++	++	-

-, insoluble; +, partial soluble; ++, soluble

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

3.7 Thermal analysis

Thermal stability was investigated by measuring weight losses of the polymers at 170°C at different times (1, 2, 3, 4, 6 and 8 h). The weight of polymers used in these experiments was 50 - 60 mg. Before testing thermal stability, all polymers were heated at 120°C for 1 hour in a hot air oven to evaporate the remaining solvents. Table 3.7 shows weight losses of polymers at different times.

Table 3.7 Weight losses of polymers at different times

Polymer codes	% Weight losses					
	1h	2h	3h	4h	6h	8h
Mn-PB	5.5	8.9	13.3	16.3	18.3	20.2
Mn-PB-X	5.1	7.9	9.6	11.5	16.2	19.2
Mn-PP	8.7	14.6	17.1	19.0	21.7	23.8
Mn-PP-X	7.8	12.0	15.2	17.3	21.4	23.2
Ni-PB	6.1	8.8	10.1	11.0	12.5	13.3
Ni-PB-X	5.5	8.9	11.3	12.6	15.0	16.3
Ni-PP	8.5	11.2	13.0	14.3	15.3	16.8
Ni-PP-X	5.2	6.6	8.6	10.4	12.8	15.0
PB-X	17.5	24.0	27.1	27.8	30.4	31.7
PP-X	17.3	24.7	28.4	31.1	34.0	35.0

Nickel-containing polymers show better thermal stability than manganese-containing polymers. M-P-X is slightly more thermally stable than M-P. M-P is expected to be more stable than M-P-X as more percent weight of ML_2 (Table 3.5) in polymer backbone. In this case, M-P-X is stabilized by more hydrogen bonding. Thermal stability of the metal-containing polymers was compared to that of the

polymers without metal which were synthesized from the reaction between *m*-xylylenediamine and PB or PP prepolymers. The result showed that metal-containing polymers exhibited better thermal stability than polymers without metal complexes.

Ni-PB was chosen for TGA study because it has the best thermal stability. The TGA thermogram and data are shown in Figure 3.17 and Table 3.8, respectively. The initial decomposition temperature (IDT) and the temperature at 50% weight loss of Ni-PB were found at 234°C and 430°C, respectively. The possible degradation of Ni-PB was shown in Scheme 3.10.

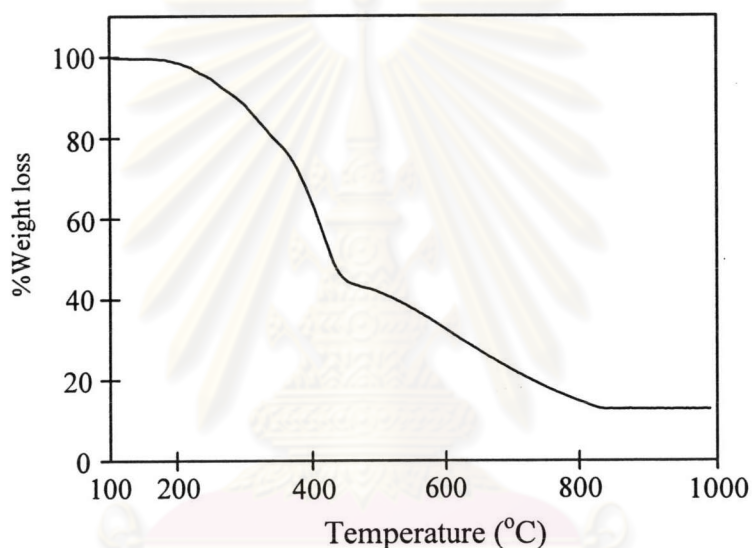
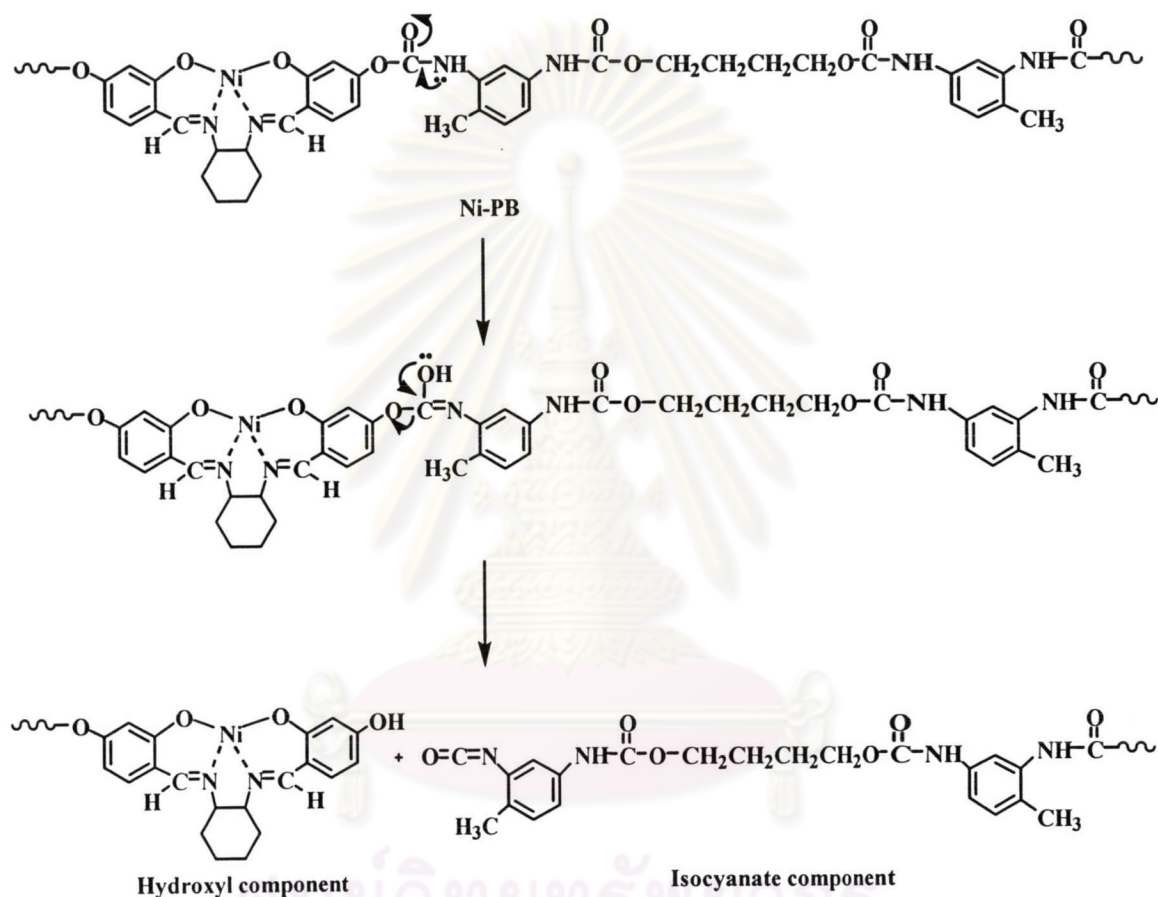


Figure 3.17 TGA thermogram of Ni-PB

Table 3.8 TGA data of Ni-PB

Polymer	% Weight loss at different temperatures (°C)							
	200	300	400	500	600	700	800	900
Ni-PB	2	11	36	58	67	77	85	87

In comparison with the previous research, the IDTs of nickel containing polyurethane-ureas[10], synthesized from Schiff base metal complexes were found between 163 - 271 °C. The temperature at 50% weight loss of these nickel containing polymers were found between 384 - 444 °C. The Ni-PB has the thermal properties in the same range as the previous research.



Scheme 3.10 Possible thermal degradation of Ni-PB