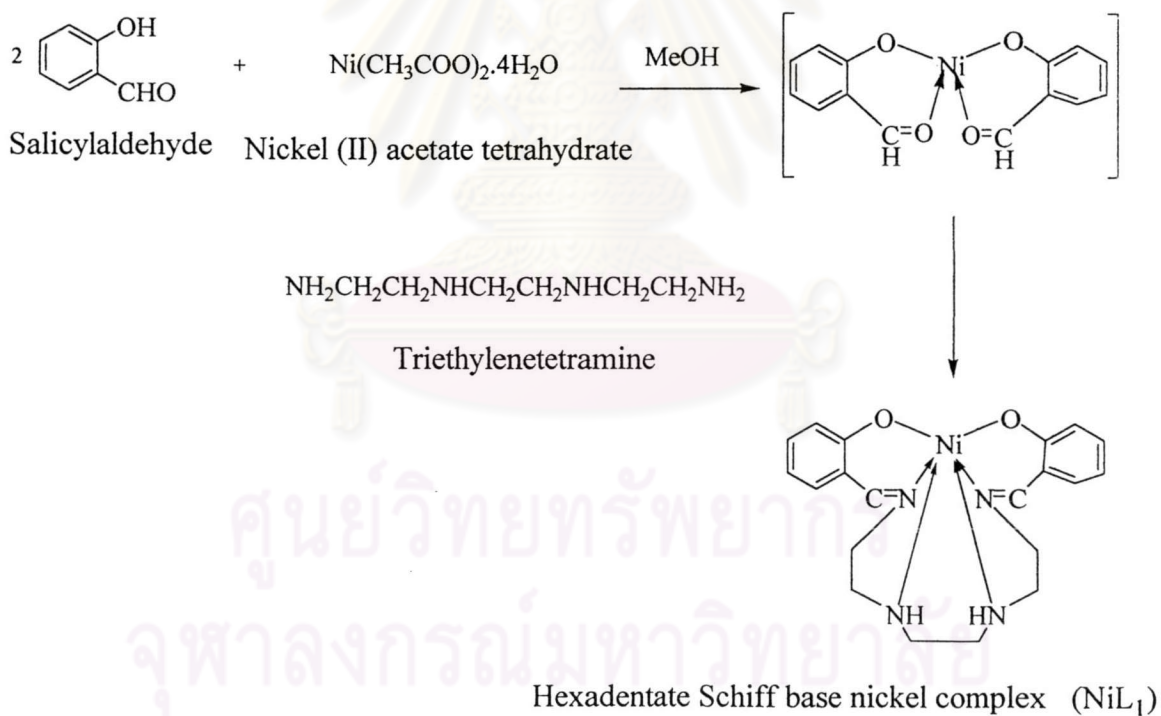


CHAPTER III

RESULTS AND DISCUSSION

3.1 Synthesis of hexadentate Schiff base nickel complex

Hexadentate Schiff base nickel complex (NiL_1) was synthesized by the reaction between salicylaldehyde and nickel (II) acetate tetrahydrate in methanol to form a template intermediate. Triethylenetetramine was then added to obtain NiL_1 (Scheme 3.1).



Scheme 3.1 Synthesis of hexadentate Schiff base nickel complex (NiL_1)

3.1.1 Characterization of NiL₁

The IR spectrum of NiL₁ in Figure 3.1 showed an absorption band of imine C=N stretching at 1642 cm⁻¹ and aromatic C-H bending at 950 cm⁻¹ which agreed with the data reported in the literature¹⁸.

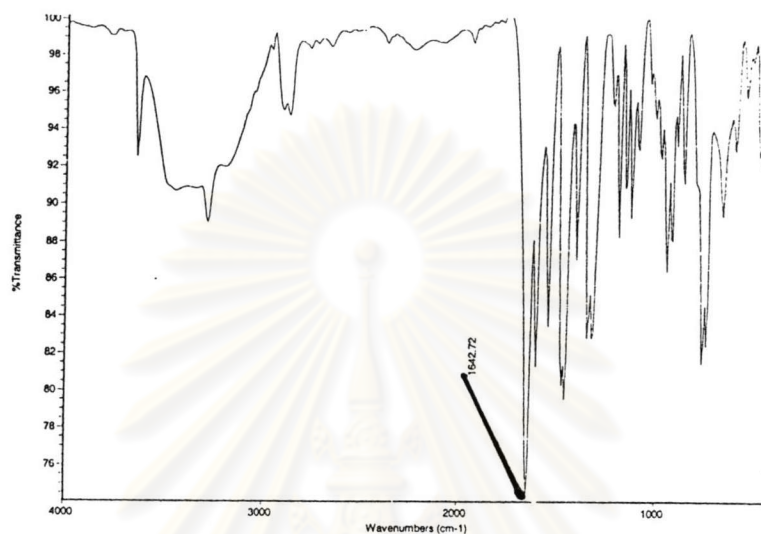


Figure 3.1 FTIR spectrum of hexadentate Schiff base nickel complex (NiL₁)

The structure of NiL₁ was determined by X-ray crystallography. The result suggested that Nickel atom in NiL₁ had an octahedral geometry¹⁸ (Figure 3.2).

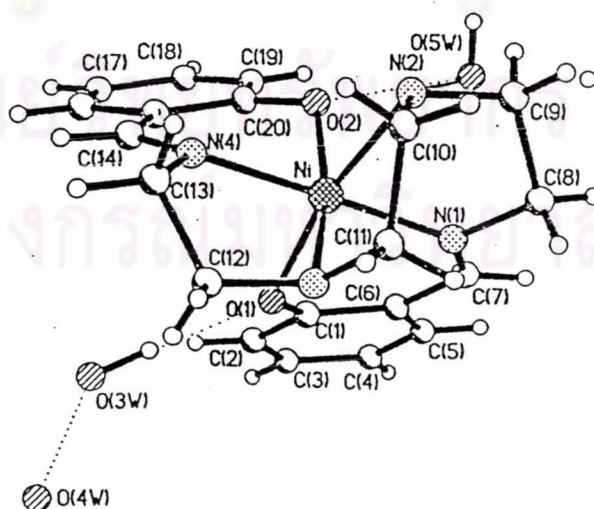


Figure 3.2 X-ray crystal structure of NiL₁

3.1.2 Thermal behavior of NiL₁

Thermal properties of NiL₁ were investigated using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

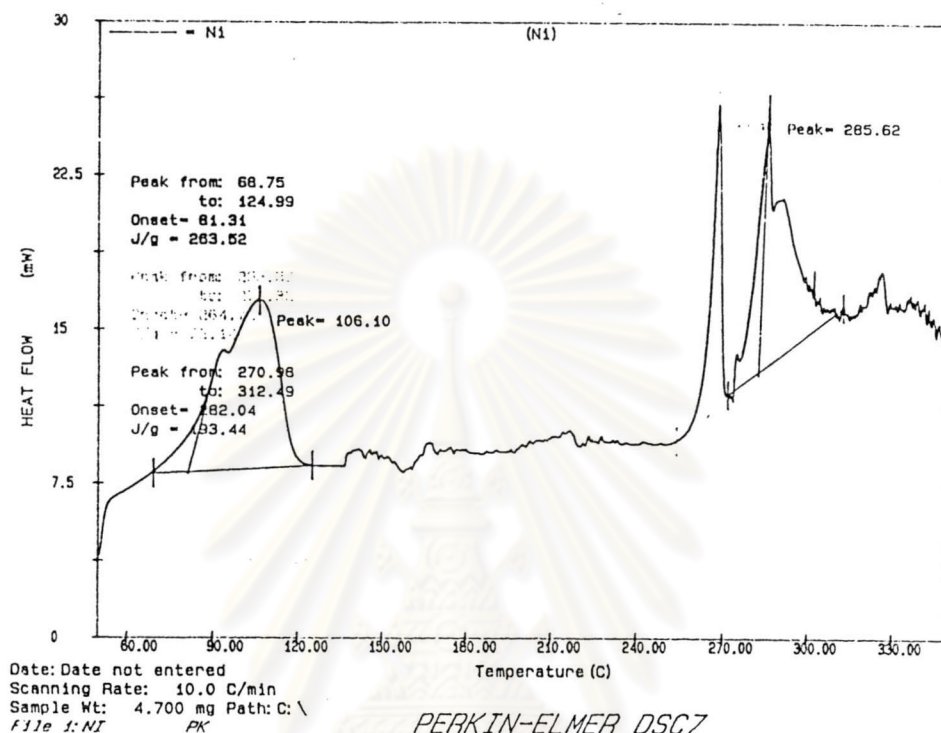


Figure 3.3 DSC thermogram of NiL₁ at a heating rate of 10 °C/min

DSC thermogram in Figure 3.3 showed a large endotherm around 106 °C and two small endotherms around 260 °C and 285.6 °C, respectively, followed by decomposition of materials.

The endothermic peak, which appeared around 106 °C, is associated with the loss of water as confirmed by TGA showed in Figure 3.4. According to endothermic peaks around 260 °C and 285.6 °C appeared on the DSC thermogram, it was possible that NiL₁ might show the liquid crystalline properties. The polarizing optical microscope (POM) was used to investigate mesogenic properties. It was found that NiL₁ did not reveal any crystal-mesophase transition at this temperature. Therefore, the POM result suggested that NiL₁ did not show liquid crystalline property.

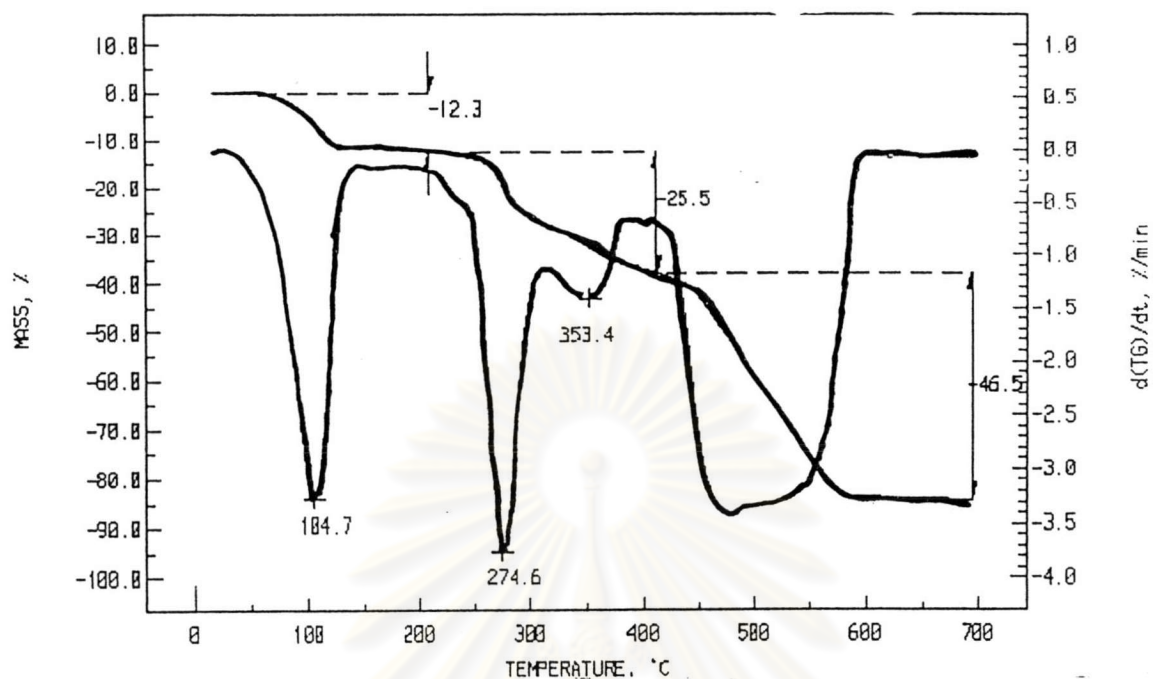


Figure 3.4 TGA thermogram of NiL₁

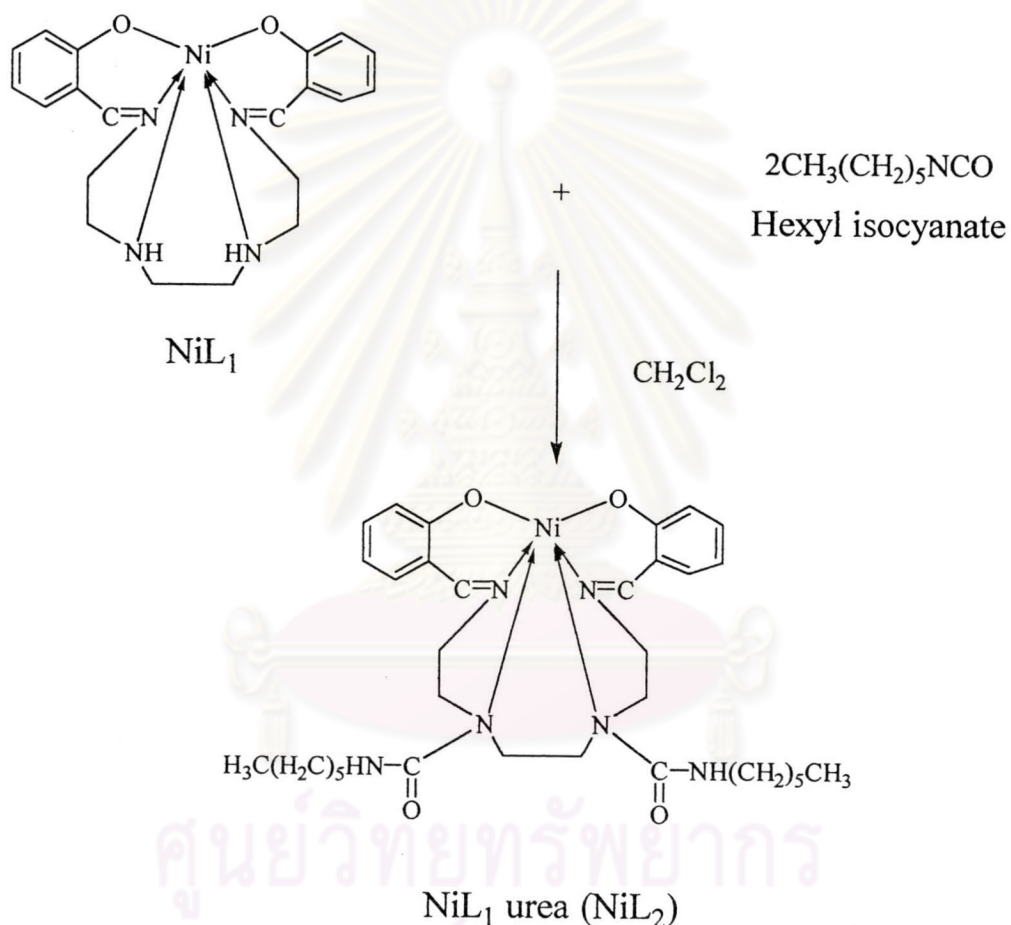
The TGA curve of NiL₁ (Figure 3.4) showed three-stage decomposition. A 50% weight loss occurred at the temperature of 450 °C. The weight loss percentages of NiL₁ at different temperatures were given in Table 3.1.

Table 3.1 TGA data of NiL₁

Temperature (°C)	300	400	500	600
Weight loss (%)	27	36	60	84

3.2 Synthesis of NiL₁ urea (NiL₂) from the reaction between NiL₁ and hexyl isocyanate

The next step was to investigate the reactivity of the amine group in NiL₁ using the reaction with hexyl isocyanate. The amine groups of NiL₁ reacted with the isocyanate group of the hexyl isocyanate to give amide groups (Scheme 3.2). The product obtained from this reaction was called NiL₂ which was a urea derivative of NiL₁.



Scheme 3.2 Reaction between NiL₁ and hexyl isocyanate to give NiL₂

Both NiL₁ and hexyl isocyanate were soluble in dichloromethane. The other advantage in using dichloromethane as solvent was the ease of its removal to obtain the product.

When the reaction was completed, it was found that the effective way to isolate NiL₂ from the reaction mixture was to leave the reaction mixture at room temperature in order to remove dichloromethane slowly by evaporation. NiL₂ would

then precipitate from the reaction mixture. The amount of dichloromethane used in the reaction was very important since NiL_2 would precipitate at the suitable concentration of the reaction mixture. The concentrated solution resulted in precipitation of NiL_2 along with the impurity. If the reaction mixture was too dilute, NiL_2 would not precipitate and the reaction mixture decomposed.

The reaction was studied by IR spectroscopy. TLC cannot be used due to decomposition of the material on the acidic silica gel. The reaction progress could be observed by the disappearance of the strong NCO absorption in hexyl isocyanate and the appearance of a new $-\text{NCON}-$ absorption band in NiL_2 .

The completeness of reaction was confirmed by the absence of the characteristic NCO peak absorption band in isocyanate at 2275 cm^{-1} and the presence of a new carbonyl ($\text{C}=\text{O}$) stretching vibration of $-\text{NCON}-$ group that usually was observed at 1711 cm^{-1} .

The condition for obtaining optimum yield of NiL_2 was determined with variations in temperature and time. The chosen reaction temperature were room temperature, $40\text{ }^\circ\text{C}$ and refluxing CH_2Cl_2 ($80\text{ }^\circ\text{C}$).

When the reaction was done at room temperature, there was the presence of a new carbonyl ($\text{C}=\text{O}$) stretching vibration of $-\text{NCON}-$ group at 1711 cm^{-1} after 3 hours. The absorption band of NCO peak at 2275 cm^{-1} was still observed after 12 hours. Therefore, the reaction was not completed. (Figure 3.5). The reaction at $40\text{ }^\circ\text{C}$ gave a similar result (Figure 3.6).

At the reaction temperature of $80\text{ }^\circ\text{C}$, the NCO absorption band disappeared completely after heating for 12 hours (Figure 3.7).

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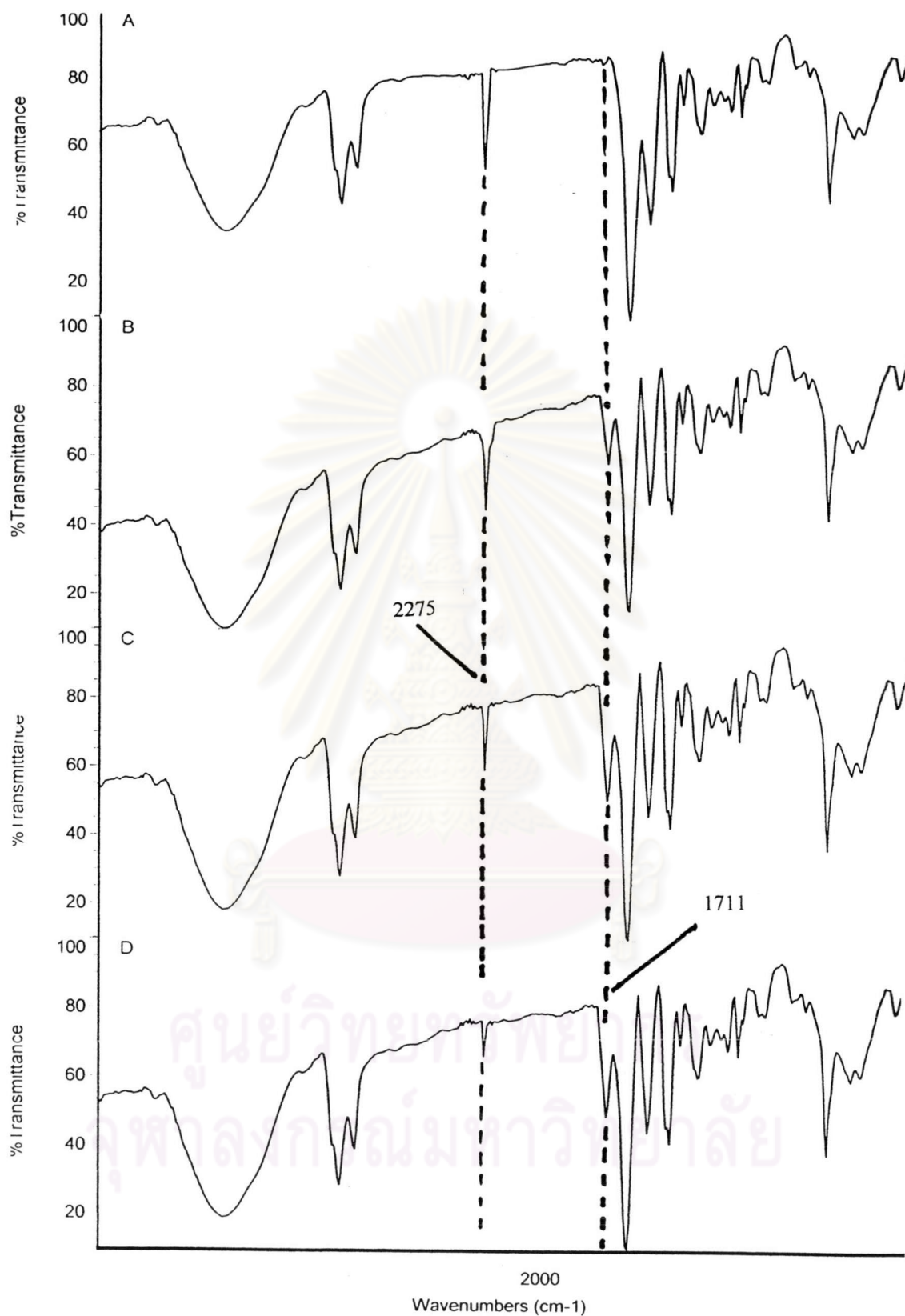


Figure 3.5 IR spectra of a reaction mixture of NiL₁: hexyl isocyanate at a mole ratio of 1:2 when the reaction was done at room temperature; (A) after 1 h (B) after 3 h (C) after 6 h and (D) after 12 h

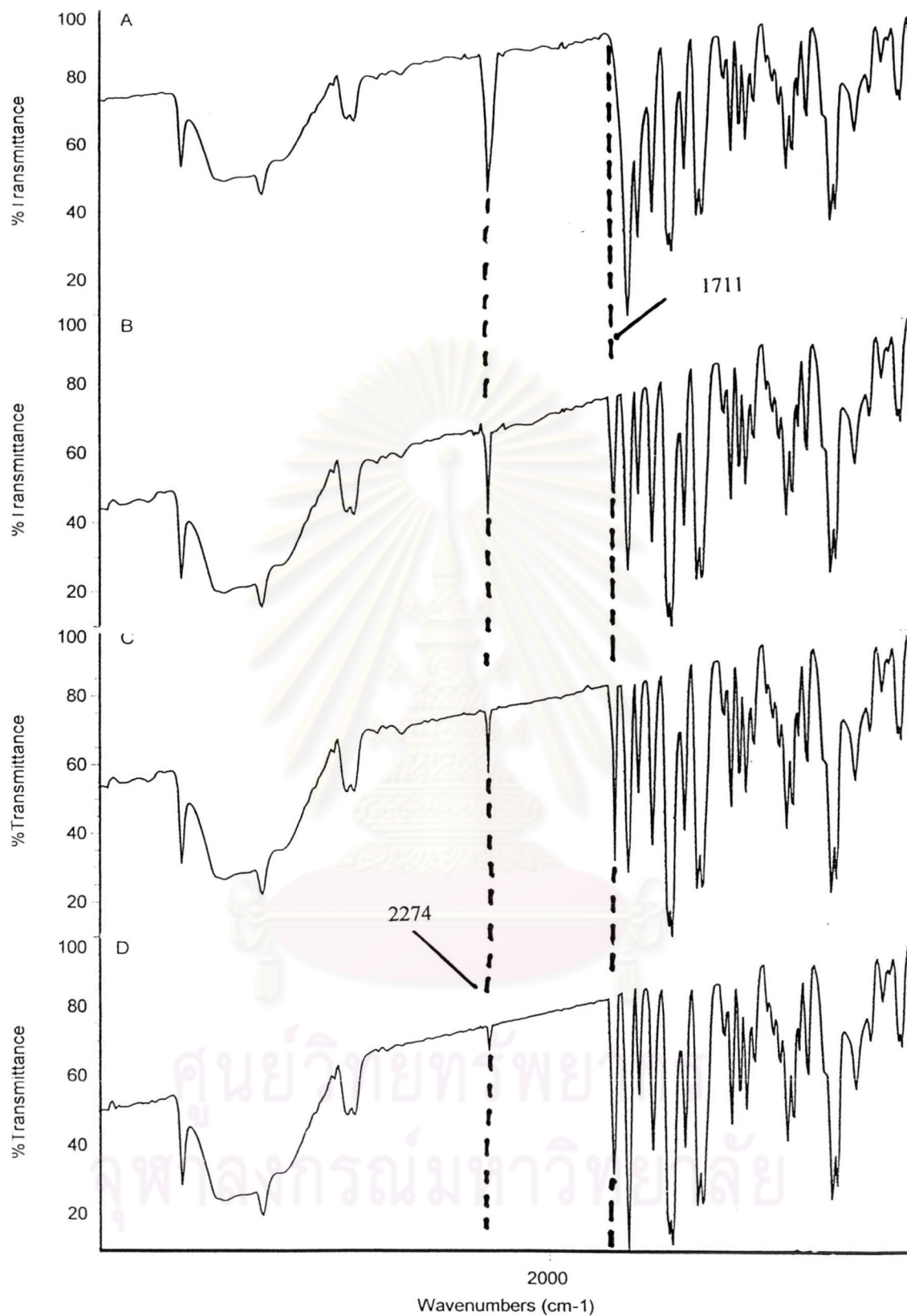


Figure 3.6 IR spectra of a reaction mixture of NiL₁: hexyl isocyanate at a mole ratio of 1:2 when the reaction was done at 40 °C; (A) after 1h (B) after 3 h (C) after 6 h and (D) after 12 h

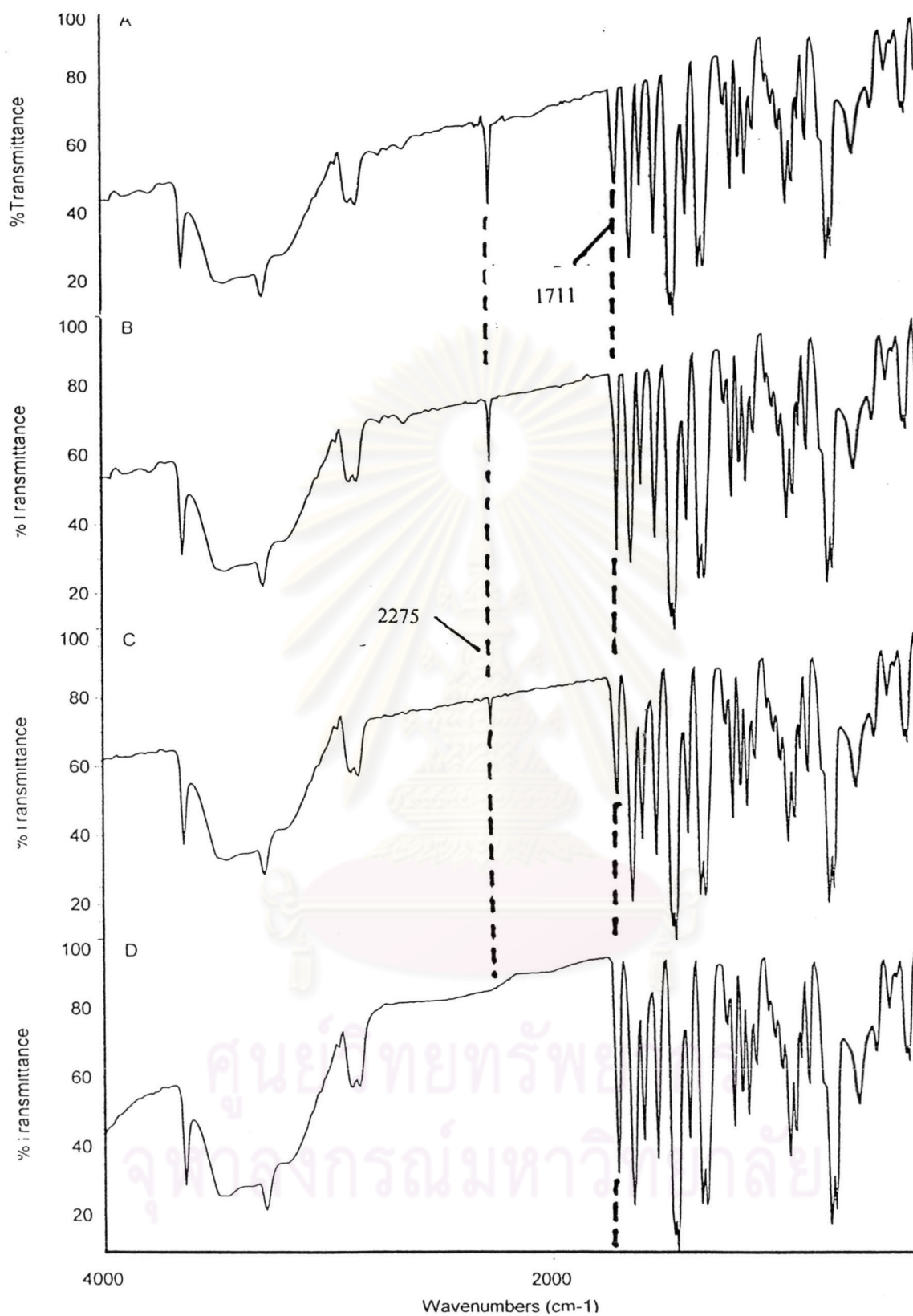


Figure 3.7 IR spectra of a reaction mixture of NiL₁: hexyl isocyanate at a mole ratio of 1:2 when reaction was done at refluxing temperature of CH₂Cl₂; (A) after 1 h (B) after 3 h (C) after 6 h and (D) after 12 h

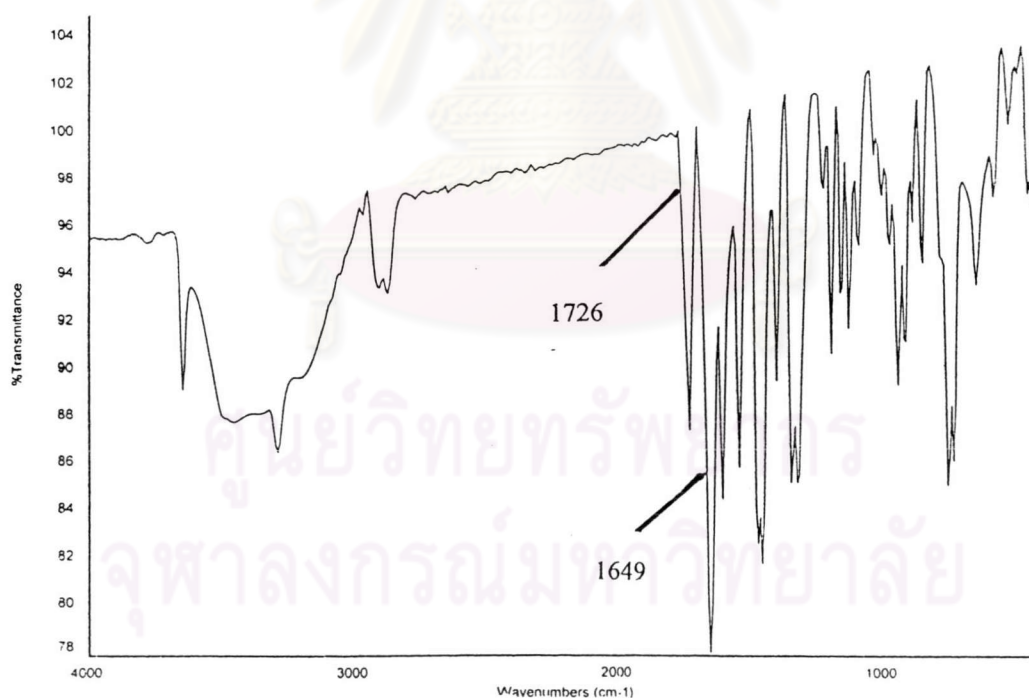
Table 3.2 Yield of NiL₂ from different reaction temperatures

Reaction temperature (°C)	Reaction duration (h)	Yield of NiL ₂ (%)
Room temperature	12	63
40	12	80
40 (reflux in CH ₂ Cl ₂)	12	90

Table 3.2 shows the yield of NiL₂ obtained from different reaction temperatures. When the reaction was performed at room temperature and 40 °C, NiL₂ was isolated in low yield since the reaction was not completed. A good yield of NiL₂ was obtained when the reaction mixture in CH₂Cl₂ was heated at reflux.

3.2.1 Characterization of NiL₂

3.2.1.1 IR spectroscopy

**Figure 3.8** FTIR spectrum of NiL₂

The IR spectrum of NiL₂ (Figure 3.8) shows the N-H stretching vibration of a urea linkage at 3300 cm⁻¹. The aliphatic C-H stretching vibration appeared at

2930 cm^{-1} and 2843 cm^{-1} . The carbonyl (C=O) stretching vibration of -NCON- group was presence at 1726 cm^{-1} . The imine (C=N) absorption band appeared at 1649 cm^{-1} , the benzene C=C stretching appeared at 1549 and 1447 cm^{-1} and the benzene C-H bending was observed at 749 cm^{-1} .

3.2.1.2 Elemental analysis

Table 3.3 shows the possible molecular formulars of NiL_2 . The experimental value agreed with the molecular formula $\text{C}_{34}\text{H}_{50}\text{N}_6\text{O}_4\text{Ni}\cdot\text{H}_2\text{O}$.

Table 3.3 Analytical data of NiL_2

Complex	Formula (molecular weight)		Elemental analysis		
			C%	H%	N%
NiL_2	$\text{C}_{34}\text{H}_{50}\text{N}_6\text{O}_4\text{Ni}$ (655.5)	Calculated	61.36	7.57	12.63
$\text{NiL}_2\cdot\text{H}_2\text{O}$	$\text{C}_{34}\text{H}_{50}\text{N}_6\text{O}_4\text{Ni}\cdot\text{H}_2\text{O}$ (682.3)	Calculated	59.75	7.67	12.30
$\text{NiL}_2\cdot 2\text{H}_2\text{O}$	$\text{C}_{34}\text{H}_{50}\text{N}_6\text{O}_4\text{Ni}\cdot 2\text{H}_2\text{O}$ (701.5)	Calculated	58.21	7.76	11.98
		Found	59.54	7.48	12.47

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3.2.2 Thermal analysis

3.2.2.1 Differential scanning calorimetry (DSC)

DSC thermogram in Figure 3.9 showed two small endotherms around 63 °C and 236 °C, respectively, followed by decomposition of the materials.

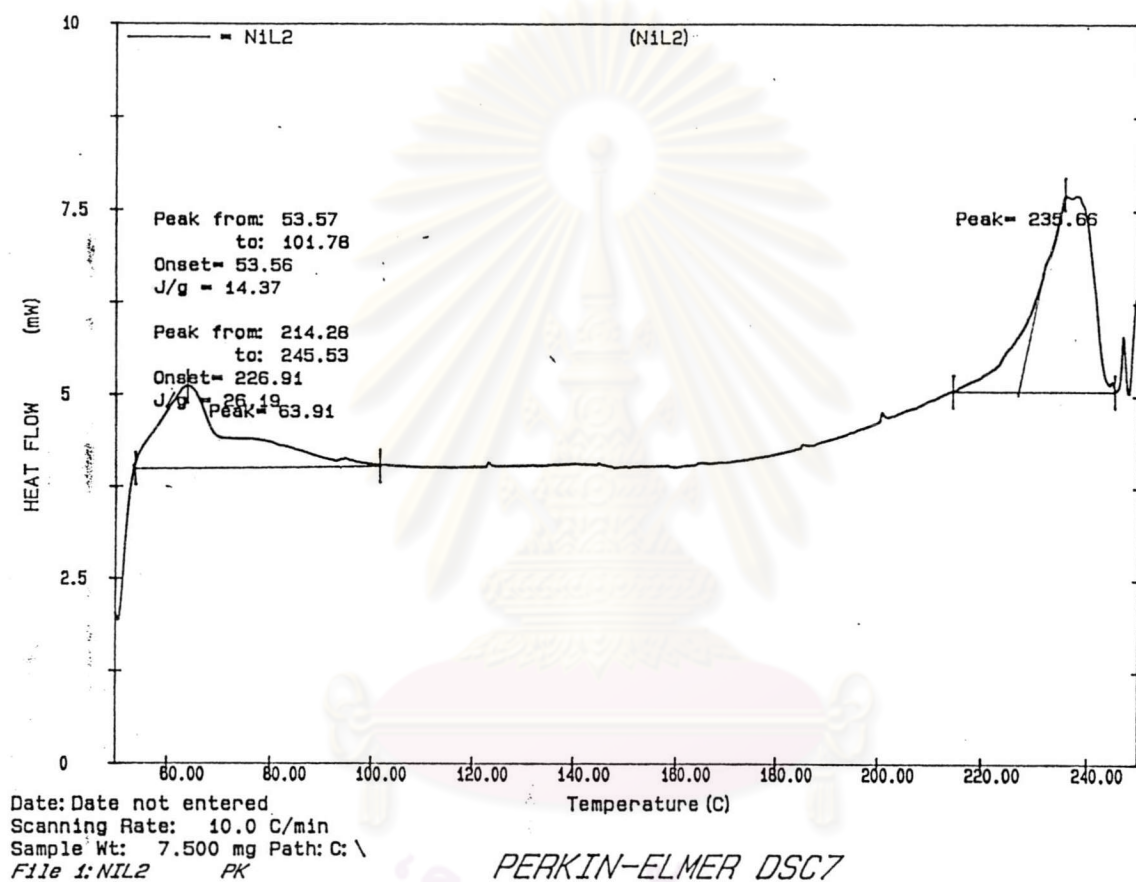


Figure 3.9 DSC thermogram of NiL₂ at a heating rate of 10 °C/min

3.2.2.2 Thermogravimetric analysis (TGA)

The TGA curve of NiL_2 is shown in Figure 3.10. NiL_2 showed two-stage decomposition.

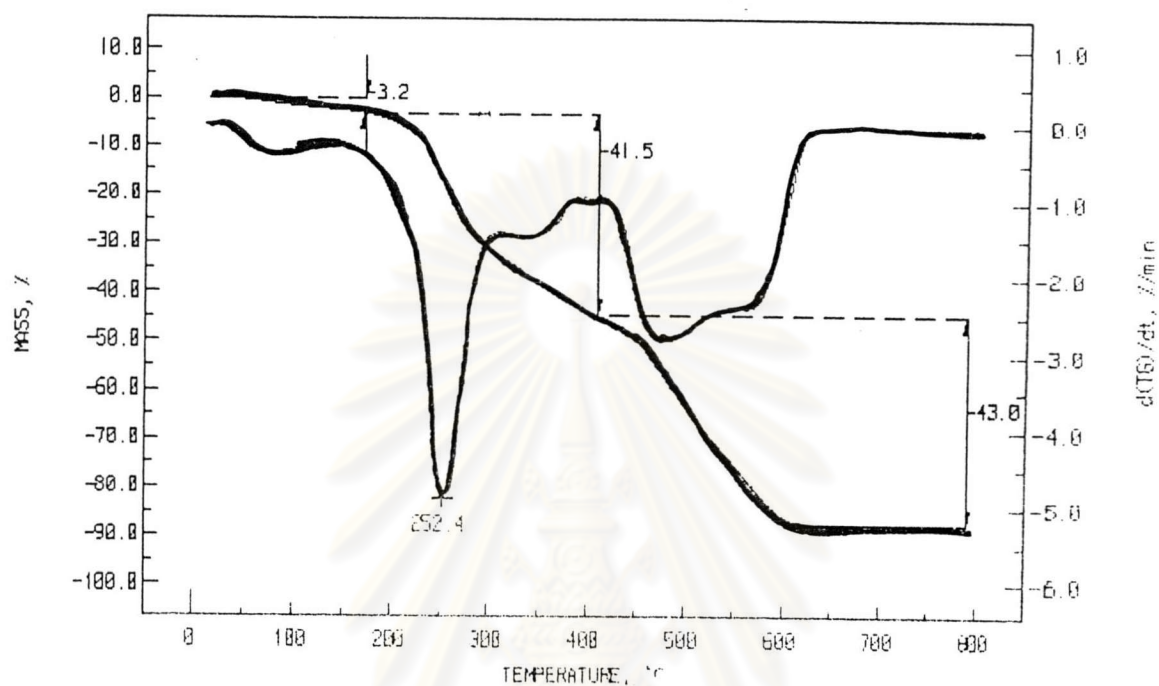


Figure 3.10 TGA thermogram of NiL_2

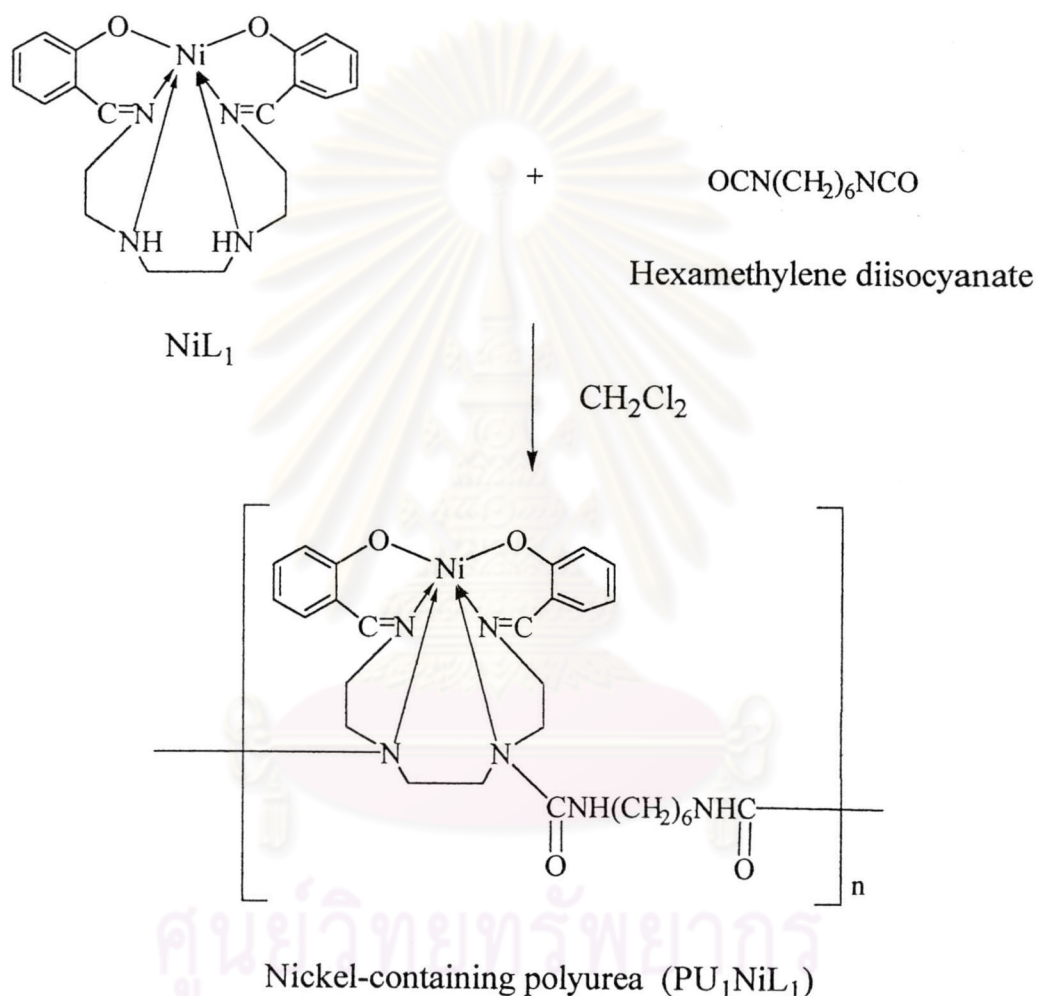
A 50% weight loss occurred at temperature of 453 °C. the % weight loss of NiL_2 at this temperature is almost equal to that of NiL_1 . However NiL_2 had slightly higher weight loss percentages at 300 and 400 °C than NiL_1 . The weight loss percentages of NiL_2 at different temperatures were given in Table 3.4.

Table 3.4 TGA data of NiL_2

Temperature (°C)	300	400	500	600
Weight loss (%)	33	43	65	84

3.3 Synthesis of nickel-containing polyurea (PU_1NiL_1) from the reaction between NiL_1 and hexamethylene diisocyanate

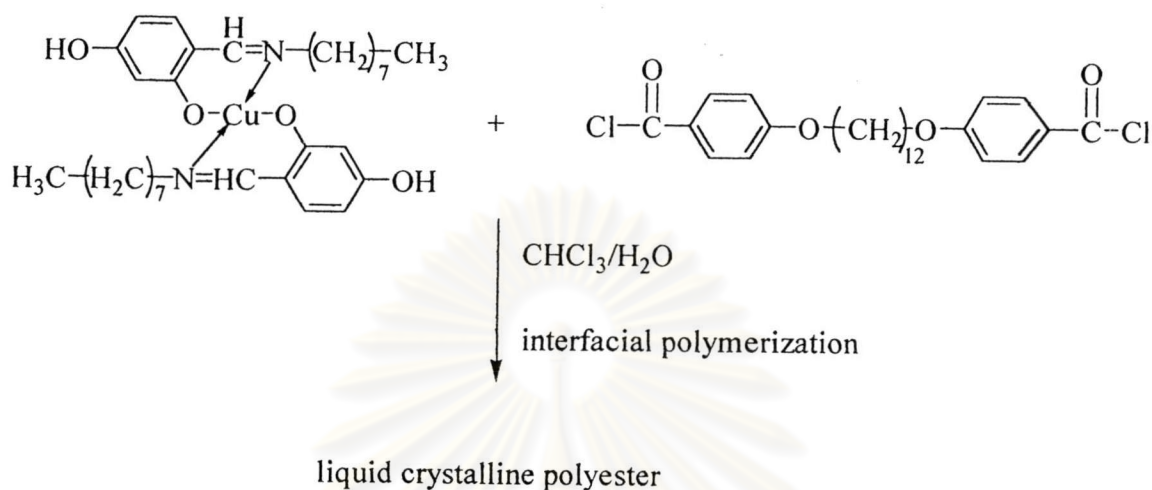
The reaction between NiL_1 and hexamethylene diisocyanate to give PU_1NiL_1 was then carried out using the same method and condition as described in section 3.2. The outline for this reaction is shown in Scheme 3.3.



Scheme 3.3 Synthesis of PU_1NiL_1

The preparative method for polyurethane-urea found in literature¹ was normally done by using polar solvents such as DMF or DMSO. After the reaction was completed, DMF or DMSO was added in large excess to dissolve the linear polymer. The crosslinked polymer was separated by filtration. The dissolved linear polymer was then precipitated by the addition of non-solvents such as methanol or water.

Another polymerization method was interfacial polymerization. In this case, metal-containing liquid crystalline polyesters was obtained from the reaction between Schiff base copper complex and diacid chloride¹⁹ as shown in Scheme 3.4.



Scheme 3.4 Synthesis of copper-containing liquid crystalline

As discussed in section 3.2, it could be seen from the reaction between NiL_1 and hexamethylene isocyanate to yield NiL_2 that the reaction was done in refluxing dichloromethane for 12 hours. Therefore, the reaction between NiL_1 and hexamethylene diisocyanate to obtain polyurea (PU_1NiL_1) was also carried out using the same condition. The mole ratio of NiL_1 : diisocyanate was as 1.1:1 to avoid crosslinking of the polymers.

The progress of reaction was followed by IR spectroscopy (Figure 3.11). The completeness of the reaction was determined by disappearance of the NCO peak of hexamethylene diisocyanate at 2269 cm^{-1} and the presence of a new carbonyl ($\text{C}=\text{O}$) stretching vibration of $-\text{NCON}-$ group at 1716 cm^{-1} . The IR spectra were obtained from heating a reaction mixture in CH_2Cl_2 at reflux for 12 hours.

After heating for 3 hours, there was the presence of a new carbonyl ($\text{C}=\text{O}$) stretching vibration of $-\text{NCON}-$ group at 1716 cm^{-1} . The completeness of polymerization was supported by the disappearance of the NCO peak at 2269 cm^{-1} after heating for 12 hours.

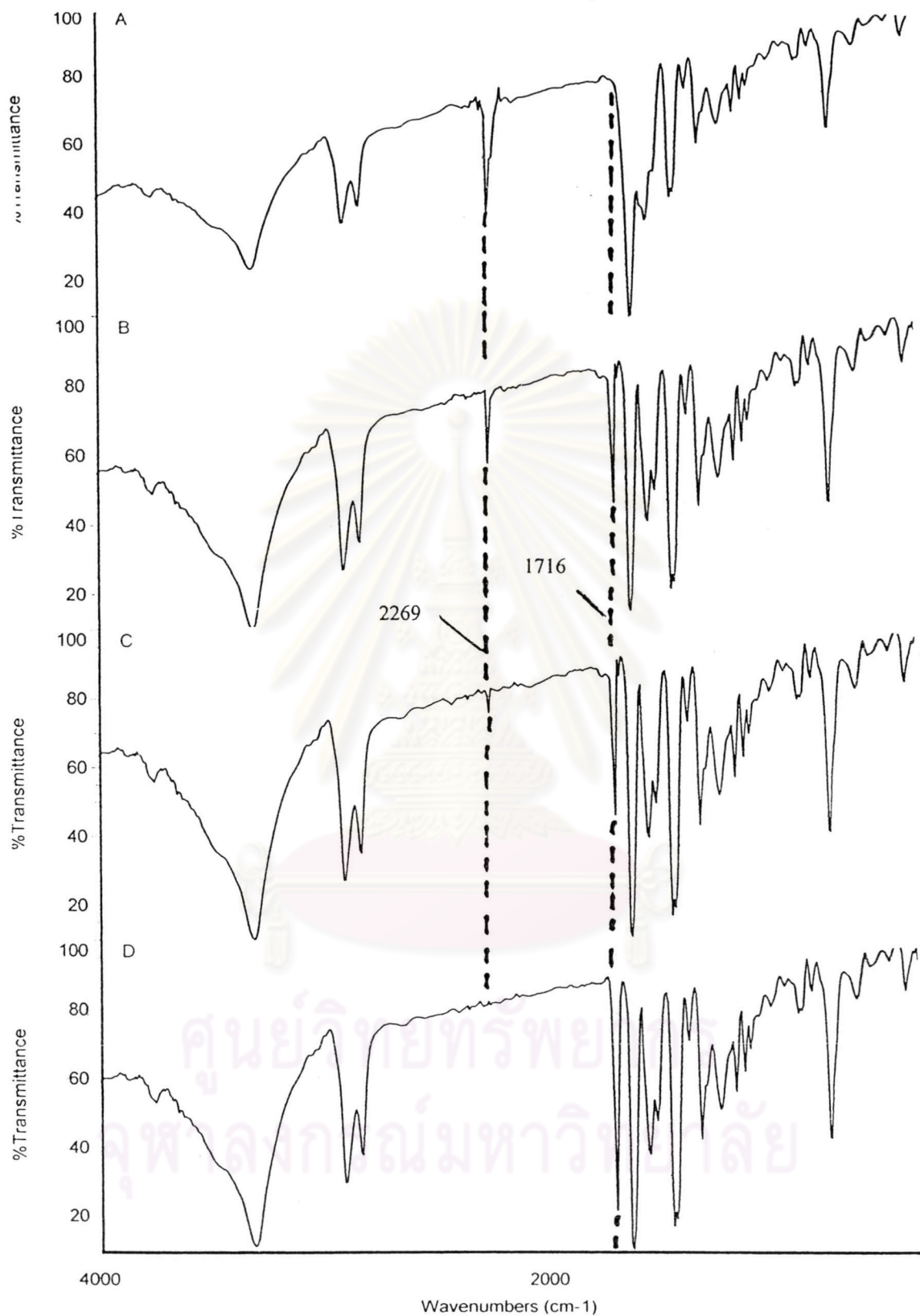


Figure 3.11 IR spectra of a reaction mixture of NiL₁: hexamethylene diisocyanate at a mole ratio of 1.1:1 when the reaction was done at refluxing temperature of CH₂Cl₂; (A) after 1 h (B) after 3 h (C) after 6 h and (D) after 12 h

3.3.1 Characterization of PU_1NiL_1

3.3.1.1 IR spectroscopy

PU_1NiL_1 was obtained as brown powder. The IR spectrum in Figure 3.12 showed the N-H band of the urea group at 3332 cm^{-1} . The C-H stretching vibrations appeared at 2924 and 2854 cm^{-1} and the carbonyl (C=O) stretching vibration of -NCON- group appeared at 1721 cm^{-1} . The imine (C=N) absorption band was observed at 1640 cm^{-1} . The benzene C=C stretching appeared at 1578 cm^{-1} and the aromatic C-H bending was observed at 763 cm^{-1} .

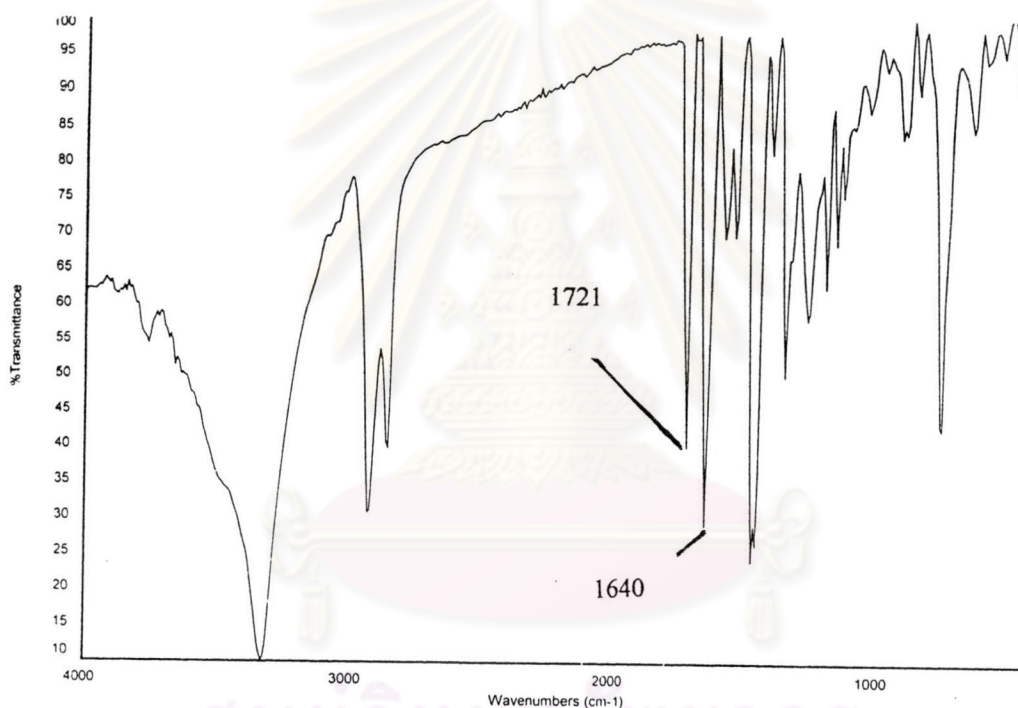


Figure 3.12 IR spectrum of nickel-containing polyurea (PU_1NiL_1)

3.3.1.2 Elemental analysis

The chemical structure of PU_1NiL_1 was confirmed by elemental analysis. Table 3.5 showed the possible molecular formula of PU_1NiL_1 . The experimental value agreed with the formula $\text{C}_{36}\text{H}_{50}\text{N}_8\text{O}_6\text{Ni}\cdot\text{H}_2\text{O}$.

Table 3.5 Analytical data of PU_1NiL_1

Polymer	Formula (Repeating unit)		Elemental analysis		
			C%	H%	N%
PU_1NiL_1	$\text{C}_{36}\text{H}_{50}\text{N}_8\text{O}_6\text{Ni}$ (748.3)	Calculated	57.73	6.73	14.97
$\text{PU}_1\text{NiL}_1\cdot\text{H}_2\text{O}$	$\text{C}_{36}\text{H}_{50}\text{N}_8\text{O}_6\text{Ni}\cdot\text{H}_2\text{O}$ (766.3)	Calculated	56.37	6.84	14.62
$\text{PU}_1\text{NiL}_1\cdot 2\text{H}_2\text{O}$	$\text{C}_{36}\text{H}_{50}\text{N}_8\text{O}_6\text{Ni}\cdot 2\text{H}_2\text{O}$ (784.3)	Calculated	55.08	6.94	14.28
		Found	56.49	6.42	14.42

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3.3.2 Thermal analysis

3.3.2.1 Differential scanning calorimetry (DSC)

DSC thermogram of PU₁NiL₁ (Figure 3.13) shows an exothermic peak at temperature of 228 °C peak that might be due to crosslinking reaction of PU₁NiL₁, therefore the crosslinking reaction of PU₁NiL₁ was investigated.

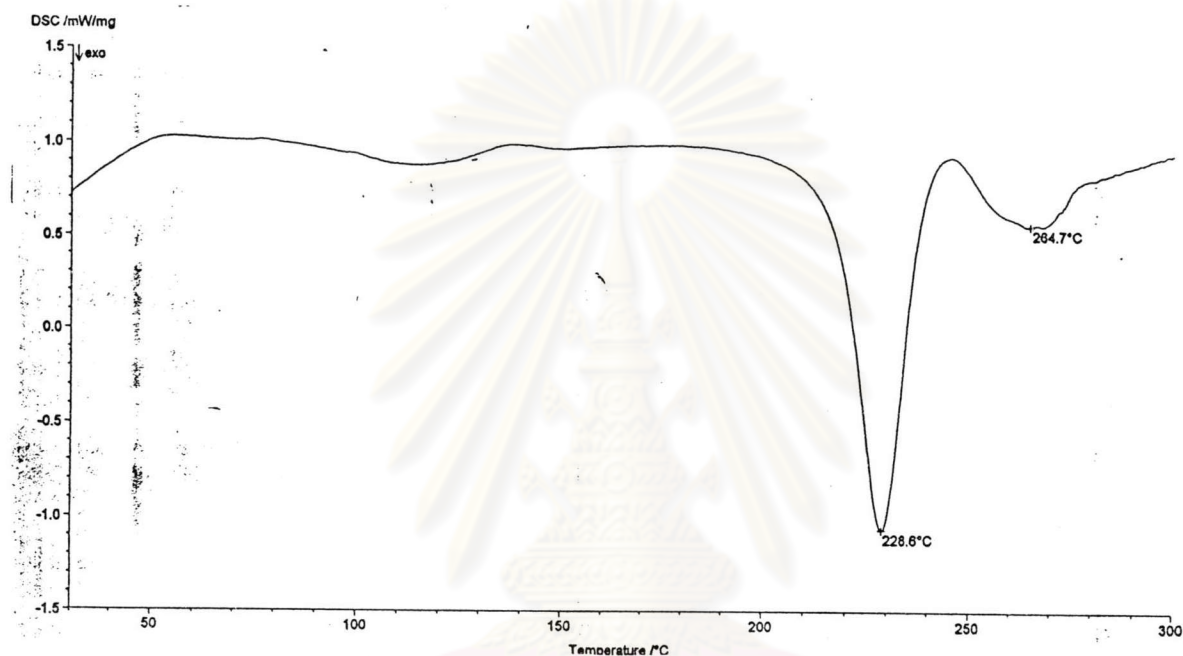


Figure 3.13 DSC thermogram of PU₁NiL₁ at a heating rate of 10 °C/min

The crosslinking reaction of PU₁NiL₁ was studied by heating at 228 °C and the resulting polymer was studied by IR, DSC and TGA.

After heating PU_1NiL_1 at 228°C for 1 hour, IR spectrum of the crosslinked PU_1NiL_1 was obtained. Comparing the IR spectra of PU_1NiL_1 with crosslinked PU_1NiL_1 , both spectra had similar pattern (Figures 3.14 a and 3.14 b).

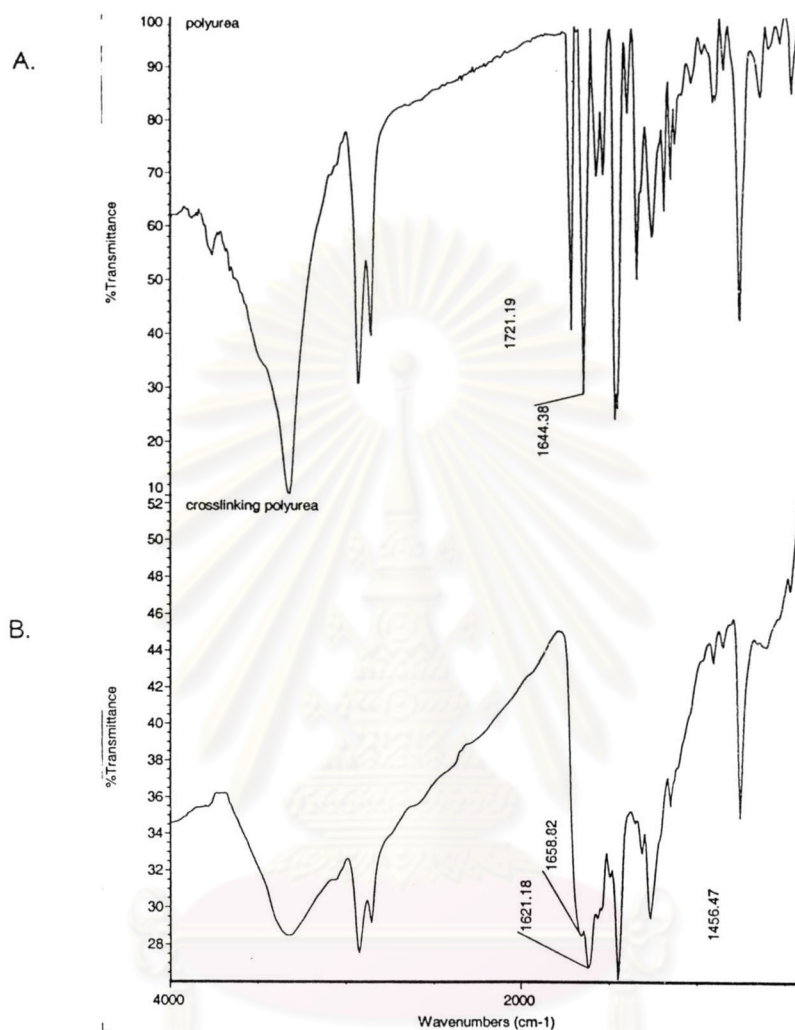


Figure 3.14 Comparison IR spectrum between PU_1NiL_1 and crosslinked PU_1NiL_1 after heat at 228°C for 1 hour

DSC thermogram of the crosslinked PU_1NiL_1 was obtained after heating PU_1NiL_1 at 228°C for 1 hour (Figure 3.15). The exothermic peak at 228°C , which was observed in the case of PU_1NiL_1 , disappeared. Therefore, it was possible that the crosslinking reaction was completed.

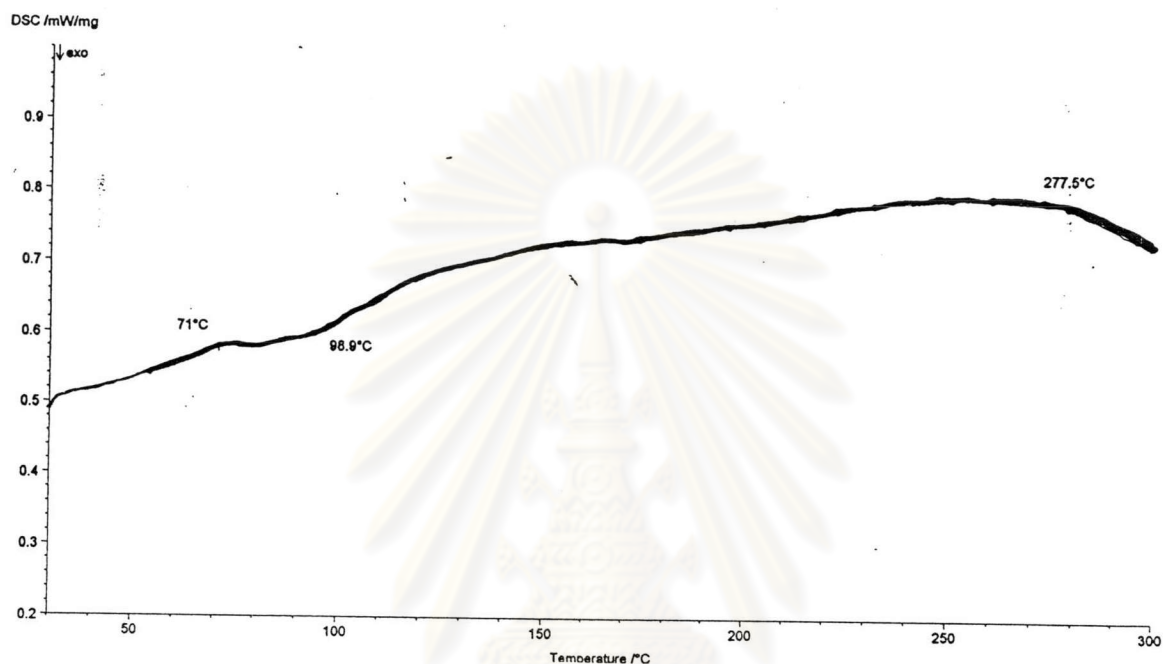


Figure 3.15 DSC thermogram of crosslinked PU_1NiL_1 after heat at 228°C for 1 hour

From IR and DSC experiments, it was possible to conclude that the PU_1NiL_1 underwent crosslinking reaction after heating.

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3.3.2.2 Thermogravimetric analysis

The TGA curve of PU_1NiL_1 was shown in Figure 3.16. The PU_1NiL_1 showed two-stage decomposition. A 50% weight loss percentage of PU_1NiL_1 occurred for PU_1NiL_1 at 480 °C.

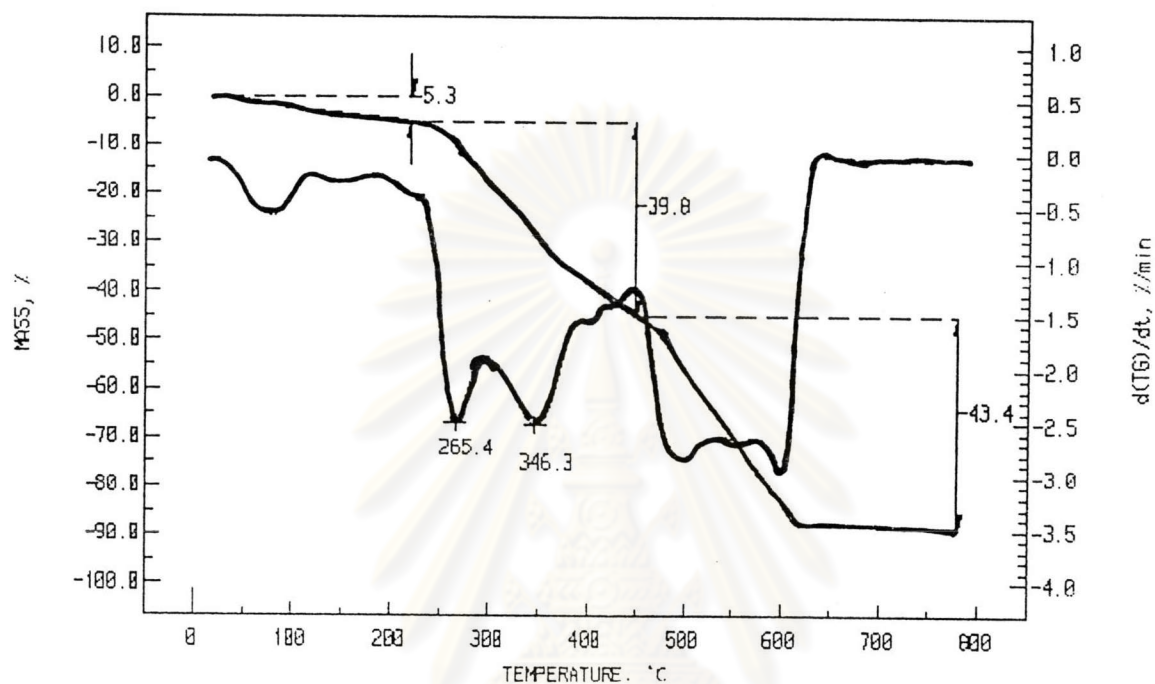


Figure 3.16 TGA thermogram of PU_1NiL_1

The weight loss percentages of PU_1NiL_1 at different temperature were given in Table 3.6.

Table 3.6 TGA data of PU_1NiL_1

Temperature (°C)	300	400	500	600
Weight loss (%)	20	40	58	88

The TGA curve of crosslinked PU_1NiL_1 was shown in Figure 3.17. The PU_1NiL_1 showed two-stage decomposition. A 50% weight loss percentage of crosslinked PU_1NiL_1 occurred for PU_1NiL_1 at 500 °C. This value was observed that crosslinked PU_1NiL_1 had lower weight loss percentage than crosslinked PU_1NiL_1 .

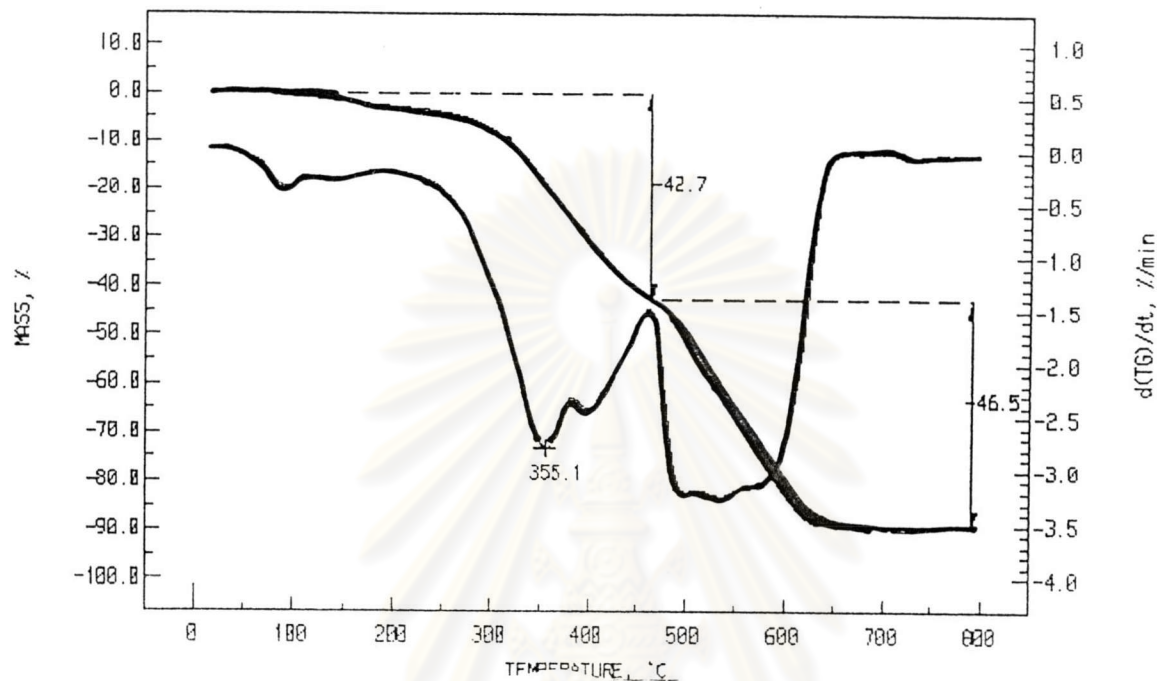


Figure 3.17 TGA thermogram of crosslinked PU_1NiL_1

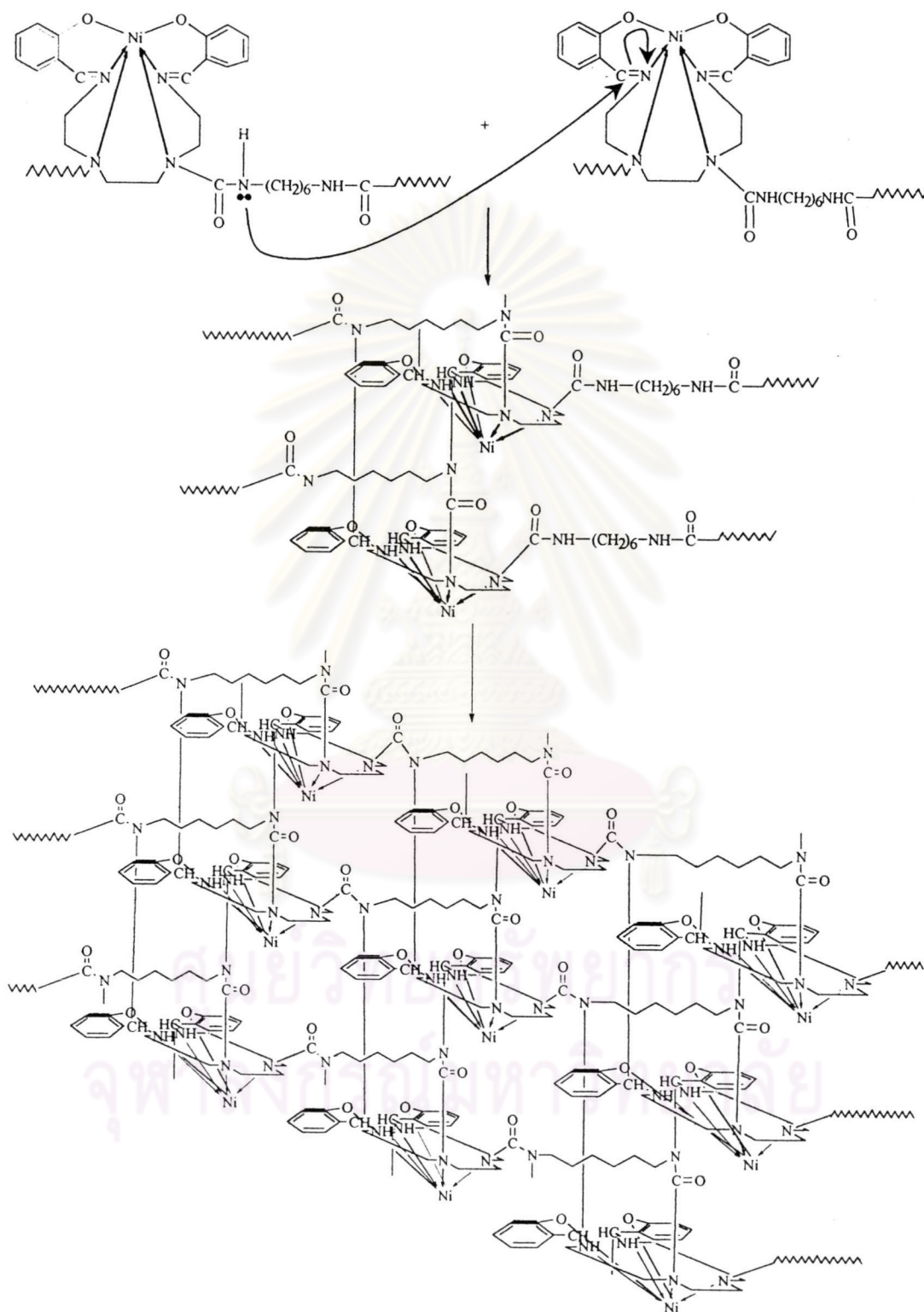
The weight loss percentages of PU_1NiL_1 at difference temperature were given in Table 3.7

Table 3.7 TGA data of crosslinked PU_1NiL_1

Temperature (°C)	300	400	500	600
Weight loss (%)	8	31	54	82

From TGA data showed that crosslinked PU_1NiL_1 had higher stability more than PU_1NiL_1 at 300-400 °C, which might be due to the crosslinked structure.

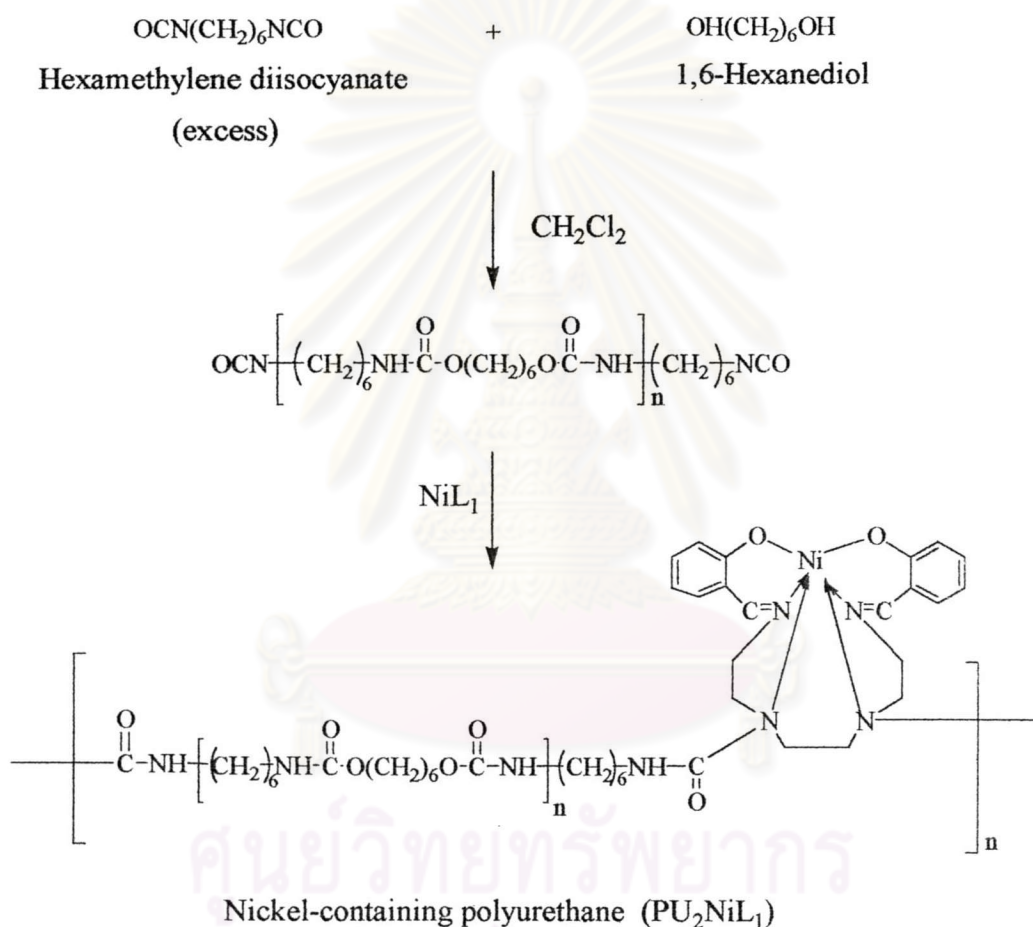
The crosslinking polyurea mechanism was proposed to involve the reaction between C=N group of PU_1NiL_1 and NH group of another PU_1NiL_1 molecule. The same reaction occurs repeatedly to produce crosslinked PU_1NiL_1 .



Scheme 3.5 Possible route to the formation of crosslinked PU_1NiL_1

3.4 Synthesis of nickel-containing polyurethane (PU₂NiL₁) from the reaction between NiL₁, hexamethylene diisocyanate and 1,6-hexanediol

PU₂NiL₁ was synthesized by using a two-staged reaction. Firstly prepolymer was synthesized from reaction between hexamethylene diisocyanate and 1,6-hexanediol. Then, the prepolymer was reacted with NiL₁ to obtain nickel-containing polyurethane (PU₁NiL₁). The outline for this reaction is shown in Scheme 3.6.



Scheme 3.6 Synthesis of PU₂NiL₁

In the prepolymer step, the extent of the reaction was determined by titration of unreacted NCO group by the known method²⁰. The reaction was stopped when one-half of the NCO groups were consumed. Titration indicated that one-half of the NCO groups were consumed after heating at refluxing temperature of CH₂Cl₂ for 8 hours, therefore prepolymer synthesis was carried out for 8 hours before NiL₁ was added. The reaction mixture in CH₂Cl₂ solution was then heated and reflux to obtain PU₂NiL₁.

IR spectroscopy was used to determine the optimum condition reaction temperature and time. The expected reaction was that the amine groups of NiL₁ reacted with the isocyanate group of prepolymer to give amide groups.

The reaction was followed by disappearance of the IR absorption band of the NCO in polymer (Figure 3.18). The IR spectra were obtained from a reaction mixture at 80 °C. It was found that after heating at 80 °C for 6 hours, prepolymer reacted with NiL₁ since the IR absorption band of the carbonyl (C=O) stretching vibration of –NCON– group at 1700 cm⁻¹ was present.

If the polymerization was completed, the IR absorption band at 2274 cm⁻¹ due to the NCO peak of isocyanate group should disappear. After heating for 18 hours, the absorption band at 2274 cm⁻¹ was completely disappeared and the optimum yield of PU₂NiL₁ was obtained.



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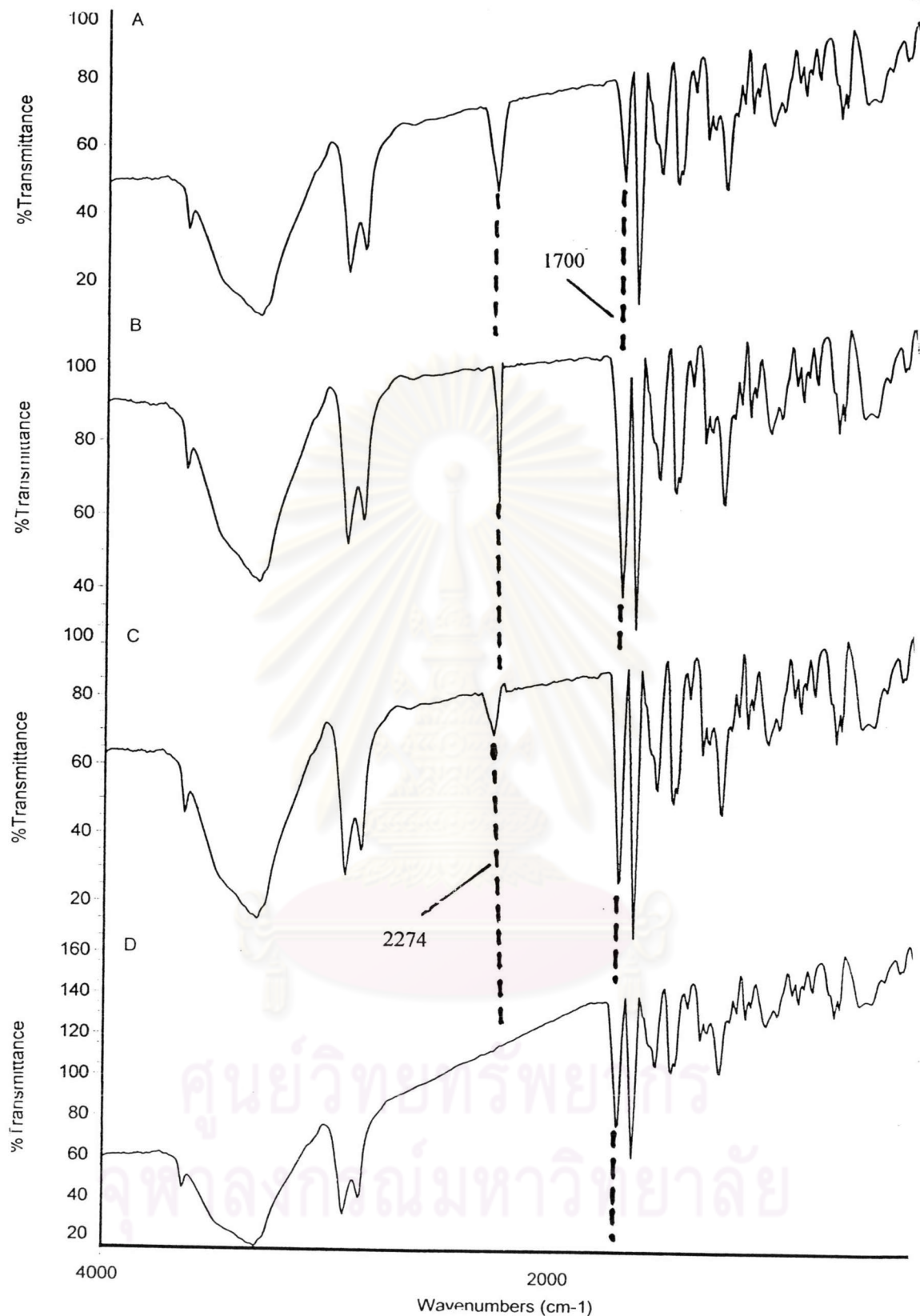


Figure 3.18 IR spectra of a reaction mixture of NiL_1 and the prepolymer obtained from hexamethylene diisocyanate and hexanediol when the reaction was done in refluxing CH_2Cl_2 ; (A) after 3 h (B) after 6 h (C) after 12 h and (D) after 18 h

3.4.1 Characterization of PU_2NiL_1

3.4.1.1 IR spectroscopy

The IR spectrum in Figure 3.19 showed the N-H band of the urea group at 3320 cm^{-1} . The C-H stretching vibrations appeared at 2924 cm^{-1} and 2866 cm^{-1} and the carbonyl (C=O) stretching vibration of -NCON- group at 1716 cm^{-1} . The imine (C=N) absorption band appeared at 1640 cm^{-1} , the benzene C=C stretching appeared at 1541 cm^{-1} and 1461 cm^{-1} and the aromatic C-H bending was observed at 742 cm^{-1}

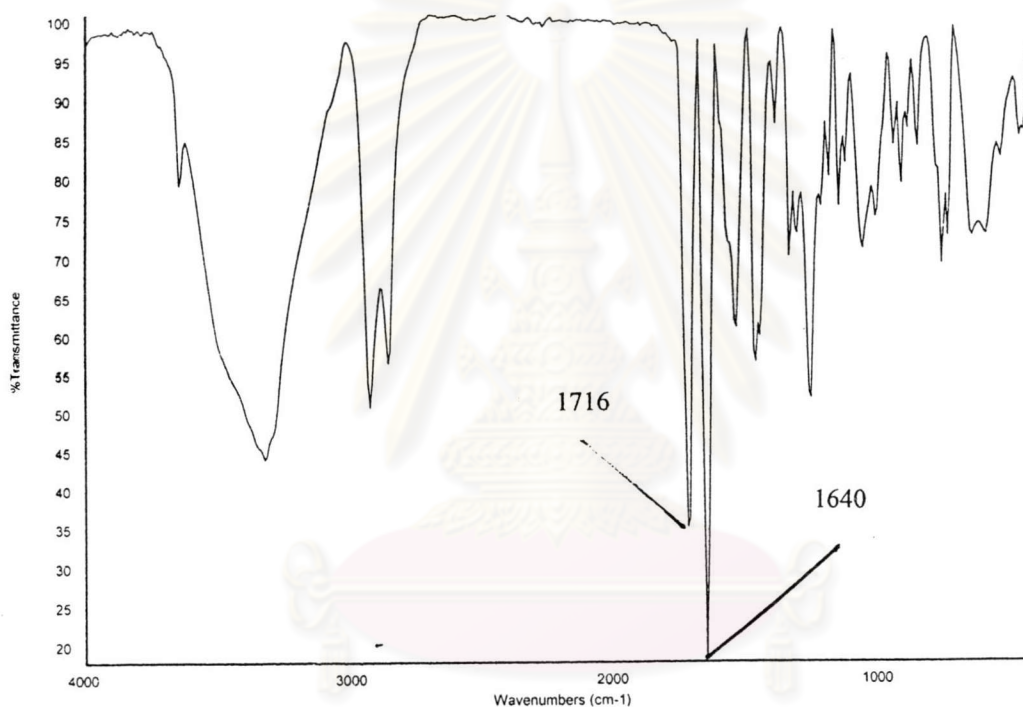


Figure 3.19 IR spectrum of nickel-containing polyurethane (PU_2NiL_1)

3.4.1.2 Elemental analysis

Elemental analysis shows that the experimentally determined percentage values of carbon, hydrogen, and metal are almost equal to the calculated values. The values were shown in Table 3.8.

Table 3.8 Analysis data of PU_2NiL_1

Complex	Formula (Repeating unit)	Elemental analysis			
		C%	H%	N%	
PU_1NiL_1	$\text{C}_{64}\text{H}_{102}\text{N}_{12}\text{O}_{14}\text{Ni}$	Calculated	58.13	7.78	12.71
	(1322.28)	Found	58.16	7.78	12.47

3.4.2 Thermal analysis

3.4.2.1 Differential scanning calorimetry characterized of PU_2NiL_1

DSC thermogram in Figure 3.20 showed the endothermic peak at 127.9 °C, followed by decomposition of the materials.

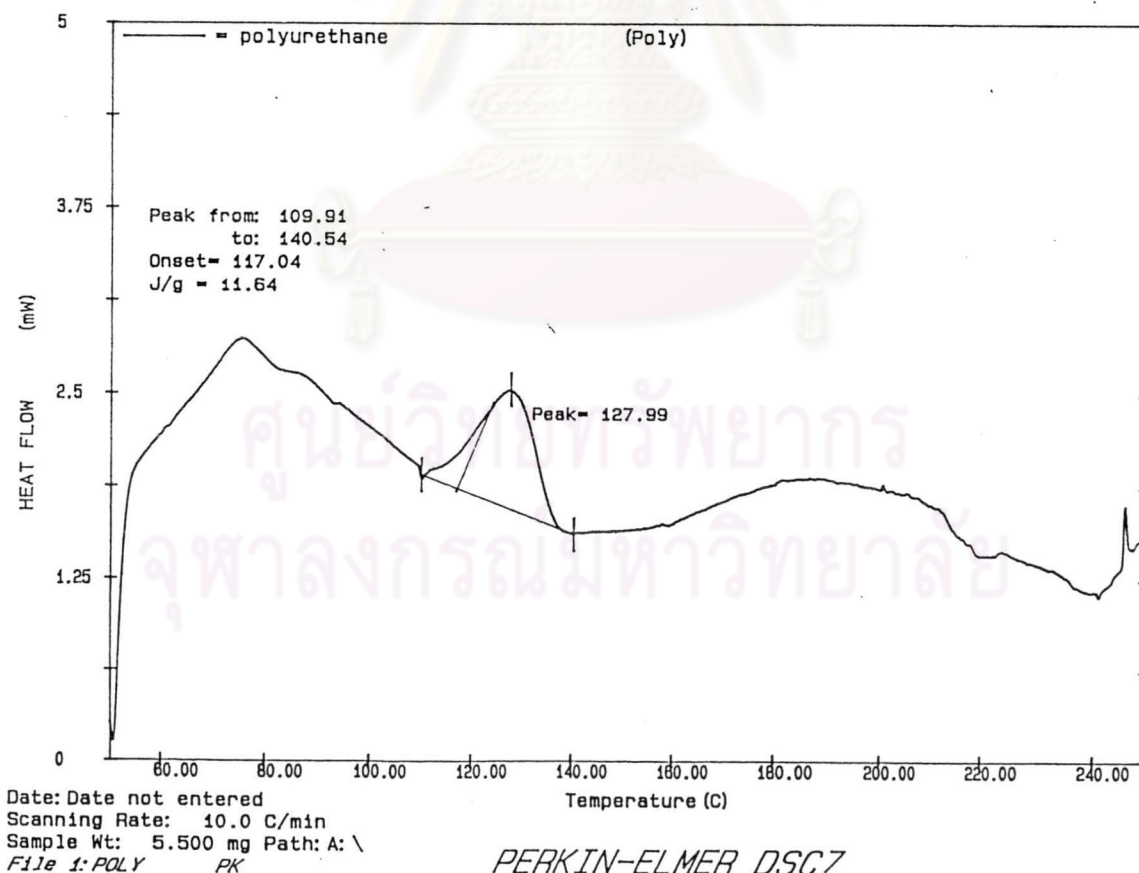


Figure 3.20 DSC thermogram of PU_2NiL_1 at a heating rate of 10 °C/min

3.4.2.2 Thermogravimetric analysis

The TGA curve of PU_2NiL_1 was shown in Figure 3.21. The PU_2NiL_1 showed three-stage decomposition.

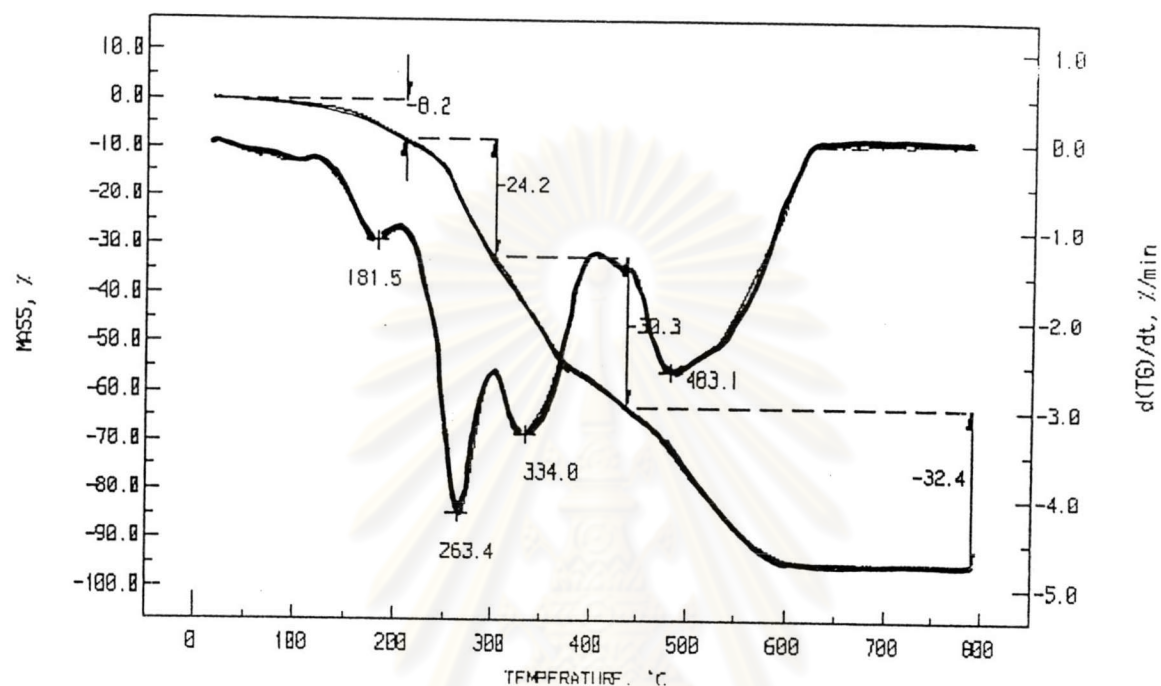


Figure 3.21 TGA thermogram of PU_2NiL_1

The weight loss percentages of PU_2NiL_1 at different temperature were given in Table 3.9.

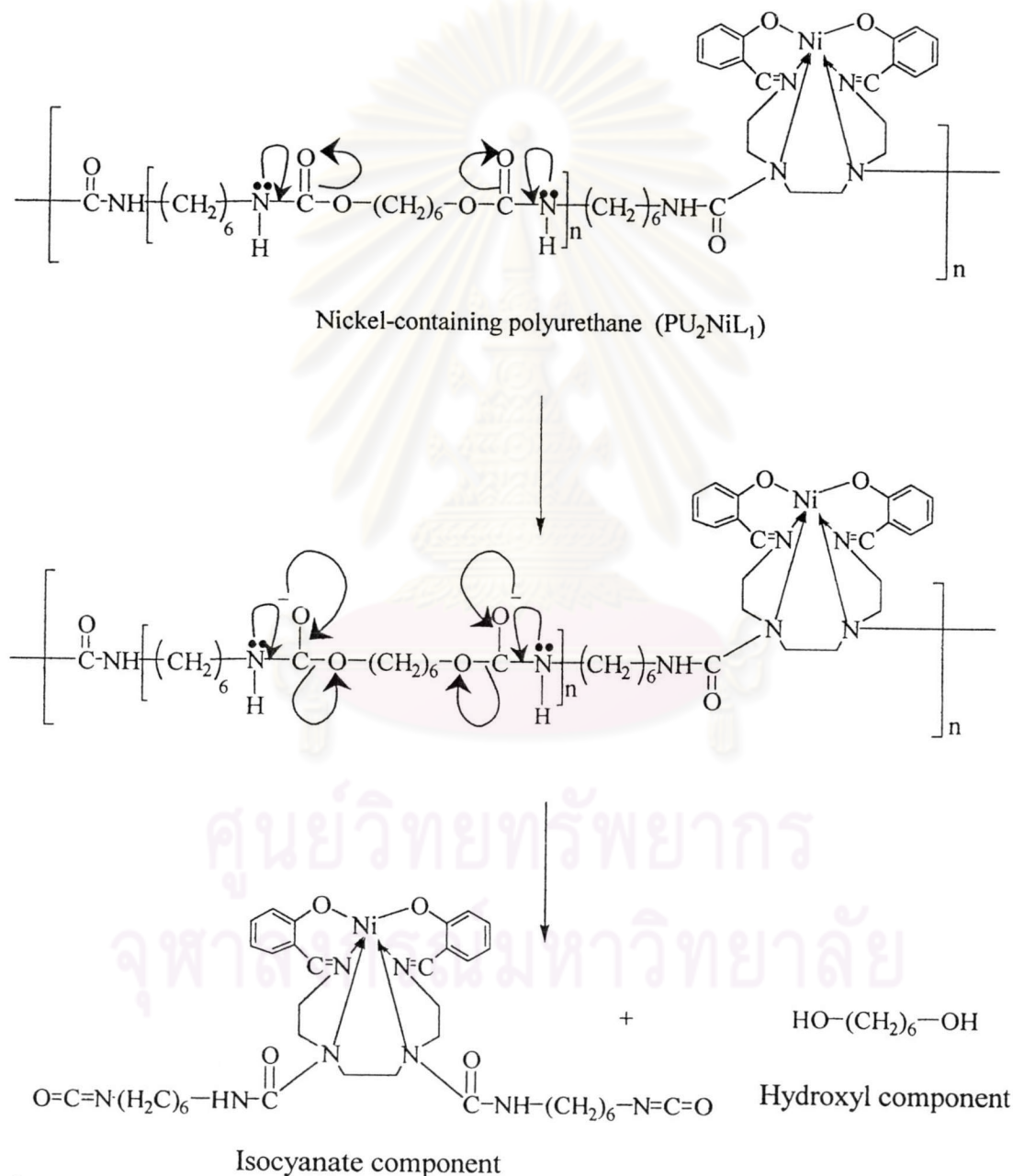
Table 3.9 TGA data of PU_2NiL_1

Temperature (°C)	300	400	500	600
Weight loss (%)	33	57	77	93

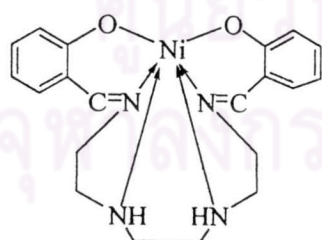
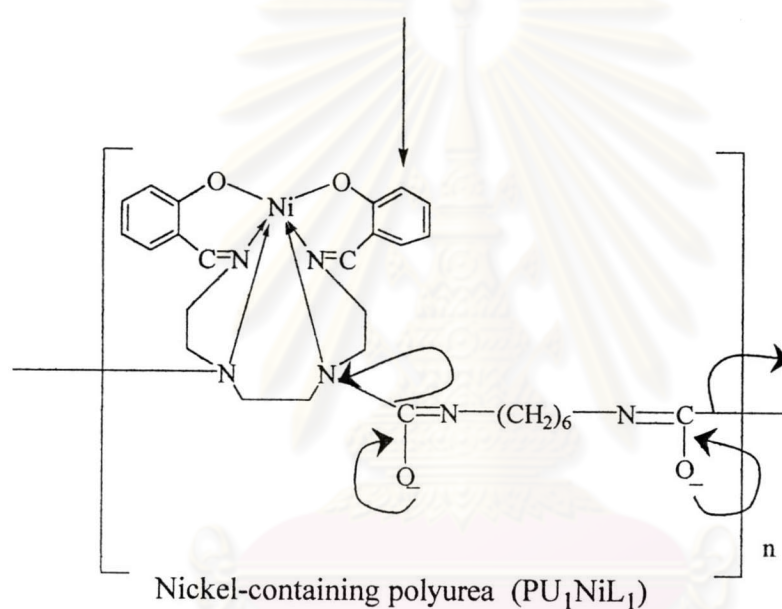
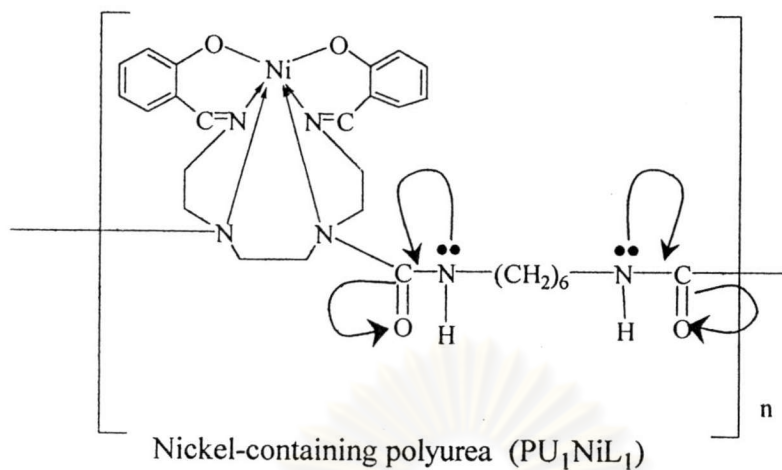
A 50% weight loss occurred for PU_2NiL_1 at the temperature of 355 °C. The result suggested that PU_2NiL_1 had higher weight loss percentages than PU_1NiL_1 at the same temperature. Therefore, nickel-containing polyurea was more stable than nickel-containing polyurethane, this might be due to the stabilization by hydrogen

bonding in polymer. In addition, DSC thermogram of PU_2NiL_2 in Figure 3.20 did not show the exothermic crosslinking, which may be explained based on our findings that PU_2NiL_2 contained less amide group than PU_1NiL_1 .

Initial thermal degradation of polyurethane (PU_1NiL_2) proceeded via urethane scission to give isocyanate and hydroxyl component while the initial thermal degradation of polyurea PU_1NiL_1 proceeded via urea scission to isocyanate and amine component (Scheme 3.7 and 3.8).



Scheme 3.7 Initial thermal degradation of PU_2NiL_1



Nikel hexadentate Schiff base complex

+



Hexamethylene diisocyanate

Scheme 3.8 Initial thermal degradation of PU_1NiL_1