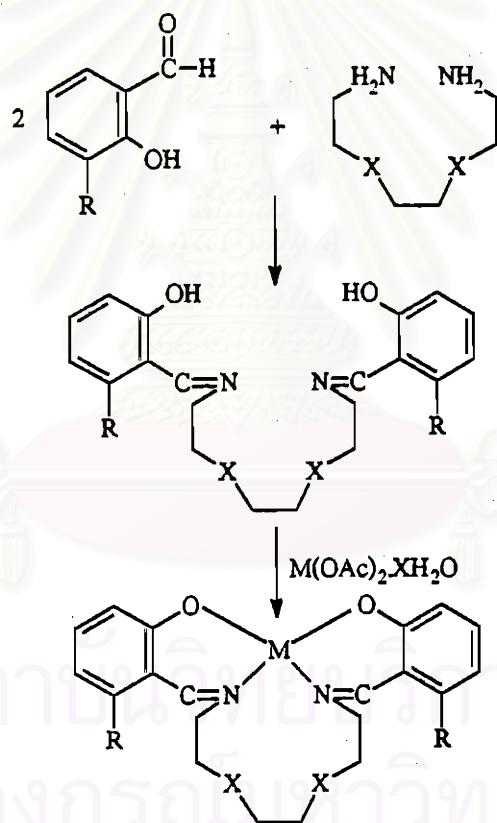


CHAPTER III

RESULTS AND DISCUSSION

The Schiff's base metal complexes could be prepared from the condensation reaction between *o*-hydroxyaromatic aldehydes and diamines as described by Marvel²² and shown in Scheme 3.1. These complexes were characterized by IR and elemental analysis.



- I. R = H , X = -S-
- II. R = CH₃, X = -S-
- III. R = H , X = -O-
- IV. R = CH₃, X = -O-
- V. R = H , X = -NH-

Scheme 3.1 Synthesis of Schiff's base metal complexes.

In this work, metal complexes NiL and ZnL were chosen as crosslinking agents for DGEBA (Figure 3.1) because of their good thermal stability and good solubility in organic solvents. Moreover, the complexes have two amino groups which are able to react with the epoxy resin to give crosslinked epoxy polymers.

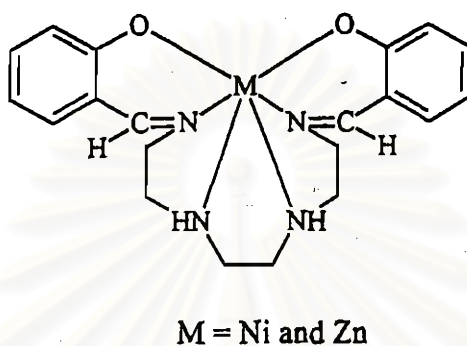
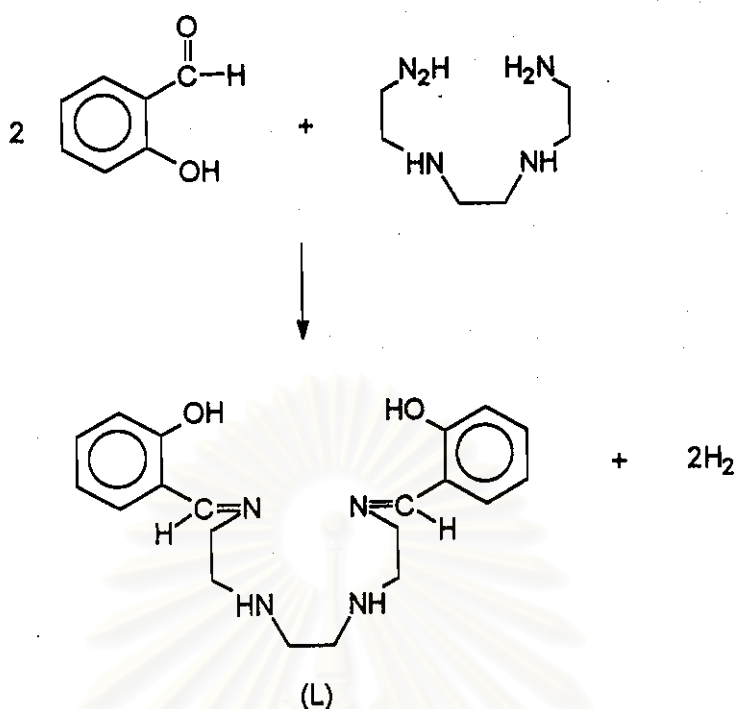


Figure 3.1 Structure of the metal complexes NiL and ZnL.

3.1 Synthesis of Schiff's Base Ligand (L)

Ligand L was synthesized by a condensation reaction between salicylaldehyde and triethylenetetramine. The amine nitrogen attacks the carbonyl carbon of the aldehyde followed by loss of water to give ligand L as shown in Scheme 3.2.

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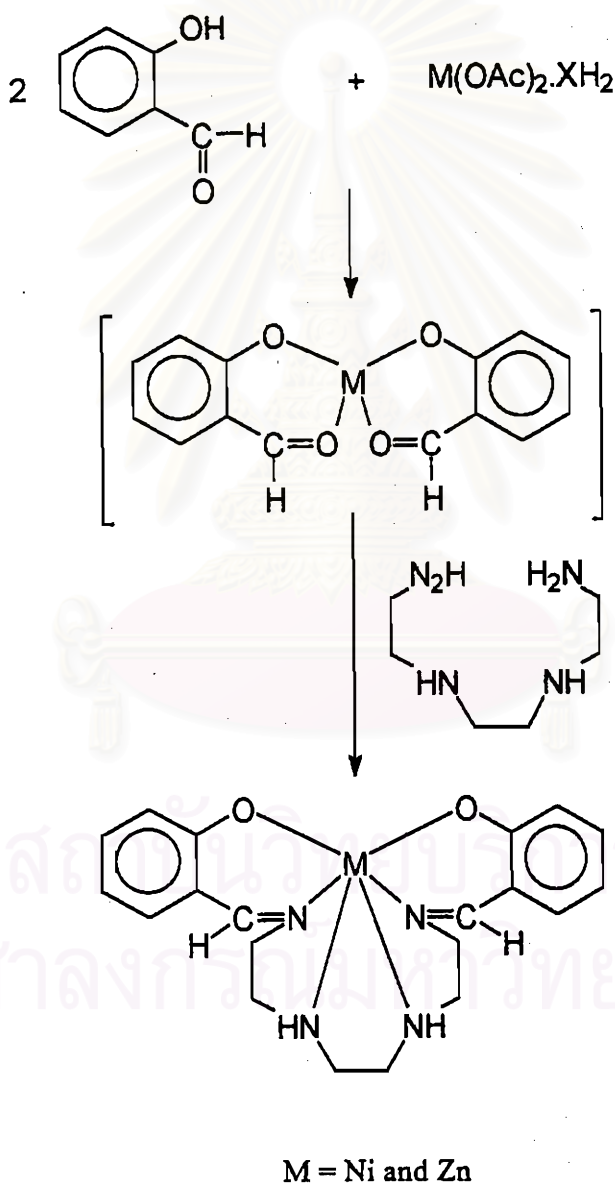
Scheme 3.2. Synthesis of ligand (L).

Ligand L was isolated as an air stable yellow solid in 85% yield. It was soluble in acetone, dichloromethane, ethanol and methanol. The spectroscopic data confirmed the structure of ligand L. The IR spectrum of ligand L showed an absorption band of imine C=N stretching at 1639 cm^{-1} . The absorption bands at 990 and 860 cm^{-1} coincided with the characteristic absorption peaks of aromatic C-H bending of a 1,2-disubstitution benzene.

^1H NMR spectrum of ligand L showed the following important proton signals: 2.57, 2.70 and 3.72 ppm assigned to three chemically unequivalent methylene protons; 6.81-7.29 ppm assigned to the aromatic protons and 8.33 ppm assigned to the Schiff's base protons. The ^{13}C NMR spectrum showed important carbon signals which could be assigned as follows : the signals at 53, 58 and 59 ppm assigned to three chemically unequivalent methylene carbons; the signals at 162, 132, 131, 118.5, 118 and 117 ppm assigned to aromatic carbons and the signal at 168 ppm assigned to the imine carbons.

3.2. Synthesis of Schiff's base Metal complexes.

The complexation was done by mixing a methanolic solution of ligand L with metal acetate to obtain Schiff's base metal complexes. The yields however were low. Therefore, the complexes were synthesized by a one-pot reaction as shown in Scheme 3.3.



Scheme 3.3. Synthesis of complexes using one-pot reaction.

Using one-pot reaction, NiL was synthesized in 89 % as a light brown solid which decomposed at 200 °C and ZnL was synthesized in 99 % as yellow solid with a melting point of 234-235 °C. Both metal complexes were soluble in acetone, hexane, dichloromethane, ethanol, methanol and water. The complexes were characterized by IR, ^1H NMR, ^{13}C NMR, and elemental analysis. The IR spectrum of NiL (Figure A.4) showed an absorption band of imine $\text{C}=\text{N}$ stretching at 1638 cm^{-1} . The absorption bands coincided with the characteristic absorption peaks of aromatic $\text{C}-\text{H}$ bending of a 1,2-disubstitution benzene were 950 and 850 cm^{-1} . MS data gave $m/z = 411.3$ corresponding to M^+ of the molecular formula ($\text{C}_{20}\text{H}_{24}\text{N}_4\text{O}_2\text{Ni}$) of the NiL complex. The structure of NiL has also been determined by X-ray crystallography and is shown in Figure 3.2.

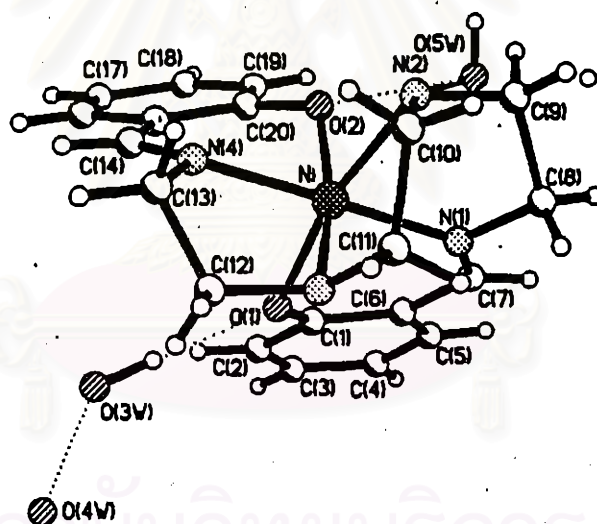


Figure 3.2. X-ray crystal structure of NiL

The IR spectrum of ZnL (Figure A.5) showed absorption bands similar to those of NiL; imine $\text{C}=\text{N}$ stretching at 1645 cm^{-1} and aromatic $\text{C}-\text{H}$ bending at 930 and 870 cm^{-1} . MS data gave $m/z = 417.3$, which is M^+ for the molecular formula ($\text{C}_{20}\text{H}_{24}\text{N}_4\text{O}_2\text{Zn}$) of the ZnL complex.

In comparison between the ^1H NMR spectrum of ZnL and ligand L, the imine protons shifted upfield from 8.33 to 8.18 ppm and the aromatic protons shifted upfield

from 6.81-7.29 to 6.31-7.10 ppm. The CH₂ signals of L appeared as a multiplet at 2.41-2.65 ppm (4H) and two triplets with J = 6.8 Hz at 3.72 ppm (4H) and 2.70 ppm (4H), while ZnL showed four multiplet CH₂ signals at 4.05-4.29 (2H), 3.21-3.48 (4H), 2.73-2.92 (2H) and 2.35-2.61 (4H). Therefore, one of the methylene protons split into two peaks which indicate the complex formation. The ¹³C NMR spectrum of ZnL showed signals similar to those of ligand L.

3.3 Crosslinking Reaction of DGEBA Epoxy Resin with Schiff's Base Metal Complexes.

DSC was employed to investigate whether crosslinking of DGEBA with metal complexes could occur. The optimum crosslinking conditions could also be determined by use of this technique. DSC experiments were performed by heating a mixture of DGEBA and metal complexes at the equivalent weight ratio of 6:1 in a DSC cell using a closed aluminum pan in the air. The temperature range was 40-300°C at a heating rate of 20°C / min. Figures 3.3 and 3.4 are the thermograms obtained where the metal complexes were NiL and ZnL, respectively. From Figures 3.3 and 3.4, each thermograms gave a large exothermic crosslinking peak at 171 and 194°C respectively which indicated that the crosslinking reaction occurred. The crosslinking range of NiL and ZnL were 123-215 and 119-279°C, respectively. Therefore, in the preparation of epoxy polymers, the temperature in the crosslinking reaction of DGEBA with NiL at the equivalent weight ratio of 6:1 was chosen at 190°C and in the crosslinking reaction of DGEBA with ZnL at the same equivalent weight ratio was chosen at 180°C.

Isothermal crosslinking behavior of DGEBA with metal complex was investigated. Isothermal crosslinking of DGEBA with the NiL complex and the ZnL complex at the equivalent weight ratio of 6:1 were done at a constant temperature of 180°C. The crosslinking reaction of DGEBA with NiL completed within 9 minutes (Figure 3.5) and that of ZnL completed within 11 minutes.(Figure 3.6), which indicated that NiL required less crosslinking time than ZnL.

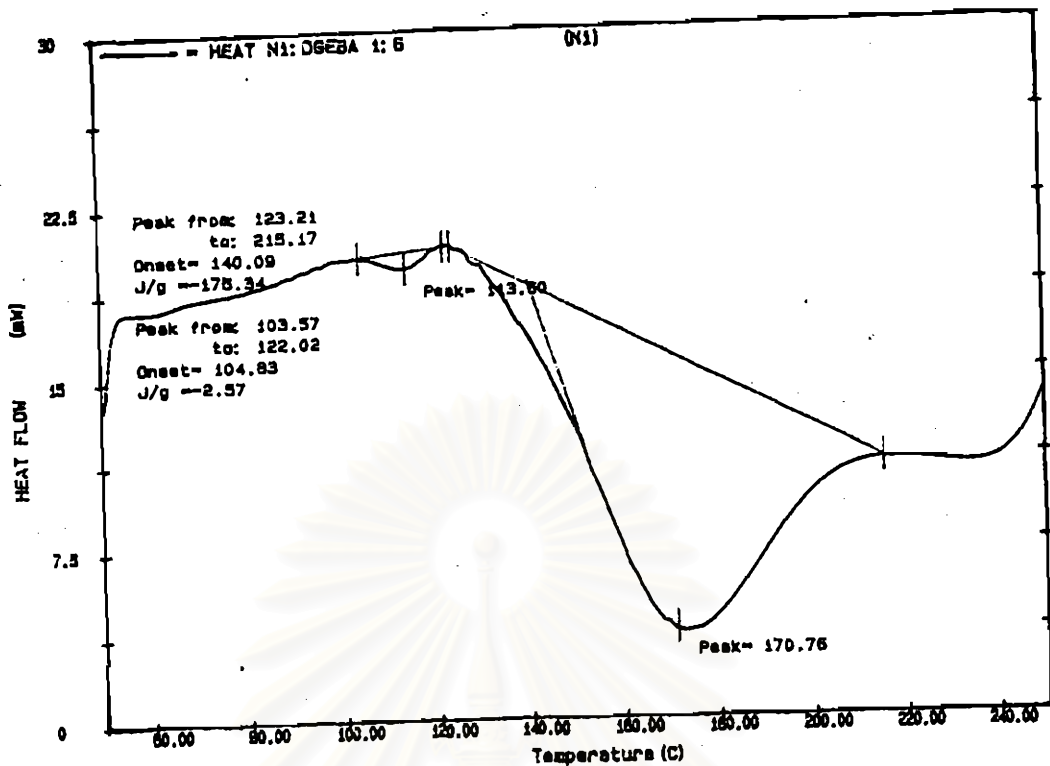


Figure 3.3. DSC thermogram of NIL:DGEBA at the equivalent weight ratio of 1 : 6

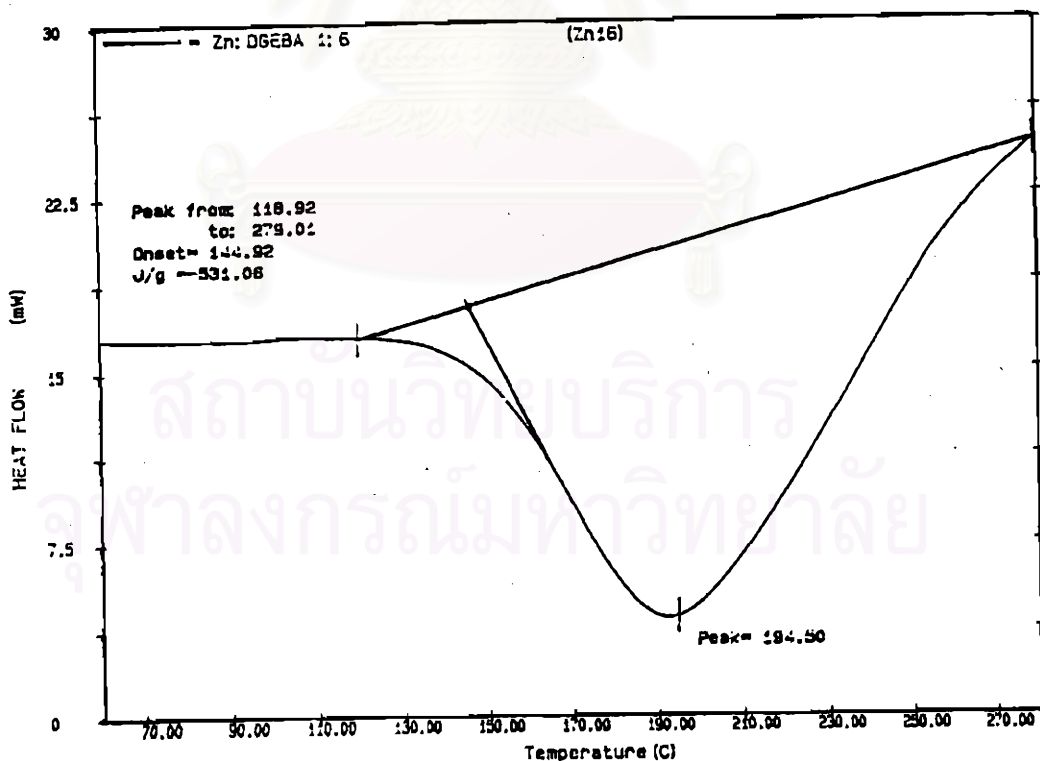


Figure 3.4. DSC thermogram of ZnL:DGEBA at the equivalent weight ratio of 1 : 6

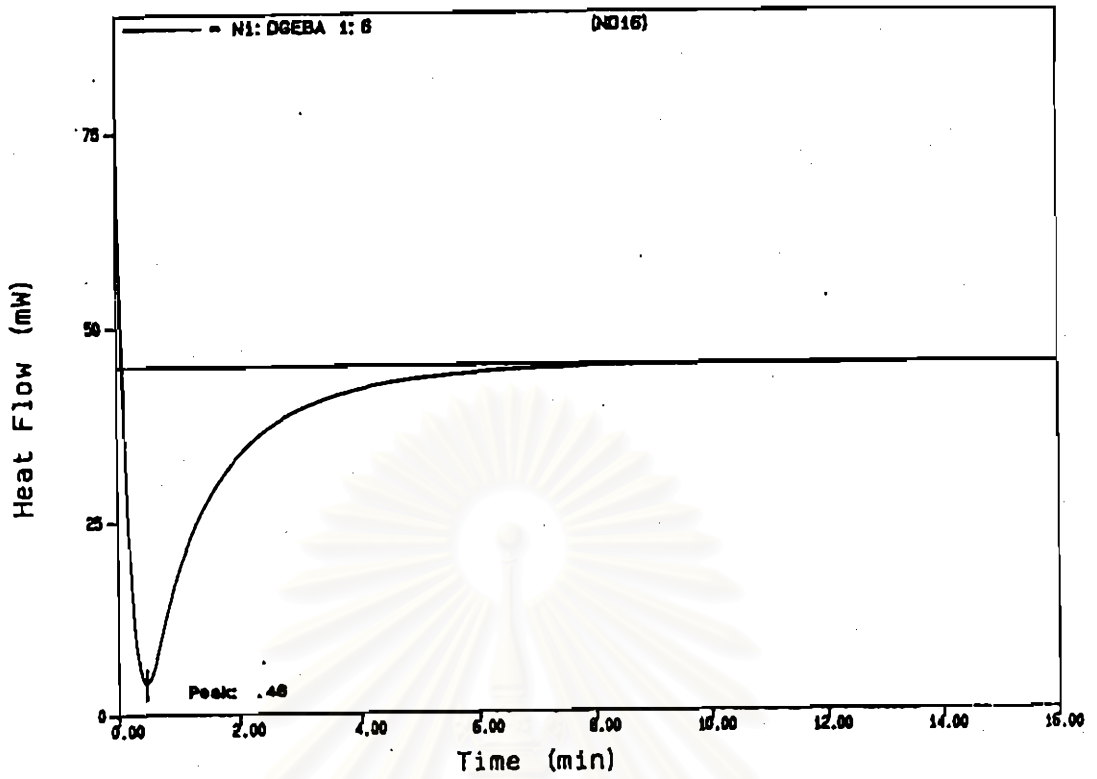


Figure 3.5. Isothermal DSC thermogram at 180°C of NiL:DGEBA at the equivalent weight ratio of 1:6

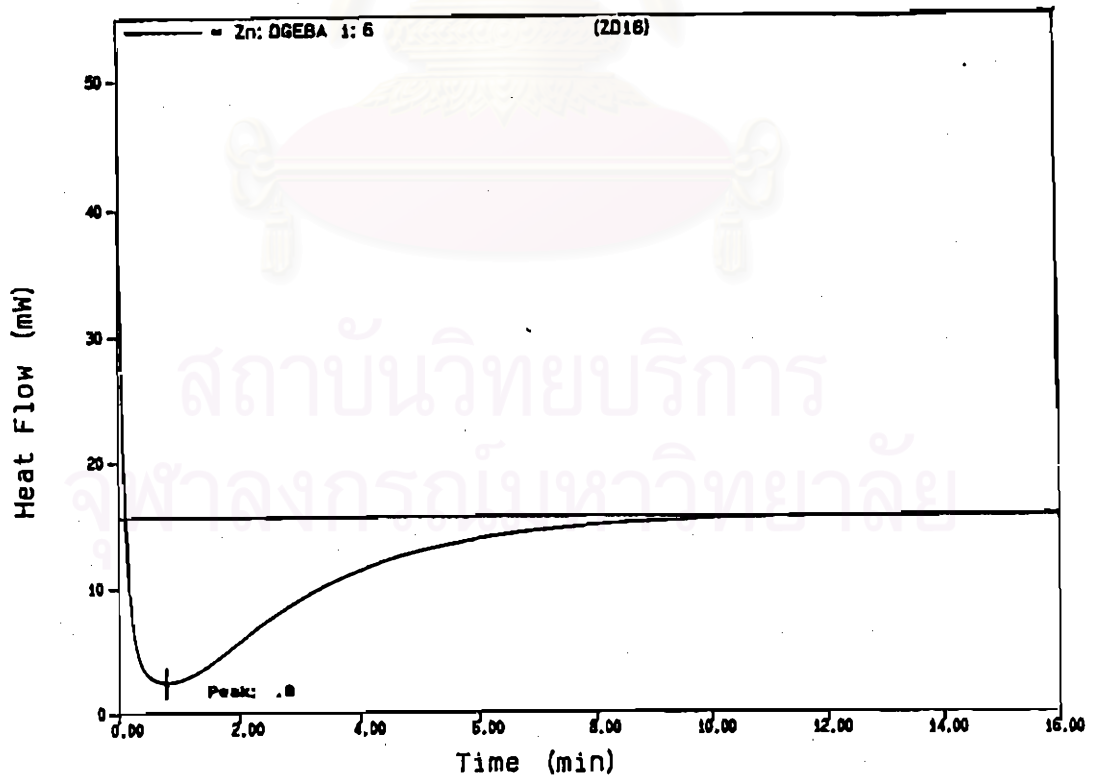


Figure 3.6. Isothermal DSC thermogram at 180°C of ZnL:DGEBA at the equivalent weight ratio of 1:6

Since the metal complexes are 6-coordinate, chelation between NH and metal must be broken before the crosslinking reaction can occur. This was confirmed by performing DSC experiments of NIL and ZnL as shown in Figures 3.7 and 3.8, respectively. Both thermograms of NIL and ZnL gave endothermic peaks at 135°C and 110°C, respectively, which might be due to the loss of water from the complex overlapping with the dissociation of the metal complexes.

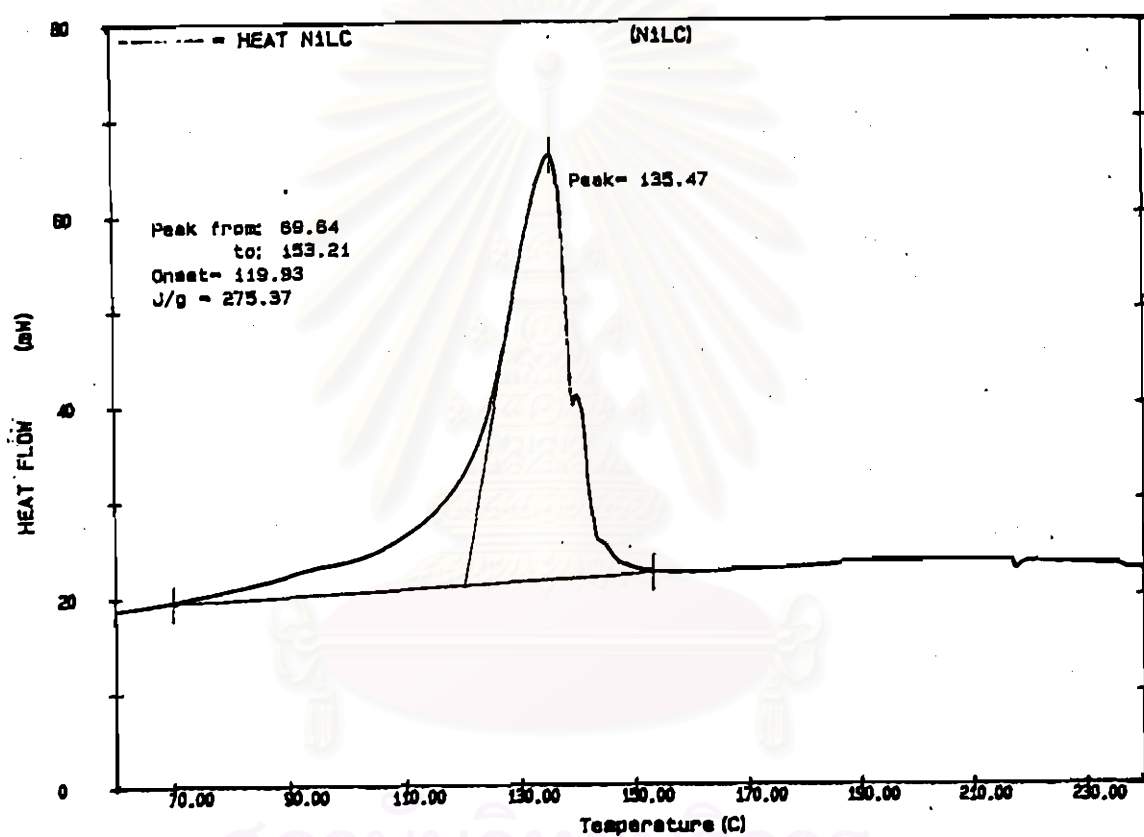


Figure 3.7. DSC thermogram of NIL

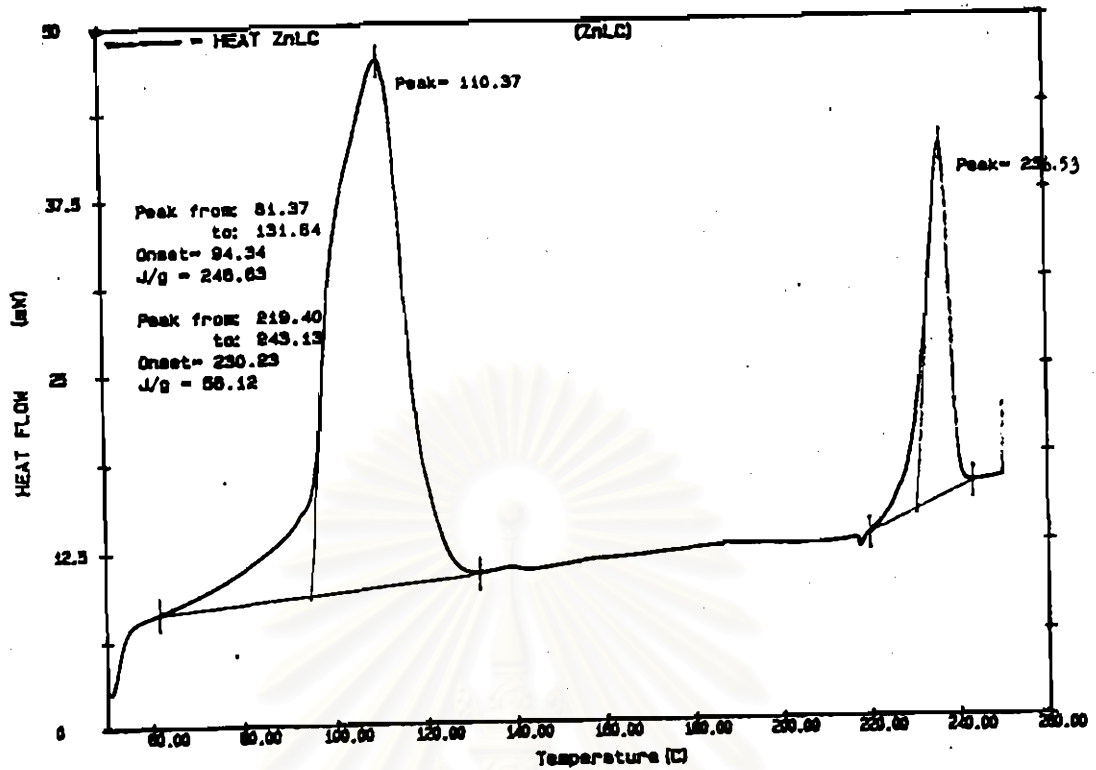
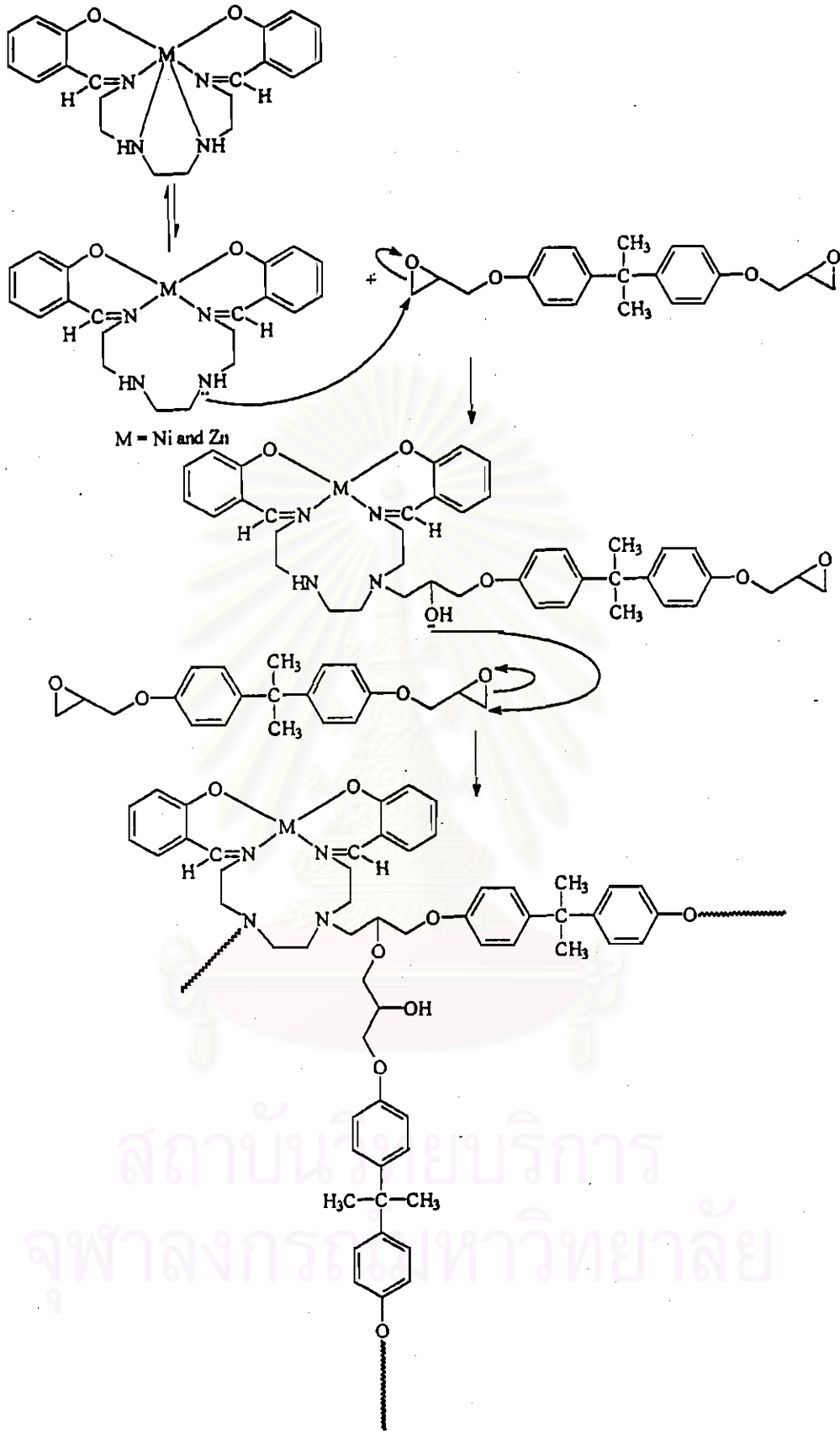


Figure 3.8. DSC thermogram of ZnL

The crosslinking mechanism was proposed to involve a ring opening of the epoxy group of DGEBA by an amino group of the metal complex to give a secondary alcohol. Another nitrogen of the metal complexes or an oxygen of the newly formed secondary alcohol can then attack an epoxy group of another DGEBA molecule. The same reaction occurs repeatedly to produce crosslinked epoxy polymer containing metal complexes (Scheme 3.4).



metal-containing epoxy polymer

Scheme 3.4. Possible mechanism of the crosslinking reaction of DGEBA with metal complexes.

3.4. Effect of Tetrabutyl Ammonium Hydroxide (Bu₄NOH)

From the previous results, the reaction between DGEBA and metal complexes occurs at high temperature which is difficult for mold casting. As reported in the literature, the reaction between DGEBA and phenol²³⁻²⁴ can be catalyzed with bases such as NaOH, tertiary amines and quarternary ammonium salts. Tetrabutyl ammonium hydroxide (Bu₄NOH) was chosen as a catalyst for the crosslinking reaction between DGEBA and the metal complexes in our study. The optimum crosslinking conditions could, again, be determined by DSC. Figures 3.9 and 3.10 are the thermograms obtained from heating a mixtures of metal complexes, DGEBA and Bu₄NOH at the equivalent weight ratio of 1 : 6 : 0.2.

From Figures 3.9 and 3.10, both thermograms gave exothermic crosslinking peaks which indicated that the crosslinking reaction had occurred. The temperature range of the crosslinking peak of NiL and ZnL were 81-233^oC and 91-231^oC, respectively and maximum peaks for NiL complex and ZnL were 151 and 153^oC, respectively. These are lower temperatures than in the crosslinking reactions without Bu₄NOH.

Isothermal crosslinking behavior of DGEBA with metal complexes in the Bu₄NOH was investigated at 140^oC. The equivalent weight ratio of NiL : DGEBA : Bu₄NOH was 6:1:0.2. Crosslinking reaction with NiL finished in about 11 minutes (Figure 3.11) and that of ZnL finished in about 7 minutes (Figure 3.12). Therefore, when Bu₄NOH was employed in the crosslinking reaction, ZnL required less crosslinking time than NiL.

Therefore, in the preparation of epoxy polymers, the temperature in the crosslinking reaction of DGEBA with NiL and ZnL in the presence of Bu₄NOH was chosen to be 140^oC

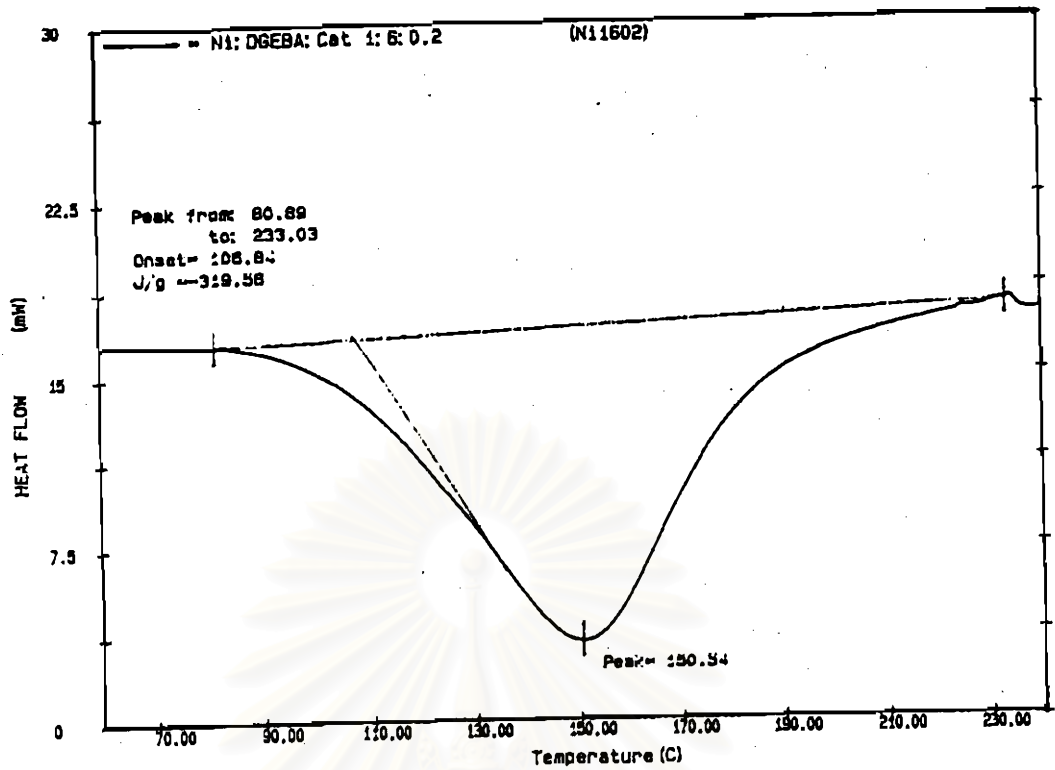


Figure 3.9. DSC thermogram of the mixture of NIL : DGEBA : Bu₄NOH at the equivalent weight ratio of 1 : 6 : 0.2.

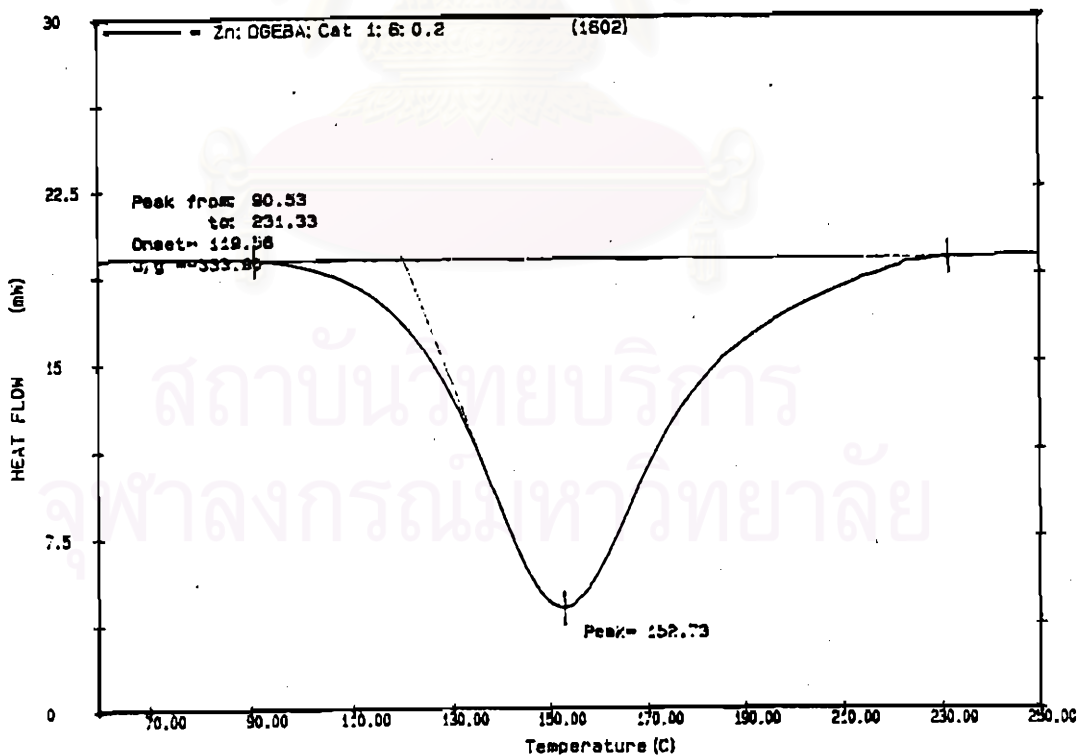


Figure 3.10. DSC thermogram of the mixture of ZnL : DGEBA : Bu₄NOH at the equivalent weight ratio of 1 : 6 : 0.2.

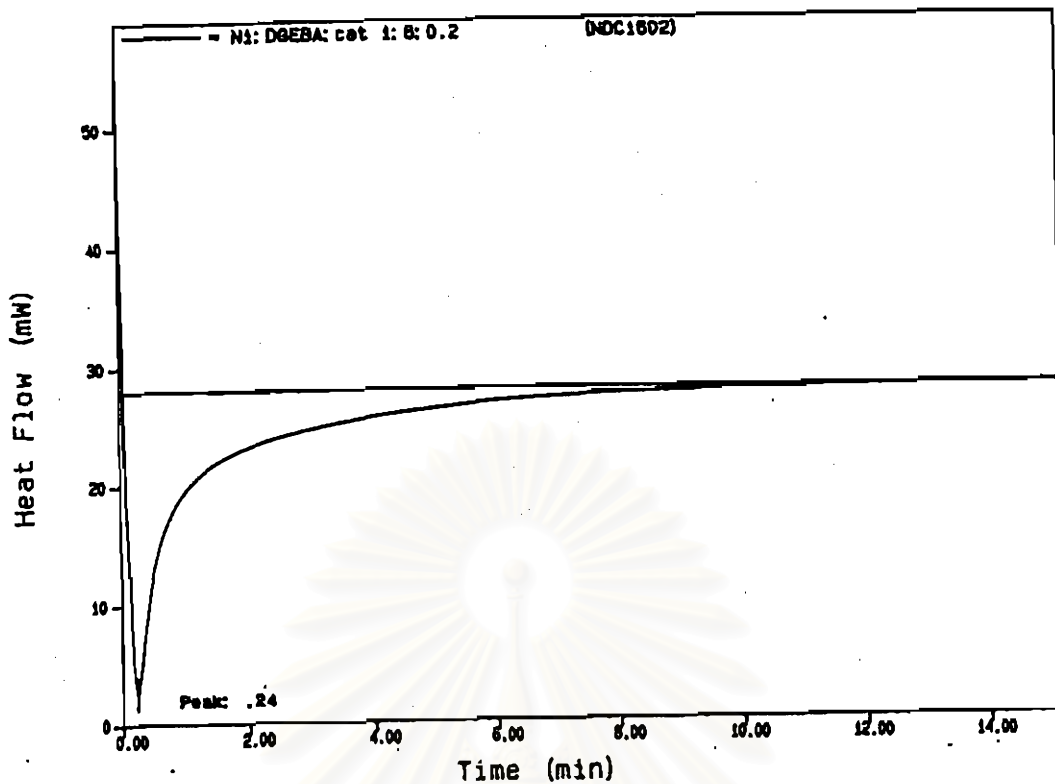


Figure 3.11. Isothermal DSC thermogram at 140 °C of NiL:DGEBA:Bu₄NOH at the equivalent weight ratio of 1:6:0.2.

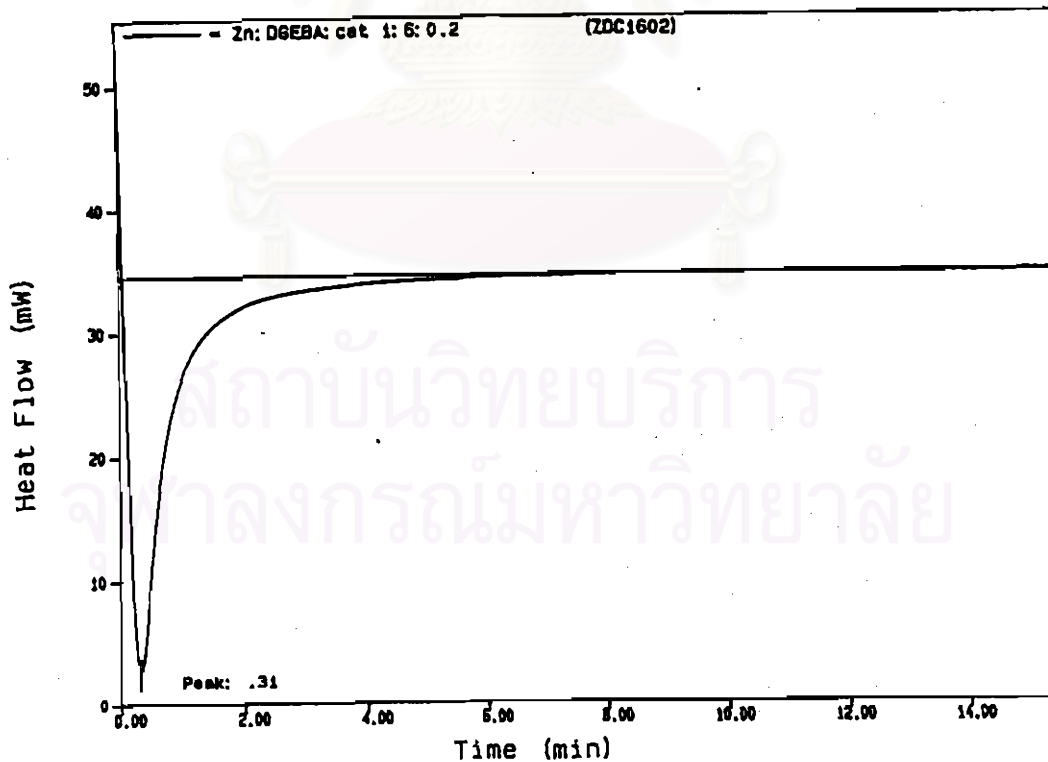
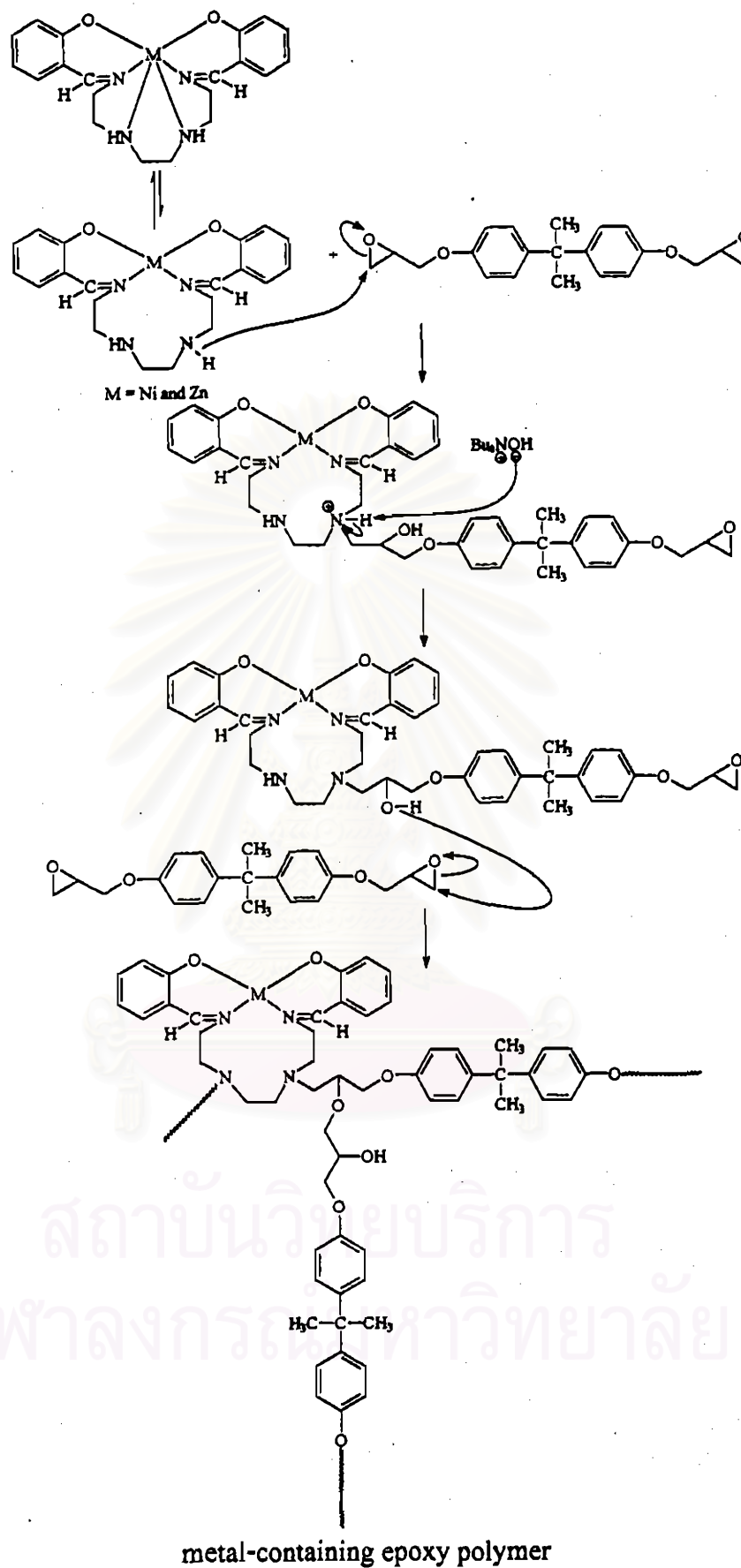


Figure 3.12. Isothermal DSC thermogram at 140 °C of ZnL:DGEBA:Bu₄NOH at the equivalent weight ratio of 1:6:0.2.

Tetrabutyl ammonium hydroxide probably acts as a basic catalyst. The metal complex first dissociated then the amine group opened the epoxide ring of DGEBA. Bu_4NOH probably could remove a proton from the ammonium salt. This results in faster polymerization to give the metal-containing polymers. A possible mechanism of crosslinking reaction in the presence of Bu_4NOH is shown in Scheme 3.5.



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Scheme 3.5. Possible mechanism of the crosslinking reaction of DGEBA with metal complexes in the presence of Bu₄NOH.

3.5. Characterization of Metal-containing Epoxy Polymers

3.5.1 Physical Properties

The next step was to prepare samples of crosslinked DGEBA for further characterization. The samples were prepared as described in the experimental section. The completeness of the crosslinking reaction could be observed by disappearance of characteristic IR band of the epoxide group at 917 cm^{-1}

The ratios between DGEBA : metal complexes : Bu_4NOH employed were 6:1:0, 6:1:0.2, 8:1:0.2, 10:1:0.2 and 12:1:0.2 in order to determine the optimum ratio that yielded polymers with the best properties.

The epoxy polymers were characterized by IR spectroscopy and thermal analysis. All complexes gave similar IR absorption bands as follows an absorption band of imine $\text{C}=\text{N}$ stretching at 1650 cm^{-1} ; absorption bands of aromatic $\text{C}-\text{H}$ bending of a 1,2-disubstitution benzene at 800 cm^{-1} .

Maleic anhydride and diethylenetriamine were also employed as crosslinking agents for DGEBA in order to compare the properties of the metal-containing epoxy polymer with the known system.

The thermal properties of the crosslinked epoxy polymers were studied using DMA and TGA. The Glass transition temperature (T_g) could be obtained from DMA by observing the maximum value of loss modulus. DMA thermograms of Ni and Zn-containing epoxy polymers were shown in Figure A.13-A.24. The values of T_g of crosslinked epoxy polymers obtained from different weight ratios of DGEBA and metal complexes without Bu_4NOH and in the presence of Bu_4NOH are shown in Table 1.

Table 3.1. Glass transition temperature of crosslinked epoxy polymers obtained from different weight ratios of DGEBA and metal complexes.

Crosslinking agent	Equivalent weight ratio of ML : DGEBA : Bu ₄ NOH	T _g (°C)
NiL	1 : 6 : 0	133
	1 : 6 : 0.2	127
	1 : 8 : 0.2	121
	1 : 10 : 0.2	110
	1 : 12 : 0.2	102
	1 : 14 : 0.2	69
ZnL	1 : 6 : 0	167
	1 : 6 : 0.2	144
	1 : 8 : 0.2	145
	1 : 10 : 0.2	151
	1 : 12 : 0.2	135
	1 : 14 : 0.2	120
Maleic anhydride	a	143
Diethylenetriamine	b	96

^a equivalent weight ratio of DGEBA : maleic anhydride was 1 : 2.8 and 0.1 phr of dimethylbenzylamine was used as a catalyst

^b equivalent weight ratio of diethylenetriamine : DGEBA was 1 : 1

TGA thermograms of DGEBA crosslinked with NiL complex at mole ratio between NiL : DGEBA : Bu₄NOH of 1 : 6 : 0.2 showed 0.5 % weight loss at the temperature range of 0-200 °C. The first step of weight loss indicates a small amount of water in the metal complexes. The rapid second weight loss at the temperature range 280-363 °C is due to decomposition of the polymer chain.

TGA thermograms of DGEBA crosslinked with different mole ratios of NiL and different mole ratios of ZnL gave similar results. Table 2 shows amount of weight loss at NiL and ZnL containing epoxy polymers at different temperatures.

Table 3.2. Heat resistance of Ni and Zn containing epoxy polymers.

Metal Complexes	ratio of complexes: DGEBA : Bu ₄ N OH	Beginning Temperature (°C)	Temperature which weight loss occurs (°C)			
			5%	10%	20%	30%
NiL	1:6:0	100	285	304	330	352
	1:6:0.2	150	293	311	337	363
	1:8:0.2	150	270	300	326	350
	1:10:0.2	150	263	300	326	344
	1:12:0.2	211	296	319	341	367
	1:14:0.2	214	300	321	343	364
ZnL	1:6:0	100	178	285	319	344
	1:6:0.2	150	269	300	330	352
	1:8:0.2	150	289	315	337	356
	1:10:0.2	150	250	300	330	350
	1:12:0.2	175	285	304	333	363
	1:14:0.2	200	285	311	337	363

To determine the thermal stability of the metal-containing epoxy polymers, an isothermal study at 250°C for 48 hours in air was employed. Table 3 shows weight loss of Ni- and Zn-containing epoxy polymers at different times. The metal-containing

epoxy polymers with the best thermal stability were those prepared when the ratios of ML:DGEBA:Bu₄NOH were 1:8:0.2, 1:10:0.2 and 1:12:0.2.

Table 3.3. Thermal stability of Ni and Zn containing epoxy polymers at 250 °C.

Crosslinking Agent	Ratio of ML : DGEBA : Bu ₄ NOH	% Weight loss at different time			
		12 h	24 h	36 h	48 h
NIL	1:6:0	1.6	2.8	3.9	5.1
	1:6:0.2	1.4	2.1	2.9	3.4
	1:8:0.2	1.0	1.7	2.3	2.7
	1:10:0.2	0.8	1.4	1.9	2.3
	1:12:0.2	0.9	1.8	2.1	2.7
	1:14:0.2	0.9	2.0	2.6	3.2
ZnL	1:6:0	2.0	4.1	6.2	7.7
	1:6:0.2	1.4	2.4	3.4	4.1
	1:8:0.2	1.1	2.1	2.9	3.6
	1:10:0.2	1.1	2.1	3.0	3.7
	1:12:0.2	0.9	2.2	2.9	3.7
	1:14:0.2	1.0	2.2	3.1	4.0
Maleic anhydride	a	1.9	2.7	3.4	4.0
Diethylenetriamine	b	9.1% within 2 hours			

^a equivalent weight ratio of DGEBA : maleic anhydride was 1 : 2.8 and 0.1 phr of dimethylbenzylamine was used as a catalyst

^b equivalent weight ratio of diethylenetriamine : DGEBA was 1 : 1

3.5.2. Mechanical Properties

The epoxy polymers obtained from ML:DGEBA:Bu₄NOH at the equivalent weight ratios of 1 : 8 : 0.2 and 1 : 10 : 0.2 were chosen since they have good thermal stability. Table 4 shows tensile strength of the metal containing epoxy polymers.

Table 3.4 Mechanical properties of metal containing epoxy polymers.

Crosslinking agent	Ratio of ML:DGEBA:Bu ₄ NOH	Tensile strength (N/mm ²)
NiL	1 : 8 : 0.2	44
	1 : 10 : 0.2	45
ZnL	1 : 8 : 0.2	42
	1 : 10 : 0.2	41
Maleic anhydride	a	56
Diethylene triamine	b	44

^a equivalent weight ratio of DGEBA : maleic anhydride was 1 : 2.8 and 0.1 phr of dimethylbenzylamine was used as a catalyst

^b equivalent weight ratio of diethylenetriamine : DGEBA was 1 : 1

In comparison between using metal complexes and diethylenetriamine as crosslinking agents for DGEBA, the advantages of using metal complexes as crosslinking agent are higher T_g values and better thermal stability of epoxy polymers could be obtained. The disadvantage is that a higher crosslinking temperature is needed.

Comparing to maleic anhydride-DGEBA system, the metal-containing epoxy polymers were obtained at a lower crosslinking temperature while possessing comparable thermal stability and tensile strength.