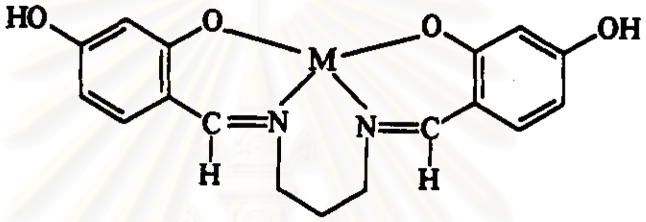
CHAPTER III

RESULTS AND DISCUSSION

A general structure of metal complexes in this work is shown in Figure 3.



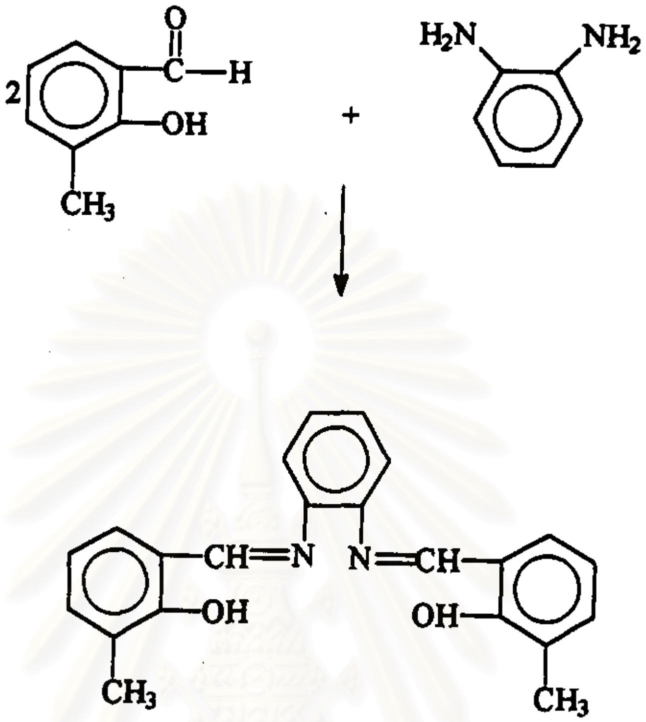
M = Co, Ni and Cu

Figure 3. Structure of the metal complexes.

The above complex was chosen because of its stability. The **Co-1**, **Ni-1** and **Cu-1** complexes exist in monomer with stable square planar geometry. Moreover, the complexes have two phenolic groups which are able to react with the epoxy resin to give epoxy polymers. The metal may also donate electron and therefore make the phenolic groups more nucleophilic.

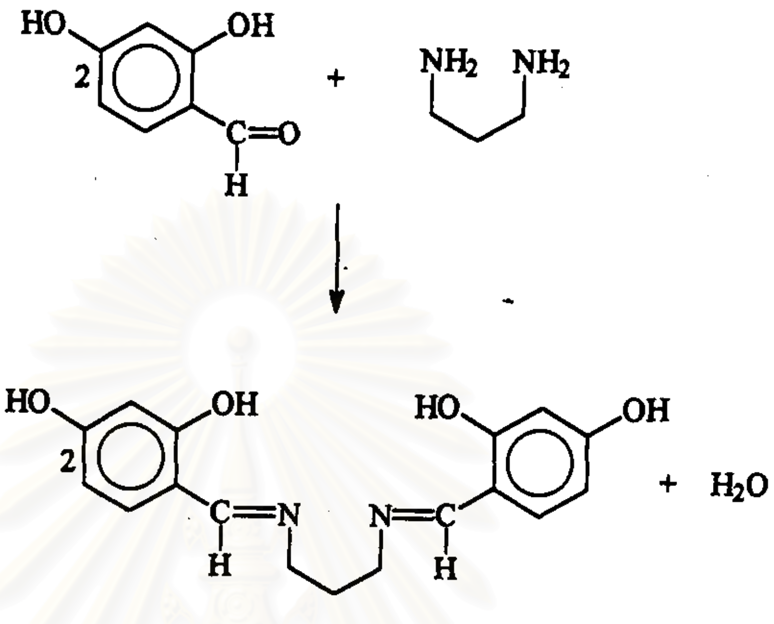
3.1 Synthesis of Tetradentate Schiff's Base Ligand

It is well known that tetradentate Schiff's base ligand, such as 1,2-Bis-(2-hydroxy-3-methylbenzylideneamino)-benzene, can be synthesized by condensation reaction of amine with aldehyde[20]. The reaction produces the imine N=C or Schiff's base compound and water. The reaction proceeds smoothly with high yield as shown in Scheme 9.



Scheme 9. Synthesis of 1,2-Bis-(2-hydroxy-3-methylbenzylideneamino)- benzene.

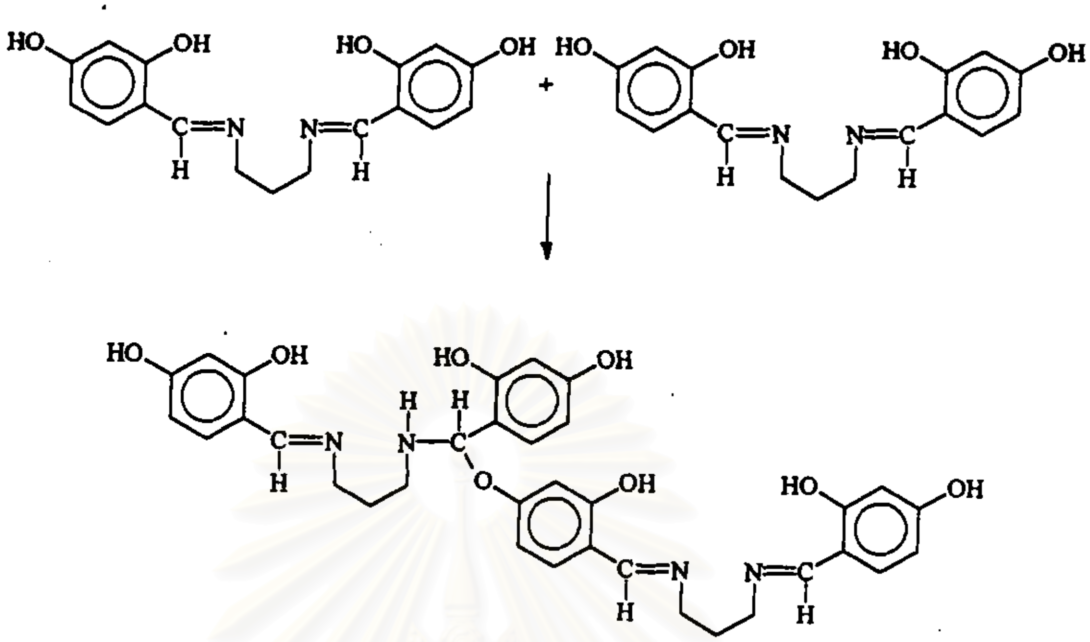
In our study, ligand (1) was synthesized by using the similar reaction as shown in Scheme 9. Starting from 2,4-dihydroxybenzaldehyde and 1,3-diaminopropane, a lone pair of electrons on the amine nitrogen attacks on carbonyl carbon of aldehyde following by the loss of water to give ligand (1) as shown in Scheme 10.



(1)

Scheme 10. Synthesis of ligand (1).

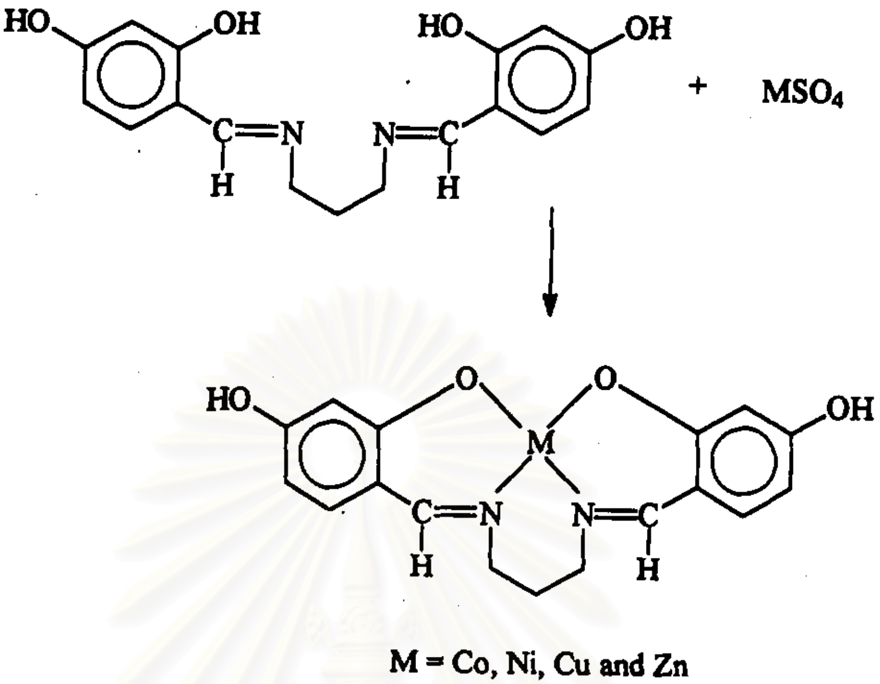
The ligand (1) was stable in solution but unstable as a solid with out solvent. When the solution of (1) was evaporated to dryness, it decomposed to give a viscous product. The decomposition might be due to the reaction between phenolic groups and imine groups shown in Scheme 11. Therefore, the ligand(1) had to be kept in methanolic solution and used in the next steps without purification.



Scheme 11. Possible decomposition reaction of ligand (1).

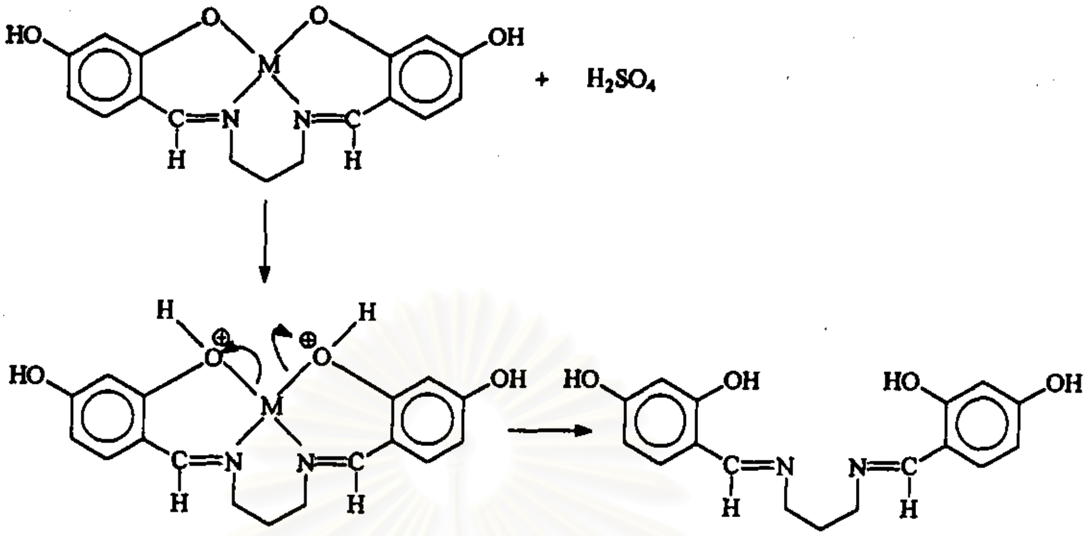
3.2 Synthesis of Tetradentate Schiff's Base Metal Complexes

The complexation reaction was done by mixing the methanolic solution of ligand (1) with metal sulfates to obtain tetradentate Schiff's base metal complexes shown in Scheme 12.



Scheme 12. Synthesis of complexes using metal sulfates.

When metal sulfates were used, the %yield of **Ni-1**, **Cu-1**, **Zn-1** and **Co-1** complexes were 60%, 50%, 40% and 35%, respectively. The purity of complexes were poor and the purification could not be performed effectively. This might be due to the formation of sulfuric acid as a by-product which caused protonation of the imime nitrogen or the phenolic oxygen of the complexes as shown in Scheme 13. Therefore, the obtained product might be a mixture of various forms of complexes and the free ligand (**1**).



Scheme 13. Protonation of Schiff's base metal complexes by H_2SO_4.

The obtained complexes were characterized by IR spectroscopy and elemental analysis. All complexes gave similar IR absorption bands shown in Tables 1-4 and their spectra are shown in the appendix.

Table 1. IR absorption characteristic of **Co-1** complex.

Absorption band (cm^{-1})	Assignment
3494	OH stretching, strong
3000-3200	aromatic C-H stretching, weak
2800-3000	aliphatic C-H stretching, weak
1617	C=N stretching, strong
1400-1600	aromatic C=C stretching, medium
1233	aromatic C-O stretching, strong
985, 845	aromatic C-H bending, medium

Table 2. IR absorption characteristic of Ni-1 complex.

Absorption band (cm^{-1})	Assignment
3467	OH stretching, strong
3000-3100	aromatic C-H stretching, weak
2800-3000	aliphatic C-H stretching, weak
1615	C=N stretching, strong
1400-1600	aromatic C=C stretching, medium
1234	aromatic C-O stretching, strong
990, 844	aromatic C-H bending, medium

Table 3. IR absorption characteristic of Cu-1 complex.

Absorption band (cm^{-1})	Assignment
3494	OH stretching, strong
3000-3100	aromatic C-H stretching, weak
2800-3000	aliphatic C-H stretching, weak
1611	C=N stretching, strong
1400-1600	aromatic C=C stretching, medium
1227	aromatic C-O stretching, strong
990, 844	aromatic C-H bending, medium

Table 4. IR absorption characteristic of **Zn-1** complex *.

Absorption band (cm^{-1})	Assignment
3440	OH stretching, strong
3000-3100	aromatic C-H stretching, weak
2800-3000	aliphatic C-H stretching, strong
1632	C=N stretching, medium
1400-1600	aromatic C=C stretching, medium
1223	aromatic C-O stretching, strong
943, 846	aromatic C-H bending, weak

Elemental analyses of the complexes are shown in Table 5. The results indicate that all complexes have water in their composition. All complexes exist in monomer forms and the empirical formular of **Co-1**, **Ni-1** and **Cu-1** complexes are $C_{17}H_{16}N_2O_4Co{\bullet}4H_2O$, $C_{17}H_{16}N_2O_4Ni{\bullet}2H_2O$ and $C_{17}H_{16}N_2O_4Cu{\bullet}2H_2O$, respectively.

Table 5 Elemental analyses of the metal complexes

Complexes	%C found (cald.)	%H found (cald.)	%N found (cald.)	%M found (cald.)
Co-1	46.75(46.06)	5.46(5.25)	6.32(6.55)	12.09(13.29)
Ni-1	50.19(50.16)	4.80(4.95)	6.65(6.88)	13.45(14.42)
Cu-1	48.74(49.57)	4.63(4.89)	6.34(6.80)	15.84(15.43)

* For **Zn-1** complex, the data from elemental analysis is not matched with the calculated result.

3.3 Crosslinking Reaction of DGEBA Epoxy Resin with Tetradentate Schiff's base Metal Complexes

It is known that DGEBA can be crosslinked using a variety of phenolic compounds such as bisphenol-A and 1,7-dihydroxynapthalene to obtain epoxy polymers.[9-10] Therefore, it is possible to crosslink DGEBA with the use of metal complexes by similar reactions.

The DSC technique was employed in order to investigate whether crosslinking of DGEBA with metal complexes can occur. The suitable crosslinking condition could also be determined by using this DSC 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 closed aluminum pan in air. The temperature range was 25-400 °C at a heating rate of 20 °C/min. Figures 4, 5 and 6 are the thermograms obtained from heating mixtures between **Co-1** , **Ni-1** and **Cu-1** complexes and DGEBA, respectively.

From Figures 4-6, all thermograms gave exothermic crosslinking peaks which indicated that the crosslinking reaction occurred.[23] **Co-1** complex gave crosslinking peak at the range of 160-250 °C with the maximum peak at 185 °C. **Ni-1** complex gave crosslinking peak at the range of 200-280 °C with the maximum peak at 255 °C. **Cu-1** complex gave crosslinking peak at the range of 170-230 °C with the maximum peak at 200 °C. Zn complex gives crosslinking peak at the range of 220-340 °C with the maximum peak at 287 °C. Therefore, in order to prepare epoxy polymers, the crosslinking temperature in the crosslinking reaction of DGEBA with **Co-1** and **Cu-1** complexes was chosen at 200 °C and the crosslinking temperature of DGEBA with **Ni-1** complex was chosen at 240 °C. Crosslinking of DGEBA with Zn complex could not be done since the crosslinking temperature was too high for the available apparatus.

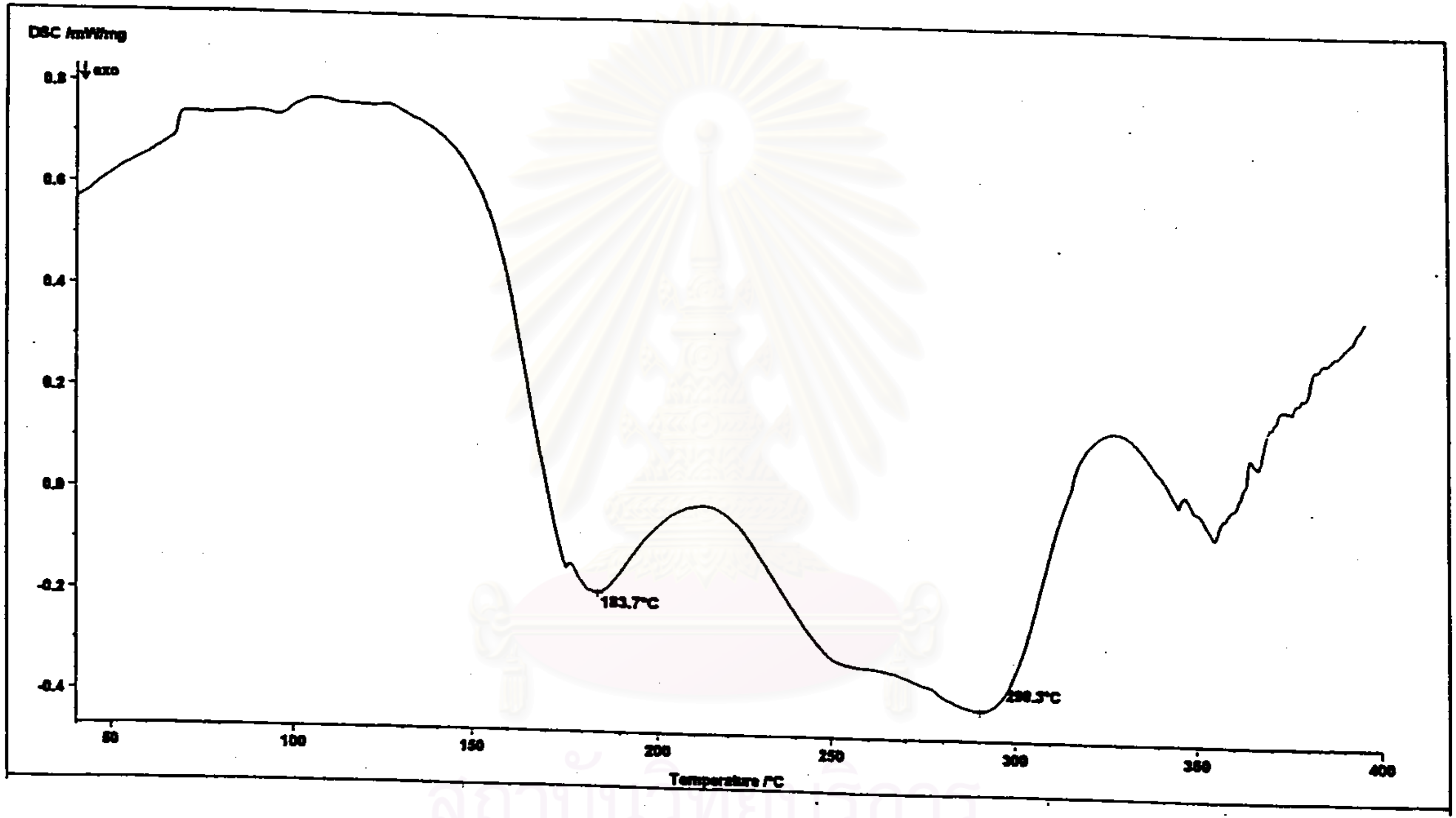


Figure 4. DSC thermogram of the mixture of **Co-1** and DGEBA at **Co-1**:DGEBA ratio of 1:6

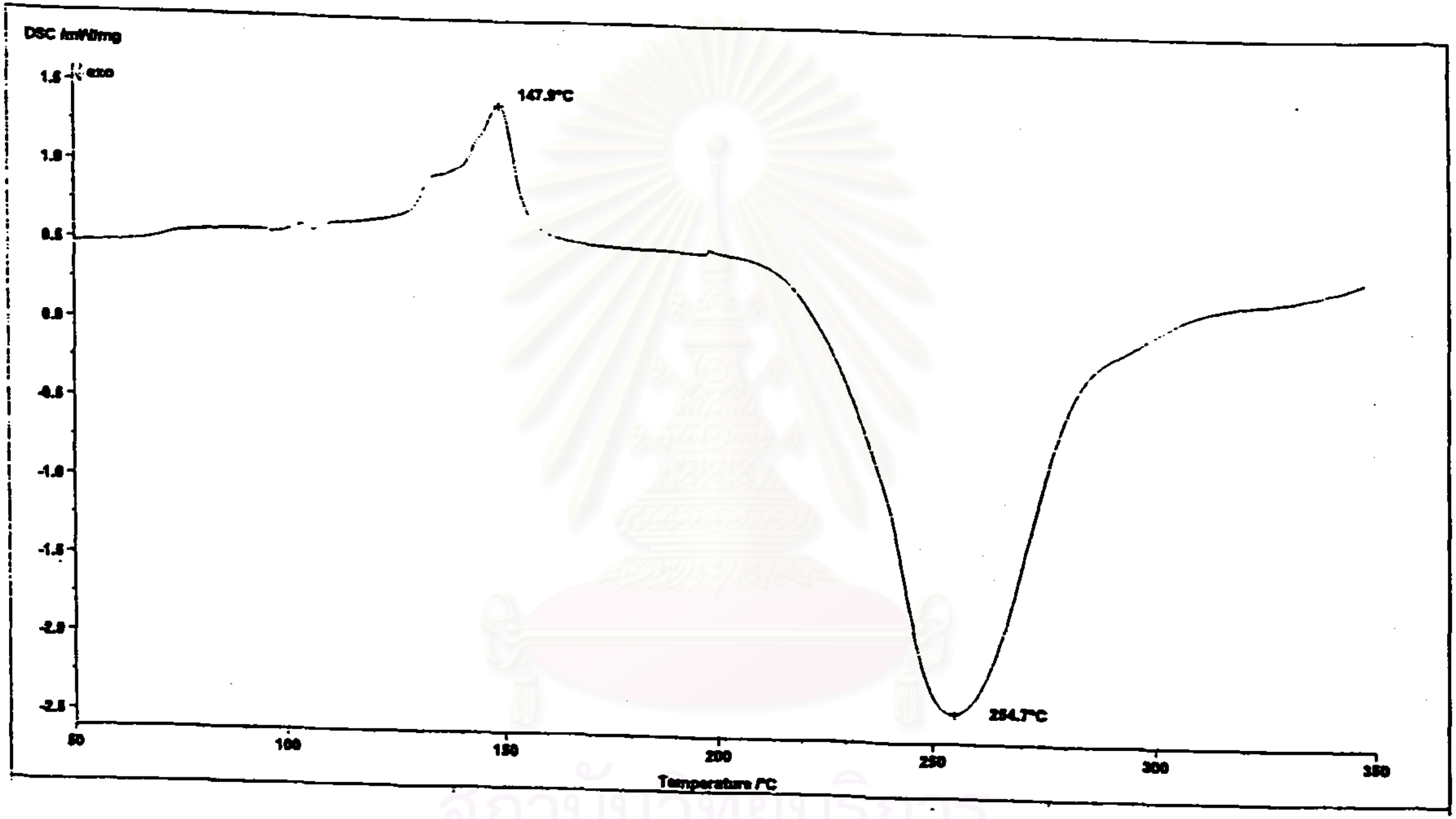


Figure 5. DSC thermogram of the mixture of Ni-1 and DGEBA at Ni-1:DGEBA ratio of 1:6.

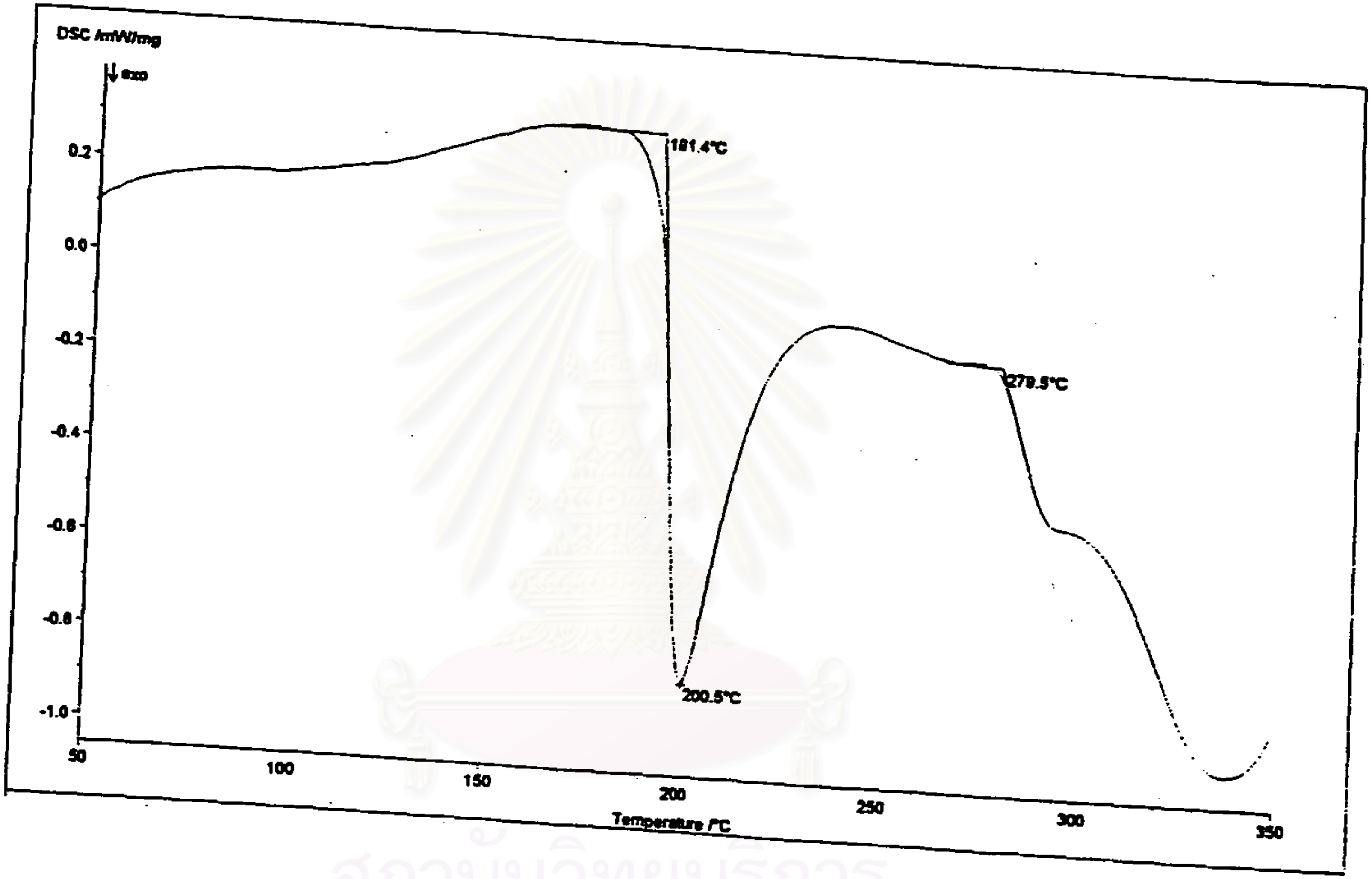


Figure 6. DSC thermogram of the mixture of Cu-1 and DGEBA at Cu-1:DGEBA ratio of 1:6.

Isothermal crosslinking behavior of DGEBA with different mole ratios of metal complexes was investigated. Isothermal crosslinking of DGEBA with **Cu-1** complex was done at a constant temperature of 200 °C. When mole ratio between **Cu-1** complex and DGEBA was 1:6, crosslinking reaction finished in about 13 minutes (Figure 7). At the higher mole ratio of 1:1.67, crosslinking reaction took 1.25 minutes, which is shorter since there was more **Cu-1** complex to react with DGEBA (Figure 8). Isothermal crosslinking behavior of DGEBA with **Ni-1** and **Co-1** complexes are done at 250 °C and 200 °C, respectively and the results are similar to the **Cu-1** case (Figures 9-12).

The next step was to prepare samples of crosslinked DGEBA for further characterization of physical propreties. The samples were prepared as described in the experiment section. The time used for crosslinking reaction was 3 hours to ensure the completed reaction, which could be observed by disapperance of characteristic IR band of epoxide group at 920 cm^{-1}.

The crosslinking mechanism is proposed to involve a ring opening of epoxy group of DGEBA by the phenolic hydroxy oxygen of the metal complex giving a secondary alcohol product. Another phenolic hydroxy oxygen of the metal complex then attacks the epoxy group of another molecule of DGEBA and opens the epoxy ring. The same reaction occurs repeatedly producing epoxy polymer containing metal complexes shown in Scheme 14.

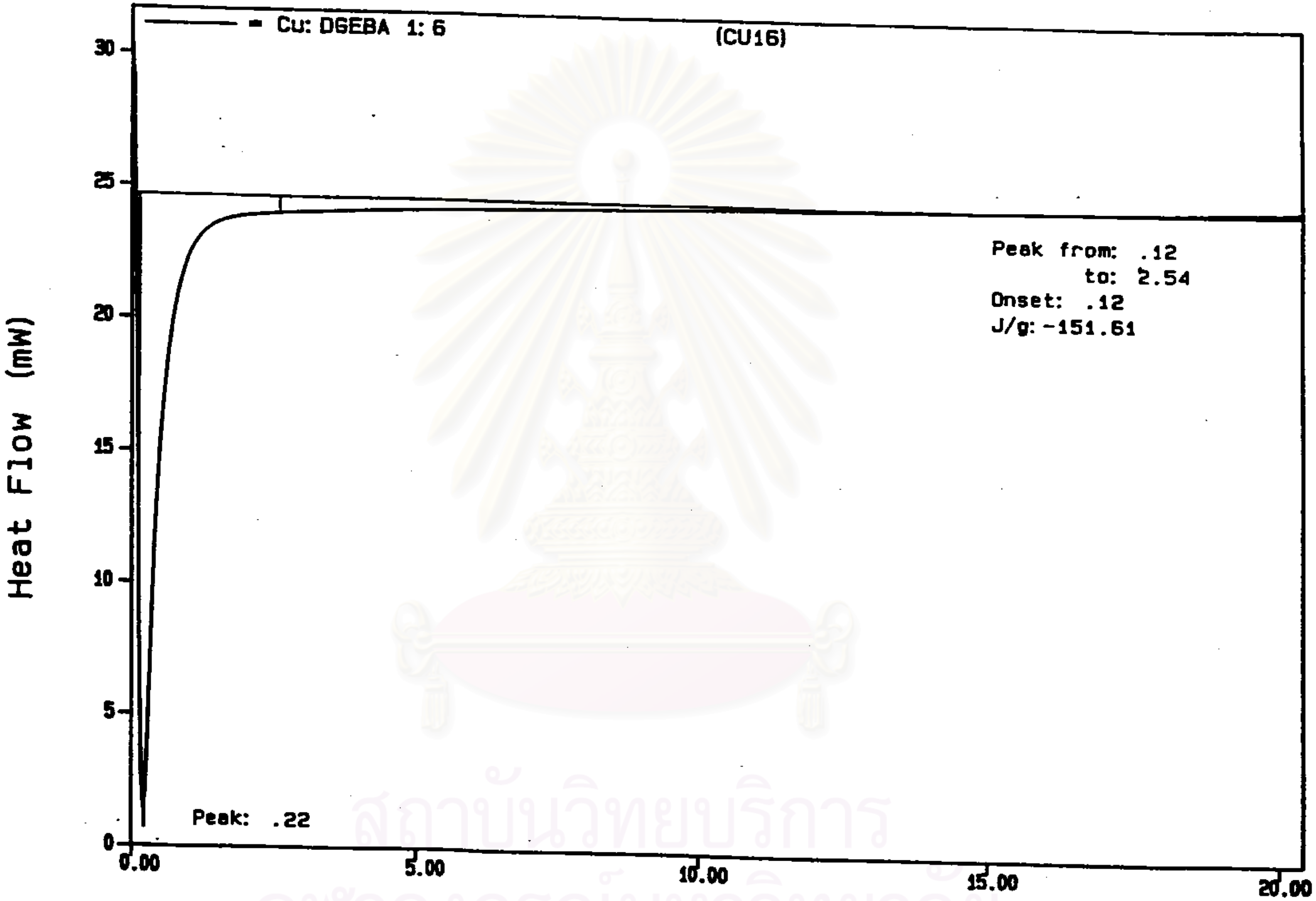


Figure 7. Isothermal (200 °C) DSC thermogram of the mixture of Cu-1 and DGEBA at Cu-1:DGEBA ratio of 1:6.

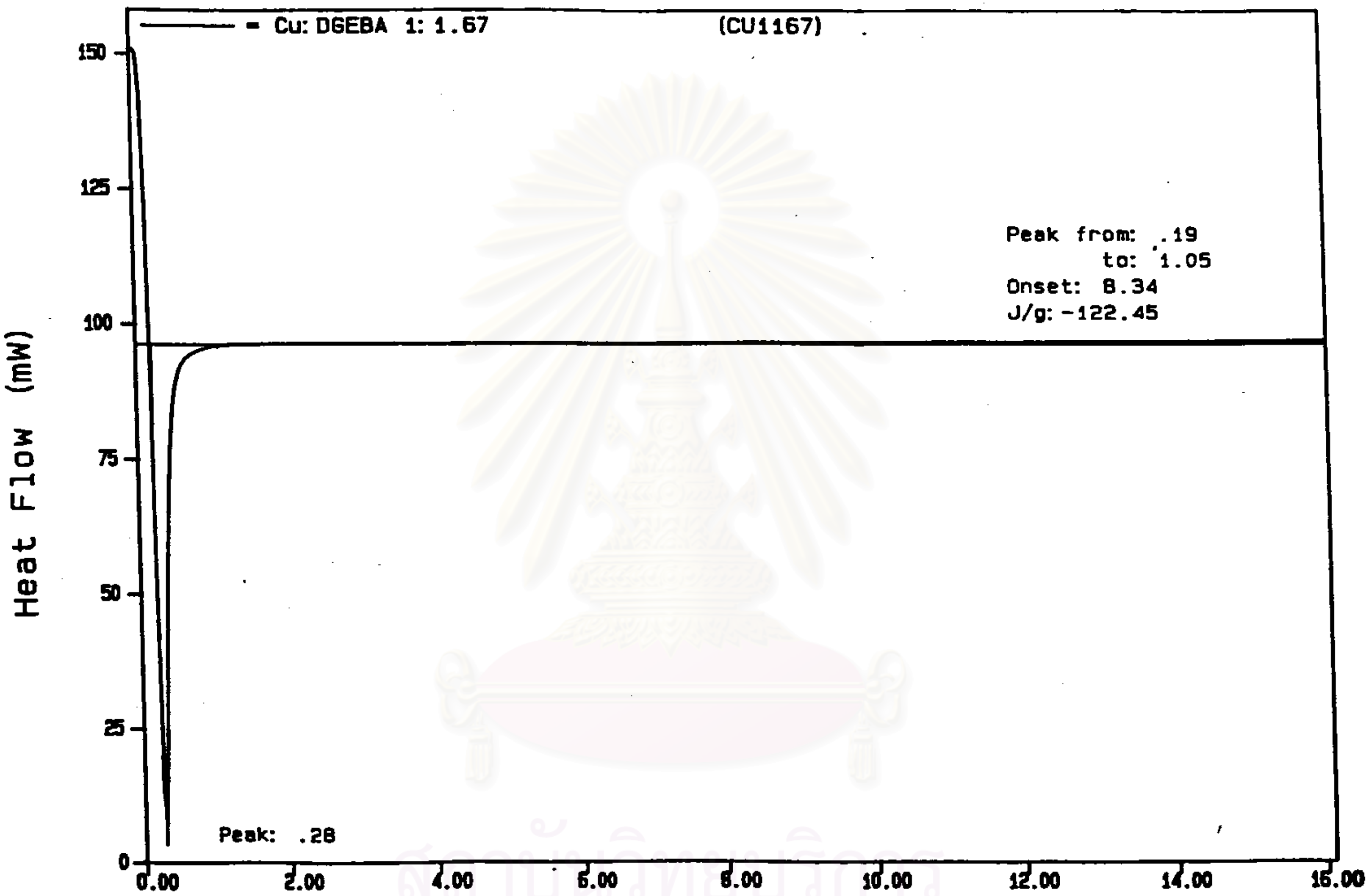


Figure 8. Isothermal (200 °C) DSC thermogram of the mixture of Cu-1 and DGEBA at Cu-1:DGEBA ratio of 1:1.67.

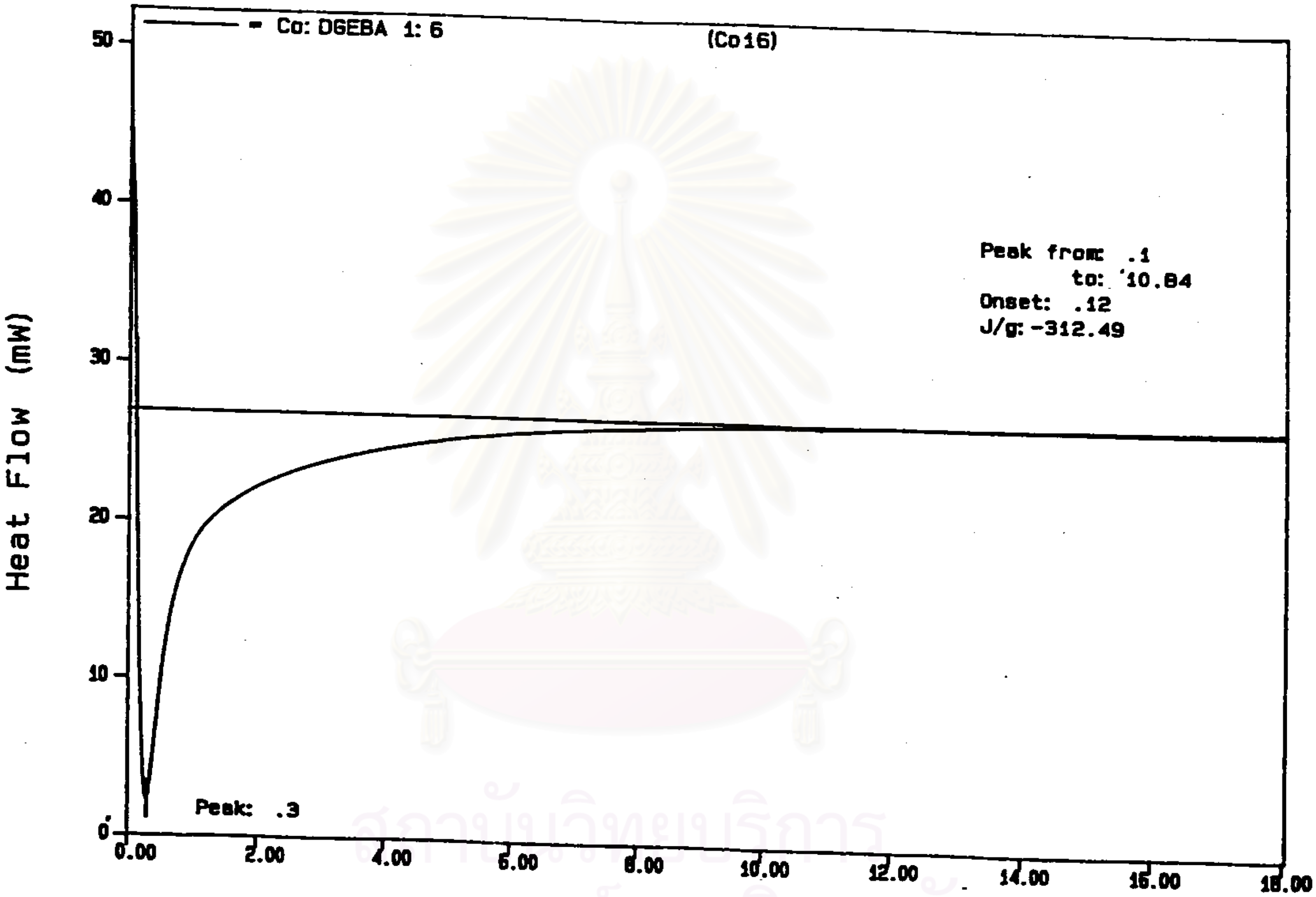


Figure 9. Isothermal (200 °C) DSC thermogram of the mixture of Co-1 and DGEBA at Co-1:DGEBA ratio of 1:6

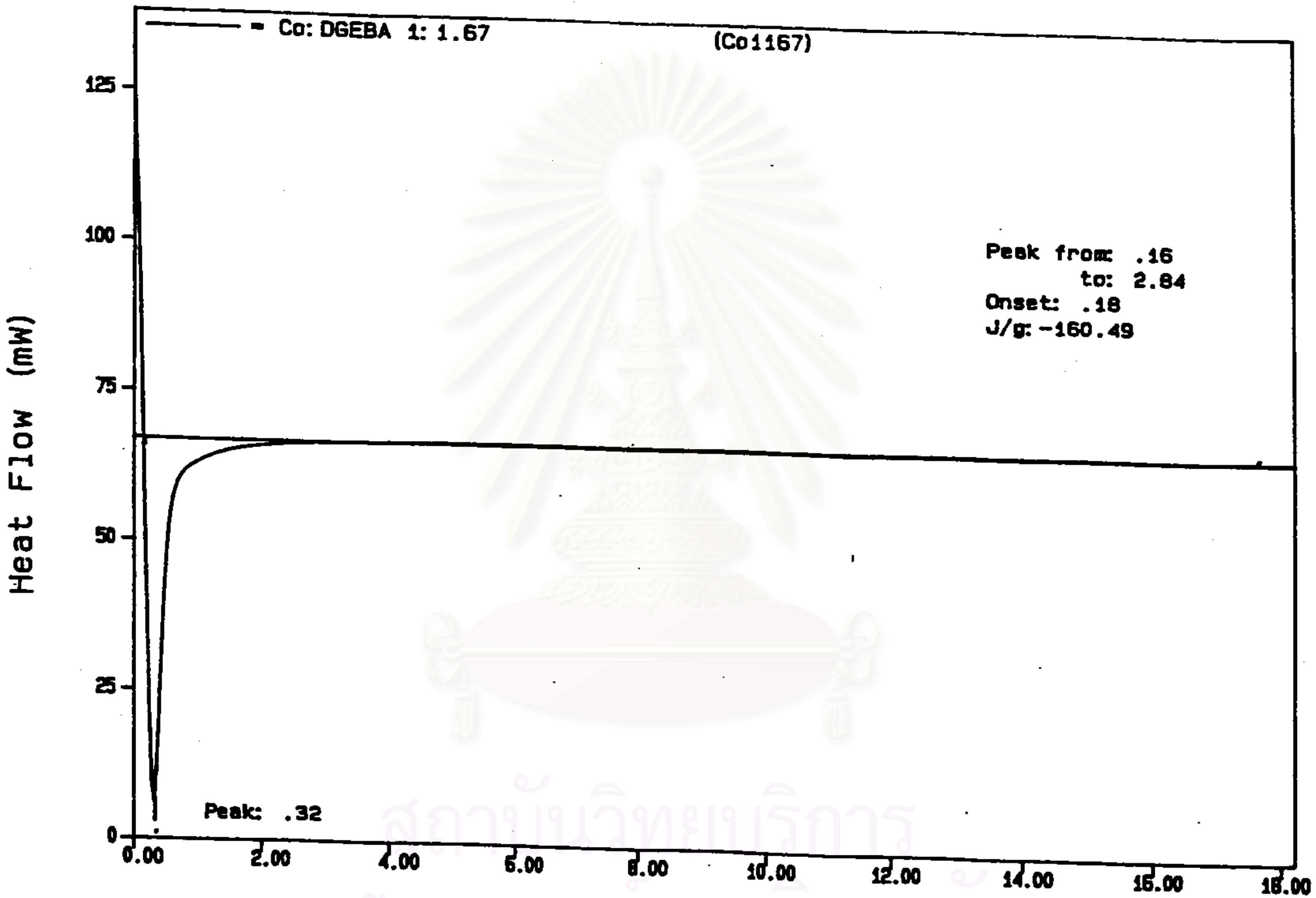


Figure 10. Isothermal (200 °C) DSC thermogram of the mixture of Co-1 and DGEBA at Co-1:DGEBA ratio of 1:1.67.

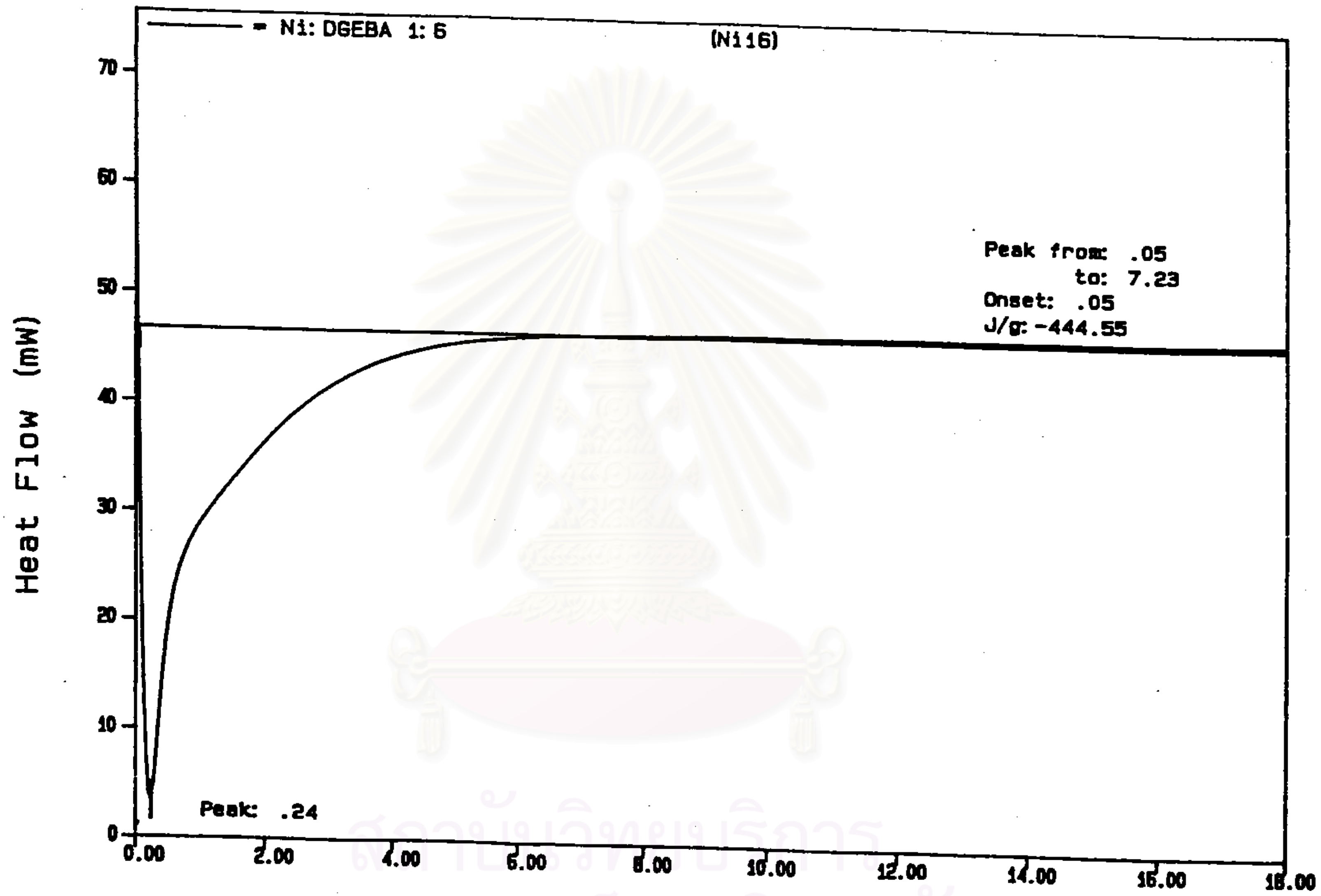


Figure 11. Isothermal (250 °C) DSC thermogram of the mixture of Ni-1 and DGEBA at Ni-1:DGEBA ratio of 1:6.

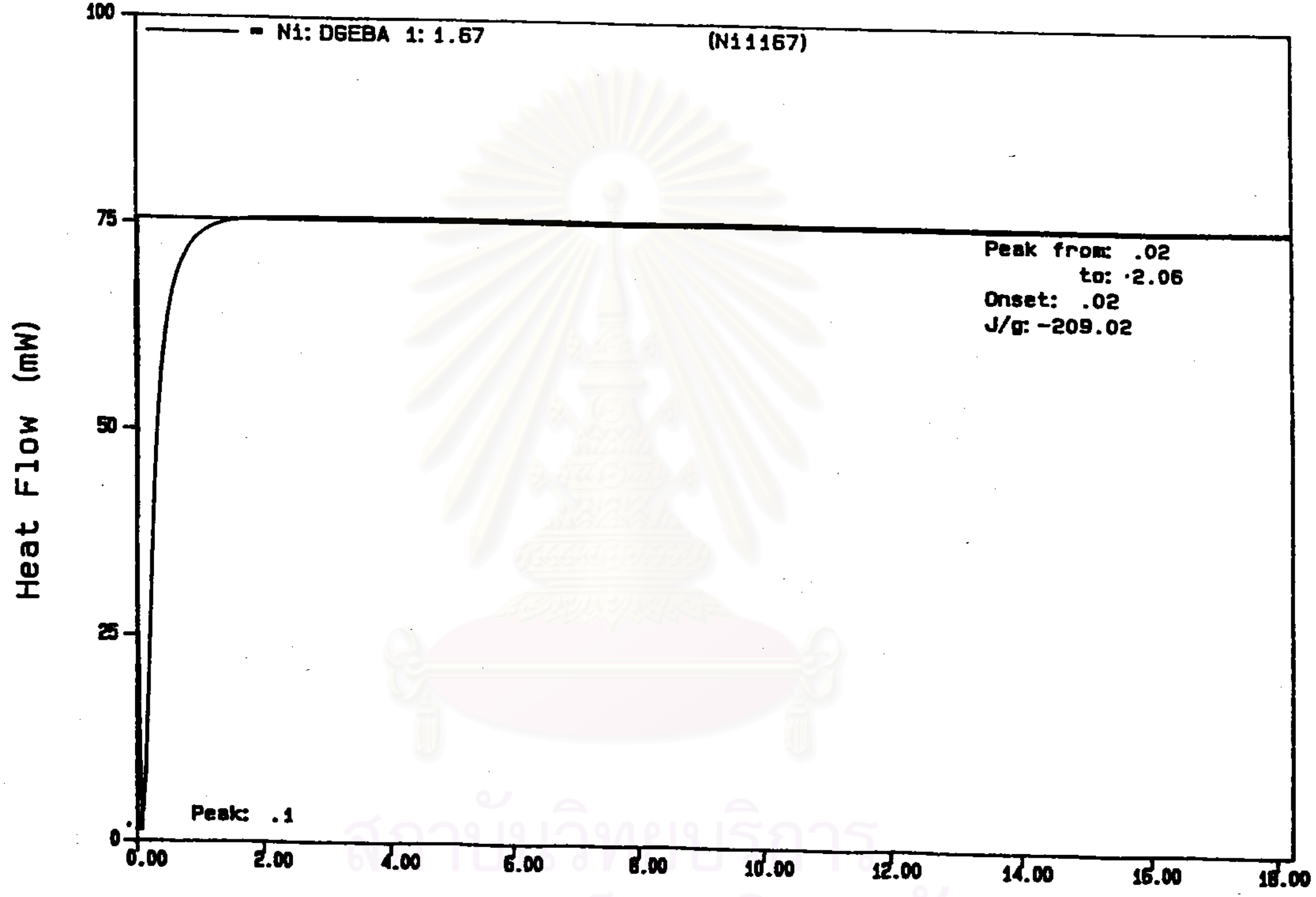
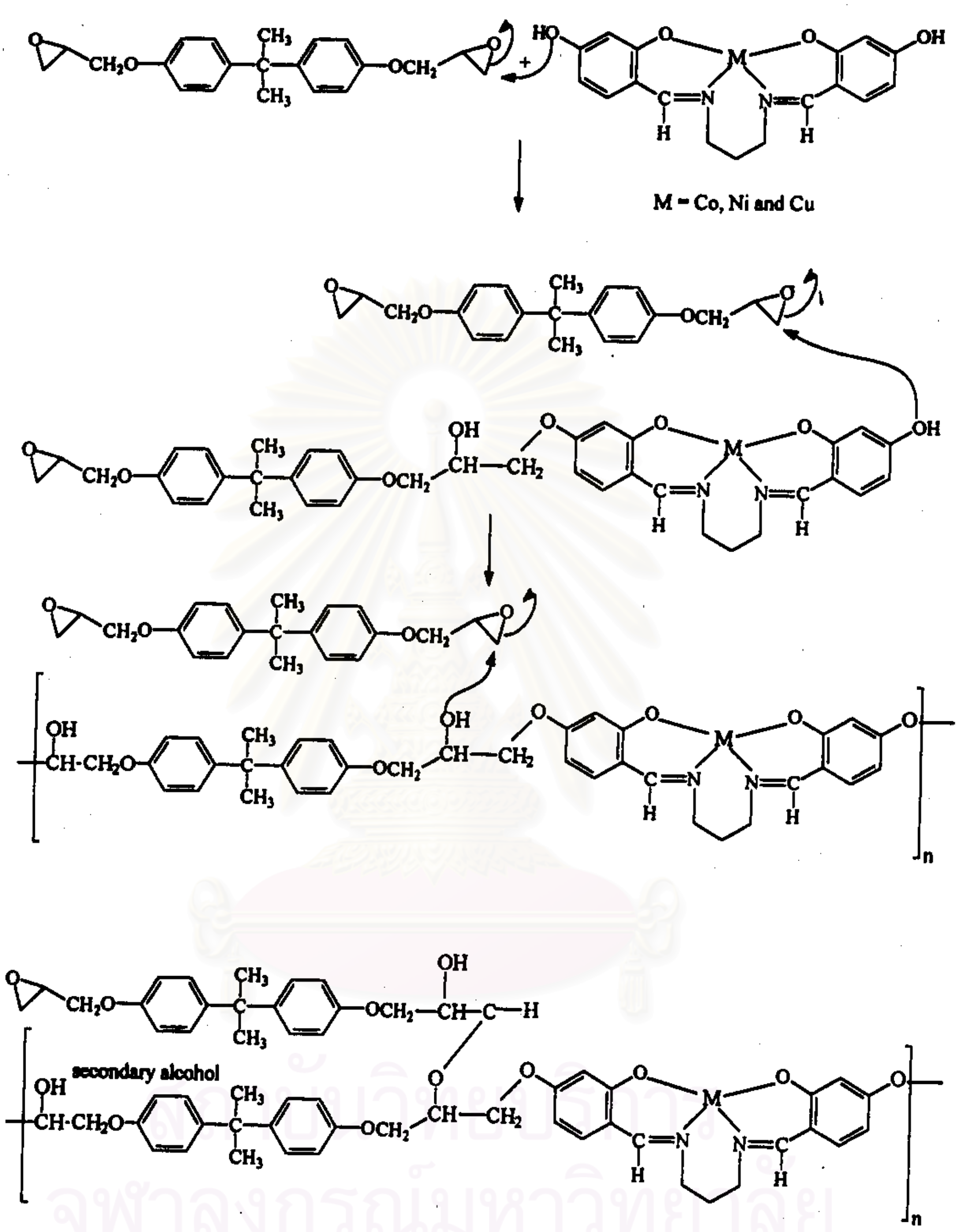


Figure 12. Isothermal (250 °C) DSC thermogram of the mixture of Ni-1 and DGEBA at Ni-1:DGEBA ratio of 1:1.67.



Scheme 14. Possible mechanism of the reaction of metal complexes with DGEBA.

The results from DSC experiments also indicate that the order of reactivity of metal complexes towards DGEBA are **Co-1 > Cu-1 > Ni-1 > Zn-1**. The Co(II), Ni(II) and Cu(II) ion may enhance the nucleophilicity of the phenolic hydroxy groups of the complexes. The **Co-1**, **Ni-1** and **Cu-1** complexes are thus reactive to DGEBA . While

Zn(II) ion has fully occupied d orbital. The metal center has less effect on the enhancement of the nucleophilicity of the hydroxy group. **Zn-1** complex is thus less reactive than **Co-1, Ni-1** and **Cu-1** complexes .

In comparison with similar crosslinking agents which do not contain metals, bisphenol-A, phenol groups in metal complexes are more reactive than those in bisphenol-A. This also supports the ability of a metal ion to augment the nucleophilicity of the phenolic groups.

In the preparation of crosslinked epoxy polymers, the ratios between DGEBA and metal complexes were varied 6:1, 4:1, 2:1, 1.67:1 and 1:1 to determine the optimum ratio of the starting material that gave crosslinked polymers with the best physical properties.

The obtained epoxy polymers were characterized by IR spectroscopy and thermal analysis. All complexes gave similar IR absorption bands as shown in Table 6 and their spectra were shown in Figures A. 5-18.

Table 6. IR absorption characteristic of epoxy polymers.

Absorption band (cm^{-1})	Assignment
3300-3500	OH stretching, broad strong
3000-3100	aromatic C-H stretching, weak
2800-3000	aliphatic C-H stretching, medium
1600-1650	C=N stretching, strong
1400-1600	aromatic C=C stretching, medium
1228	aromatic C-O stretching, strong
825	aromatic C-H bending, strong

The thermal property of crosslinked epoxy polymers obtained from the crosslinking reaction of DGEBA with different equivalent weight ratios of **Co-1, Ni-1** and **Cu-1** complexes were studied using DMA and TGA. Glass transition temperature

(T_g) could be obtained from DMA technique by observing the maximum value of loss modulus. DMA thermograms of Co, Ni and Cu-containing epoxy polymers were showed in the Figures A. 19-23. The values of glass transition temperature (T_g) of crosslinked epoxy polymers obtained from different weight ratios of DGEBA and different complexes are shown in Table 7 and Figures 13-15.

Table 7 Glass transition temperature of crosslinked epoxy polymer obtained from different weight ratios of DGEBA and different metal complexes

Complexes curing agent	Glass transition temperature (T_g)				
	1:6	1:4	1:2	1:1.67	1:1
Co	102	108	118	126	-
Ni	95	120	143	141	145
Cu	78	133	150	162	-

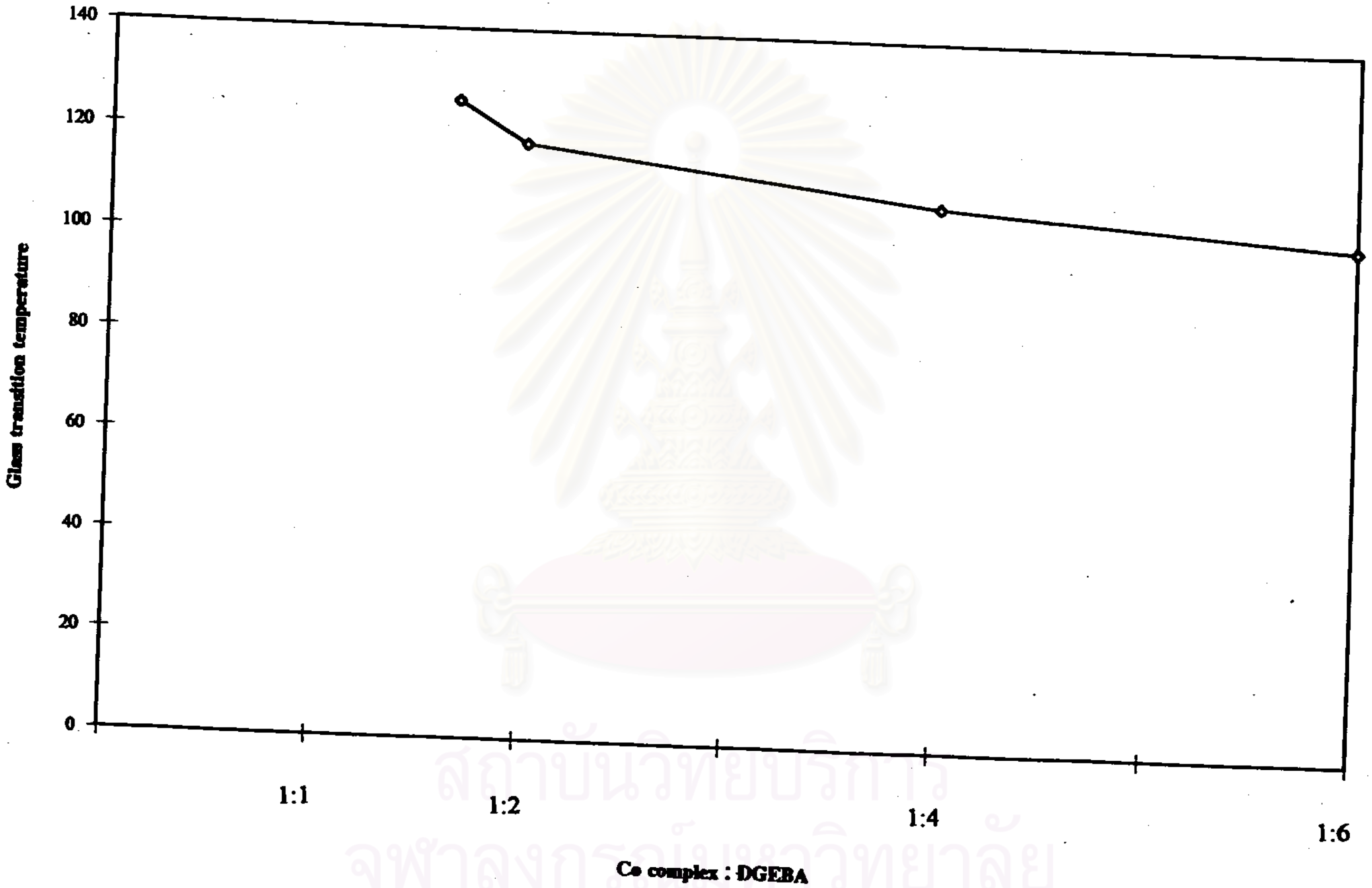


Figure 13. Relationship between T_g values of Co-containing epoxy polymers and mole ratio of Co-1:DGEBA

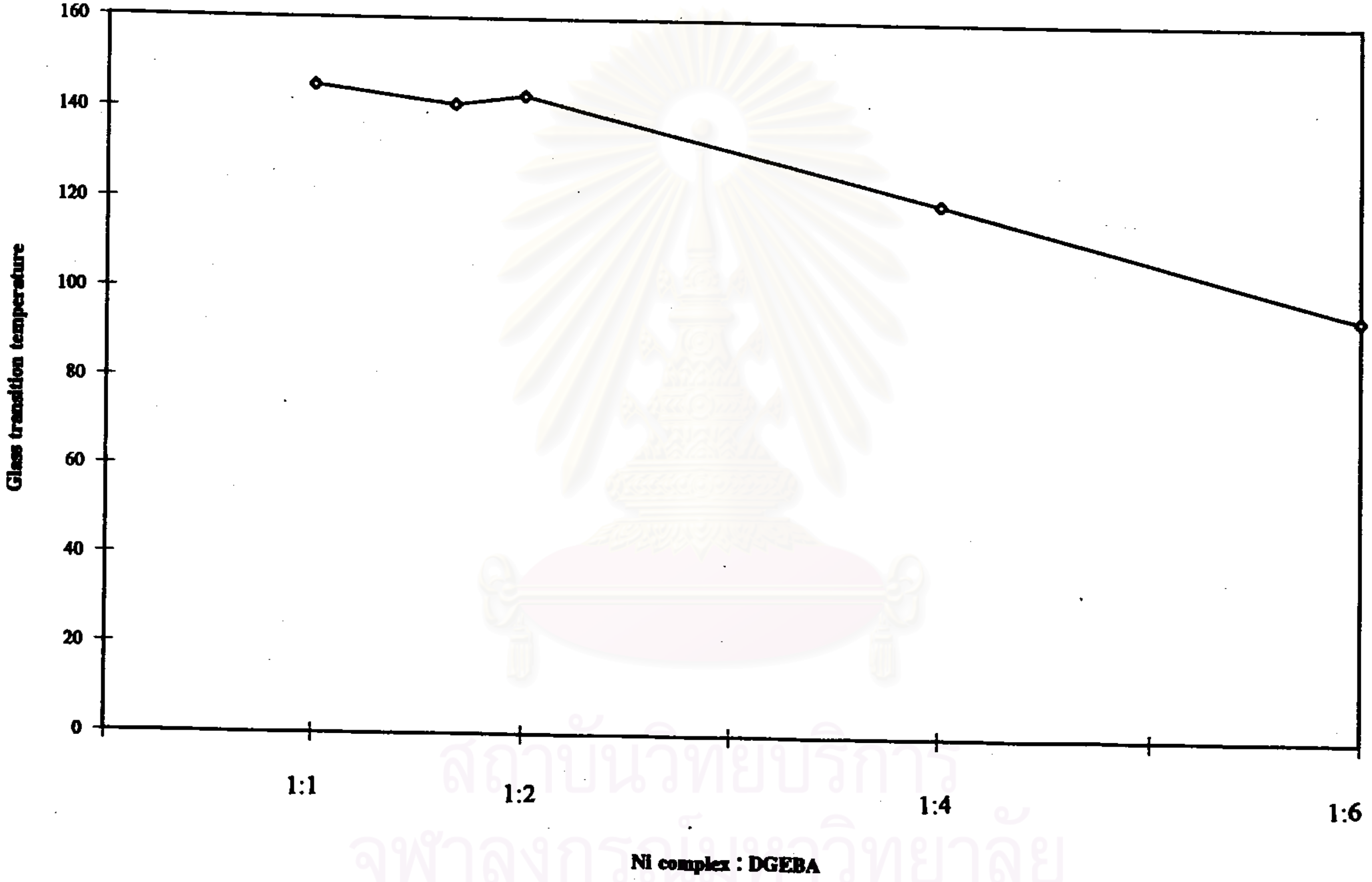


Figure 14. Relationship between T_g values of Ni-containing epoxy polymers and mole ratio of Ni-1:DGEBA

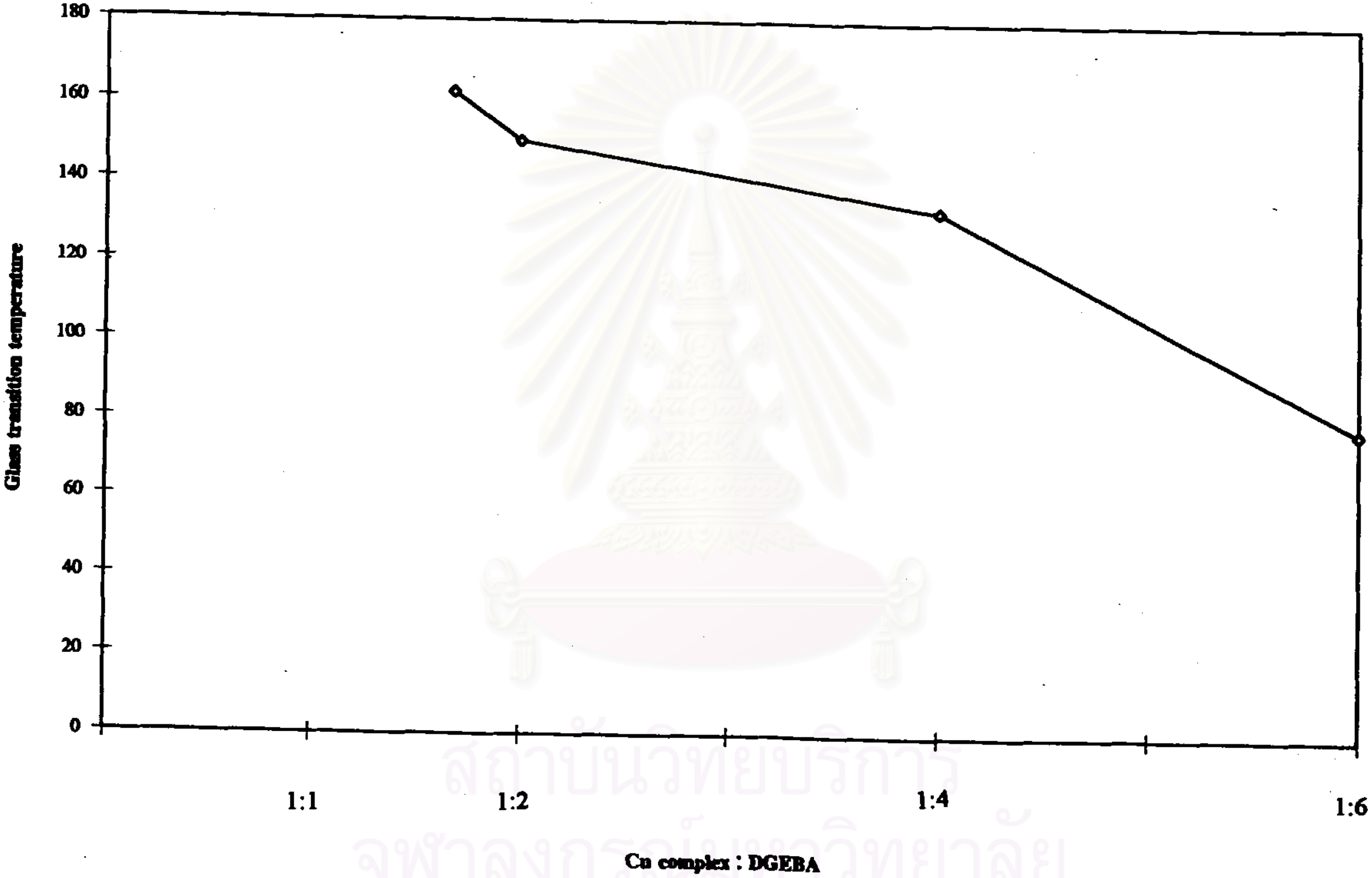


Figure 15. Relationship between T_g values of Cu-containing epoxy polymers and mole ratio of Cu-1:DGEBA

TGA thermograms of DGEBA crosslinked with **Cu-1** complex at mole ratio between **Cu-1** complex and DGEBA of 1:1.67 showed 0.65 % weight loss at the temperature range of 100-150 °C. The first step of weight loss indicates small amount of water in metal complexes. The rapid second weight loss at the temperature range 280-432 °C is due to decomposition of polymer chain (Figure 16). TGA thermograms of DGEBA crosslinked with other mole ratios of **Cu-1** complex and different mole ratios of **Ni-1** and **Co-1** complexes gave similar results (Figures A. 24-35). Table 8 shows amount of weight loss of **Co-1**, **Ni-1** and **Cu-1** containing epoxy polymers at different temperatures.

Table 8. Heat resistance of Co, Ni and Cu containing epoxy polymers.

Metal complexes	Ratio of complexes : DGEBA	Beginning temperature (°C)	Temperature which weight loss occurs (°C)			
			5%	10%	20%	30%
Co-1 complex	1:6	250	282	311	339	368
	1:4	240	280	316	340	370
	1:2	240	270	308	338	370
	1:1.67	240	260	300	338	380
Ni-1 complex	1:6	250	279	307	343	368
	1:4	250	286	311	345	378
	1:2	243	250	300	332	371
	1:1.67	261	293	322	350	393
	1:1	255	268	300	336	369
Cu-1 complex	1:6	239	285	309	350	369
	1:4	240	286	312	361	400
	1:2	246	286	321	365	402
	1:1.67	280	365	400	414	432

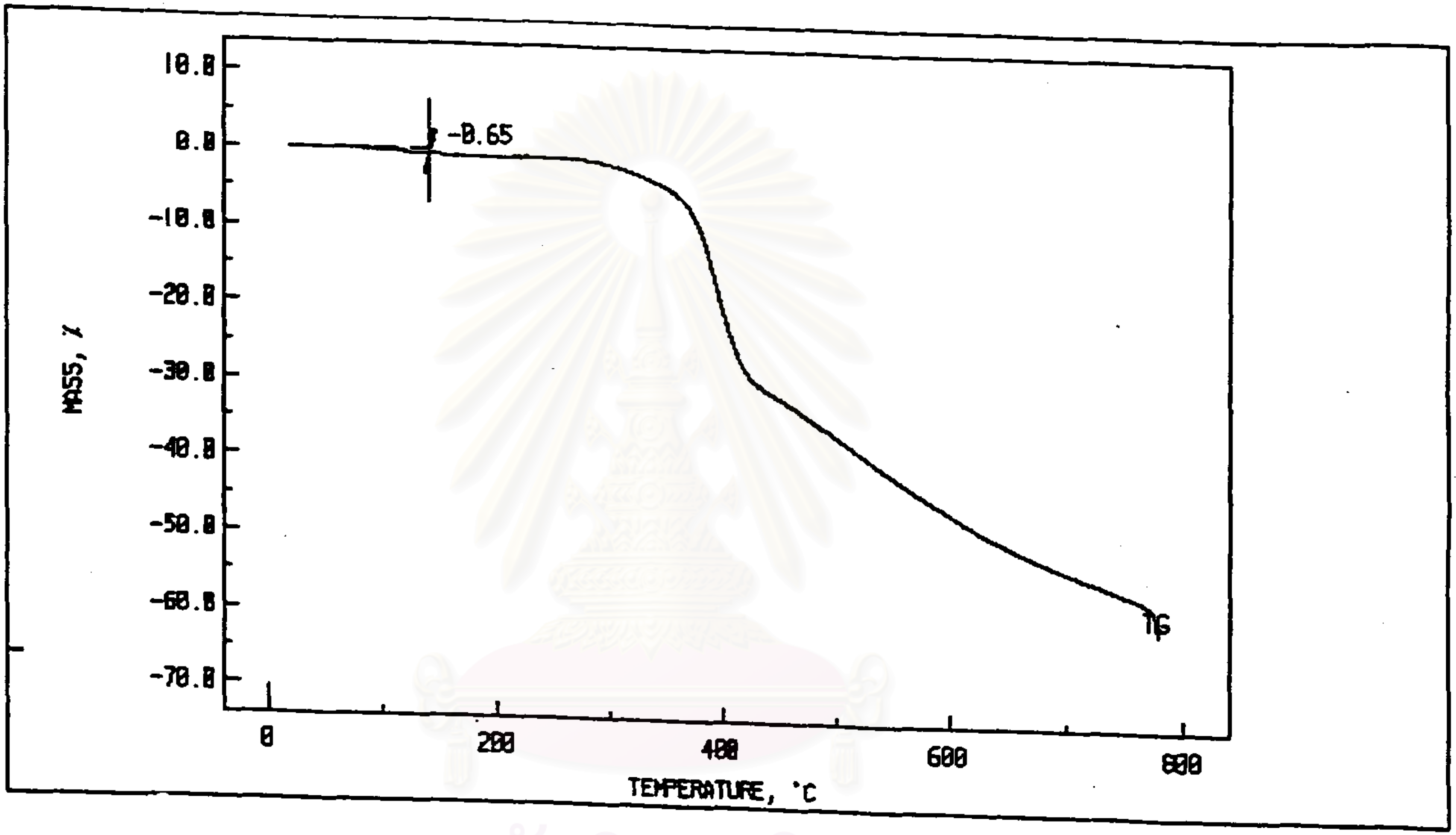


Figure 16. TGA thermogram of Cu-containing epoxy polymer at Cu-1:DGEBA ratio of 1:1.67

From the above TGA data, the results indicate that Cu containing epoxy polymer gives less weight loss than Co and Ni containing epoxy polymers. The lowest weight loss was obtained when mole ratio of DGEBA and **Cu-1** complex was 1:1.67.

To determine thermal stability of metal-containing epoxy polymers, isothermal study at 245 °C for 48 hours was employed. Table 9 shows weight loss of Co, Ni and Cu containing epoxy polymers at different time. The results indicate that the Ni containing epoxy polymer gives the best thermal stability.

Table 9. Thermal stability of Co, Ni and Cu containing epoxy polymers at 245 °C.

Metal complexes	Ratio of complexes: DGEBA	%weight loss at different time		
		time (h)		
		16	36	48
Co-1 complex	1:6	1.95	2.61	2.81
	1:4	2.55	3.16	3.43
	1:2	2.18	2.72	3.18
	1:1.67	3.76	4.58	5.09
Ni-1 complex	1:6	1.05	2.24	2.68
	1:4	1.01	1.75	2.11
	1:2	0.94	1.54	1.88
	1:1.67	1.34	1.80	2.01
	1:1	1.19	1.44	1.65
Cu-1 complex	1:6	2.36	3.03	3.22
	1:4	2.00	2.61	2.73
	1:2	3.53	5.10	5.45
	1:1.67	3.45	5.18	5.59

The experimental results from using metal complexes as crosslinking agents for DGEBA were compared to well-known crosslinking agents, bisphenol A and 2,7-dihydroxynaphthalene,[13] which are used to prepare thermally stable epoxy polymers. These two phenolic crosslinking were chosen since they have phenol groups that undergo the same crosslinking reaction as the tetradentate Schiff's base metal complexes(Scheme 14).

Crosslinking behaviors of DGEBA with bisphenol A and 2,7-dihydroxynaphthalene at a mole ratio of 1:1 were investigated. Isothermal DSC experiments were done at a constant temperature of 250 °C. By using 2,7-dihydroxynaphthalene, crosslinking reaction took about 9 minutes to complete (Figure 17). In case of bisphenol A, the reaction was very slow (Figure 18). When **Co-1** and **Ni-1** complexes were used as crosslinking agents, the reactions were faster at the same temperature. Crosslinking reactions by using **Cu-1** complex occurred at lower temperature and took much less time to complete. This faster crosslinking reactions of metal complexes may be explained by electroactive nature of Co, Ni and Cu which elevate the nucleophilicity of the phenolic group of the metal complexes. From the isothermal experiments, **Cu-1** complex took much less time than **Co-1** complex. The order of reactivity varies as, **Co-1 ≈ Cu-1 > Ni-1 > Zn-1**.

Two epoxy polymers were then prepared by crosslinking of DGEBA with bisphenol A and 2,7-dihydroxynaphthalene at the mole ratio of at 250 °C for 6 and 4 hours, respectively. The epoxy polymer obtained from using bisphenol A as crosslinking agent was brittle and it was impossible to determine its T_g value by DMA. The T_g value of polymer obtained from using 2,7-dihydroxynaphthalene as crosslinking agent was 90 °C as determined by DMA. Thermal stability of two epoxy polymers was studied by using the same isothermal condition as mentioned earlier at a temperature of 245 °C for 48 hours. Table 10 shows weight loss of the epoxy polymers crosslinked by using bisphenol A and 2,7-dihydroxynaphthalene at different time. The results indicate that 2,7-dihydroxynaphthalene gives better thermal stability than bisphenol A.

Table 10. Heat resistance of epoxy polymers using bisphenol A and 2,7-dihydroxynaphthalene.

Crosslinking agent	Time (h)		
	16	36	48
bisphenol A	3.09 %	5.15 %	5.41%
2,7-dihydroxynaphthalene	0.83 %	1.44 %	1.52 %

In comparison between using metal complexes and phenols as crosslinking agents for DGEBA, the Ni-containing epoxy polymer possesses comparable thermal stability to the 2,7-dihydroxynaphthalene. Co and Cu-containing epoxy polymers possess comparable thermal stability to the bisphenol A. The advantage of using metal complexes as crosslinking agent are (1) the reaction occurs much faster and (2)higher T_g values of epoxy polymers could be obtained. The only disadventage of using metal complexes as crosslinking agent is that the mixture of metal complexes with DGEBA at high mole ratio is difficult to prepare because of high viscousity.

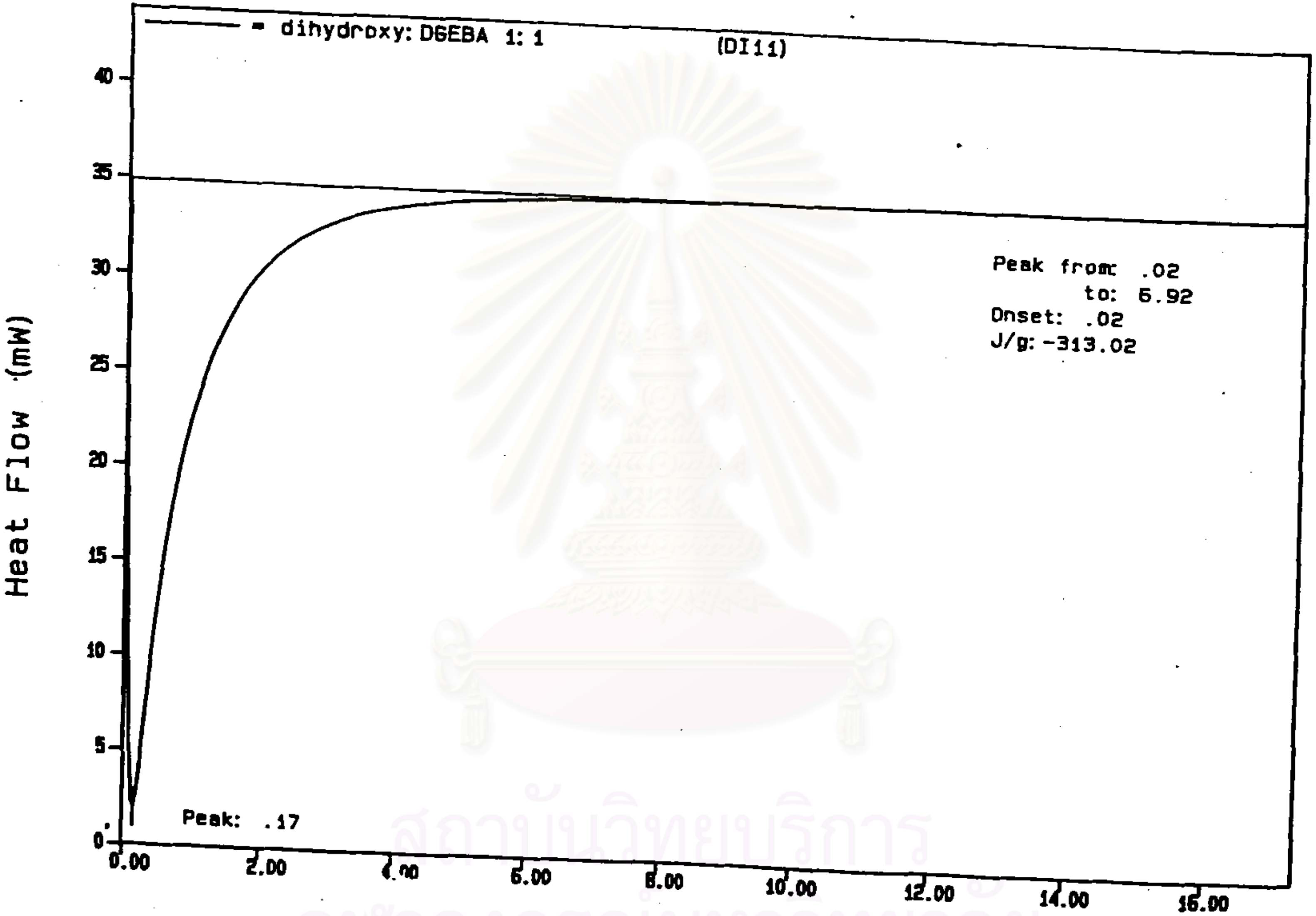


Figure 17. Isothermal (250°C) DSC thermogram of the mixture of 2,7-dihydroxynaphthalene and DGEBA at 2,7-dihydroxynaphthalene :DGEBA ratio of 1:1

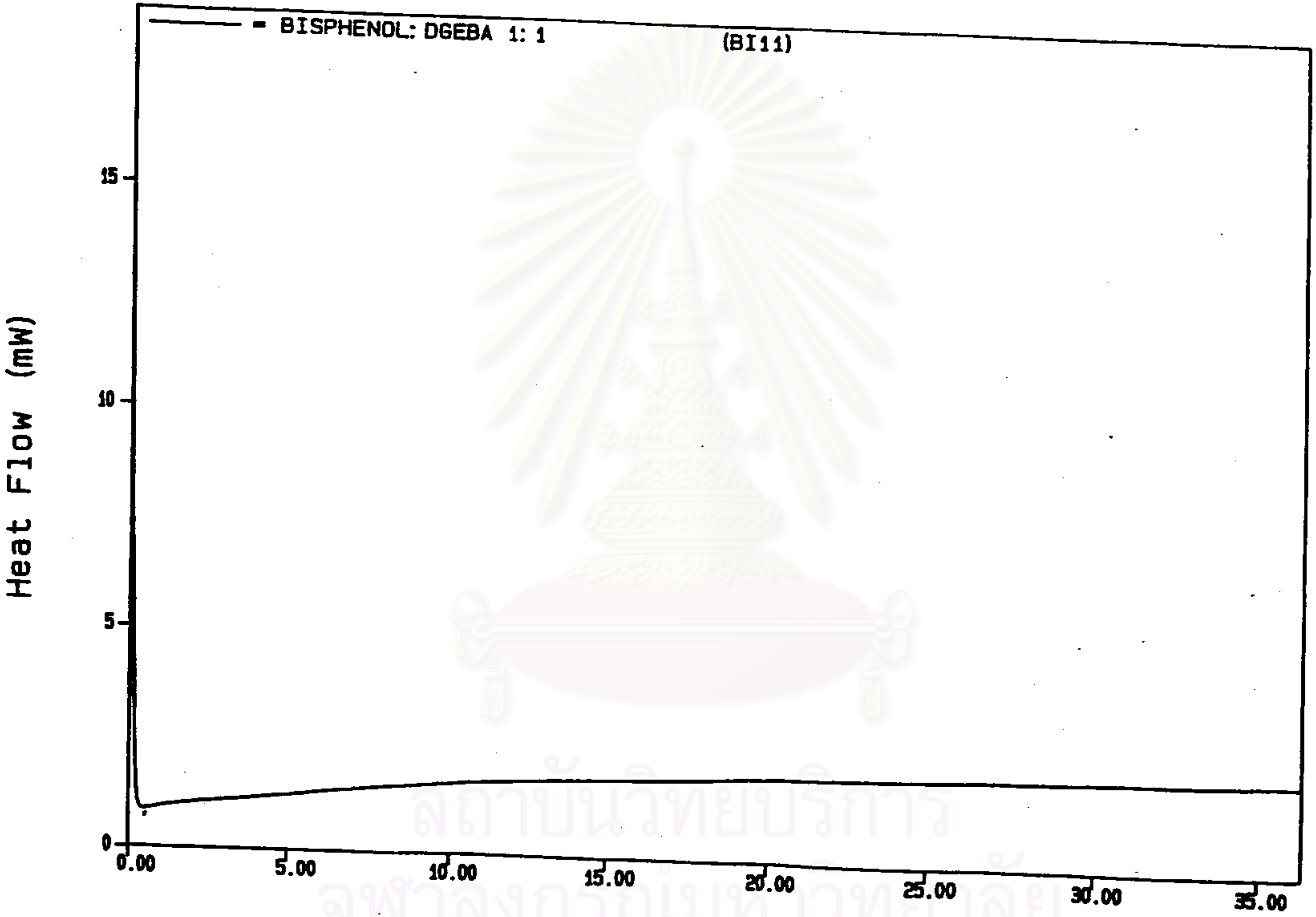


Figure 18. Isothermal (250°C) DSC thermogram of the mixture of bisphenol A and DGEBA at bisphenol A:DGEBA ratio of 1:1