

การใช้สารประกอบเชิงซ้อนของโลหะประเภทเฮกซาเดนเตตซีฟเบส  
และมาลิกแอโนไฮไดรด์เป็นสารเชื่อมขวางสำหรับเอพอกซีเรซิน



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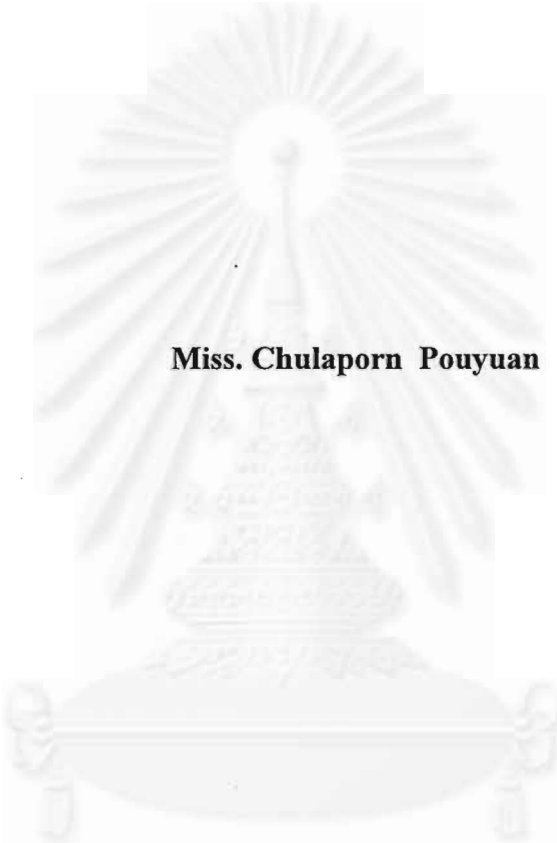
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**APPLICATION OF HEXADENTATE SCHIFF BASE METAL COMPLEXES  
AND MALEIC ANHYDRIDE AS CROSSLINKING AGENTS  
FOR EPOXY RESIN**



**Miss. Chulaporn Pouyuan**

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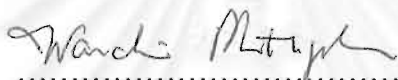
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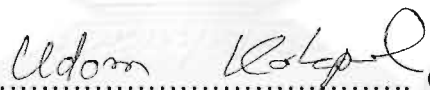
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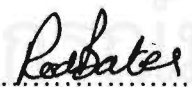
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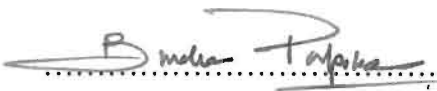
  
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การสังเคราะห์เอพอกซีพอลิเมอร์ที่มีนิกเกิลและสังกะสีเป็นส่วนประกอบสามารถทำได้โดยการทำ  
ปฏิกิริยาเชื่อมขวางของไดโกลซิดิลอีเทอร์ของบิสฟีนอลเอ (ดีจีอีพีเอ) ด้วยสารประกอบเชิงซ้อนของโลหะ  
ประเภทเฮกซะเดนเตทซึฟเบสและมาลิกแอนไฮไดรด์ โดยมีเตตระบิวทิลแอมโมเนียมไฮดรอกไซด์เป็นตัวเร่ง  
ปฏิกิริยาที่เหมาะสมต่อการทำปฏิกิริยาเชื่อมขวางเนื่องจากสามารถทำให้อุณหภูมิของการเกิดปฏิกิริยาเชื่อมขวาง  
ลดลง ผลการทดลองจากอินฟราเรดสเปกโตรสโคปีระบุว่า สภาวะที่เหมาะสมในการทำปฏิกิริยาเชื่อมขวาง คือ  
110 องศาเซลเซียส เป็นเวลา 8 ชั่วโมง การศึกษาสมบัติของพอลิเมอร์ทำได้โดยใช้ไดนามิกเมคคานิคอลแอนนา  
ไลซิส เทอร์โมกราวิเมตริกแอนาไลซิสและการทดสอบความทนแรงดึง เอพอกซีพอลิเมอร์ที่มีโลหะเป็น  
ส่วนประกอบมีความเสถียรต่ออุณหภูมิสูงและมีสมบัติเชิงกลที่ดี เอพอกซีพอลิเมอร์ที่มีนิกเกิลเป็นส่วนประกอบที่  
เตรียมจากอัตราส่วนระหว่าง ดีจีอีพีเอ : สารประกอบเชิงซ้อนของโลหะนิกเกิล : มาลิกแอนไฮไดรด์ เท่ากับ  
1 : 0.15 : 0.15 มีค่าความทนแรงดึง 48 นิวตันต่อตารางมิลลิเมตร เมื่อให้ความร้อนที่อุณหภูมิ 250 องศาเซลเซียส  
เป็นเวลา 48 ชั่วโมง พอลิเมอร์จะสูญเสียน้ำหนักไปร้อยละ 7.7 ซึ่งเมื่อเปรียบเทียบกับเอพอกซีพอลิเมอร์ที่เป็นที่  
รู้จักกันดี เอพอกซีพอลิเมอร์ที่มีนิกเกิลเป็นส่วนประกอบจะมีความเสถียรต่ออุณหภูมิสูงมากกว่าพอลิเมอร์ที่เตรียม  
จากดีจีอีพีเอ-ไดเอทิลีนไตรเอมีน

สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย

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CHULAPORN POUYUAN : APPLICATION OF HEXADENTATE  
SCHIFF BASE METAL COMPLEXES AND MALEIC ANHYDRIDE  
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Nickel- and Zinc-containing epoxy polymers were synthesized by crosslinking of diglycidyl ether of bisphenol A (DGEBA) with hexadentate Schiff base metal complexes and maleic anhydride. Tetrabutylammonium hydroxide was found to be a suitable catalyst for the crosslinking reaction since it decreased the crosslinking temperature. The results from infrared spectroscopy experiments indicated that the optimum crosslinking conditions were 110°C for 8 hours. The polymer properties were studied using dynamic mechanical analysis, thermogravimetric analysis and tensile testing. The metal-containing polymers showed high thermal stability and good mechanical properties. The Nickel-containing polymer obtained from DGEBA : nickel complex : maleic anhydride at the mole ratio of 1 : 0.15 : 0.15 showed tensile strength of 48 N/mm<sup>2</sup>. Upon heating at 250°C for 48 hours, the weight loss of the polymer was 7.7%. In comparison to the known epoxy polymer obtained from DGEBA-diethylenetriamine system, the nickel-containing polymer showed much higher thermal stability.

สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย

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Chulaporn Pouyuan

จุฬาลงกรณ์มหาวิทยาลัย

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## LIST OF ABBREVIATIONS

Bu <sub>4</sub> NOH	Tetrabutylammonium hydroxide
DETA	Diethylenetriamine
DGEBA	Diglycidyl ether of bisphenol A
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimetry
MA	Maleic anhydride
ML	Schiff base metal complex
NiL	Schiff base nickel complex
T <sub>g</sub>	Glass transition temperature
ZnL	Schiff base zinc complex
phr	part per hundred



## CHAPTER I

### INTRODUCTION



#### 1.1 Epoxy Polymers

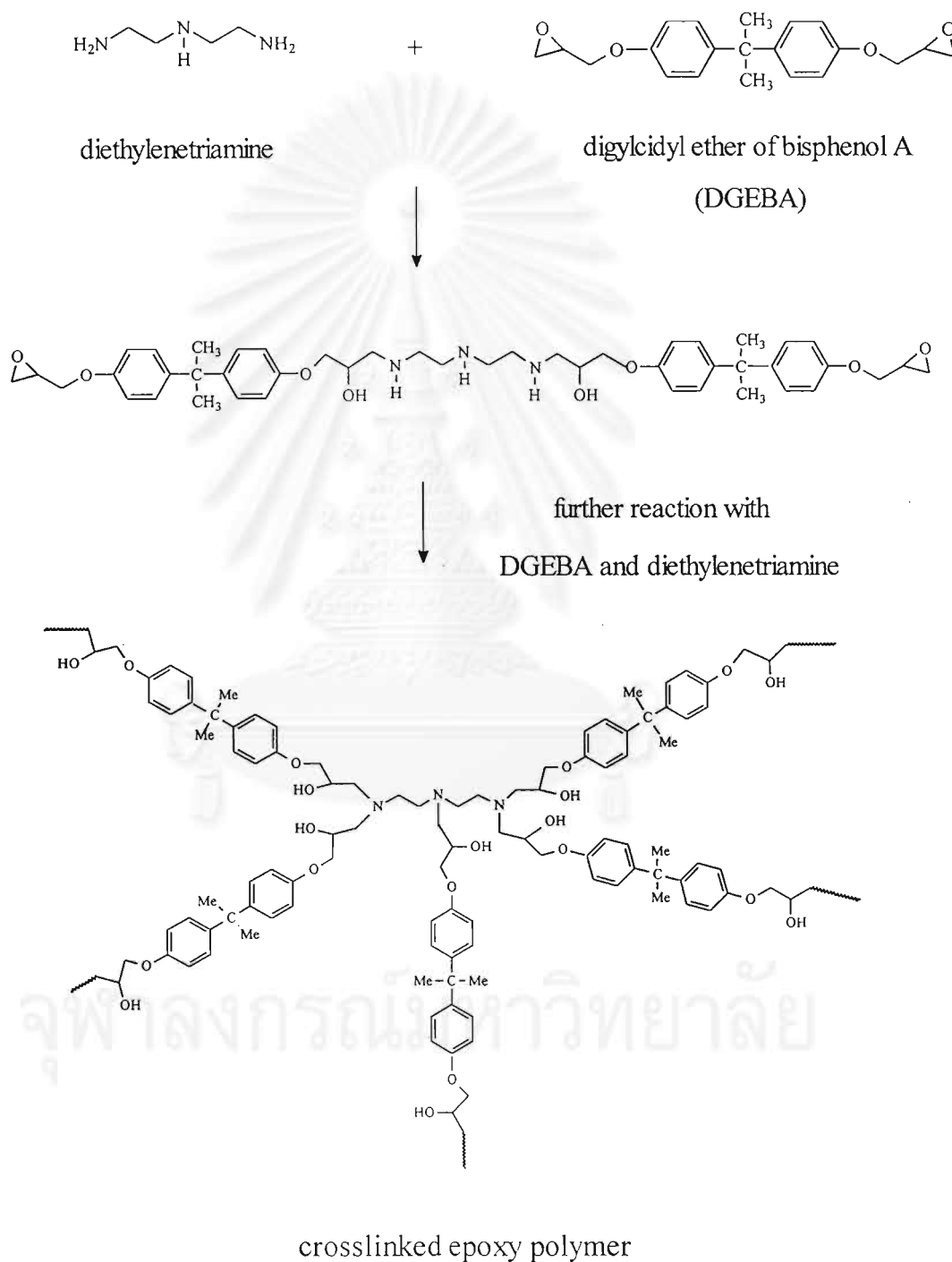
Epoxy polymers are thermosetting polymers formed through the reaction between epoxy resin and a crosslinking agent.

Epoxy polymers are being increasingly used in structural applications since these polymers offer many advantages. Epoxy polymers are highly chemical and corrosion – resistant. They also exhibit low shrinkage during the crosslinking process. Such factors are important for many applications. Epoxy polymers are used in many areas such as adhesive bonding, construction materials, coating, laminates, molding, textile finishing air, printed circuit boards and aerospace.<sup>1-3</sup>

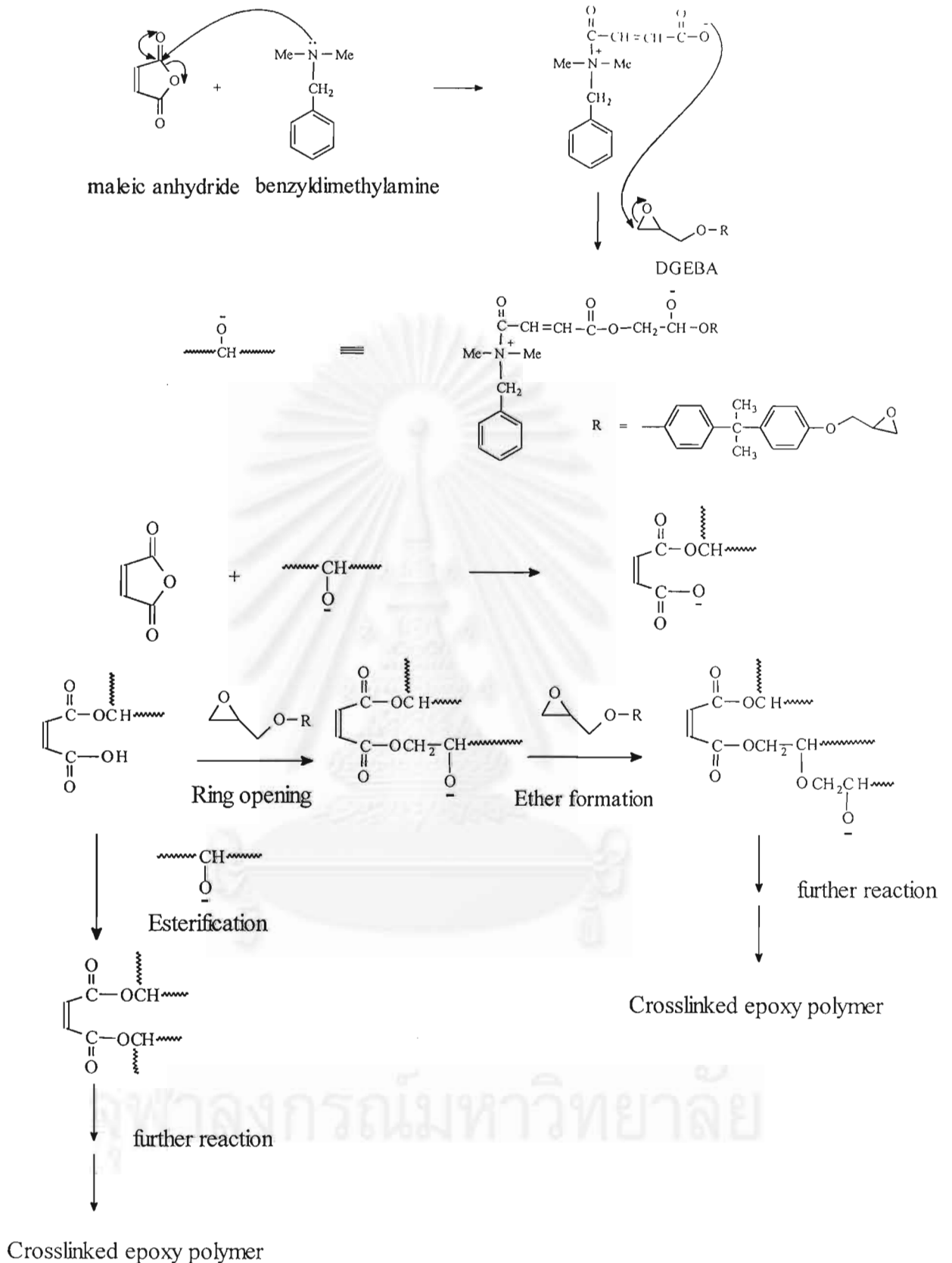
In general, crosslinking of the diglycidyl ether of bisphenol – A epoxy resin (DGEBA) can be done using proper crosslinking agents such as amines, phenols, organic acids and acid anhydrides.<sup>4-6</sup> For example, diethylenetriamine reacts by nucleophilic addition to the epoxide ring in DGEBA to give a crosslinked epoxy polymer (Scheme 1.1.)

Acid anhydrides are extensively used as crosslinking agents in the crosslinking reaction of DGEBA. They contribute excellent properties to the resulting epoxy polymers such as good thermal, electrical properties and long useful pot lives.<sup>6-10</sup> In the crosslinking reaction, acid anhydrides can react with the epoxy group in the presence of the accelerators such as alcohols and amines. For example, crosslinking of DGEBA with maleic anhydride in the presence of benzyldimethylamine is shown in Scheme 1.2.

Ring opening by the amines produces carboxylate groups which can react with the epoxide rings in DGEBA to generate hydroxyl groups which undergo further reaction with maleic anhydride and DGEBA to give crosslinked epoxy polymers.



**Scheme 1.1** Crosslinking reaction of DGEBA with diethylenetriamine

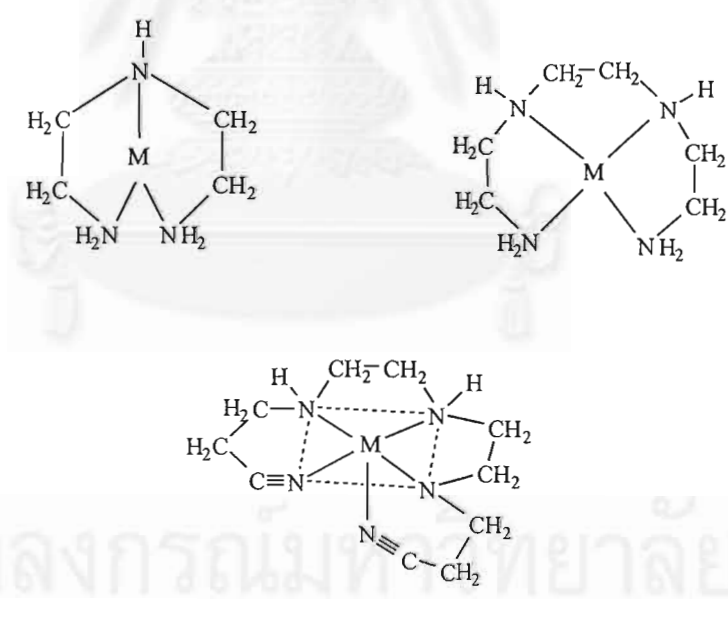


**Scheme 1.2** Possible mechanism of the crosslinking reaction of DGEBA with maleic anhydride in the presence of benzyldimethylamine

## 1.2 Metal-Containing Epoxy Polymers

Epoxy polymers are finding increasing applications in many areas. A variety of epoxy polymers are available and there are several approaches to improve the physical and mechanical properties of epoxy polymers including the use of metal complexes as crosslinking agents or accelerators. Modified epoxide polymers containing transition metals show better properties of chemical resistance, thermal resistance and electrical conductivity than the unmodified epoxy polymers.<sup>11-15</sup>

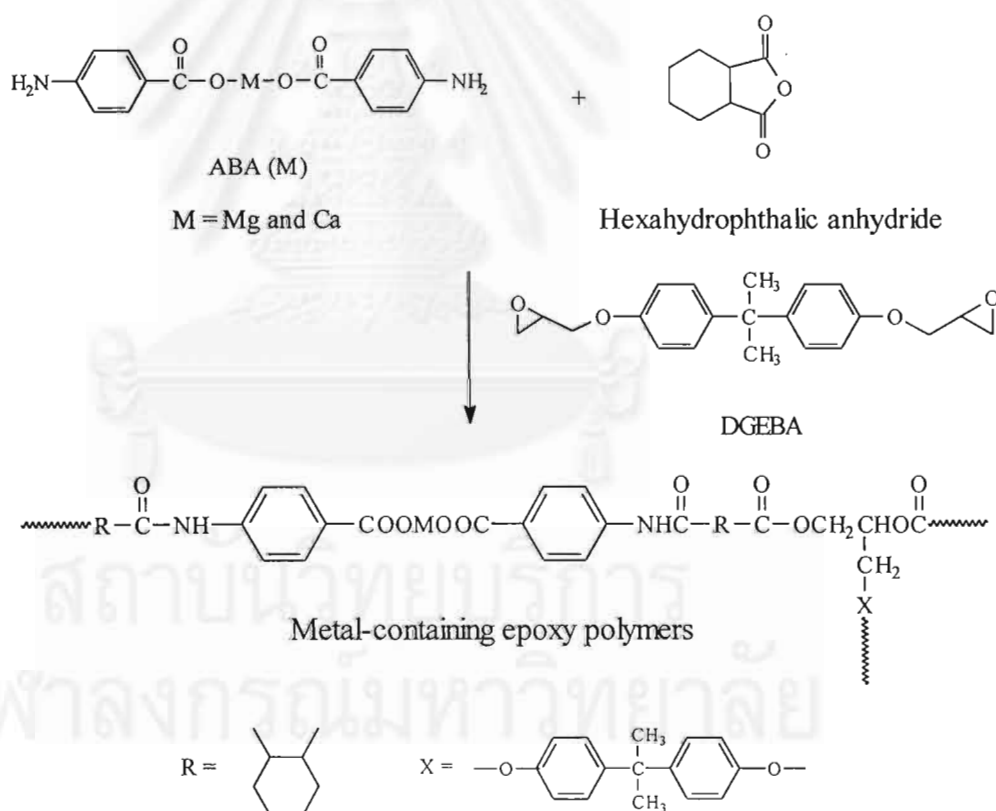
Kurnoskin<sup>16-21</sup> synthesized metal-containing epoxy polymers by crosslinking of DGEBA with metal complexes of the first row transition metals and aliphatic amines. Some of these metal complexes are shown in Scheme 1.3. The resulting metal-containing epoxy polymers showed good thermal oxidative stability, chemical resistance, heat resistance and high strength.



**Scheme 1.3** Structures of metal complexes of first row transition metal

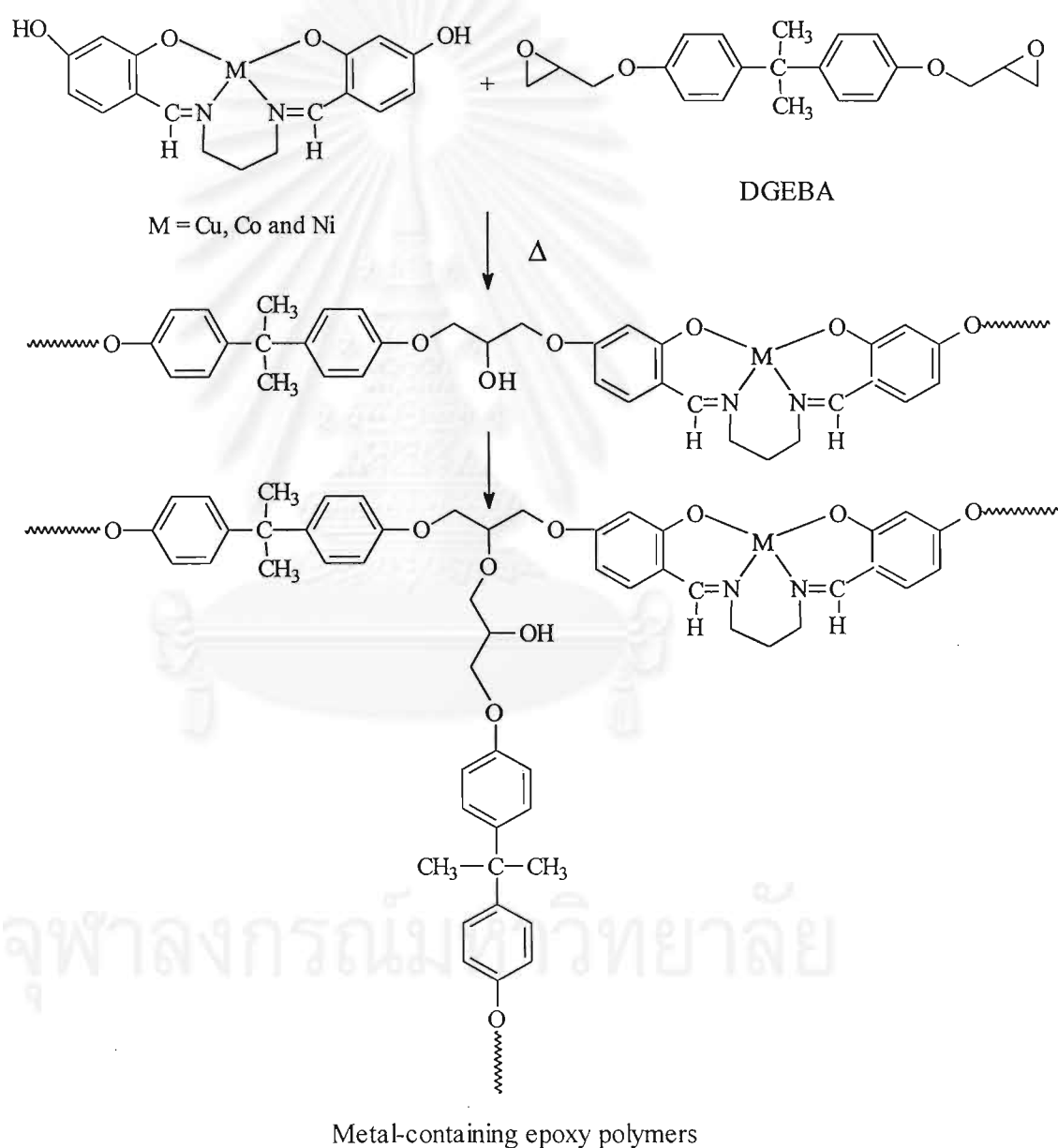
Reddy and Gowda<sup>22</sup> synthesized crosslinked epoxy polymers using copper and nickel acetylacetonates as the accelerators for the crosslinking of DGEBA with metal acetylacetonates. They showed that the use of both metal acetylacetonates decreased the crosslinking time. The epoxy polymers possessed excellent thermal and electrical insulation.

Takechi and Matsuda<sup>23</sup> synthesized metal-containing epoxy polymers by crosslinking DGEBA with the metal salts of *p*-aminobenzoic acid ABA(M) and hexahydrophthalic anhydride (Scheme 1.4). The metal-containing epoxy polymers had good thermal oxidative stability, chemical resistance, heat resistance, electrical conductivity and high impact strength.



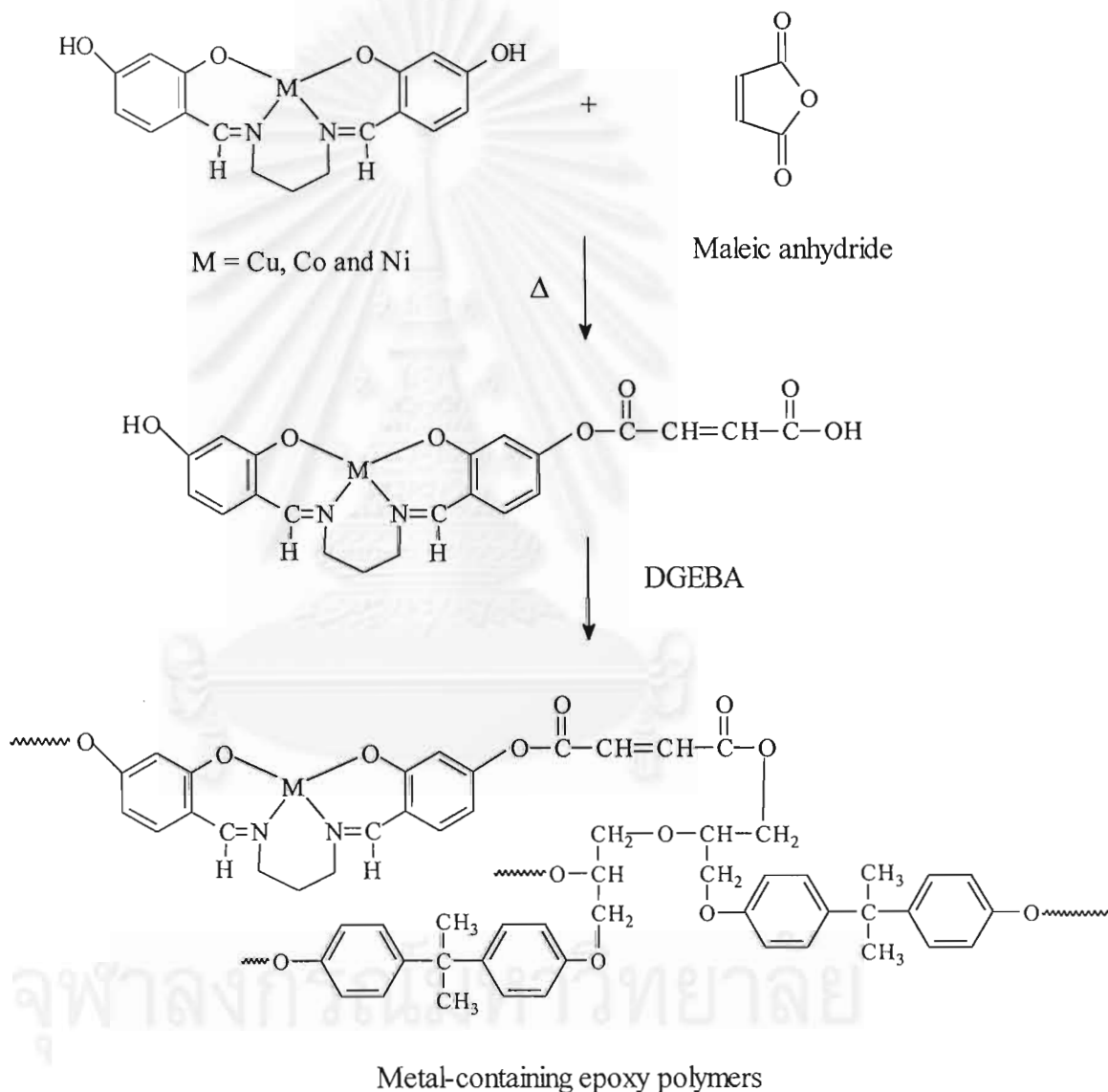
**Scheme 1.4** Synthesis of metal-containing epoxy polymers using metal salts of *p*-aminobenzoic acid and hexahydrophthalic anhydride as crosslinking agents for DGEBA

Our research group<sup>24</sup> synthesized metal-containing epoxy polymers by crosslinking DGEBA with tetradentate Schiff base metal complexes. These metal complexes have two hydroxyl groups which are able to react with DGEBA to give the crosslinked epoxy polymers (Scheme 1.5). The resulting epoxy polymers showed good thermal stability and mechanical properties.



**Scheme 1.5** Reaction of tetradentate Schiff base metal complexes with DGEBA

Further study was done on the epoxy-anhydride system.<sup>25</sup> Crosslinking of DGEBA with a mixture of maleic anhydride and tetradentate Schiff base metal complexes yielded metal-containing epoxy polymers (Scheme 1.6) which showed good thermal stability and mechanical properties.



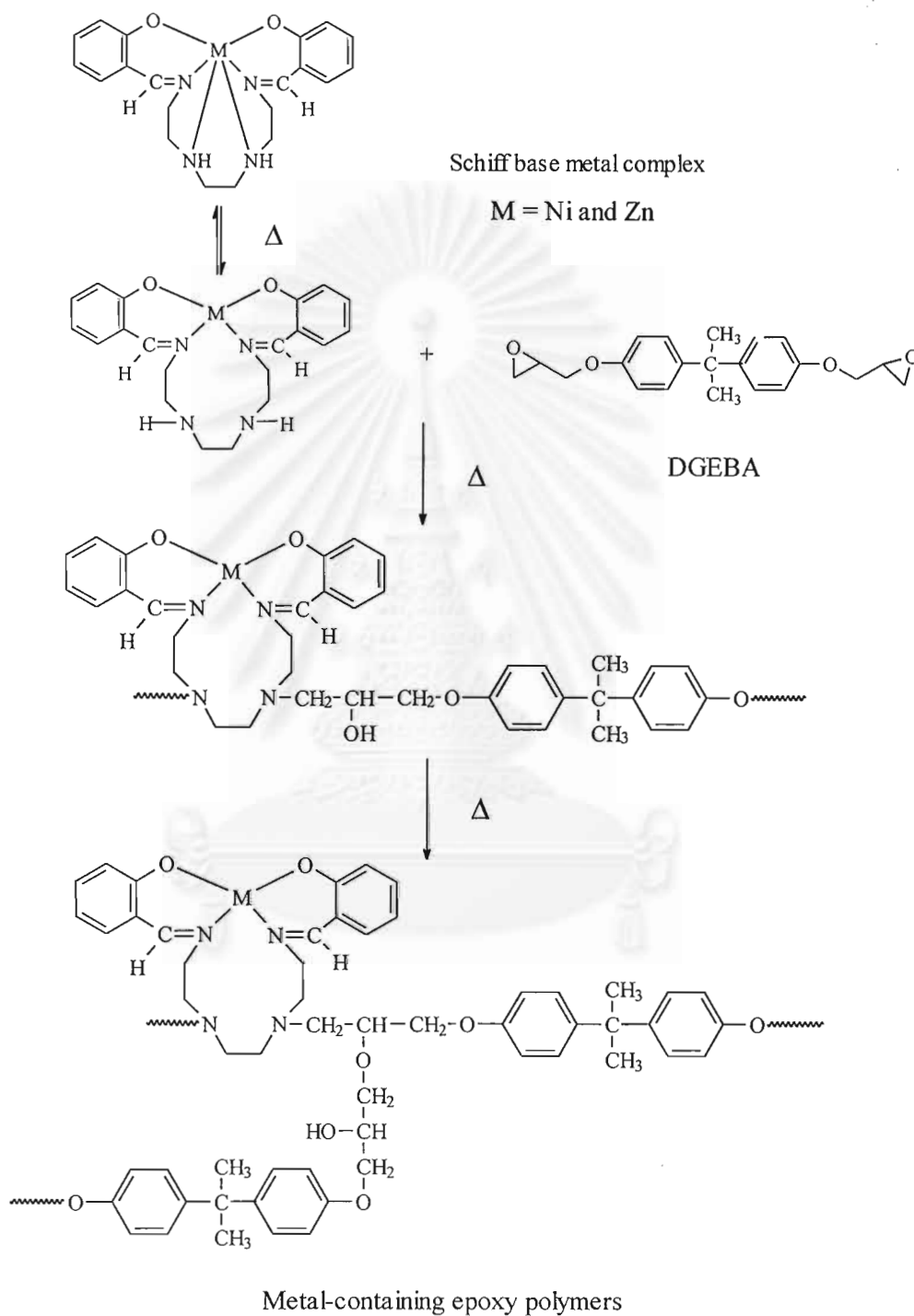
**Scheme 1.6** Reaction of DGEBA with tetradentate Schiff base metal complexes and maleic anhydride

At the same time, another type of metal-containing crosslinking agent was also synthesized in our group.<sup>26</sup> The preparation of metal-containing epoxy polymers involved crosslinking of DGEBA with hexadentate Schiff base metal complexes (Scheme 1.7). The resulting metal-containing epoxy polymers also showed good thermal stability. The advantages of using this type of metal complex is their stability and low crosslinking temperature.



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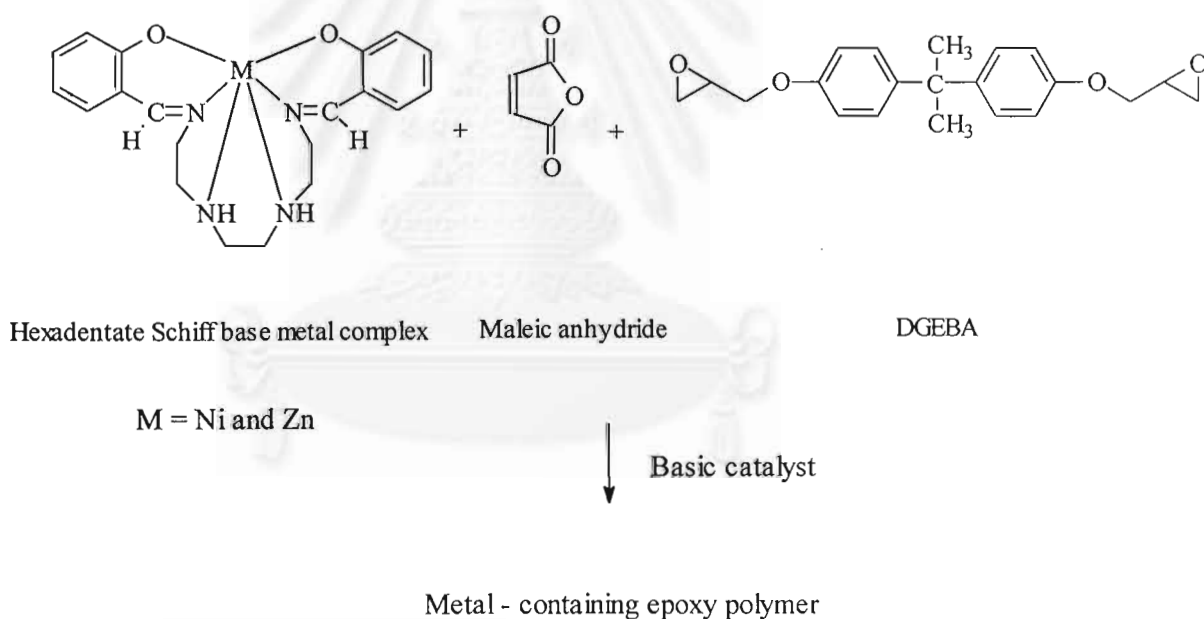




**Scheme 1.7** Possible mechanism of the crosslinking reaction of DGEBA with hexadentate Schiff base metal complexes

### 1.3 Objective and Scope of the Research

The objective of this work was synthesize heat resistant metal-containing epoxy polymers using low crosslinking temperatures. The crosslinking was done by reaction of DGEBA with hexadentate Schiff base metal complexes and maleic anhydride in the presence of a basic catalyst (Scheme 1.8). The metal complexes used were hexadentate Schiff base metal complexes. The use of maleic anhydride and a basic catalyst was expected to decrease the crosslinking temperature. The optimum conditions for the crosslinking reaction were determined and the physical and mechanical properties of the metal-containing epoxy polymers were then investigated.



**Scheme 1.8** · Synthesis of metal-containing epoxy polymers using hexadentate Schiff base metal complexes and maleic anhydride as crosslinking agents

## CHAPTER II

### EXPERIMENTS

#### 2.1 Materials

All reagents and solvents were of analytical grade quality. The solvents were obtained from Baker Chemical Company. DGEBA epoxy resin (D.E.R. 330, epoxy equivalent weight = 185), 2-hydroxybenzaldehyde, triethylenetetramine, nickel (II) acetate tetrahydrate, zinc (II) acetate dihydrate, maleic anhydride, benzyldimethylamine, tetrabutylammonium hydroxide (0.8 M in methanol) and sodium hydroxide were obtained from Fluka. All chemicals were used without further purification.

#### 2.2 Analytical Procedures

The IR spectra were recorded on a Nicolet Impact 410. Elemental analyses were carried out on a Perkin Elmer Elemental Analyzer 2400 CHN. The thermal properties of epoxy polymers were measured on a Perkin Elmer Differential Scanning Calorimeter (DSC 7) and Netzch Dynamic Mechanical Analyzer (DMA 242). Tensile strength was measured on an Instron Model 4310.

#### 2.3 Preparation of Hexadentate Schiff Base Metal Complexes (ML)

##### 2.3.1. Preparation of the Nickel Complex (NiL)

The preparation of NiL was carried out according to the method reported in the literature.<sup>26</sup> A cool (0–10°C) methanolic solution (10 ml) of triethylenetetramine (1 ml, 6.70 mmol) was added dropwise to a cooled methanolic solution (10 ml) of salicylaldehyde (1.18 g, 9.66 mmol) and nickel (II) acetate (1.03 g, 4.84 mmol). The

mixture was stirred for 10 minutes then neutralized by addition of 2 M sodium hydroxide solution (5 ml, 10 mmol) and stirred for 1 hour. Upon standing at room temperature for 7 hours, brown crystals of NiL precipitated from the solution. The NiL crystals were isolated by filtration and dried in vacuo (1.82 g, 91 %) m.p. 200°C dec. IR (KBr,  $\text{cm}^{-1}$ ); 3640 (NH), 3300, 3000, 2960, 2800, 1638 (C=N), 1601, 1448, 1250, 950, 850.

### 2.3.2. Preparation of the Zinc Complex (ZnL)

ZnL was synthesized according to the procedure described in experiment 2.3.1 using Zinc (II) acetate instead of Nickel (II) acetate. The yellow crystals of ZnL precipitated from the solution. The yellow precipitate was isolated by filtration and dried in vacuo (1.86 g, 93 %) m.p. 235°C.  $^1\text{H}$  NMR  $\delta$  (200 MHz,  $\text{CDCl}_3$ , ppm); 8.13 (2H, s, CH=N), 6.99-7.14 (4H, m, aromatic protons), 6.67-6.71 (2H, d,  $J=8.54$ , aromatic protons), 6.37-6.44 (2H, m, aromatic protons), 4.05-4.29 (2H, m, methylene protons), 3.21-3.48 (4H, m, methylene protons) 2.73-2.92 (2H, m, methylene protons), 2.35-2.61 (4H, m, methylene protons). IR (KBr,  $\text{cm}^{-1}$ ); 3646 (NH), 3300, 3000, 2800, 1645 (C=N), 1600, 1448, 1200, 930, 870.

## 2.4 Reaction between Hexadentate Schiff Base Metal Complexes and Maleic

### Anhydride

Metal complexes ( NiL and ZnL ) and maleic anhydride ( MA ) were mixed at the mole ratio of ML : MA = 1 : 1. The sample was heated at 130 °C in an oven and the progress of the reaction was followed by using IR spectroscopy.

## **2.5 Reaction between DGEBA, Hexadentate Schiff Base Metal Complexes and Maleic Anhydride**

DGEBA, metal complexes (NiL or ZnL) and maleic anhydride were mixed at the mole ratio of DGEBA : ML : MA = 1 : 0.20 : 0.20. The sample was heated in a hot air oven in air at different isothermal temperatures and the progress of the reaction was followed by IR spectroscopy. The disappearance of the IR band of the epoxide group at  $917\text{ cm}^{-1}$  was observed when the reaction was complete. The crosslinking temperature for each metal complex was chosen so that the crosslinking reaction was complete in 4 hours. It was found that the optimum temperature for both NiL and ZnL was  $130^{\circ}\text{C}$ .

## **2.6 Isothermal Study of Reaction between DGEBA, Hexadentate Schiff Base Metal Complexes and Maleic Anhydride in the Presence of $\text{Bu}_4\text{NOH}$**

DGEBA, metal complexes (NiL or ZnL), maleic anhydride and  $\text{Bu}_4\text{NOH}$  were mixed at the mole ratio of DGEBA : ML : MA. The amount of tetrabutylammonium hydroxide employed was 20 mole % of the metal complex. The sample was heated in a hot air oven at  $110$  and  $130^{\circ}\text{C}$  and the progress of the reaction was followed by IR spectroscopy to investigate the optimum crosslinking parameters for DGEBA.

## **2.7 Preparation of Metal-Containing Epoxy Polymers Using Hexadentate Schiff Base Metal Complexes and Maleic Anhydride as Crosslinking Agents in the Presence of $\text{Bu}_4\text{NOH}$**

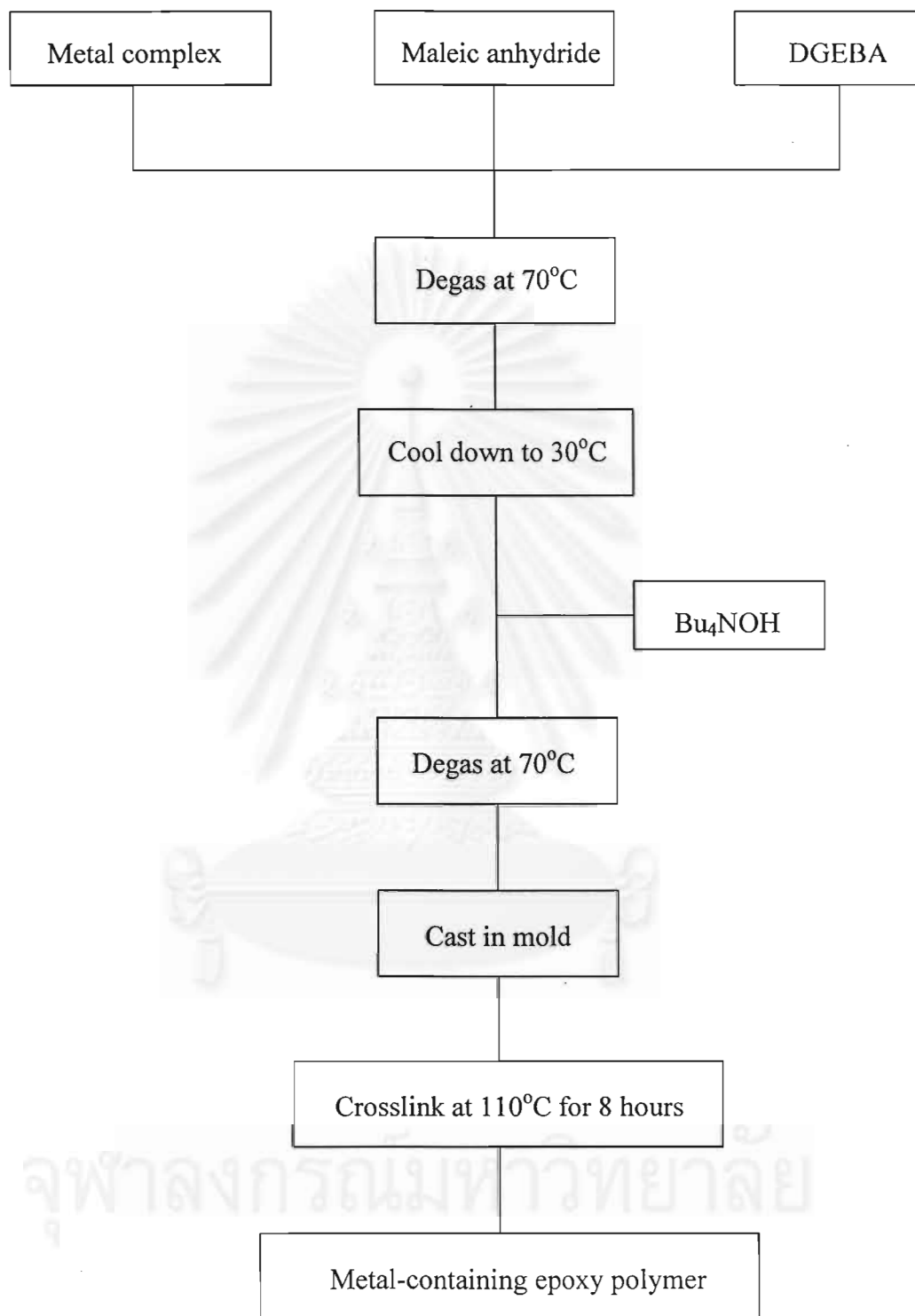
### **2.7.1. Nickel-Containing Epoxy Polymer**

NiL and maleic anhydride were used as a crosslinking agent and  $\text{Bu}_4\text{NOH}$  was used as a catalyst at the amount of 10 and 20 mole % of the metal complex.

The mole ratios of DGEBA : NiL : MA : Bu<sub>4</sub>NOH employed are shown in Table 2.1. A mixture of DGEBA, NiL and maleic anhydride was heated at 70°C and stirred to become homogeneous then degassed under vacuum until gas bubbles were not observed. The mixture was cooled to room temperature and Bu<sub>4</sub>NOH was added then stirred and degassed under vacuum at 70°C for 1 hour until gas bubbles were not observed. The degassed mixture was put into a metal or silicone rubber mold and cured at 110°C for 8 hours. The procedure for the preparation of Ni-containing epoxy polymers is shown in Scheme 2.1

**Table 2.1** Composition of starting materials in DGEBA : NiL : MA : Bu<sub>4</sub>NOH formulation

Mole ratio of DGEBA : NiL : MA	Weight of composition (g)		
	DGEBA	NiL	MA
1 : 0.20 : 0.20	3	0.76	0.16
1 : 0.15 : 0.15	3	0.56	0.12
1 : 0.10 : 0.10	3	0.38	0.08
1 : 0.05 : 0.05	3	0.19	0.04



**Scheme 2.1** Preparation scheme of metal-containing epoxy polymer

### 2.7.2. Zinc-Containing Epoxy Polymers

DGEBA was crosslinked with ZnL, maleic anhydride and Bu<sub>4</sub>NOH at 110°C for 8 hours by using the same method as described in 2.7.1. The mole ratios of DGEBA : ZnL : MA : Bu<sub>4</sub>NOH are shown in Table 2.2

**Table 2.2** Composition of starting materials in DGEBA : ZnL : MA : Bu<sub>4</sub>NOH formulation

Mole ratio of DGEBA : ZnL : MA	Weight of composition (g)		
	DGEBA	ZnL	MA
1 : 0.20 : 0.20	3	0.71	0.16
1 : 0.15 : 0.15	3	0.53	0.12
1 : 0.10 : 0.10	3	0.35	0.08
1 : 0.05 : 0.05	3	0.18	0.04

Comparative polymers obtained by using maleic anhydride, tetrabutylammonium hydroxide or diethylenetriamine as crosslinking agents were also prepared using the procedure described in the literature.<sup>25</sup> Table 2.3 shows the composition of the starting materials.



**Table 2.3** Composition of starting materials in crosslinking reaction of DGEBA  
Using maleic anhydride, tetrabutylammonium hydroxide and  
diethylenetriamine as crosslinking agents

Crosslinking agent	Mole ratio of DGEBA : Crosslinking agent	Weight of composition (g)		Crosslinking condition
		DGEBA	Crosslinking agent	
Maleic anhydride <sup>a</sup>	1 : 2.8	3	2.25	110 °C / 1 h followed by 160 °C / 4 h
Maleic anhydride <sup>b</sup>	1 : 0.2	3	0.16	110 °C / 8 h
Diethylenetriamine	1 : 1	3	0.36	100 °C / 1 h
Bu <sub>4</sub> NOH	1 : 0.2	3	0.09	110 °C / 8 h

<sup>a</sup> benzyldimethylamine 0.0053 g (0.1 phr) was employed as a catalyst

<sup>b</sup> tetrabutylammonium hydroxide was employed as a catalyst

## 2.8. Characterization of Metal-Containing Epoxy Polymers.

### 2.8.1 IR Spectroscopy

The polymers obtained were characterized by IR spectroscopy as KBr pellets.

### 2.8.2 Thermal Properties

The Glass transition temperatures ( $T_g$ ) of the epoxy polymers were measured by dynamic mechanical analysis at a heating rate of  $3^\circ\text{C} / \text{min}$ .

### 2.8.3 Thermal Stability

Heat resistance of the epoxy polymers was studied using the thermogravimetric analysis. The polymer samples ( $1 \text{ cm} \times 5 \text{ cm} \times 3 \text{ mm}$ ) were heat at  $250^\circ\text{C}$  for 48 h in a hot air oven to obtain % weight loss of polymer at different times.

### 2.8.4 Mechanical Properties

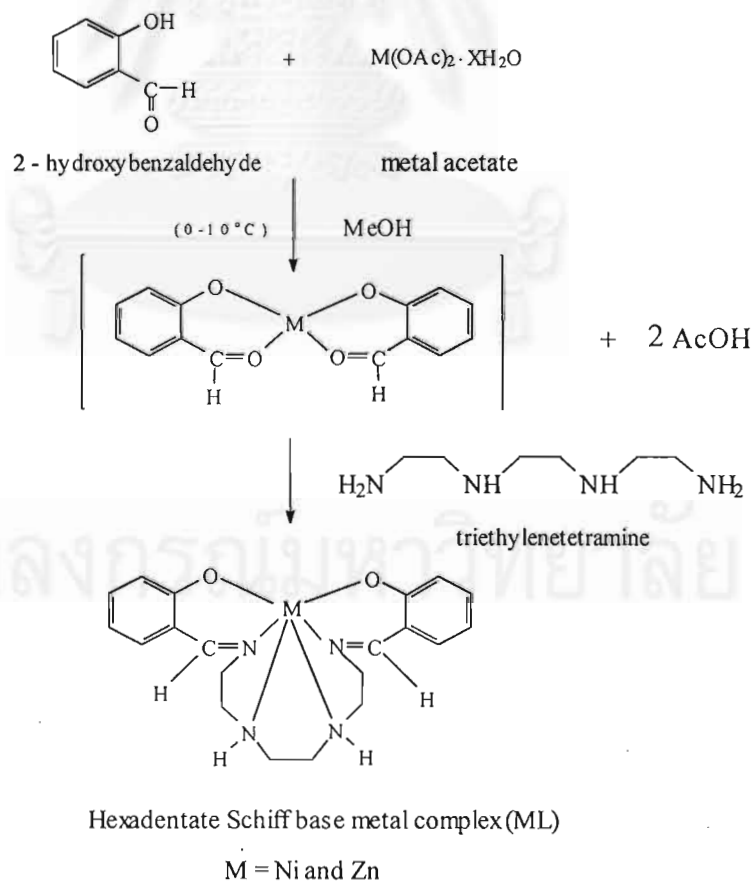
Tensile testing of the epoxy polymers was performed according to the procedure described in ASTM D 638 (tensile testing).

## CHAPTER III

### RESULTS AND DISCUSSION

#### 3.1 Synthesis of Hexadentate Schiff Base Metal Complexes (ML)

Hexadentate Schiff base metal complexes were synthesized according to the procedure described in the literature.<sup>26</sup> The proposed mechanism is that 2-hydroxybenzaldehyde and the metal acetate form an intermediate in the first step. This intermediate then undergoes condensation with triethylenetetramine to give the Schiff base metal complex (ML) (Scheme 3.1). The spectroscopic data of these metal complexes agreed with the values reported in the literature.

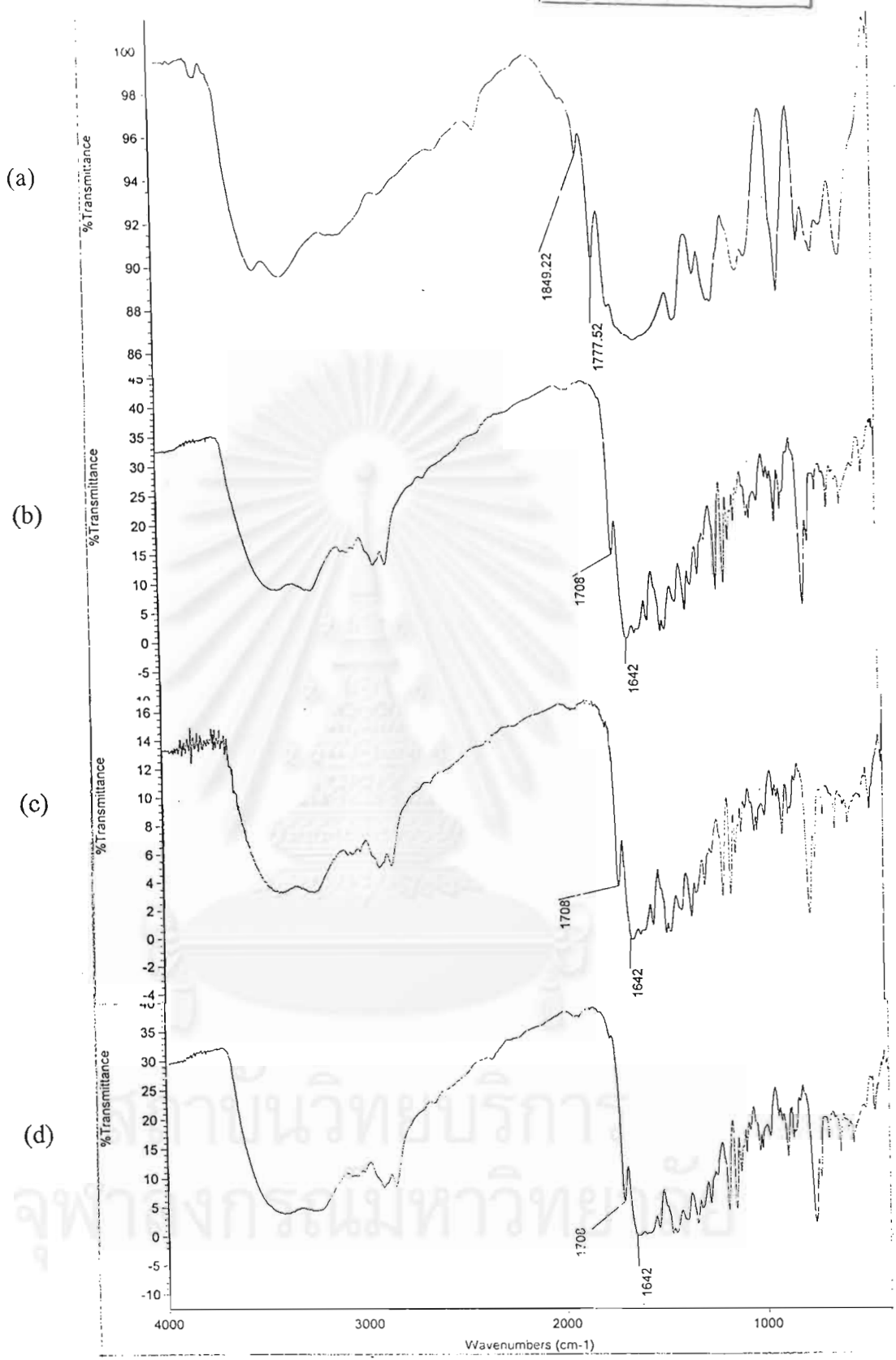


**Scheme 3.1** Synthesis of Hexadentate Schiff base metal complexes

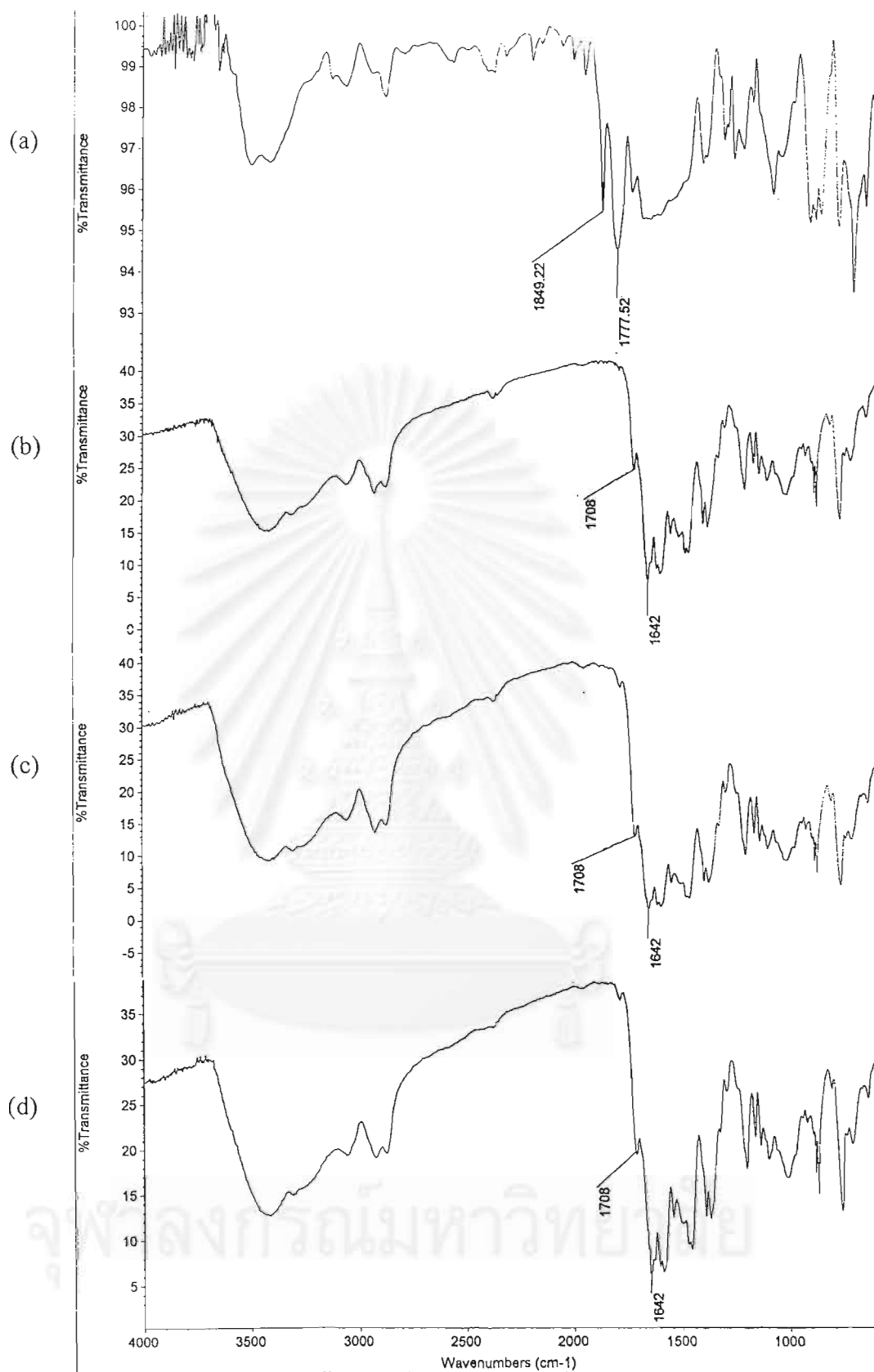
### 3.2 Reaction between Hexadentate Schiff Base Metal Complexes and Maleic Anhydride

The next step was to study the reaction between nickel and zinc complexes (NiL and ZnL) with maleic anhydride. As previously mentioned, Takechi and Matsuda<sup>23</sup> studied the crosslinking of DGEBA with divalent metal salts of *p*-aminobenzoic acid and hexahydrophthalic anhydride. The proposed mechanism is that the amino groups of the metal salts first reacted with the anhydride group to give carboxylate groups, which could then undergo further reaction with the epoxide groups of DGEBA.

Therefore, the amine groups in NiL and ZnL should be able to react in a similar way. The thermal crosslinking reaction between the metal complexes and maleic anhydride was studied by IR spectroscopy.

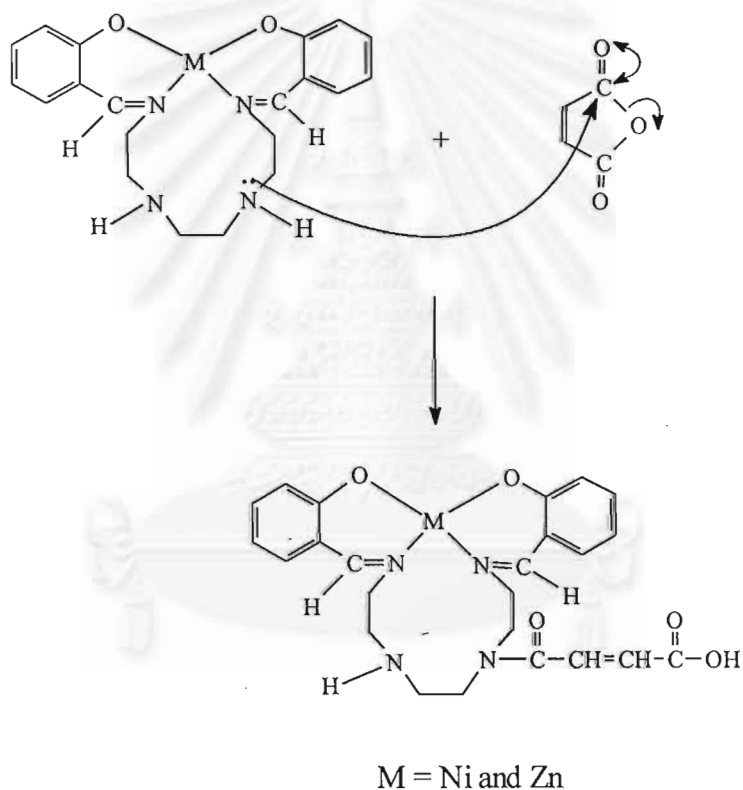


**Figure 3.1** IR spectra of a mixture of NiL and maleic anhydride at the mole ratio of 1:1 (a) initial mixture (b) after heating at 130 °C for 1 h (c) 2 h and (d) after 4 h



**Figure 3.2** IR spectra of a mixture of ZnL and maleic anhydride at the mole ratio of 1:1 (a) initial mixture (b) after heating at 130 °C for 1 h (c) 2 h and (d) after 4 h

Figure 3.1 shows the IR spectra of a mixture of NiL and maleic anhydride at a mole ratio of 1:1 before and after heating. The C=O bands of the anhydride group at 1850 and 1777  $\text{cm}^{-1}$  disappeared after heating at 130  $^{\circ}\text{C}$  for 1 hour. Therefore, the anhydride ring could be opened by the amino group of NiL to generate a carboxylic group which appears at 1708  $\text{cm}^{-1}$  and the C=N band appears at 1642  $\text{cm}^{-1}$  (Scheme 3.2). When ZnL was used, the IR study showed similar results.



**Scheme 3.2** Reaction between metal complex and maleic anhydride

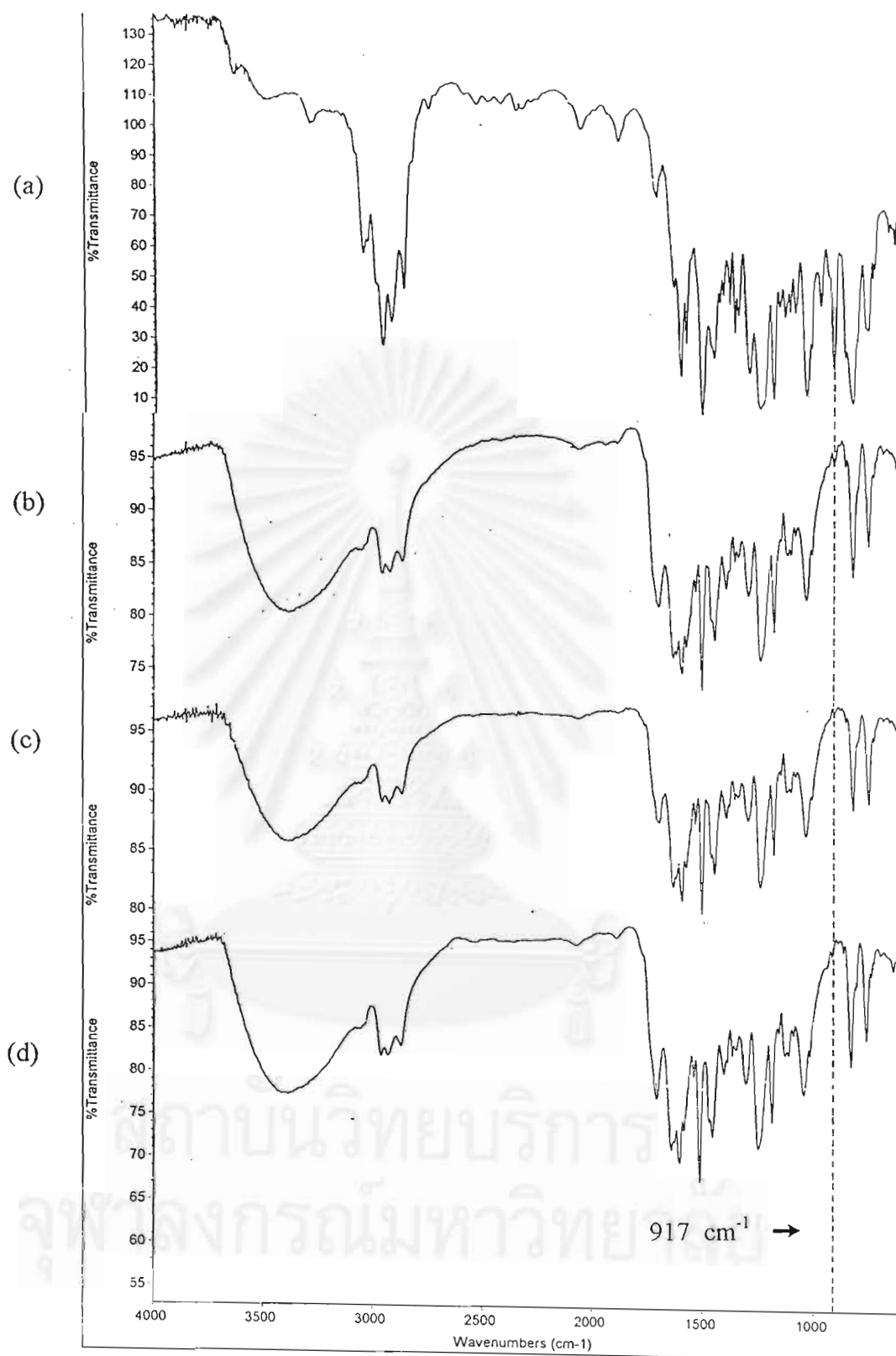
### 3.3 Crosslinking Reaction of DGEBA with Hexadentate Schiff Base Metal Complexes and Maleic Anhydride (MA)

Infrared spectroscopy was also used in this study to determine the suitable temperature for crosslinking of DGEBA with ML and maleic anhydride. The reaction was followed by observing the disappearance of the IR band of the epoxide group in DGEBA at  $917\text{ cm}^{-1}$ . In the case of NiL, the IR spectra were obtained from a mixture of DGEBA : NiL: MA at the mole ratio of 1 : 0.2 : 0.2 at the temperature of  $110^{\circ}\text{C}$  and  $130^{\circ}\text{C}$ . Figures 3.3 and 3.4 show the results from IR experiments.

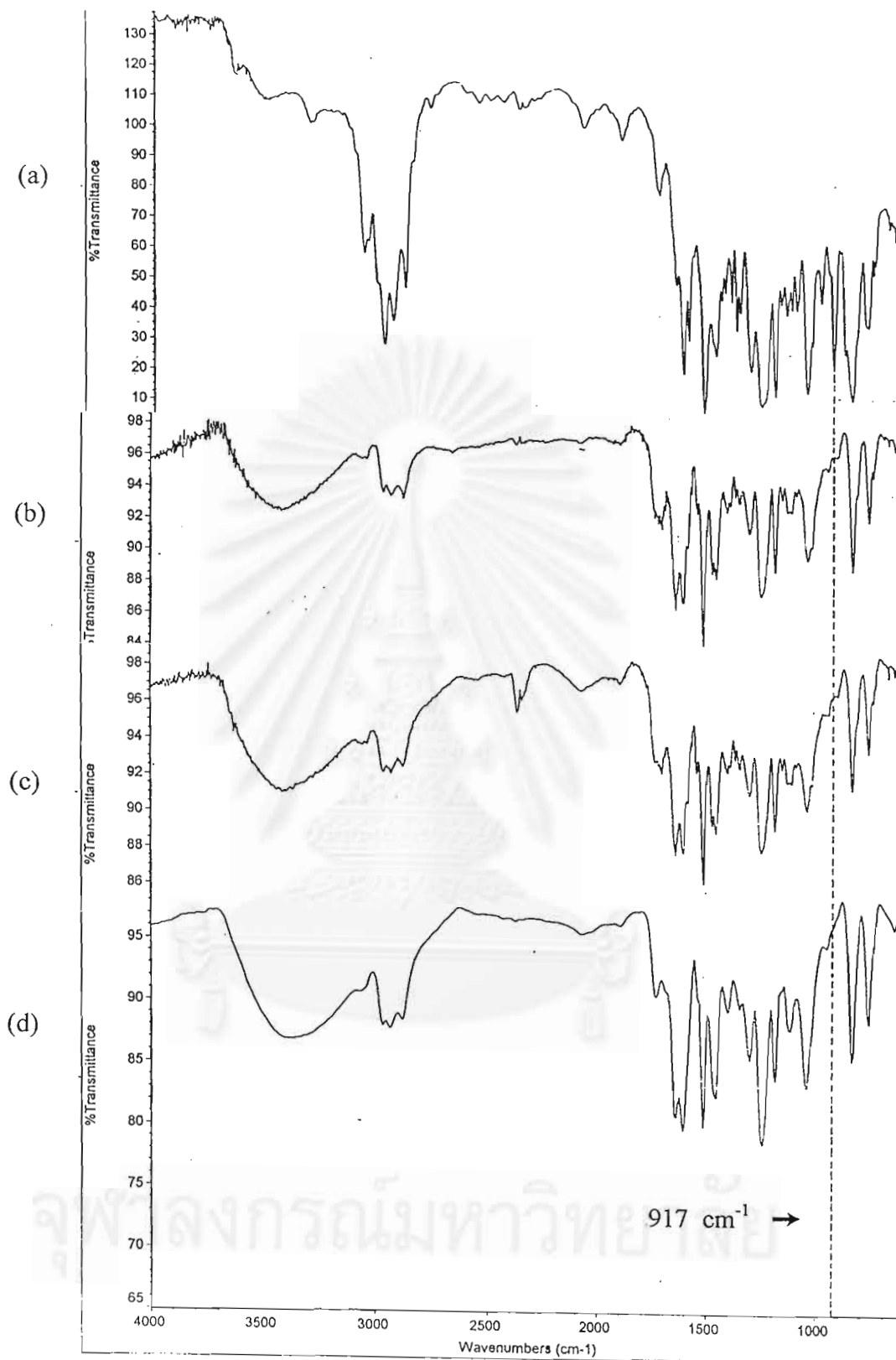
The IR spectra suggested that the crosslinking reaction at  $130^{\circ}\text{C}$  was completed after 4 hours. When the crosslinking was done at  $110^{\circ}\text{C}$  the IR band at  $917\text{ cm}^{-1}$  was still observed, which indicated that the crosslinking reaction was incomplete.

The crosslinking reaction of DGEBA with ZnL and MA was studied using the same method. Figures 3.5 and 3.6 show the results from IR experiment which were similar to those obtained in the case of NiL.

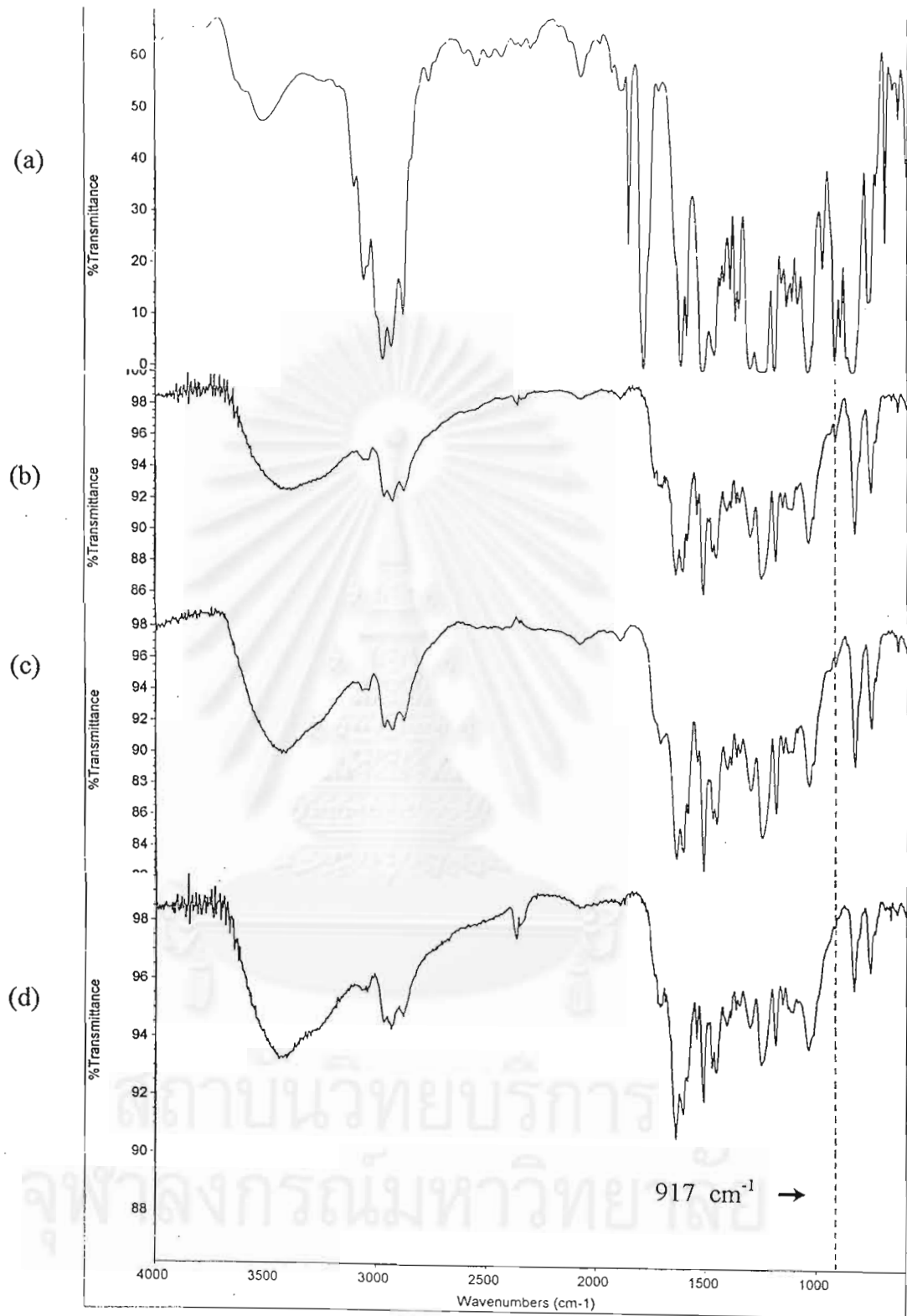




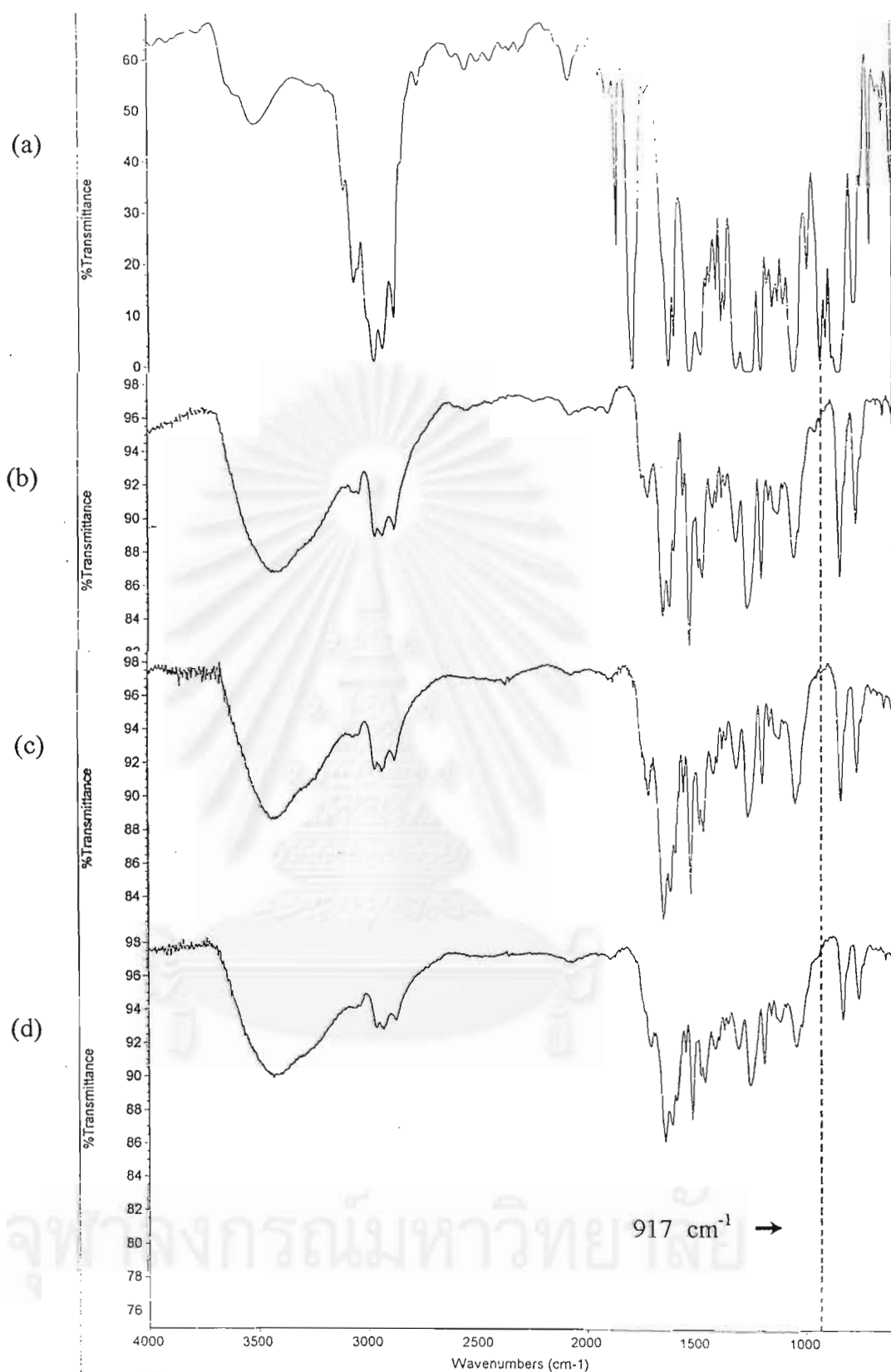
**Figure 3.3** IR spectra of DGEBA : NiL : MA mixture at the mole ratio of 1 : 0.2 : 0.2 (a) before heating (b) after heating at 110 °C 1 h (c) after 2 h and (d) after 4 h



**Figure 3.4** IR spectra of DGEBA : NiL : MA mixture at the mole ratio of 1 : 0.2 : 0.2 (a) before heating (b) after heating at 130 °C 1 h (c) after 2 h and (d) after 4 h

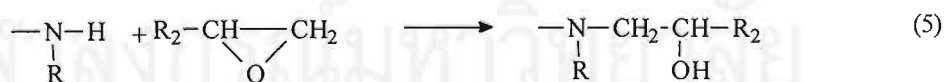
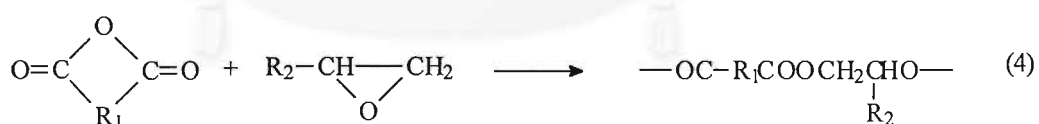
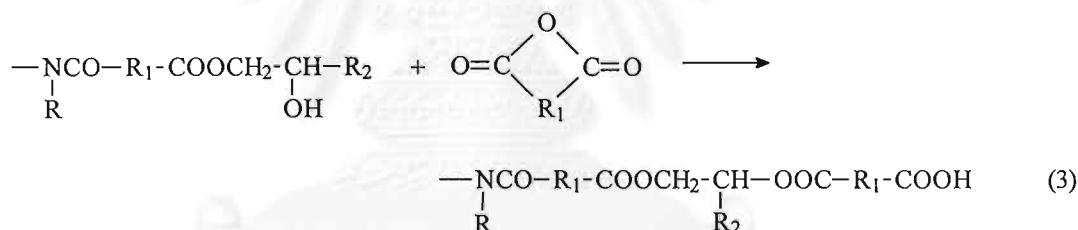
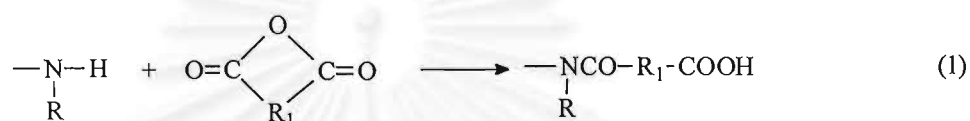


**Figure 3.5** IR spectra of DGEBA : ZnL : MA mixture at the mole ratio of 1 : 0.2 : 0.2 (a) before heating (b) after heating at 110 °C 1 h (c) after 2 h and (d) after 4 h



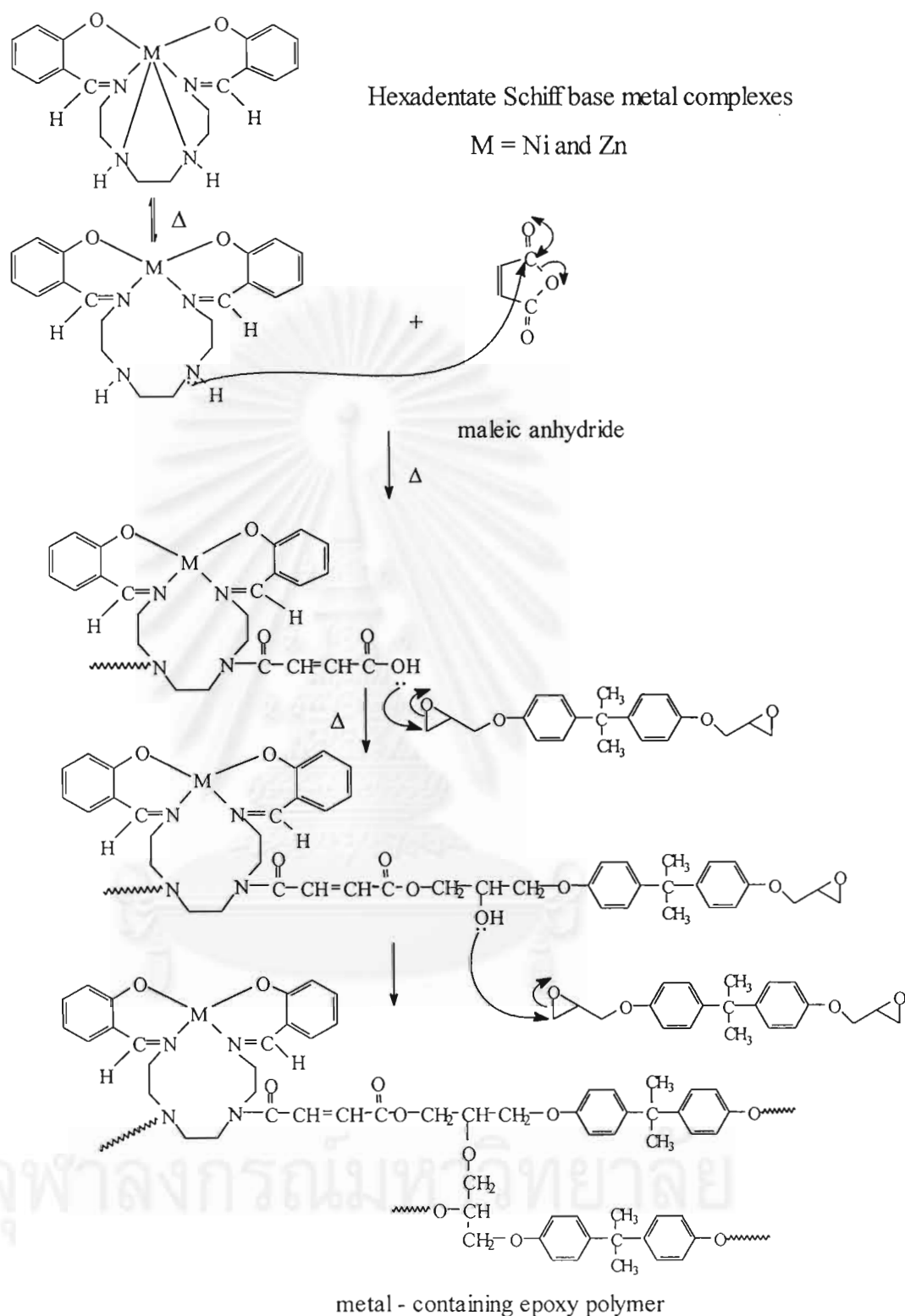
**Figure 3.6** IR spectra of DGEBA : ZnL : MA mixture at the mole ratio of 1 : 0.2 : 0.2 (a) before heating (b) after heating at 130 °C 1 h (c) after 2 h and (d) after 4 h

The results from previous research<sup>26</sup> showed that the crosslinking of DGEBA with metal complexes occurred at 180°C. Therefore, the crosslinking reaction of DGEBA with metal complexes in the presence of maleic anhydride occurred at a low temperature. The reaction of the functional groups in DGEBA, metal complexes and maleic anhydrides could be considered as follows :



Thus, the amine group in the metal complexes reacts with the acid anhydride group in maleic anhydride to form a carboxylic group [eq.(1)]; the generated carboxylic group reacts with the epoxide group in DGEBA [eq.(2)], the newly generated hydroxyl group reacts with the acid anhydride group to form a half ester [eq.(3)], the acid anhydride group reacts with the epoxide group to form an ester linkage [eq.(4)], finally, the amine group reacts with the epoxide group to form a hydroxyl group [eq.(5)].

It is well known that reaction (1) proceeds much more rapidly than reactions (3), (4) and (5).<sup>11</sup> Therefore, in the crosslinking of DGEBA-metal complex-maleic anhydride systems, it is likely that the metal complexes first dissociate the amine group, which then reacts with maleic anhydride to form a carboxylic group, which could then open the epoxide ring in DGEBA. The generated hydroxyl group could then undergo further reaction with DGEBA to give crosslinked epoxy polymer (Scheme 3.3).



**Scheme 3.3** Proposed mechanism of the crosslinking reaction of DGEBA with metal complexes and maleic anhydride

### 3.4 Effect of catalyst

It is known that crosslinking of DGEBA with NiL and ZnL can be accelerated by the use of tetrabutylammonium hydroxide (Bu<sub>4</sub>NOH) as a catalyst.<sup>26</sup> It was reported that the crosslinking reaction in the presence of Bu<sub>4</sub>NOH proceeded at a lower temperature than the crosslinking reaction without the catalyst. The suitable amount of Bu<sub>4</sub>NOH was found to be 20 mole % of the metal complex.

Therefore, Bu<sub>4</sub>NOH was chosen as a catalyst in the crosslinking reaction of DGEBA with the metal complexes and maleic anhydride in order to reduce the crosslinking temperature. The amount of Bu<sub>4</sub>NOH employed in this work was 20 mole % of the metal complex. The crosslinking reaction was studied by IR spectroscopy. The disappearance of the epoxide peak at 917 cm<sup>-1</sup> should be observed after the crosslinking was completed as before.

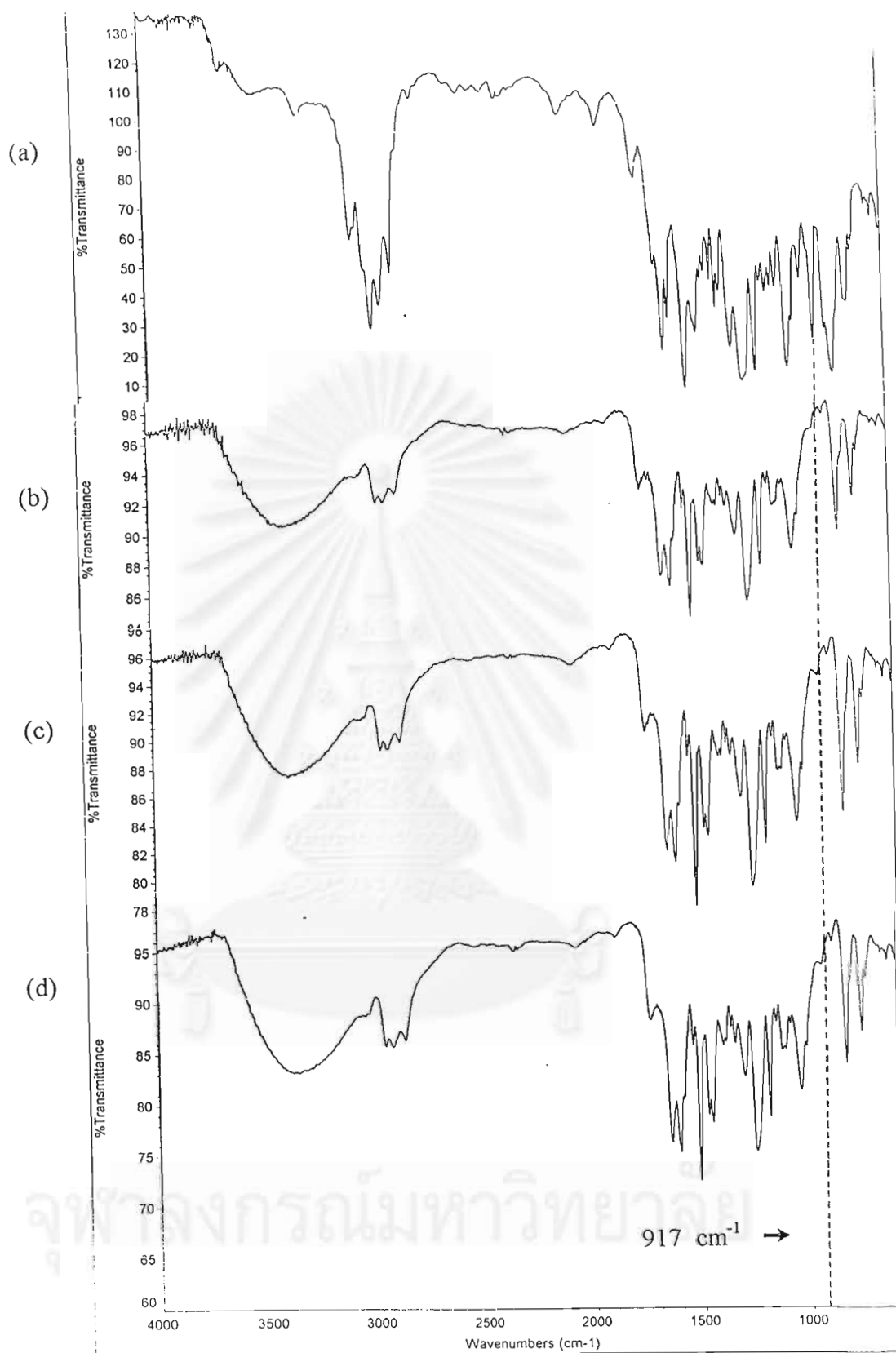
In the case of NiL, when Bu<sub>4</sub>NOH was employed at the mole ratio of DGEBA : NiL: MA = 1 : 0.2 : 0.2 and crosslinking was carried out at 130 and 110°C, the reaction was complete in 1 hour and 4 hours, respectively (Figures 3.7 and 3.8).

In comparison to the crosslinking reaction without Bu<sub>4</sub>NOH, the time of crosslinking at 130 °C decreased from 4 hours to 1 hours. When the crosslinking was carried out at 110 °C without Bu<sub>4</sub>NOH, the reaction did not finish in 4 hours.

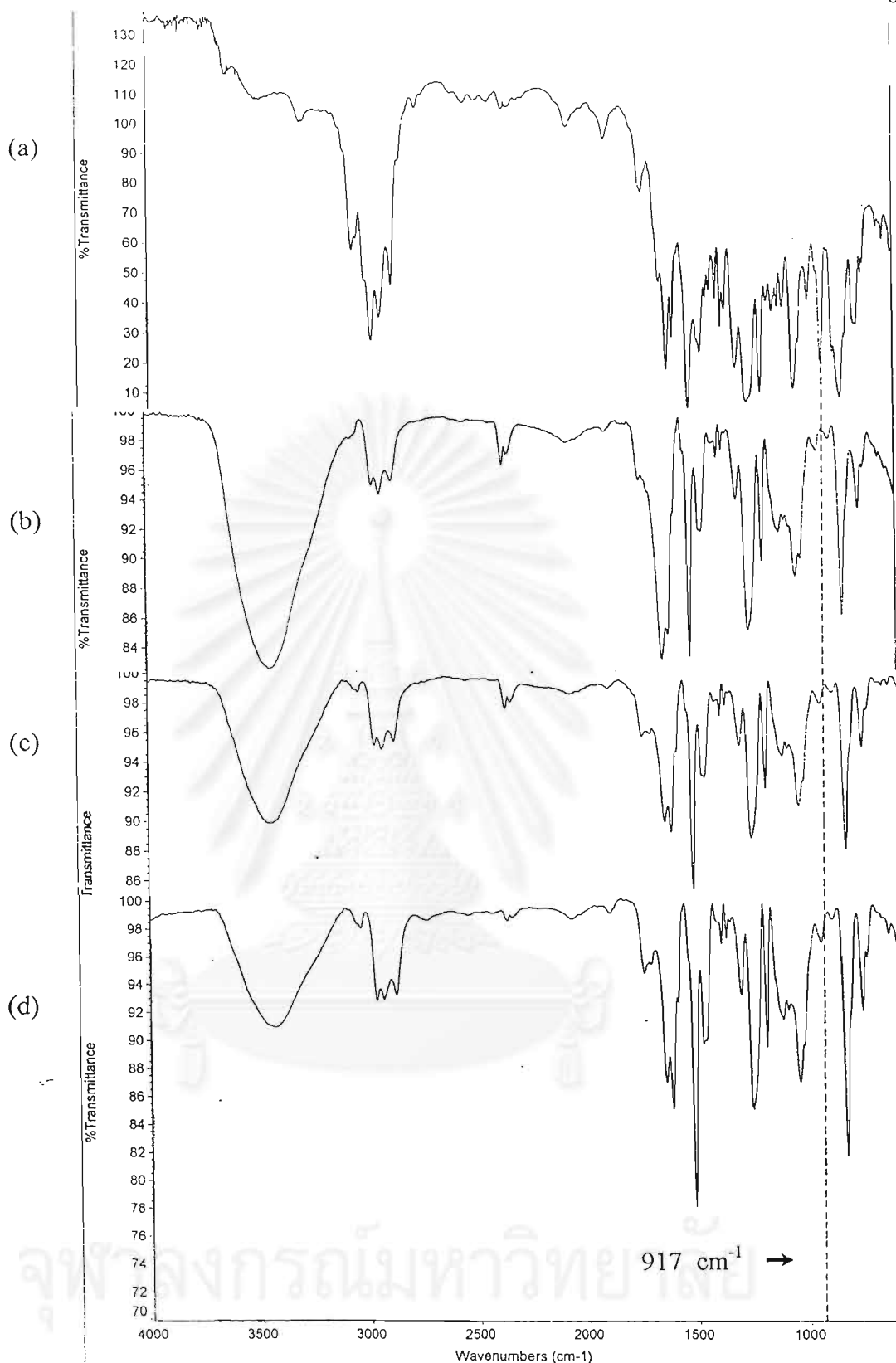
Crosslinking of DGEBA with ZnL and MA in the presence of Bu<sub>4</sub>NOH gave similar results to those of NiL (Figures 3.9 and 3.10).

A possible crosslinking mechanism in the presence of Bu<sub>4</sub>NOH is shown in Scheme 3.4. The metal complex first dissociates the amine group, which opens the maleic anhydride ring to generate a carboxylate group. Bu<sub>4</sub>NOH might accelerate the reaction by removing a proton from the ammonium salt. The carboxylate group undergoes reaction with DGEBA to give a secondary alcohol which reacts further with DGEBA to give crosslinked metal-containing epoxy polymers.

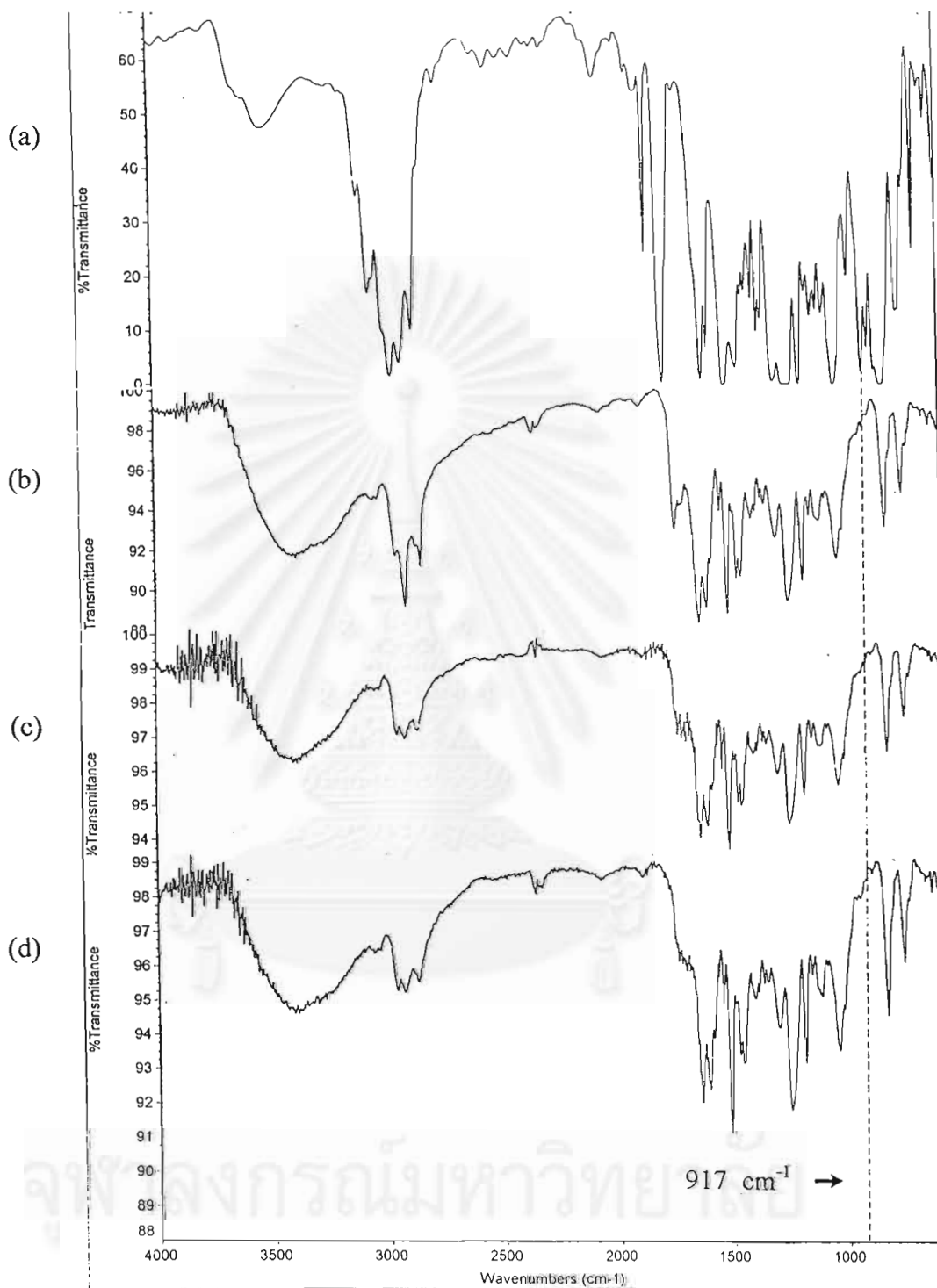




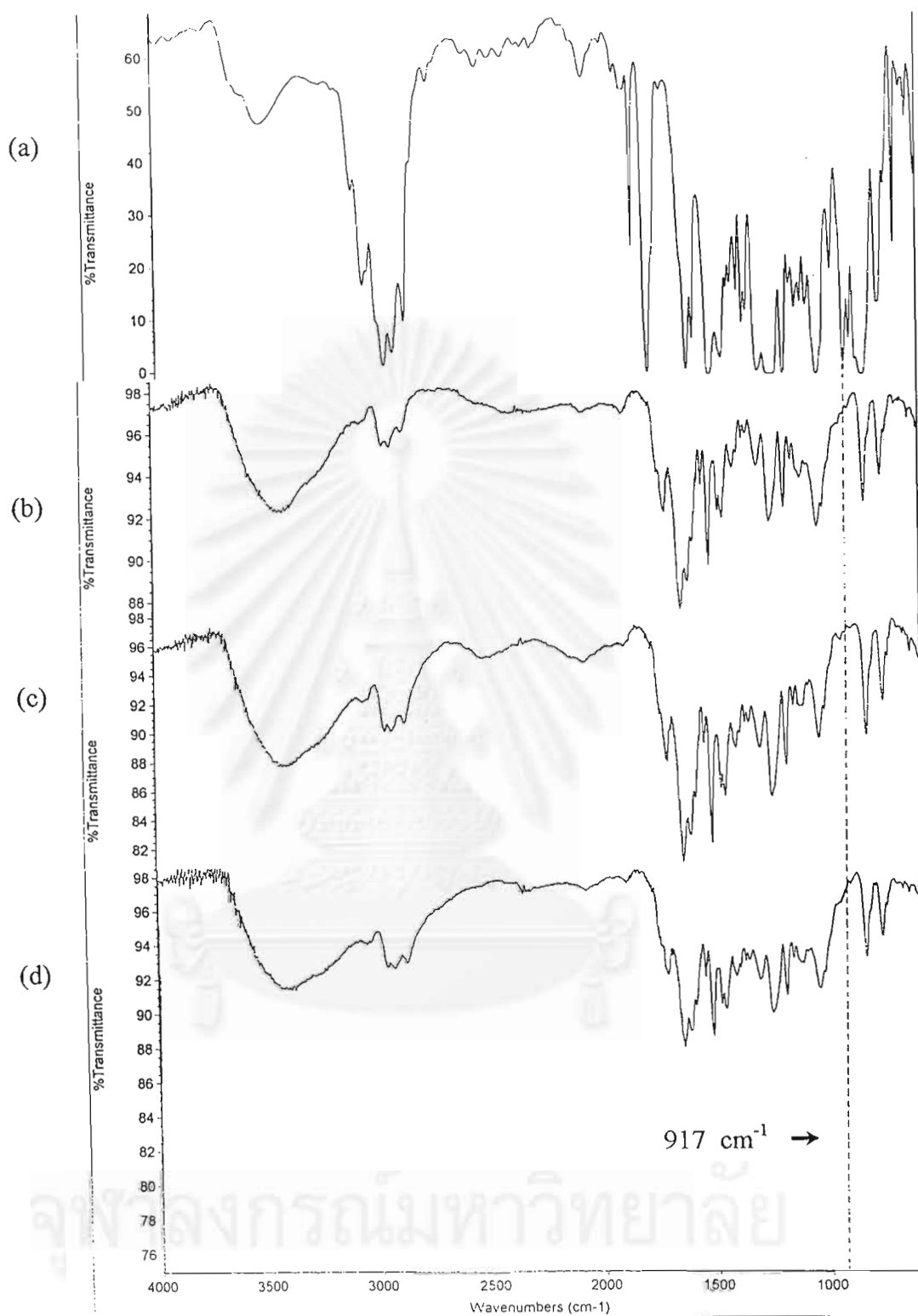
**Figure 3.7** IR spectra of DGEBA : NiL : MA mixture in the presence of 20 mole % of  $\text{Bu}_4\text{NOH}$  at the mole ratio of 1 : 0.2 : 0.2 (a) initial mixture (b) after heating at  $110^\circ\text{C}$  1 h (c) after 2 h (d) after 4 h



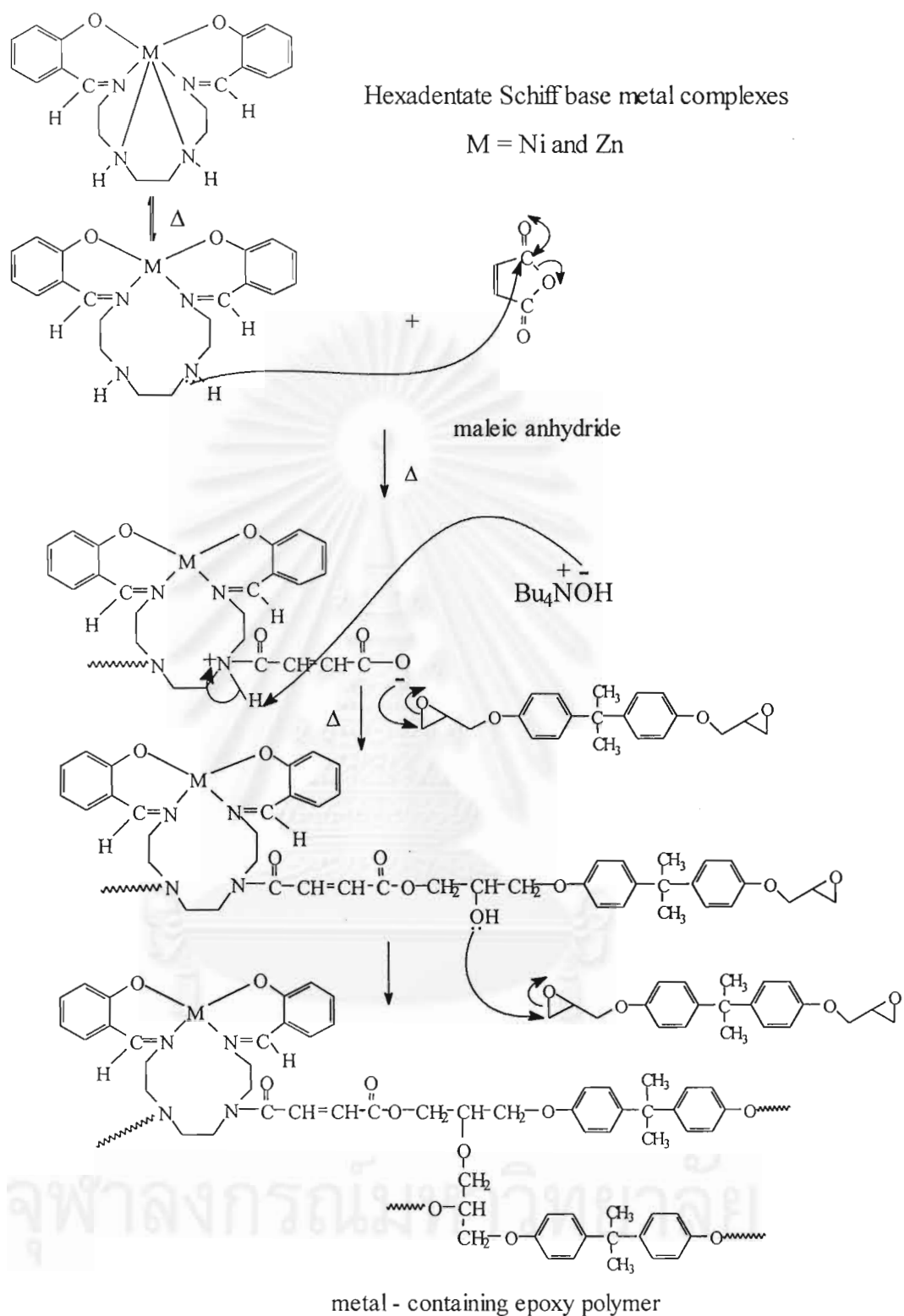
**Figure 3.8** IR spectra of DGEBA : NiL : MA mixture in the presence of 20 mole % of  $\text{Bu}_4\text{NOH}$  at the mole ratio of 1 : 0.2 : 0.2 (a) initial mixture (b) after heating at  $130\text{ }^\circ\text{C}$  1 h (c) after 2 h (d) after 4 h



**Figure 3.9** IR spectra of DGEBA : ZnL : MA mixture in the presence of 20 mole % of  $\text{Bu}_4\text{NOH}$  at the mole ratio of 1 : 0.2 : 0.2 (a) initial mixture (b) after heating at  $110\text{ }^\circ\text{C}$  1 h (c) after 2 h (d) after 4 h



**Figure 3.10** IR spectra of DGEBA : ZnL : MA mixture in the presence of 20 mole % of  $\text{Bu}_4\text{NOH}$  at the mole ratio of 1 : 0.2 : 0.2 (a) initial mixture (b) after heating at  $130 \text{ }^\circ\text{C}$  1 h (c) after 2 h (d) after 4 h



**Scheme 3.4** Proposed mechanism of crosslinking reaction of DGEBA with metal complexes and maleic anhydride in the presence of Bu<sub>4</sub>NOH

### 3.5 Preparation of Metal – Containing Epoxy Polymers

Another objective of this research was to investigate the physical and mechanical properties of the metal-containing epoxy polymers and polymer samples were prepared for this purpose. As previously described, crosslinking of DGEBA with the metal complexes and maleic anhydride in the presence of  $\text{Bu}_4\text{NOH}$  at  $110^\circ\text{C}$  was complete in 4 hours. Therefore, this crosslinking temperature was chosen for the preparation of epoxy polymer samples from both NiL and ZnL. The preparation method is described in the experimental section. The time required to complete the crosslinking process was determined by observing the disappearance of the epoxide group in DGEBA at  $917\text{ cm}^{-1}$ . It was found that the suitable crosslinking condition was  $110^\circ\text{C}$  / 4 hours followed by postcuring at the same temperature for 4 hours to ensure the complete reaction.

To determine the optimum composition that would yield polymers with good properties, the mole ratios of DGEBA : metal complex : maleic anhydride employed in this study were 1 : 0.05 : 0.05, 1 : 0.1 : 0.1, 1 : 0.15 : 0.15 and 1 : 0.2 : 0.2.  $\text{Bu}_4\text{NOH}$  was used in the amounts of 10 and 20 mole % of the metal complexes.

The properties of the polymers prepared without using  $\text{Bu}_4\text{NOH}$  was not studied since high crosslinking temperatures were required.

For comparison, different epoxy polymers were prepared using the known crosslinking agents, namely maleic anhydride and diethylenetriamine.

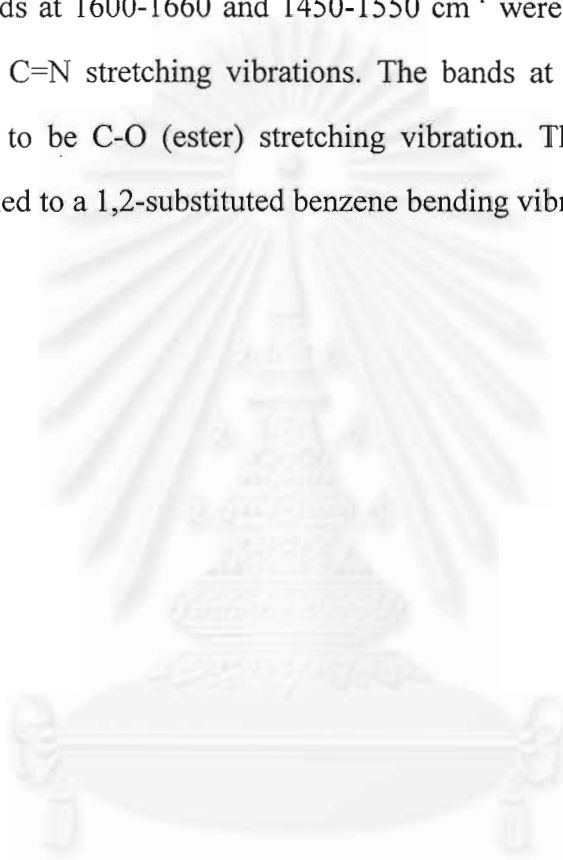
### 3.6 Characterization of Metal – Containing Epoxy Polymers

#### 3.6.1 IR spectroscopy

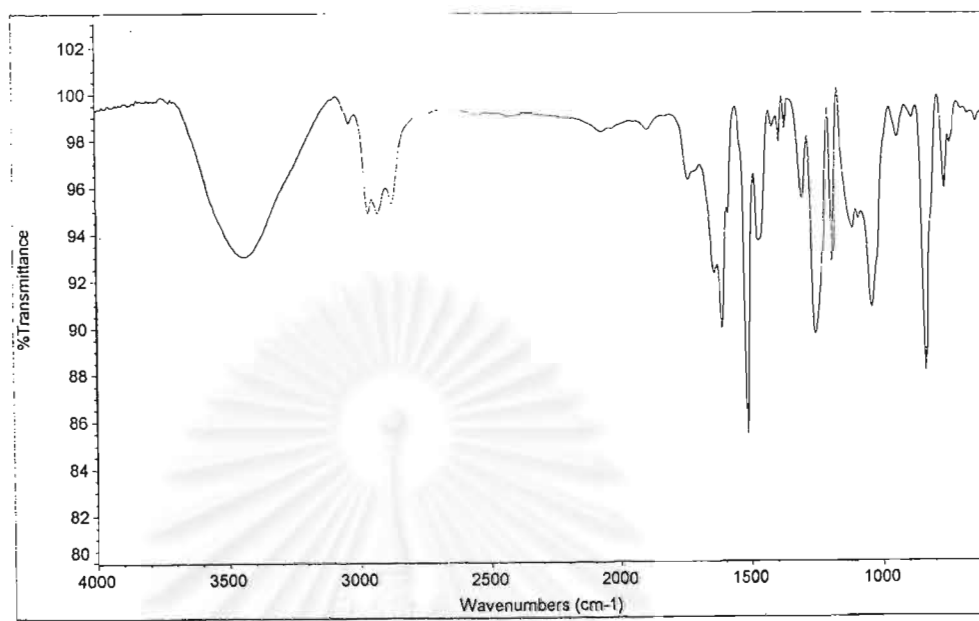
The metal – containing epoxy polymers obtained from different ratios of DGEBA : ML : MA were characterized by IR spectroscopy. All epoxy polymers gave

similar spectra. Examples of IR spectrum of the polymers obtained from DGEBA : NiL : MA and DGEBA : ZnL : MA are shown in Figures 3.11 and 3.12.

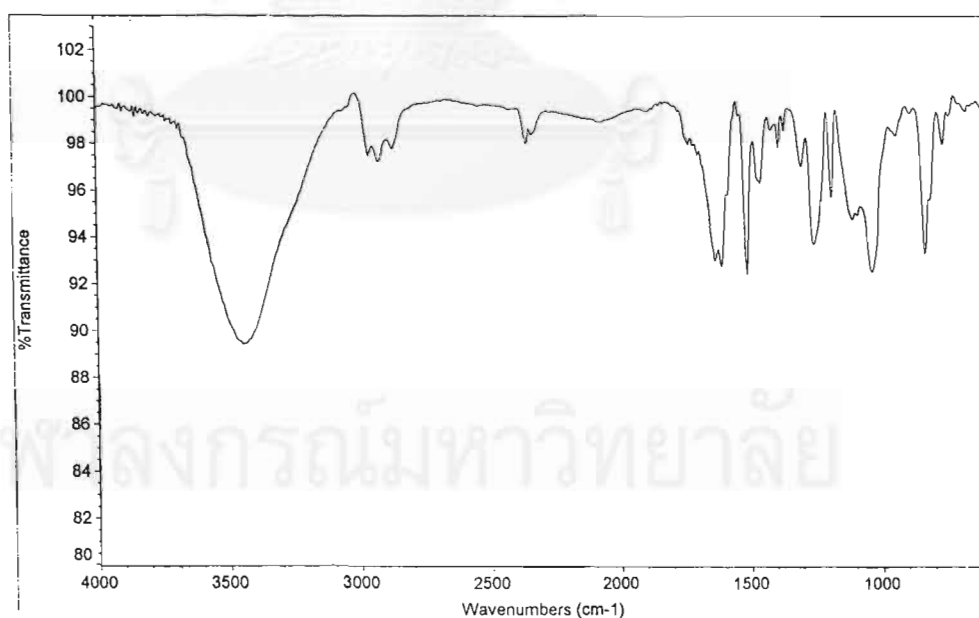
In the IR spectrum the O-H absorption band of a secondary alcohol at 3300-3500  $\text{cm}^{-1}$  and the band of C=O stretching vibration at 1730-1735  $\text{cm}^{-1}$  were apparent. The absorption bands at 1600-1660 and 1450-1550  $\text{cm}^{-1}$  were due to the C=C stretching vibrations and C=N stretching vibrations. The bands at 1100-1300 and 1250  $\text{cm}^{-1}$  were assigned to be C-O (ester) stretching vibration. The absorption band at 830  $\text{cm}^{-1}$  was assigned to a 1,2-substituted benzene bending vibration.



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**Figure 3.11** IR spectrum of Ni-containing epoxy polymer at the mole ratio of DGEBA : NiL : MA = 1 : 0.15 : 0.15 with 20 mole % of Bu<sub>4</sub>NOH employed as catalyst



**Figure 3.12** IR spectrum of Zn-containing epoxy polymers at the mole ratio of DGEBA : ZnL : MA = 1 : 0.15 : 0.15 with 20 mole % of Bu<sub>4</sub>NOH employed as catalyst



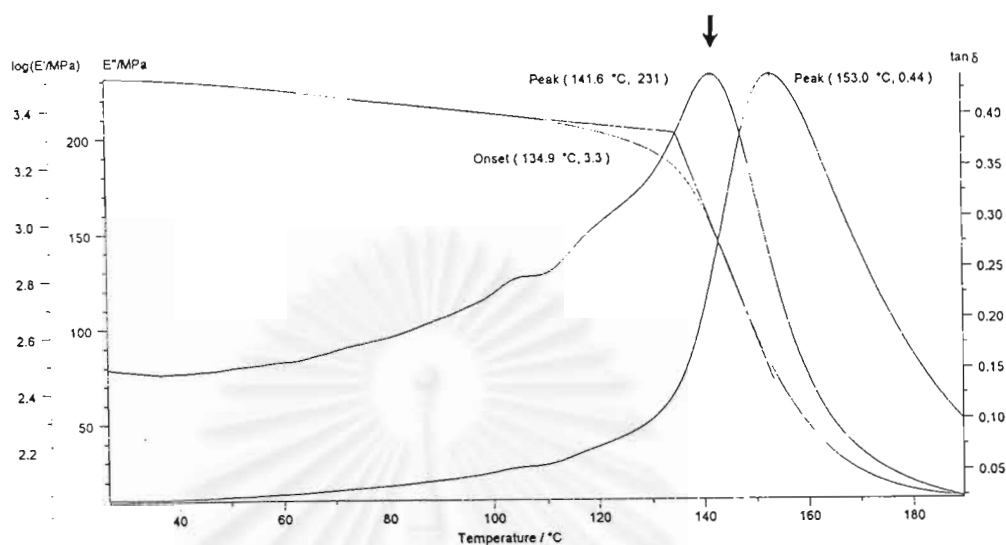
### 3.6.2 Glass Transition Temperature ( $T_g$ )

The glass transition temperature of the metal – containing epoxy polymers were studied using dynamic mechanical analysis (DMA) by observing the maximum value of the loss modulus. For example, DMA thermograms of Ni – and Zn – containing epoxy polymers obtained from DGEBA : metal complex : MA at the ratio of 1 : 0.15 : 0.15 showed  $T_g$  at 139 and 131 °C, respectively (Figures 3.13 and 3.14). The thermograms of other metal – containing epoxy polymers are shown in Figures A.6 – 25.

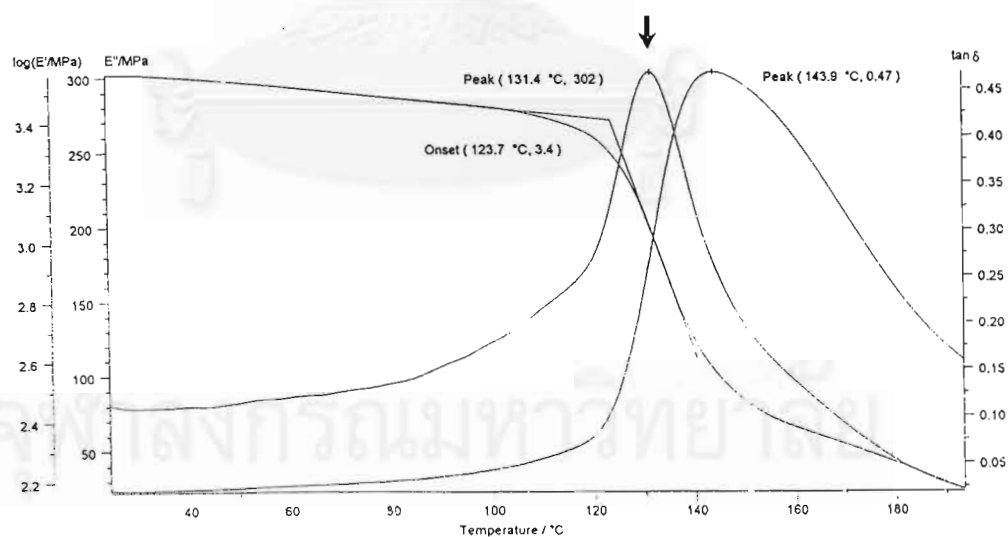
Table 3.1 shows the glass transition temperatures of metal – containing epoxy polymers obtained from different formulations. It can be seen that both Ni – and Zn – containing epoxy polymers exhibited good  $T_g$  values at the mole ratio of DGEBA : metal complex : MA = 1 : 0.2 : 0.2, 1 : 0.15 : 0.15 and 1 : 0.1 : 0.1. Ni – containing polymers had higher  $T_g$  than Zn-containing polymers. Variation of the  $Bu_4NOH$  amount did not effect the  $T_g$  values.

Very low  $T_g$  values were obtained at the ratio of 1 : 0.05 : 0.05 since there were only small amounts of metal complexes and maleic anhydride available for the crosslinking reaction, resulting in low crosslinking densities of the polymers. The ratio of 1 : 0.3 : 0.3 was not studied because mixing of the starting materials to obtain homogenous samples was difficult due to the high viscosity.

In comparison to the epoxy polymers obtained from the known systems, namely maleic anhydride and diethylenetriamine, the metal-containing polymers showed higher  $T_g$ . Crosslinking was also possible with  $Bu_4NOH$ , however, the resulting polymer was a brittle material with low  $T_g$ .



**Figure 3.13** DMA thermogram of Ni – containing epoxy polymer at the mole ratio of DGEBA : NiL : MA = 1 : 0.15 : 0.15 with 20 mole % of  $\text{Bu}_4\text{NOH}$  employed as catalyst



**Figure 3.14** DMA thermogram of Zn – containing epoxy polymers at the mole ratio of DGEBA : ZnL : MA = 1 : 0.15 : 0.15 with 20 mole % of  $\text{Bu}_4\text{NOH}$  employed as catalyst

**Table 3.1** Glass transition temperature ( $T_g$ ) of the metal – containing epoxy polymers

Metal complex (ML)	Mole ratio of DGEBA : ML : MA	$T_g$ (°C)	
		10 Mole % of Bu <sub>4</sub> NOH	20 mole % of Bu <sub>4</sub> NOH
NiL	1 : 0.20 : 0.20	130	133
	1 : 0.15 : 0.15	142	139
	1 : 0.10 : 0.10	124	119
	1 : 0.05 : 0.05	85	91
ZnL	1 : 0.20 : 0.20	129	129
	1 : 0.15 : 0.15	128	131
	1 : 0.10 : 0.10	114	132
	1 : 0.05 : 0.05	86	106
Maleic anhydride <sup>a</sup>	-	69	
Maleic anhydride <sup>b</sup>	-	114	
Diethylenetriamine <sup>c</sup>	-	125	
Tetrabutylammonium hydroxide <sup>d</sup>	-	95	

<sup>a</sup> mole ratio of DGEBA : MA : Bu<sub>4</sub>NOH was 1 : 0.2 : 0.2

<sup>b</sup> mole ratio of DGEBA : MA was 1 : 2.8 and 0.1 phr of benzyldimethylamine was employed as a catalyst

<sup>c</sup> mole ratio of DGEBA : DETA was 1 : 1

<sup>d</sup> mole ratio of DGEBA : Bu<sub>4</sub>NOH was 1 : 0.2

### 3.6.3 Thermal Stability

The thermal stability of the metal-containing epoxy polymers was determined by heating the polymers at 250 °C for 48 hours in air. Table 3.5 shows the weight loss of the epoxy polymers at different times.

The results indicated that the Ni-containing polymer had higher thermal stability than the Zn-containing polymers. The optimum ratio for both epoxy polymers that gave the highest thermal stability was 1 : 0.15 : 0.15 when 20 mole % of Bu<sub>4</sub>NOH was employed.

Ni-containing epoxy polymers exhibited much higher thermal stability than the epoxy polymers synthesized from DGEBA – DETA system.

In comparison to the polymer obtained from DGEBA : MA and benzyldimethylamine as catalyst, the metal-containing polymer showed slightly higher thermal stability. In the case of the two polymers obtained from DGEBA : MA : Bu<sub>4</sub>NOH and DGEBA : Bu<sub>4</sub>NOH, they showed good thermal stability but these polymers were soft and brittle materials with low T<sub>g</sub>.

**Table 3.2** Thermal stability at 250 °C of the metal-containing epoxy polymers obtained from different mole ratios of DGEBA : ML : MA and Bu<sub>4</sub>NOH was employed as a catalyst

Metal complex (ML)	Mole ratio of DGEBA : ML : MA	% Weight loss 10 mole % Bu <sub>4</sub> NOH				% Weight loss 20 mole % Bu <sub>4</sub> NOH			
		12 h	24 h	36 h	48 h	12 h	24 h	36 h	48 h
NiL	1 : 0.20 : 0.20	8.0	8.9	9.7	10.1	7.7	8.5	9.2	9.5
	1 : 0.15 : 0.15	6.1	7.1	7.8	8.4	5.9	6.7	7.3	7.7
	1 : 0.10 : 0.10	6.6	9.2	11.0	12.3	6.7	8.2	10.2	11.9
	1 : 0.05 : 0.05	8.8	11.1	14.3	15.8	8.5	11.5	18.1	19.6
ZnL	1 : 0.20 : 0.20	10.0	12.9	15.2	17.0	8.9	11.1	13.0	14.6
	1 : 0.15 : 0.15	6.5	8.6	10.3	11.7	6.2	8.0	9.4	10.5
	1 : 0.10 : 0.10	9.6	13.9	17.6	19.7	9.3	14.1	17.5	19.6
	1 : 0.05 : 0.05	9.5	13.1	16.3	19.1	9.9	13.6	17.5	19.8
Maleic anhydride <sup>a</sup>	-	-	-	-	-	6.1	6.9	7.4	7.7
Maleic anhydride <sup>b</sup>	-	-	-	-	-	6.6	8.1	9.5	9.8
Diethylenetriamine <sup>c</sup>	-	-	-	-	-	7.3	20.7	25.3	26.6
Tetrabutylammonium hydroxide <sup>d</sup>	-	-	-	-	-	4.6	5.1	5.5	5.9

<sup>a</sup> mole ratio of DGEBA : MA : Bu<sub>4</sub>NOH was 1 : 0.2 : 0.2

<sup>b</sup> mole ratio of DGEBA : MA was 1 : 2.8 and 0.1 phr of benzyldimethylamine was employed as a catalyst

<sup>c</sup> mole ratio of DGEBA : DETA was 1 : 1

<sup>d</sup> mole ratio of DGEBA : Bu<sub>4</sub>NOH was 1 : 0.2

### 3.6.3 Mechanical Properties

Mechanical properties of the metal-containing epoxy polymers obtained from different equivalent mole ratios of metal complexes and  $\text{Bu}_4\text{NOH}$  were investigated. Tensile testing was performed and the values obtained are shown in Table 3.6.

**Table 3.6** Tensile strength of the metal-containing epoxy polymers obtained from different mole ratios of DGEBA : ML : MA and  $\text{Bu}_4\text{NOH}$  was employed as a catalyst

Metal complex (ML)	Mole ratio of DGEBA : ML : MA	Tensile strength ( $\text{N/mm}^2$ )	
		10 mole % of $\text{Bu}_4\text{NOH}$	20 mole % of $\text{Bu}_4\text{NOH}$
NiL	1 : 0.20 : 0.20	42	43
	1 : 0.15 : 0.15	45	48
	1 : 0.10 : 0.10	58	61
	1 : 0.05 : 0.05	35	38
ZnL	1 : 0.20 : 0.20	44	48
	1 : 0.15 : 0.15	49	51
	1 : 0.10 : 0.10	57	59
	1 : 0.05 : 0.05	52	53
Maleic anhydride <sup>a</sup>	-	30	
Maleic anhydride <sup>b</sup>	-	56	
Diethylenetriamine <sup>c</sup>	-	57	
Tetrabutylammonium Hydroxide <sup>d</sup>	-	64	

<sup>a</sup> mole ratio of DGEBA : MA :  $\text{Bu}_4\text{NOH}$  was 1 : 0.2 : 0.2

<sup>b</sup> mole ratio of DGEBA : MA was 1 : 2.8 and 0.1 phr of benzyldimethylamine was employed as a catalyst

<sup>c</sup> mole ratio of DGEBA : DETA was 1 : 1

<sup>d</sup> mole ratio of DGEBA :  $\text{Bu}_4\text{NOH}$  was 1 : 0.2

The results suggest that variation of the Bu<sub>4</sub>NOH amount has no effect on tensile strength. At the same mole ratio of DGEBA : ML : MA Ni- and Zn-containing epoxy polymers prepared from 10 mole% of Bu<sub>4</sub>NOH show the same tensile strength as those prepared from 20 mole% of Bu<sub>4</sub>NOH.

In the case of Ni-containing epoxy polymers obtained from the equivalent mole ratio of DGEBA : NiL : MA = 1 : 0.2 : 0.2, 1 : 0.15 : 0.15 and 1 : 0.1 : 0.1, it was found that the tensile strength decreased when the amount of NiL and MA were increased. This might be due to the increase in viscosity of the mixture before crosslinking. Therefore, it was difficult to get a homogenous mixture. The tensile strength of Zn-containing epoxy polymers showed a similar trend. The optimum ratio of Ni- and Zn-containing epoxy polymers that gave the highest tensile strength was the polymers obtained from the ratio of 1 : 0.1 : 0.1, which possessed the same tensile strength as the epoxy polymers obtained from DGEBA – MA, DGEBA – diethylenetriamine and DGEBA – Bu<sub>4</sub>NOH systems.

## CHAPTER IV

### CONCLUSION AND SUGGESTION FOR FUTURE WORK

#### 4.1 Conclusion

Metal-containing epoxy polymers were synthesized by crosslinking of the diglycidyl ether of bisphenol A (DGEBA) with hexadentate Schiff base metal complexes and maleic anhydride. The metal complexes employed were NiL and ZnL. In comparison to the crosslinking reaction of DGEBA with the metal complexes without the use of maleic anhydride, the reaction in the presence of maleic anhydride reduced the crosslinking temperature from 180°C to 130 °C. Tetrabutylammonium hydroxide was found to be a suitable catalyst for the crosslinking reaction since it decreased the crosslinking temperature to 110 °C.

The progress of the crosslinking reaction was followed by using IR spectroscopy. It was found that the optimum crosslinking condition for the preparation of nickel- and zinc-containing epoxy polymers was 110 °C/ 8 hours. The polymers were investigated for their physical and mechanical properties, namely glass transition temperature, thermal stability and tensile strength. The metal-containing polymers showed good thermal stability and high tensile strength.

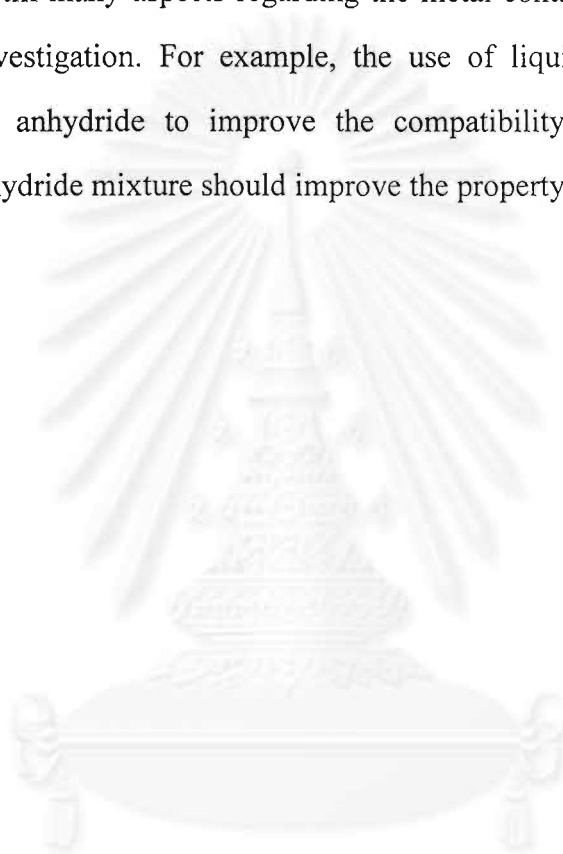
Nickel-containing epoxy polymers had better properties than zinc-containing epoxy polymers. The polymer which showed good properties was the nickel-containing epoxy polymer obtained from DGEBA : nickel complex : maleic anhydride at the mole ratio of 1 : 0.15 : 0.15. The glass transition temperature and tensile strength of the polymer were 142 °C and 48 N/mm<sup>2</sup>, respectively. Upon heating at 250 °C for 48 hours, the weight loss of the polymer was 7.7%, which indicated much higher thermal stability compared to the known epoxy polymer obtained from DGEBA-diethylenetriamine system. The polymer which showed good tensile strength was the nickel-containing epoxy polymer obtained from DGEBA : nickel complex : maleic anhydride at the mole



ratio of 1 : 0.1 : 0.1. The tensile strength of the polymer was  $61 \text{ N/mm}^2$ , then the glass transition temperature and the weight loss of the polymer were  $119 \text{ }^\circ\text{C}$  and 11.9%, respectively.

#### 4.2 Suggestion for Future Work

There are still many aspects regarding the metal-containing epoxy polymers that require further investigation. For example, the use of liquid acid anhydride such as hexahydrophthalic anhydride to improve the compatibility of the DGEBA : metal complex : acid anhydride mixture should improve the property of the polymers.



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**APPENDIX**

สถาบันวิทยบริการ  
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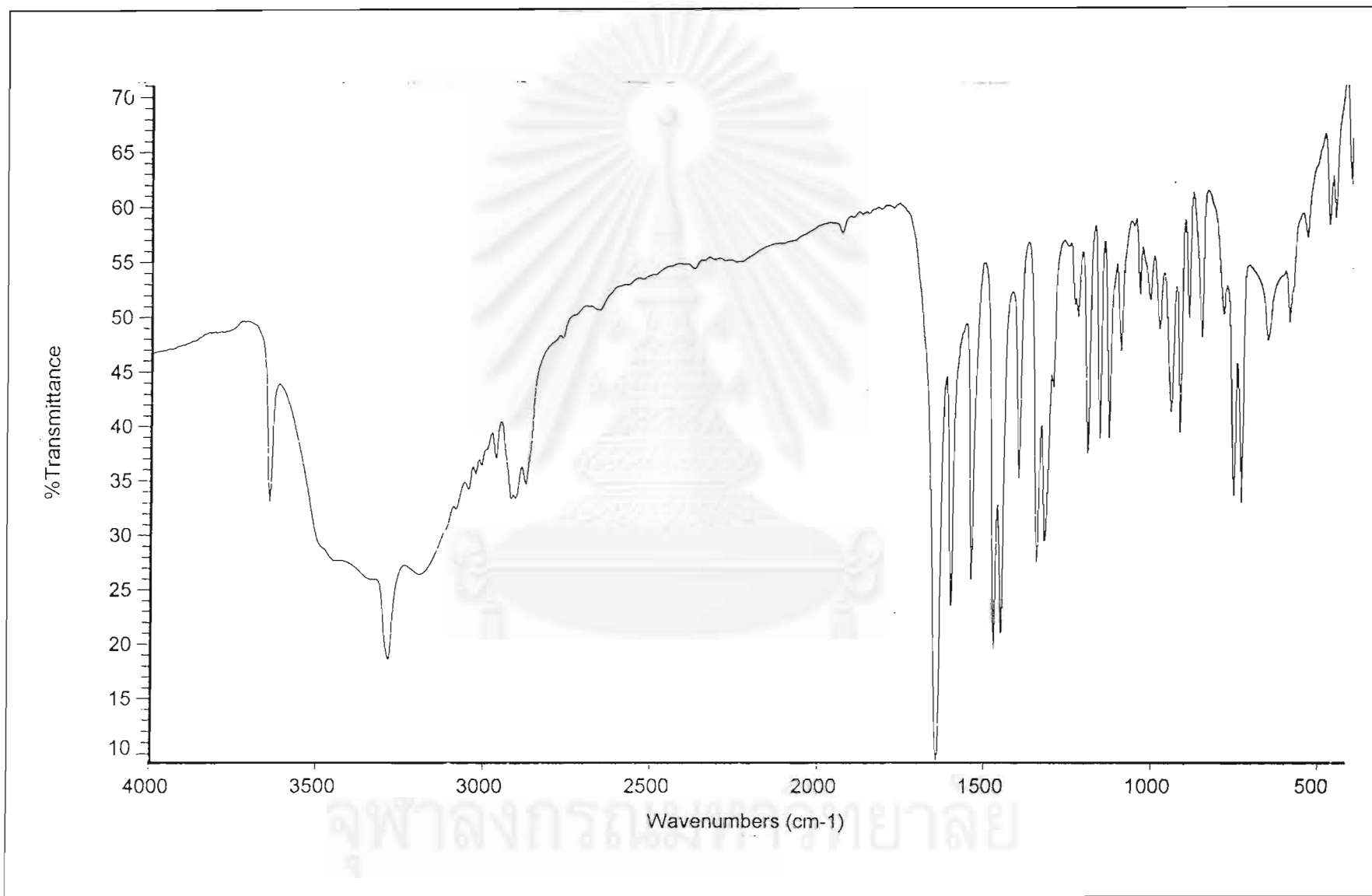


Figure A. 1 IR spectrum of NiL

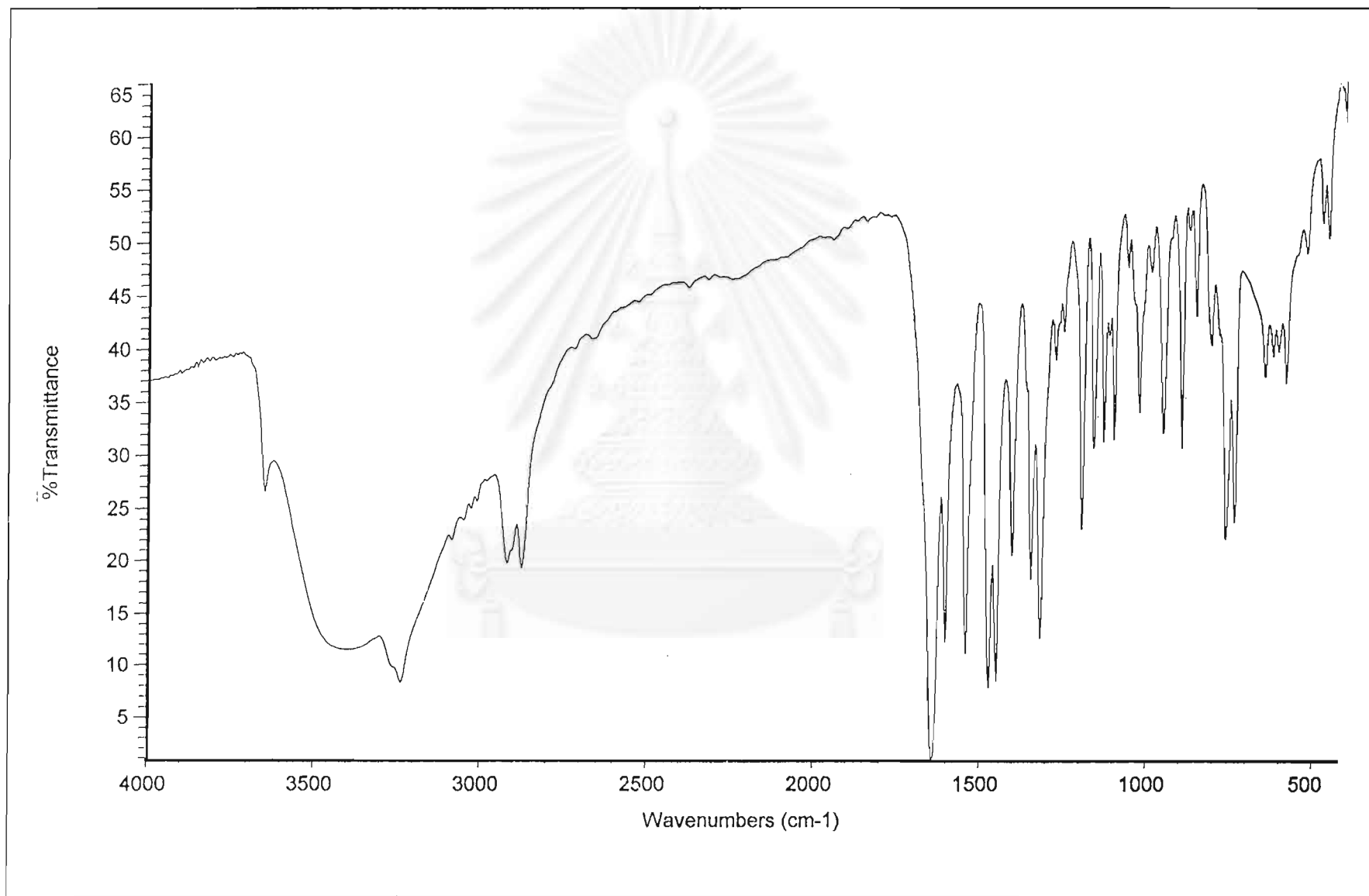


Figure A. 2 IR spectrum of **ZnL**

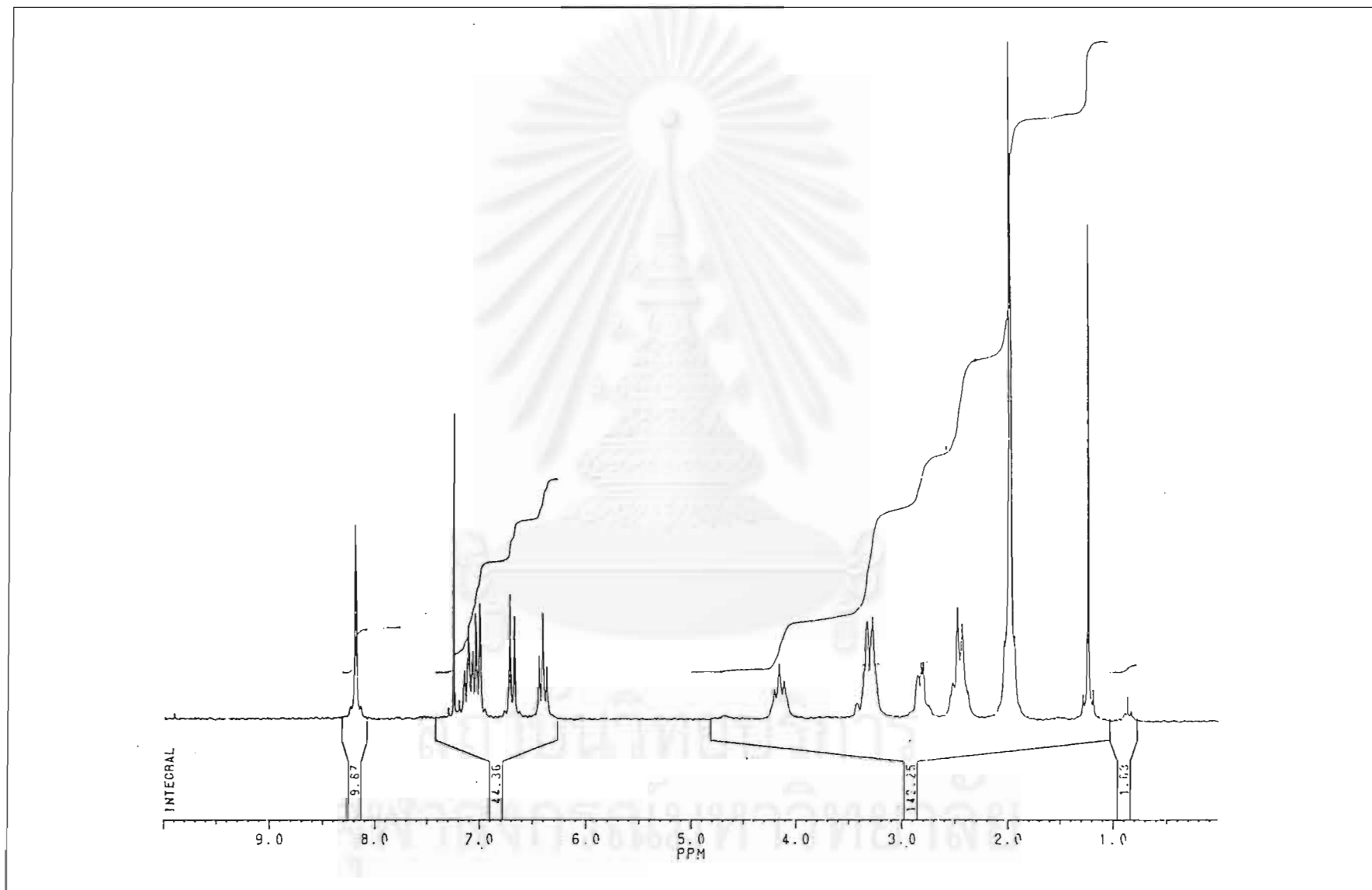


Figure A. 3  $^1\text{H}$  NMR spectrum of **ZnL**



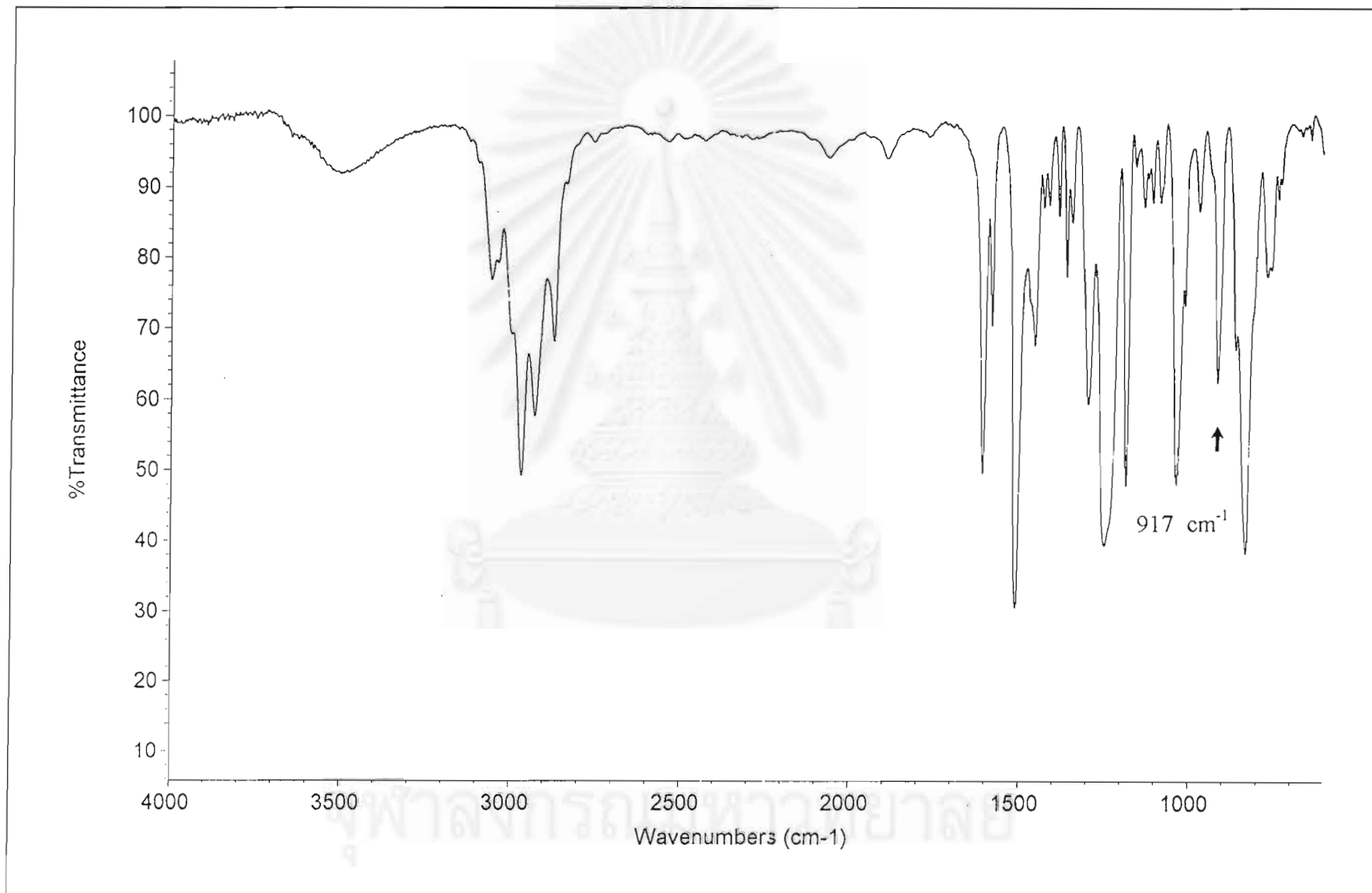


Figure A. 4 IR spectrum of **DGEBA**

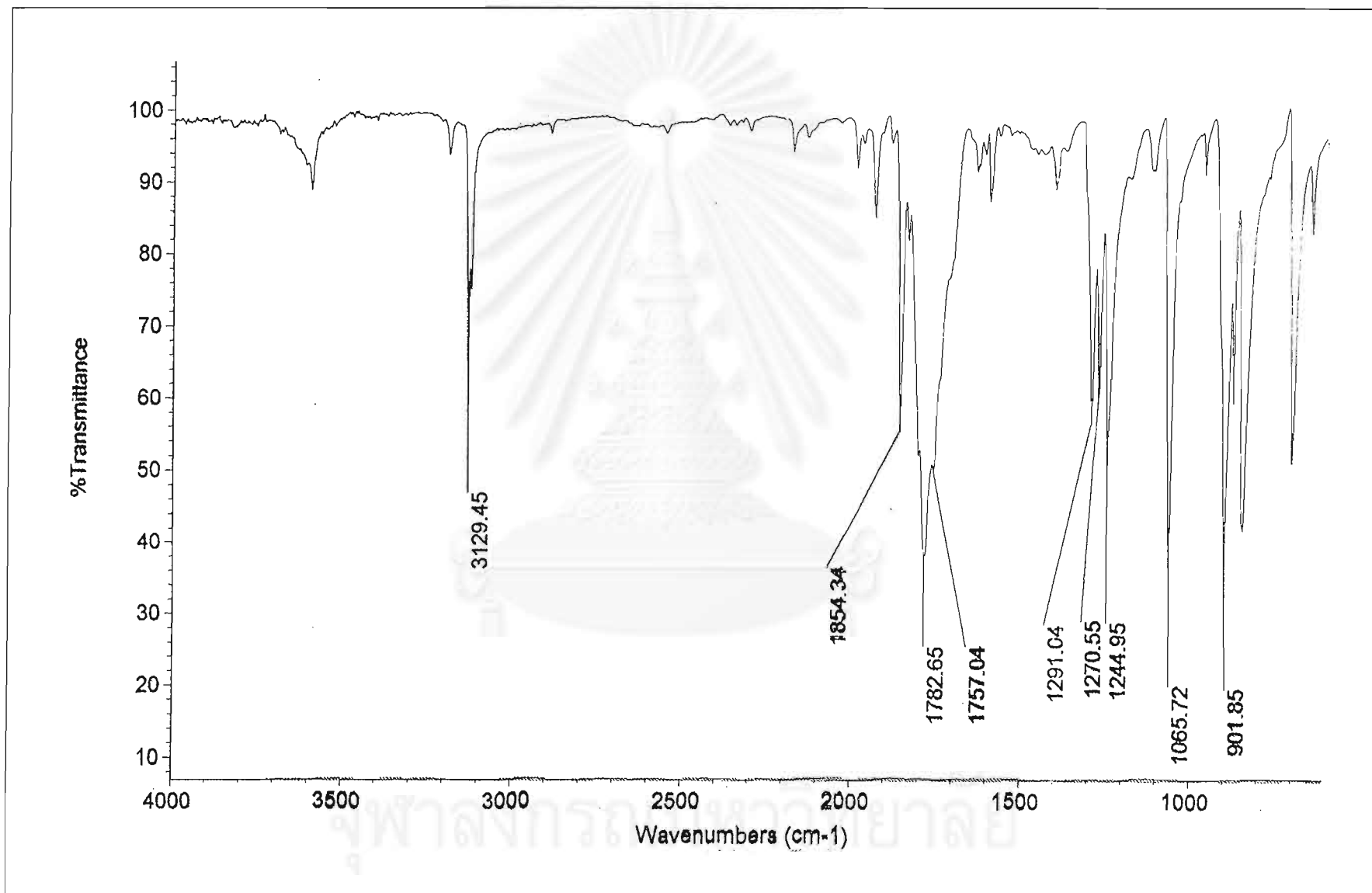


Figure A. 5 IR spectrum of Maleic anhydride

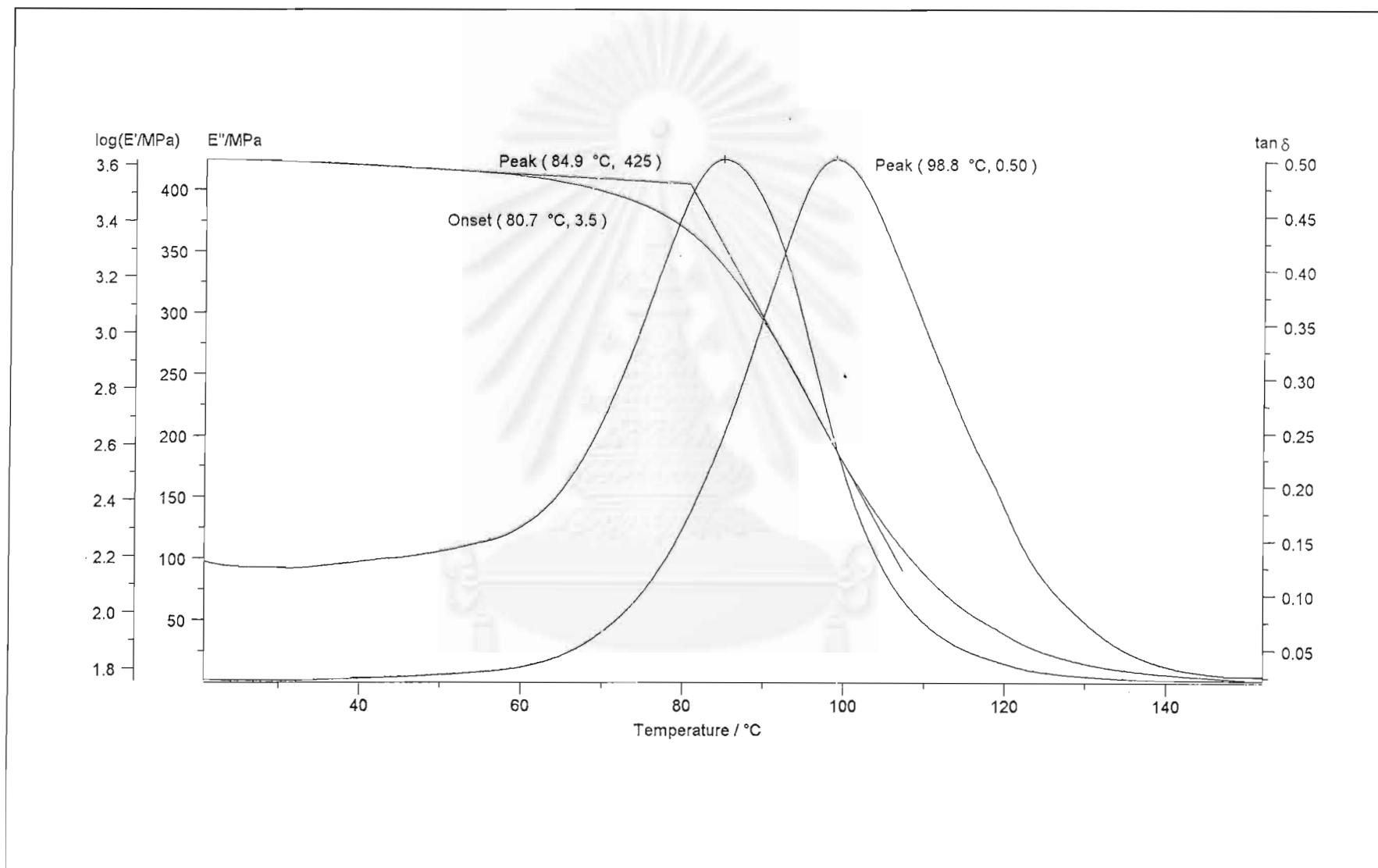


Figure A. 6 DMA thermogram of Ni-containing epoxy polymer at the mole ratio of DGEBA : NiL : MA = 1 : 0.05 : 0.05 with 10 mole % of Bu<sub>4</sub>NOH employed as catalyst

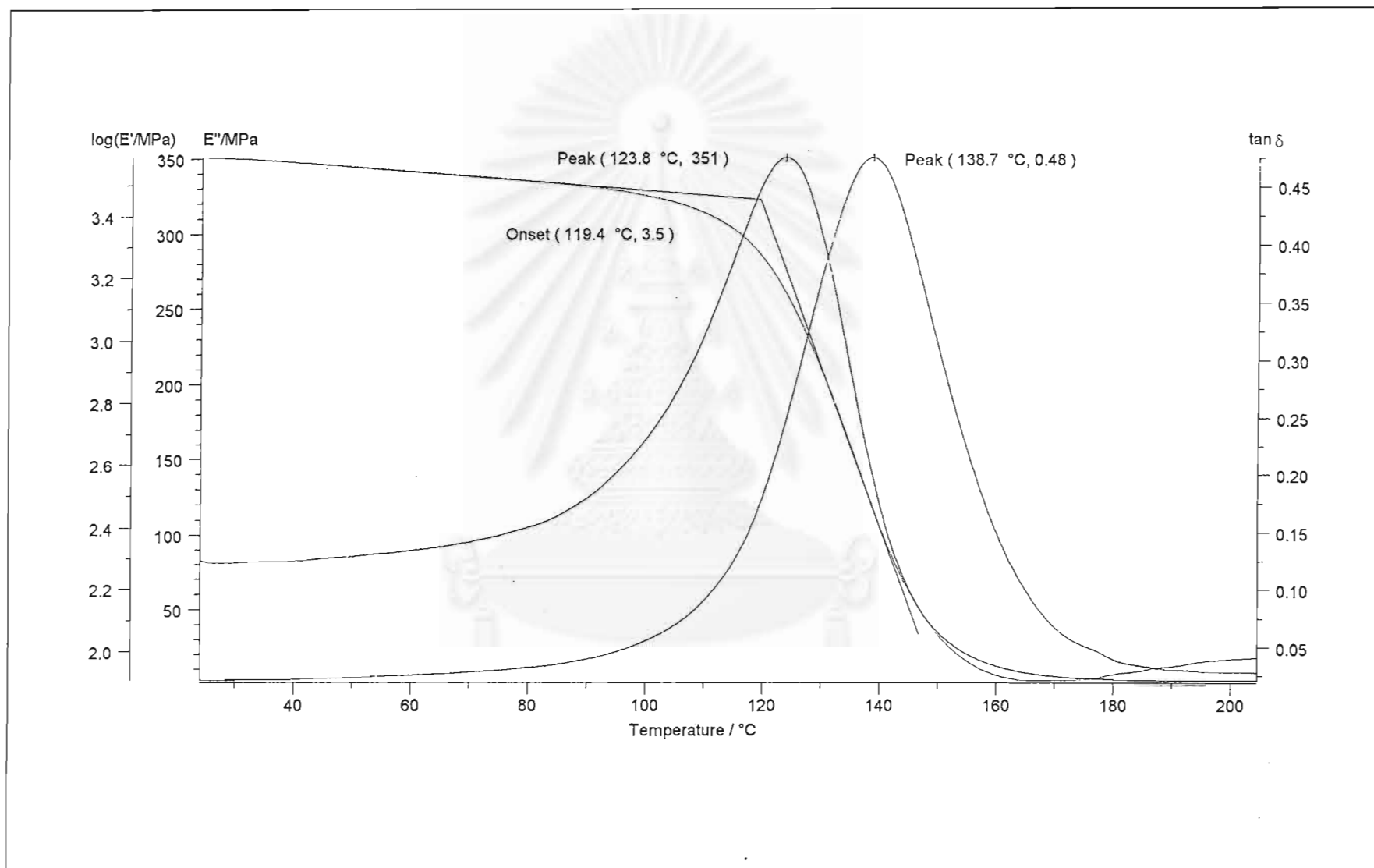


Figure A. 7 DMA thermogram of Ni-containing epoxy polymer at the mole ratio of DGEBA : NiL : MA = 1 : 0.10 : 0.10 with 10 mole % of  $\text{Bu}_4\text{NOH}$  employed as catalyst

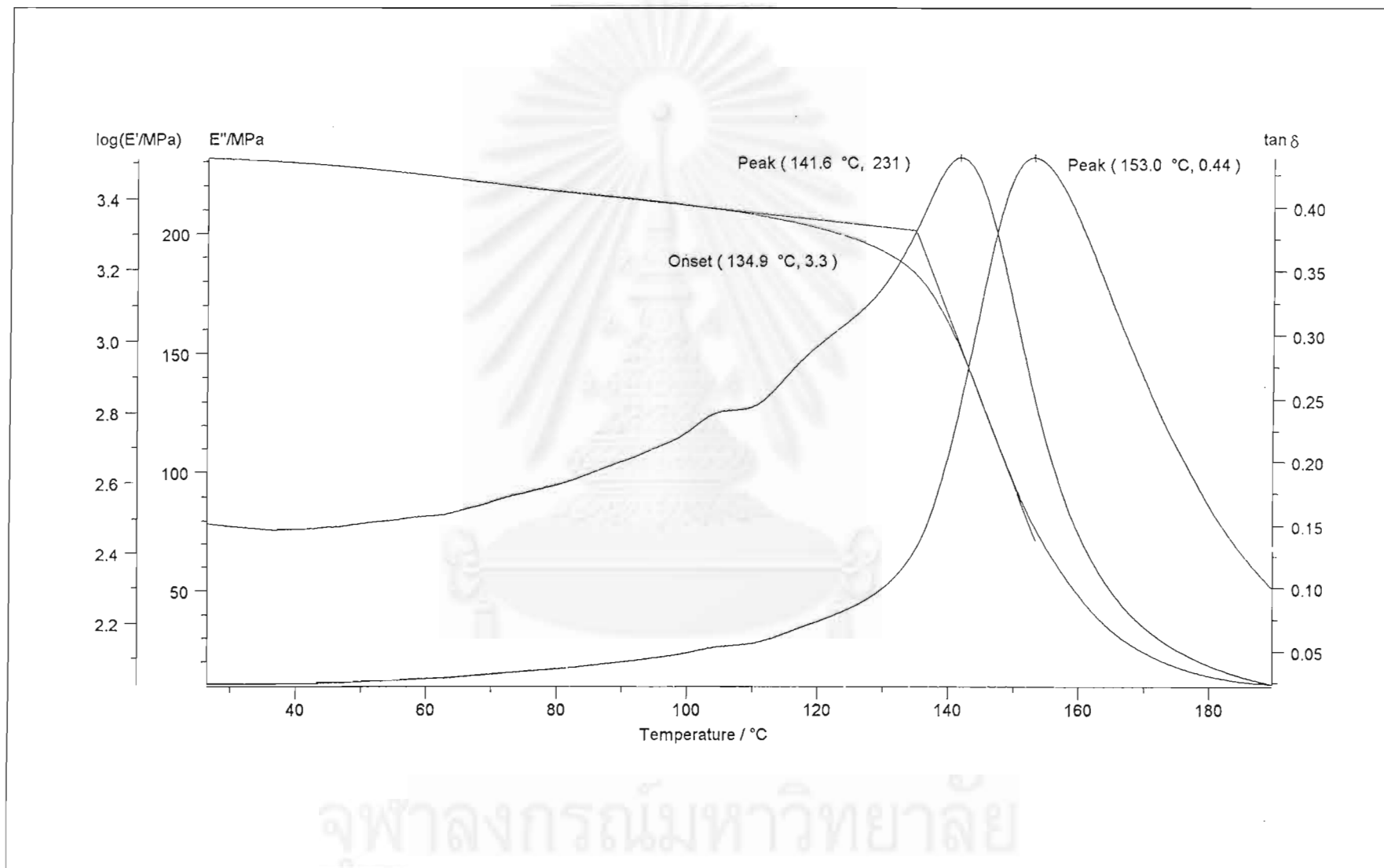


Figure A. 8 DMA thermogram of Ni-containing epoxy polymer at the mole ratio of DGEBA : NiL : MA = 1 : 0.15 : 0.15 with 10 mole % of Bu<sub>4</sub>NOH employed as catalyst

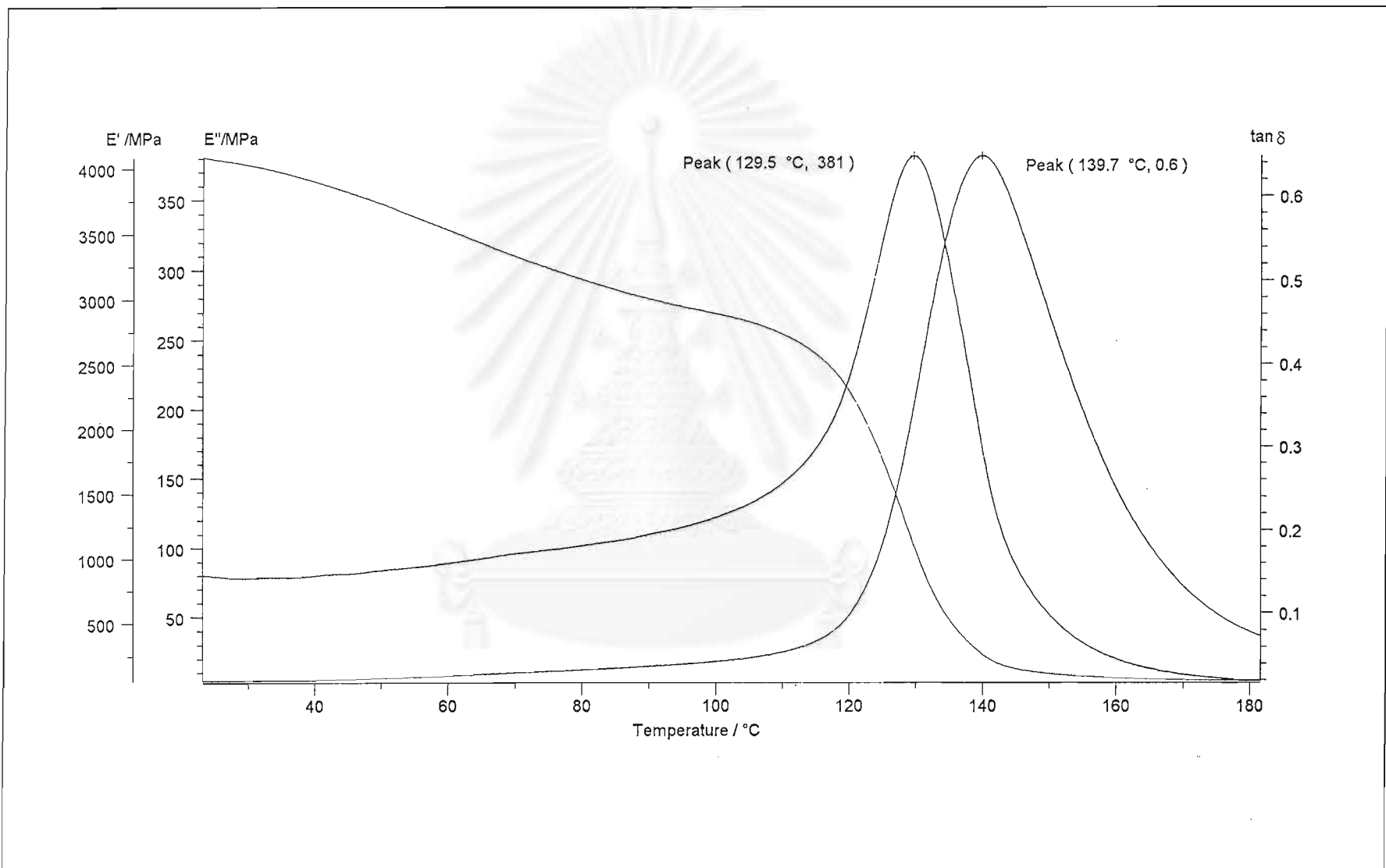


Figure A. 9 DMA thermogram of Ni-containing epoxy polymer at the mole ratio of DGEBA : NiL : MA = 1 : 0.20 : 0.20 with 10 mole % of Bu<sub>4</sub>NOH employed as catalyst

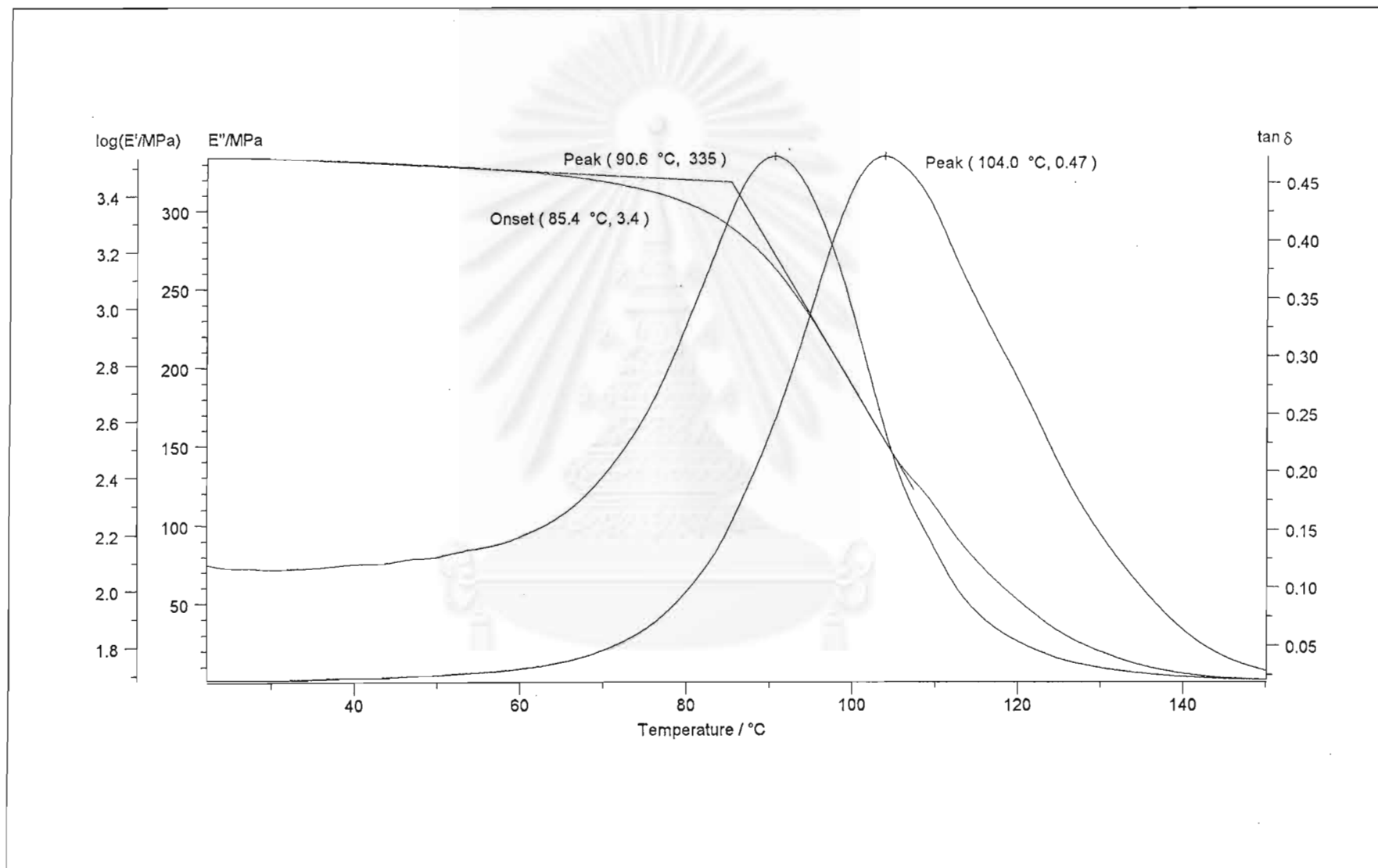


Figure A. 10 DMA thermogram of Ni-containing epoxy polymer at the mole ratio of DGEBA : NiL : MA = 1 : 0.05 : 0.05 with 20 mole % of Bu<sub>4</sub>NOH employed as catalyst

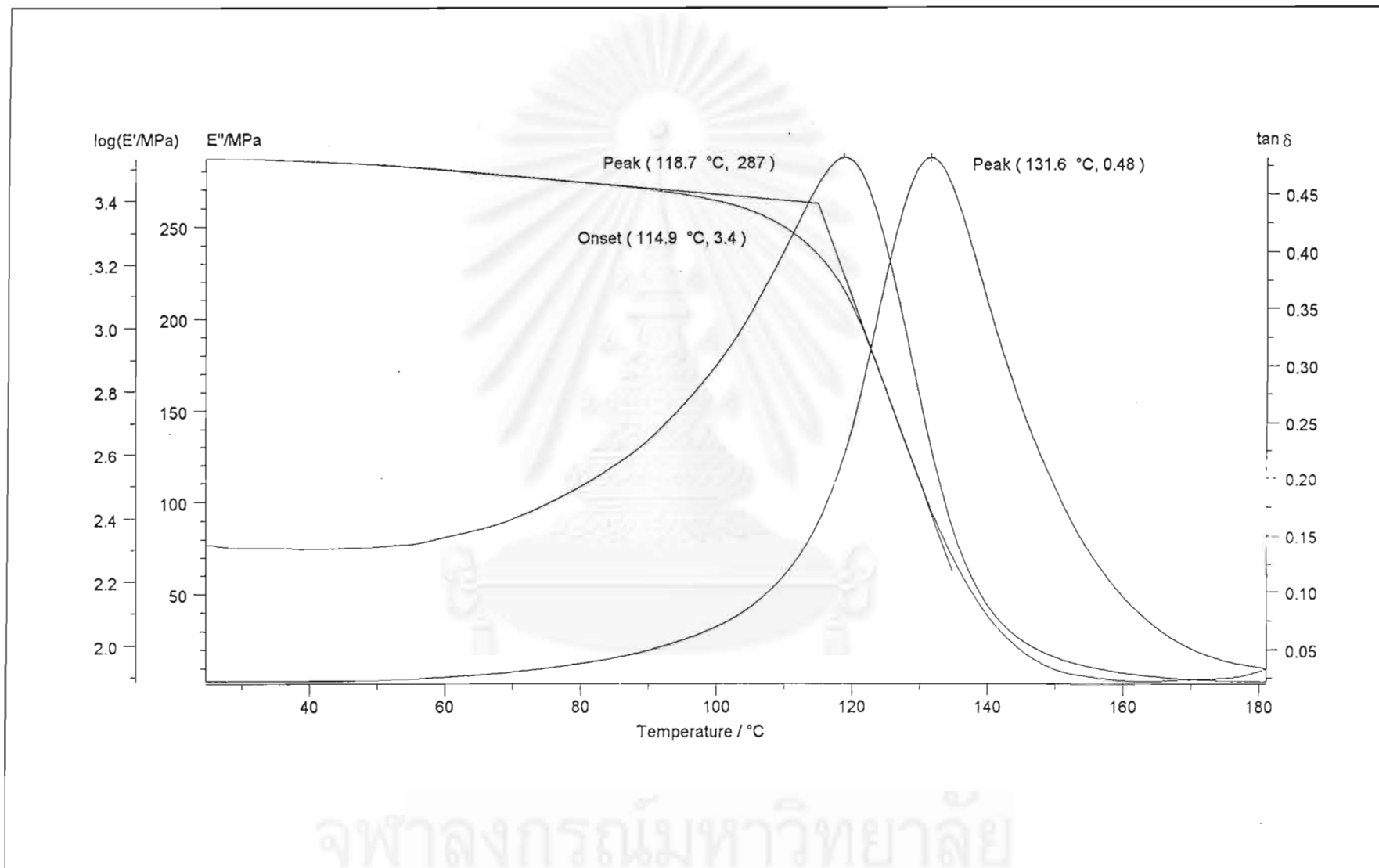


Figure A. 11 DMA thermogram of Ni-containing epoxy polymer at the mole ratio of DGEBA : NiL : MA = 1 : 0.10 : 0.10 with 20 mole % of Bu<sub>4</sub>NOH employed as catalyst



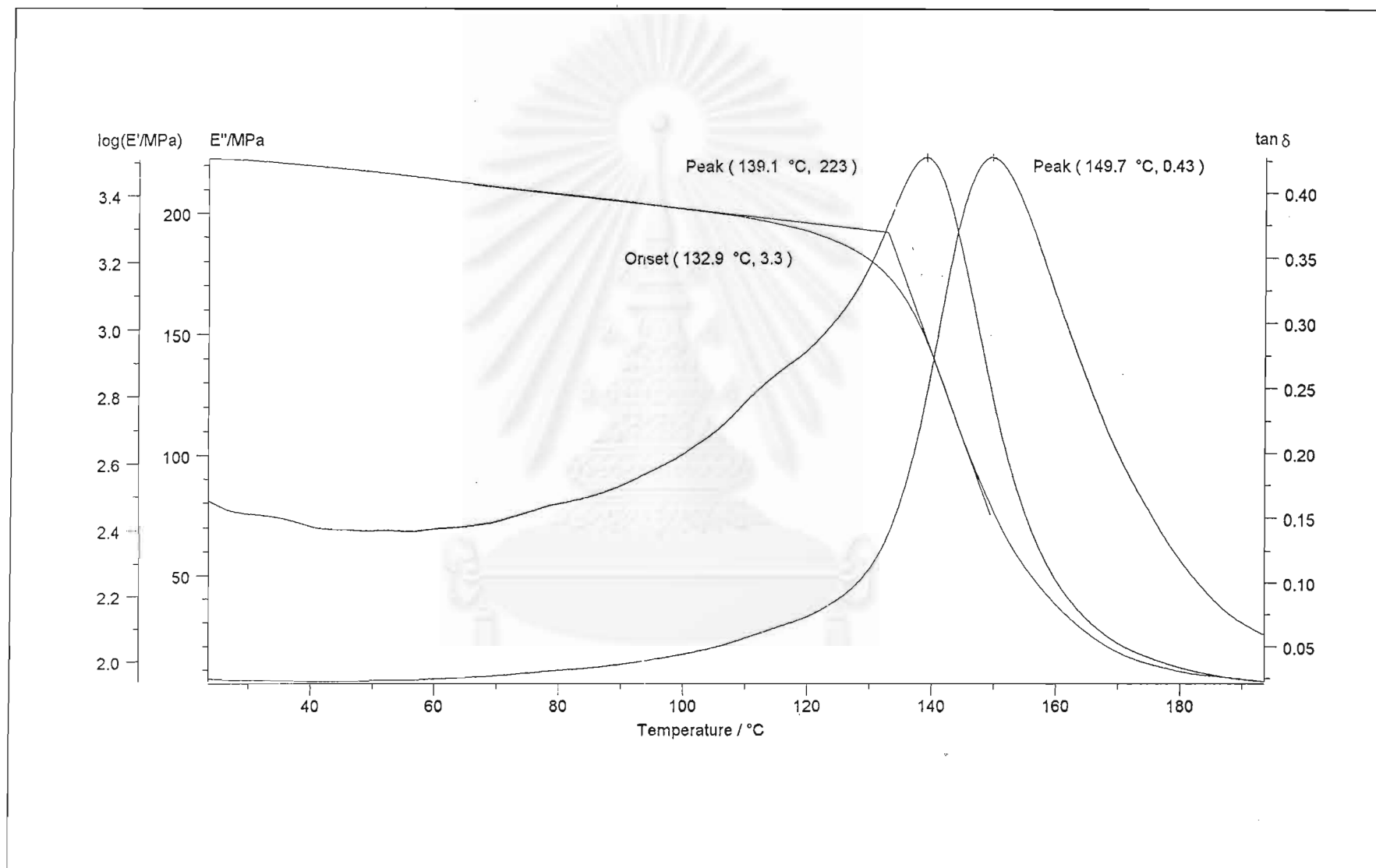


Figure A. 12 DMA thermogram of Ni-containing epoxy polymer at the mole ratio of DGEBA : NiL : MA = 1 : 0.15 : 0.15 with 20 mole % of Bu<sub>4</sub>NOH employed as catalyst

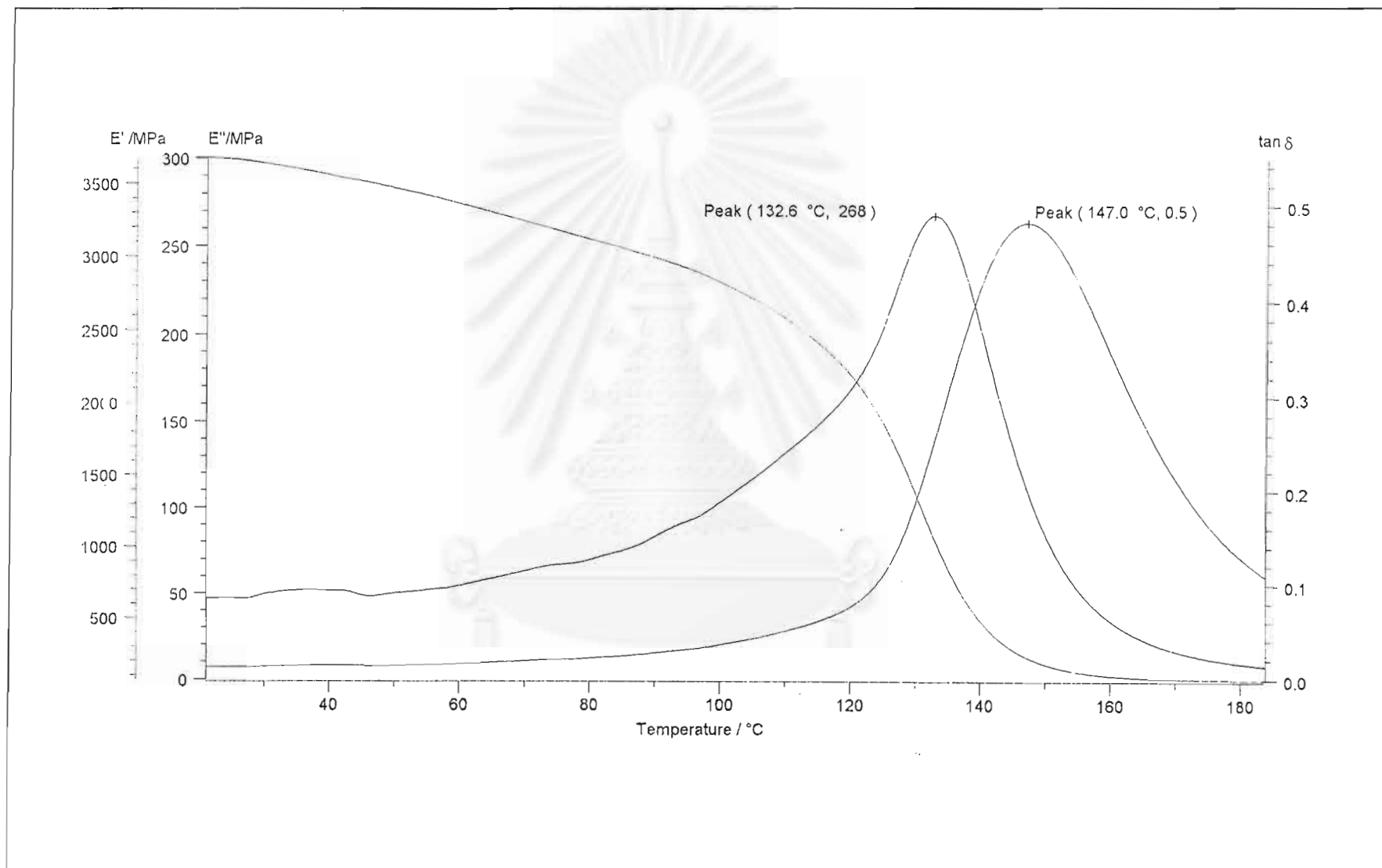


Figure A. 13 DMA thermogram of Ni-containing epoxy polymer at the mole ratio of DGEBA : NiL : MA = 1 : 0.20 : 0.20 with 20 mole % of Bu<sub>4</sub>NOH employed as catalyst

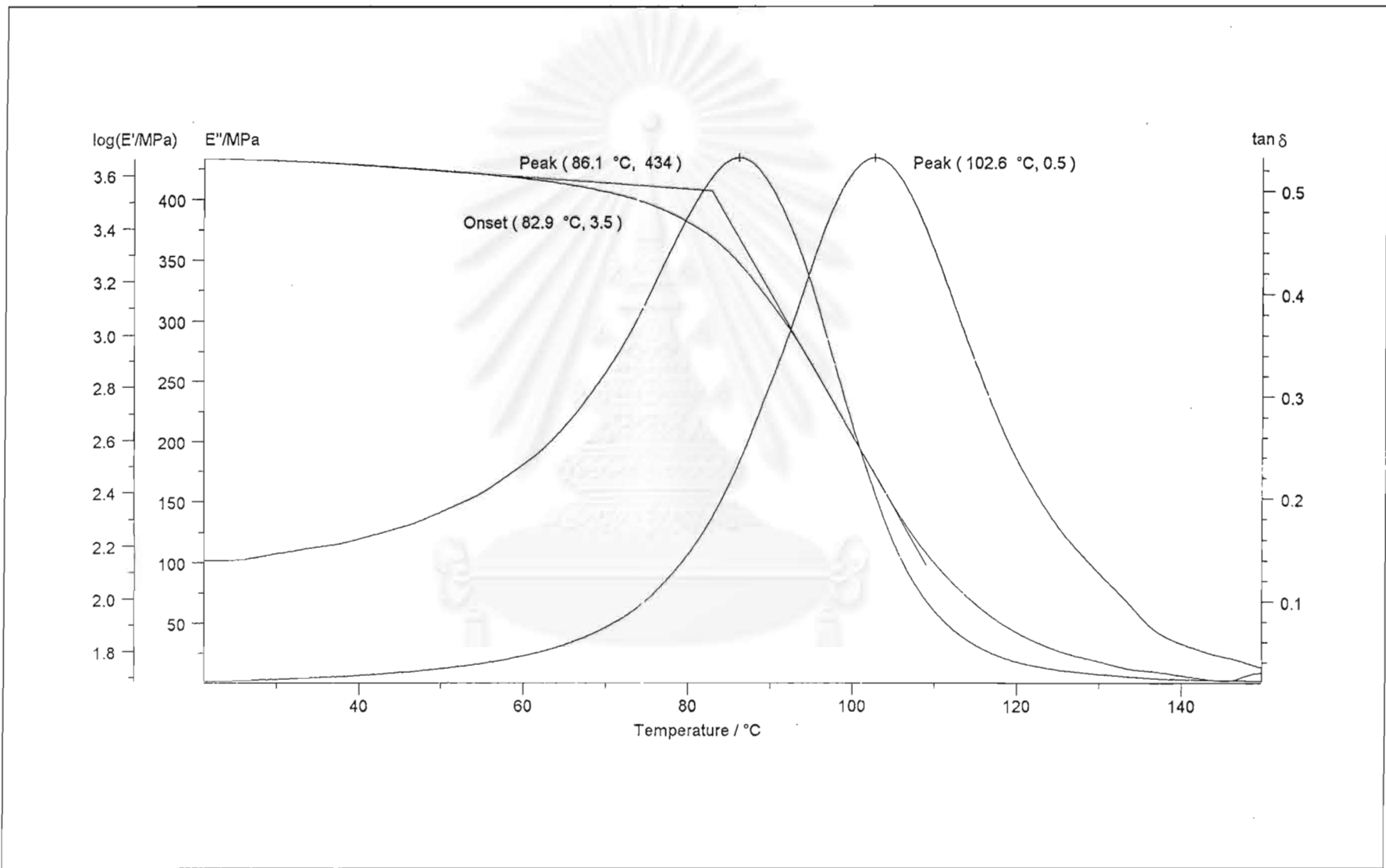


Figure A. 14 DMA thermogram of Zn-containing epoxy polymer at the mole ratio of DGEBA : ZnL : MA = 1 : 0.05 : 0.05 with 10 mole % of Bu<sub>4</sub>NOH employed as catalyst

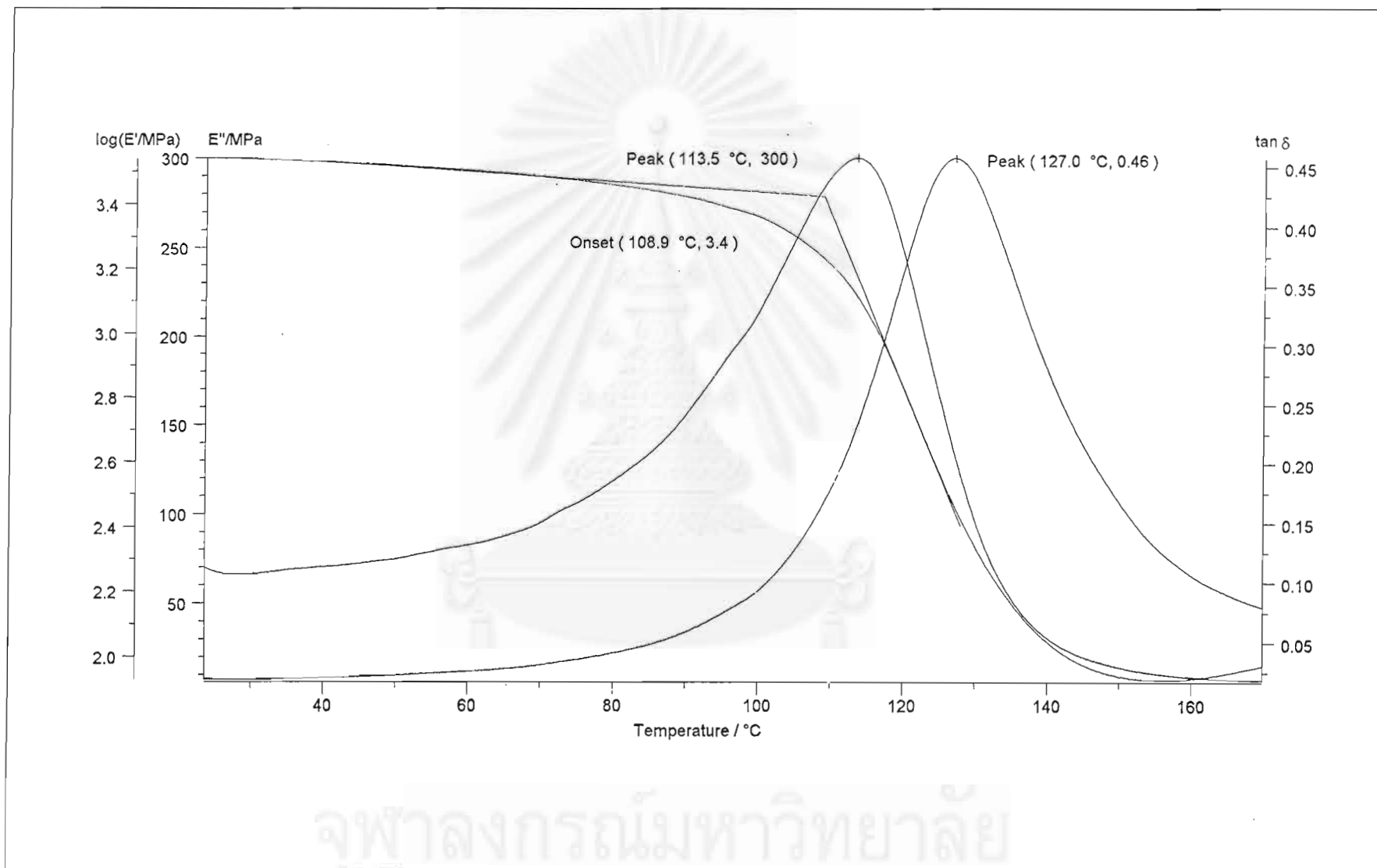


Figure A. 15 DMA thermogram of Zn-containing epoxy polymer at the mole ratio of DGEBA : ZnL : MA = 1 : 0.10 : 0.10 with 10 mole % of Bu<sub>4</sub>NOH employed as catalyst

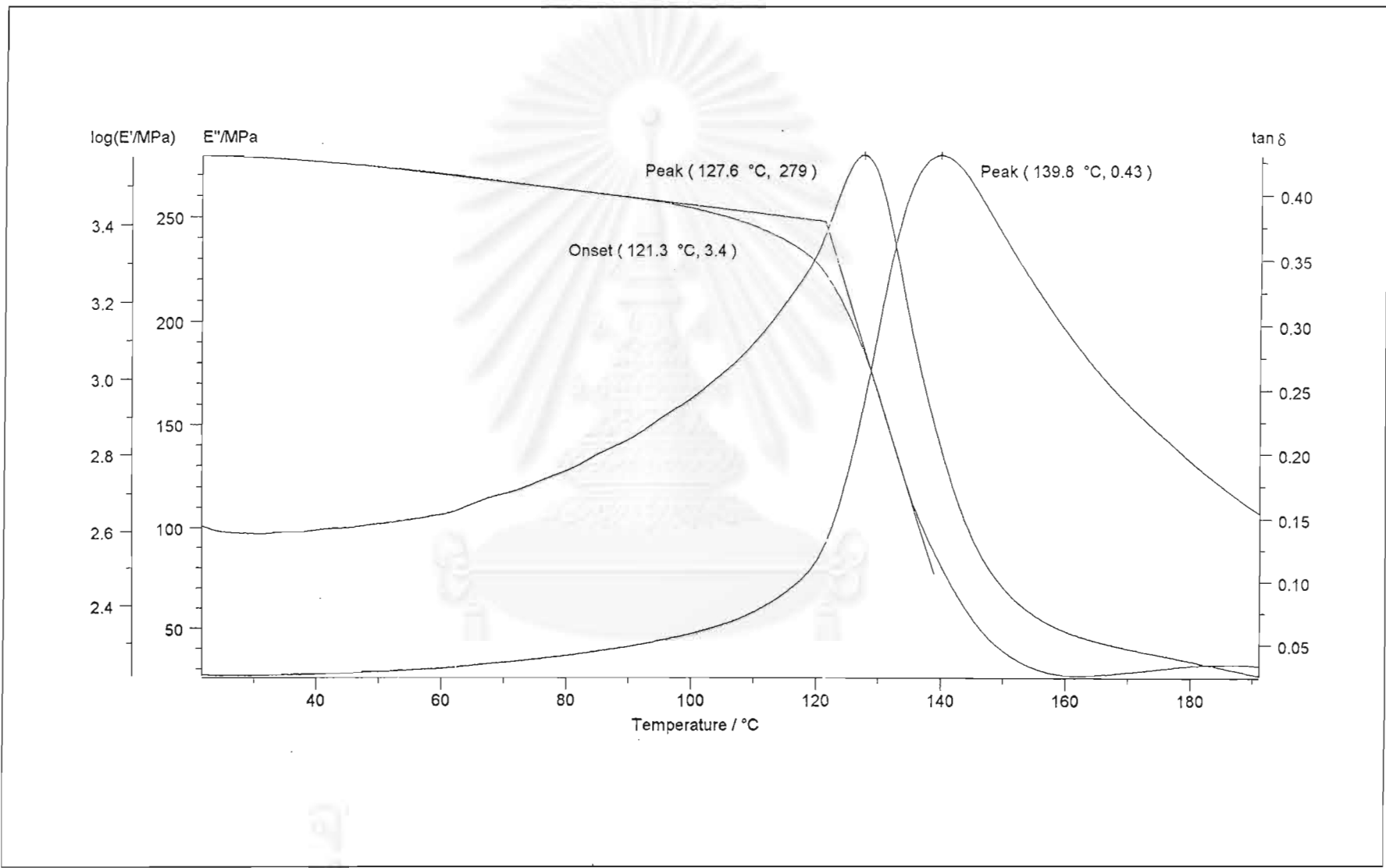


Figure A. 16 DMA thermogram of Zn-containing epoxy polymer at the mole ratio of DGEBA : ZnL : MA = 1 : 0.15 : 0.15 with 10 mole % of Bu<sub>4</sub>NOH employed as catalyst

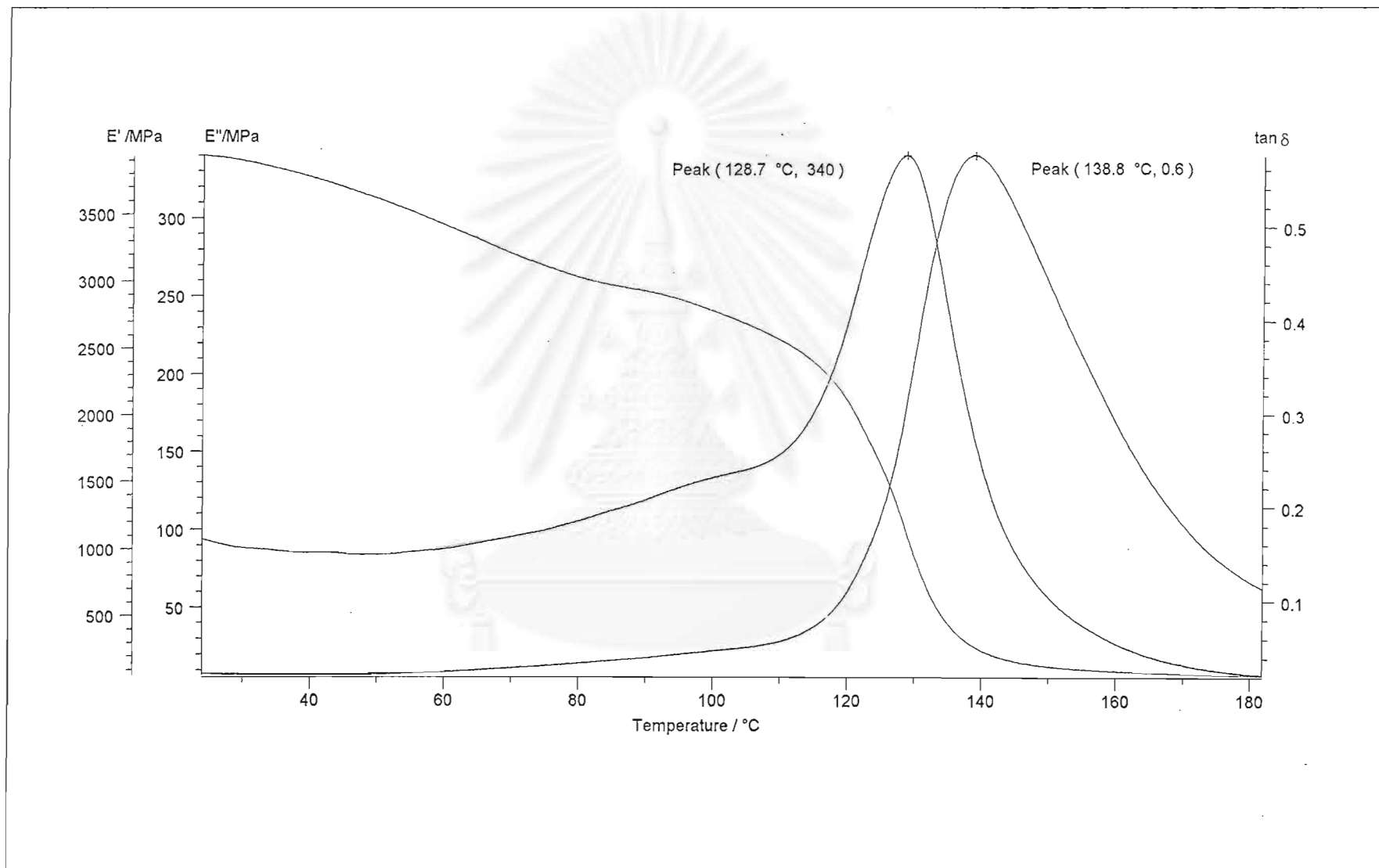


Figure A. 17 DMA thermogram of Zn-containing epoxy polymer at the mole ratio of DGEBA : ZnL : MA = 1 : 0.20 : 0.20 with 10 mole % of Bu<sub>4</sub>NOH employed as catalyst

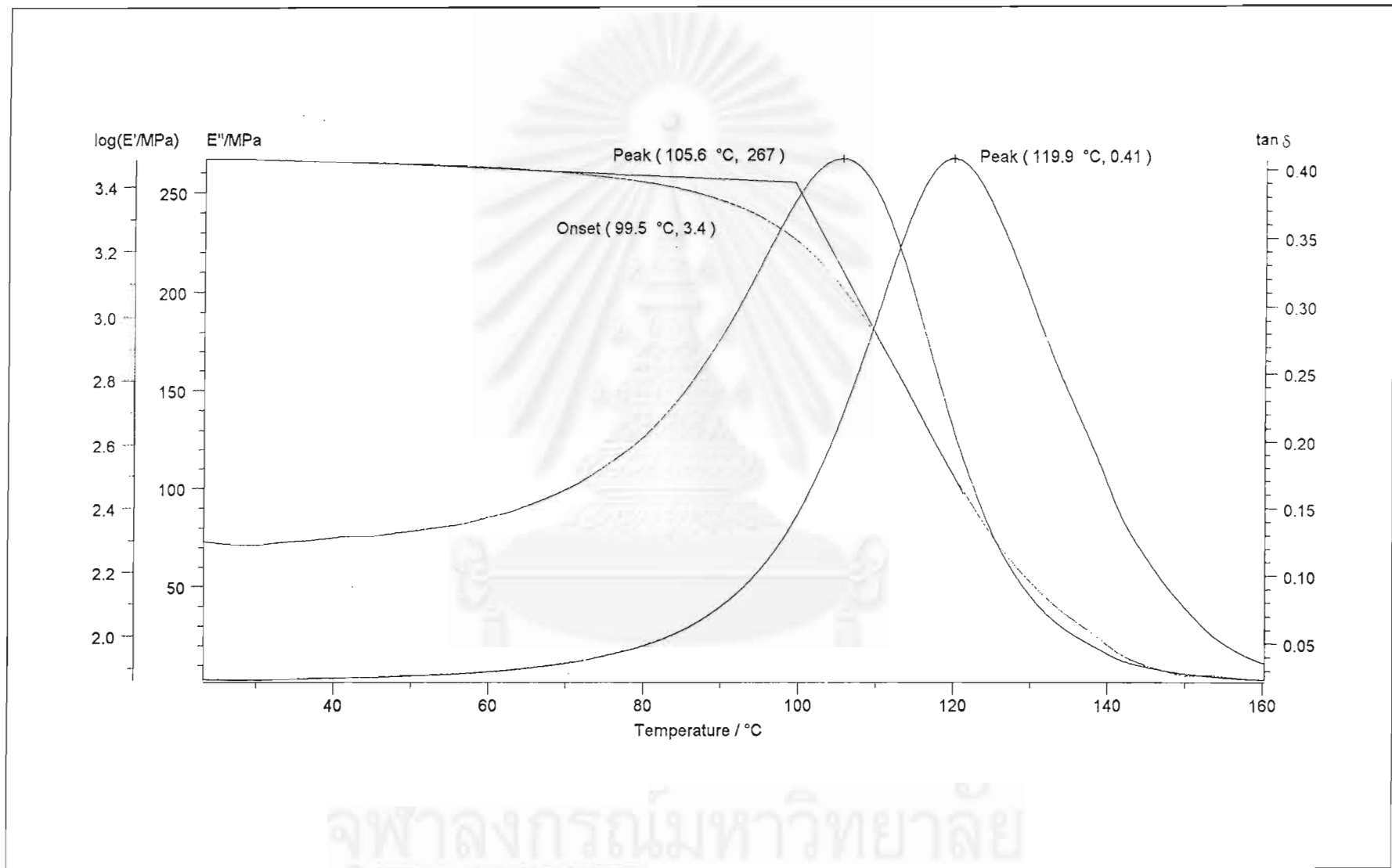


Figure A. 18 DMA thermogram of Zn-containing epoxy polymer at the mole ratio of DGEBA : ZnL : MA = 1 : 0.05 : 0.05 with 20 mole % of Bu<sub>4</sub>NOH employed as catalyst

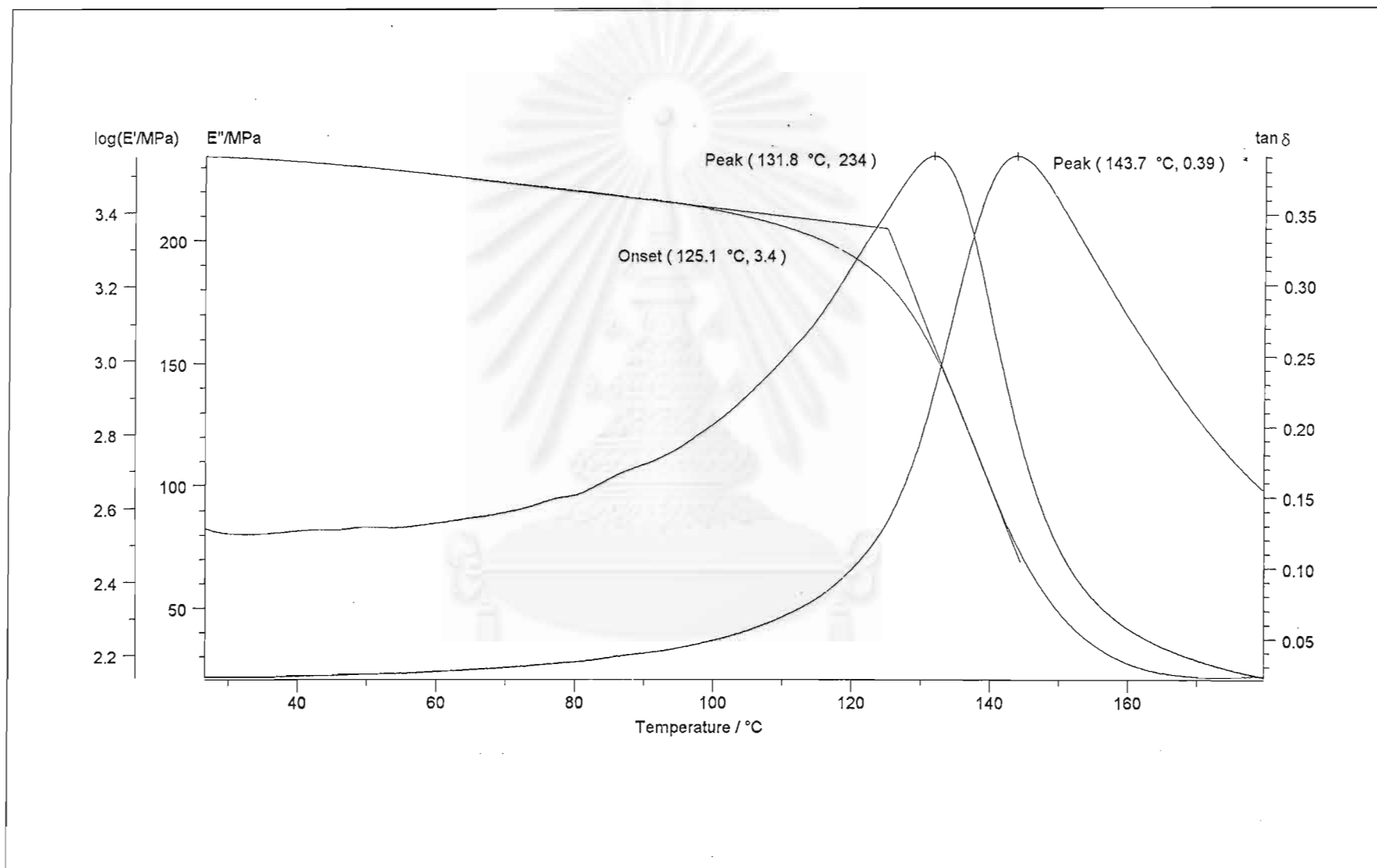


Figure A. 19 DMA thermogram of Zn-containing epoxy polymer at the mole ratio of DGEBA : ZnL : MA = 1 : 0.10 : 0.10 with 20 mole % of Bu<sub>4</sub>NOH employed as catalyst



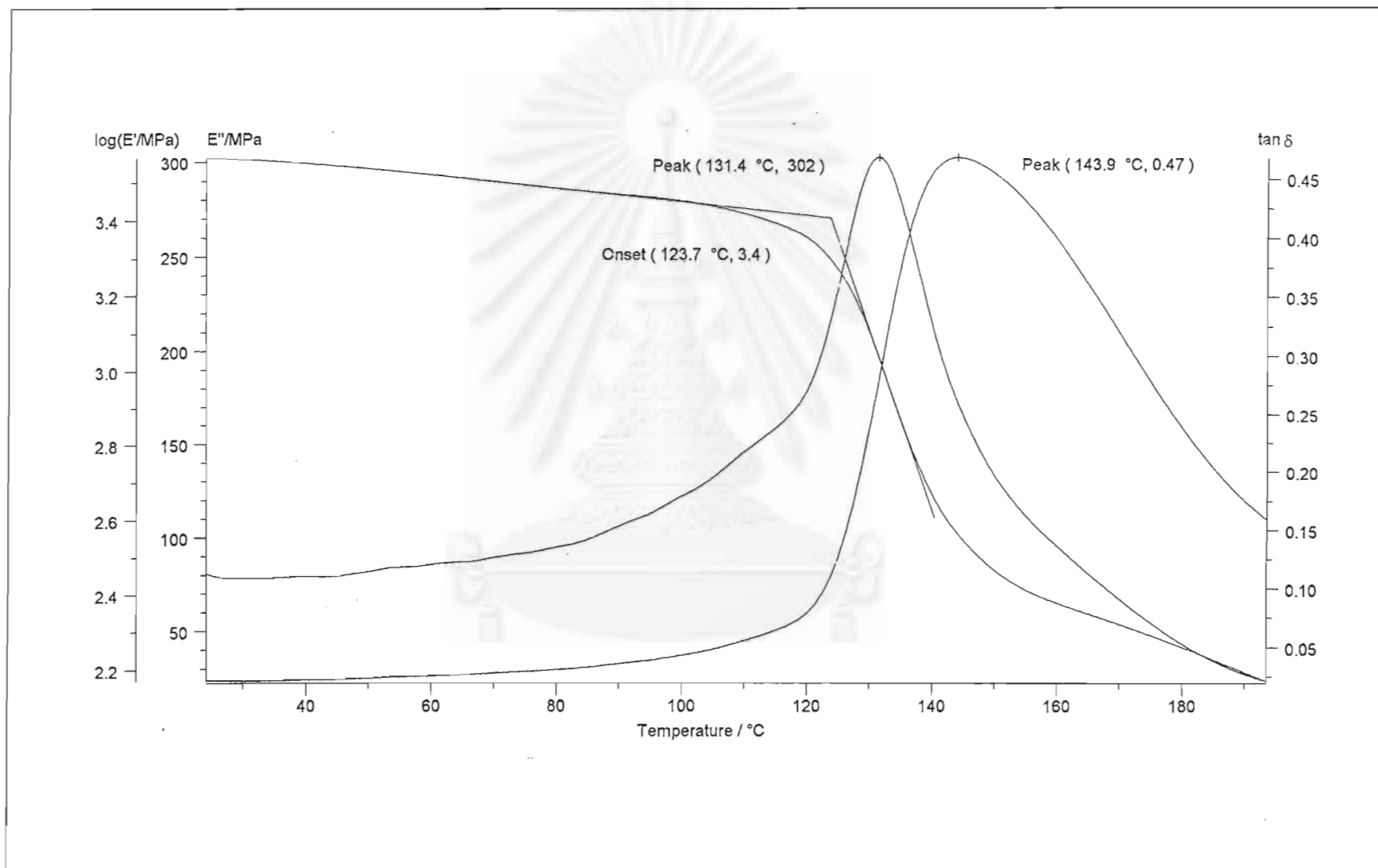


Figure A. 20 DMA thermogram of Zn-containing epoxy polymer at the mole ratio of DGEBA : ZnL : MA = 1 : 0.15 : 0.15 with 20 mole % of Bu<sub>4</sub>NOH employed as catalyst

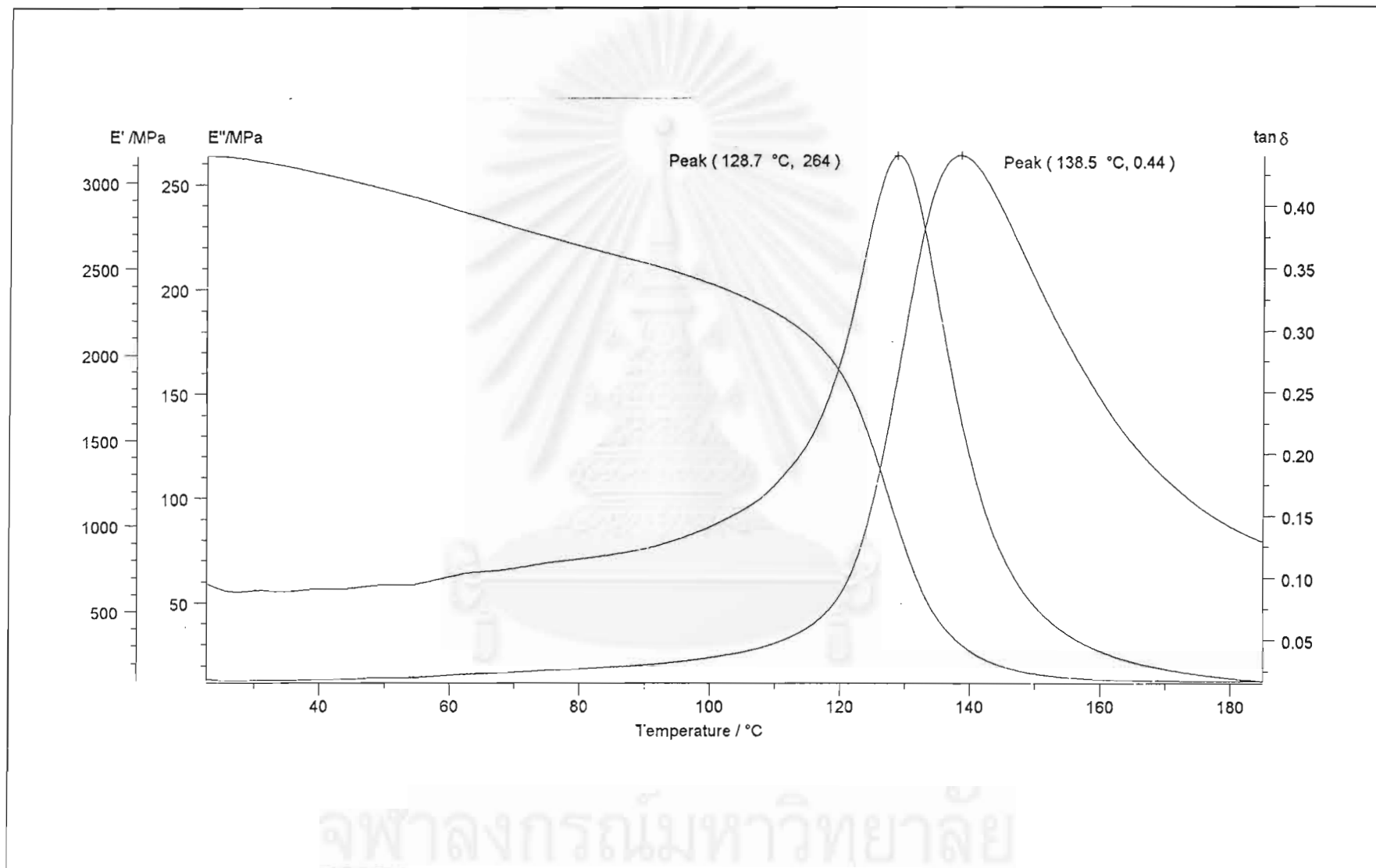


Figure A. 21 DMA thermogram of Zn-containing epoxy polymer at the mole ratio of DGEBA : ZnL : MA = 1 : 0.20 : 0.20 with 20 mole % of Bu<sub>4</sub>NOH employed as catalyst

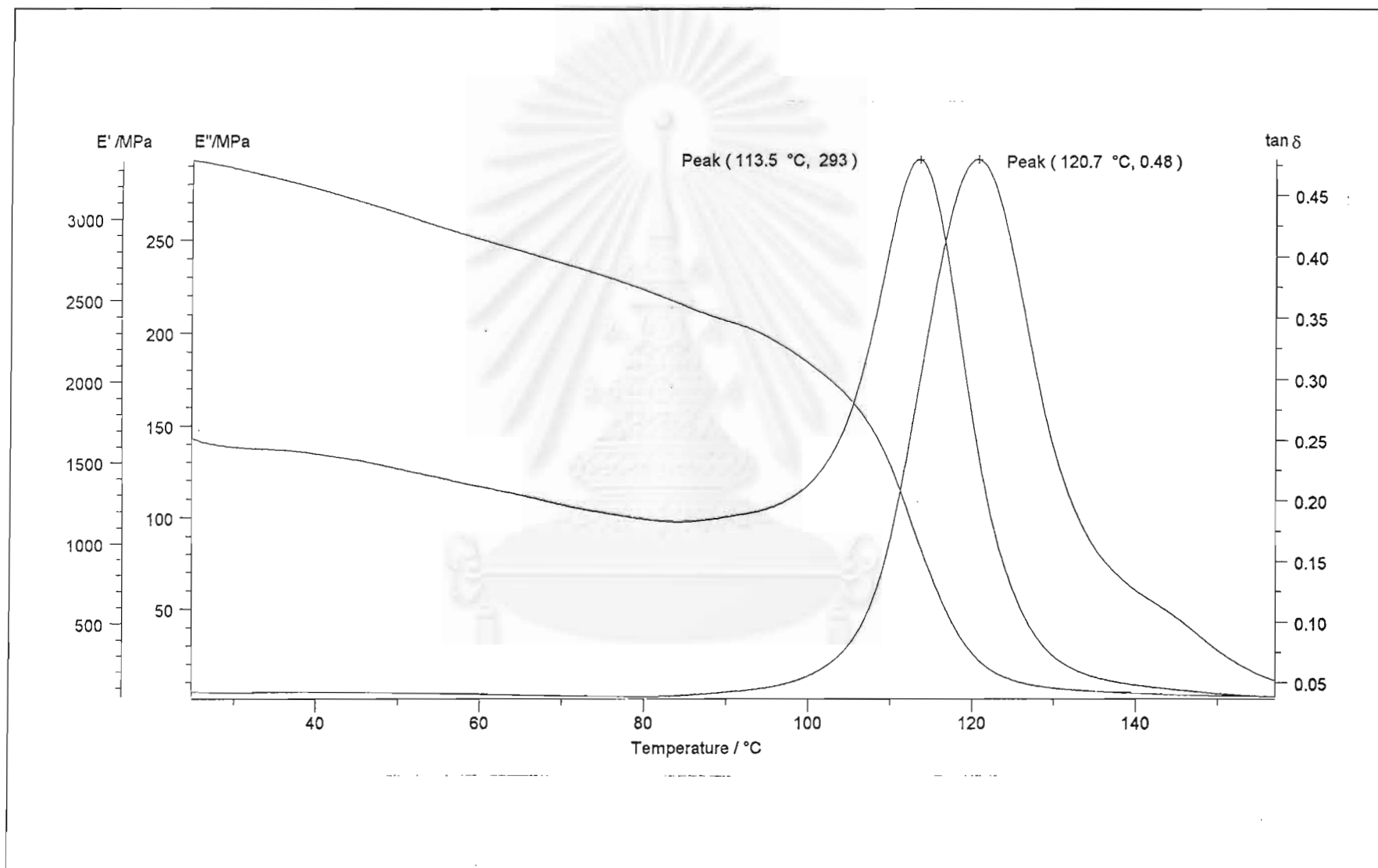


Figure A. 22 DMA thermogram of DGEBA-MA system at DGEBA : MA ratio of 1 : 2.8 with BDMA employed as catalyst

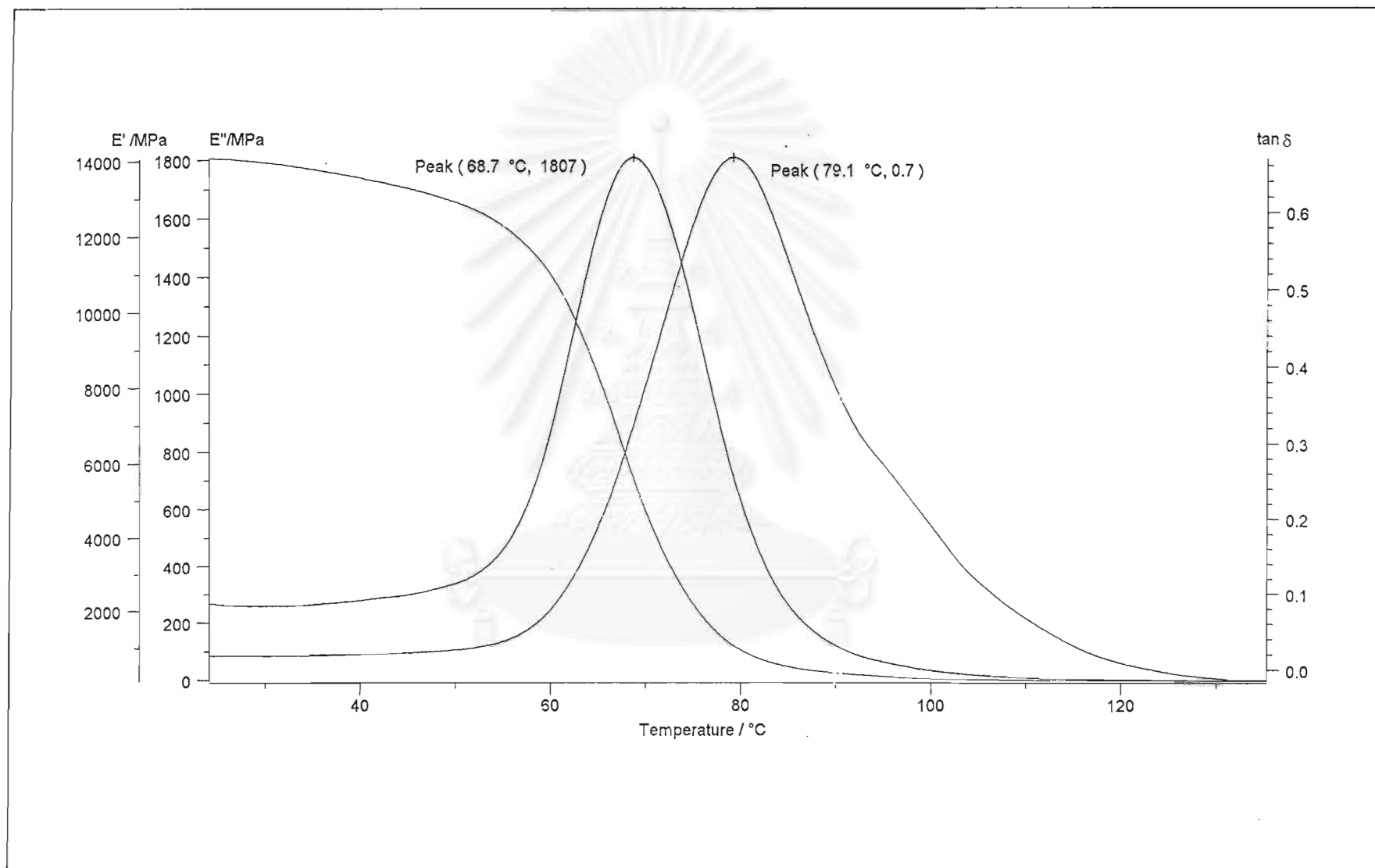


Figure A. 23 DMA thermogram of DGEBA-MA system at DGEBA : MA ratio of 1 : 0.2 with  $\text{Bu}_4\text{NOH}$  employed as catalyst

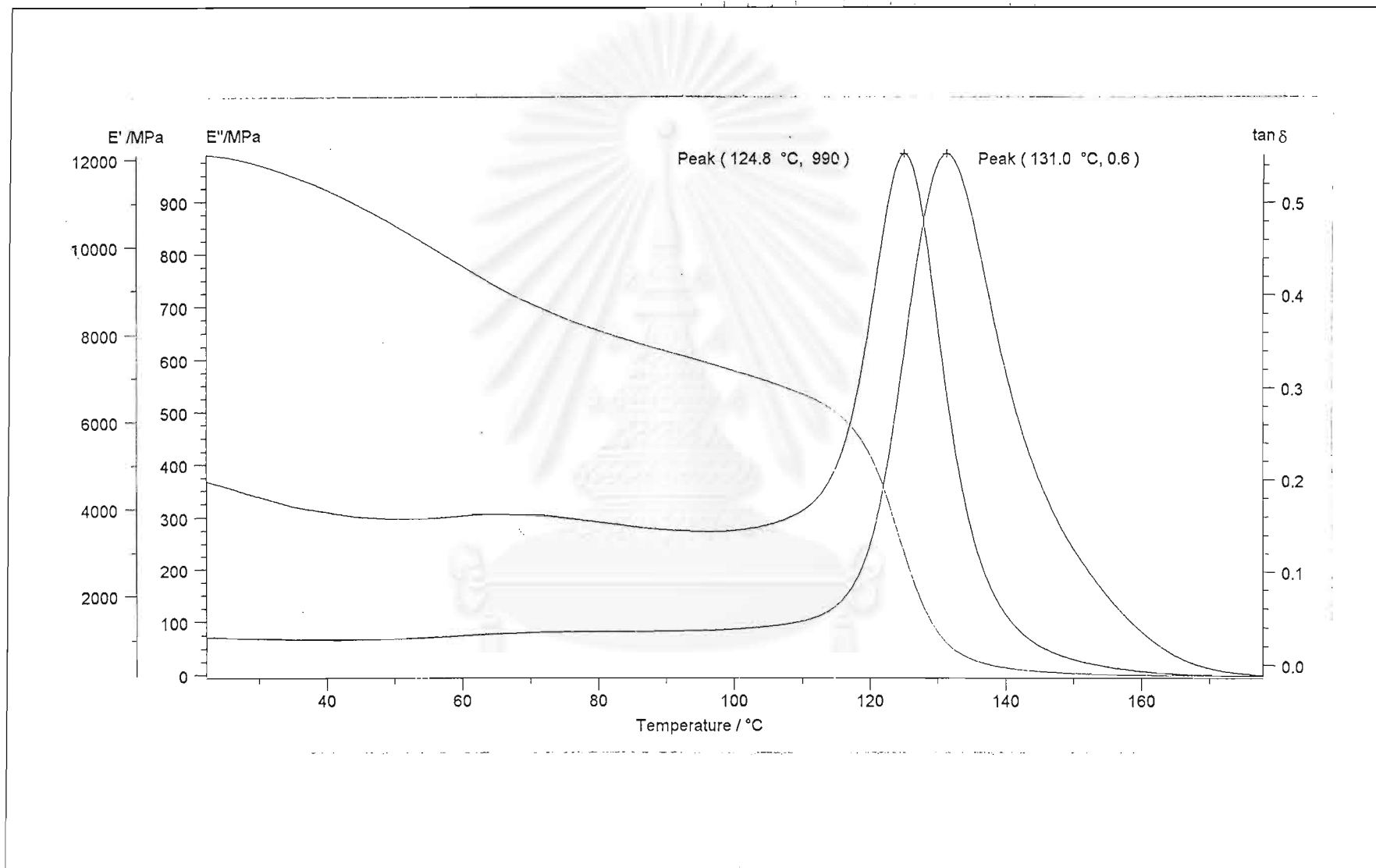


Figure A. 24 DMA thermogram of DGEBA-DETA system at DGEBA : DETA at 1 : 1

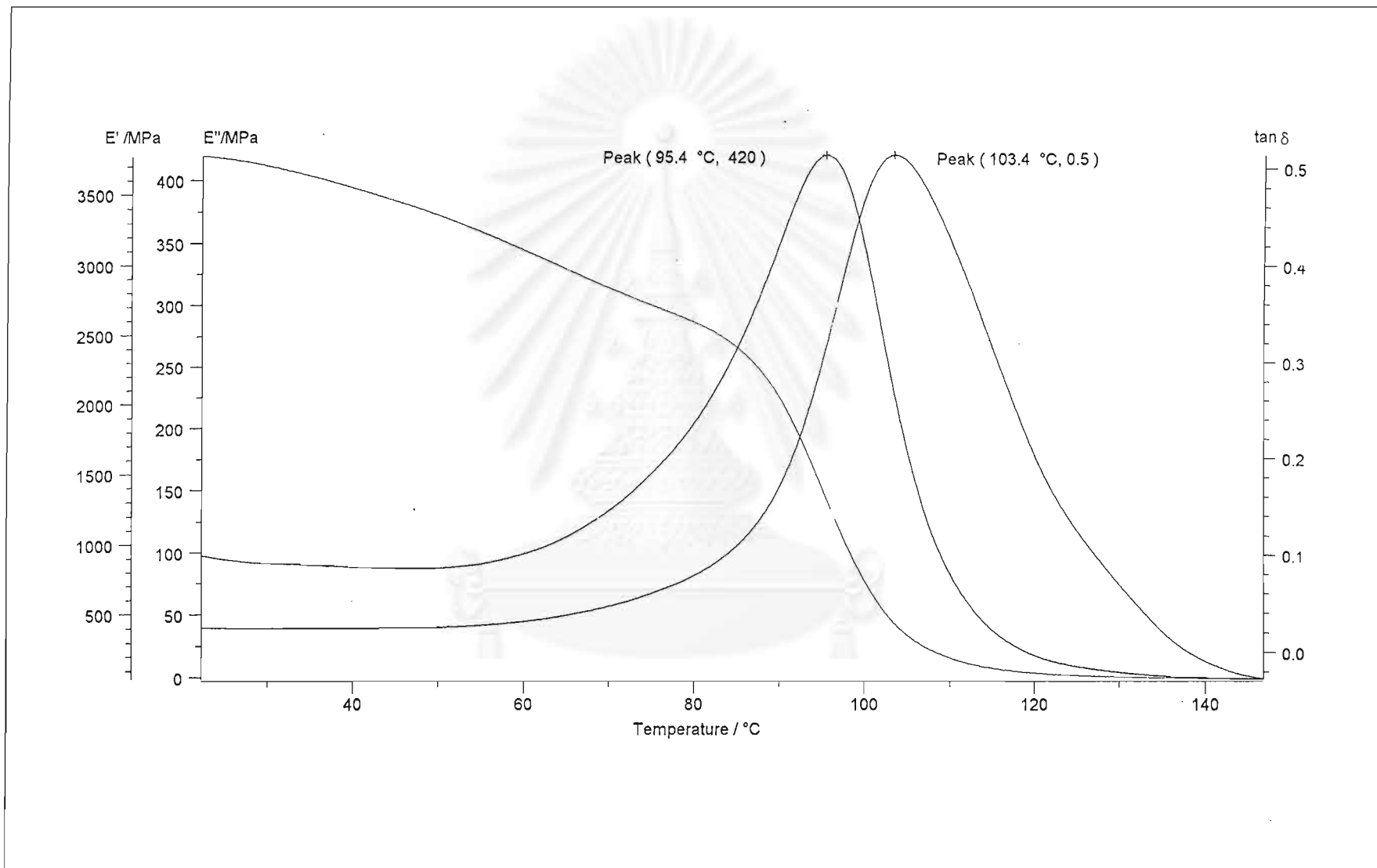
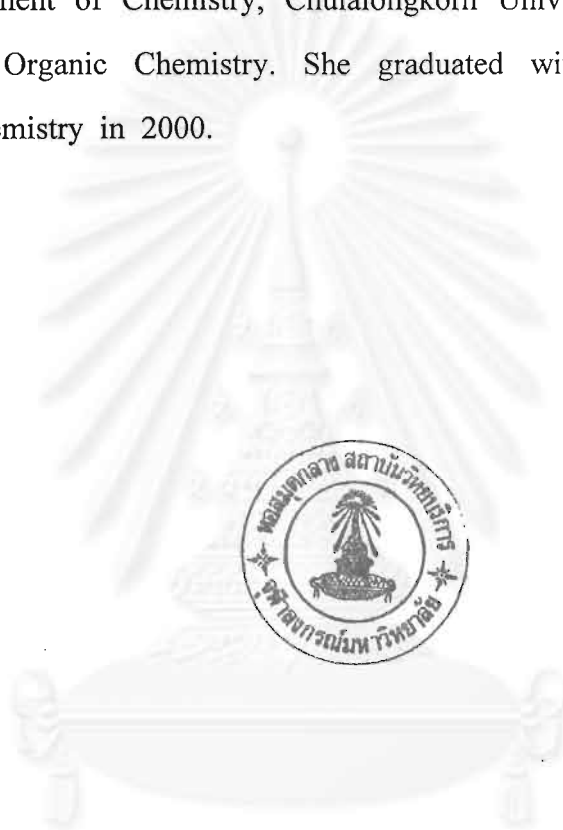


Figure A. 25 DMA thermogram of DGEBA-Bu<sub>4</sub>NOH system at DGEBA : Bu<sub>4</sub>NOH ratio of 1 : 20 mole % of Bu<sub>4</sub>NOH

## VITA

Chulaporn Pouyuan was born on June 21, 1975 in Nakhonnayok, Thailand. She received a Bachelor's Degree of Science in Chemistry from Chulalongkorn University in 1997. Since 1997 she has been a graduate student in the Department of Chemistry, Chulalongkorn University and has studied in the field of Organic Chemistry. She graduated with a Master's Degree of Science in chemistry in 2000.



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