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SYNTHESIS OF FERROCENE-CONTAINING EPOXY POLYMERS

Miss. Roongtip Patrathiranond

**A Thesis Summitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Petrochemistry and Polymer Science
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รุ่งทิพย์ ภัทรธีรานนท์ : การสังเคราะห์เอพอกซีพอลิเมอร์ที่มีเฟอโรซีน (SYNTHESIS OF FERROCENE-CONTAINING EPOXY POLYMERS) อ. ที่ปรึกษา : ผศ. ดร. นวลพรรณ จันทรศิริ, 106 หน้า, ISBN 974-346-910-9

การสังเคราะห์เอพอกซีพอลิเมอร์ที่มีเฟอโรซีนเป็นส่วนประกอบสามารถทำได้โดยการทำปฏิกิริยาเชื่อมขวางของไดไกลซิดิลอีเทอร์ของบิสฟีนอลเอ (ดีจีอีบีเอ) ด้วยอนุพันธ์ของเฟอโรซีน คือ 1,1′-บิส(ไฮดรอกซีเอทิล)เฟอโรซีน และ 1,1′-เฟอโรซีนไดคาร์บอกซิลิกแอซิด โดยมีมาลีอิกแอนไฮไดร์ดในระบบของดีจีอีบีเอ/1,1′-บิส(ไฮดรอกซีเอธิล)เฟอโรซีน ตัวเร่งปฏิกิริยาที่ใช้ คือ เตตระบิวทิลแอมโมเนียมไฮดรอกไซด์ การศึกษาด้วยเทคนิคอินฟราเรดสเปกโตรสโคปี และดิฟเฟอเรนเชียล สแกนนิง แคลอริเมตรี ทำให้ทราบสภาวะที่เหมาะสมสำหรับปฏิกิริยาเชื่อมขวาง การศึกษาสมบัติทางกายภาพและสมบัติเชิงความร้อนของพอลิเมอร์ทำได้โดยใช้ไดนามิกแมคคานิคอลแอนนาไลซิส และเทอร์โมกราวิเมตริกแอนนาไลซิส โพลิเมอร์ที่ได้จาก 1,1′-เฟอโรซีนไดคาร์บอกซิลิกแอซิด มีค่าอุณหภูมิกลาสทรานซิชันสูงกว่าโพลิเมอร์ที่ได้จาก 1,1′-บิส(ไฮดรอกซีเอทิล)เฟอโรซีน เมื่อให้ความร้อนกับโพลิเมอร์ที่อุณหภูมิ 250 องศาเซลเซียส เป็นเวลา 48 ชั่วโมง พอลิเมอร์ที่ได้จาก 1,1′-บิส(ไฮดรอกซีเอธิล)เฟอโรซีน มีความเสถียรต่ออุณหภูมิสูงกว่าพอลิเมอร์ที่ได้จาก 1,1′-เฟอโรซีนไดคาร์บอกซิลิกแอซิด

หลักสูตร ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต..........
สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่ออาจารย์ที่ปรึกษา..........
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ROONGTIP PATRATHIRANOND : SYNTHESIS OF FERROCENE-CONTAINING EPOXY POLYMERS. THESIS ADVISOR : ASSIST.PROF.NUANPHUN CHANTARASIRI, Ph.D. 106 pp., ISBN 974-346-910-9

Ferrocene-containing epoxy polymers were synthesized by crosslinking of diglycidyl ether of bisphenol A (DGEBA) with ferrocene derivatives, namely 1,1′–bis(hydroxyethyl)ferrocene and 1,1′–ferrocenedicarboxylic acid. Maleic anhydride (MA) was used in the system of DGEBA/1,1′–bis(hydroxyethyl)ferrocene. The catalyst employed was tetrabutylammonium hydroxide (Bu_4NOH). Infrared spectroscopy and differential scanning calorimetry were employed to determine the crosslinking reaction conditions. Physical and thermal properties of the polymers were studied by dynamic mechanical analysis and thermogravimetric analysis. The polymers obtained from 1,1′–ferrocenedicarboxylic acid exhibited higher glass transition temperatures (T_g) than the polymers obtained from 1,1′–bis(hydroxyethyl)ferrocene. Upon heating at 250°C for 48 hours, the polymers obtained from 1,1′–bis(hydroxyethyl)ferrocene showed higher thermal stability than those obtained from 1,1′–ferrocenedicarboxylic acid.

Program of Petrochemistry and Polymer Science	Student's signature...........................
Field of study Petrochemistry and Polymer Science	Advisor's signature……...................
Academic year 2000	

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This thesis could not have been completed without the generous help of Assistant Professor Dr. Thawatchai Tuntulani and the staff of the Supramolecular Physico-Chemical Laboratory.

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Roongtip Patrathiranond

CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SCHEMES

LIST OF ABBREVIATIONS

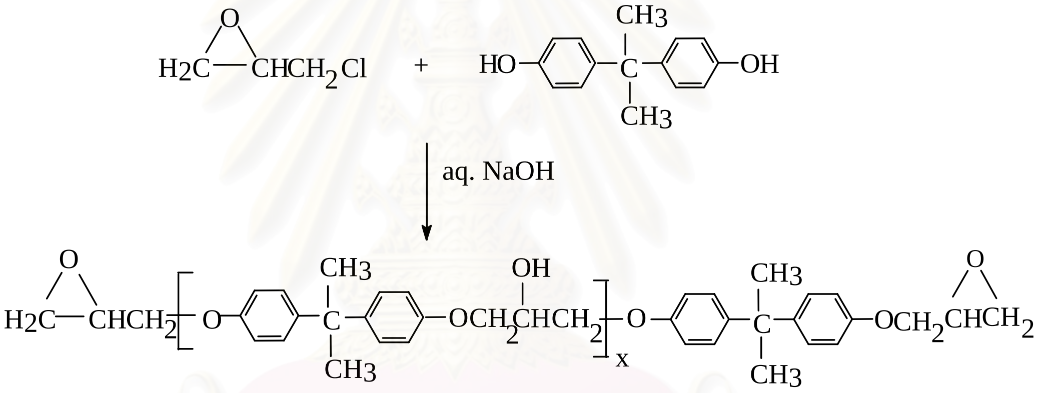
DGEBA	Diglycidyl ether of bisphenol A
DMA	Dynamic mechanical analysis
DSC	Differential Scanning Calorimetry
F_c	Ferrocene
MA	Maleic anhydride
T_g	Glass transition temperature
TGA	Thermogravimetric analysis

CHAPTER I

INTRODUCTION

1.1 Epoxy Polymers

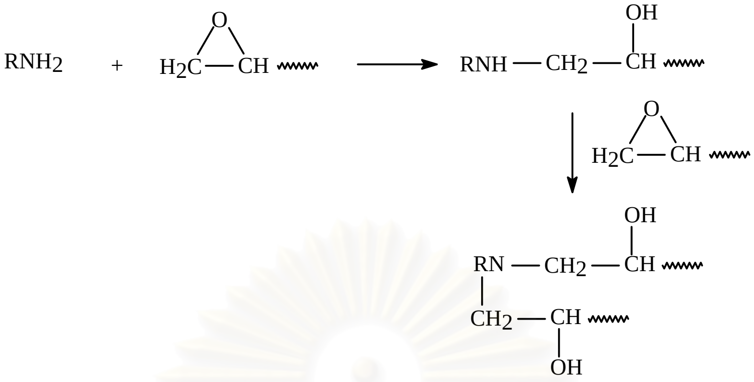
Epoxy resins are typically formed by the reaction of bisphenol A and epichlorohydrin as shown in Scheme 1.1.



Diglycidyl ether of bisphenol A epoxy resin (DGEBA)

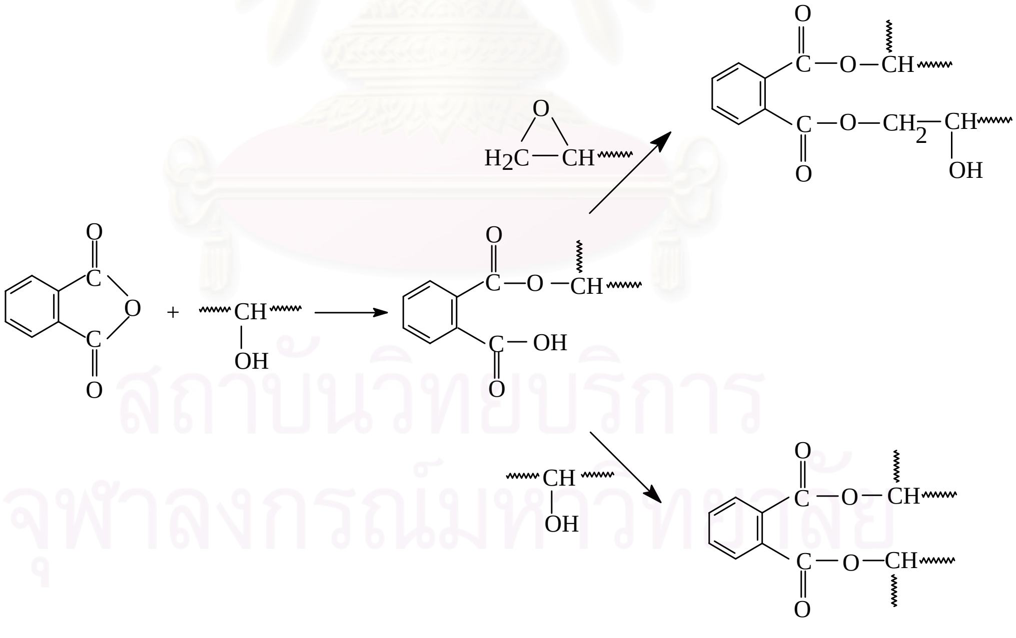
Scheme 1.1 Synthesis of DGEBA epoxy resin

Epoxy polymers are thermosetting polymers formed through the reaction between epoxy resin and a crosslinking agent. The crosslinking of the diglycidyl ether of bisphenol A epoxy resin (DGEBA) can be done using many types of crosslinking agents, including amines, amides, acids and acid anhydrides.[1-2] For example, the reaction with amines involves opening the epoxide ring through nucleophilic addition to give a β-hydroxyamino linkage as shown in Scheme 1.2.



Scheme 1.2 Crosslinking reaction of an epoxy resin by amine

Carboxylic acid anhydrides such as phthalic anhydride can react with pendant hydroxyl groups in DGEBA to give ester acids, which can then react with epoxide or other hydroxyl groups to create additional ester groups (Scheme 1.3).



Scheme 1.3 Crosslinking reaction of an epoxy resin by phthalic anhydride

Epoxy polymers are being increasingly used in industrial since they offer many advantages such as high chemical and corrosion resistance, toughness and flexibility, good adhesion to many different substrates and good mechanical and electrical behavior. The applications for epoxides fall into two categories: coatings and structural.[1-3] Coating applications include marine, maintenance, drum and can coatings. Structural composites are used in the military, aircraft, automobiles and pipes in oil, gas, chemical and mining industries. Laminates are used in the electrical and electronic industries. Other applications include repair of highway concrete cracks, coating for roads and bridges, industrial foaming and a wide range of adhesive applications.

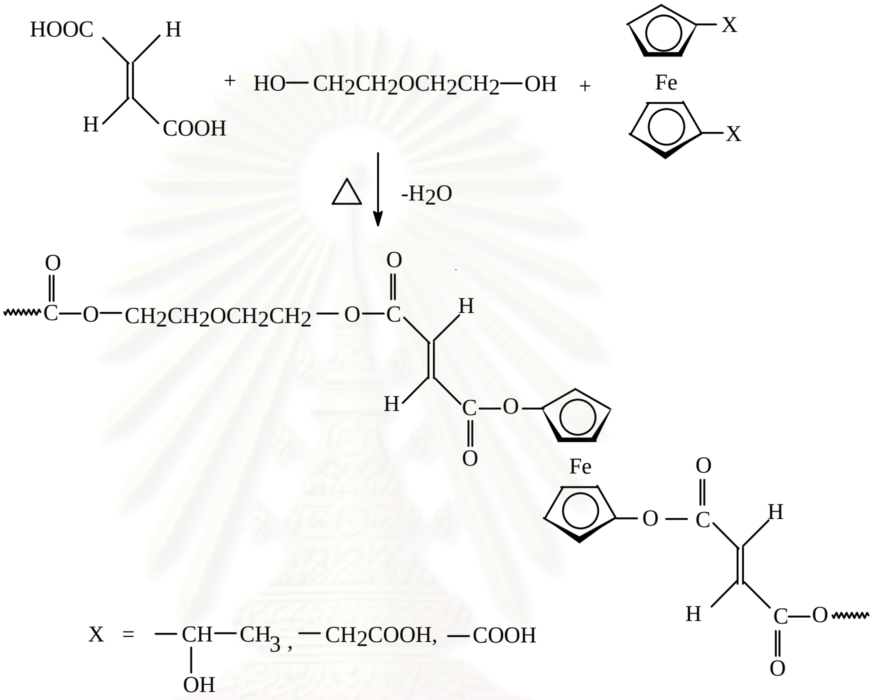
1.2 Ferrocene-Containing Epoxy Polymers

Epoxy polymers have highly increasing applications in many areas. Several attempts have been made to improve the physical and mechanical properties of epoxy polymers. Introduction of metal complexes as crosslinking agents is a method to improve the polymer properties.

Ferrocene is a metal complex that is used in polymer synthesis since it has high thermal stability.[4] Thus, the ferrocene-containing polymers provide high thermal stability. 1,1′–Bis(hydroxyethyl)ferrocene and 1,1′- ferrocenedicarboxylic acid are derivatives of ferrocene that were introduced to many polymers to improve the properties of the polymers.

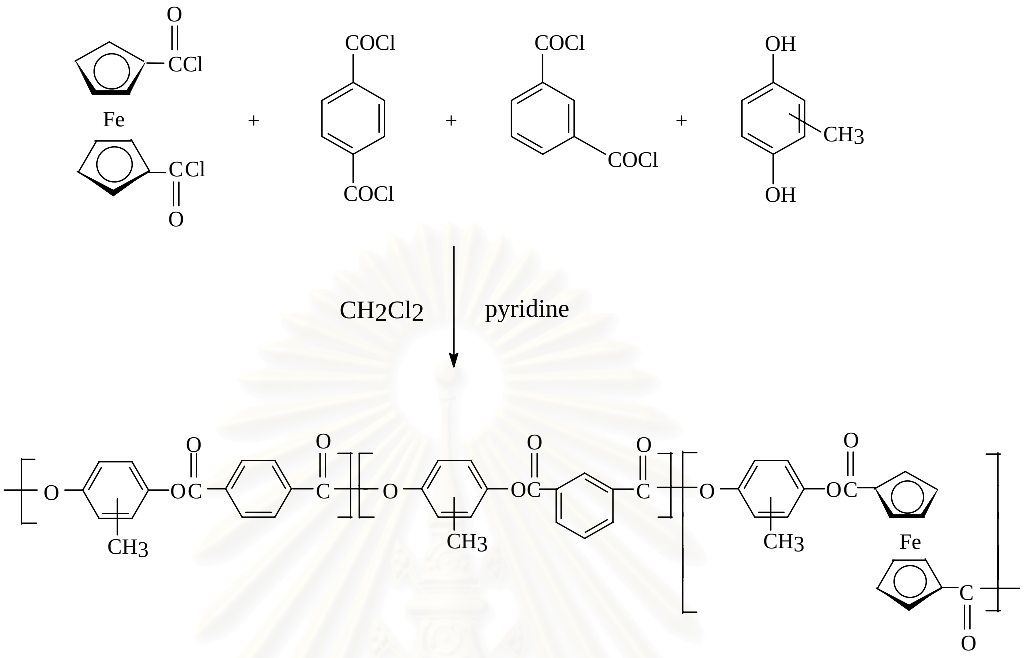
1.2.1 Ferrocene-Containing Polyesters

Jada and Reed[5] synthesized ferrocene–bound polyester resins using derivatives of ferrocene as accerelators and initiators such as 1,1′–bis(hydroxyethyl)ferrocene, 1,1′-ferrocenedicarboxylic acid and 1,1′–ferrocenediacetic acid. The dispersion of the derivative of ferrocene in the polymer matrix was improved by bonding between the derivatives of ferrocene and polyester chains (Scheme 1.4). The incorporation of ferrocene increased the rate of the polyesterification reaction. Copolymerization of ferrocene-bound polyester and styrene yielded a copolymer with high tensile strength and hardness.



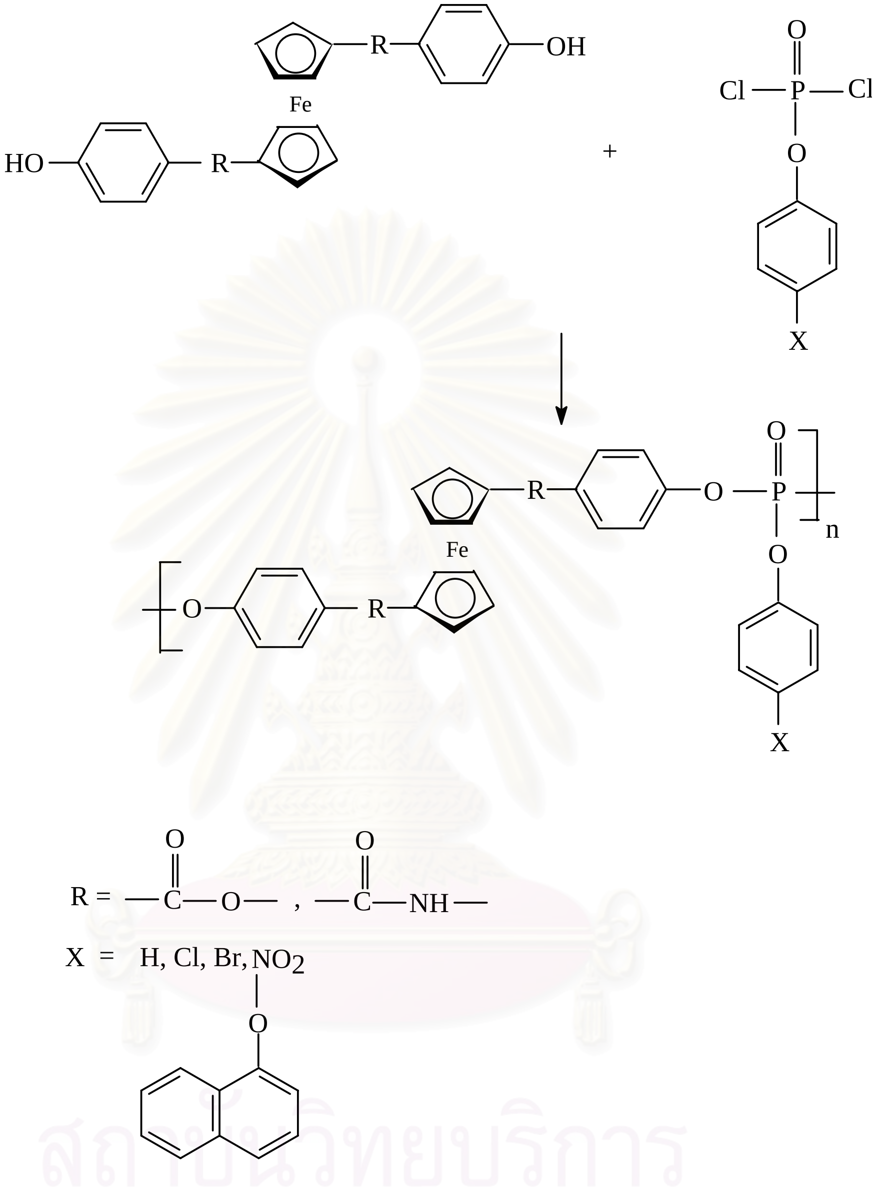
Scheme 1.4 Synthesis of ferrocene-bound polyester

Singh et al.[6] synthesized ferrocene-containing aromatic copolyesters from 1,1′-(dichlorocarbonyl)ferrocene, terephthaloyl chloride, isophthaloyl chloride and methylhydroquinone (Scheme 1.5). It was found that the ferrocene-containing polymers had higher thermal stability than the polymers without ferrocene units.



Scheme 1.5 Synthesis of ferrocene-containing aromatic copolyesters

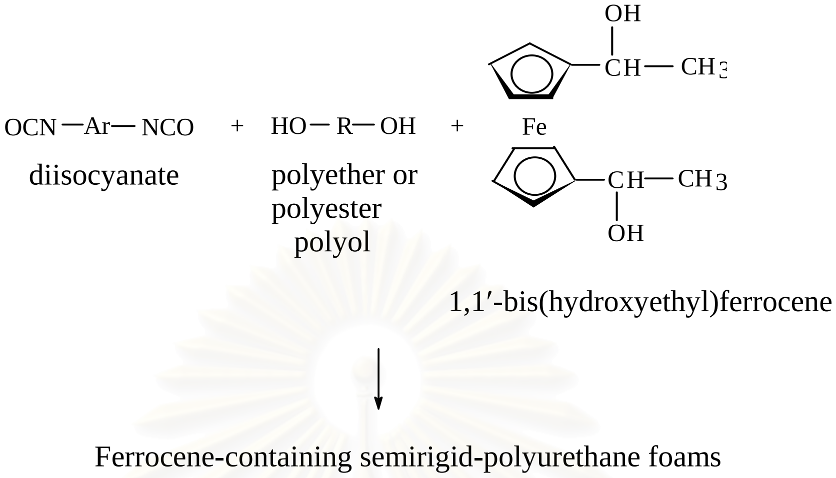
Kishore et al.[7] synthesized ferrocene-containing polyphosphate esters from 1,1′-bis(*p*-hydroxyphenylamido)ferrocene and 1,1′-bis(*p*-hydroxyphenoxycarbonyl)-ferrocene with aryl phosphorodichloridates (Scheme 1.6). The polymers obtained had high thermal and flame resistance. Additionally, the polyamide-phosphate esters showed better thermal stability than the polyester-phosphate esters.



Scheme 1.6 Synthesis of polyphosphate esters

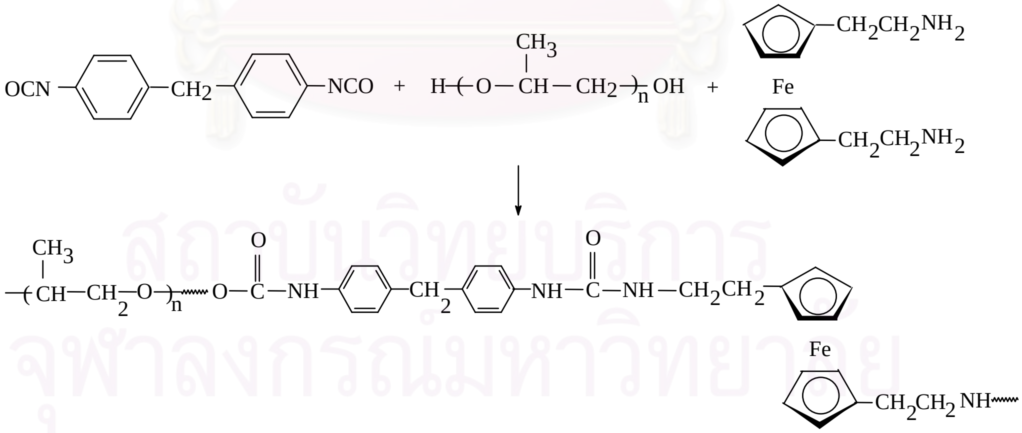
1.2.2 Ferrocene-Containing Polyurethanes

Fawcett et al.[8] synthesized semirigid–polyurethane foams by using 1,1′–bis(hydroxyethyl)ferrocene as shown in Scheme 1.7. Thermal and mechanical properties of the polyurethanes were improved.



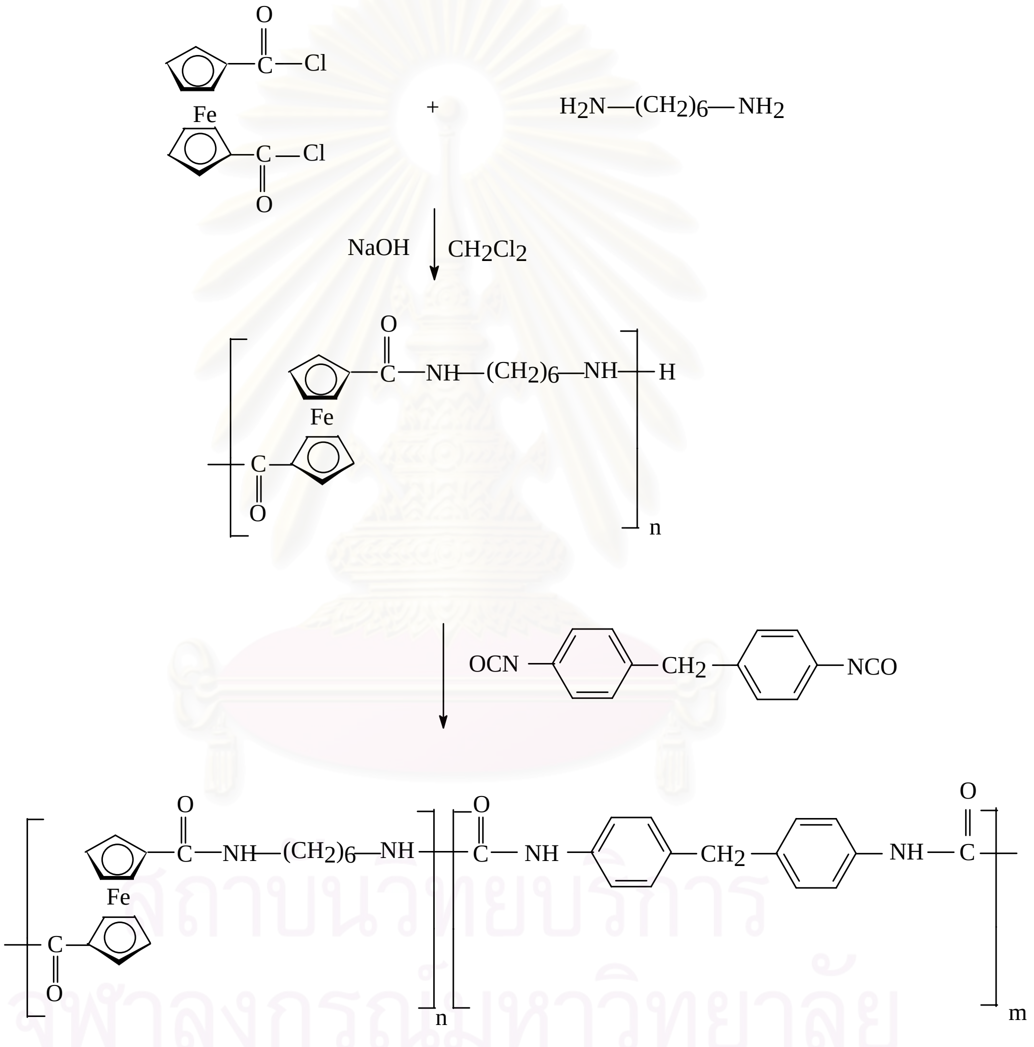
Scheme 1.7 Synthesis of ferrocene-containing polyurethanes

Gonsalves and Rausch[9] synthesized ferrocene-containing segmented poly(urea urethanes) from polypropylene glycol, diphenylmethane-4,4′-diisocyanate and 1,1′-bis(β-aminoethyl)ferrocene (Scheme 1.8). The polymers showed high thermal stability.



Scheme 1.8 The structure of ferrocene-containing poly(urea urethanes)

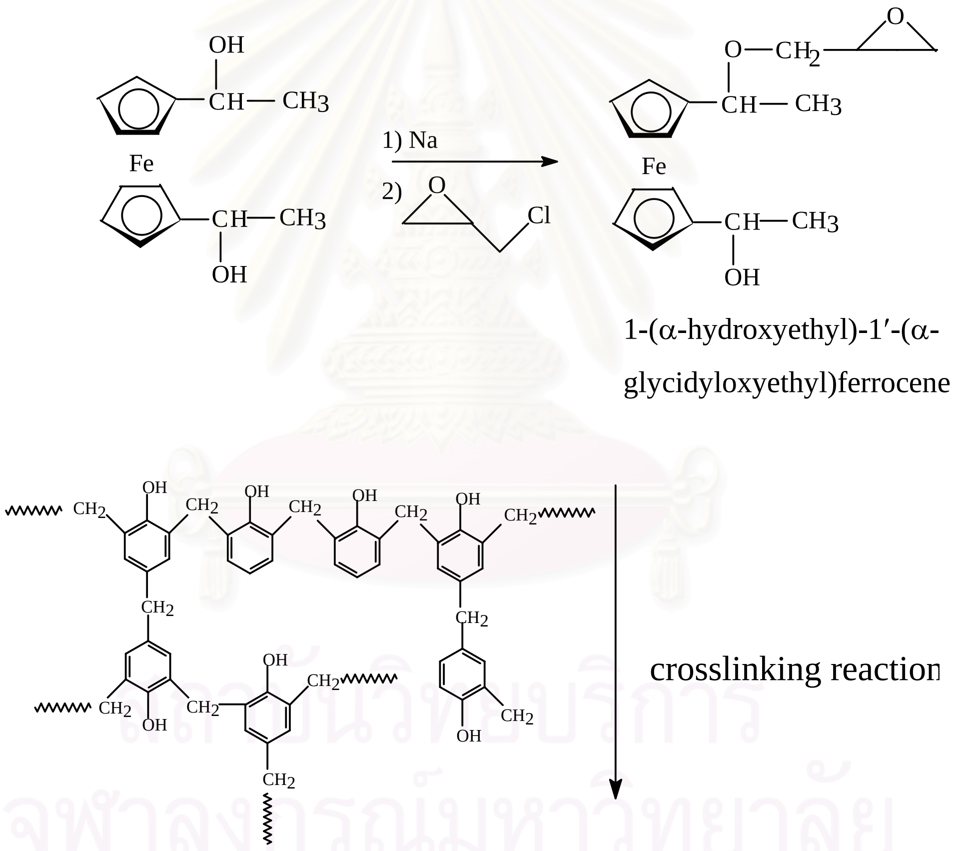
Mohajeri et al.[10] synthesized ferrocene urethane block copolymers based on diphenylmethane-4,4′-diisocyanate and ferrocene-containing amine terminated propolymers (Scheme 1.9). It was found that introduction of the $FcNH_2$ moiety into the structure of block copolymers increased their thermal stability.



Scheme 1.9 Synthesis of ferrocene urethane block copolymer

1.2.3 Ferrocene-Containing Phenol-Formaldehyde Polymers

Galkina et al.[11] synthesized 1-(α-hydroxyethyl)-1′-(α-glycidyloxyethyl)-ferrocene from 1,1′–bis(hydroxyethyl)ferrocene and epichlohydrin which was used as crosslinking agent for the crosslinking reaction of phenol–formaldehyde novolak resins. The resulting resins had high heat resistance (Scheme 1.10).



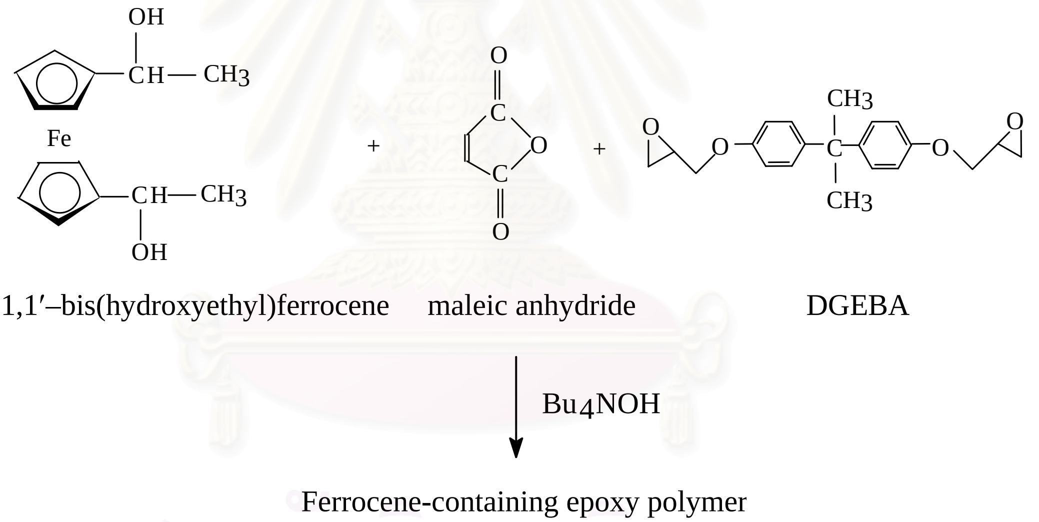
1-(α-hydroxyethyl)-1′-(α-glycidyloxyethyl)ferrocene

Ferrocene-containing phenol-formaldehyde novolak resin

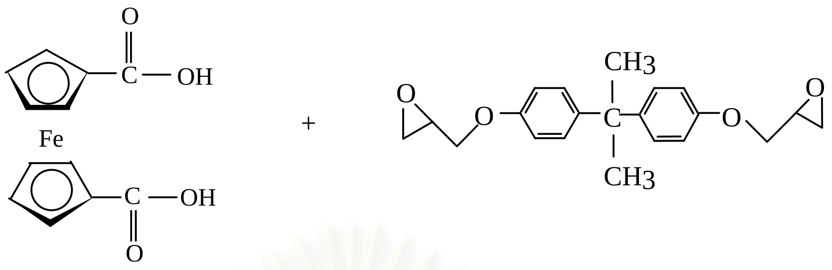
Scheme 1.10 Synthesis of ferrocene-containing phenol-formaldehyde novolak resins

1.3 Objective and Scope of the Research

The objective of this work was to synthesize ferrocene–containing epoxy polymers. The crosslinking was done by the reaction of DGEBA with 1,1′–bis(hydroxyethyl)ferrocene or 1,1′-ferrocenedicarboxylic acid in the presence of tetrabutylammonium hydroxide (Bu_4NOH) as a basic catalyst (Schemes 1.11 and 1.12). The optimum conditions for the crosslinking reaction were determined and thermal properties of the ferrocene–containing epoxy polymers were then investigated.



Scheme 1.11 Synthesis of ferrocene-containing epoxy polymers using 1,1′–bis(hydroxyethyl)ferrocene and maleic anhydride as a crosslinking agent



1,1′–ferrocenedicarboxylic acid

$\downarrow Bu_4NOH$

Ferrocene-containing epoxy polymer

Scheme 1.12 Synthesis of ferrocene-containing epoxy polymers using 1,1′–ferrocenedicarboxylic acid as a crosslinking agent

CHAPTER II

EXPERIMENTAL

2.1 Materials

All reagents and solvents were of analytical grade quality. The solvents were obtained from Baker Chemical company. Dichloromethane (CH_2Cl_2) was refluxed over calcium hydride (CaH_2) and distilled immediately before use. Diglycidyl ether of bisphenol A (DGEBA) epoxy resin (D.E.R. 330, epoxy equivalent weight = 185), maleic anhydride, tetrabutylammonium hydroxide (0.8 M in methanol) and ferrocene 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. NMR spectra were recorded in $CDCl_3$ and DMSO solution on an ACF 200 MHz Bruker instrument. The thermal properties of epoxy polymers were measured on a Netzsch dynamic mechanical analyzer (DMA 242), a Netzsch differential scanning calorimeter (DSC 200) and a Netzsch thermogravimetric analyzer (STA 409 C).

2.3 Preparation of Ferrocene Derivatives

2.3.1 Preparation of 1,1′-diacetylferrocene

0.84 g (7 mmole) of anhydrous aluminium chloride and 30 ml of dried methylene was placed in a flask. To this mixture, 0.58 ml (9 mmole) of acetyl chloride was added followed by 0.50 g (3 mmole) of ferrocene. The solution was stirred at room temperature for 30 minutes. An additional portion of 0.84 g (7 mmole) of anhydrous aluminium chloride and 0.58 ml (9 mmole) of acetyl chloride was added. The solution was stirred for 15 minutes, then, the reaction mixture was poured into ice water and was neutralized with 25% sodium hydroxide solution. The neutralized solution was extracted with methylene chloride and washed with water. The solution was dried with anhydrous sodium sulfate and the methylene chloride was evaporated to yield 0.62 g (85%) of 1,1′- diacetylferrocene. m.p. 130-131°C (lit.[12] 130-131°C). IR (KBr, cm^{-1}); 1656 (C=O), 1458, 1375 ($-CH_3$), 1280, 1117, 1055. ^1H NMR δ (200 MHz, $CDCl_3$, ppm); 4.74 (4H, s, C_p), 4.48 (4H, s, C_p), 2.33 (6H, s, CH_3).

2.3.2 Preparation of 1,1′ –bis(hydroxyethyl)ferrocene

To 30 ml of methanol, was added 0.50 g (1.84 mmole) of 1,1′–diacetylferrocene. To this solution, 0.28 g (7.35 mmole) of sodium borohydride was added. The mixture was stirred at room temperature for 15 minutes. Cold hydrochloric acid (3M) was added dropwise until there were no further hydrogen gas bubbles. The aqueous mixture was extracted with methylene chloride and the organic extract was washed with water. The solution was dried with anhydrous sodium sulfate and the methylene chloride was evaporated to yield 0.46 g (91%) of 1,1′–bis(hydroxyethyl)ferrocene. m.p. 69-71°C (lit.[13] 69-70°C). IR (KBr, cm^{-1}); 3500-3300 (OH), 2970-2860 (CH), 1650, 1454 (C=C), 1375 ($-CH_3$), 1280, 1100 (C-O). ^1H NMR δ (200 MHz, $CDCl_3$, ppm); 4.00-4.26 (8H, m, aromatic protons), 4.31 (1H, q, J=6.7, $C\underline{H}OH$), 3.81 (1H, q, J=6.7, $C\underline{H}OH$), 1.52 (3H, d, J=6.7, CH_3), 1.46 (3H, d, J=6.7, CH_3). ^{13}C NMR δ (200 MHz, $CDCl_3$, ppm); 90.5, 88.7, 72.1, 71.2, 70.1, 69.9, 69.3, 68.2, 67.3, 65.1, 62.7, 29.7, 22.2, 19.2.

2.3.3 Preparation of 1,1′- ferrocenedicarboxylic acid

To 10 ml of commercial 5.25 % sodium hypochlorite solution was added 0.50 g (1.84 mmole) of 1,1′- diacetylferrocene with rapid stirring. The temperature was maintained between 44 and 50°C. Additional 5 ml portions of sodium hypochlorite solution was added after 1 and 1.5 hrs. Following the final addition of hypochlorite, the reaction mixture was stirred 1 hr at 44-50°C, and then filtered while still warm. The clear orange filtrate obtained was treated with aqueous bisulfite and acidified with dilute hydrochloric acid to yield 0.43 g (85%) of orange precipitate. m.p. 240°C (dec.) (lit.[14] 240°C dec.). IR (KBr, cm^{-1}); 2625, 2545 (OH), 1720, 1680 (C=O), 1492, 1405 (C=C), 1374, 1300 (C-O), 1166 (C-C), 1025, 914 (OH). ^1H NMR δ (200 MHz, DMSO, ppm); 4.68 (4H, s, C_p), 4.46 (4H, s, C_p).

2.3.4 Reaction between 1,1′- ferrocenedicarboxylic acid and Styrene Oxide in the Presence of Bu_4NOH

To 0.13 g (1.09 mmole) of styrene oxide was added 0.15 g (0.55 mmole) of 1,1′- ferrocenedicarboxylic acid. To this mixture 0.14 mol (0.11 mmole) of Bu_4NOH was added. The mixture was stirred until it was homogeneous. The mixture was heated in an oven at 130°C for 2 hours to give a black solid which was purified by column chromatography. Silica gel was used as the stationary phase. A mixed solvent of 30% ethyl acetate and 70% hexane was used as the mobile phase. A yellow solid was obtained as the product (0.03 g, 12%). IR (KBr, cm^{-1}); 3500-3300 (OH), 1700 (C=O), 1280, 1150 (C-O). ^1H NMR δ (200 MHz, $CDCl_3$, ppm); 7.50-7.24 (10H, m, Ph), 5.12 (2H, m, $C\underline{H}OH$), 4.81 (4H, m, CH_2), 4.51-4.27 (8H, m, C_p), 3.73 (2H, s, OH). ^{13}C NMR δ (200 MHz, $CDCl_3$, ppm) ; 171.1 (C=O); 140.1, 128.5, 128.0, 126.3 (Ph), 72.7, 72.3, 72.2 (C_p), 72.1 (CH_2); 69.7 (CH).

2.4 Reaction between 1,1′–bis(hydroxyethyl)ferrocene and Maleic Anhydride

1,1′–Bis(hydroxyethyl)ferrocene and maleic anhydride (MA) were mixed at the mole ratio of 1,1′–bis(hydroxyethyl)ferrocene : MA = 1 : 2. The sample was heated at 120°C in an oven. The progress of the reaction was followed by using IR spectroscopy.

2.5 Reaction between DGEBA, 1,1′–bis(hydroxyethyl)ferrocene and Maleic Anhydride

DGEBA, 1,1′–bis(hydroxyethyl)ferrocene and maleic anhydride were mixed at the mole ratio of DGEBA : 1,1′-ferrocenedicarboxylic acid : MA = 1 : 0.20 : 0.20. The sample was heated in an oven at 140°C and 180°C. The progress of the reaction was followed by using IR spectroscopy.

2.6 Isothermal study of Reaction between DGEBA, Maleic Anhydride and 1,1′–bis(hydroxyethyl)ferrocene in the Presence of Bu_4NOH

DGEBA, maleic anhydride, 1,1′–bis(hydroxyethyl)ferrocene and Bu_4NOH were mixed at the mole ratio of DGEBA : MA : 1,1′–bis(hydroxyethyl)ferrocene : Bu_4NOH = 1 : 0.20 : 0.20 : 0.04 . The sample was heated in a hot air oven at 120 °C and the progress of the reaction was followed by using IR spectroscopy.

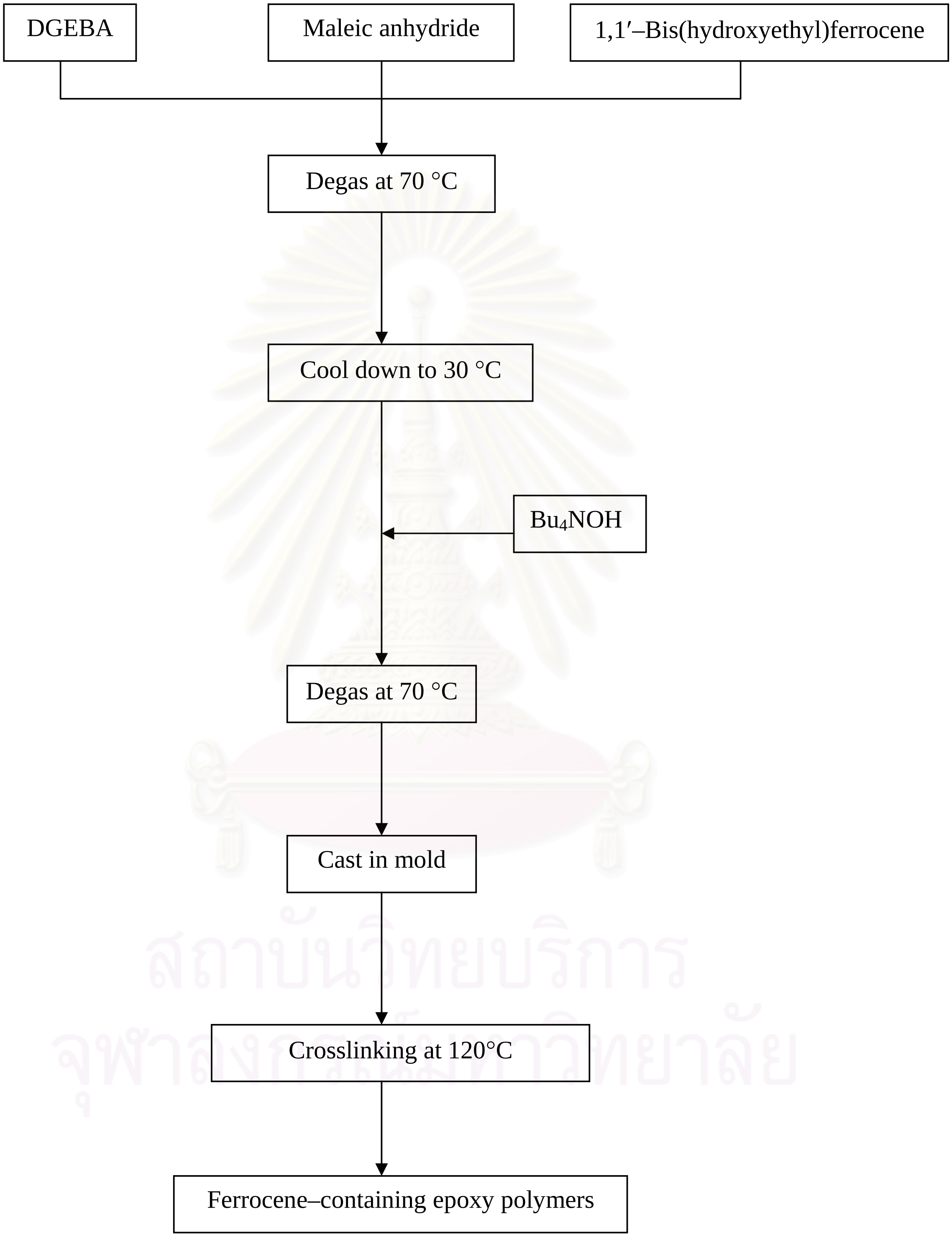
2.7 Preparation of Ferrocene-Containing Epoxy Polymers Using 1,1′–bis(hydroxyethyl)ferrocene and Maleic Anhydride as Crosslinking Agents in the Presence of Bu_4NOH

1,1′–bis(hydroxyethyl)ferrocene and maleic anhydride were used as the crosslinking agents and Bu_4NOH was used as a catalyst. The mole ratios of DGEBA: MA : 1,1′-ferrocenedicarboxylic acid : Bu_4NOH employed are shown in Table 2.1. The mixture of 1,1′–bis(hydroxyethyl)ferrocene and maleic anhydride was added to the degassed DGEBA. The mixture was heated at 70°C and stirred to become homogeneous then degassed under vacuum until gas bubbles were not observed. The mixture was cooled down to room temperature. Bu_4NOH was added with stirring and degassed under vacuum at 70°C until gas bubbles were not observed. The degassed mixture was put into a metal mold and cured at 120°C. The time required to complete the crosslinking reaction was 8 hours for the mole ratio of DGEBA : MA :

1,1′–bis(hydroxyethyl)ferrocene at 1 : 0.20 : 0.40, 1 : 0.20 : 0.30 and 1 : 0.20 : 0.20. For the mole ratio of 1 : 0.20 : 0.15, the crosslinking condition was 140°C for 10 hours. The procedure for the preparation of ferrocene-containing epoxy polymers is shown in Scheme 2.1

Table 2.1 Composition of starting materials in DGEBA : MA : 1,1′–bis(hydroxyethyl)ferrocene ($C_{14}H_{18}FeO_2$) : Bu_4NOH formulation

Mole ratio of DGEBA : MA: $C_{14}H_{18}FeO_2$: Bu_4NOH	Weight of composition (g)			
	DGEBA	**MA**	$C_{14}H_{18}FeO_2$	Bu_4NOH (ml)
1 : 0.20 : 0.40 : 0.08	3	0.16	0.88	0.81
1 : 0.20 : 0.30 : 0.06	3	0.16	0.66	0.61
1 : 0.20 : 0.20 : 0.04	3	0.16	0.44	0.41
1 : 0.20 : 0.15 : 0.03	3	0.16	0.33	0.30



Scheme 2.1 Preparation of ferrocene-containing epoxy polymers using 1,1′-bis(hydroxyethyl)ferrocene as a crosslinking agent

2.8 Reaction between DGEBA and 1,1′-ferrocenedicarboxylic acid

2.8.1 Differential Scanning Calorimetry (DSC)

DGEBA and 1,1′-ferrocenedicarboxylic acid were mixed at the mole ratio of DGEBA : 1,1′-ferrocenedicarboxylic acid = 1 : 0.80 and 1 : 0.20. The sample was then heated in DSC cell using a closed aluminium pan under nitrogen. The temperature range was 40-300°C at a heating rate of 10°C/min.

2.8.2 Infrared Spectroscopy (IR)

DGEBA and 1,1′-ferrocenedicarboxylic acid were mixed at the mole ratio of DGEBA : 1,1′-ferrocenedicarboxylic acid = 1 : 0.20. The sample was heated in an oven at 180°C and the progress of the reaction was followed by IR spectroscopy. The disappearance of the IR absorption band of the epoxide group at 917 cm^{-1} was observed when the reaction was complete.

2.9 Isothermal study of Reaction between 1,1′-ferrocenedicarboxylic acid and Bu_4NOH

1,1′-ferrocenedicarboxylic acid and Bu_4NOH were mixed at the mole ratio of 1,1′-ferrocenedicarboxylic acid : Bu_4NOH = 1 : 0.50. The sample was heated in a hot air oven at 130 °C and the progress of the reaction was followed by IR spectroscopy.

2.10 Reaction between DGEBA and 1,1′-ferrocenedicarboxylic acid in the Presence of Bu_4NOH

2.10.1 Differential Scanning Calorimetry (DSC)

DGEBA, 1,1′-ferrocenedicarboxylic acid and Bu_4NOH were mixed at the different mole ratio of 1,1′-ferrocenedicarboxylic acid and Bu_4NOH. The sample was then heated in DSC cell using a closed aluminium pan under nitrogen. The temperature range was 40-300°C at a heating rate of 10°C/min. The optimum crosslinking condition was determined.

2.10.2 Infrared Spectroscopy (IR)

DGEBA, 1,1′-ferrocenedicarboxylic acid and Bu_4NOH were mixed at mole ratio of DGEBA : 1,1′-ferrocenedicarboxylic acid : Bu_4NOH = 1 : 0.20 : 0.02 , 1 : 0.20 : 0.04 and 1 : 0.20 : 0.08. The sample was heated in a hot air oven at 130 °C. The progress of the reaction was followed by IR spectroscopy to investigate the optimum crosslinking parameters for the DGEBA.

2.11 Preparation of Ferrocene-Containing Epoxy Polymers Using 1,1′-ferrocenedicarboxylic acid as Crosslinking Agents in the Presence of Bu_4NOH

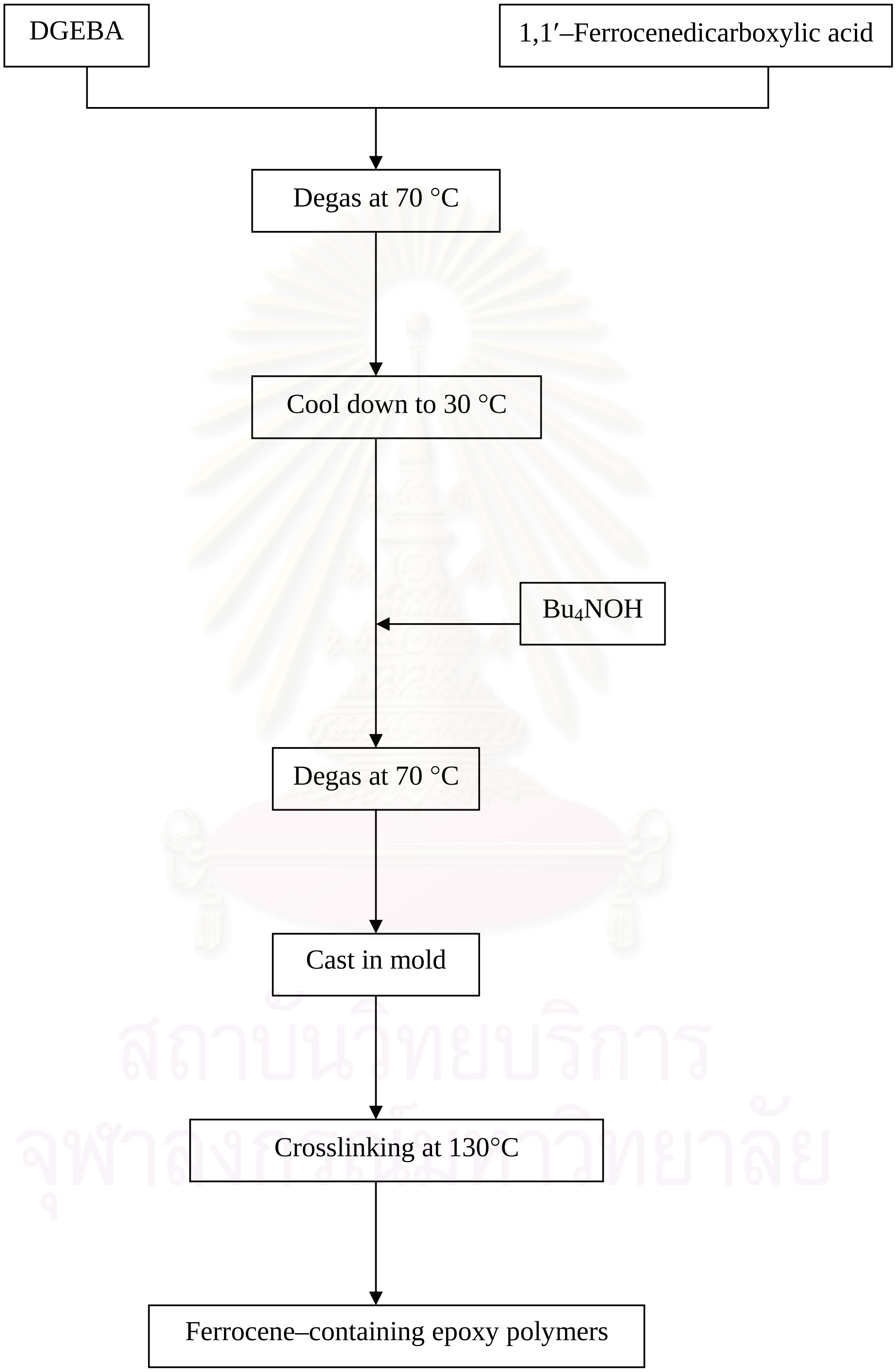
DGEBA was crosslinked with 1,1′-ferrocenedicarboxylic acid and Bu_4NOH at 130°C by the same method as described in 2.7. The time required to complete the crosslinking reaction was 12 hours for the mole ratio of DGEBA : 1,1′-ferrocenedicarboxylic acid : Bu_4NOH at 1 : 0.30 : 0.04, 1 : 0.20 : 0.04 and 1 : 0.10 : 0.04, 18 hours for the mole ratio of 1 : 0.05 : 0.04 and 30 hours for the ratio of 1 : 0.025 : 0.02 and 1 : 0.0125 : 0.02. The mole ratios of DGEBA : 1,1′-

ferrocenedicarboxylic acid : Bu_4NOH employed are shown in Table 2.2. The procedure for the preparation of ferrocene-containing epoxy polymers is shown in Scheme 2.2.

Table 2.2 Composition of starting materials in DGEBA : 1,1′–ferrocenedicarboxylic acid ($C_{12}H_{10}FeO_4$) : Bu_4NOH formulation

Mole ratio of DGEBA : $C_{12}H_{10}FeO_4$: Bu_4NOH	Weight of composition (g)		
	DGEBA	$C_{12}H_{10}FeO_4$	Bu_4NOH (ml)
1 : 0.30 : 0.04	3	0.67	0.41
1: 0.20 : 0.04	3	0.44	0.41
1 : 0.10 : 0.04	3	0.22	0.41
1 : 0.05 : 0.04	3	0.11	0.41
1 : 0.025 : 0.02	3	0.06	0.20
1 : 0.0125 : 0.02	3	0.03	0.20

Comparative polymers obtained by using maleic anhydride, tetrabutylammonium hydroxide or diethylenetriamine as crosslinking agents were also prepared using the procedures described in the literature.[1,15] Table 2.3 shows the composition of the starting materials.



Scheme 2.2 Preparation of ferrocene-containing epoxy polymers using 1,1′-ferrocenedicarboxylic acid as a crosslinking agent

Table 2.3 Composition of starting materials in the 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[a]	1 : 0.20	3	0.16	110°C/8h
Diethylenetriamine	1 : 1	3	0.36	100°C/1h
Bu_4NOH	1 : 0.04	3	0.09	110°C/8h

[a]tetrabutylammonium hydroxide was employed as a catalyst

2.12 Characterization of Ferrocene-Containing Epoxy Polymers

2.12.1 IR Spectroscopy

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

2.12.2 Thermal Properties

The glass transition temperatures (T_g) of the epoxy polymers were measured by dynamic mechanical analysis (DMA). The length, width and thickness of the polymer samples were 4, 1 and 0.3 cm, respectively.

2.12.3 Thermal Stability

To study the heat resistance of the epoxy polymers, the polymer samples were heated at 250 °C for 48 h in a hot air oven to obtain % weight loss of polymer at different times

2.12.4 Thermogravimetric Analysis (TGA)

The heat resistance of the epoxy polymers was studied using the thermogravimetric analysis.

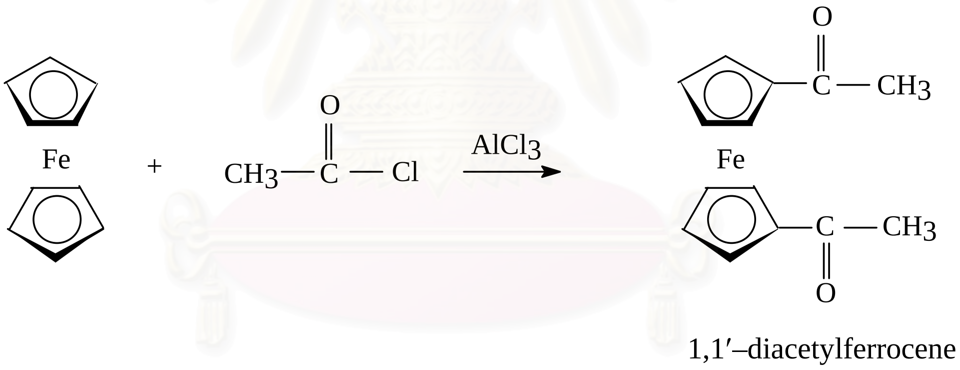
CHAPTER III

RESULTS AND DISCUSSION

Part 1 Use of 1,1′–bis(hydroxyethyl)ferrocene as a Crosslinking Agent

3.1 Synthesis of 1,1′–diacetylferrocene

1,1′–Diacetylferrocene was synthesized by the Friedel-Crafts acylation of ferrocene with acetyl chloride in the presence of aluminium chloride[16] which acted as a Lewis acid (Scheme 3.1).

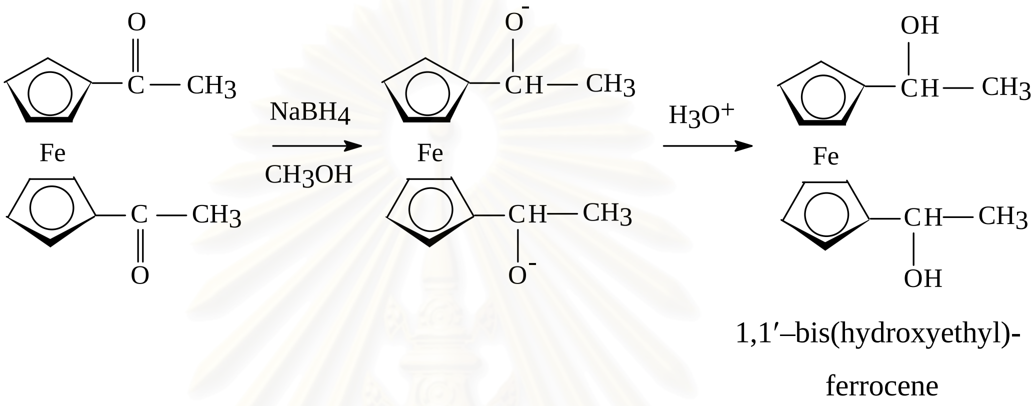


Scheme 3.1 Synthesis of 1,1′–diacetylferrocene

IR spectrum of 1,1′–diacetylferrocene (Figure A.1) showed the absorption band of C=O stretching vibration at 1656 cm^{-1}. ^1H NMR spectrum (Figure A.2) showed the aromatic protons signals as two singlets at 4.74 ppm (4H) and 4.48 ppm (4H). The methyl protons also appeared as a singlet at 2.33 ppm (6H).

3.2 Synthesis of 1,1′–bis(hydroxyethyl)ferrocene

1,1′–Bis(hydroxyethyl)ferrocene was synthesized by the reduction of 1,1′–diacetylferrocene with $NaBH_4$[17] (Scheme 3.2).



Scheme 3.2 Synthesis of 1,1′–bis(hydroxyethyl)ferrocene

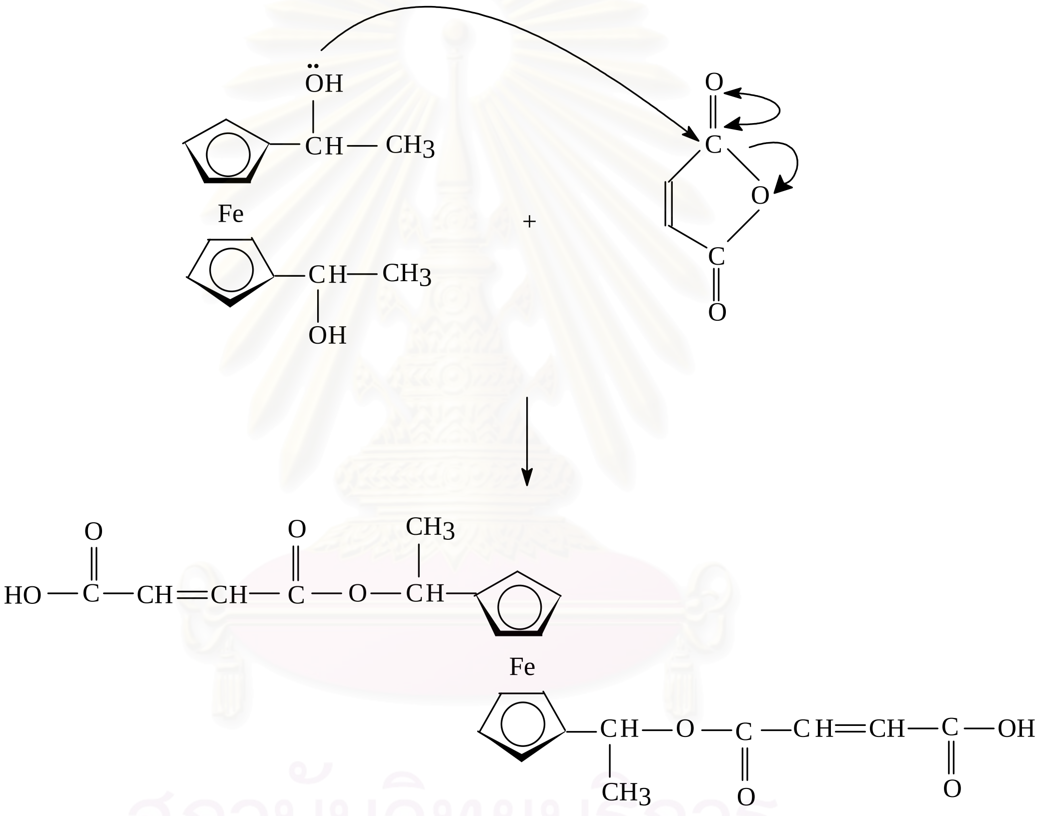
From the IR spectrum (Figure A.3), the absorption band at 3500-3300 cm^{-1} belongs to the O-H stretching vibration. The absorption band at 1100 cm^{-1} is assigned to be C-O stretching vibration of secondary alcohol.

^1H NMR spectrum (Figure A.4) shows the aromatic proton signals as multiplet at 4.00-4.26 ppm. The methine protons signals appear as two quartets since there were meso and d,l isomers. These quartets appear at 4.31 ppm and 3.81 ppm with J = 6.7 Hz. The signals of the methyl groups appear as two doublets at 1.52 ppm and 1.46 ppm with J = 6.7 Hz.

^{13}C NMR spectrum (Figure A.5) shows the signals of C_p quaternary carbons at 90.5 and 88.7 ppm. The methyl carbons signals were observed at 22.2 and 19.2 ppm.

3.3 Reaction between 1,1′–bis(hydroxyethyl)ferrocene and Maleic Anhydride

Infrared spectroscopy was used to study the reaction between 1,1′–bis(hydroxyethyl)ferrocene and maleic anhydride. The expected reaction is that the hydroxyl groups of the 1,1′–bis(hydroxyethyl)ferrocene react with the anhydride group of maleic anhydride to give ester groups and carboxylic groups (Scheme 3.3).



Scheme 3.3 Reaction between 1,1′–bis(hydroxyethyl)ferrocene and maleic anhydride

When a mixture of 1,1′–bis(hydroxyethyl)ferrocene : maleic anhydride at the mole ratio of 1 : 2 was heated at 120°C for 4 hours, the absorption bands of the anhydride group at 1854 cm^{-1} and 1777 cm^{-1} disappeared. There was an appearance of the new ester group at 1739 cm^{-1} (Figure 3.1).

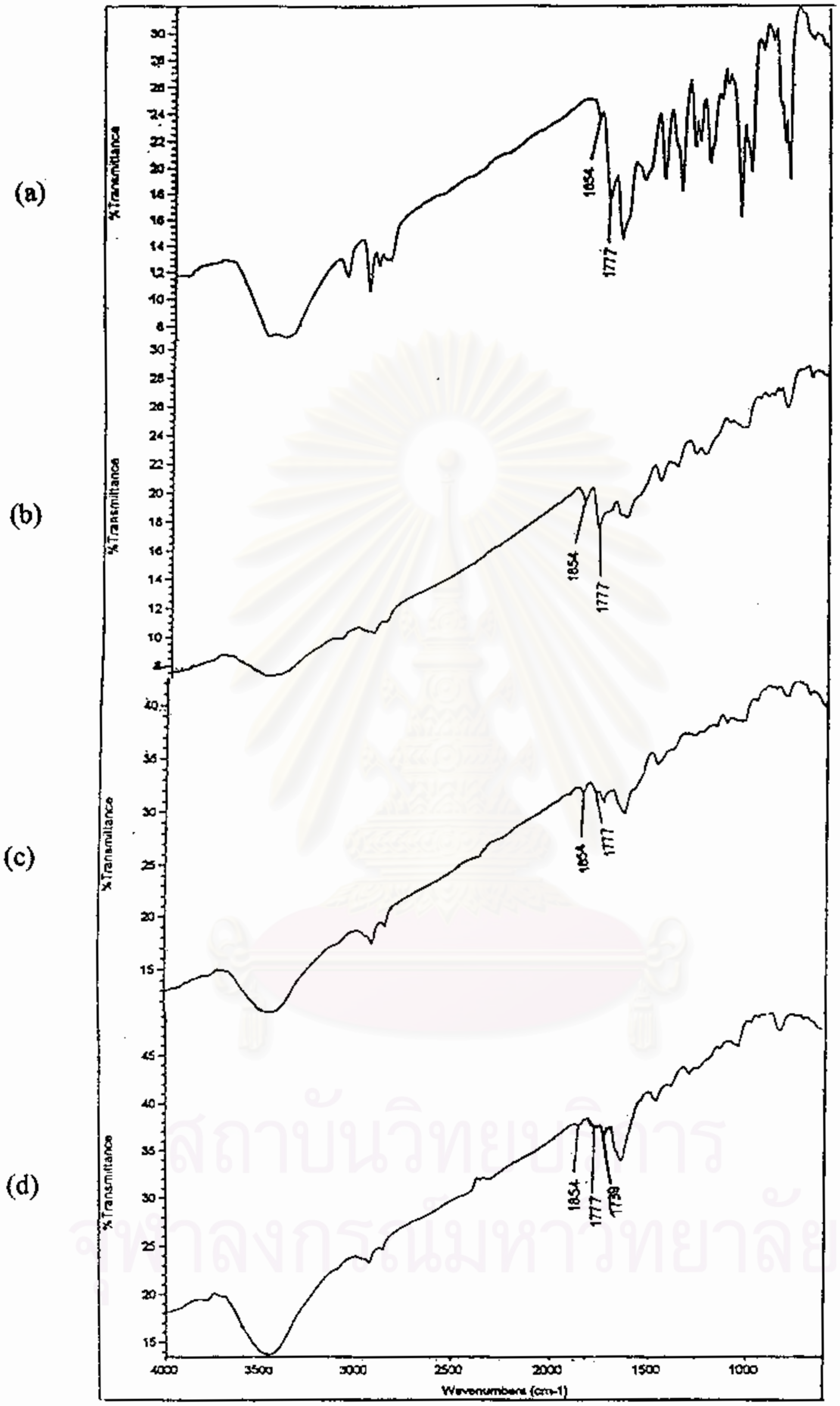


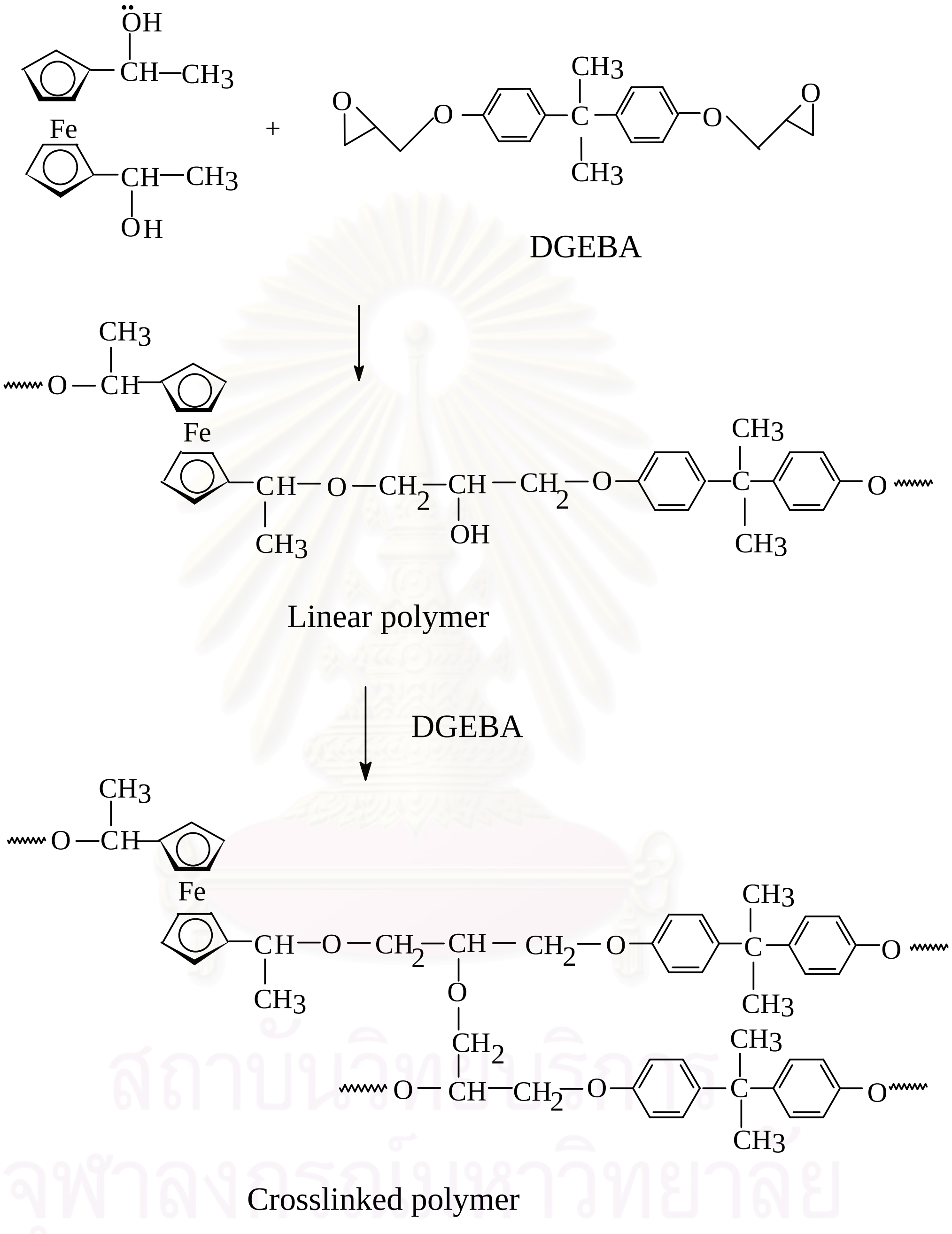
Figure 3.1 IR spectra of 1,1′–bis(hydroxyethyl)ferrocene : MA at the mole ratio of 1 : 2 (a) before heating (b) after heating at 120°C for 1 h (c) after 2 h and (d) after 4 h

3.4 Crosslinking Reaction of DGEBA with 1,1′–bis(hydroxyethyl)ferrocene and Maleic Anhydride (MA)

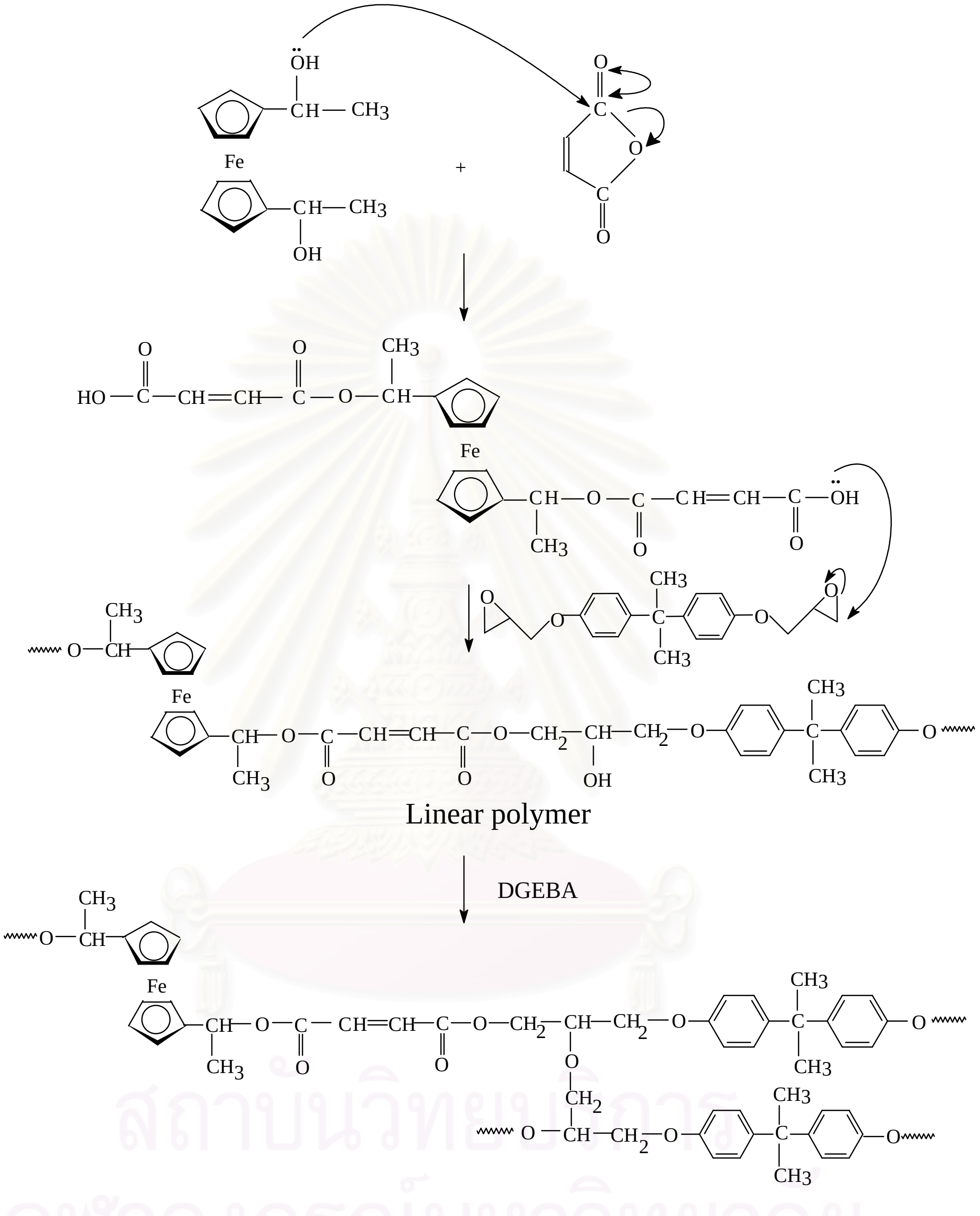
Since there were three starting materials, several reactions could occur during the polymerization: the reaction between 1,1′–bis(hydroxyethyl)ferrocene and maleic anhydride (Scheme 3.3) and the reaction between 1,1′–bis(hydroxyethyl)ferrocene and DGEBA (Scheme 3.4).

For the reaction between 1,1′–bis(hydroxyethyl)ferrocene and DGEBA (Scheme 3.4), the proposed mechanism is the ring opening of DGEBA by the hydroxyl groups in 1,1′–bis(hydroxyethyl)ferrocene to give a linear polymer. The generated hydroxyl groups could then undergo further reaction with DGEBA to give a crosslinked polymer. It has been known that the reaction in Scheme 3.3 proceeds more rapidly than that in Scheme 3.4. Furthermore, the IR experiment (Figure 3.1) also confirmed that 1,1′–bis(hydroxyethyl)ferrocene could react with maleic anhydride. When a mixture of DGEBA : 1,1′–bis(hydroxyethyl)ferrocene : maleic anhydride was heated, the IR experiment (Figure 3.2) showed that maleic anhydride reacted first since the C=O absorption bands of maleic anhydride group at 1854 and 1777 cm^{-1} disappeared while the IR absorption band of epoxide group at 917 cm^{-1} was still observed. Therefore, during the crosslinking process of DGEBA/1,1′–bis(hydroxyethyl)-ferrocene/maleic anhydride system, 1,1′–bis(hydroxyethyl)-ferrocene reacts first with maleic anhydride to form carboxylic groups which can then open the epoxide rings in DGEBA. The generated hydroxyl groups can then undergo further reaction with DGEBA to give the crosslinked polymer (Scheme 3.5).

Since the mole ratio of 1,1′–bis(hydroxyethyl)ferrocene employed in the experiment was equal to that of maleic anhydride, therefore 1,1′–bis(hydroxyethyl)ferrocene was not all converted to disubstituted carboxylic product. There would be monosubstituted carboxylic product which could also undergo the crosslinking reaction with DGEBA.



Scheme 3.4 Reaction between DGEBA and 1,1′–bis(hydroxyethyl)ferrocene



Scheme 3.5 Proposed mechanism of the crosslinking reaction of DGEBA with 1,1′–bis(hydroxyethyl)ferrocene and maleic anhydride

Infrared spectroscopy was used to study the crosslinking condition. The completeness of the crosslinking reaction was confirmed by the disappearance of the characteristic absorption band of the epoxide groups in DGEBA at 917 cm^{-1}. The IR spectra were obtained from heating a mixture of DGEBA : 1,1′–bis(hydroxyethyl)ferrocene : MA at the mole ratio of 1 : 0.20 : 0.20 at 140°C and 180°C (Figures 3.2 and 3.3).

When the mixture was heated at 140°C, the IR absorption band of epoxide group at 917 cm^{-1} was still observed. Therefore, the crosslinking reaction was not completed. However, the C=O absorption bands of the anhydride group at 1854 cm^{-1} and 1777 cm^{-1} disappeared. This indicated that the anhydride ring was opened by the hydroxyl groups of 1,1′–bis(hydroxyethyl)ferrocene to generate carboxylic groups. There was the appearance of a new ester group at 1731 cm^{-1} after heating for 1 hour. When the crosslinking was done at 180°C, the IR absorption band of the epoxide ring at 917 cm^{-1} disappeared completely after heating for 4 hours.

(a)

(b)

(c)

(d)

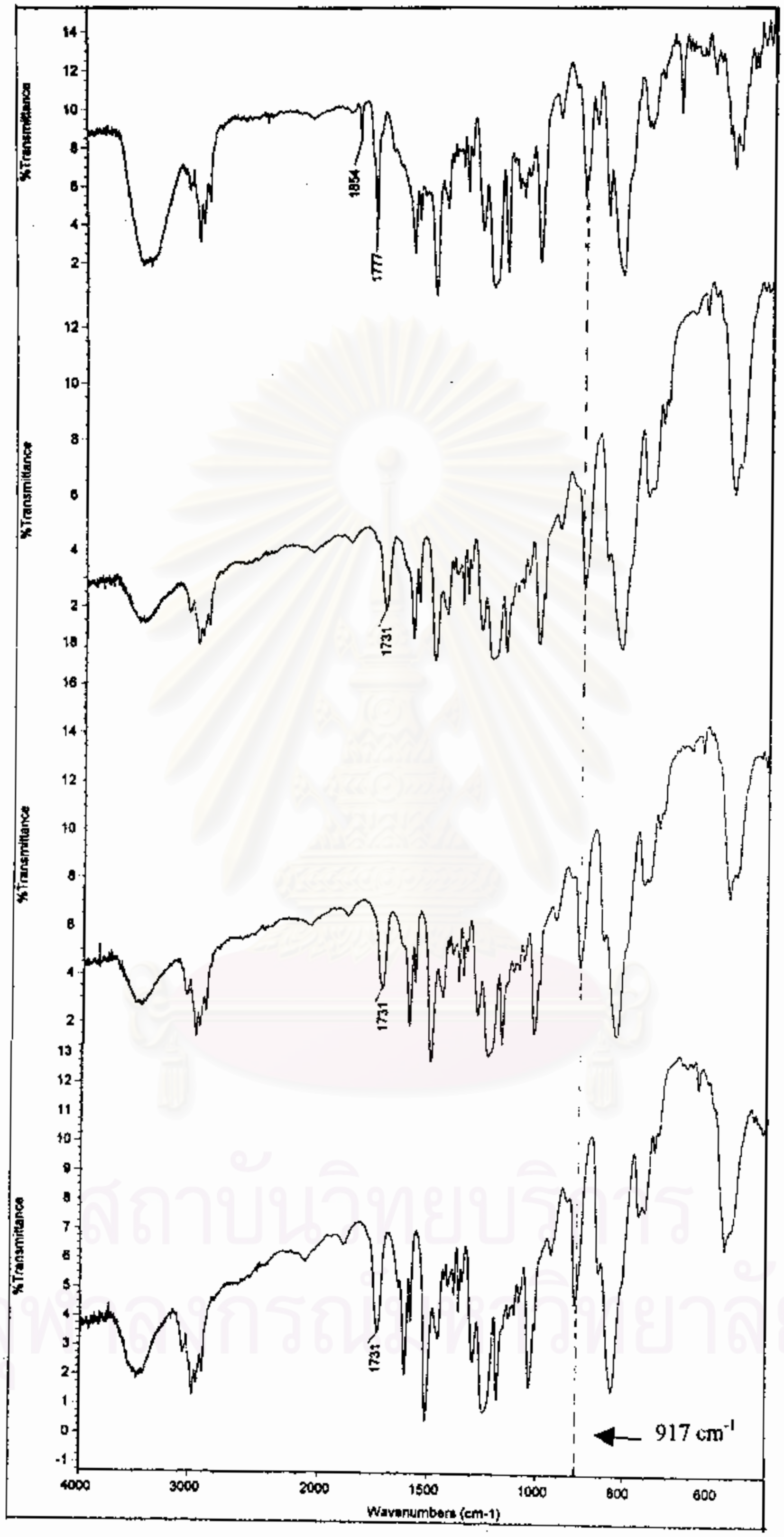


Figure 3.2 IR spectra of DGEBA : 1,1′–bis(hydroxyethyl)ferrocene : MA at the mole ratio of 1 : 0.20 : 0.20 (a) before heating (b) after heating at 140°C for 1 h (c) after 2 h and (d) after 4 h

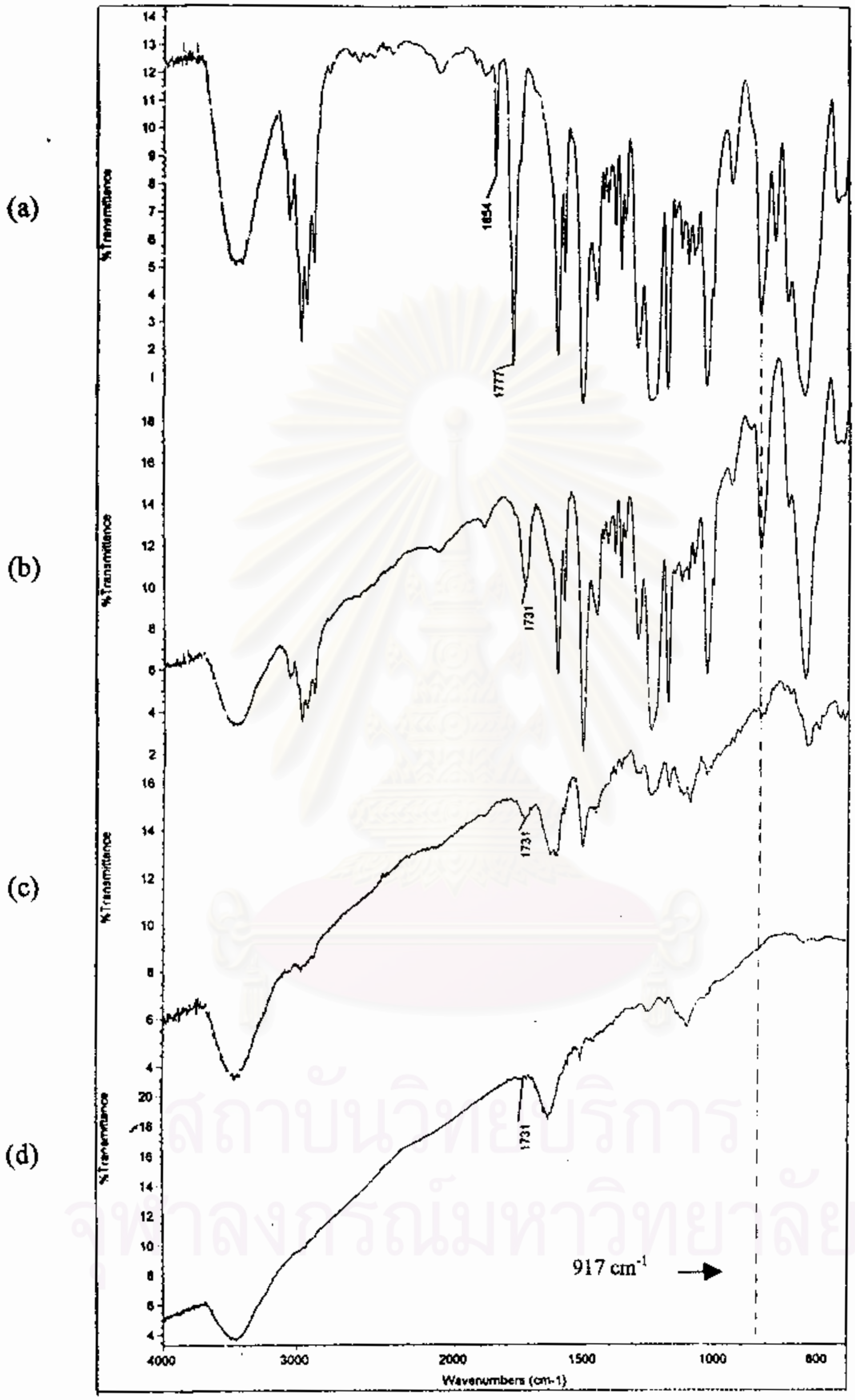
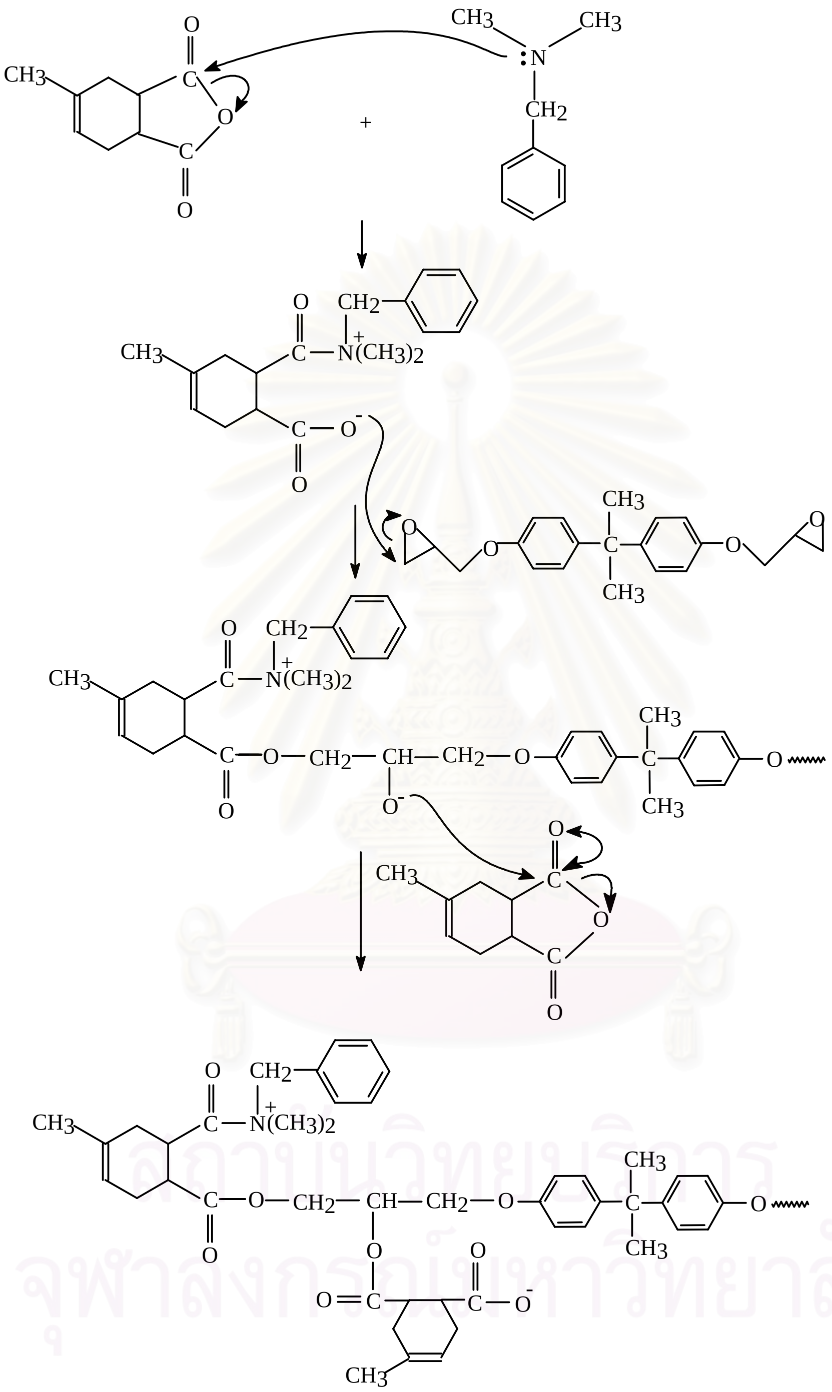


Figure 3.3 IR spectra of DGEBA : 1,1′–bis(hydroxyethyl)ferrocene : MA at the mole ratio of 1 : 0.20 : 0.20 (a) before heating (b) after heating at 180°C for 1 h (c) after 2 h and (d) after 4 h

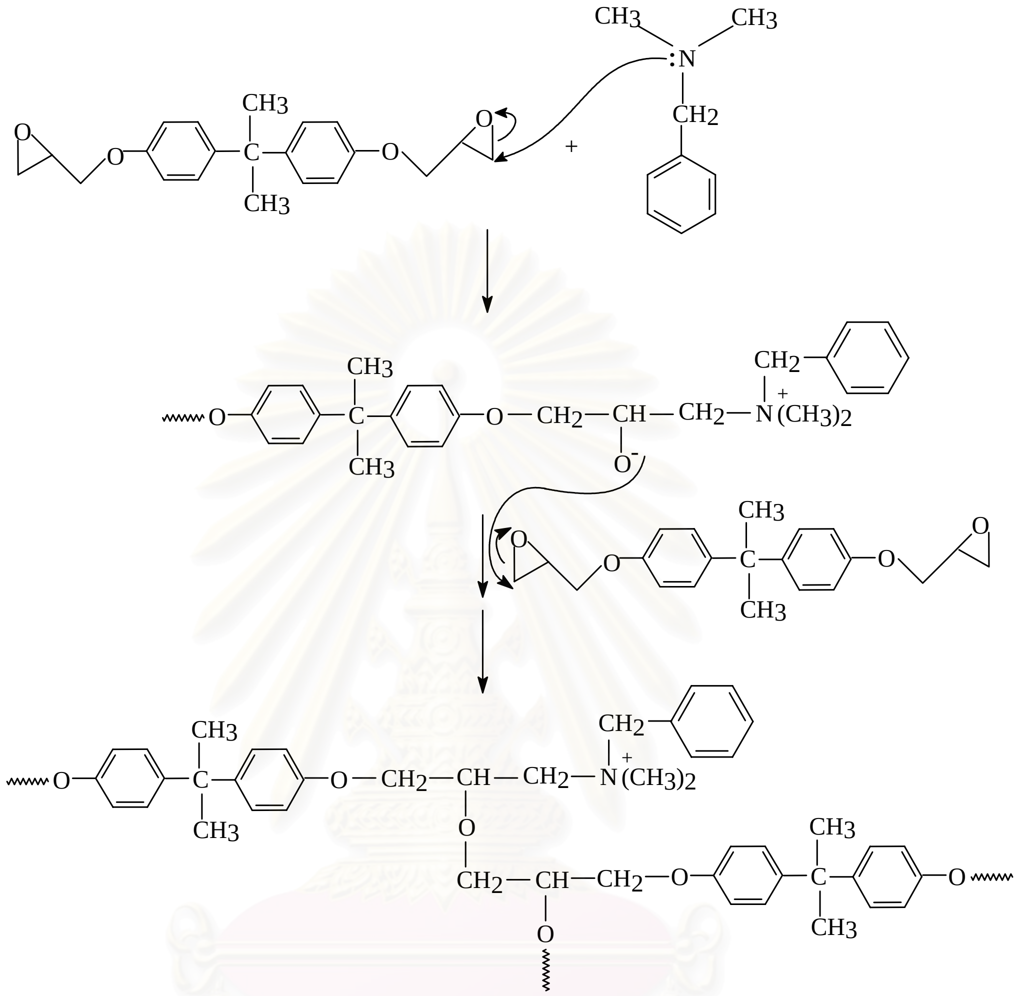
3.5 Reaction between DGEBA, Maleic Anhydride and 1,1′-bis(hydroxyethyl)-ferrocene in the Presence of Bu_4NOH

From Figure 3.3, it was shown that the crosslinking reaction was completed after heating at 180°C for 4 hours. It is known that the temperature required for the crosslinking reaction of DGEBA with phenolic crosslinking agents can be reduced by the use of Bu_4NOH as a catalyst.[1] Since the crosslinking temperature of DGEBA with 1,1′-bis(hydroxyethyl)ferrocene and maleic anhydride was high, tetrabutylammonium hydroxide (Bu_4NOH) was employed as a catalyst in order to decrease the crosslinking temperature.

Ma et al.[18] proposed the crosslinking mechanisms of DGEBA using methyl tetrahydrophthalic anhydride as a crosslinking agent catalyzed by benzyl dimethylamine. The crosslinking reaction of the system can be considered as two sequential stages: (1) an anionic copolymerization of cyclic anhydride and epoxy resin (Scheme 3.6) and (2) a homopolymerization of epoxide initiated by a quaternary ammonium salt zwitter ion (Scheme 3.7). The proposed mechanism of copolymerization (Scheme 3.6) was a nucleophilic attack of anhydride by the tertiary amine to form the quaternary ammonium salt zwitter ion, which then reacted with DGEBA to yield an alkoxide anion. This alkoxide anion could then open the anhydride ring to yield a carboxylate ion, which could undergo reaction with epoxide to yield an alkoxide anion. In comparison to homopolymerization (Scheme 3.7), the copolymerization proceeds more rapidly.



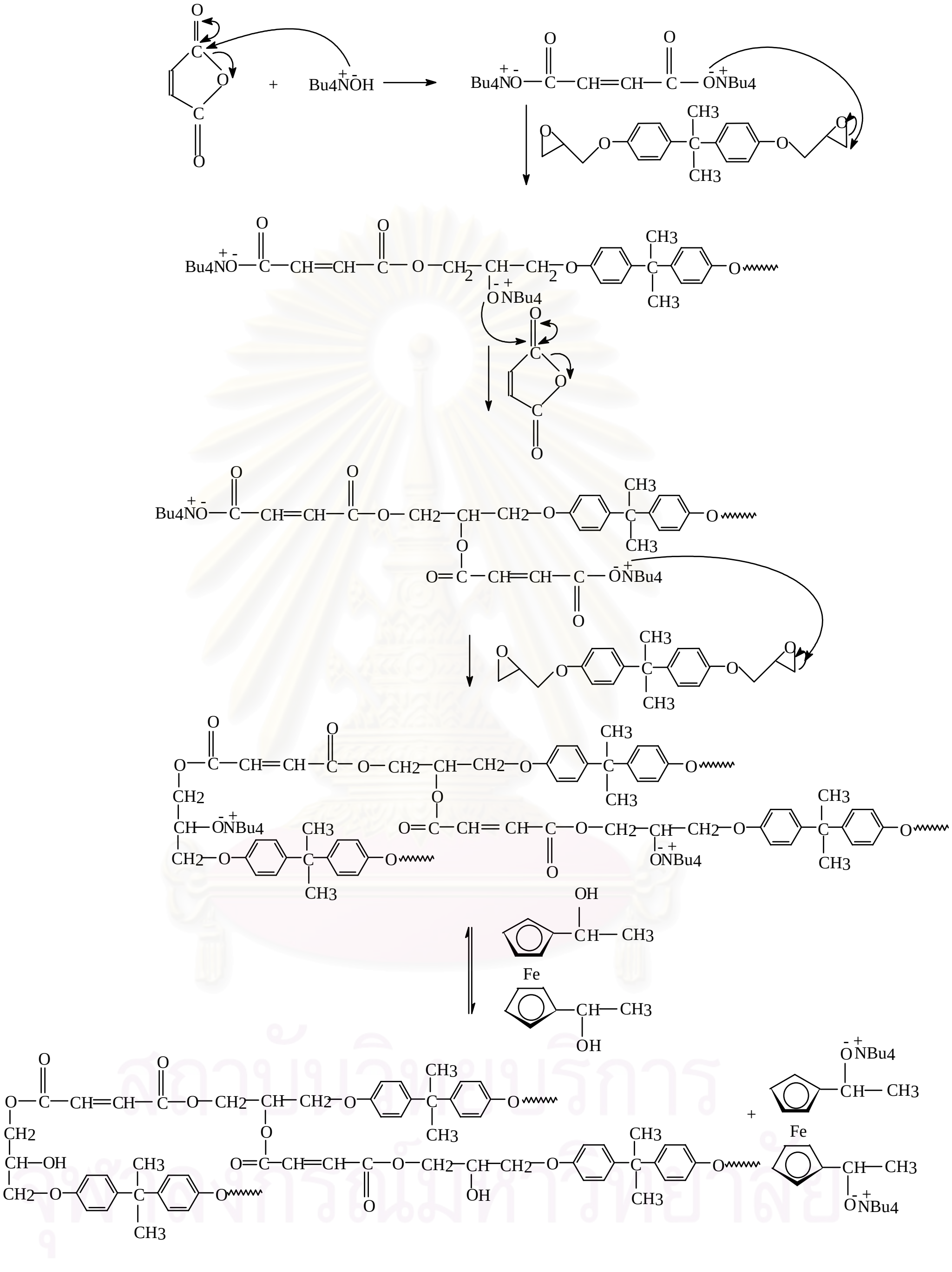
Scheme 3.6 Copolymerization of DGEBA with methyl tetrahydrophthalic anhydride and benzyl dimethylamine



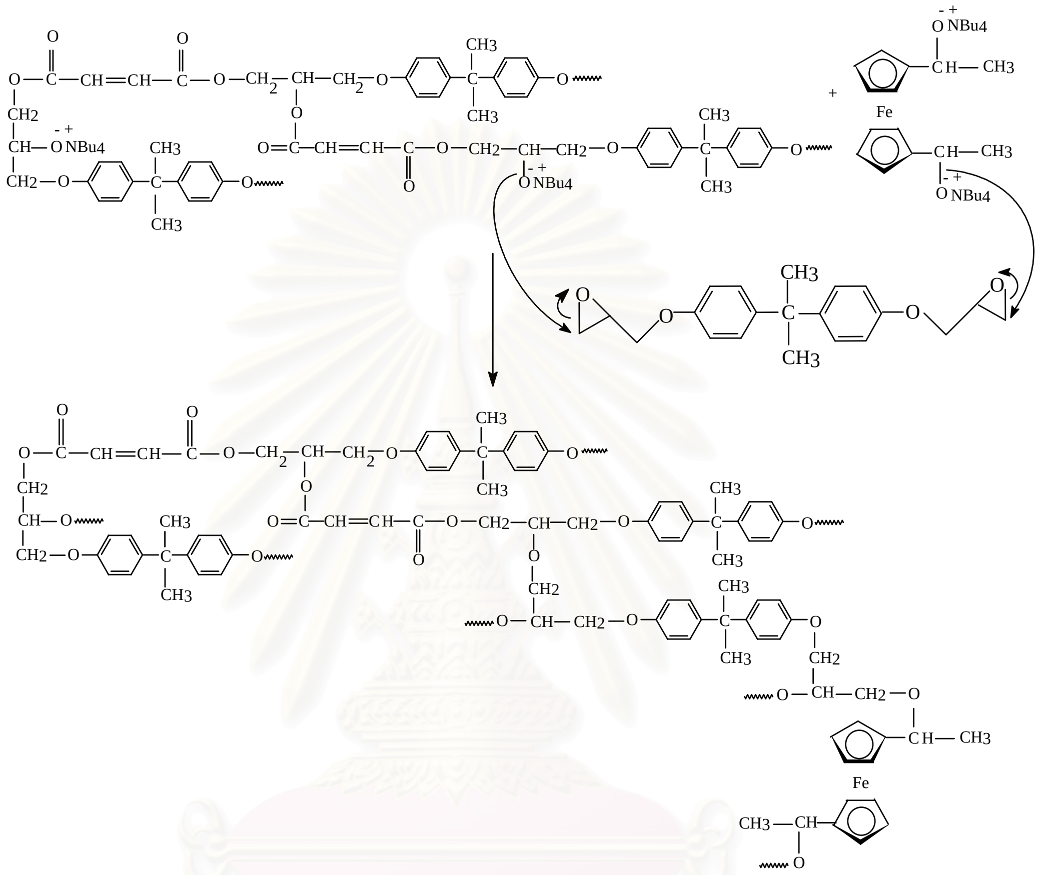
Scheme 3.7 Homopolymerization of DGEBA and benzyl dimethylamine

Therefore, when DGEBA was crosslinked with maleic anhydride and 1,1′–bis(hydroxyethyl)ferrocene in the presence of Bu_4NOH, the expected reaction is the ring opening of maleic anhydride by Bu_4NOH to give carboxylate ions, which can then undergo reaction with DGEBA to give alkoxide groups. These alkoxide groups then open the anhydride rings to yield carboxylate ions, which react with DGEBA to give alkoxide anions. When maleic anhydride was completely reacted, the proton exchange reaction between alkoxide groups and hydroxyl groups of 1,1′–bis(hydroxyethyl)ferrocene would occur. Thus, the alkoxide groups on the polymer chain and those resulting from 1,1′–bis(hydroxyethyl)ferrocene could then open the epoxide rings of DGEBA to yield the crosslinked polymers (Schemes 3.8 and 3.9).

When a mixture of DGEBA : 1,1′–bis(hydroxyethyl)ferrocene : maleic anhydride : Bu_4NOH at the mole ratio of 1 : 0.20 : 0.20 : 0.04 was heated at 120°C for 4 hours (Figure 3.4), the IR absorption band at 917 cm^{-1} became shorter after heating for 1 hour and disappeared after 4 hours. When the reaction was done without catalyst, the IR absorption band at 917 cm^{-1} was still observed after heating at 120°C for 4 hours and the temperature required to complete the reaction was 180°C for 4 hours. This indicated that the crosslinking temperature decreased from 180°C to 120°C when Bu_4NOH was used. The C=O absorption bands of the anhydride group at 1854 and 1777 cm^{-1} also disappeared and there was an appearance of a new ester band at 1731 cm^{-1}.



Scheme 3.8 Proposed mechanism of reaction between DGEBA, 1,1′–bis(hydroxyethyl)ferrocene and maleic anhydride in the presence of Bu_4NOH



Scheme 3.9 Proposed mechanism of the crosslinking reaction of DGEBA with the alkoxide groups on the polymer chain and those generated from 1,1′–bis(hydroxyethyl)ferrocene

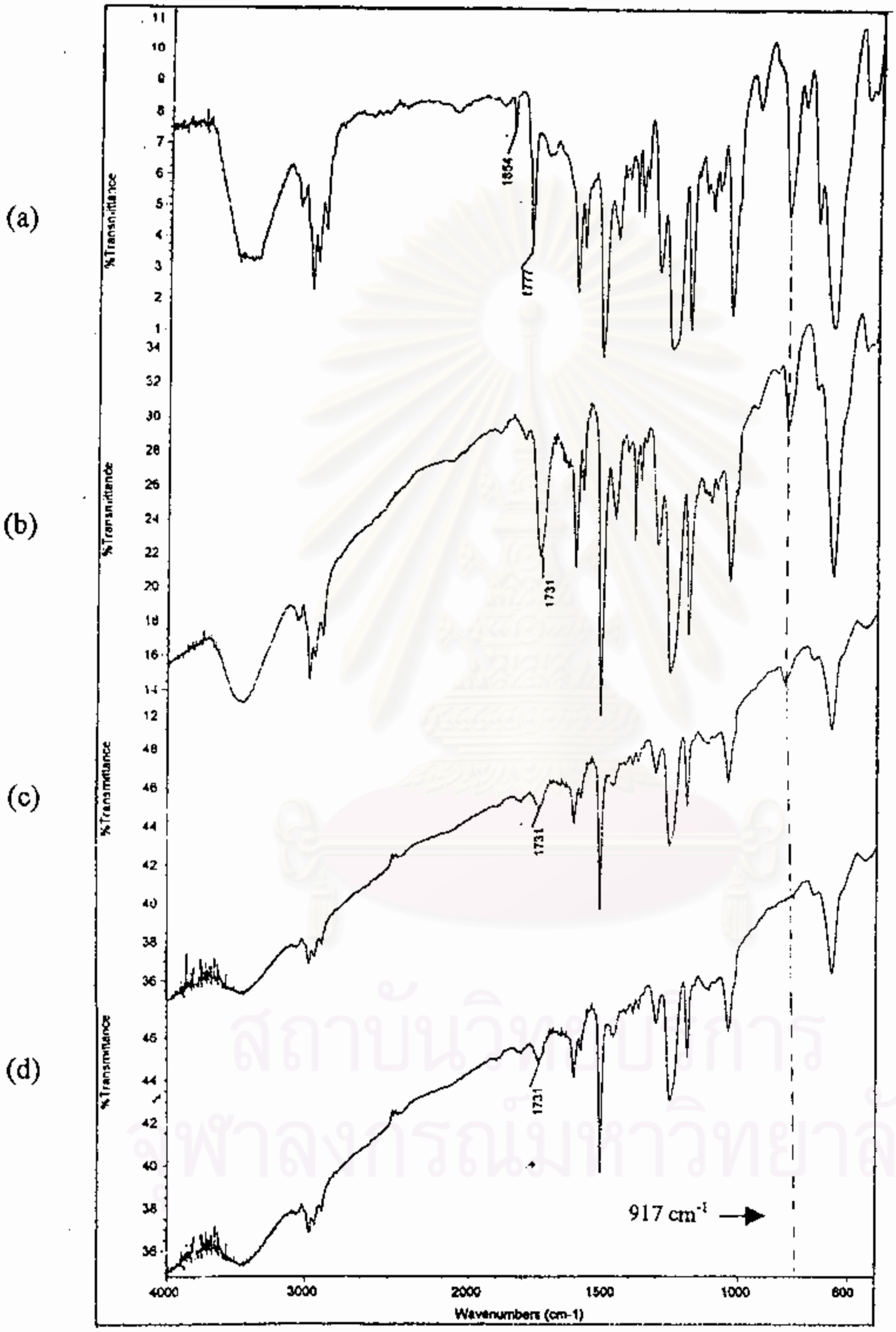


Figure 3.4 IR spectra of DGEBA : 1,1′–bis(hydroxyethyl)ferrocene : MA : Bu_4NOH at the mole ratio of 1 : 0.20 : 0.20 : 0.04 (a) before heating (b) after heating at 120°C for 1 h (c) after 2 h and (d) after 4 h

3.6 Preparation of Ferrocene-Containing Epoxy Polymers

From the previous results, it was found that the crosslinking reaction of DGEBA with the 1,1′–bis(hydroxyethyl)ferrocene and maleic anhydride in the presence of Bu_4NOH at 120°C was completed in 4 hours. Therefore, this crosslinking temperature was chosen in the preparation of polymer samples. The preparation method is described in the experimental section. The time required to complete the crosslinking reaction was determined by observing the disappearance of the IR absorption band of the epoxide ring at 917 cm^{-1}. The ratios of DGEBA : 1,1′–bis(hydroxyethyl)ferrocene : MA were varied to determined the optimum ratio that yielded the polymers with good properties and Bu_4NOH was used in the amount of 20 mole% of 1,1′–bis(hydroxyethyl)ferrocene. For the mole ratio of DGEBA : 1,1′–bis(hydroxyethyl)ferrocene : MA = 1 : 0.20 : 0.20 , 1 : 0.30 : 0.20 and 1 : 0.40 : 0.20, the crosslinking condition was 4 hours at 120°C followed by postcuring at the same temperature for 4 hours. For the mole ratio of DGEBA : 1,1′–bis(hydroxyethyl)ferrocene : MA = 1 : 0.15 : 0.20, the crosslinking condition was 4 hours at 140°C followed by postcuring at the same temperature for 6 hours. This ratio required higher crosslinking temperature and longer time than the other ratios because there was small amount of 1,1′–bis(hydroxyethyl)ferrocene for the crosslinking reaction.

The properties of the polymers prepared without using Bu_4NOH were not studied since high crosslinking reaction temperatures were required.

3.7 Characterization of Ferrocene-Containing Epoxy Polymers

3.7.1 IR Spectroscopy

The ferrocene-containing epoxy polymers obtained from various ratios of DGEBA : 1,1′–bis(hydroxyethyl)ferrocene : MA : Bu_4NOH were characterized by IR spectroscopy. All epoxy polymers gave similar spectra. An example of the IR spectrum of the polymer obtained from the ratio of DGEBA : 1,1′–

bis(hydroxyethyl)ferrocene : MA : Bu_4NOH = 1 : 0.20 : 0.20 : 0.04 is shown in Figure 3.5.

The IR spectrum shows the O-H absorption band of the secondary alcohol at 3300-3500 cm^{-1} and the absorption band of C=O stretching vibration of the ester group at 1731 cm^{-1}. The absorption band at 1634 cm^{-1} is due to C=C stretching vibration. The absorption bands at 1100-1300 cm^{-1} are assigned to be C-O stretching vibrations of ester.

3.7.2 Dynamic Mechanical Analysis (DMA)

Dynamic Mechanical Analysis was employed to determine the glass transition temperature (T_g) of the ferrocene-containing epoxy polymers by observing the maximum value of loss modulus. For example, DMA thermogram of epoxy polymer at the mole ratio of DGEBA : 1,1′–bis(hydroxyethyl)ferrocene : MA = 1 : 0.20 : 0.20 showed a T_g at 81°C (Figure 3.6). The thermogram of ferrocene-containing epoxy polymers obtained from other ratios of starting materials are shown in Figures A.6-8.

Table 3.1 shows the glass transition temperatures of ferrocene-containing epoxy polymers obtained from various formulations. The ratio of 1 : 0.20 : 0.20 exhibit the highest T_g value. When the amount of 1,1′–bis(hydroxyethyl)ferrocene was increased to 0.30 and 0.40, the T_g decreased to 70°C and 59°C, respectively since there might be unreacted 1,1′–bis(hydroxyethyl)ferrocene remaining in the epoxy polymer. The mole ratio of 1 : 0.15 : 0.20 also gave the low T_g since there was only a small amount of 1,1′–bis(hydroxyethyl)ferrocene to undergo the crosslinking reaction.

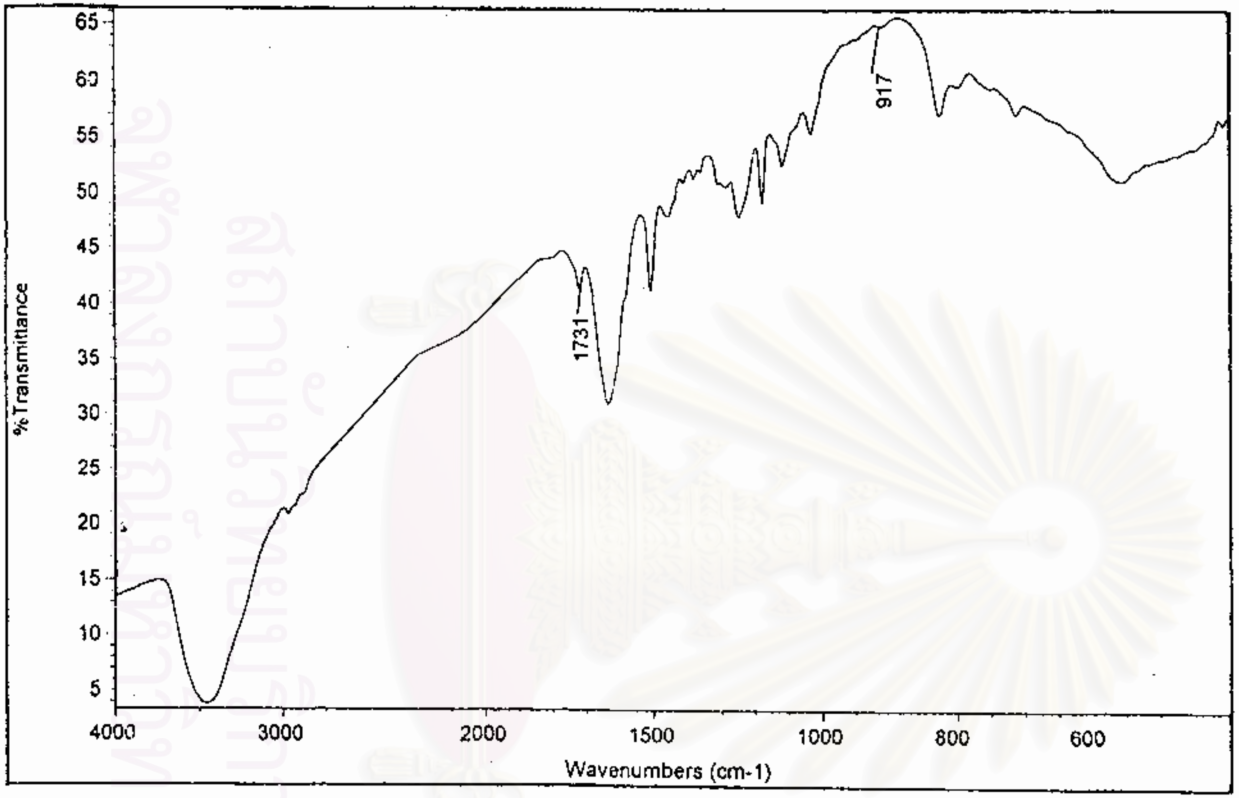


Figure 3.5 IR spectrum of ferrocene-containing epoxy polymer at the mole ratio of DGEBA : 1,1'–bis(hydroxyethyl)ferrocene : MA : Bu_4NOH = 1 : 0.20 : 0.20 : 0.04

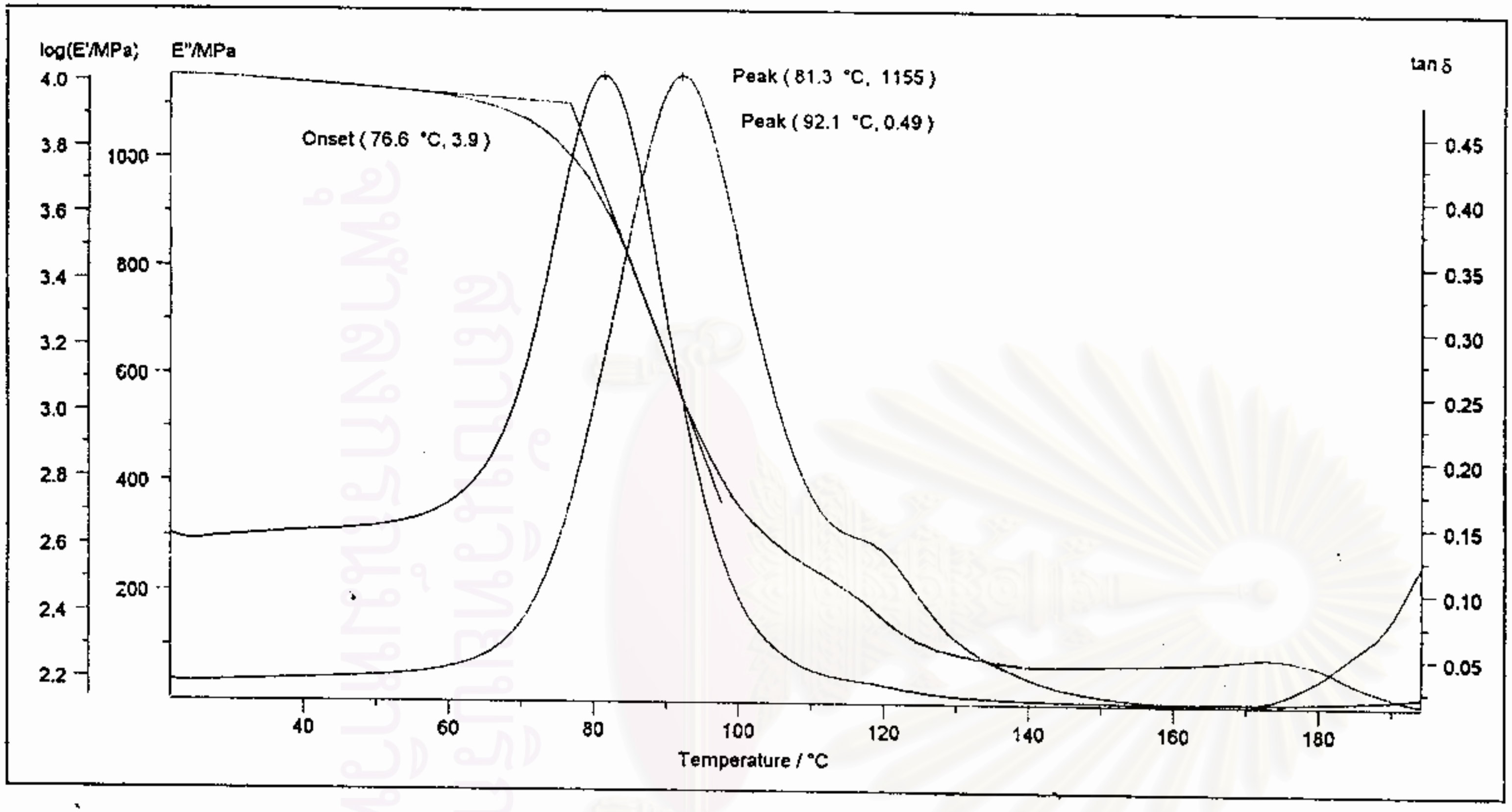


Figure 3.6 DMA thermogram of ferrocene-containing epoxy polymer at the mole ratio of DGEBA : 1,1′–bis(hydroxyethyl)ferrocene : MA : Bu_4NOH = 1 : 0.20 : 0.20 : 0.04

Table 3.1 Glass transition temperature (T_g) of ferrocene-containing epoxy polymers obtained from various mole ratios of DGEBA : 1,1′–bis(hydroxyethyl)ferrocene ($C_{14}H_{18}FeO_2$) : maleic anhydride (MA) : Bu_4NOH

Crosslinking Agent	**Mole ratio of** DGEBA : $C_{14}H_{18}FeO_2$: MA : Bu_4NOH	T_g (°C)
$C_{14}H_{18}FeO_2$ and MA	1 : 0.40 : 0.20 : 0.08	59
	1 : 0.30 : 0.20 : 0.06	70
	1 : 0.20 : 0.20 : 0.04	81
	1 : 0.15 : 0.20 : 0.03	71
Maleic anhydride	1 : 0 : 0.20 : 0.04	81
Diethylenetriamine[a]	-	125
Bu_4NOH	1 : 0 : 0 : 0.04	93

[a] mole ratio of DGEBA : DETA was 1 : 1

3.7.3 Thermal Stability

The thermal stability of the ferrocene-containing epoxy polymers was determined by heating the polymers at 250°C for 48 hours in air. Since T_g of the obtained epoxy polymers were very low, only the mole ratio of 1 : 0.20 : 0.20 was chosen for the study since it had highest glass transition temperature. Table 3.2 shows the weight loss of the epoxy polymers at different times.

Table 3.2 Thermal stability at 250°C of the ferrocene-containing epoxy polymer obtained at the mole ratio of DGEBA : $C_{14}H_{18}FeO_2$: MA : Bu_4NOH = 1 : 0.20 : 0.20 : 0.04

Crosslinking Agent	Mole ratio of DGEBA : $C_{14}H_{18}FeO_2$: MA : Bu_4NOH	% Weight loss at different time			
		12 h	24 h	36 h	48 h
$C_{14}H_{18}FeO_2$ and MA	1 : 0.20 : 0.20 : 0.04	6.9	9.5	11.9	14.3
Maleic anhydride	1 : 0 : 0.20 : 0.04	6.1	6.9	7.4	7.7
Diethylenetriamine[a]	-	7.3	20.7	25.3	26.6
Bu_4NOH	1 : 0 : 0 : 0.04	4.6	5.1	5.5	5.9

[a] mole ratio of DGEBA : DETA was 1 : 1

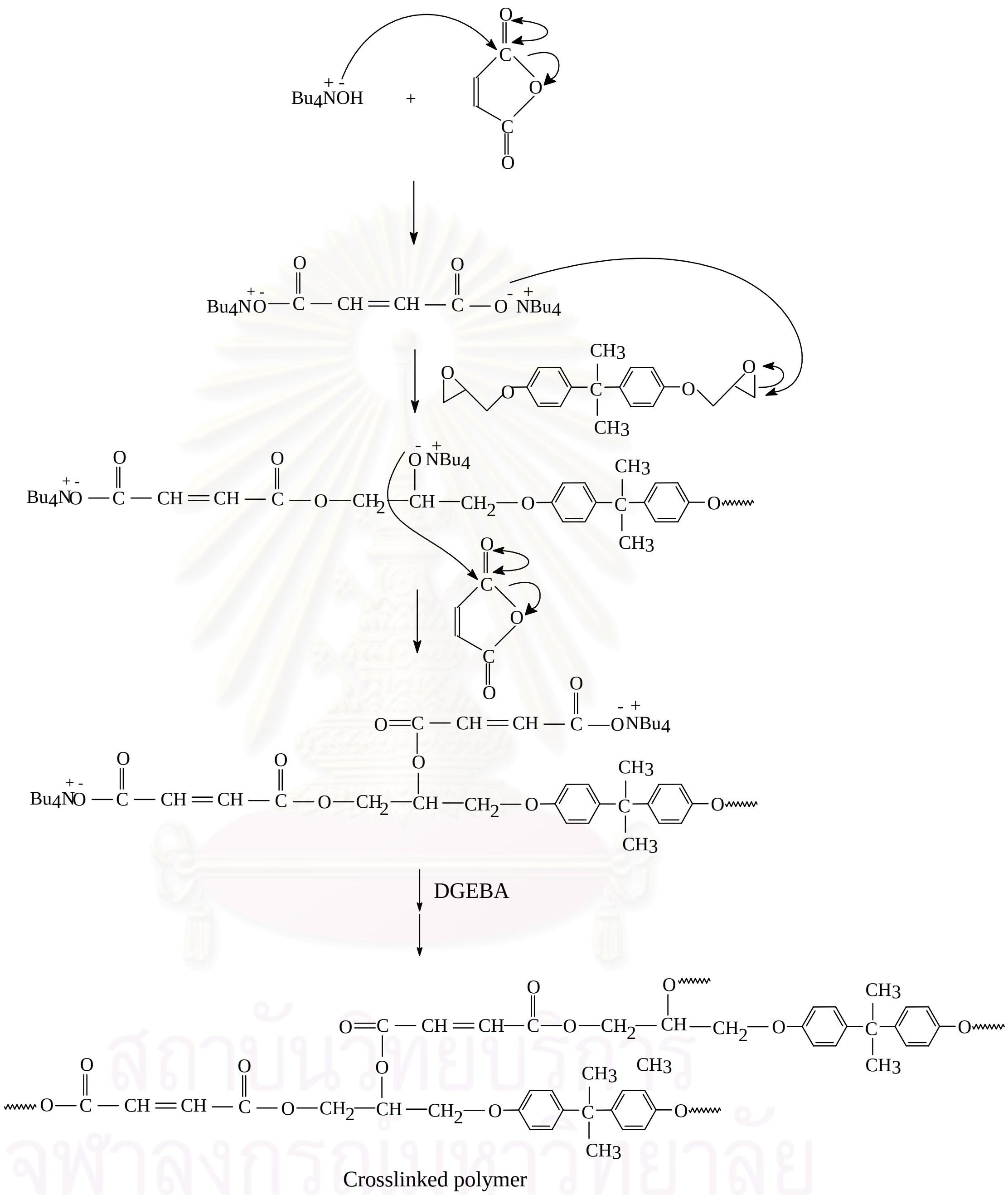
The results indicated that the ferrocene-containing polymers had low T_g and low thermal stability compared with the known polymers obtained from DGEBA : MA : Bu_4NOH and DGEBA : Bu_4NOH. This was probably because of side reactions that occurred during the polymerization. These side reactions could be the crosslinking of DGEBA with maleic anhydride in the presence of Bu_4NOH and the crosslinking of DGEBA with Bu_4NOH (Schemes 3.10 and 3.11). These side crosslinking reactions could occur as well as the expected reaction.

The proposed mechanism of crosslinking of DGEBA with maleic anhydride in the presence of Bu_4NOH is the nucleophilic ring-opening polymerization of maleic anhydride by Bu_4NOH, which could act as a nucleophile to give carboxylate ion which could undergo further reaction with DGEBA to give alkoxide anion. This alkoxide anion could then open the anhydride ring to yield a carboxylate ion, which could undergo reaction with epoxide to yield a crosslinked polymer (Scheme 3.10).

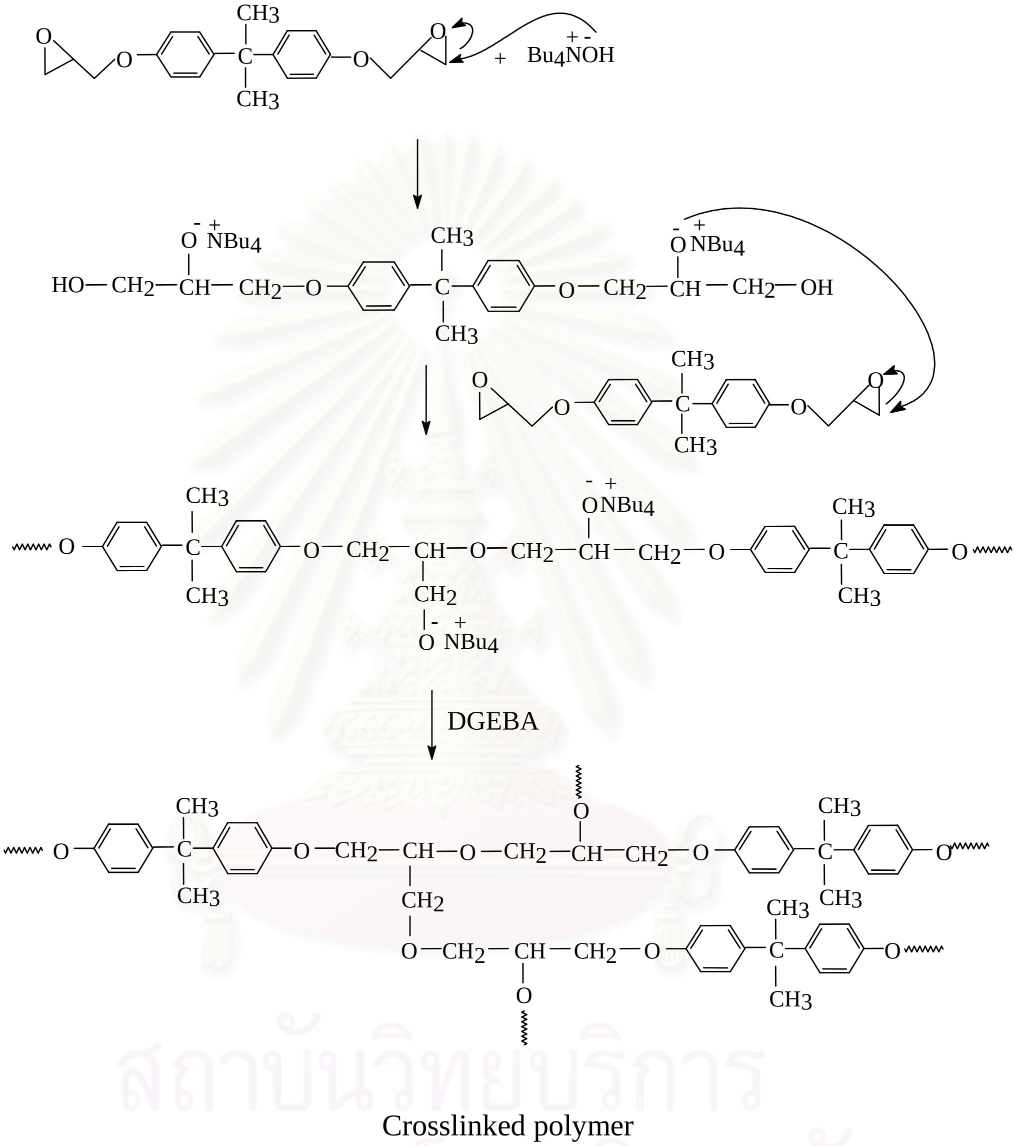
The crosslinking reaction of DGEBA with Bu_4NOH is also a nucleophilic ring-opening polymerization. Bu_4NOH reacted with epoxide ring of DGEBA to give the alkoxide anion, This alkoxide anion could then undergo further reaction with DGEBA. Finally the crosslinked polymer was obtained (Scheme 3.11).

Additionally, 1,1′–bis(hydroxyethyl)ferrocene could remain in the polymer since the proton exchange reaction between the alkoxide groups on the polymer chain and 1,1′–bis(hydroxyethyl)ferrocene might not complete because of the steric effect.

DSC thermograms of DGEBA : Bu_4NOH at the ratios of 1 : 0.04 and 1 : 0.16 are shown in Figures 3.7 and 3.8. The exothermic crosslinking peaks were observed at 113°C and 97°C, respectively. Increase of Bu_4NOH amount resulted in decrease of the crosslinking temperature. If Bu_4NOH underwent a crosslinking reaction with DGEBA, unreacted 1,1′–bis(hydroxyethyl)ferrocene and maleic anhydride would remain in the polymer. As a result, the obtained polymers would have low molecular weight and low degree of crosslinking. Therefore, the synthesized polymer would have low T_g and poor thermal stability.



Scheme 3.10 Crosslinking of DGEBA with maleic anhydride in the presence of Bu_4NOH



Scheme 3.11 Crosslinking of DGEBA with Bu_4NOH

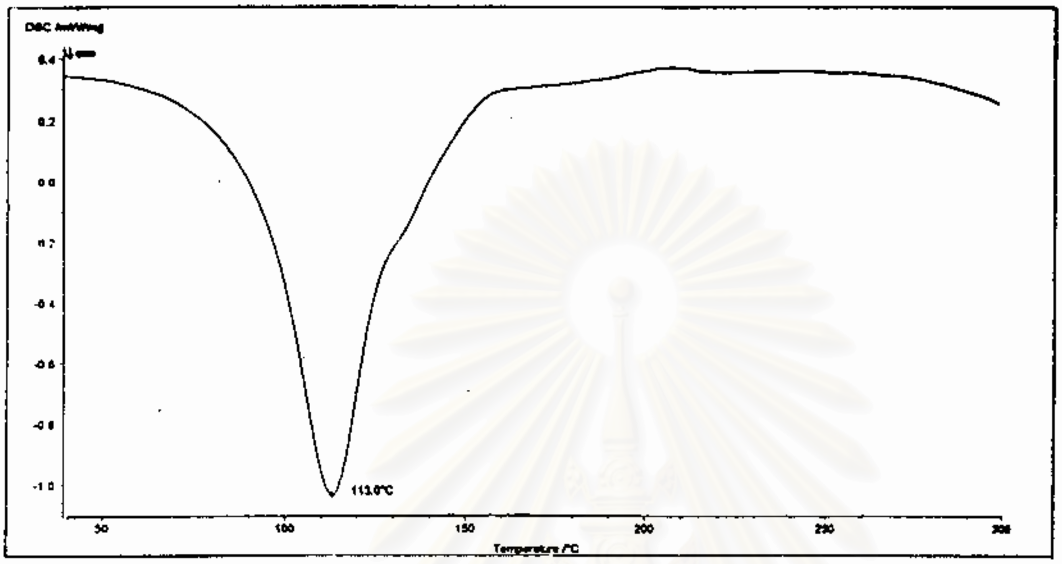


Figure 3.7 DSC thermogram of DGEBA : Bu_4NOH at the mole ratio of 1 : 0.04

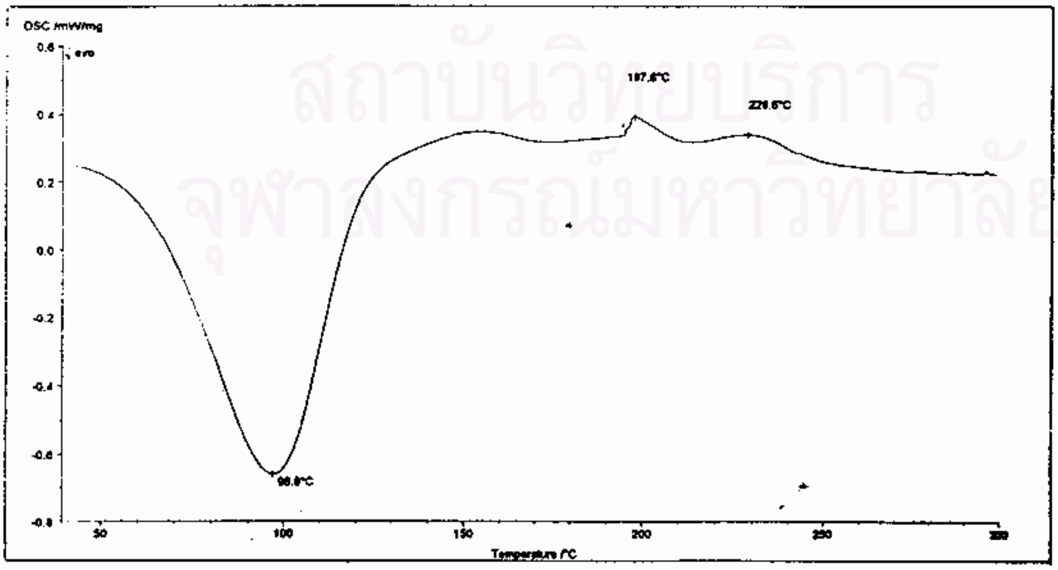
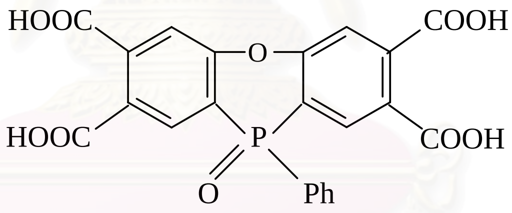


Figure 3.8 DSC thermogram of DGEBA : Bu_4NOH at the mole ratio of 1 : 0.16

Part 2 Use of 1,1′-ferrocenedicarboxylic acid as a Crosslinking Agent

The results from the previous part showed that use of 1,1′–bis(hydroxyethyl)ferrocene as a crosslinking agent gave polymers with low T_g and poor thermal stability. Moreover, 1,1′–bis(hydroxyethyl)ferrocene was difficult to prepare and purify. Therefore, 1,1′-ferrocenedicarboxylic acid was considered since it was easy to prepare and to purify. In this part, the use of 1,1′-ferrocenedicarboxylic acid as a crosslinking agent for DGEBA was studied.

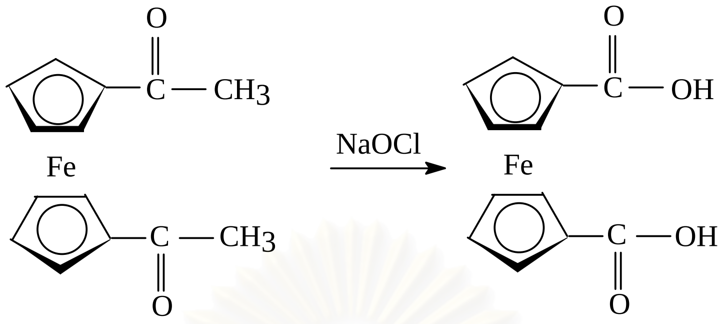
Crosslinking of DGEBA with carboxylic acid derivatives is known. Wang and Shau[19] synthesized phosphorylated epoxy polymer by crosslinking of DGEBA with 10-phenylphenoxa-phosphine-3,8-tetracarboxylic acid-10-oxide (PDAC) (Scheme 3.12). The resulting polymers showed good thermal stability and flame resistance. Therefore, 1,1′-ferrocenedicarboxylic acid should be able to undergo the crosslinking reaction with DGEBA in the same manner as PDAC.



Scheme 3.12 The structure of PDAC

3.8 Synthesis of 1,1′-ferrocenedicarboxylic acid

1,1′-Ferrocenedicarboxylic acid was synthesized from 1,1′-diacetylferrocene using sodium hypochlorite an oxidizing agent[20] (Scheme 3.13).



Scheme 3.13 Synthesis of 1,1′-ferrocenedicarboxylic acid

The 1,1′-ferrocenedicarboxylic acid was characterized by IR and ^{1}H NMR spectroscopy. In IR spectrum (Figure A.9), the absorption band at 3500-3300 cm^{-1} is due to the O-H stretching vibration. The absorption band of C=O stretching vibration at 1680 cm^{-1} is apparent.

^{1}H NMR spectrum (Figure A.10) shows that the aromatic protons signals appear as two singlets at 4.68 ppm (4H) and 4.46 ppm (4H).

3.9 Reaction between DGEBA and 1,1′-ferrocenedicarboxylic acid

3.9.1 Differential Scanning Calorimetry (DSC)

DSC was employed to determine the crosslinking reaction temperature. The DSC thermograms were obtained from mixtures of DGEBA : 1,1′-ferrocenedicarboxylic acid at the mole ratios of 1 : 0.20 and 1 : 0.80 (Figures 3.9 and 3.10). It was found that the mole ratio 1 : 0.20 and 1 : 0.80 gave exothermic crosslinking peaks with the maxima at 227 and 235°C, respectively, followed by decomposition of the materials.

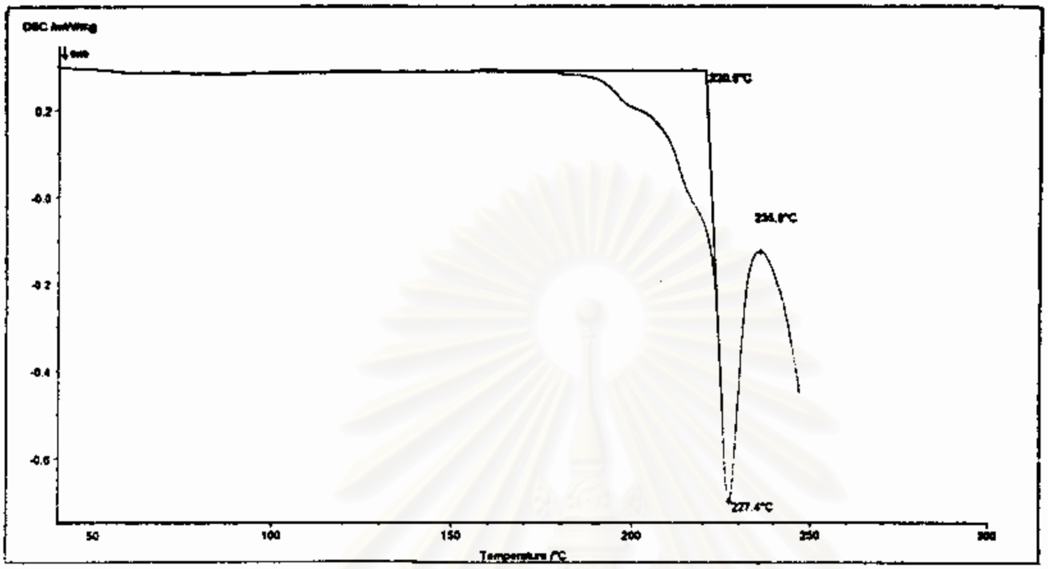


Figure 3.9 DSC thermogram of DGEBA : 1,1′-ferrocenedicarboxylic acid at the mole ratio of 1 : 0.20

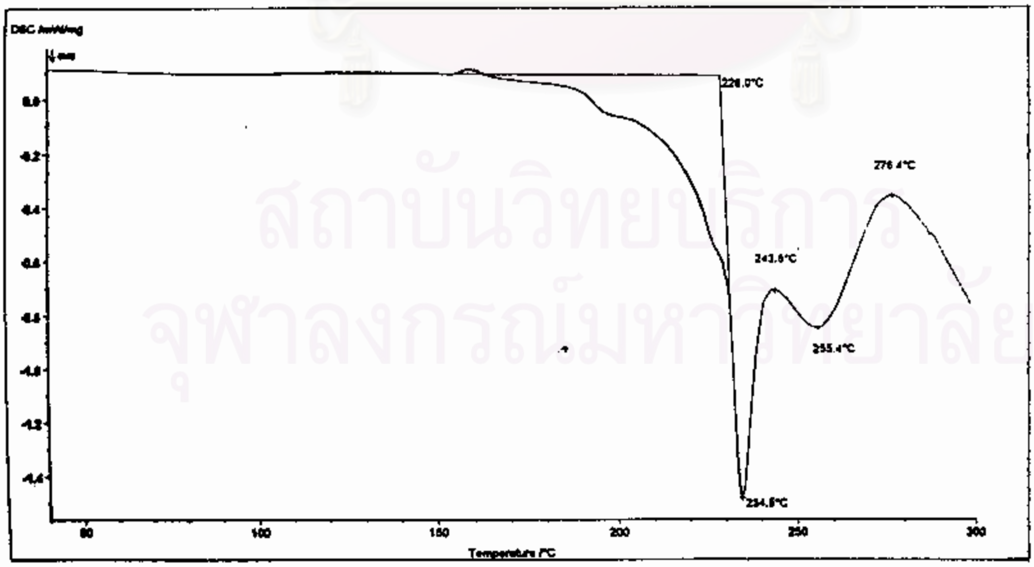


Figure 3.10 DSC thermogram of DGEBA : 1,1′-ferrocenedicarboxylic acid at the mole ratio of 1 : 0.80

3.9.2 Infrared Spectroscopy (IR)

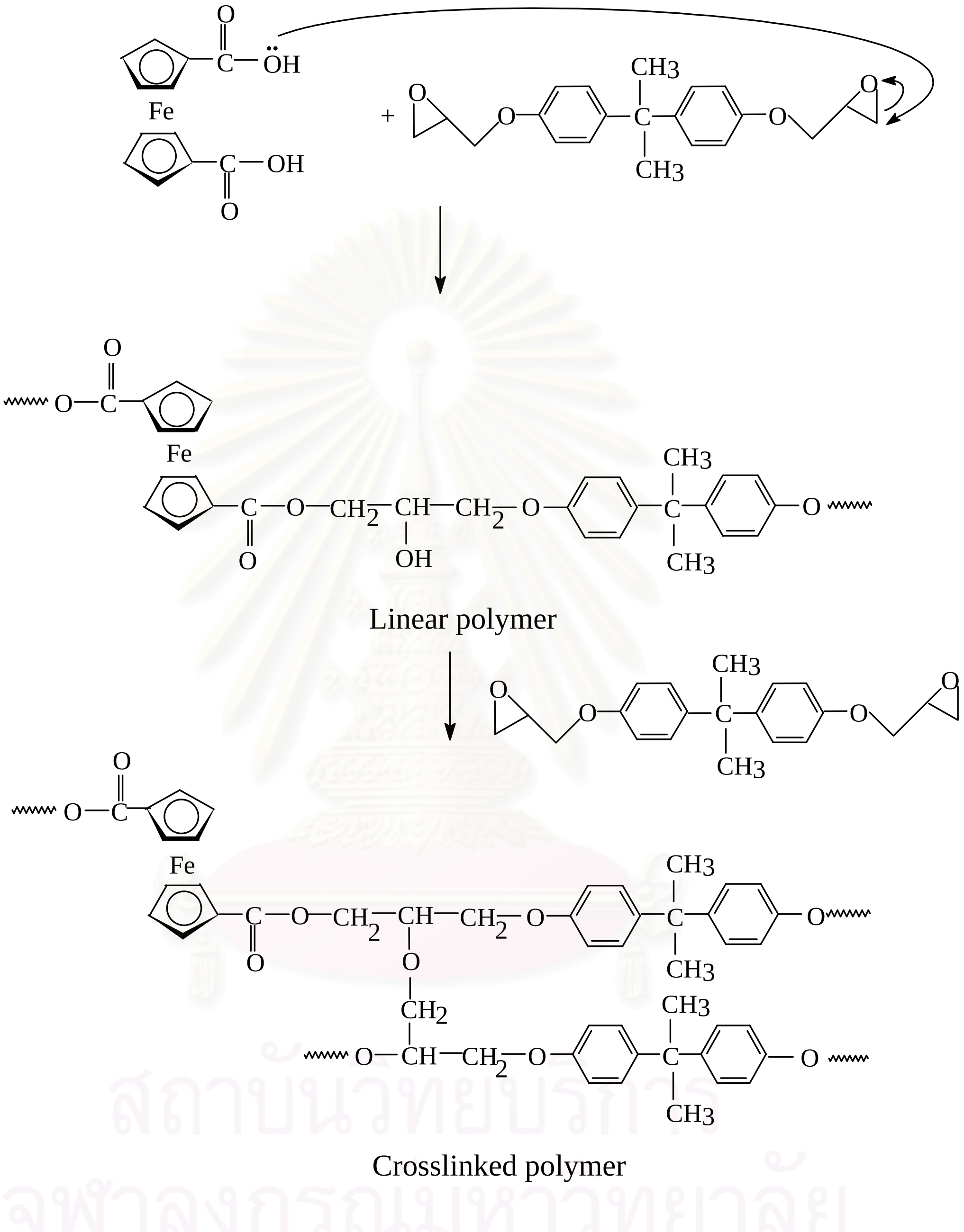
IR was used to determine the optimum crosslinking temperature and time. The proposed crosslinking mechanism is that the carboxylic groups of 1,1′-ferrocenedicarboxylic acid react with DGEBA by opening the epoxide rings to give linear polymer. Then, the generated hydroxyl groups undergo further reaction with DGEBA to give the crosslinked polymer that contains ferrocene unit in the polymer chain (Scheme 3.14).

The reaction was followed by disappearance of the IR absorption band of the C=O of the carboxylic group of 1,1′-ferrocenedicarboxylic acid and the epoxide group of DGEBA.

From previous DSC thermograms, the reaction of DGEBA : 1,1′-ferrocenedicarboxylic at the mole ratio of 1 : 0.20 showed the initial temperature of the crosslinking peak at 180°C. Therefore, this temperature was chosen for the crosslinking reaction, since the crosslinked material decomposed at high temperature.

The IR spectra were obtained from a mixture of DGEBA : 1,1′-ferrocenedicarboxylic acid at the mole ratio of 1 : 0.20 at the temperature of 180°C (Figure 3.11). It was found that after heating at 180°C for 1 hour, 1,1′-ferrocenedicarboxylic acid reacted with DGEBA since the IR absorption band of the carboxylic group of 1,1′-ferrocenedicarboxylic acid at 1680 cm^{-1} disappeared and ester groups at 1710 cm^{-1} could be observed.

If the crosslinking reaction was completed, the IR absorption band at 917 cm^{-1} due to the epoxide groups of DGEBA should disappear. After heating for 4 hours, the absorption band at 917 cm^{-1} was still observed. Therefore, the crosslinking reaction was not completed.



Scheme 3.14 Proposed mechanism of reaction between DGEBA and 1,1′–ferrocenedicarboxylic acid

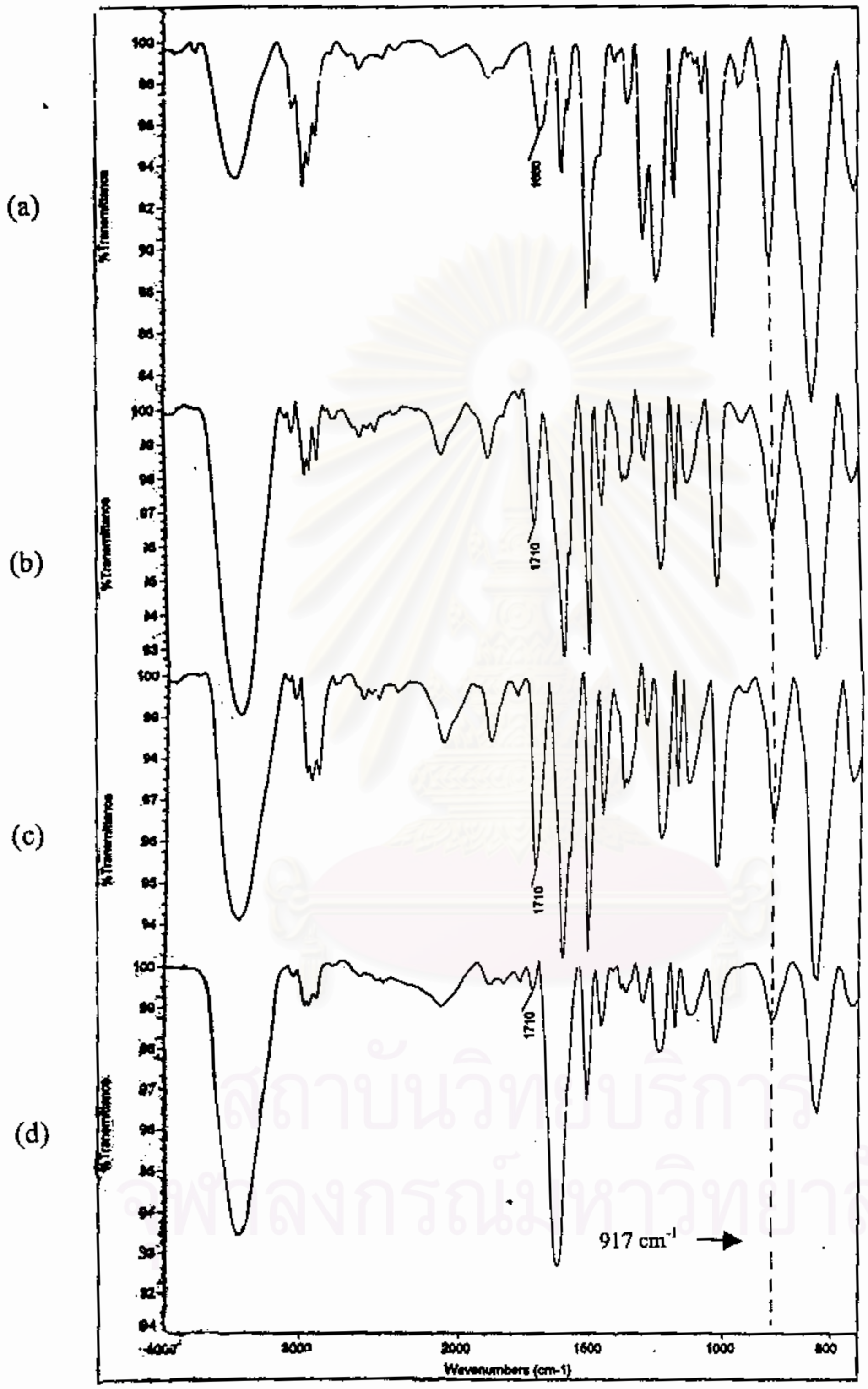


Figure 3.11 IR spectra of DGEBA : 1,1′–ferrocenedicarboxylic acid at the mole ratio of 1 : 0.20 (a) before heating (b) after heating at 180°C for 1 h (c) after 2 h and (d) after 4 h

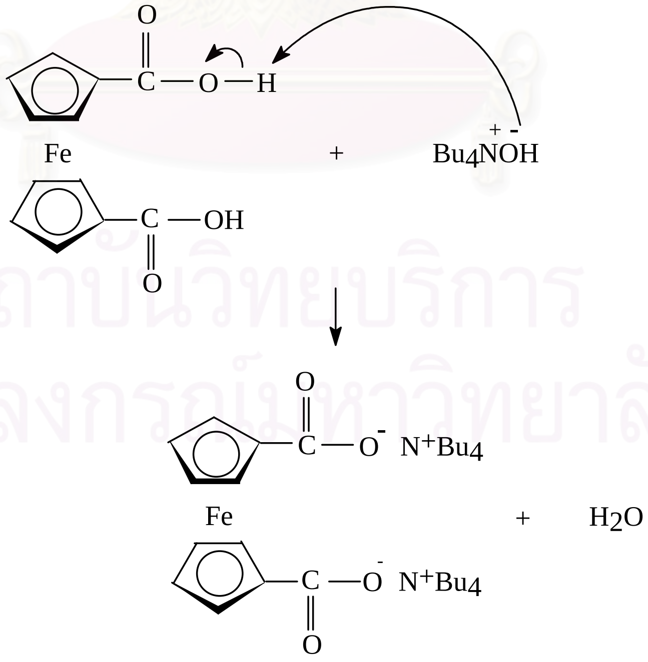
3.10 Effect of Catalyst

The previous DSC and IR experiments showed that the crosslinking reaction of DGEBA and 1,1′-ferrocenedicarboxylic acid required high temperature. Therefore, tetrabutylammonium hydroxide (Bu_4NOH) was chosen as a catalyst in order to reduce the crosslinking temperature.

3.10.1 Reaction between 1,1′-ferrocenedicarboxylic acid and Bu_4NOH

It was important to study the reaction between Bu_4NOH and 1,1′-ferrocenedicarboxylic acid. The expected reaction is the proton removal from of the carboxylic group by Bu_4NOH to form 1,1′- ferrocenedicarboxylate (Scheme 3.15).

When a mixture of 1,1′- ferrocenedicarboxylic acid : Bu_4NOH at the mole ratio of 1 : 0.50 was heated at 130°C for 3 hours, the IR spectra (Figure 3.12) showed that the band intensity of carboxylic band at 1680 cm^{-1} decreased. Two new absorption bands at 1644 and 1560 cm^{-1} due to carboxylate ion could be observed.



Scheme 3.15 Reaction between 1,1′-ferrocenedicarboxylic acid and Bu_4NOH

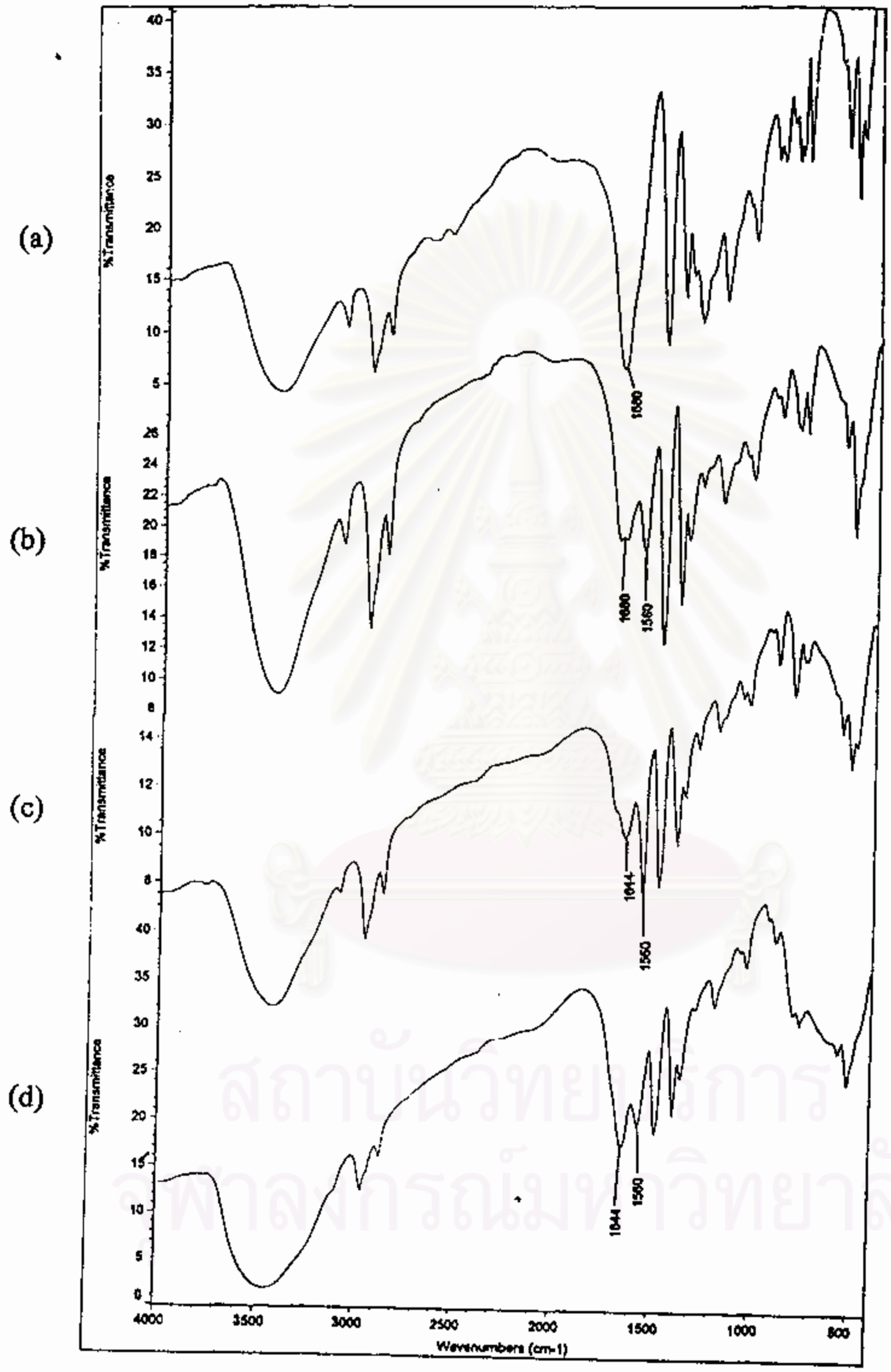
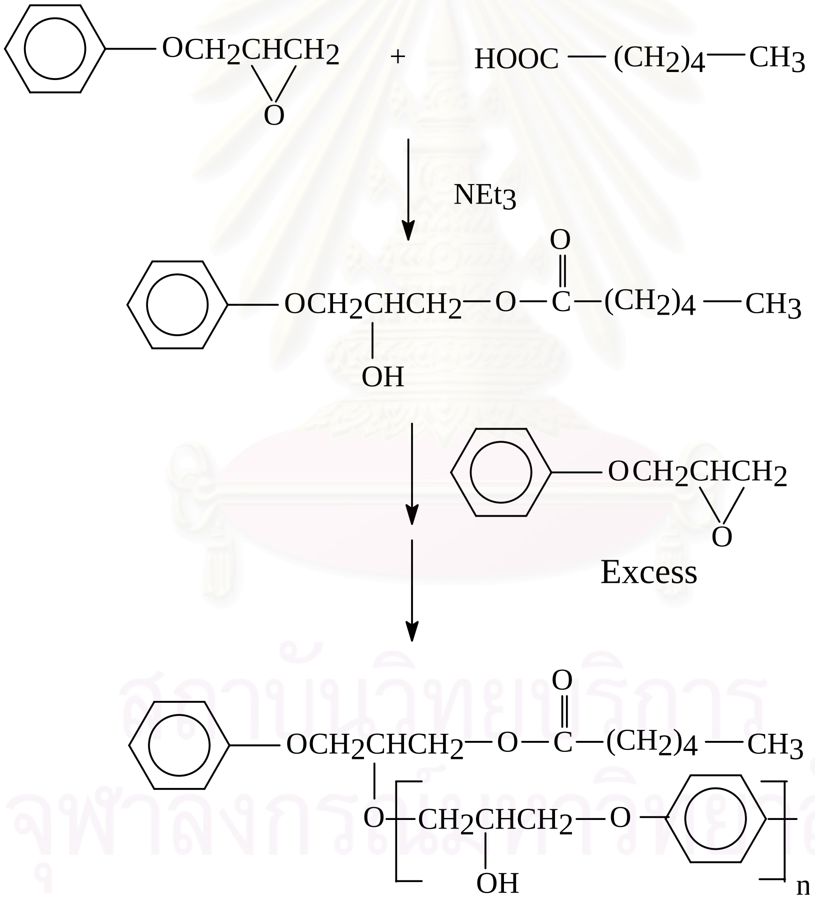


Figure 3.12 IR spectra of 1,1′–ferrocenedicarboxylic acid : Bu$_4$NOH at the mole ratio of 1 : 0.50 (a) before heating (b) after heating at 130°C for 30 min (c) after 1 h and (d) after 3 h

3.10.2 Reaction between Styrene Oxide and 1,1′-ferrocenedicarboxylic acid in the Presence of Bu_4NOH

Matejka et al.[21] studied the base catalyzed reaction between epoxide and a carboxylic acid using a model system of phenylglycidyl ether and caproic acid in the presence of triethylamine (Scheme 3.16). The reaction between phenylglycidyl ether and caproic acid was markedly preferred. With phenylglycidyl ether in excess, polyether was formed only after caproic acid had been consumed.



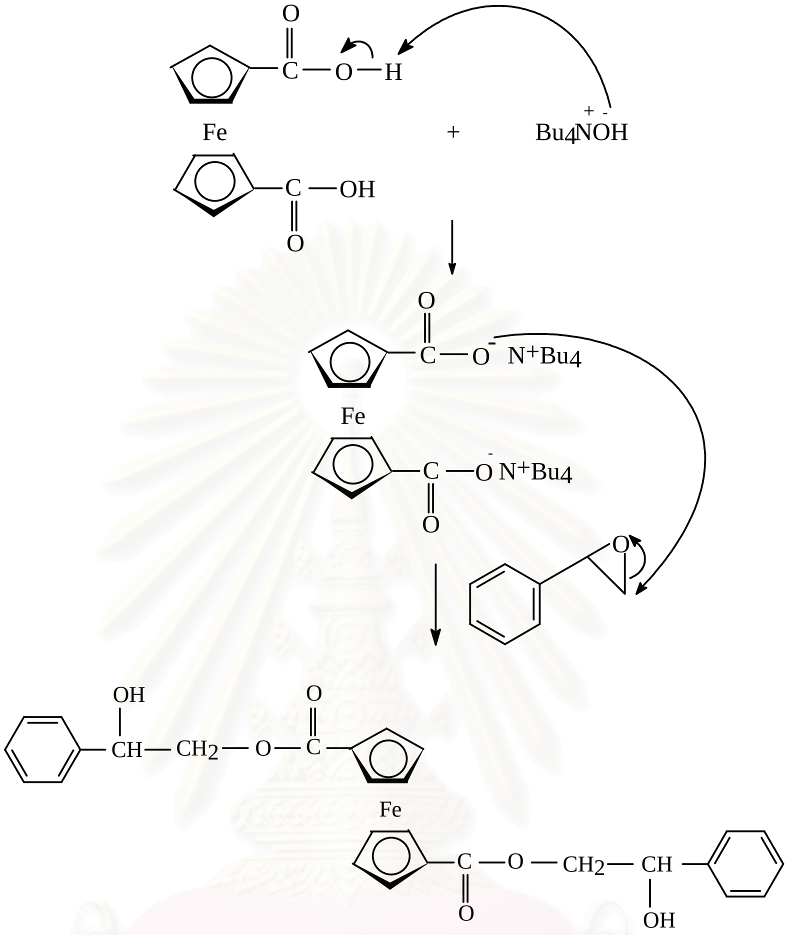
Scheme 3.16 Reaction of phenylglycidyl ether and caproic acid in the presence of triethylamine

Therefore, in the case of the reaction between 1,1′-ferrocenedicarboxylic acid and DGEBA, the reaction between 1,1′-ferrocenedicarboxylic acid and styrene oxide in the presence of Bu_4NOH was studied as the model system. The expected reaction is the ring opening of epoxide ring in styrene oxide by the carboxylic group in 1,1′-ferrocenedicarboxylic acid to give 1,1′-(2-hydroxy-2-phenyl ethylcarboxylate)-ferrocene (Scheme 3.17).

The product was characterized by IR, ^{1}H NMR and ^{13}C NMR spectroscopy. From IR spectrum (Figure A.11), the absorption band at 3500-3300 cm^{-1} is due to the O-H stretching vibration. The absorption band of C=O stretching vibration of the ester group at 1700 cm^{-1} is apparent. The absorption bands at 1280 and 1150 cm^{-1} are C-O stretching vibration of the ester group.

^{1}H NMR spectrum (Figure A.12) indicated that the aromatic proton signals of benzene and ferrocene units appear as multiplets at 7.50-7.24 and 4.51-4.27 ppm, respectively. The methine protons signal appears as multiplet at 5.12 ppm. The methylene protons signal appears as multiplet at 4.81 ppm. The hydroxyl protons signal appears as a broad singlet at 3.73 ppm.

^{13}C NMR spectrum (Figure A.13) shows the signal of the ester carbon at 171.1 ppm. The ferrocene carbons signals appear at 72.7, 72.3 and 72.2 ppm. The aromatic carbons signals of benzene rings appear at 140.1, 128.5, 128.0 and 126.3 ppm. The methylene and methine carbon signals can be observed at 72.1 and 69.7 ppm, respectively.



Scheme 3.17 Reaction between 1,1′-ferrocenedicarboxylic acid and styrene oxide in the presence of Bu_4NOH

3.10.3 Reaction between DGEBA and 1,1′-ferrocenedicarboxylic acid in the Presence of Bu_4NOH

3.10.3.1 Differential Scanning Calorimetry (DSC)

The DSC thermograms were obtained from different mole ratios of 1,1′-ferrocenedicarboxylic acid and Bu_4NOH. The mole ratio of DGEBA : 1,1′-ferrocenedicarboxylic acid employed was 1 : 0.20 and the amounts of Bu_4NOH

employed were 0.40, 0.16, 0.12, 0.08 and 0.04. All thermograms (Figures 3.13-3.17) showed exothermic peaks in the range of 101-129°C which were due to the crosslinking reaction of DGEBA with 1,1′-ferrocenedicarboxylate. The crosslinking temperature decreased when the amount of the Bu$_4$NOH was increased.

When the reaction mixture contained a high amount of Bu$_4$NOH (Figure 3.13), the crosslinked polymer decomposed at the starting temperature of 210°C. This is probably due to the side reaction, since Bu$_4$NOH would react with DGEBA instead of 1,1′- ferrocenedicarboxylic acid (Scheme 3.11). Thus, the resulting polymer would have a low molecular weight and low degree of crosslinking.

When the amount of Bu$_4$NOH was 0.04, there was another exothermic peak with the peak maximum at 197°C. This is because the amount of Bu$_4$NOH was not enough to convert all of 1,1′-ferrocenedicarboxylic acid to 1,1′-ferrocenedicarboxylate. Therefore, the unreacted 1,1′-ferrocenedicarboxylic acid underwent the crosslinking reaction with DGEBA at 197°C which was in the same temperature range observed in DSC thermogram of the crosslinking reaction without Bu$_4$NOH (Figure 3.9).

When the amount of Bu$_4$NOH was increased to 0.08, 0.12 and 0.16, the exothermic peak at 197°C disappeared since there was enough Bu$_4$NOH to convert all of 1,1′- ferrocenedicarboxylic acid to carboxylate ion.

Comparing between Figures 3.14 and 3.18, when the amount of 1,1′-ferrocenedicarboxylic acid was increased from 0.20 to 0.80, the crosslinking peak maximum of the reaction between 1,1′- ferrocenedicarboxylate and DGEBA shifted from 110°C to 126°C. This probably because there was not enough Bu$_4$NOH to convert all 1,1′- ferrocenedicarboxylic acid to its carboxylate ion. This was supported by the observation of the crosslinking peak at 197°C due to the reaction between DGEBA and 1,1′- ferrocenedicarboxylic acid. Furthermore, the crosslinked polymer that contained high amount of 1,1′- ferrocenedicarboxylic acid showed more decomposition because there might be unreacted 1,1′- ferrocenedicarboxylic acid left in the polymer.

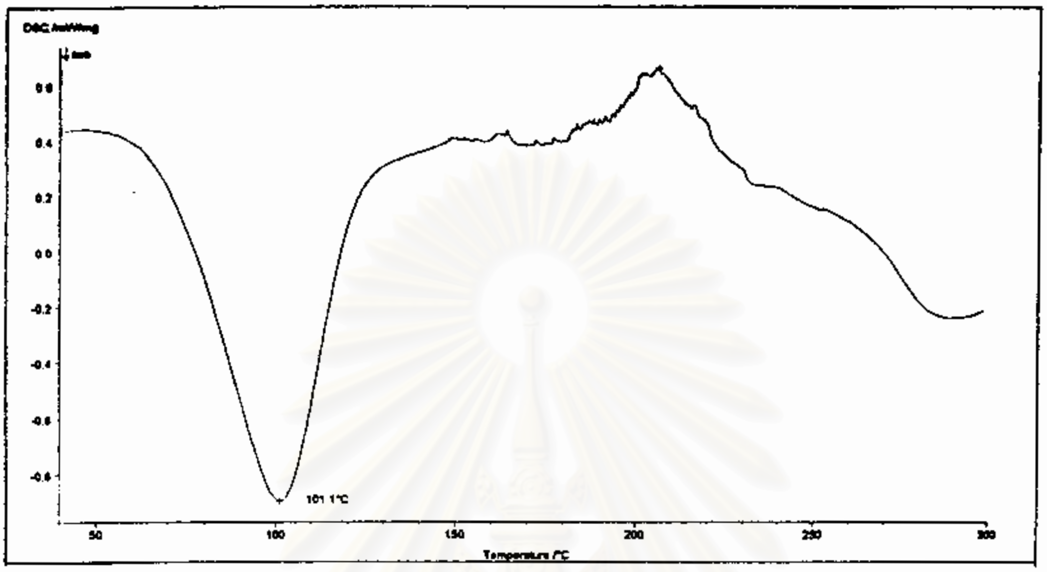


Figure 3.13 DSC thermogram of DGEBA : 1,1′-ferrocenedicarboxylic acid : Bu_4NOH at the mole ratio of 1 : 0.20 : 0.40

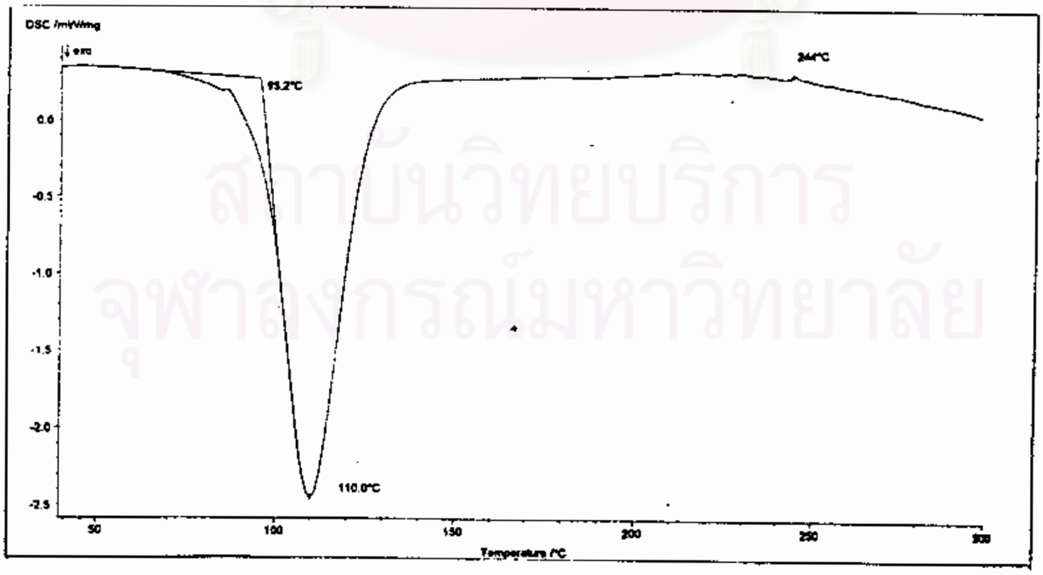


Figure 3.14 DSC thermogram of DGEBA : 1,1′-ferrocenedicarboxylic acid : Bu_4NOH at the mole ratio of 1 : 0.20 : 0.16

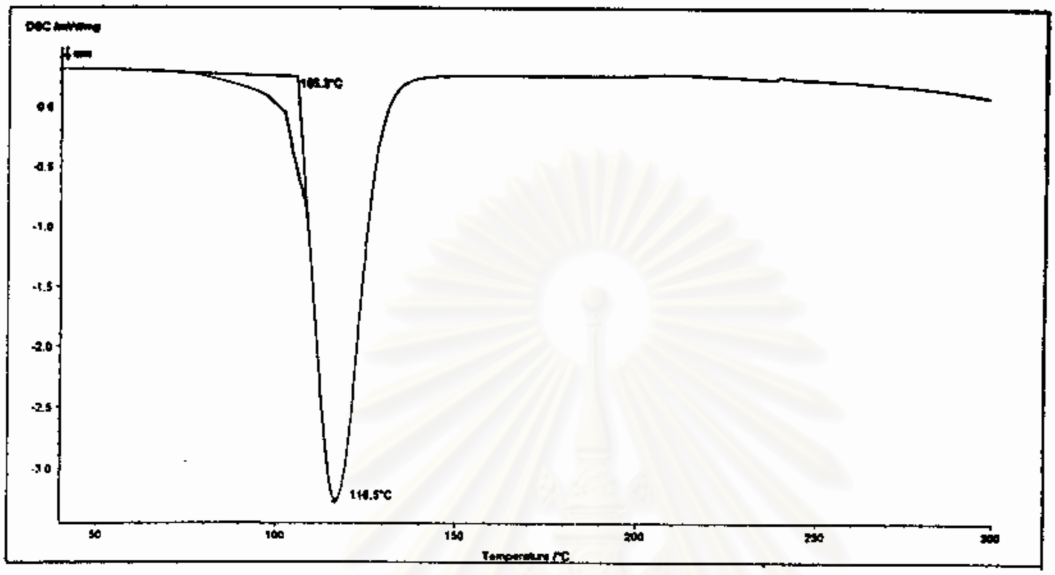


Figure 3.15 DSC thermogram of DGEBA : 1,1′-ferrocenedicarboxylic acid : Bu_4NOH at the mole ratio of 1 : 0.20 : 0.12

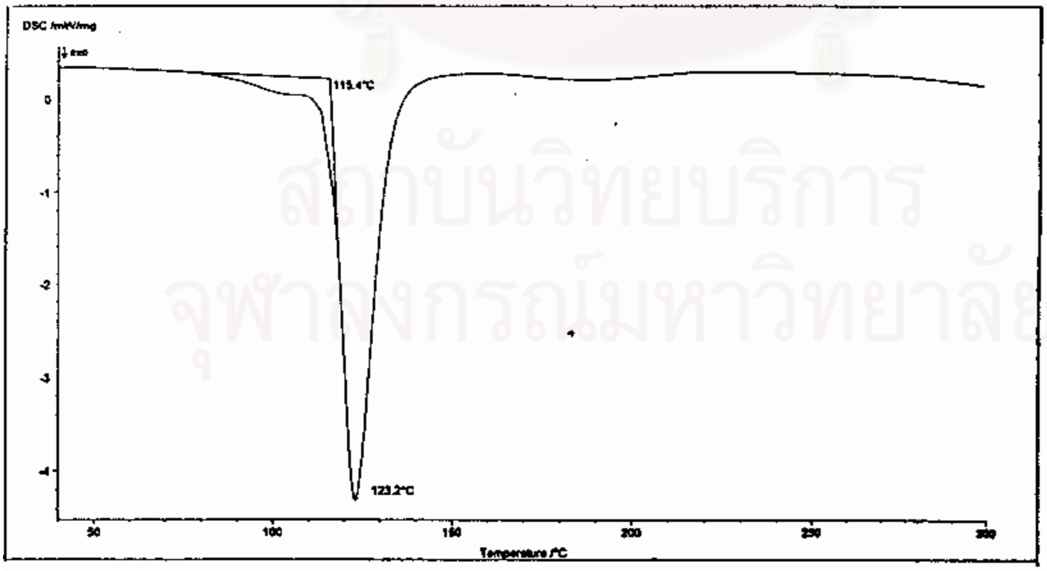


Figure 3.16 DSC thermogram of DGEBA : 1,1′-ferrocenedicarboxylic acid : Bu_4NOH at the mole ratio of 1 : 0.20 : 0.08

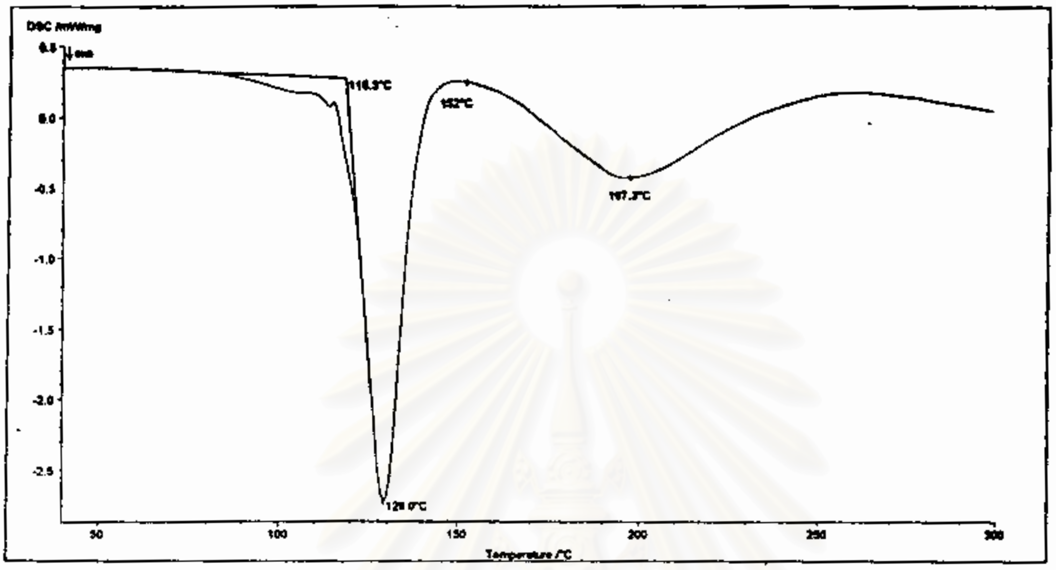


Figure 3.17 DSC thermogram of DGEBA : 1,1′-ferrocenedicarboxylic acid : Bu_4NOH at the mole ratio of 1 : 0.20 : 0.04

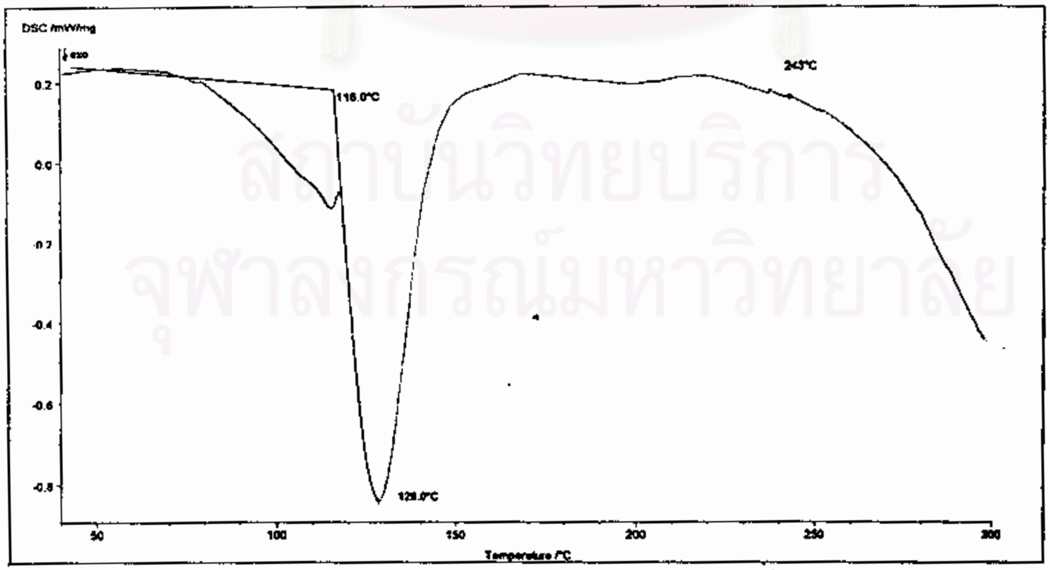


Figure 3.18 DSC thermogram of DGEBA : 1,1′-ferrocenedicarboxylic acid : Bu_4NOH at the mole ratio of 1 : 0.80 : 0.16

3.10.3.2 Infrared Spectroscopy (IR)

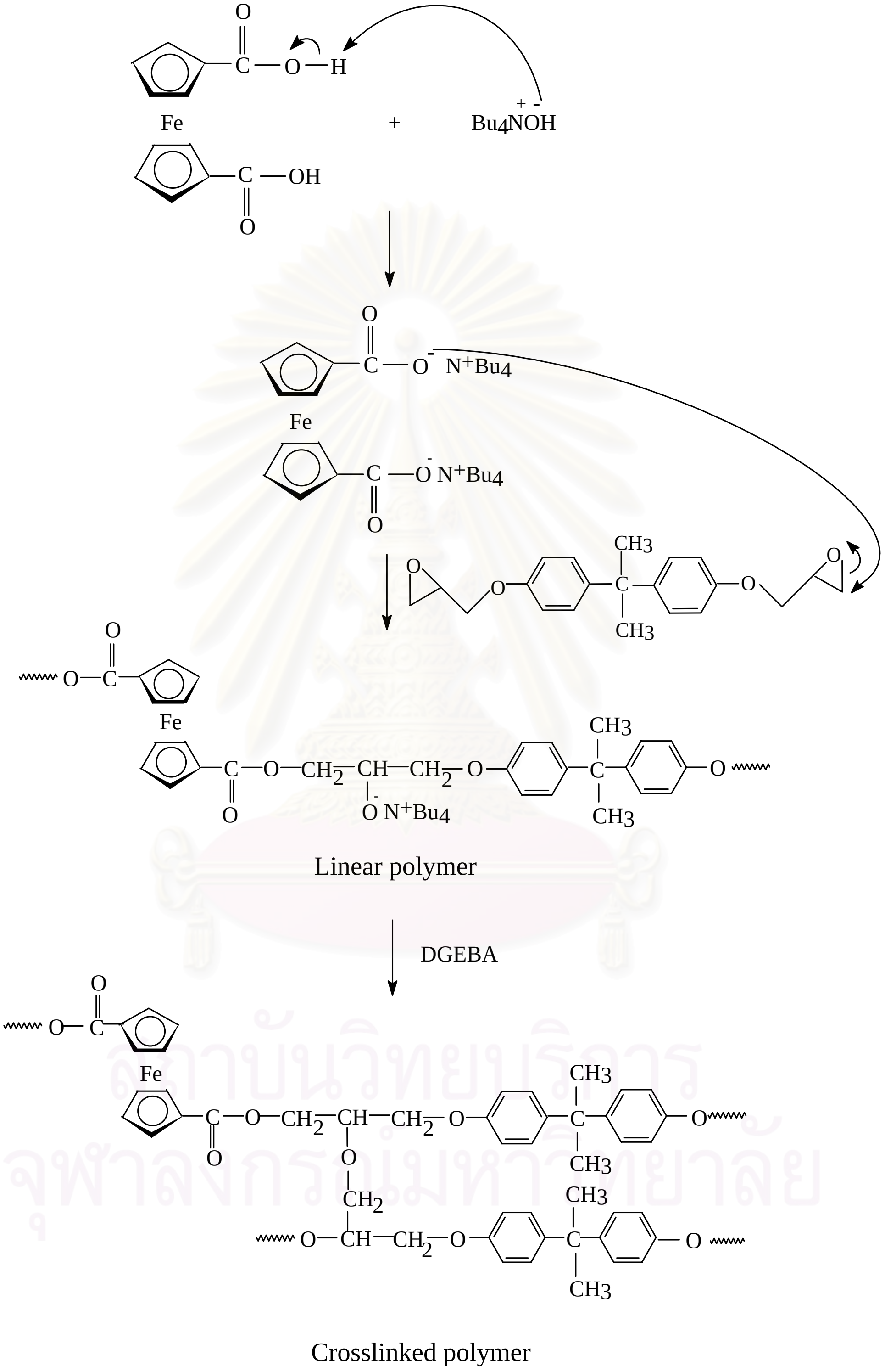
IR was used to determine the optimum crosslinking temperature and time. The proposed crosslinking mechanism is that Bu_4NOH abstracts protons from 1,1′-ferrocenedicarboxylic acid to give the carboxylate ions as discussed in 3.10.1 which undergo reaction with DGEBA to give crosslinked polymers (Scheme 3.18).

When a mixture of DGEBA : 1,1′-ferrocenedicarboxylic acid : Bu_4NOH at the mole ratio of 1 : 0.20 : 0.02 was heated at 130°C (Figure 3.19), the IR absorption band of epoxide ring at 917 cm^{-1} disappeared after heating for 7 hours. The IR absorption band of the carboxylic group at 1680 cm^{-1} also decreased after 1 hour. There was an appearance at 1710 cm^{-1} of the ester group resulting from the reaction of carboxylate ion and DGEBA.

If the amount of Bu_4NOH was increased to 0.04 (Figure 3.20), the IR absorption band at 917 cm^{-1} disappeared after heating at 130°C for 3 hours. IR absorption band of the carboxylic group at 1680 cm^{-1} also decreased after 1 hour.

If the amount of Bu_4NOH was increased to 0.08 (Figure 3.21), the IR absorption band at 917 cm^{-1} disappeared after heating at 130°C only 30 minutes. IR absorption band of the carboxylic group at 1680 cm^{-1} disappeared after 30 minutes.

If the amount of the Bu_4NOH was increased, the time required to complete the reaction would decrease. Furthermore, the reaction at higher temperature would be completed faster than that at the lower temperature. These results agreed with those obtained from the DSC experiments (section 3.10.3.1)



Scheme 3.18 Proposed mechanism of reaction between DGEBA and 1,1′-ferrocenedicarboxylic acid in the presence of Bu_4NOH

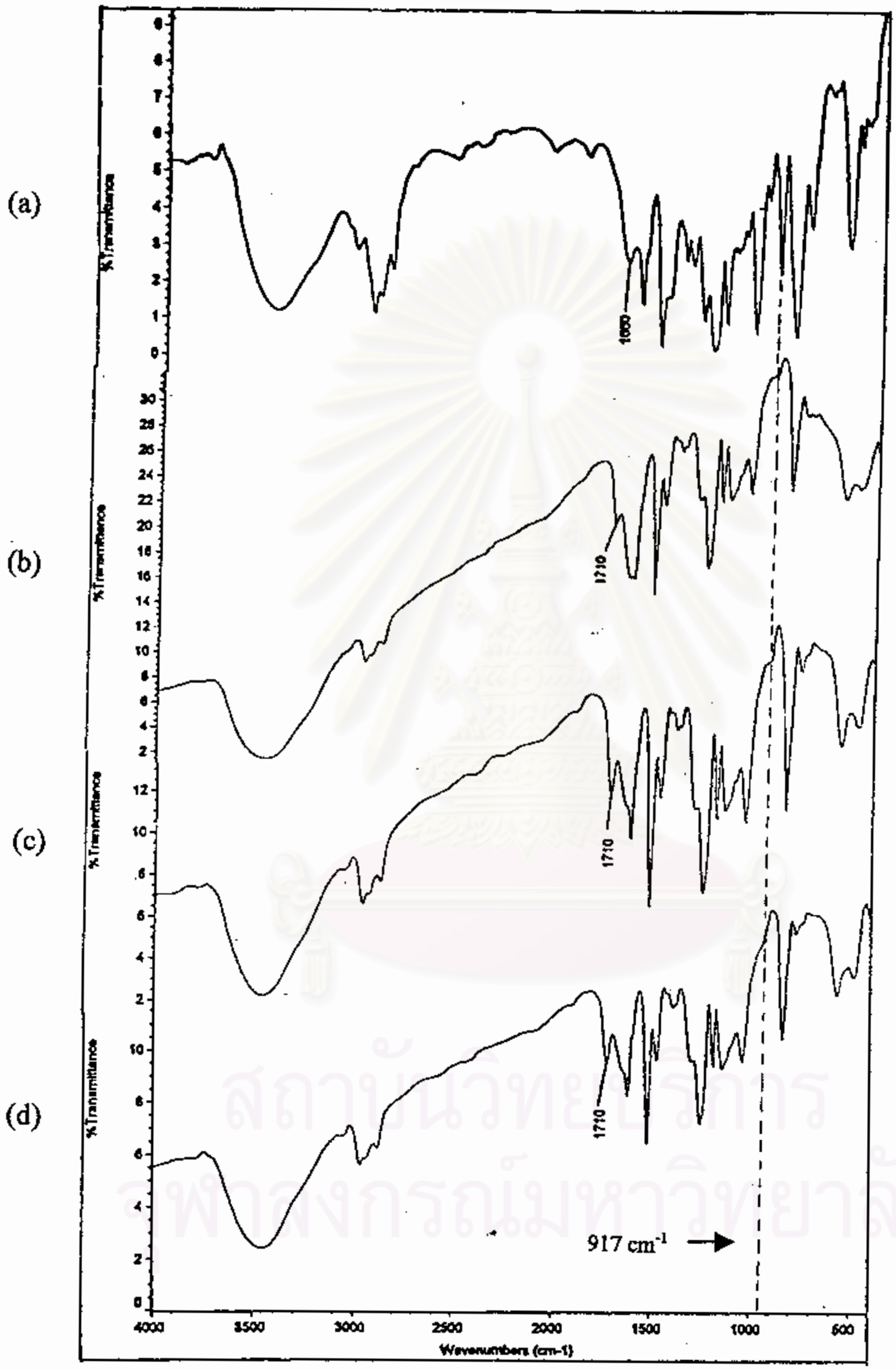


Figure 3.19 IR spectra of DGEBA : 1,1′–ferrocenedicarboxylic acid : Bu_4NOH at the mole ratio of 1 : 0.20 : 0.02 (a) before heating (b) after heating at 130°C for 1 h (c) after 4 h and (d) after 7 h

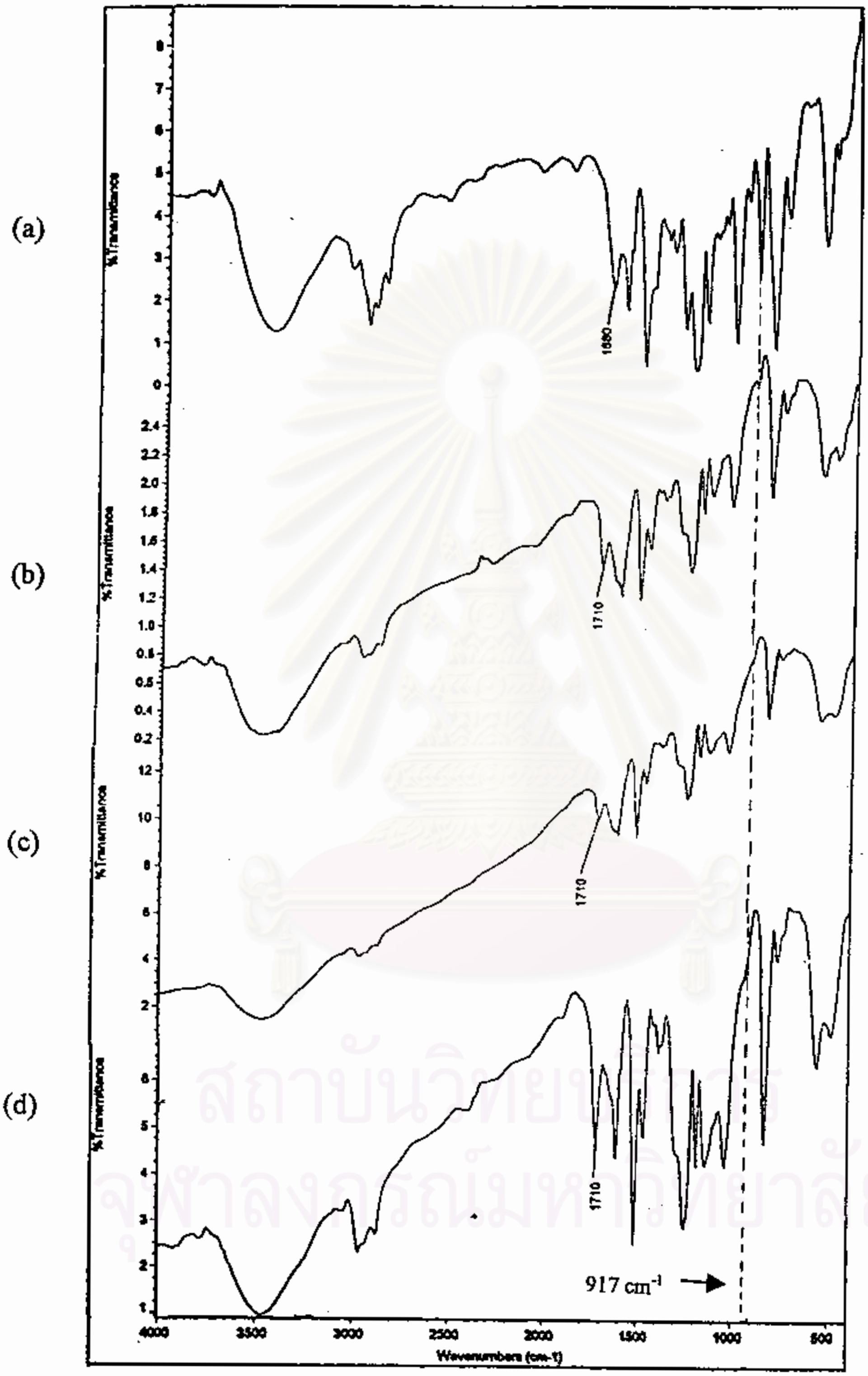


Figure 3.20 IR spectra of DGEBA : 1,1′–ferrocenedicarboxylic acid : Bu$_4$NOH at the mole ratio of 1 : 0.20 : 0.04 (a) before heating (b) after heating at 130°C for 1 h (c) after 2 h and (d) after 3 h

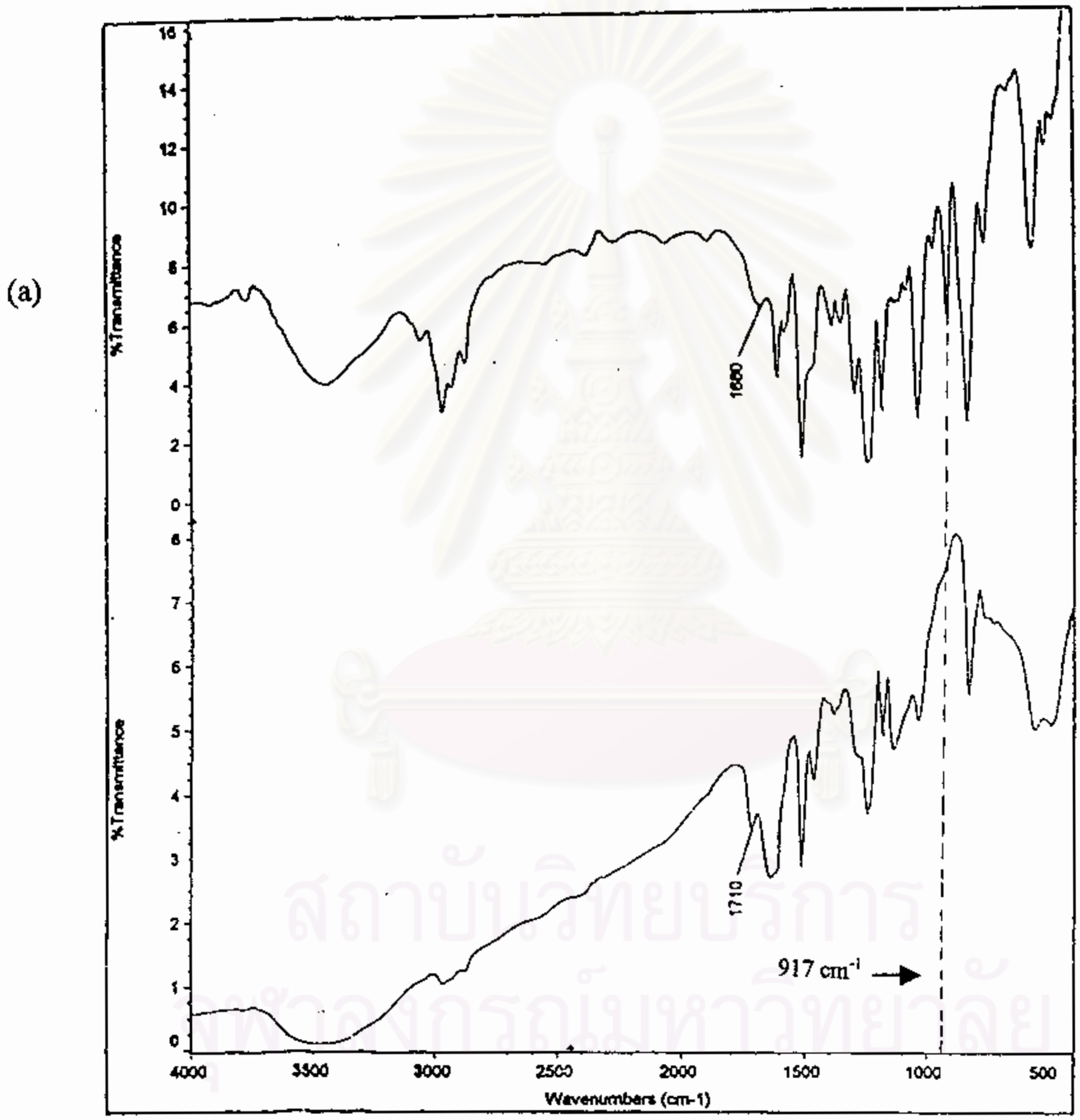


Figure 3.21 IR spectra of DGEBA : 1,1′–ferrocenedicarboxylic acid : Bu_4NOH at the mole ratio of 1 : 0.20 : 0.08 (a) before heating and (b) after heating at 130°C for 30 minutes

3.11 Preparation of Ferrocene-Containing Epoxy Polymers

In the preparation of polymer samples, the crosslinking temperature and time were chosen from the DSC and IR experiments. From IR spectra of DGEBA : 1,1′–ferrocenedicarboxylic acid : Bu_4NOH at the mole ratio of 1 : 0.20 : 0.04, it was found that the time required to complete the crosslinking reaction at 130°C was 3 hours. The mole ratio of 1 : 0.20 : 0.08 was prepared but it was difficult to obtain a homogeneous mixture because of high viscosity. Thus, the amount of Bu_4NOH employed was 0.04. To determine the composition that would provide good polymer properties, the mole ratios of DGEBA : 1,1′–ferrocenedicarboxylic acid : Bu_4NOH employed were 1 : 0.30 : 0.04, 1 : 0.20 : 0.04, 1 : 0.10 : 0.04, 1 : 0.05 : 0.04, 1 : 0.025 : 0.02 and 1 : 0.0125 : 0.02. For the mole ratio of DGEBA : 1,1′–ferrocenedicarboxylic acid at the mole ratio of 1 : 0.025 and 1 : 0.0125, the employed Bu_4NOH was decreased to 0.02 due to high viscosity of the mixture.

The time required to complete the crosslinking reaction was determined by observing the disappearance of the IR absorption band of the epoxide ring at 917 cm^{-1}. For the mole ratios of 1 : 0.30, 1 : 0.20 and 1 : 0.10 it was found that the time required to complete the reaction was 12 hours. When the amount of the 1,1′–ferrocenedicarboxylic acid was decreased the time required to complete the reaction increased, since there was low amount of crosslinking reagent to complete the crosslinking reaction.

The properties of the polymers prepared without using Bu_4NOH were not studied since high crosslinking reaction temperatures were required.

Reference polymers were also prepared to compare with the synthesized polymer using maleic anhydride as a crosslinking agent and without crosslinking agent.

3.12 Characterization of Ferrocene-Containing Epoxy Polymers

3.12.1 IR Spectroscopy

The ferrocene-containing epoxy polymers obtained from various ratios of DGEBA : 1,1′–ferrocenedicarboxylic acid : Bu_4NOH were characterized by IR spectroscopy. All epoxy polymers gave similar spectrum. An example of IR spectrum of the polymer obtained from DGEBA : 1,1′–ferrocenedicarboxylic acid : Bu_4NOH at the mole ratio of 1 : 0.20 : 0.04 is shown in Figure 3.22

The IR spectrum show the O-H absorption band of the secondary alcohol at 3300-3500 cm^{-1} and the absorption band of C=O stretching vibration of the ester group at 1710 cm^{-1}. The absorption band at 1600-1660 cm^{-1} and 1450-1550 cm^{-1} were due to C=C stretching vibrations. The absorption bands at 1100-1300 cm^{-1} were assigned to be C-O (ester) stretching vibration.

3.12.2 Dynamic Mechanical Analysis (DMA)

Dynamic Mechanical Analysis (DMA) was employed to determine the glass transition temperature (T_g) of the ferrocene-containing epoxy polymers by observing the maximum value of loss modulus. For example, DMA thermogram of the epoxy polymer obtained from the mole ratio of DGEBA : 1,1′–ferrocenedicarboxylic acid : Bu_4NOH = 1 : 0.20 : 0.04 showed T_g at 126°C (Figure 3.23). The thermogram of other ratios of ferrocene-containing epoxy polymers were shown in Figures A.14-18.

Table 3.3 shows the glass-transition temperatures of ferrocene-containing epoxy polymers. The mole ratio of 1 : 0.20 : 0.04 exhibits the highest T_g value.

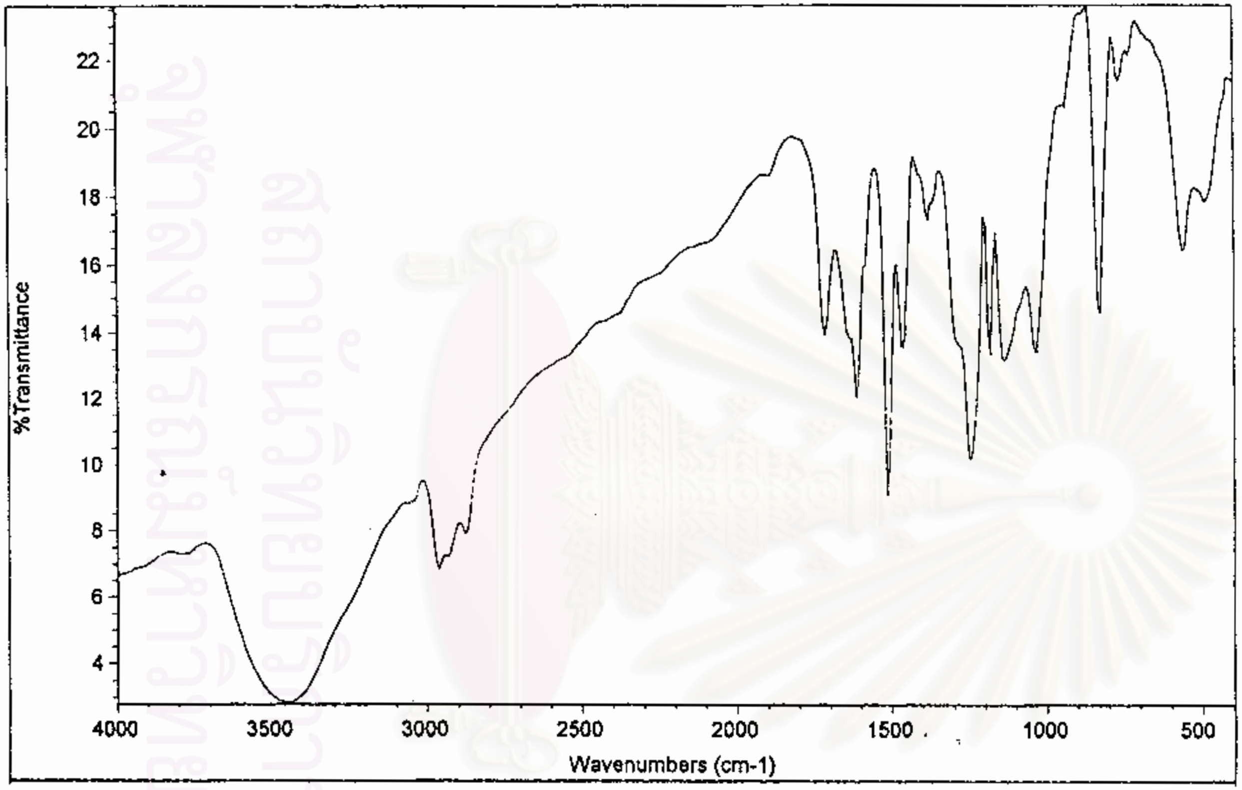


Figure 3.22 IR spectrum of ferrocene-containing epoxy polymer at the mole ratio of DGEBA : 1,1′–ferrocenedicarboxylic acid : Bu_4NOH = 1 : 0.20 : 0.04

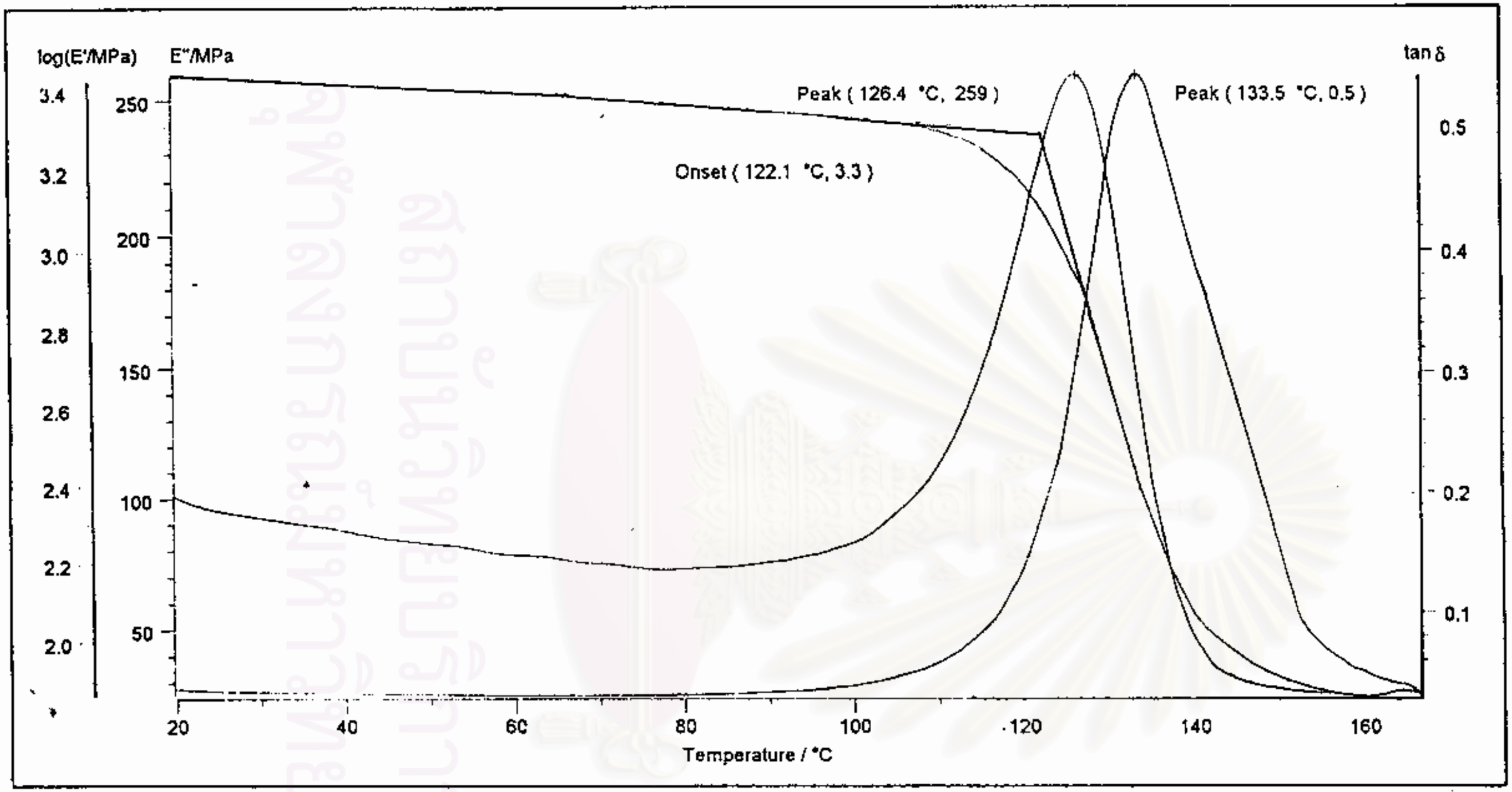


Figure 3.23 DMA thermogram of ferrocene-containing epoxy polymer at the mole ratio of DGEBA : 1,1'–ferrocenedicarboxylic acid : Bu_4NOH = 1 : 0.20 : 0.04

Table 3.3 Glass transition temperature (T_g) of ferrocene-containing epoxy polymer obtained from various mole ratios of DGEBA : 1,1′–ferrocenedicarboxylic acid ($C_{12}H_{10}FeO_4$) : Bu_4NOH

Crosslinking Agent	**Mole ratio of** DGEBA : $C_{12}H_{10}FeO_4$: Bu_4NOH	T_g (°C)
$C_{12}H_{10}FeO_4$	1 : 0.30 : 0.04	124
	1 : 0.20 : 0.04	126
	1 : 0.10 : 0.04	119
	1 : 0.05 : 0.04	116
	1 : 0.025 : 0.02	90
	1 : 0.0125 : 0.02	66
Maleic anhydride[a]	-	81
Diethylenetriamine[b]	-	125
Bu_4NOH	1 : 0 : 0.04	93

[a] mole ratio of DGEBA : MA : Bu_4NOH was 1 : 0.20 : 0.04

[b] mole ratio of DGEBA : DETA was 1 : 1

3.12.3 Thermal Stability

The thermal stability of the ferrocene-containing epoxy polymers was determined by heating the polymers at 250°C for 48 hours in air. Table 3.4 shows the weight loss of the epoxy polymers at different times. The ratio of 1 : 0.025 : 0.02 and 1 : 0.0125 : 0.02 was not studied because they provided very low T_g and the resulting polymers were soft materials.

Table 3.4 Thermal stability at 250°C of ferrocene-containing epoxy polymers obtained from different mole ratio of DGEBA : $C_{12}H_{10}FeO_4$: Bu_4NOH

Crosslinking Agent	**Mole ratio of DGEBA : $C_{12}H_{10}FeO_4$: Bu_4NOH**	% Weight loss at different time			
		12 h	24 h	36 h	48 h
$C_{12}H_{10}FeO_4$	1 : 0.30 : 0.04	13.6	23.1	27.7	33.8
	1 : 0.20 : 0.04	10.7	21.8	27.3	32.8
	1 : 0.10 : 0.04	9.0	20.9	27.0	31.9
	1 : 0.05 : 0.04	7.1	15.0	21.0	26.4
Maleic anhydride[a]	-	6.1	6.9	7.4	7.7
Diethylenetriamine[b]	-	7.3	20.7	25.3	26.6
Bu_4NOH	1 : 0 : 0.04	4.6	5.1	5.5	5.9

[a] mole ratio of DGEBA : MA : Bu_4NOH was 1 : 0.20 : 0.04

[b] mole ratio of DGEBA : DETA was 1 : 1

Thermogravimetric analysis (TGA) was also used to determine thermal stability of ferrocene-containing epoxy polymers. TGA thermogram (Figure A.19) of the polymer obtained from the mole ratio of DGEBA : 1,1′–ferrocenedicarboxylic acid : Bu_4NOH = 1 : 0.20 : 0.04 showed 100% decomposition at 600°C. For the ratios of 1 : 0.10 : 0.04 and 1 : 0.05 : 0.04 (Figures A.20 and A.21), this temperature increased to 700°C.

It could be seen that the polymers showed poor thermal stability since the carboxylate anion of 1,1′–ferrocenedicarboxylic acid had low solubility in DGEBA. Thus, the mixture was not homogeneous and poor material was obtained. DGEBA could also undergo crosslinking reaction with Bu_4NOH as shown in Scheme 3.11. Thus, 1,1′–ferrocenedicarboxylic acid would remain in the polymer.

From DSC thermogram (Figure 3.17), it was shown that the crosslinking reaction was not completed at 130°C but the IR experiment (Figure 3.20) showed that the crosslinking was completed. This is probably because the DSC experiment took a short time and the unreacted 1,1′–ferrocenedicarboxylic acid reacted with DGEBA at 197°C. But when the polymer was crosslinked at the longer time, all of 1,1′–ferrocenedicarboxylic acid could react with DGEBA.

CHAPTER IV

CONCLUSION

4.1 Conclusion

Part 1 Use of 1,1′–bis(hydroxyethyl)ferrocene as a Crosslinking Agent

Ferrocene-containing epoxy polymers using 1,1′–bis(hydroxyethyl)ferrocene as a crosslinking agent were synthesized by crosslinking of the diglycidyl ether of bisphenol A (DGEBA) with 1,1′–bis(hydroxyethyl)ferrocene and maleic anhydride. The employed catalyst was tetrabutyl ammonium hydroxide (Bu_4NOH). The progress of the crosslinking reaction was followed by IR spectroscopy. It was found that the optimum crosslinking condition for the preparation of ferrocene-containing epoxy polymers was 120°C/ 8 hours for the mole ratio of DGEBA : 1,1′–bis(hydroxyethyl)ferrocene : MA = 1 : 0.20 : 0.20, 1 : 0.30 : 0.20 and 1 : 0.40 : 0.20. When the lower amount of 1,1′–bis(hydroxyethyl)ferrocene was used at the mole ratio of 1 : 0.15 : 0.20, the reaction required higher crosslinking temperature and longer time.

The polymers were investigated for their physical properties, namely glass transition temperature (T_g) and thermal stability. The mole ratio of DGEBA : 1,1′–bis(hydroxyethyl)ferrocene : MA at 1 : 0.20 : 0.20 exhibited the highest T_g value of 81°C. Upon heating at 250°C for 48 hours, the polymer showed 14.3% weight loss. The results indicated that ferrocene-containing epoxy polymers had low T_g and low thermal stability compared with the known polymers obtained from DGEBA : MA : Bu_4NOH and DGEBA : Bu_4NOH. This was probably because of side reactions that occurred during the polymerization. These side reactions were the crosslinking reaction of DGEBA with maleic anhydride in the presence of Bu_4NOH and the crosslinking of DGEBA with Bu_4NOH.

Part 2 Use of 1,1′-ferrocenedicarboxylic acid as a Crosslinking Agent

Ferrocene-containing epoxy polymers using 1,1′–ferrocenedicarboxylic acid as a crosslinking agent were synthesized by crosslinking of the diglycidyl ether of bisphenol A (DGEBA) with 1,1′–ferrocenedicarboxylic acid. Tetrabutyl ammonium hydroxide (Bu_4NOH) was employed as a catalyst. The optimum crosslinking conditions were determined by differential scanning calorimetry (DSC) and IR spectroscopy. It was found that the optimum crosslinking temperature for the preparation of ferrocene-containing epoxy polymers was 130°C. The time required to complete the crosslinking reaction depended on the amount of 1,1′–ferrocenedicarboxylic acid.

The polymers were investigated for their glass transition temperature (T_g) and thermal stability. The mole ratio of DGEBA : 1,1′–ferrocenedicarboxylic acid : Bu_4NOH at 1 : 0.20 : 0.04 exhibited the highest T_g value of 126°C. Upon heating at 250°C for 48 hours, the polymer showed 32.8% weight loss which indicated that the polymers had poor thermal stability. High %weight loss could result from unreacted 1,1′–ferrocenedicarboxylic acid. Since the carboxylate anion of 1,1′–ferrocenedicarboxylic acid had low solubility in DGEBA. Thus, the mixture was not homogeneous and poor material was obtained. Furthermore, a side reaction that could occur during polymerization is the crosslinking of DGEBA with Bu_4NOH.

4.2 Suggestion For Future Work

The ferrocene derivative for further investigation as crosslinking agent for DGEBA should be 1,1′–ferrocenedicarboxylic acid since it was more easily prepared and purified than 1,1′–bis(hydroxyethyl)ferrocene. Since one of the problems in this research was the low solubility of the ferrocene compounds, addition of monoepoxide compounds such as butyl glycidyl ether, phenyl glycidyl ether and allyl glycidyl ether should reduce the viscosity. Other catalysts for the crosslinking reaction such as benzyl dimethylamine can be used instead of Bu_4NOH.

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APPENDIX

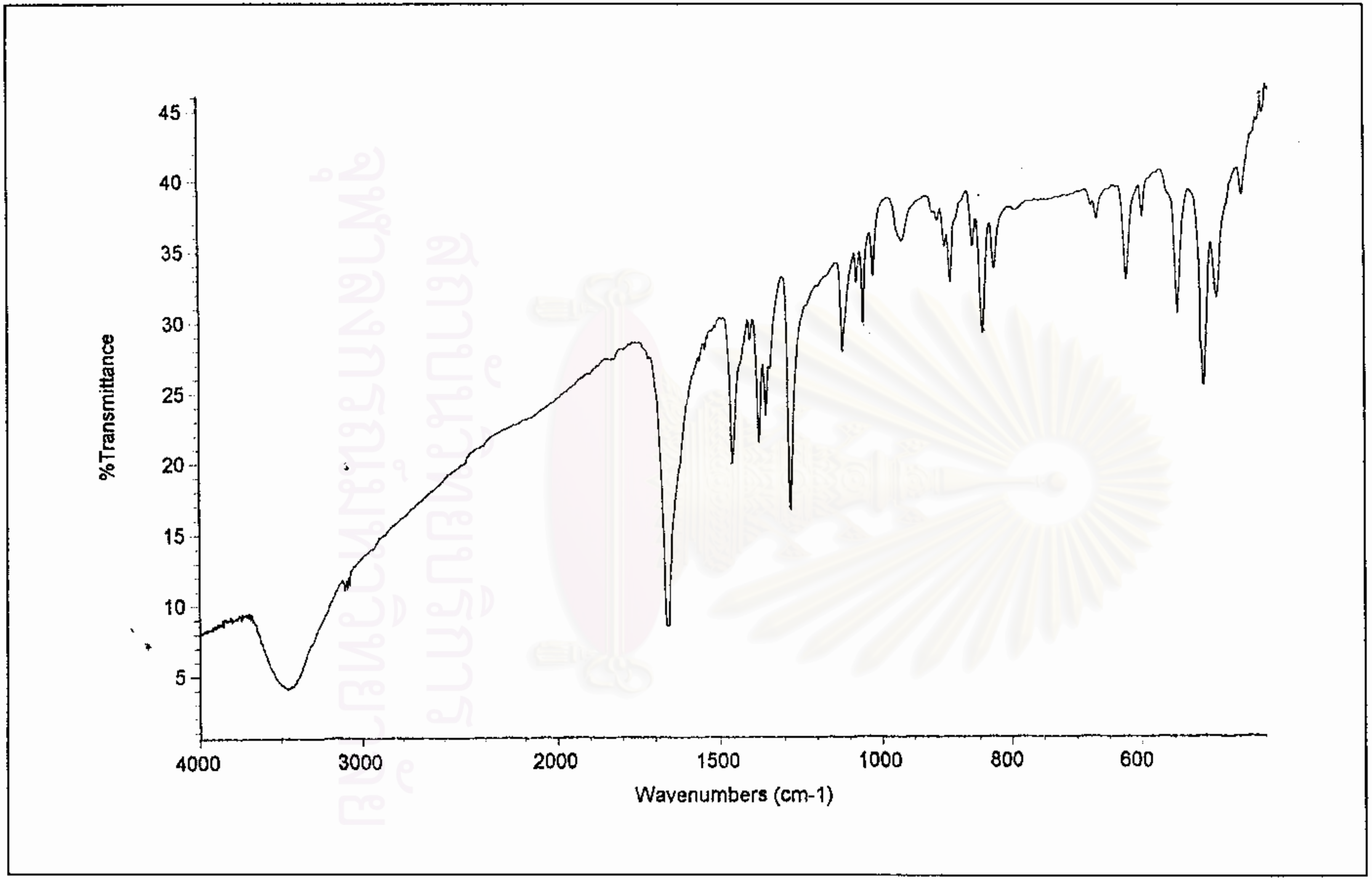


Figure A.1 IR spectrum of 1,1′-diacetylferrocene

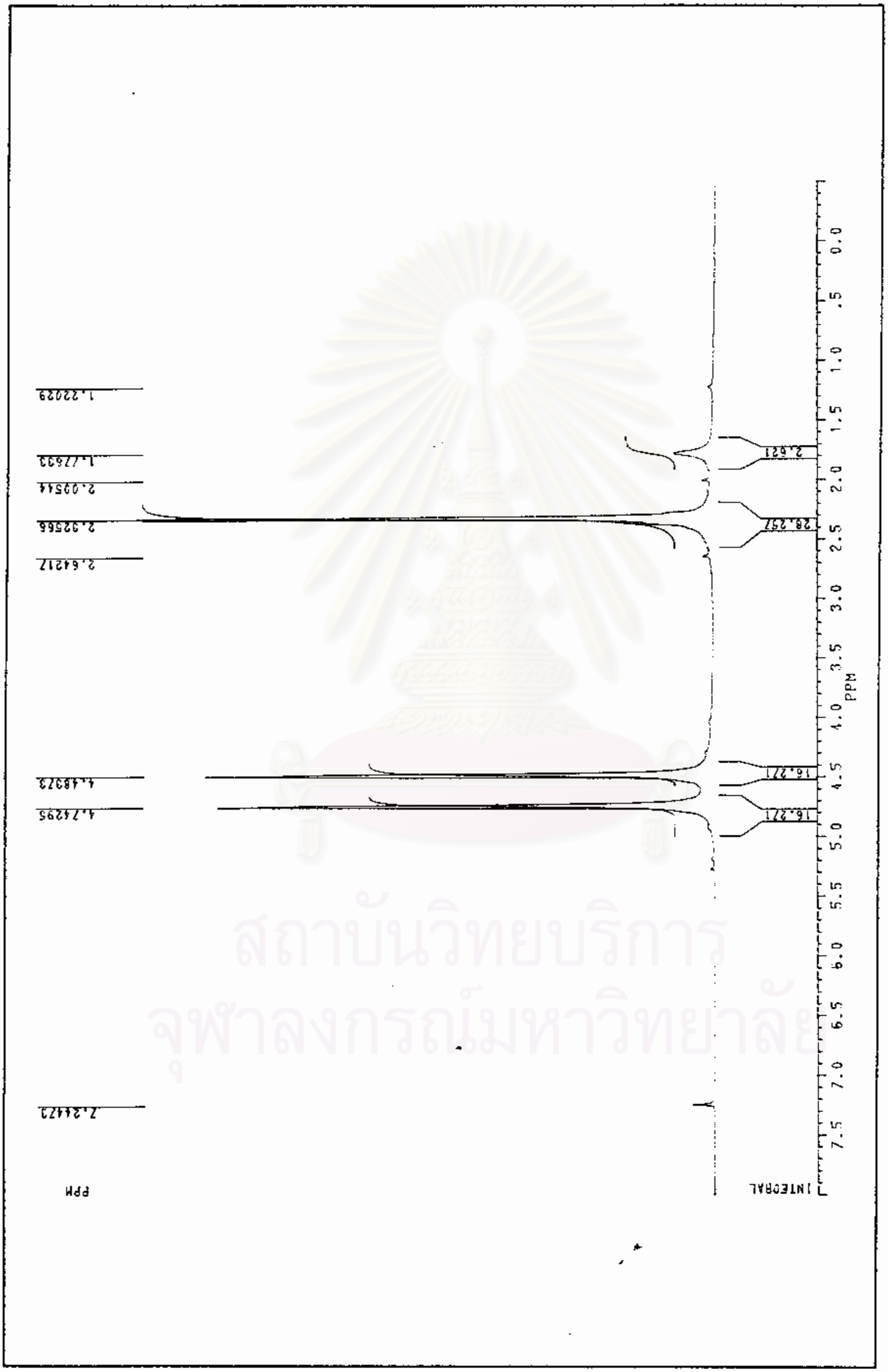


Figure A.2 ^{1}H NMR spectrum of 1,1′–diacetylferrocene

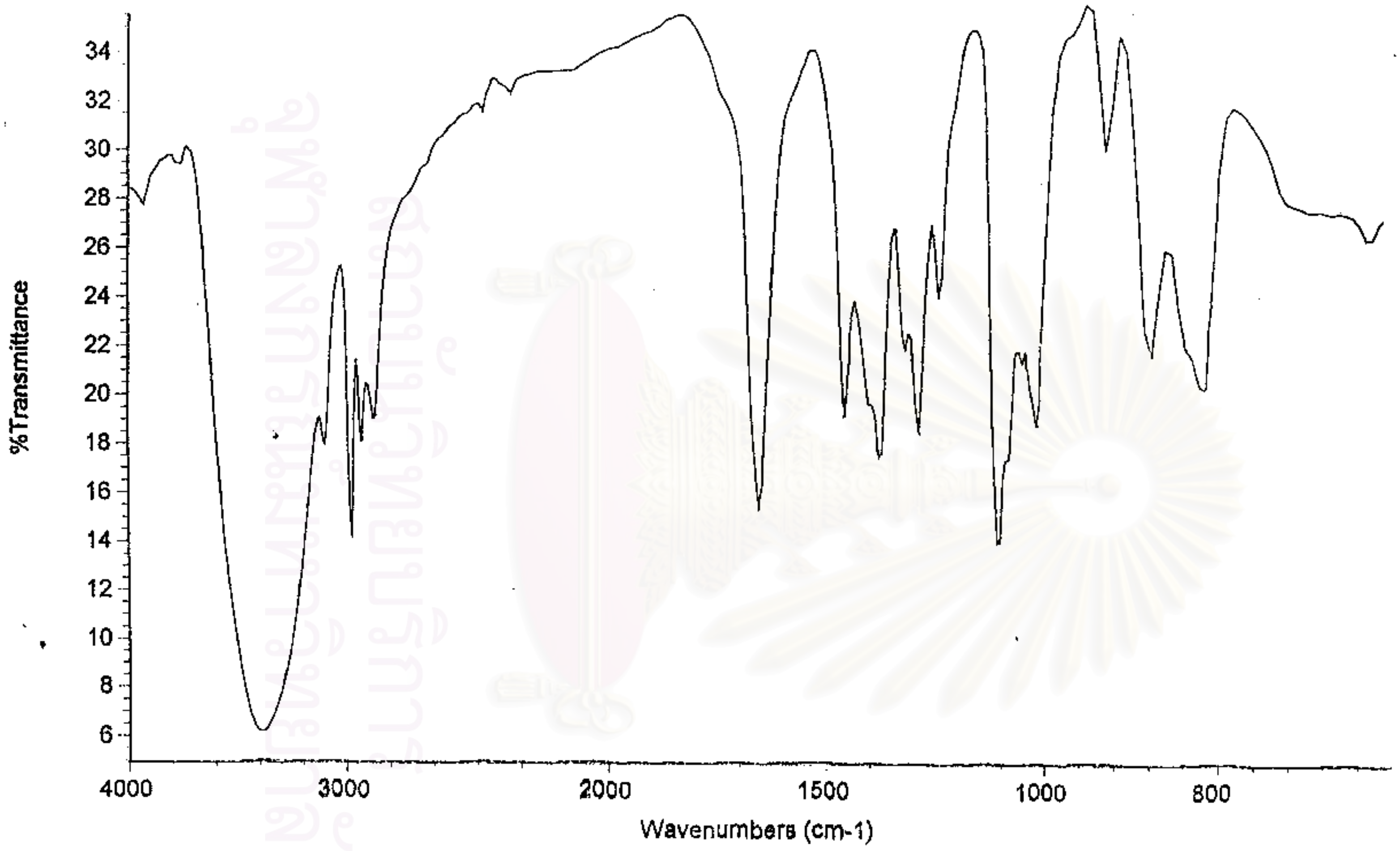


Figure A.3 IR spectrum of 1,1′–bis(hydroxyethyl)ferrocene

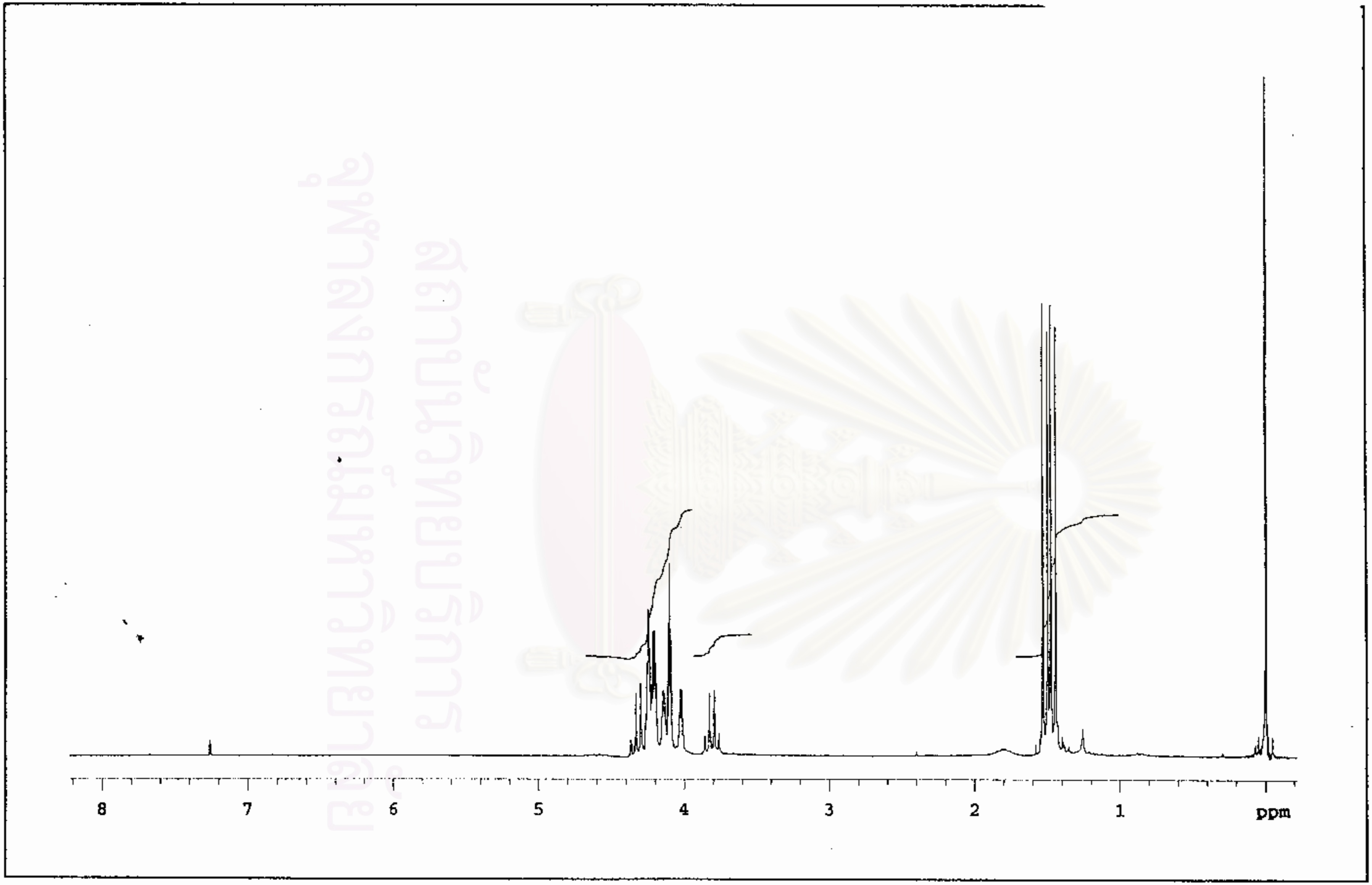


Figure A.4 ^{1}H NMR spectrum of 1,1′–bis(hydroxyethyl)ferrocene

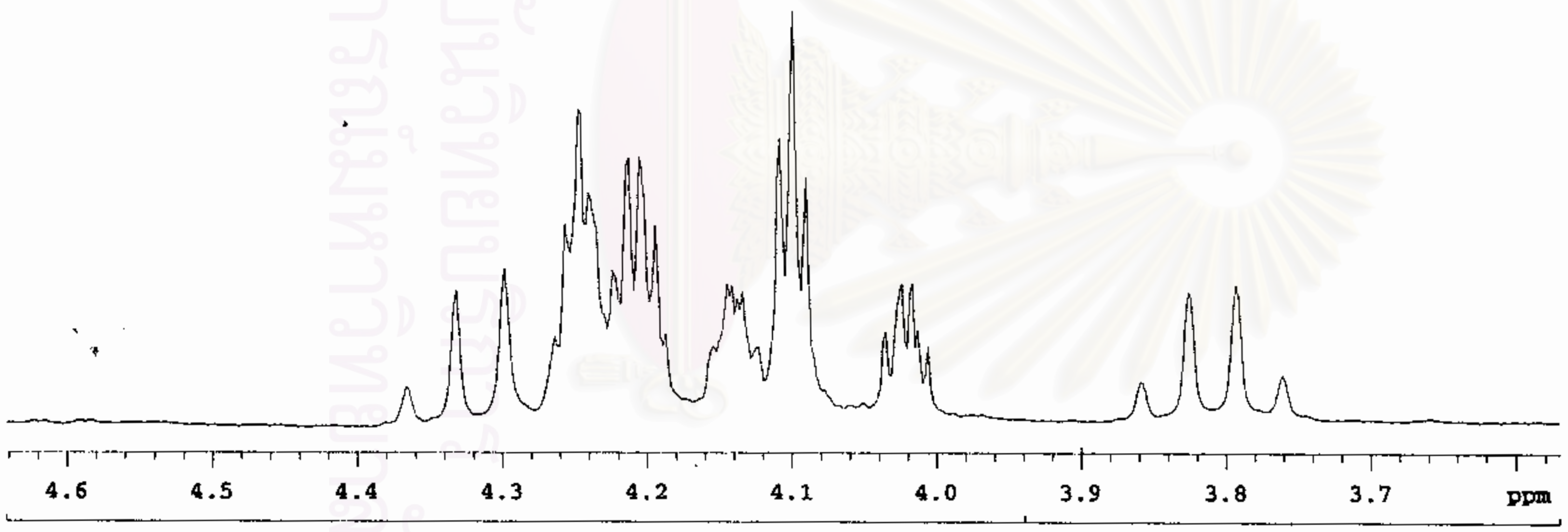


Figure A.4 (continued) ^{1}H NMR spectrum of 1,1′–bis(hydroxyethyl)ferrocene

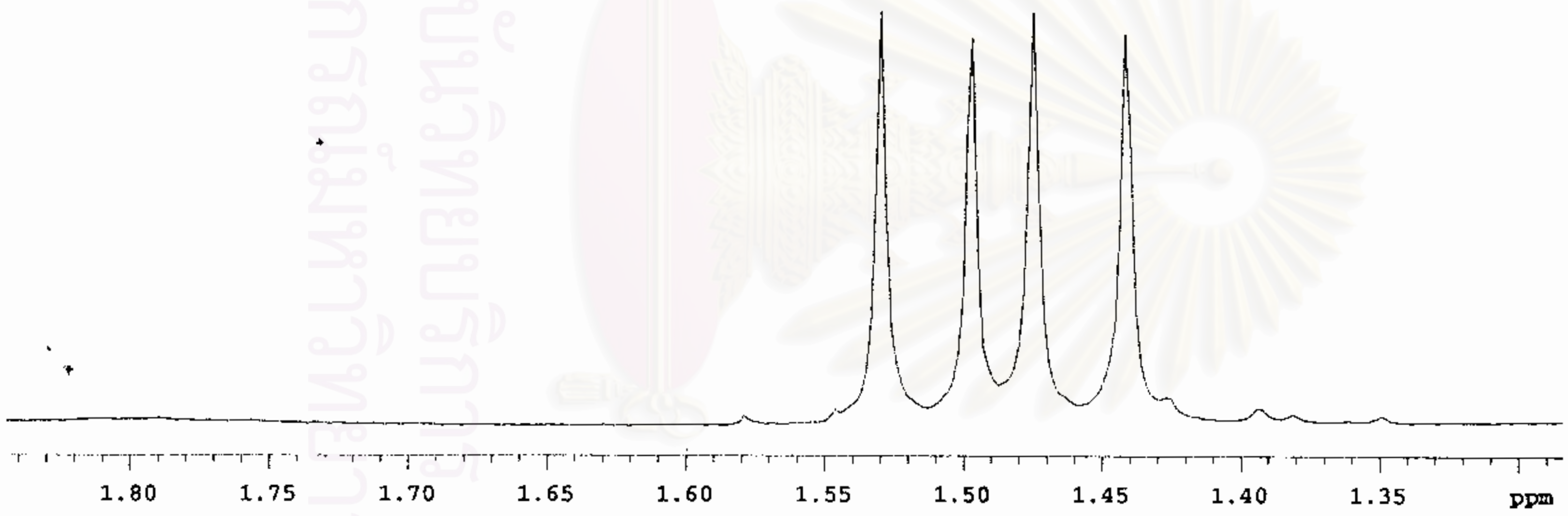


Figure A.4 (continued) ^{1}H NMR spectrum of 1,1′–bis(hydroxyethyl)ferrocene

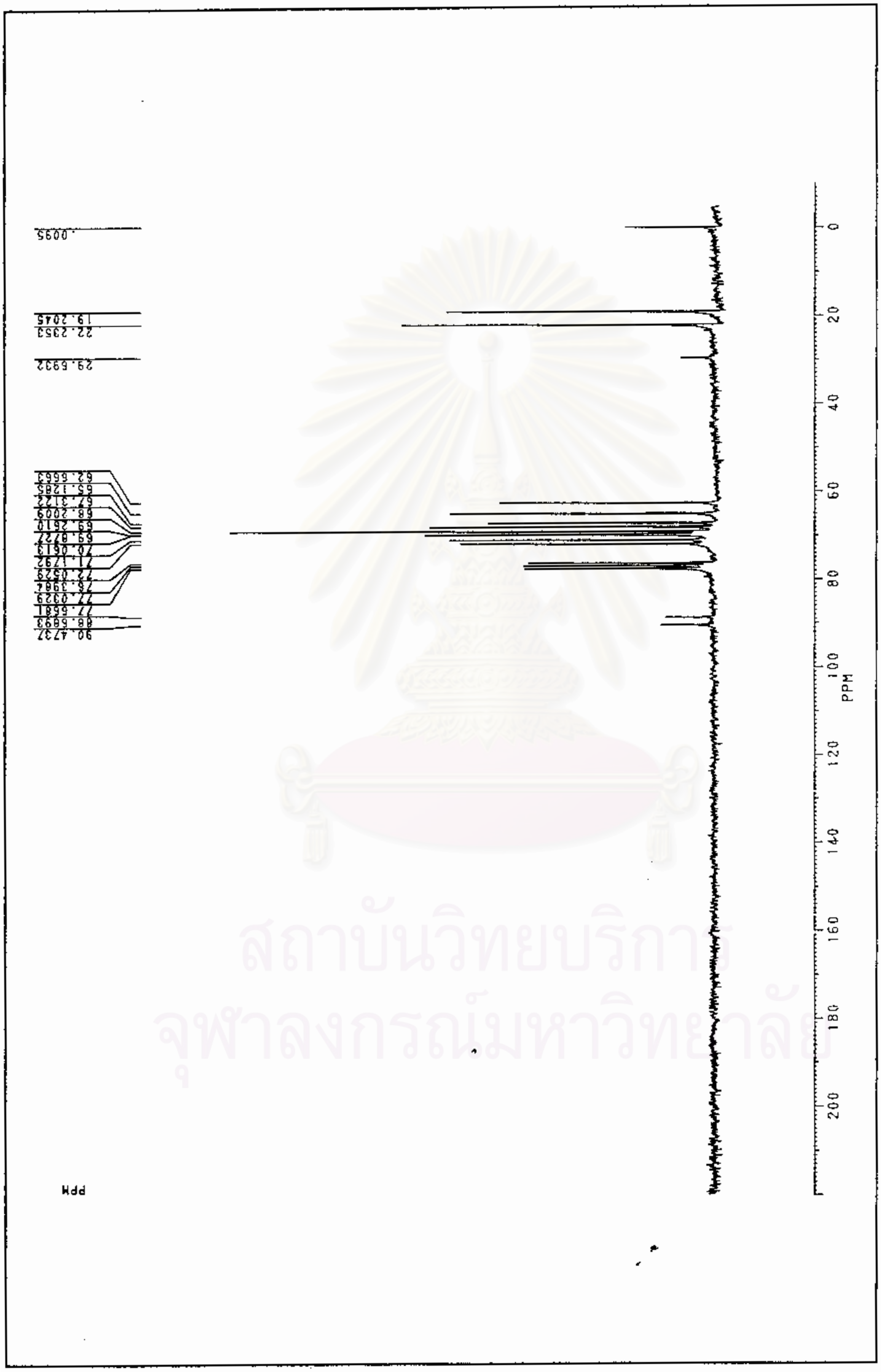


Figure A.5 ^{13}C NMR spectrum of 1,1′-bis(hydroxyethyl)ferrocene

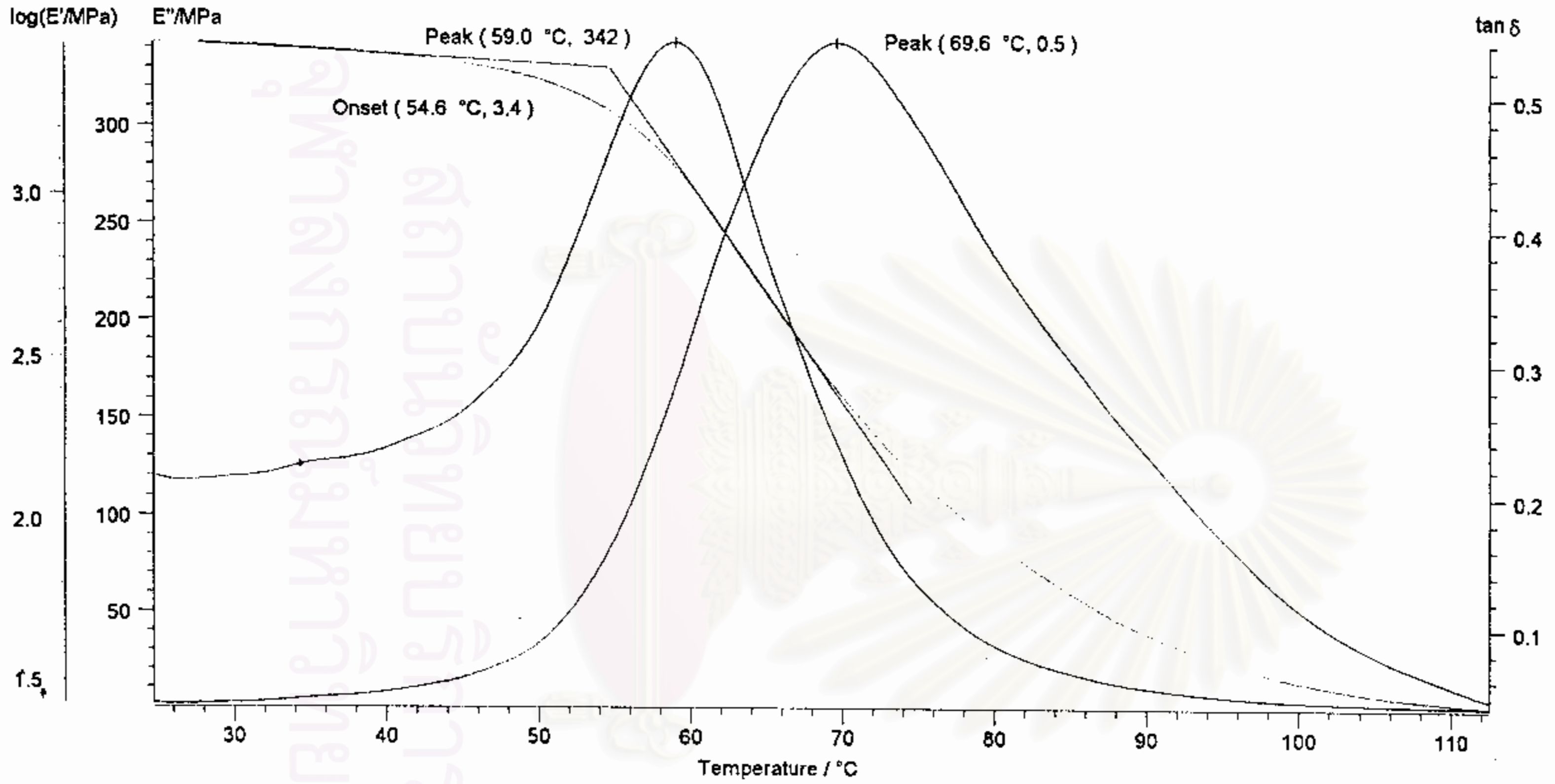


Figure A.6 DMA thermogram of ferrocene-containing epoxy polymer at the mole ratio of DGEBA : 1,1′–bis(hydroxyethyl)ferrocene : MA : Bu_4NOH = 1 : 0.40 : 0.20 : 0.08

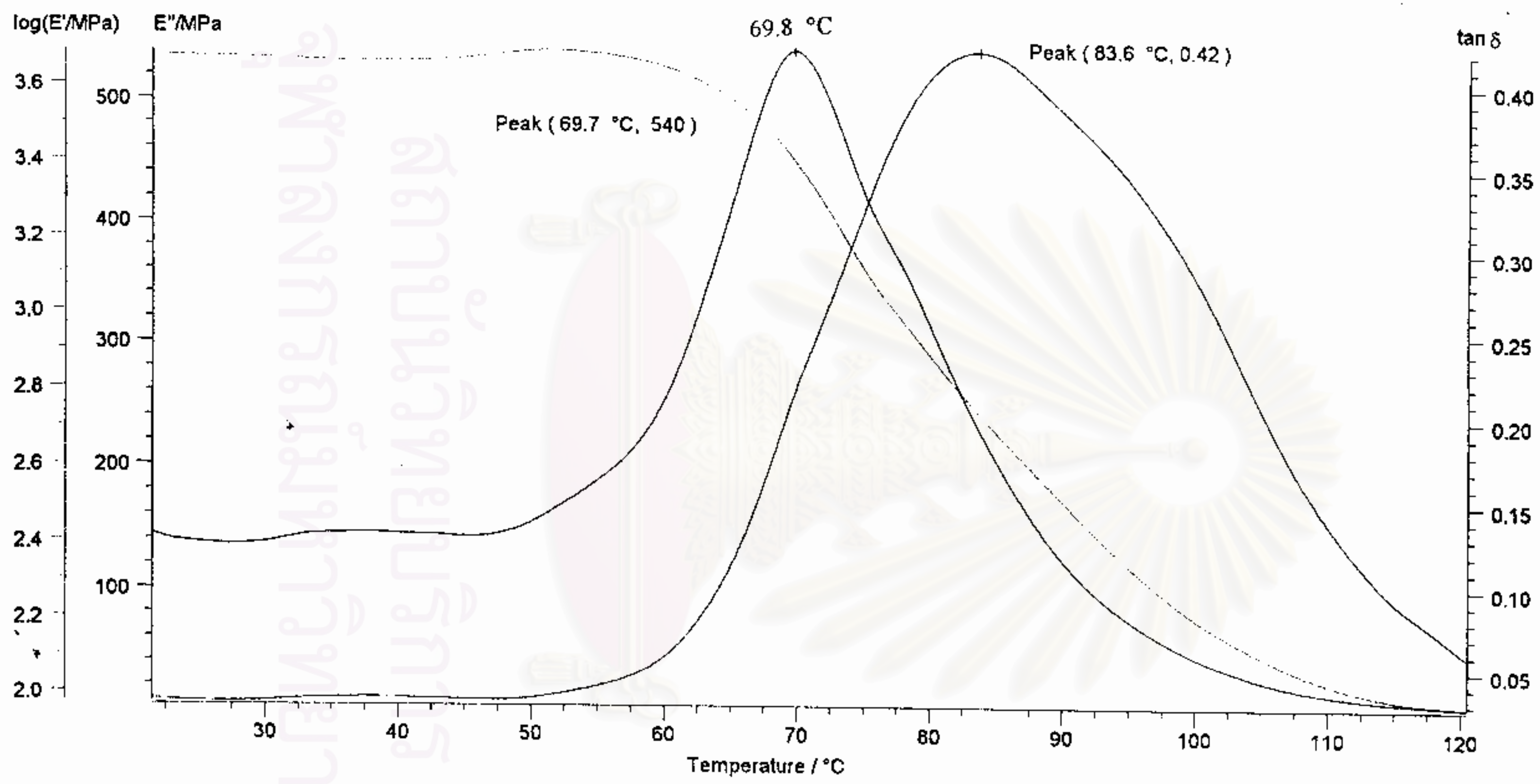


Figure A.7 DMA thermogram of ferrocene-containing epoxy polymer at the mole ratio of DGEBA : 1,1′–bis(hydroxyethyl)ferrocene : MA : Bu_4NOH = 1 : 0.30 : 0.20 : 0.06

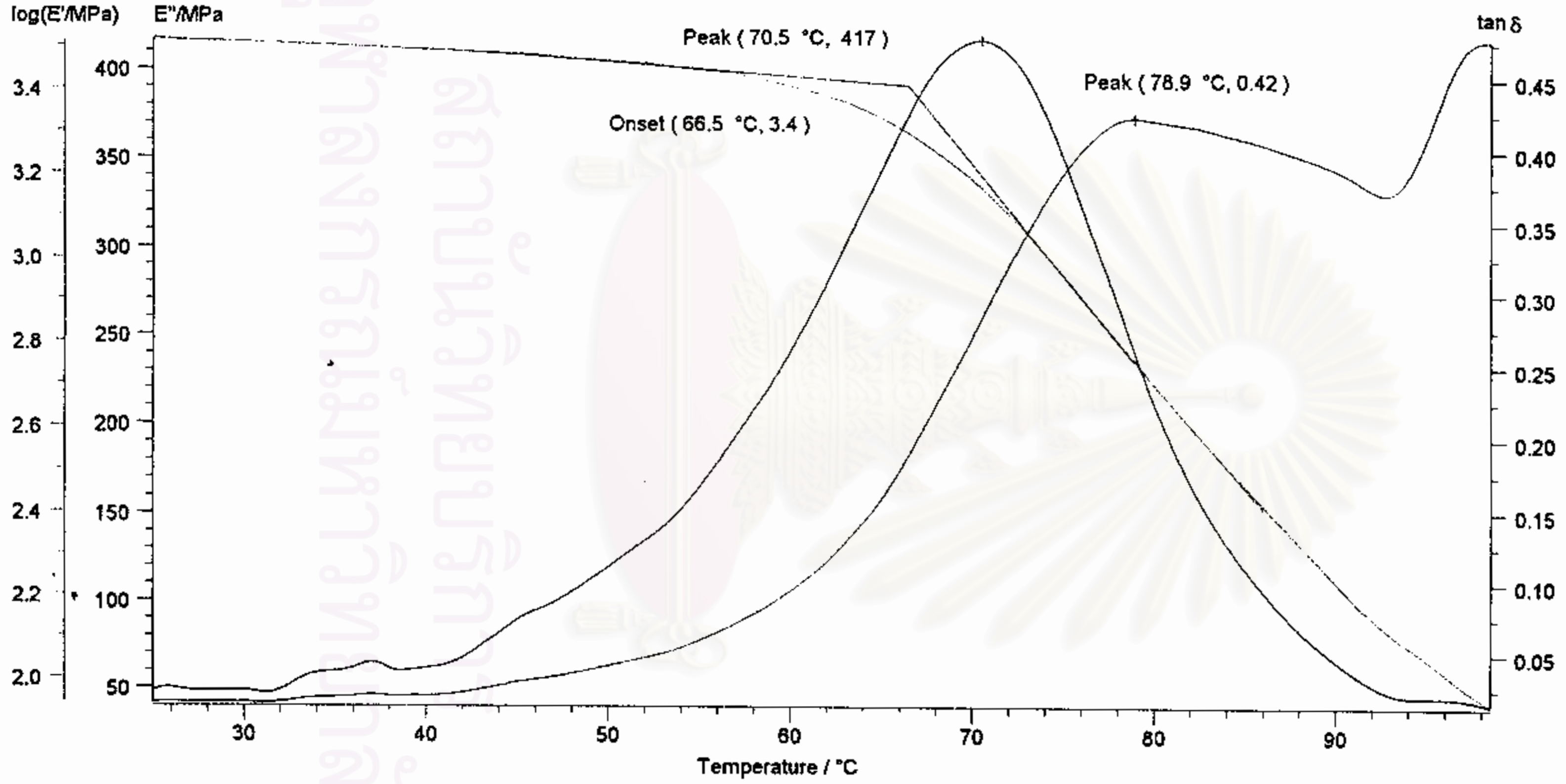


Figure A.8 DMA thermogram of ferrocene-containing epoxy polymer at the mole ratio of DGEBA : 1,1'–bis(hydroxyethyl)ferrocene : MA : Bu_4NOH = 1 : 0.15 : 0.20 : 0.03

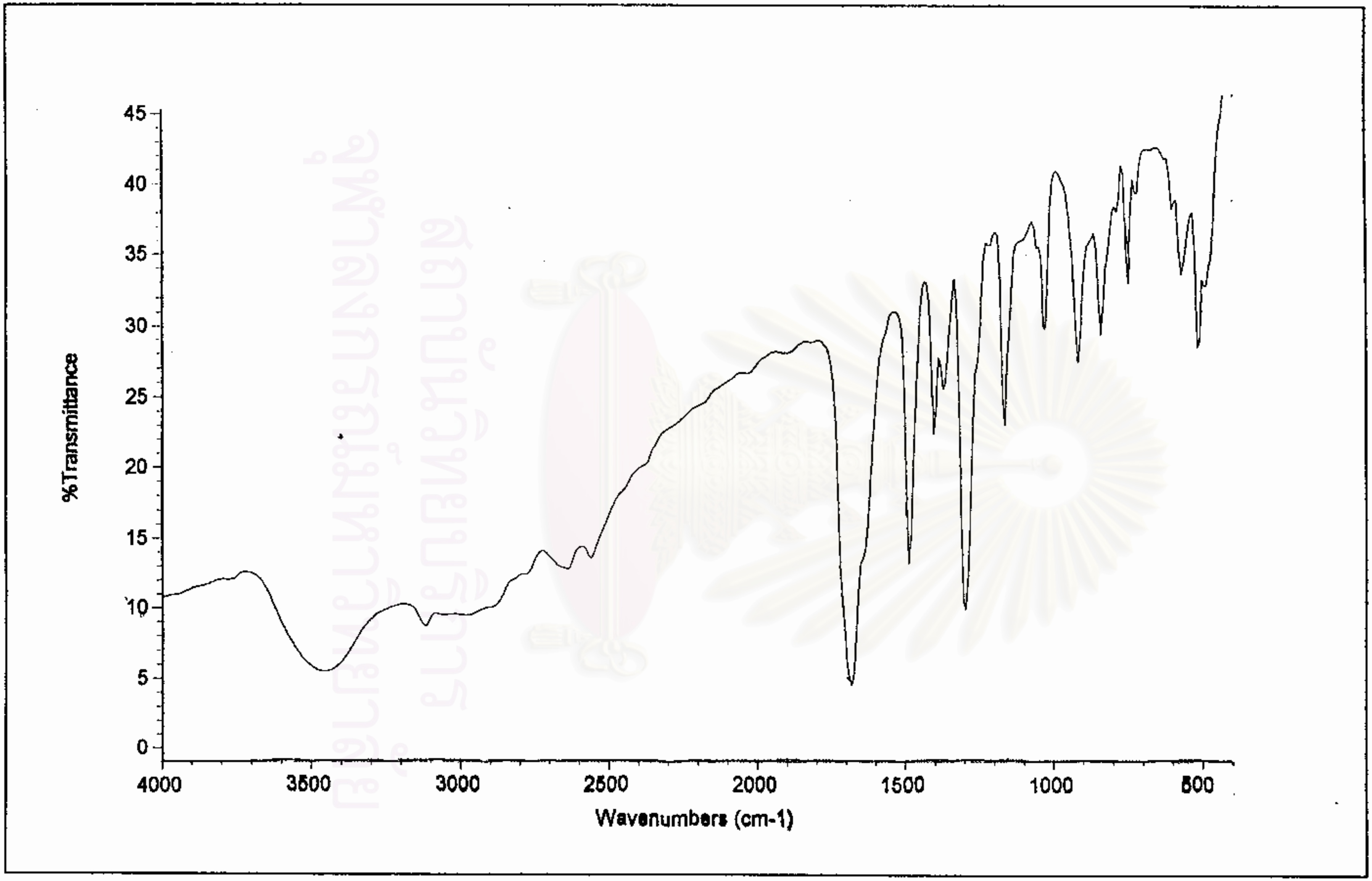


Figure A.9 IR spectrum of 1,1′-ferrocenedicarboxylic acid

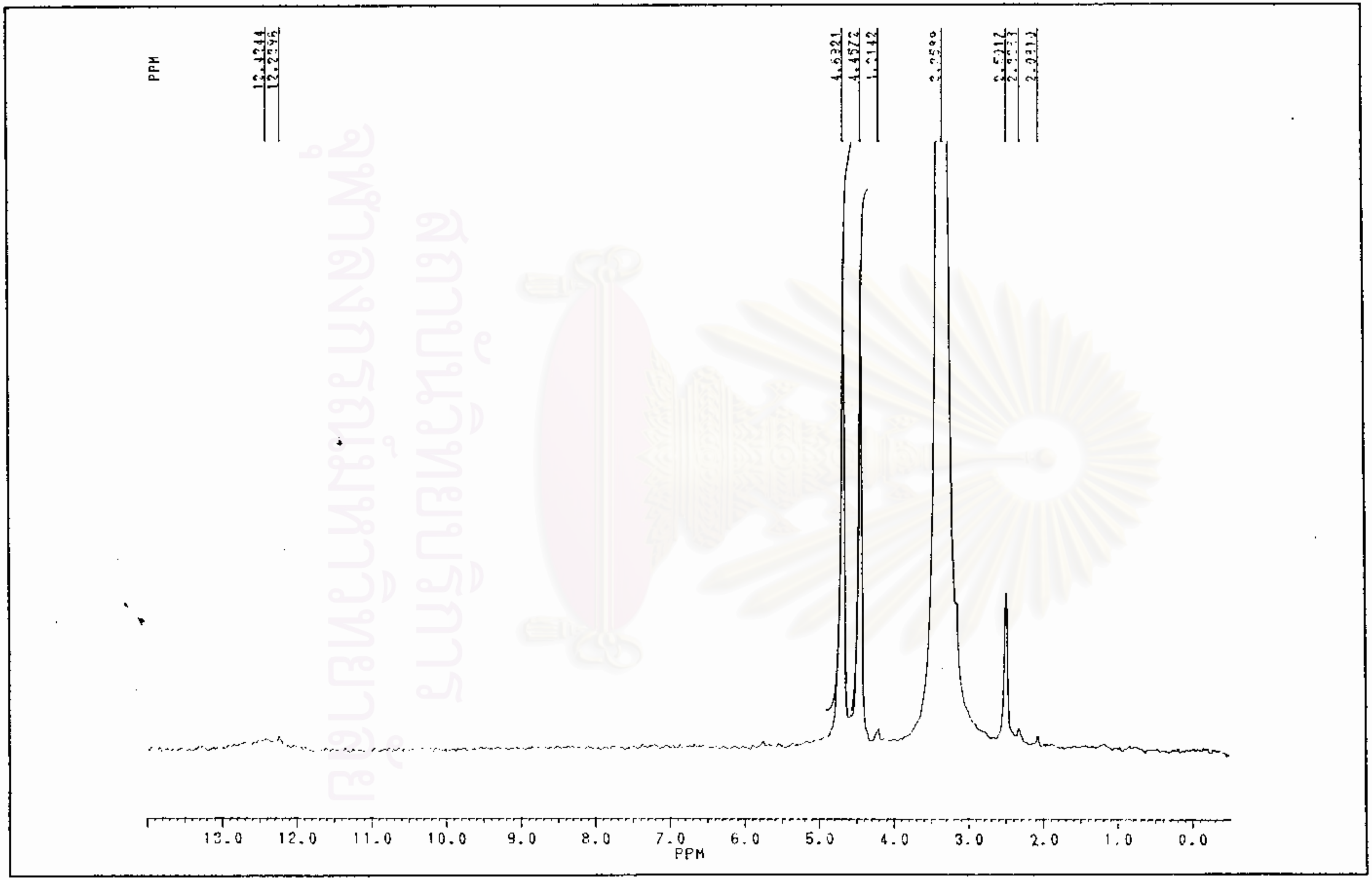


Figure A.10 ^{1}H NMR spectrum of 1,1′-ferrocenedicarboxylic acid

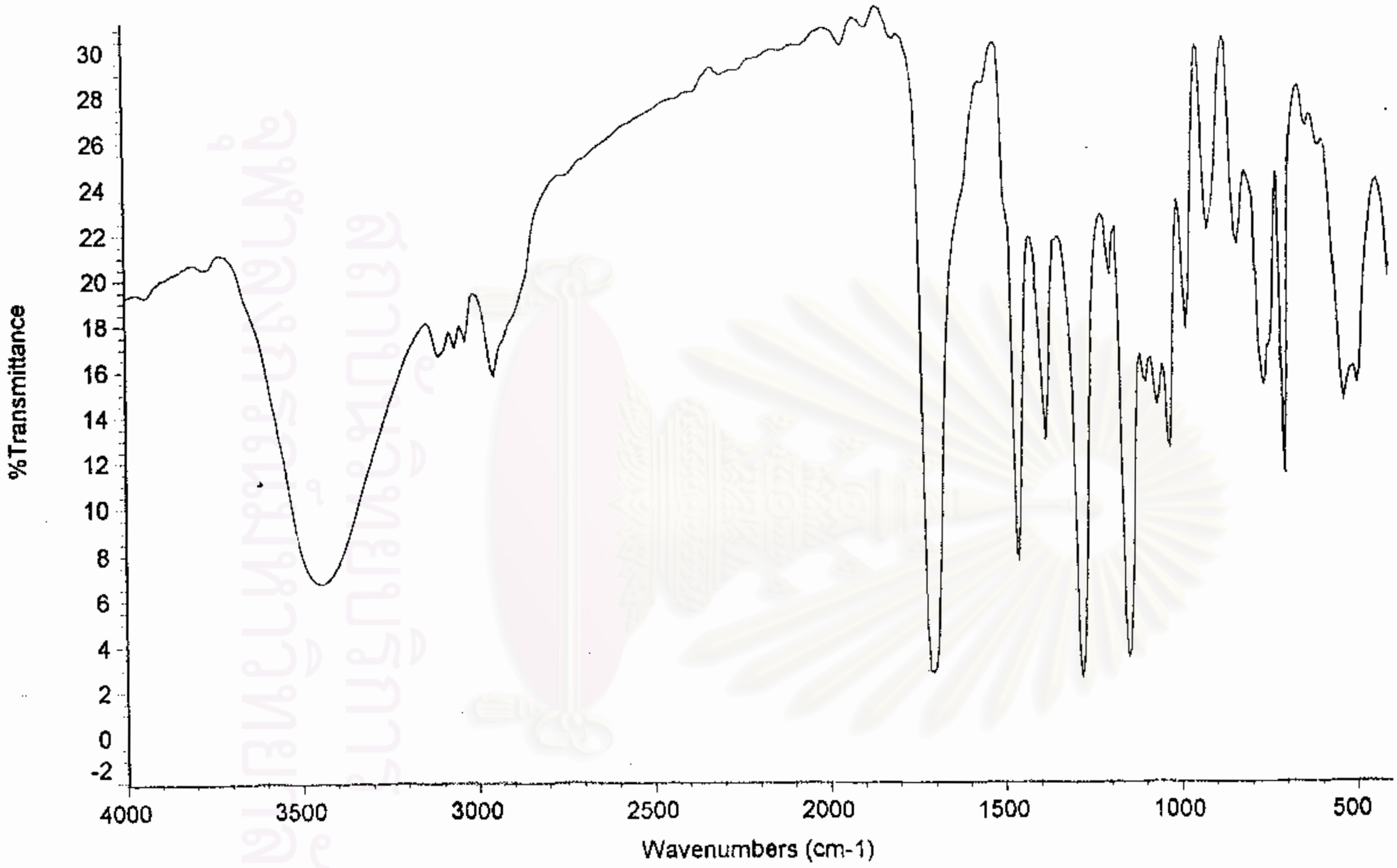


Figure A.11 IR spectrum of 1,1′-(2-hydroxy-2-phenyl ethylcarboxylate)-ferrocene

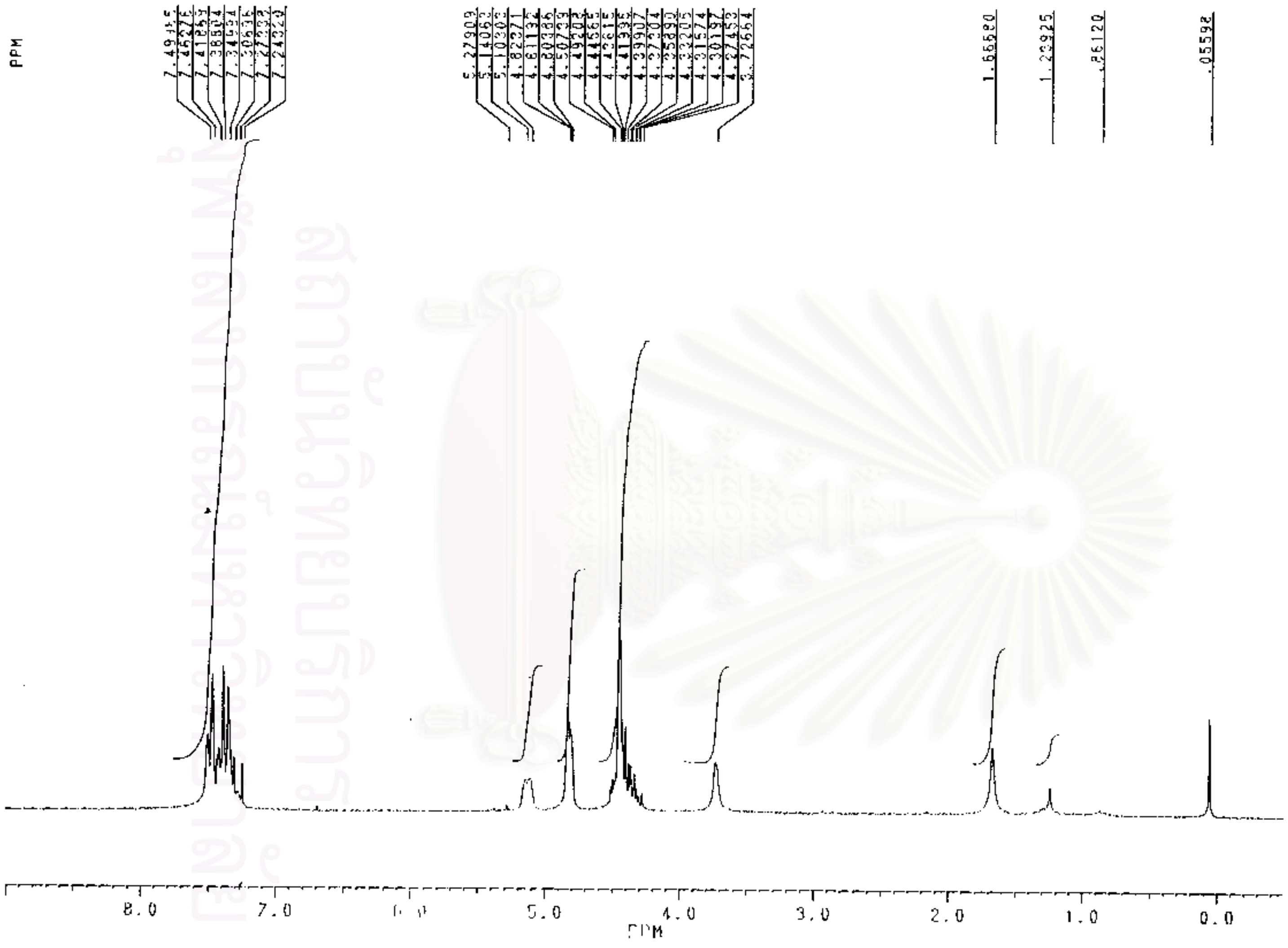


Figure A.12 ^{1}H NMR spectrum of 1,1′-(2-hydroxy-2-phenyl ethylcarboxylate)-ferrocene

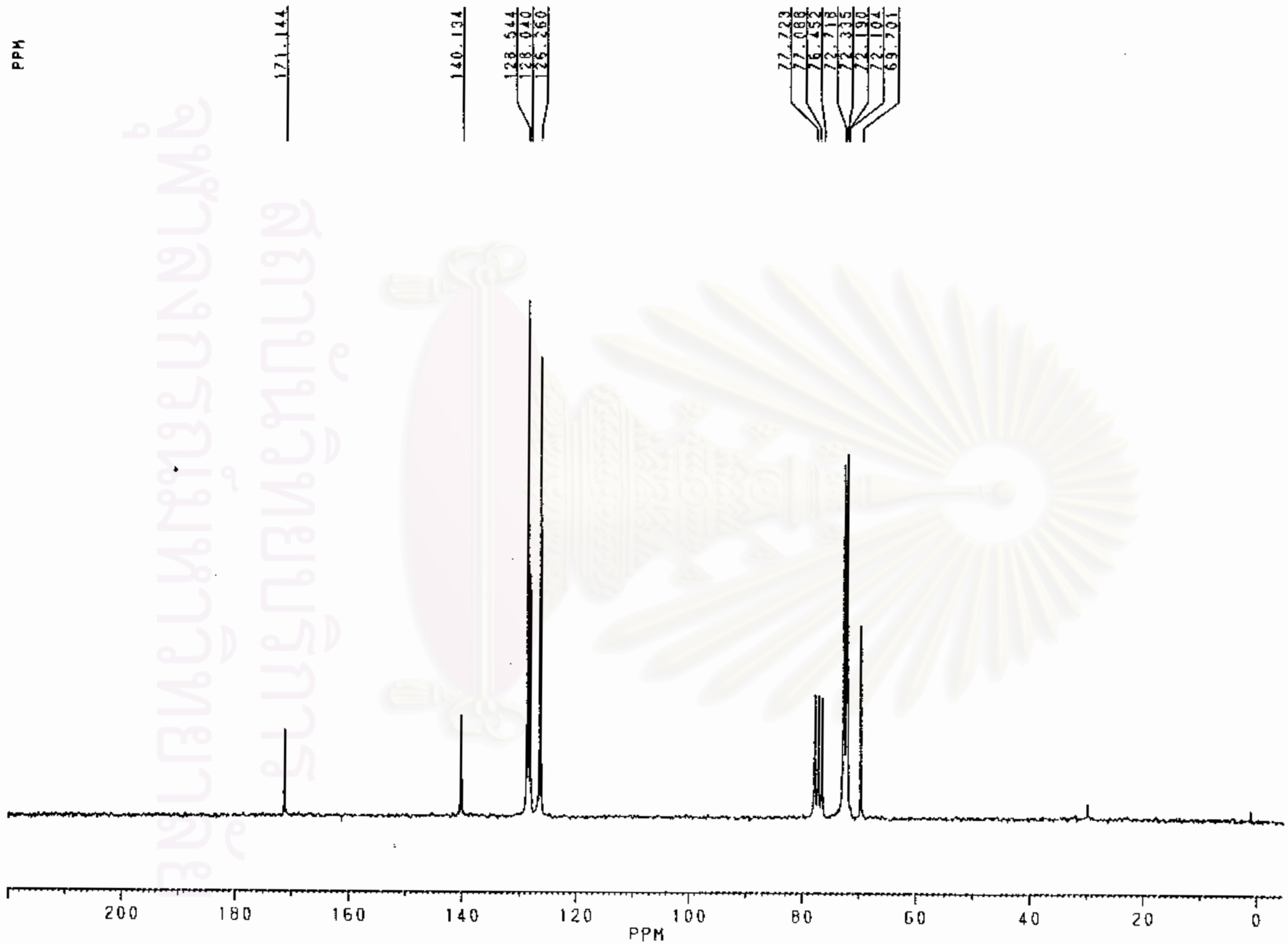


Figure A.13 ^{13}C NMR spectrum of 1,1′-(2-hydroxy-2-phenyl ethylcarboxylate)-ferrocene

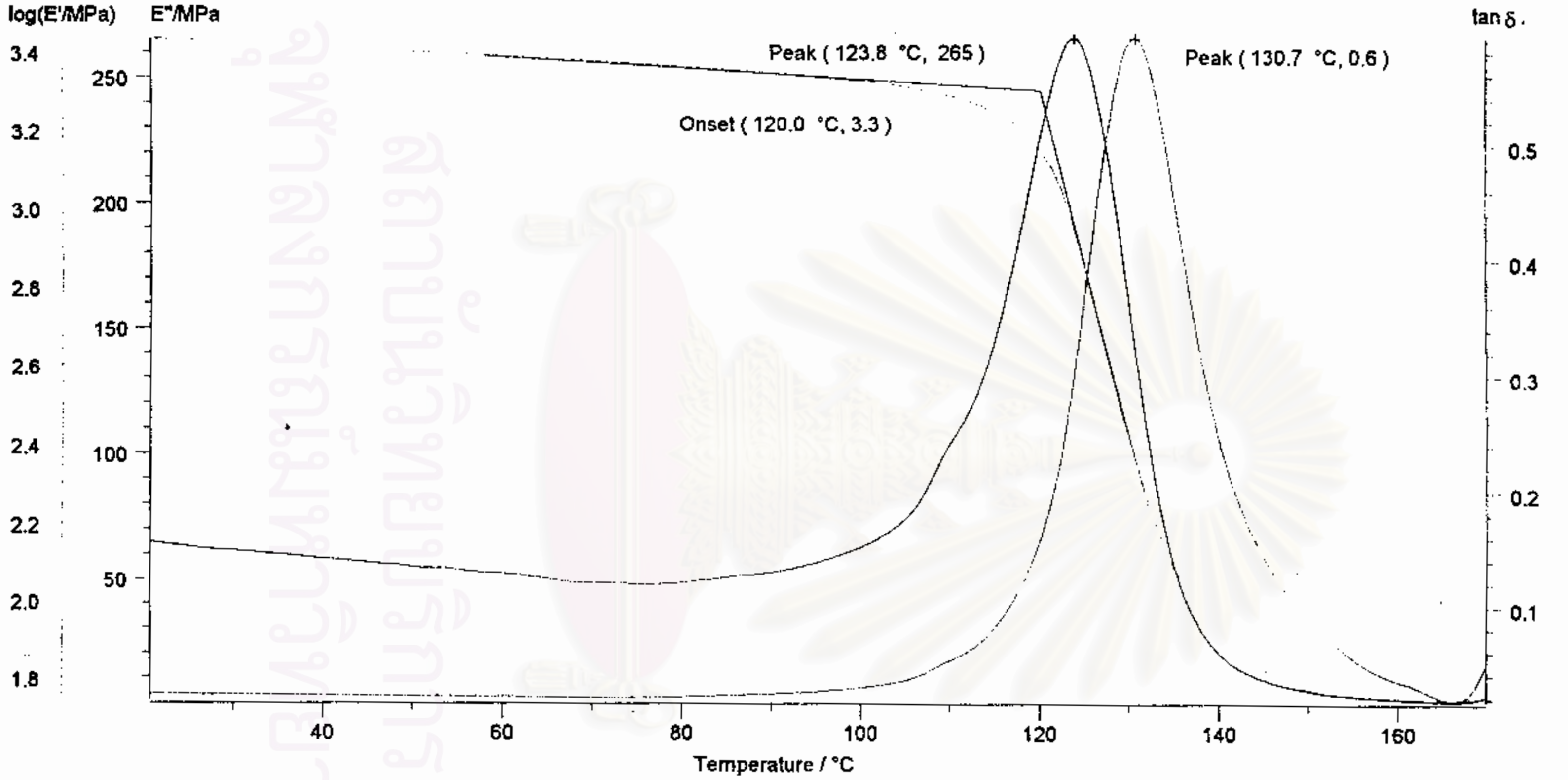


Figure A.14 DMA thermogram of ferrocene-containing epoxy polymer at the mole ratio of DGEBA : 1,1′– ferrocenedicarboxylic acid : Bu_4NOH = 1 : 0.30 : 0.04

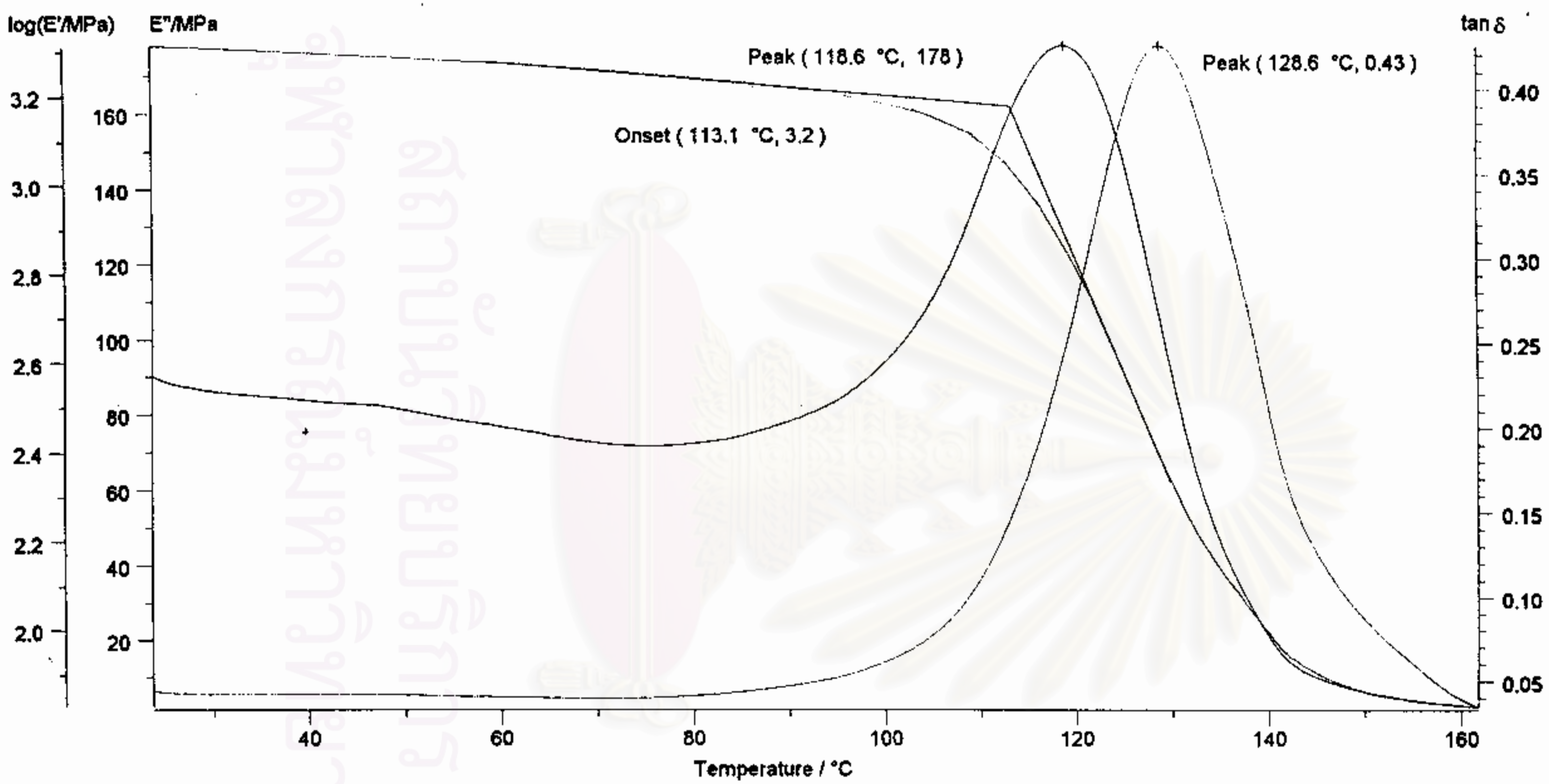


Figure A.15 DMA thermogram of ferrocene-containing epoxy polymer at the mole ratio of DGEBA : 1,1'– ferrocenedicarboxylic acid : Bu_4NOH = 1 : 0.10 : 0.04

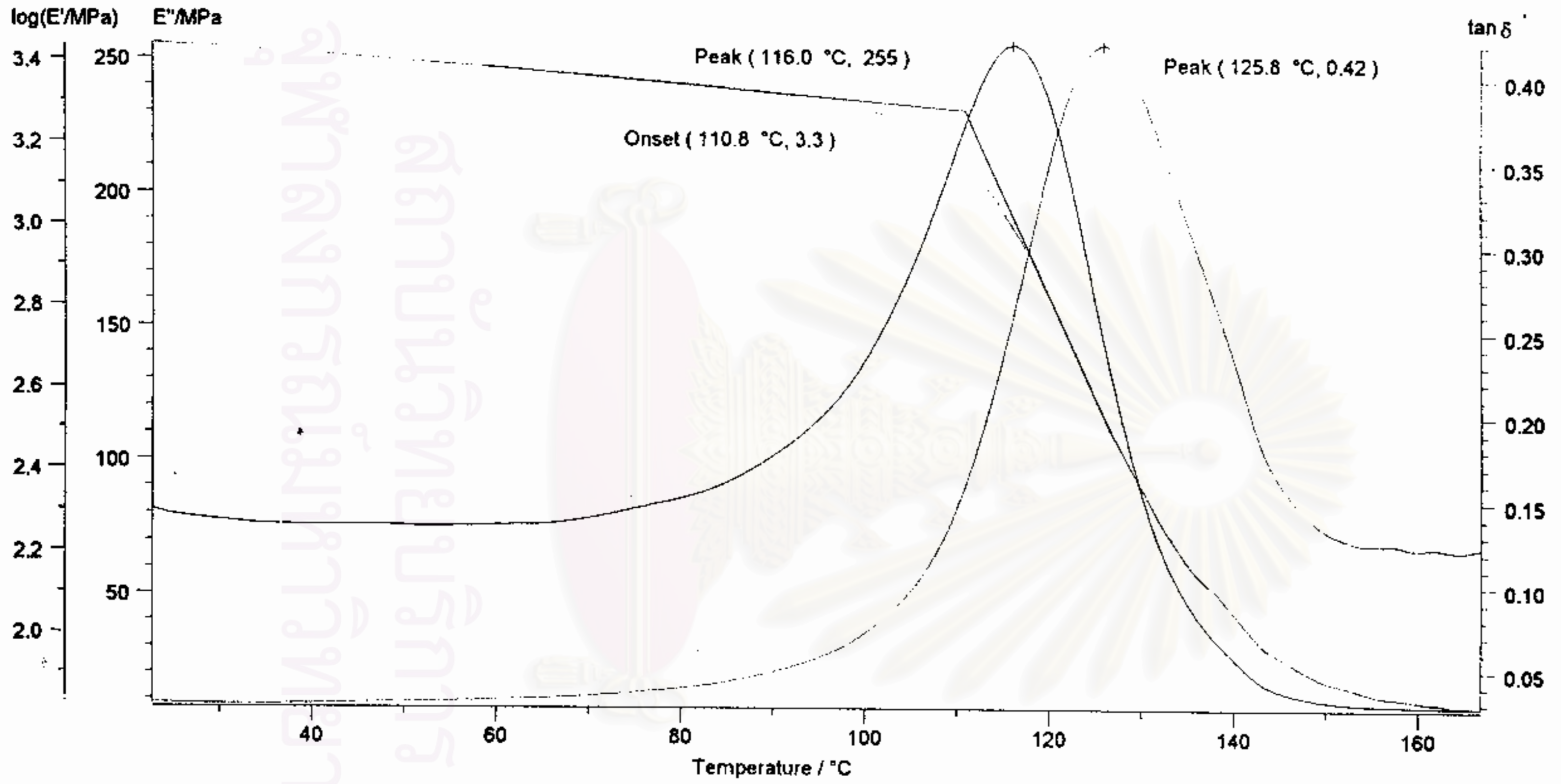
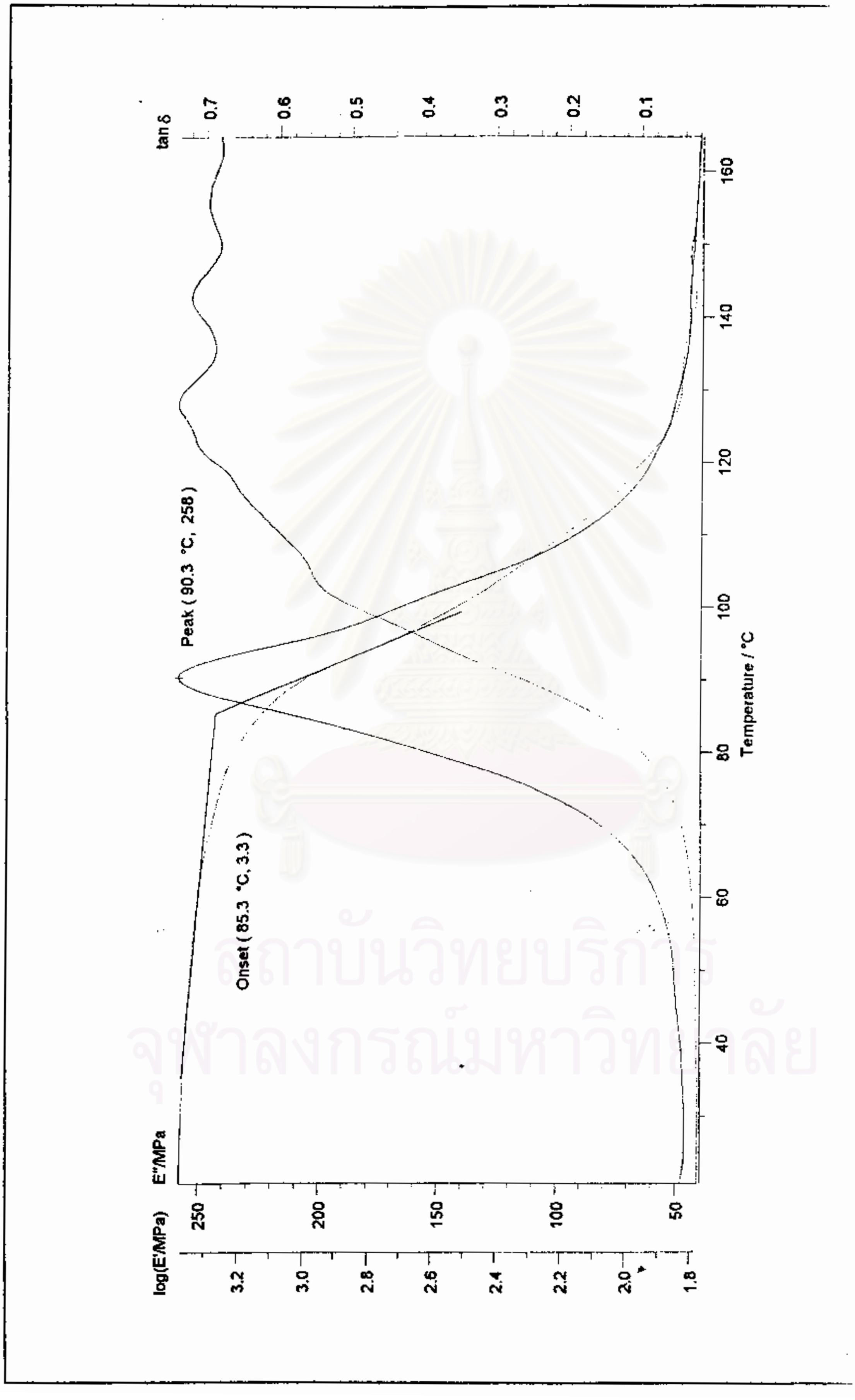


Figure A.16 DMA thermogram of ferrocene-containing epoxy polymer at the mole ratio of DGEBA : 1,1′– ferrocenedicarboxylic acid : Bu_4NOH = 1 : 0.05 : 0.04


log(E'/MPa)
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
E''/MPa
250
200
150
100
50
tan δ
0.7
0.6
0.5
0.4
0.3
0.2
0.1
Peak (90.3 °C, 258)
Onset (85.3 °C, 3.3)
40
60
80
100
120
140
160
Temperature / °C

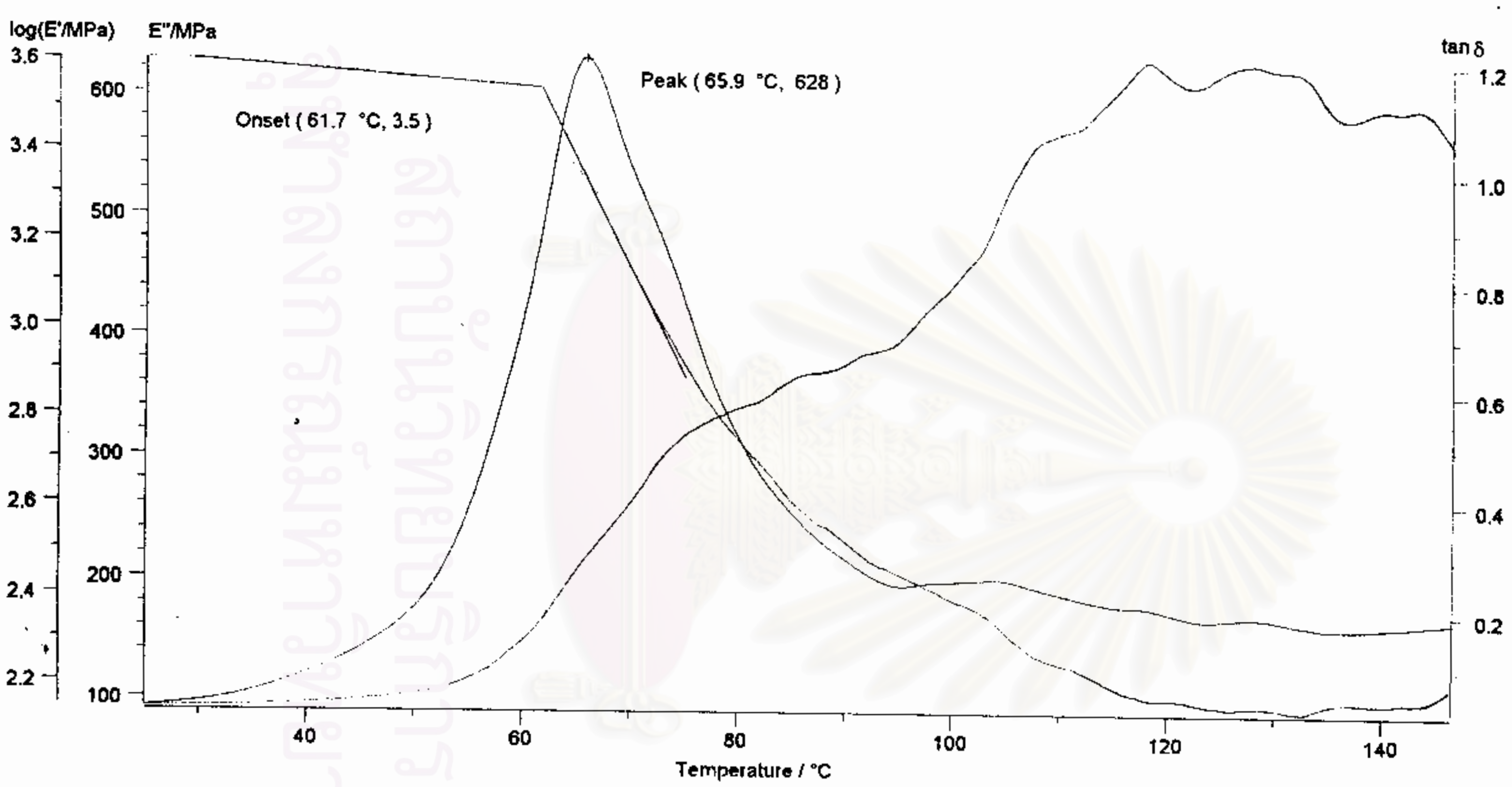


Figure A.18 DMA thermogram of ferrocene-containing epoxy polymer at the mole ratio of DGEBA : 1,1'– ferrocenedicarboxylic acid : Bu_4NOH = 1 : 0.0125 : 0.02

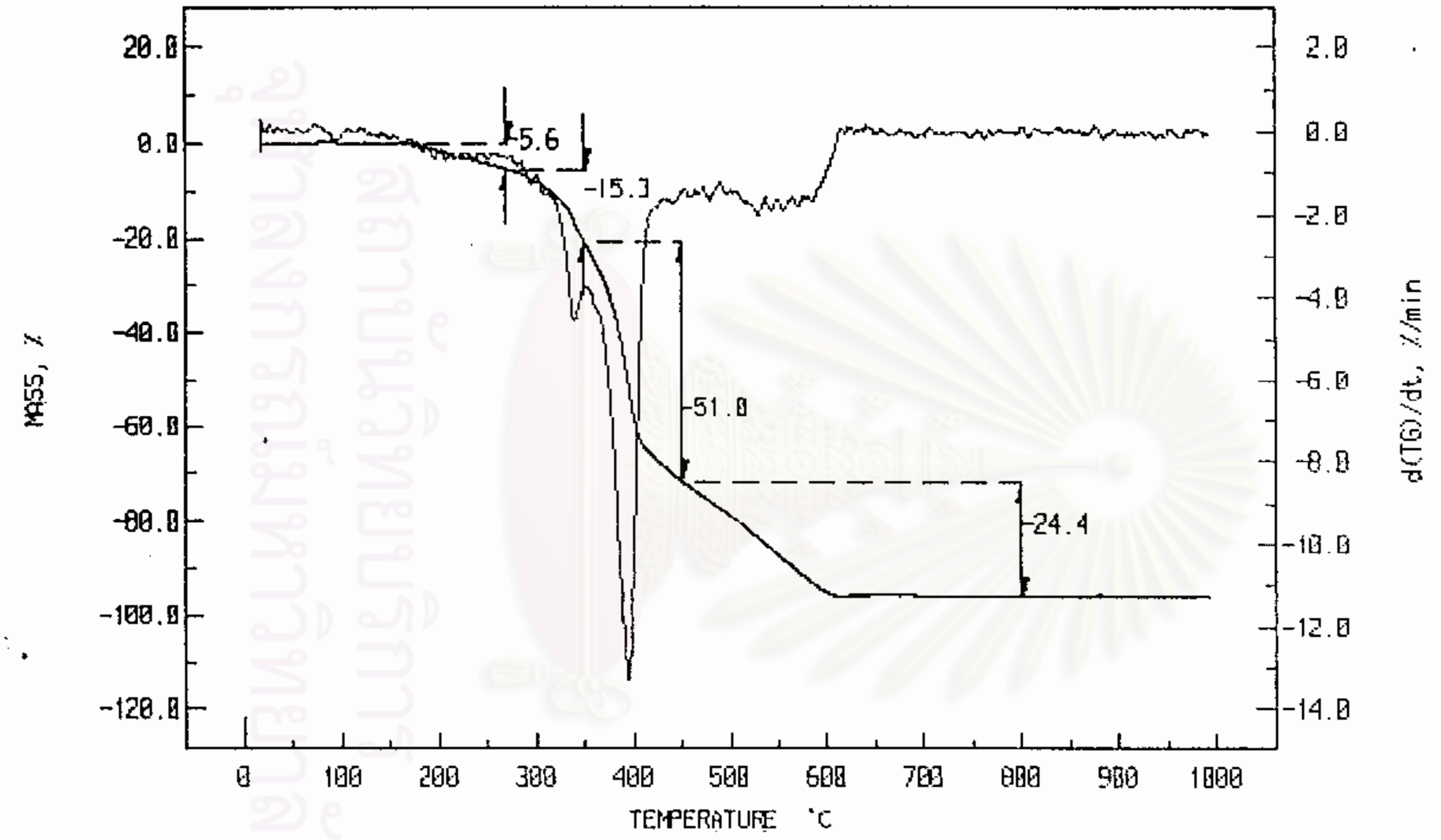


Figure A.19 TGA thermogram of ferrocene-containing epoxy polymer at the mole ratio of DGEBA : 1,1′– ferrocenedicarboxylic acid : Bu_4NOH = 1 : 0.20 : 0.04

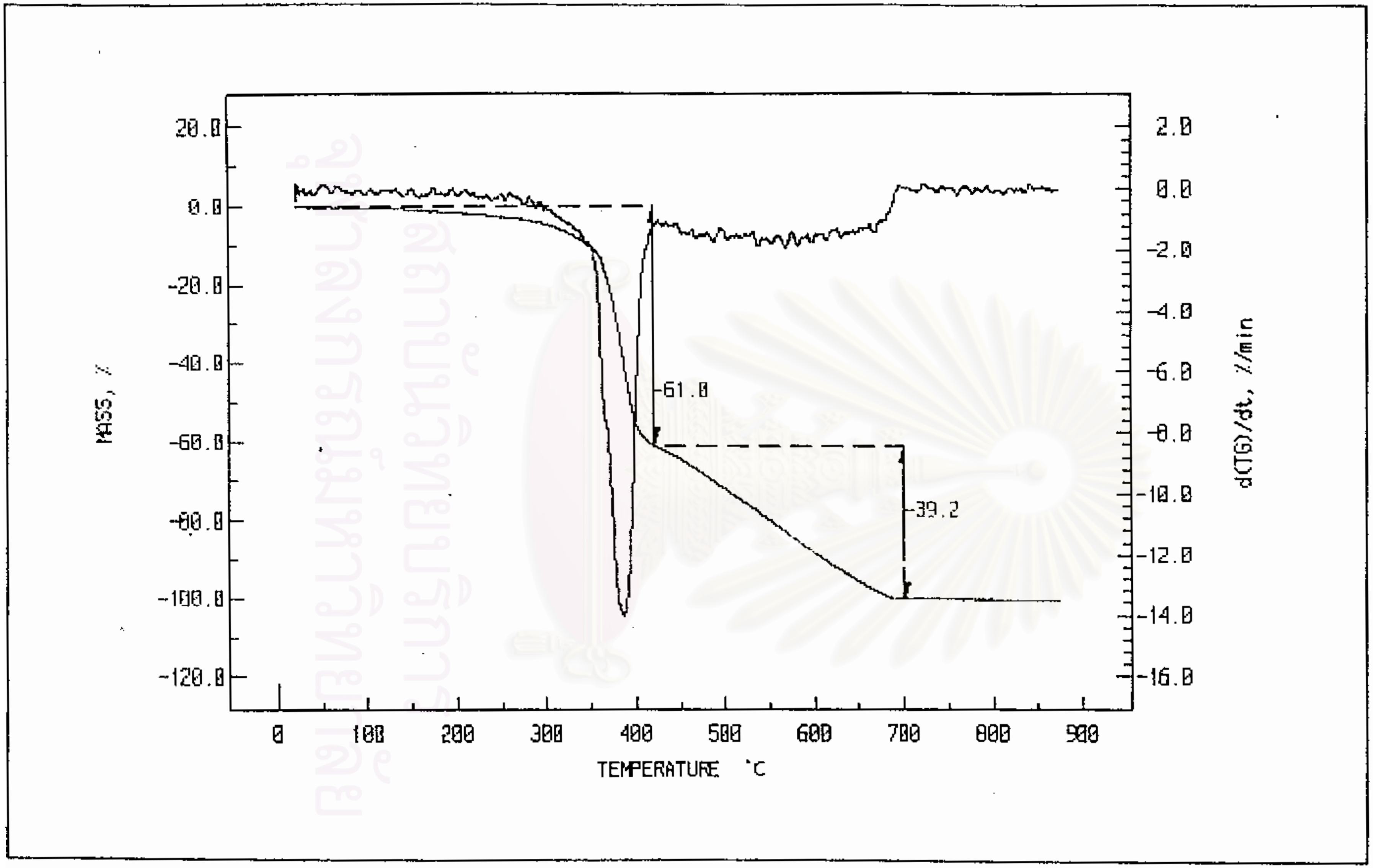


Figure A.20 TGA thermogram of ferrocene-containing epoxy polymer at the mole ratio of DGEBA : 1,1′– ferrocenedicarboxylic acid : Bu_4NOH = 1 : 0.10 : 0.04

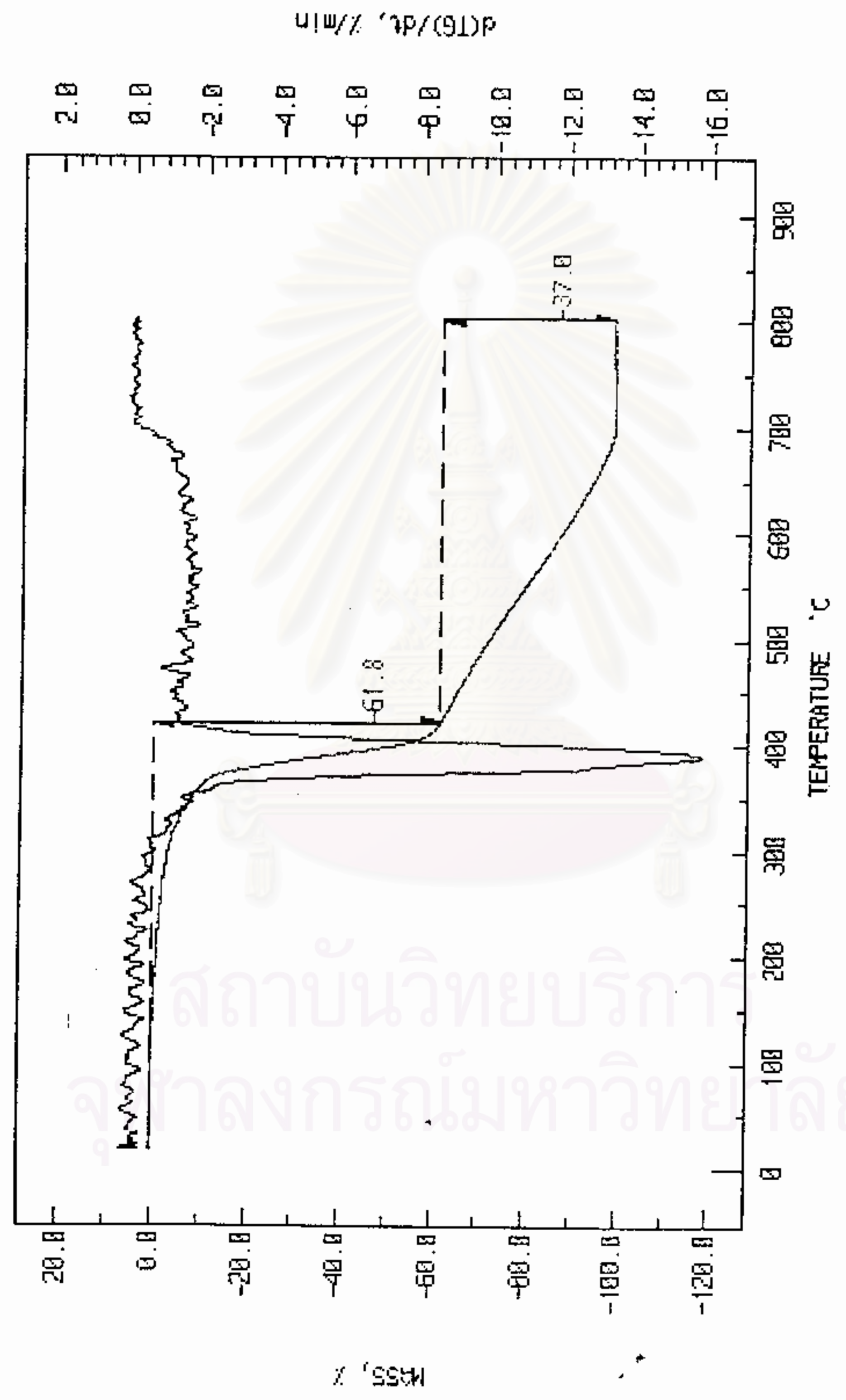


Figure A.21 TGA thermogram of ferrocene-containing epoxy polymer at the mole ratio of DGEBA : 1,1′-ferrocenedicarboxylic acid : Bu_4NOH = 1 : 0.05 : 0.04

VITA

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