EFFICIENCY ENHANCEMENT OF CHEMICAL RECYCLING PROCESS OF DEGRADABLE POLYLACTIC ACID BY EMPLOYING MICROWAVE AND MAGNETIC NANOPARTICLE CATALYST

BY

THERAKANYA SRIPHO

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF MASTER OF
ENGINEERING (ENGINEERING TECHNOLOGY)
SIRINDHORN INTERNATIONAL INSTITUTE OF TECHNOLOGY
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Approved as to style and content by

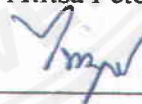Advisor and Chairperson of Thesis Committee _____

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October 2015

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Abstract

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THERAKANYA SRIPHO

Bachelor of Engineering (Chemical Engineering), Mahidol University, 2012

The aim of this research is enhancement PLA chemical recycling efficiency. Glycolysis reaction via ethylene glycol was selected as chemical recycling method. Microwave irradiation and magnetic nano particle (MNPs) catalyst were introduced to improve the performance of glycolysis reaction. ^{1}H-NMR, GPC, FT-IR, and SEM were used for characterization chemical structure and degree of polymerization (DP) of products. The results reveal that glycolyzed PLA (GlyPLA) is the main products from this recycling process. The reaction time can be dramatically decreased when microwave irradiation is employed. Additionally, dramatic decreasing of GlyPLA chain lengths is achieved when MNPs catalyst is introduced in the reaction.

However, chemical structures of the GlyPLA are not affected by employing microwave irradiation and MNPs catalyst. Therefore, employing microwave irradiation as a heating source and MNPs as a catalyst can enhance the performance of PLA chemical recycling.

Keywords: PLA, Chemical recycling, Glycolysis, Microwave irradiation, Magnetic nano particle (MNPs)

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Chapter 1

Introduction

1.1 Statement of the problems

The amount of polymers production (mainly plastics) increases dramatically during the last decade, as shown in figure 1.1, because of a wide range of plastic applications such as packaging, construction, medicine, and electronics (Hamad et al., 2013). A huge demand of plastic use all over the world is forecasted to continue rising rapidly in the future. Moreover, raw materials for production plastics, at the present, are mainly derived from fossil sources, which are non-renewable, and whose limited supply make them become higher prices in the future. Additionally, petroleum-based plastics also lead to other serious environmental problems, especially increasing greenhouse gases from burning fossil fuels via production processes and increasing amount of non-degradable plastic waste after used(Chuensangjun et al., 2013).
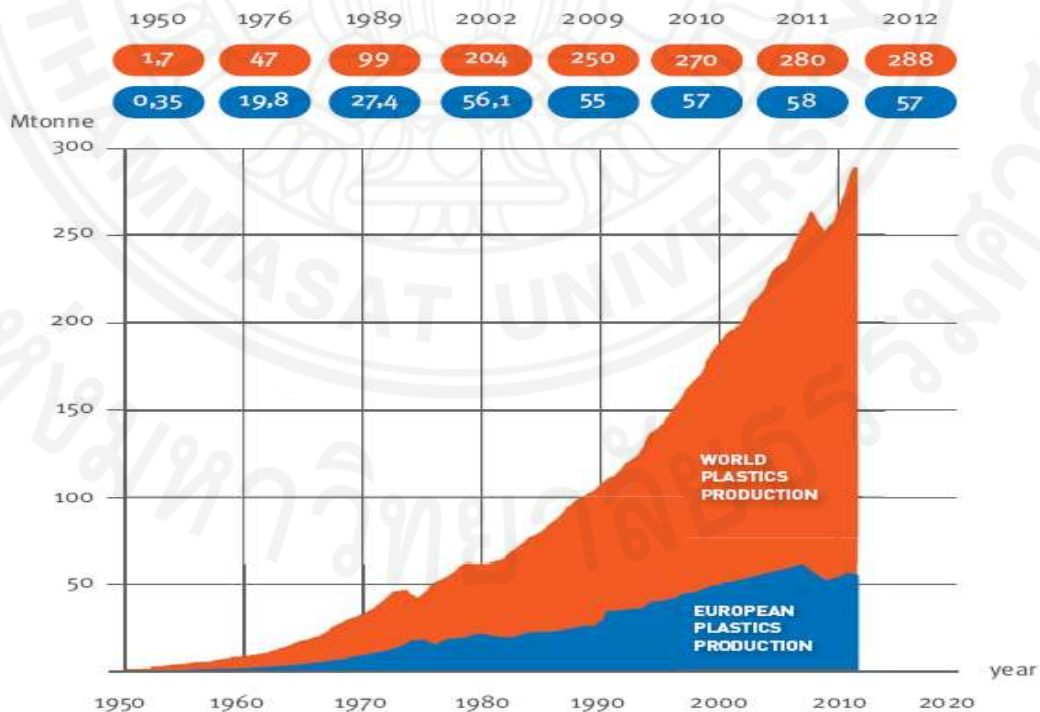
Figure 1.1 Data of world plastic production from 1950 to 2012 (PlasticsEurope, 2013).

In order to address these problems, bio-based plastics become more attractive because its monomer raw materials can be produced from agricultural sources, which are renewable. Furthermore, using bio-based plastics can also help reducing the amount of carbon dioxide emission via fossil fuel combustion (Santosh Madival, 2009).

Polylactic acid (PLA) is one of the most important bio-based plastics because of its properties, such as good biocompatibility, good mechanical properties, and rapid bio-degradability. PLA is a significant material in biomedical applications such as drug delivery and medical devices because of its biocompatibility. Comparing with other commodity polymers, PLA exhibits interesting mechanical properties, as summarized in table1.1 (Carrasco et al., 2010). Therefore, PLA is widely used to produce domestic goods such as bags, cups, food and cosmetic packaging, textile and outdoor novelties as an alternative to petroleum based plastics. Most importantly, although, the end use of bio-based plastics and petroleum - based plastics are similar, using PLA plastic products can help reducing the amount of plastic waste accumulation in the environment, according to its biodegradable properties. On the other hand, waste from petroleum based plastics may remain in the environment for more than several decades. PLA is, therefore, well-known as environmental friendly material.

Table1.1 Comparison of mechanical properties of PLA and other commodity polymers (Carrasco et al., 2010).

Mechanical Properties	PLA	PS	i-PP	PET
Tensile yield strength (MPa)	48-110	34-46	21-37	47
Tensile modulus (GPa)	3.5-3.8	2.9-3.5	1.1-1.5	3.1
Tensile elongation (%)	2.5-100	3-4	20-800	50-300
Notched Izod impact, 23ºC (J/m)	13		72	79

Because of its wide range applications and unlimited supplies of raw materials, the demand of PLA production is predicted to increase higher than other bio-based plastics, as shown in figure 1.2(Lee Tin Sin, 2013). In the near future, the amount of PLA's products seems to increase significantly, which directly impact to PLA waste accumulation. Although PLA is degradable after used, recycling and reusing its waste products are required in order to cope with waste accumulation and increase efficiency of waste utilization (Hirao et al., 2010a, Lee Tin Sin, 2013). Thus, the development of PLA recycling processes is an important aspect in order to enhance efficiency of the process and decrease environmental impacts from the recycling process.
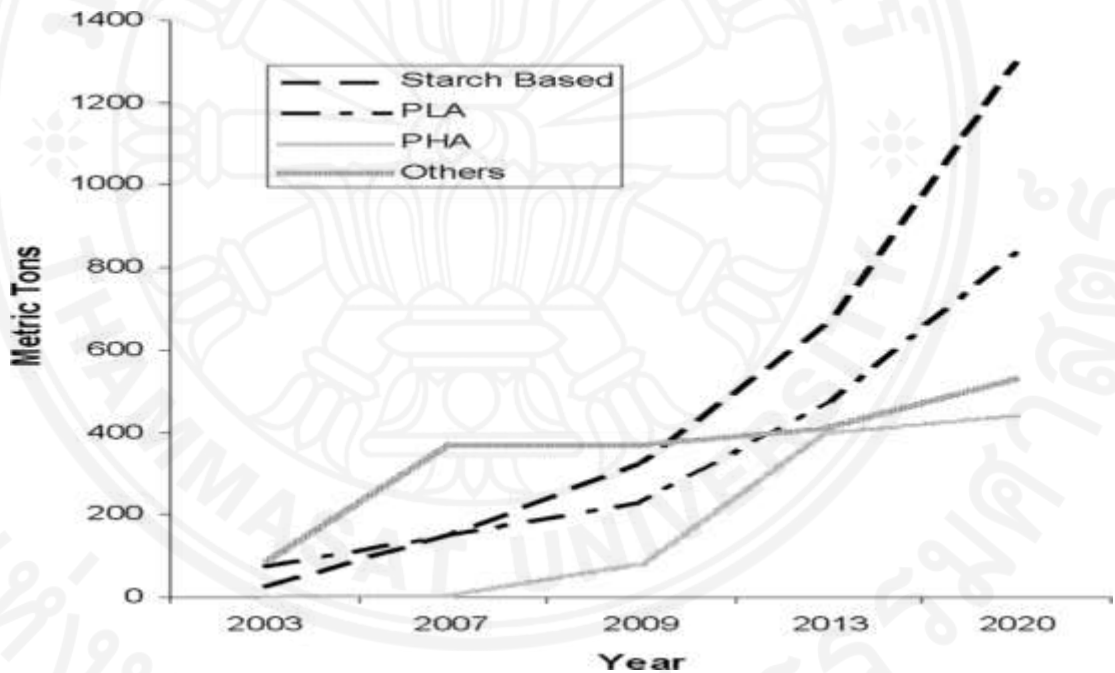
Figure 1.2 World productions of renewable biodegradable polymers in 2003 to 2020(Lee Tin Sin, 2013)

1.2 Objective

The main objectives of this study are as follows:

1.2.1 To chemical recycling of polylactic acid (PLA) and produce PLA glycolized products for the use as starting materials in the productions of other valuable products.

1.2.2 To enhance the performance of the chemical recycling process by using microwave irradiation as a heating source.

1.2.3 To enhance performance of the chemical recycling process by using magnetic nano-particles as a catalyst.

1.3 Scope of work

This research is aim to enhance the chemical recycling efficiency of PLA by glycolysis reaction, employing microwave heating source and magnetic nanoparticles catalyst. Effects of glycolysis conditions, types of catalyst on chemical structures of the glycolysis products will be investigated. The scopes of this research are as follows:

1.3.1 Develop a chemical recycling process for PLA (4043D) via glycolysis reaction using ethylene glycol as a reagent, microwave as a heating source, and magnetic nanoparticle as a catalyst.

1.3.2 Develop a separation technique and characterization of the PLA glycolyzed products.

1.3.3 Investigate the glycolysis mechanisms of PLA in the presence of the magnetic nanoparticle catalyst.

1.4 Significance of the research

This research will provide important scientific information on a new approach for PLA recycling, which can be further exploited by researchers, and applied in many industrial applications. Moreover, this research gives the benefit to the

environment in terms of more environmental friendly recycling process. These can be described, as follows:

1.4.1 Research community

The results from this work can be used as a guideline for researchers, who are interested in PLA chemical recycling processes in order to further develop chemical recycling processes for other polymers. GlyPLA production process illustrated in this work is rapid and less time-consuming process. Therefore, this research can be used as a guideline for the production of GlyPLA, which can be used as an additive to improve bio-degradable properties of plastics.

1.4.2 Industrial sector

Industries can adopt and applied this new approach of PLA recycling and the GlyPLA products. Higher production rate and lower energy consumption of PLA recycling can be achieved by employing this method because of shorter reaction time. Therefore, energy cost can be reduced. This will intensely benefit the setup of this process in industrial scaled-production. In addition, this process is more environmental friendly, so a waste treatment cost might be reduced.

1.4.3 Environment

Increasing efficiency of PLA waste utilization can be achieved, leading to decreasing of PLA waste accumulation in the environment. Therefore, the requirement of landfill, which is generally used for waste dumping, will decrease. Alternatively, this land area can be used for other purposes with higher economic values. As this is a more environmental friendly recycling process, environmental impacts from the PLA chemical recycling process can be reduced by this development because of less energy consumption and less toxic emission.

Chapter 2
Literature Review

2.1 Glycolysis reaction

Glycolysis method is an important chemical recycling process, especially for PET, which is carried out most frequently using ethylene glycol, diethylene glycol, propylene glycol, and dipropylene glycol. The glycolysis reaction is the molecular degradation of PET polymer by glycols, in the presence of trans-esterification catalysts, mainly metal acetates, where ester linkages are broken and replaced with hydroxyl terminals (López-Fonseca et al., 2010, Sinha et al., 2008). Mechanism of the reaction is shown in figure 2.1. Bis (2- hydroxyethyl terephthalate) (BHET) and other oligomers of PET were the main products from this method (Sinha et al., 2008).
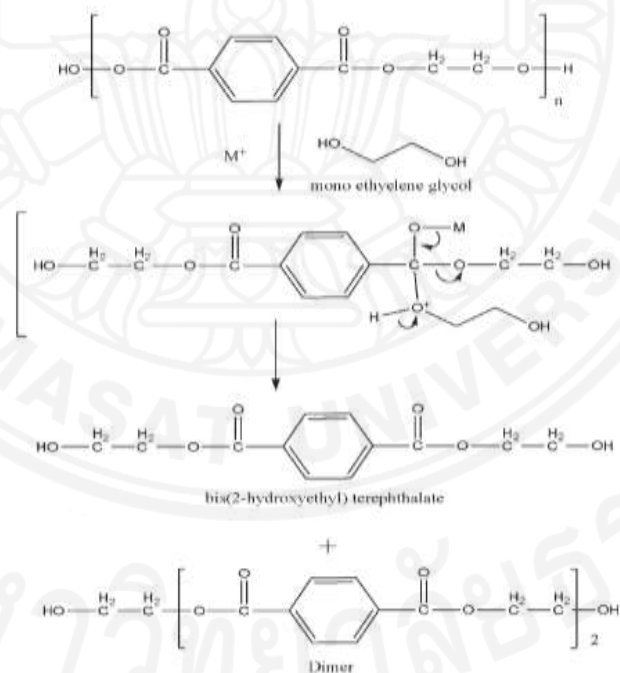
Figure 2.1 Mechanisms of glycolytic depolymerization of PET (Pingale et al., 2010).

Effect of reaction parameters, such as temperature, pressure, and PET to EG ratio on the reaction rate have been investigated by many researches. There were good agreements that reaction temperature around 180 to 190°C, and reaction time 2 to 4

hours was optimum depolymerization conditions (Viana et al., 2011, JONG-WU CHEN, 1998a). Catalysts also play an important role to the reaction rate and yield of the products, as shown in figure 2.2 (a).

Among all the catalysts, zinc acetate ($Zn(Ac)_2$) was the most popular. It was confirmed by many studies that zinc acetate was the most effective catalyst for the glycolysis reaction (C.Y. Kao 1996, JONG-WU CHEN, 1998b, Carné Sánchez and Collinson, 2011)(Pingale and Shukla, 2008), as shown in figure2.2 (b). The reason was that the activation energy was lowered by adding zinc acetate catalyst. Kao et al. reported that polymer bond was broken by facilitation of zinc acetate, subsequently enhance the depolymerization rate (C.Y. Kao 1996).
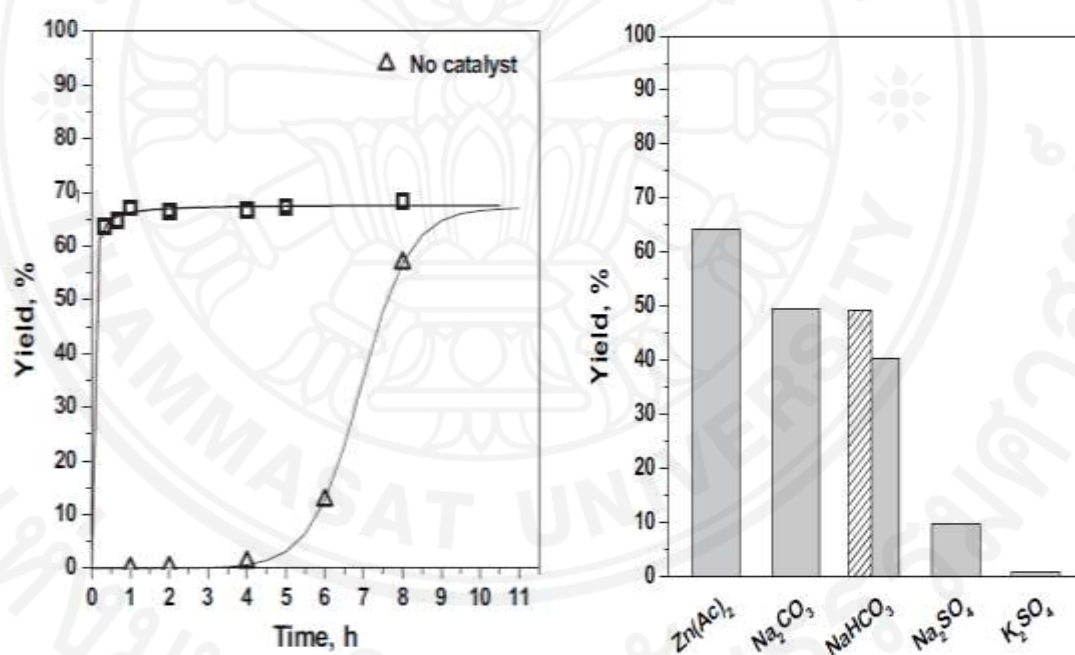
Figure 2.2 Effect of catalysts on depolymerization of PET (a) Evolution of BHET yield with time in the presence and absence of zinc acetate (EG: PET molar ratio 7.6:1, PET: $Zn(Ac)_2$ molar ratio 100:1) (b) BHET yield in the glycolysis of clear PET catalysed by several metal salts (196 °C, EG:PET molar ratio 7.6:1, PET: catalyst molar ratio 380:1) (solid bars). The conversion value for a PET:NaHCO$_3$ molar ratio of 190:1 is also included (lined bar) adapted from R. Lopez at al. (López-Fonseca et al., 2010)

In addition, many researches indicated that amount of liquid ethylene glycol, concentration of catalyst, and reaction temperature were also significant factors to enhance glycolysis efficiency. As a result of kinetic study, amount of liquid ethylene glycol and ethylene diester groups highly affected rate of reaction (A. S. Goje, 2003). The influence of catalyst concentration on monomer yield was shown in figure 2.3. This study revealed that higher concentration of zinc acetate in glycolysis of PET increased yield of PET monomer. Moreover, this trend was also found in other types of catalyst such as sodium carbonate (Na_2CO_3)(R. López-Fonseca a, 2010). Recently, M. E. Viana et al. found that temperature of glycolysis reaction in presence of zinc acetate affected conversion percentages of initial polymer. The conversion percentages of PET increased close to 100% at temperature above 180°C. However, yields of recovered monomer after separation catalyst decreased due to a difficulty of catalyst separation methods(Viana et al., 2011).
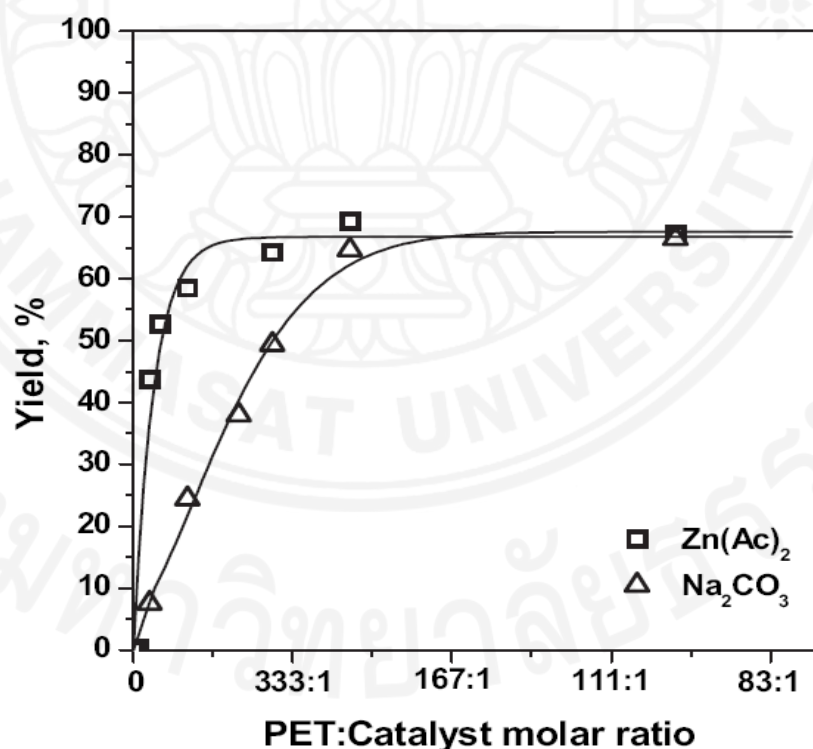
Figure 2.3 Effect of catalyst concentration on PET monomer yields (196 °C, EG:PET molar ratio 7.6:1, 1 hr.) (R. López-Fonseca a, 2010)

As a result of high efficiency of zinc acetate, in 2011, A. C. Sanchez et al. employed this catalyst in chemical recycling of PLA by alcoholysis. They reported that zinc acetate was an important factor to increase monomer yields, as illustrated in table 2.1. However, this study could not achieve 100% conversion of solid PLA. Moreover, they found that there was a contamination of spent catalyst in products, which correlated to decreased product purity(Carné Sánchez and Collinson, 2011).

Table 2.1 Results of alcoholysis of PLA in presence and absence of zinc acetate catalyst(Carné Sánchez and Collinson, 2011)

Solvent	Waste PLA	
	Monomer yield (%)	**Recovered plastic (%, appearance)**
Methanol	0	100 crystalline material
	70	5 powder (containing zinc lactate as an impurity)
Ethanol	0	100 chips
	21	10 powder (containing zinc lactate as an impurity)

Although zinc acetate was efficient catalyst, environmental impacts from toxic zinc were an importance disadvantage of this catalyst. Therefore, many attempts have been developed several eco-friendly catalysts for glycolysis reaction such as mild alkalis and metal chlorides, but, until present, the efficiency of alternative catalysts was lower than zinc acetate (Leian Bartolome and Kim, 2012, López-Fonseca et al., 2010, Bartolome et al., 2014).

Glycolysis of PLA was studied by P. Sukpuang. In this study, PLA resin (Naturework 4042D) was glycolyzed by ethylene glycol at 196°C for 30 minutes with a PLA: EG weight ratio of 1:3. Subsequently, the so-called glycolyzed PLA (GlyPLA) was obtained by dissolving products in chloroform and re-precipitating in petroleum ether (P. Sukpuang, 2009, Sukpuang P., 2009). ^{1}H-NMR spectra of GlyPLA showed chemical shifts ~ 1.2, 3.8, 4.2 and 5.1 ppm, respectively (Olewnik et

al., 2007, P. Sukpuang, 2009, J. L. Espartero, 1996), which refer to the chemical structure of GlyPLA, as shown in figure 2.4. Furthermore, calculation of the number average molecular weight of GlyPLA was around 3.8×10^3 g/mol. These studies can confirm that glycolysis can be employed as chemical recycling of PLA.

Effect of glycolysis conditions conducted by employing ethylene glycol (EG) on structure and properties of GlyPLA was studied by J. Tounthai et al. in 2013. Reaction temperature was fixed at 195 and 168 ^{0}C, while other reaction conditions were varied. Then, GlyPLA products were recovered by dissolving in chloroform, followed by re-precipitation in methanol. From GPC results, the lowest number (Mn) and weight (Mw) average molecular weight is 3,600 and 4,800, respectively. This was performed with the reaction time 30 minutes, the operation temperature 170^{0}C and the PLA: EG weight ratio 1:2. After varying reaction time, temperature, and PLA: EG ratios, found that the M_W reduction of the products was obtained by increasing the EG content, the reaction time and the temperature. In addition, the diol concentration was the key parameter to achieve lower MW, which had been reported by N. Nakruangsri et al in 2009 (Tounthai et al., 2013, N. Nakruangsri, 2009).

Procedures for GlyPLA recovery was another factor that affected the molecular weight of GlyPLA and yield, as reported by N. Nakruangsri. et al. In this study two different procedures of recovery were applied: 1) water recovery and 2) recovery by chloroform and methanol. Lower yield but higher molecular weights of the GlyPLA products were obtained from the second recovery process. Since lower solubility of GlyPLA in water, especially low molecular weight, than methanol, there was loss of the products in the second recovery process (Karst and Yang, 2005, N. Nakruangsri, 2009). Moreover, it was reported that GlyPLA can be used as a raw material for the synthesis of other copolymers and in other processes (N. Nakruangsri, 2009, Sukpuang P., 2009, Tounthai et al., 2013, P. Sukpuang, 2009).
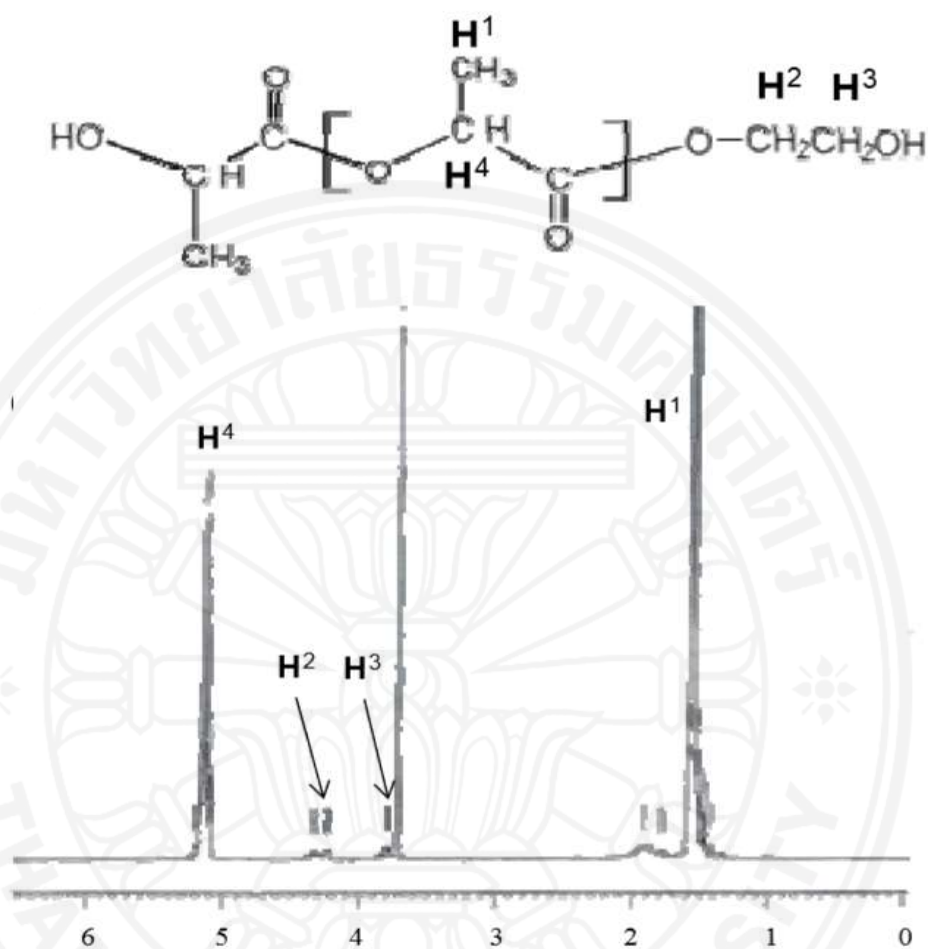
Figure 2.4 ^{1}H-NMR spectrum and proposed chemical structure of GlyPLA
(Sukpuang P., 2009)

2.2 Microwave irradiation in polymer chemical recycling processes

In 1998, Krzan reported the use of microwave irradiation for PET recycling, which was first mentioned in chemical recycling of PET (Hynek Bene, 2013, KRZAN, 1997). Nikje et al. studied the effects of microwave irradiation on the reaction time of alcoholysis reaction of PET. In this work, microwave power, types of alcohol solvents, and types of catalysts were varied. They suggested that the major advantage of using microwave heating was shorter reaction time and a cleaner process. Undesirable products from the side reaction such as oxidation of ethylene glycol were eliminated (Nikje and Nazari, 2006). Another alcoholysis

depolymerization of PET was studied by dqui et al. in 2012 (Siddiqui et al., 2012). In the experiments, a methanolysis reaction under microwave irradiation and zinc acetate catalyst were employed. Compared to conventional heating methods, microwave irradiation heating had lower polymerization time. Moreover, it was found that increasing the microwave power led to raise reaction temperature, subsequently increasing degradation rate of PET. In addition, high degradation rate was investigated at the beginning of reaction (around 5–10 minutes) due to rapid increasing of reaction temperature, as shown in figure 2.5. Furthermore, this work indicated that, under microwave irradiation, glycolysis reaction was the most efficiency chemical recycling process of PET, as illustrated in figure 2.6 (Siddiqui et al., 2012).
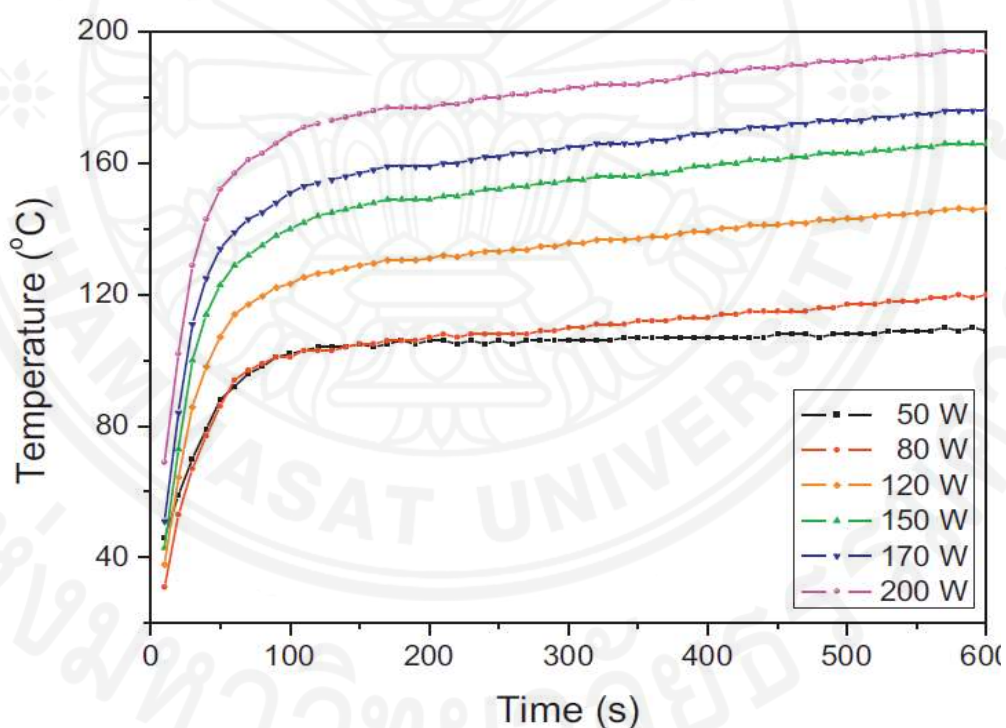
Figure 2.5 Methanolysis of PET under microwave irradiation at various reaction microwave power (Siddiqui et al., 2012).
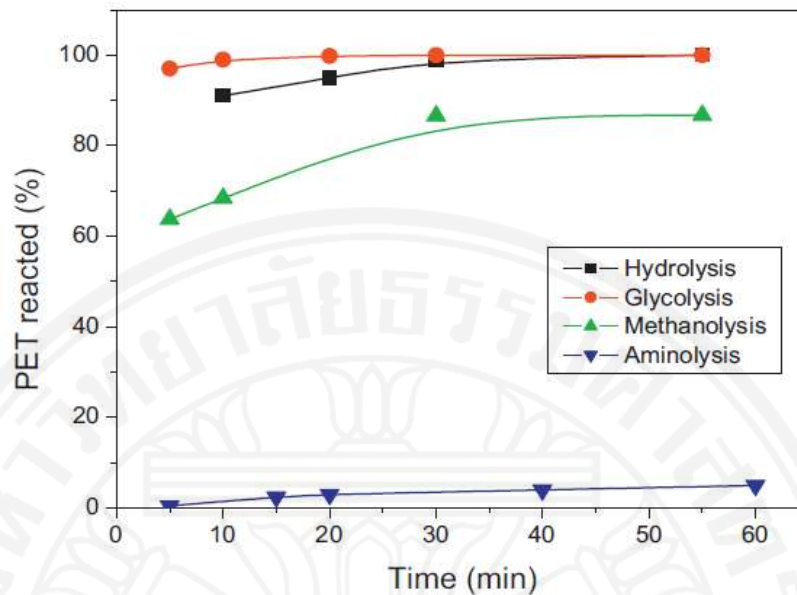
Figure 2.6 Compared the effect of different reagent types on PET degradation under microwave irradiation at 180 °C for 60 minutes (N.D. Pingale, 2009, Siddiqui et al., 2012).

Using microwave irradiation was not only applicable for PET chemical recycling, but this heating technique was also been used in chemical recycling of PLA and showed a good result. Typically, microwave irradiation heating technique had been used for synthesis of PLA (Hirao and Ohara, 2011). Chemical recycling of PLA employed microwave irradiation in order to enhance recycling performance by decreasing the reaction time. Koichi Hirao et al. studied hydrolyzed of PLLA using microwave irradiation. The aim of this study was to compare yields of lactic acid after depolymerization between conventional heating and microwave irradiation heating. The same reaction temperature and PLA: water ratio was introduced in both heating systems. They reported that the similar yields of lactic acid were obtained from both cases; around 45%. The reaction time around 800 minutes was required in conventional heating, while microwave irradiation technique could achieve the same yield within 120 minutes, as shown in figure 2.7 (Hirao et al., 2010b).
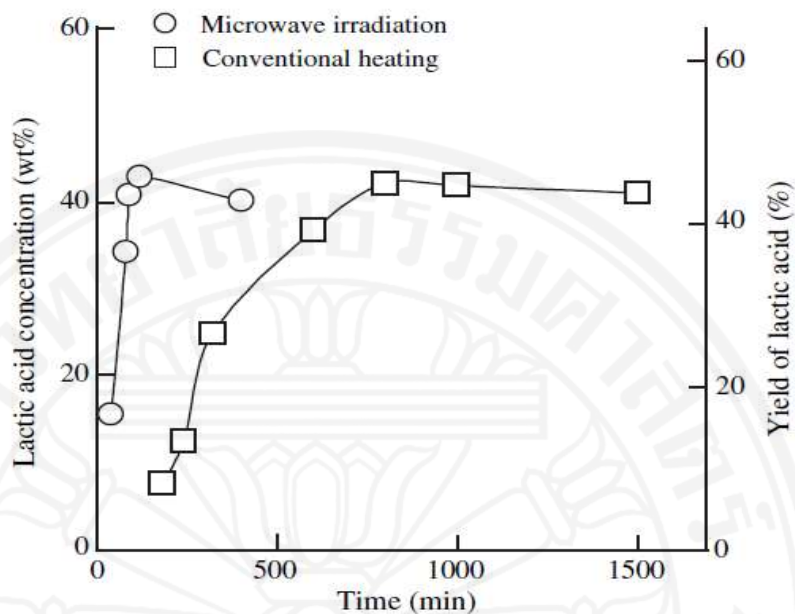
Figure 2.7 Results on lactic acid concentration (left axis) and yield (right axis) from hydrolysis under microwave irradiation (circles) and conventional heating (squares) at 170°C with PLLA: water weight ratio of 3:1, as a function of time adapted by Hirao et. al. (Hirao et al., 2010b).

Although the number average molecular weight of the products obtained from conventional heating for 240 minutes and the use of under microwave irradiation for 13 minutes was almost the same (1.2 x 10^4 and 1.4 x 10^4), GPC curves of the products were different. Binary distribution curve of GPC curve was investigated when conventional heating was employed. On the other hand, microwave irradiation illustrated one peak, as shown in figure 2.8. They explained the reason of splatted curve that hydrolysis in conventional heating slowly started in amorphous zones then crystalline zone of material was depolymerized. (Hirao et al., 2010b).
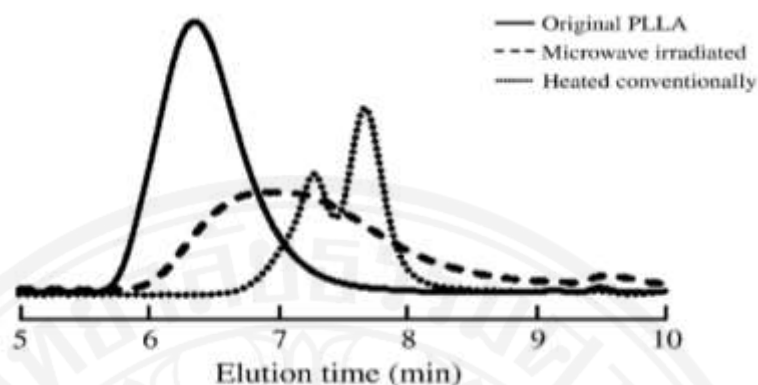
Figure 2.8 Compared GPC curves of the original PLLA, PLLA irradiated microwave for 13 min, and PLLA heated conventionally for 240 min adapted from Hirao et al. (Hirao et al., 2010b).

In the following year, alcoholysis recycling of PLA under microwave irradiation was studied by Hirao et al. The aim of this study was the same as previous study. However, in this study, ethanol and butanol were used as the solvent, with the reaction temperatures between 130 – 210 °C and a PLA: alcohol molar ratio of 1:10. The results were concluded that effects of reaction time and temperature on the number average molecular weight of products from both of the heating techniques were not different. However, the rate of depolymerization in alcoholysis reaction was increased by the introduction of microwave irradiation heating technique. Interestingly, racemization, which reflected in the results of optical purity, of the products was not influenced by employing microwave irradiation, (Hirao et al., 2010a).

2.3 Magnetic nanoparticle

In these past few years, there are more concerns about environmental problems. An enhancement of environmental friendly catalyst has gained attention from researchers and industrial sector. Less toxic catalyst has become important in many production processes. Compared with other metal catalysts, an iron catalyst is an interesting catalyst due to its availability and low toxicity.

Synthesis of magnetic nanoparticle (MNPs) is a critical process that affects size and shape of MNPs. Typically, co-precipitation, thermal decomposition, microemulsion, and hydrothermal synthesis are popular methods for synthesis MNPs, which are summarized in appendix A. Co-precipitation method is the simplest process and requires shortest reaction time when compared with other methods. Thus, there has been growing interest in the development of co-precipitation synthesis procedure of MNPs in order to control particle size, size distribution and shape of MNPs (W.H.Cheng, 1998).

Monodispersion of MNPs was an importance aspect. Organic additives were used as a stabilizer in order to prepare monodispersednMNPs. In 1996, Lee et al. reported that 4– 10 nm of MNPs can be stabilized in an aqueous solution of 1 wt% polyvinlyalcohol (PVA). Chain link clusters were formed in this study (Jiwon Lee, 1996). However, the stabilizer, organic solvent remained on the surface of MNPs surface was the limitation of this method. In 2006, K. Nishio et al. succeeded in synthesizing size-controlled MNPs around 30 - 100 nm, with size distribution around 15 percent by surfactant-free oxidation process in NaOH solution. Sodium nitrate as an oxidant and ferrous chloride aqueous solution were added (Nishio et al., 2007). Utilizing waste from other processes as a raw material for synthesis MNPs was studied by Kim et al. in 2009 (Kim et al., 2008) and Giri et al. in 2011 (Giri et al., 2011). In Giris study shown that super paramagnetic behavior of MNPs can be produced by employing co-precipitation of recovered waste iron ore tailings with acidic solution under inert atmosphere. In addition, high stability and monodispersion of MNPs in medium were investigated in this work. In addition, SEM images and TEM images indicated that the shape controllable synthesis was achieved. MNPs with spherical or cubic ranging from 8.3 to 23.0 nm were found (Giri et al., 2011).

Chapter 3

Research Methodology

3.1 Materials and Chemicals

- Polylactic acid resin pallet (NatureWork4043D)

- Ethylene glycol(EG), analytical grade (Carlo Erba)

- Chloroform, analytical grade (Lab Scan)

- Methanol, commercial grade,

- Methanol, analytical grade, (Lab Scan)

- Silica gel, RS-CHROM (Carlo Erba)

- Tetrahydrofuran (THF), analytical grade (Carlo Erba)

- Chloroform-D, D 99.8% (Cambridge Isotope Laboratories)

- Iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), analytical grade

- Iron(II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), analytical grade

- Ammonia analytical grade

- Distilled water

3.2 Equipment and Instrumental

- Samsung domestic microwave

- Round bottom flask, 250 ml

- Glass condenser

- Burette 50 ml

- Glass micro filter paper (Washman)

- Chemistry laboratory glassware

- Hot plate

- Agitator

3.3 Analytical instruments

- Proton nuclear magnetic resonance (^{1}H-NMR spectrometer), AV-500,

  Bruker Biospin

- Fourier Transform Infrared Spectrometer (FTIR), Nicolet 6700

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- Gel permeation chromatography (GPC), Waters e2695

- Scaning eletron microscope (SEM), JEOL JSM-5410LV

- High-performance liquid chromatography (HPLC), Agilent 1260 Infinity

series

- Inductively coupled plasma (ICP), Perkin-Elmer Optima 8000

3.4 Experimental

The overall experimental procedures in this study can be divided into 2 parts; PLA de-polymerization by glysolysis reaction and separation of the result GlyPLA products by column chromatography.

3.4.1 De-polymerization of PLA by glysolysis reaction

3.4.1.1 Glycolysis of PLA by using microwave irradiation

(1) Ethylene glycol (EG) and PLA resin, at percent weight described in table 3.1 was mixed in a 250 ml round bottom flask.

(2) This round bottom flask was put in a microwave oven – equipped with an open position on the top.

(3) The round bottom flask was connected to a condenser. Each batch of glycolysis conditions was conducted with the reaction conditions as summarized in table 3.1.

(4) After the completion of the glycolysis reaction, the glycolysed products (GlyPLA) were dissolved in chloroform and re-precipitated in methanol and filtrated by glass micro filter paper.

(5) The precipitant was washed by warm water before drying in a vacuum oven at 60^0C for 15 hours.

(6) The chemical structure of the resulting products were characterized GlyPLA by ^{1}H-NMR and GPC.

The overall experimental process of this work is shown in figure 3.1.

Table 3.1 A summary of glycolysis conditions of PLA.

Sample No	Power (Watt)	Temperature (°C)	Time (min)	PLA:EG (weight percent)
A1	600	190	5	1:2
A2	600	190	7	1:2
A3	600	190	10	1:2
A4	750	200	7	1:2
A5	750	200	10	1:2
A6	600	190	10	1:0.5

PLA
↓

EG ———→ Glycolysis under microwave irradiation

———————→ Excess EG

↓

Chloroform ———→ Dissolve

↓

Methanol ———→ Re-precipitation

↓

Filtration

———————→ Methanol

↓

Warm Water ———→ Washing

↓

Drying

↓

GlyPLA
↓

Characterization
- ^{1}H-NMR
- GPC
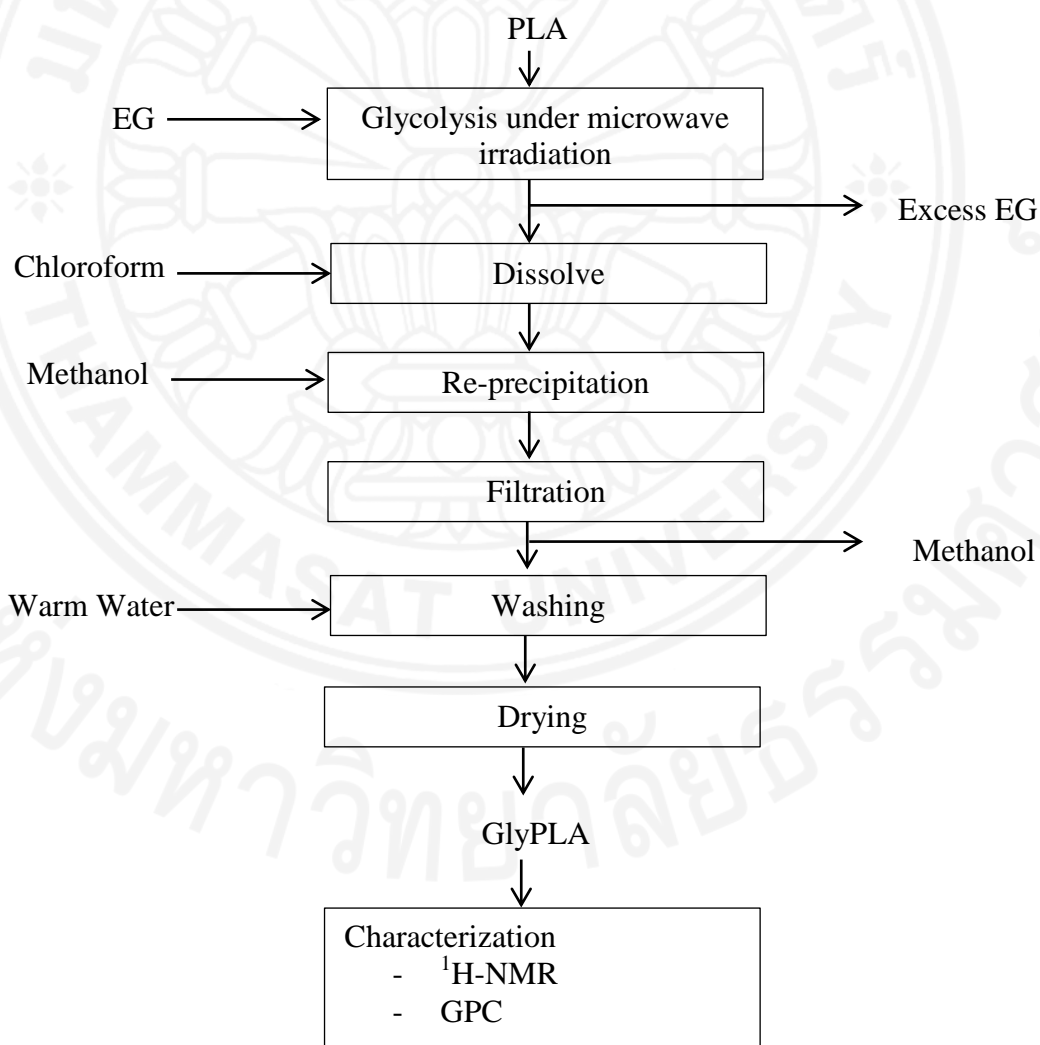
Figure 3.1 Overall experimental procedures of glycolysis of PLA under microwave irradiation.

3.4.1.2 Glycolysis of PLA by using microwave irradiation and magnetic nano particle (MNPs) catalyst

This section is divided into 2 parts; the synthesis of MNPs by the co-precipitation method, followed by the glycolysis reaction, as follows;

(1) 2 g of $FeCl_3 \cdot 6H_2O$ and 3 g of $FeSO_4 \cdot 7H_2O$ were dissolved into 100 mL deionized water.

(2) 25 ml ammonia was slowly dropped into the solution while stirring for 1.5 hours.

(3) The resulting MNPs were washed with distilled water and ethanol until the pH of the washed solvent reached 7.

(4) EG, MNPs, and PLA resin was prepared separately according to table 3.2. The mixture was then added to a 250 ml round bottom flask.

(5)   The round bottom flask was put in microwave and connected to a condenser.

(6) After the completion of the reaction, MNPs were separated from GlyPLA solution by applying magnetics bar.

(7) The separated MNPs were stored in chloroform, and GlyPLA in a PET bottle for future use.

(8) The chemical structure of GlyPLA products was characterized by HPLC, ^{1}H-NMR, and FTIR spectroscopy.

(9) The surface morphology of spent MNPs catalyst was characterized GlyPLA by SEM.

The summary of experimental procedures is illustrated following figure 3.2.

Table 3.2 Glycolysis condition of PLA with microwave irradiation and magnetic nanoparticle (MNPs).

No	MNPs (g)	PLA:MNPs	PLA:EG	Time (min.)	Power (Watt)	Temperature (°C)
B1	1.0	10:1	1:2	10	600	190
B2	0.5	20:1	1:2	10	600	190
B3	0.1	100:1	1:2	10	600	190
B4	1.0	10:1	1:1	10	600	190
B5	0.5	20:1	1:1	10	600	190
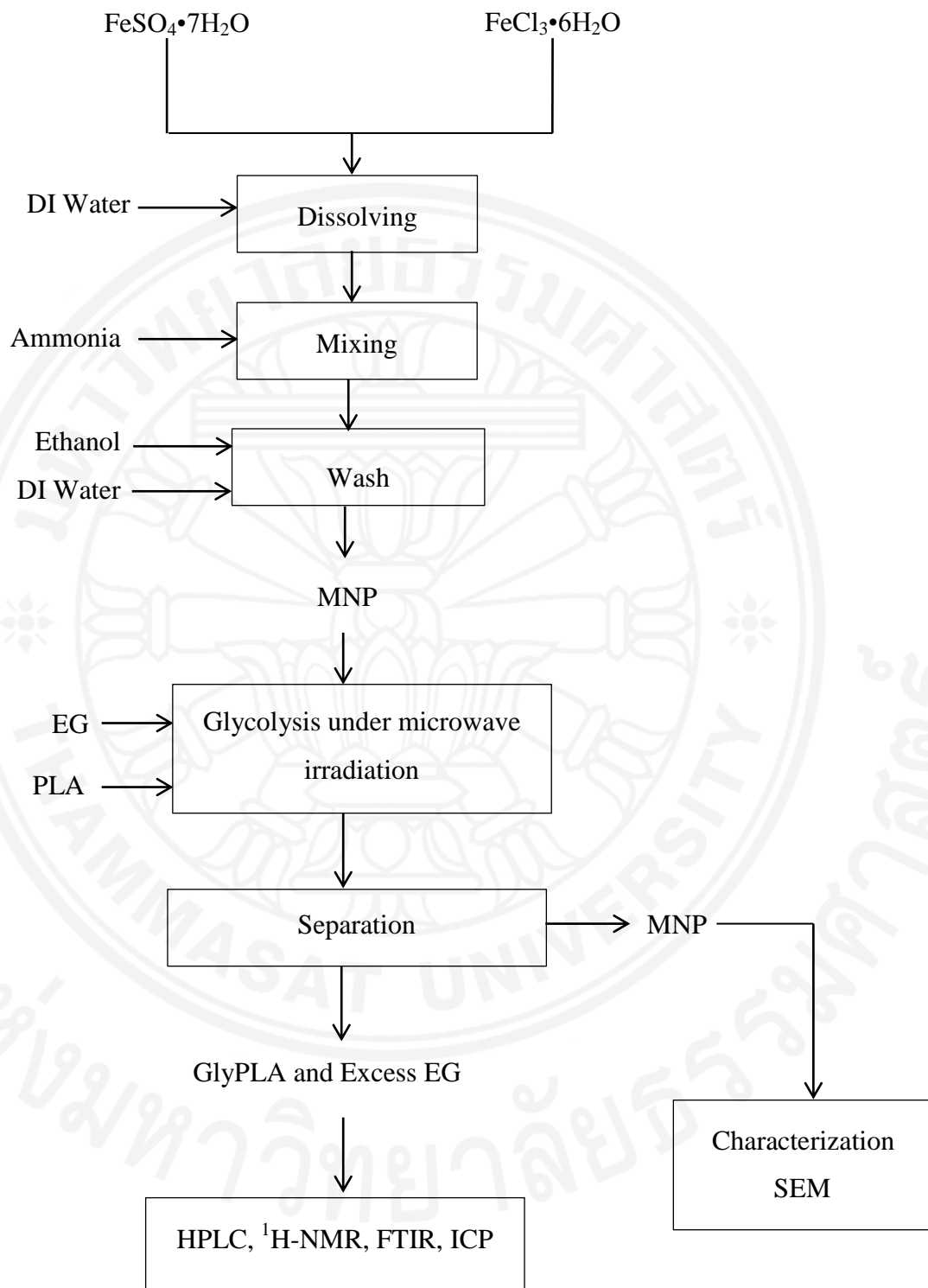
Figure 3.2 Experimental procedures of glycolysis reactions of PLA under microwave irradiation and MNPs catalyst.

3.4.3 Separation of GlyPLA products by column chromatography

Separation of GlyPLA components was conducted by column chromatography employing 50 ml burette packed with silica gel by a slurry packing method. GlyPLA products from the reaction with condition B1 were used to study the effects of the type of eluting solvent. Procedures of the experiment are explained below;

(1)   Cotton wool was plugged at the bottom of the column to prevent the loss of silica gel.

(2)   Methanol was filled into the column around one third of the column height.

(3)   A mixture of 12 ml of silica gel and 30 ml of methanol was prepared in a beaker, and the slurry was slowly poured into the column. The solvent was allowed to drain to prevent overflowing, while aware too much draining in order to prevent column run dry.

(4)   The column was tapped gently to allow air bubbles to rise to the top of the column, and the silica to settle and well packed.

(5)   Excess methanol in the column was drained until the methanol level was nearly even with the surface of the silica gel, after well-setting of silica in the column.

(6)   GlyPLA solution sample was prepared by diluting 2 ml of B1 sample into 8 ml of methanol, then pipetted this eluent in to the column, then followed by 10 ml of pure methanol in order to wash the column.

(7)   Different fractions of the sample were collected every 5 minutes, and characterized by FTIR and ^{1}H-NMR.

(8)   Repeat step 1 to 7, but the mixed solvent was changed to THF and mixture of THF and methanol at a volume ratio of 1:1.

Conditions of column chromatography are summarized followed table 3.3

Table 3.3 The summary of column chromatography conditions.

Condition	Type of sample	Amount of sample (ml)	Absorbance	Type of solve	Amount of solvent (ml)
C1	B1	2	12 ml of silica gel	Methanol	18
C2	B1	2	12 ml of silica gel	THF	18
C3	B1	2	12 ml of silica gel	Mixed solvent Methanol :THF (1:1)	18

Chapter 4
Results and Discussion

4.1 De-polymerization of PLA by glycolysis reaction

The effects of microwave irradiation and MNPs catalyst on PLA glycolysis reaction were investigated. Chemical structures of the products (GlyPLA) and the effect of glycolysis conditions are discussed below;

4.1.1 Glycolysis of PLA with microwave irradiation

4.1.1.1 Chemical structures of glycolyzed products (GlyPLA)

^{1}H-NMR spectrum of GlyPLA is shown in figure 4.1. The spectra of the products from every reaction condition illustrate a similar pattern, in which a selected spectrum is shown in Figure 4.1. Four significant chemical shifts are the spectra at 1.6, 3.8, 4.2 and 5.1ppm. The chemical shift 1.6 and 5.1 ppm also appear in original PLA, which indicates resonances of methane (-OC**H**CH$_3$C=O) at 5.1 ppm and methyl (-OCHC**H$_3$**C=O) at 1.6 ppm. On the other hand, the signals at 3.8 (O=COCH$_2$C**H$_2$**OH) and 4.2 ppm (O=COC**H$_2$**CH$_2$OH) do not appear in the starting PLA. These chemical shifts might be assigned to resonances of methylene protons originated from ethylene glycol. Moreover, ^{1}H-NMR spectrum of GlyPLA also shows chemical shifts around 4.3 ppm, which assigned to (HOC**H**CH$_3$C=O) end groups. Therefore, the chemical structure of GlyPLA from glycolysis with microwave irradiation seems to be presented followed figure 4.1, which is related to the previous studies from J. Tounthai et al. and N. Nakruangsri et al. Furthermore, the proposed mechanism of PLA glycolysis reaction via transesterification and chemical structures of GlyPLA products are shown in Figure 4.2, which agrees with our previous reports. All of ^{1}H-NMR spectra from glycolysis condition A1 – A6 were shown in appendix B.
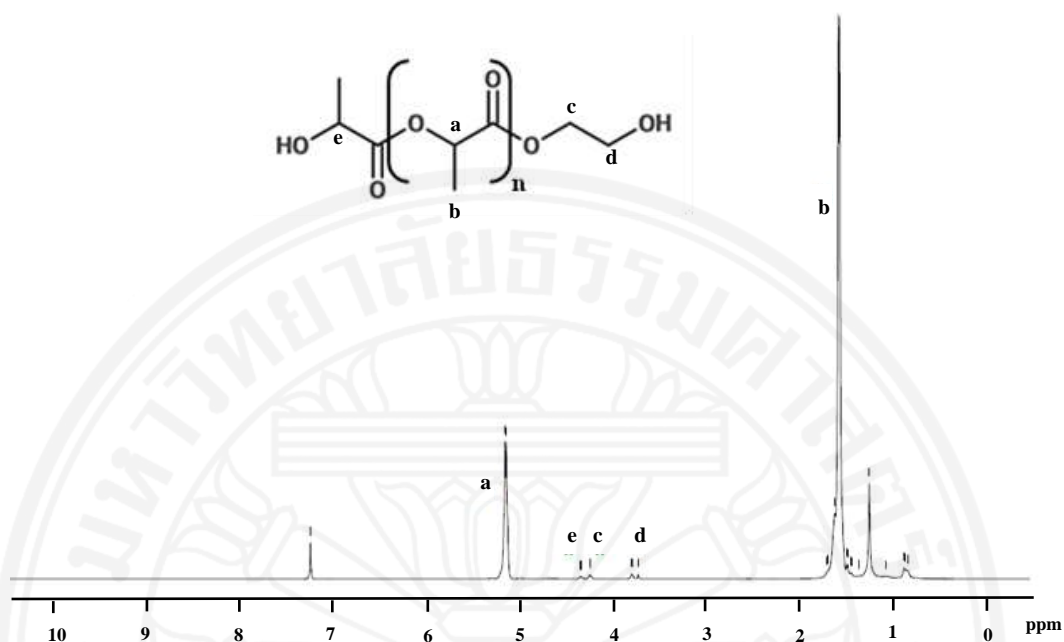
Figure 4.1 ¹H NMR spectrum and chemical structure of GlyPLA (PLA: EG 1:2, 5min, 600W) and chemical structure of GlyPLA.
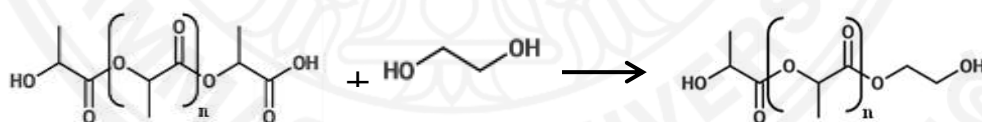
Figure 4.2 Reaction of glycolysis reaction of PLA.

4.1.1.2 Effect of glycolysis reaction conditions

From ¹H-NMR results, we can calculate degree of polymerization (DP) and number-average molecular weight (Mn) by using equations 1 and 2. The results from this calculation are summarized in table 4.1

$$DP = H^a/H^e \qquad \text{................} \quad Eq1$$
$$Mn \ (g/mol) = DP \times 72 \ + 62 \qquad \text{................} \quad Eq2$$

When;

H^a is intensity of GlyPLA at chemical shift 5.1 ppm

H^e is intensity of GlyPLA at chemical shift 4.3 ppm

Table 4.1 Results on DP and Mn of GlyPLA products obtained from glycolysis of PLA at various reaction conditions.

No	Power (Watt)	Temperature (^{o}C)	Time (min)	PLA:EG (% wt.)	DP	Mn
A1	600	190	5	1:2	63	4,561
A2	600	190	7	1:2	27	2,007
A3	600	190	10	1:2	27	2,007
A4	750	200	7	1:2	34	2,544
A5	750	200	10	1:2	46	3,334
A6	600	190	10	1:0.5	23	1,724

The results of Mn of GlyPLA products prepared from different glycolysis conditions in table 4.1 clearly indicate that Mn of GlyPLA from all of glycolysis reactions (A1 to A6) decreases when compared with that of raw material (84,000 g/mol^{-1}). A similar trend is also observed from the GPC results, which is shown in table 4.2. These reflect that the PLA chains are degraded by successive transesterification reactions of the hydroxyl groups in EG molecules.

Table 4.2 Molecular weight of GlyPLA by GPC (conditions: 200°C, 10 min., PLA: EG 1:2).

Reaction condition	Peak Number	Mn	Mw
A3	1	2,417	3,977
A5	1	10,112	17,135
	2	1,160	1,247

The data on Mn of GlyPLA products prepared from different glycolysis conditions clearly indicate that the EG:PLA feed ratios, and glycolysis temperature and time have strong influence on chemical structures and Mn of GlyPLA, which are discussed below;

(1) Effect of EG: PLA weight ratios

In conventional heating, higher EG: PLA feed ratios are employed. GlyPLA products with shorter chain length are obtained. The high diol content leads to higher degree of transesterification of the chains. However, compared the result of DP between glycolysis condition A3 and A6 can be indicated that there are slightly different DP values when microwave irradiation was introduced.

(2) Effect of glycolysis temperature and reaction time

When the reaction temperature is kept at 190°C, depolymerization of PLA via transesterification occurs with formation of product chemical structure following figure 4.1. An increase in the reaction time at this temperature produces the products with lower molecular weight.

However, an opposite trend of Mn is found when the reaction temperature is raised to 200°C. The results from conditions A3 and A5 show that at this temperature, products with higher Mn are obtained when the reaction time increases. This is likely due to re-combination of short glycolized oligomers by transesterification, which occurs at high temperature conditions. Similar results are also observed in conditions A2 and A4. When the same reaction time is applied in conditions A2 and A4,

products with lower Mn is obtained at the lower temperature (190°C). This phenomenon can be observed by GPC results, as shown in table 4.2, and figure 4.3.
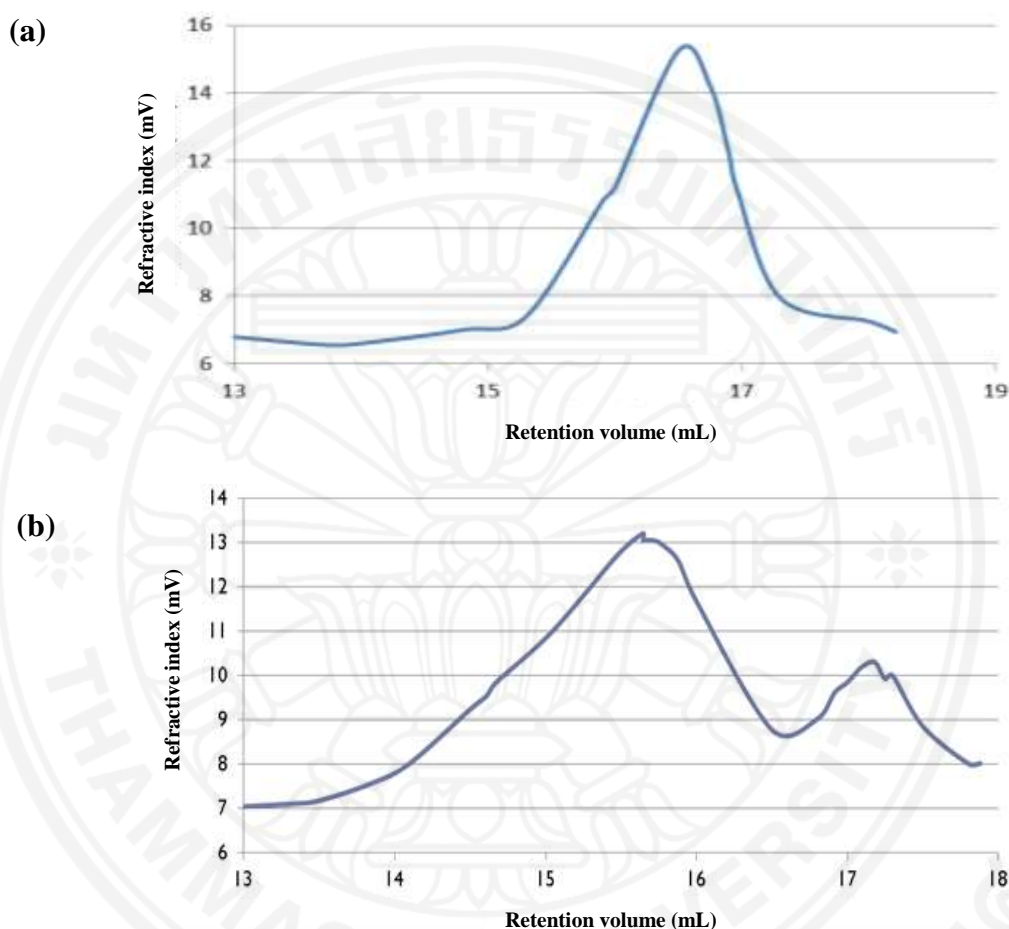
Figure 4.3 Molecular weight distribution curves of GlyPLA obtained by GPC
     experiments; a) 190°C, 10 min., PLA:EG 1:2 and b) 200°C, 10 min.,
     PLA:EG 1:2.

From GPC results, GlyPLA obtained at 200°C shows bi-modal distribution of Mn whereas GlyPLA from reaction temperature 190°C has only one range. Two peaks of GPC are obtained at Mn 10,112 and Mn 1,160 g/mol. Generally, the lower Mn is the result from a typical glycolysis reaction, same as the previous reaction and illustrated in figure 4.1. In contrast, higher Mn in condition A5 is generated from the reaction between end groups of GlyPLA with another end group of GlyPLA, as

shown in figure 4.4. This is likely due to re-combinations of short glycolized oligomers by transesterification, which occurs at high temperature conditions. The proposed chemical structure of the products from re-transesterification is also illustrated in figure 4.4. The similar chemical structure was previously reported by J. Tounthai et al (Tounthai et al., 2013). Additionally, at this temperature, an increased in the reaction time leads to Mn increasing of the products, as reflected from glycolysis condition A4 and A5.
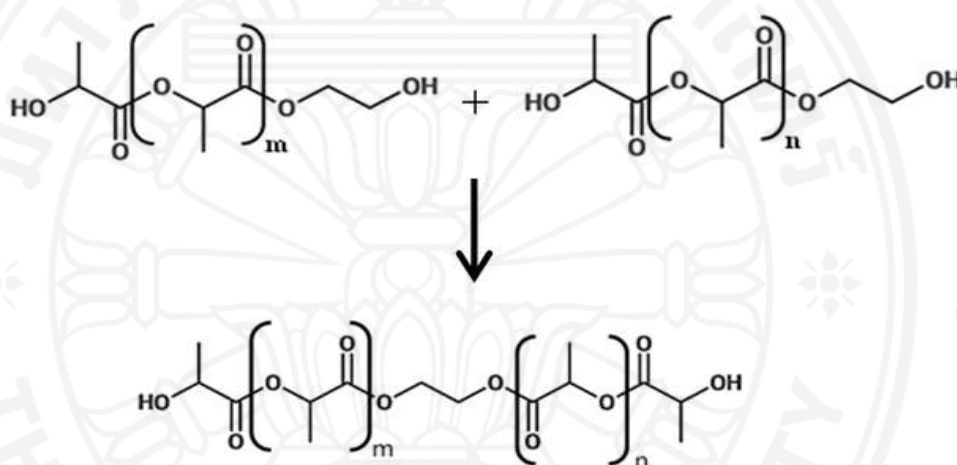
Figure 4.4 Reaction of GlyPLA reaction when reaction temperature is raised to 200°C.

(3) Effect of microwave irradiation

Results on reaction time required in the reaction using conventional heating and microwave irradiation reveal that both of heating sources can be applied to recycling of PLA via glycolysis reaction. Chemical structure of the products from both heating sources is significantly similar. However, the remarkable difference in the reaction time is observed. At the same reaction temperature, GlyPLA with Mn around 5,000 g/mol can be achieved within 5 minutes by using microwave irradiation. On the other hand, 60 minutes is required in order to achieve same number average molecular weight.

4.1.2 Glycolysis of PLA employing microwave irradiation and MNPs catalyst

When MNPs are introduced to the glycolysis reaction, the products after the reactions (condition B1, B2, B4 and B5) cannot be re-precipitated by methanol, similar to those of A1 to A6. Only GlyPLA obtained from the reaction condition B3 can be re-precipitated by methanol. This reveals that GlyPLA generated from the use of MNPs consists of higher ratio of oligomers and shorter polymer chain than those of GlyPLA from the glycolysis without MNPs. This is because the product cannot be re-precipitated into solid form. Therefore, HPLC was used to determine the components of the products from the reaction with B1, B2, B4 and B5 conditions.

4.1.2.1 Separation of GlyPLA components by HPLC

HPLC chromatograms of all of GlyPLA in figure 4.5 show a range of retention time around 6 to 8 minutes. The results from all samples consist of six significant peaks, which show the same retention time at 6.0, 6.2, 6.4, 6.7, 7.2 and 8.0 minutes. This indicates the difference in hydrophobic properties of each component. Longer polymer chains or more hydrophobic components are eluted at lower retention times. On the other hand, shorter polymer chains, which are more hydrophilic according to the higher contents of hydroxyl groups at the end of chain, are eluted later, and refer to higher retention time. Therefore, signal in HPLC chromatogram at the same retention time correspond to each particular component in GlyPLA products, which has different chain lengths.

HPLC chromatogram also demonstrates the contents of each component in GlyPLA, which can be calculated from the peak area at each retention time. The compositions of the six components in GlyPLA obtained from all reaction conditions are shown in table 4.3, which illustrates the same trend of peak area in every glycolysis conditions. The major component of products from glycolysis conditions is obtained at the longest retention time (8 minute), followed by 7.2, 6.7 and 6.4 minutes, respectively. During the first two peaks of chromatogram; 6.0 and 6.2 minute, little amount of GlyPLA component can be found. Therefore, the GlyPLA from these four reaction conditions consist of similar components, and each component at the same retention time have the same polymer length and chemical

structure. So, there are four majorities of components in this GlyPLA. Moreover, the highest proportion of components from all of glycolysis reactions is present at the retention time equal to 8 minute.
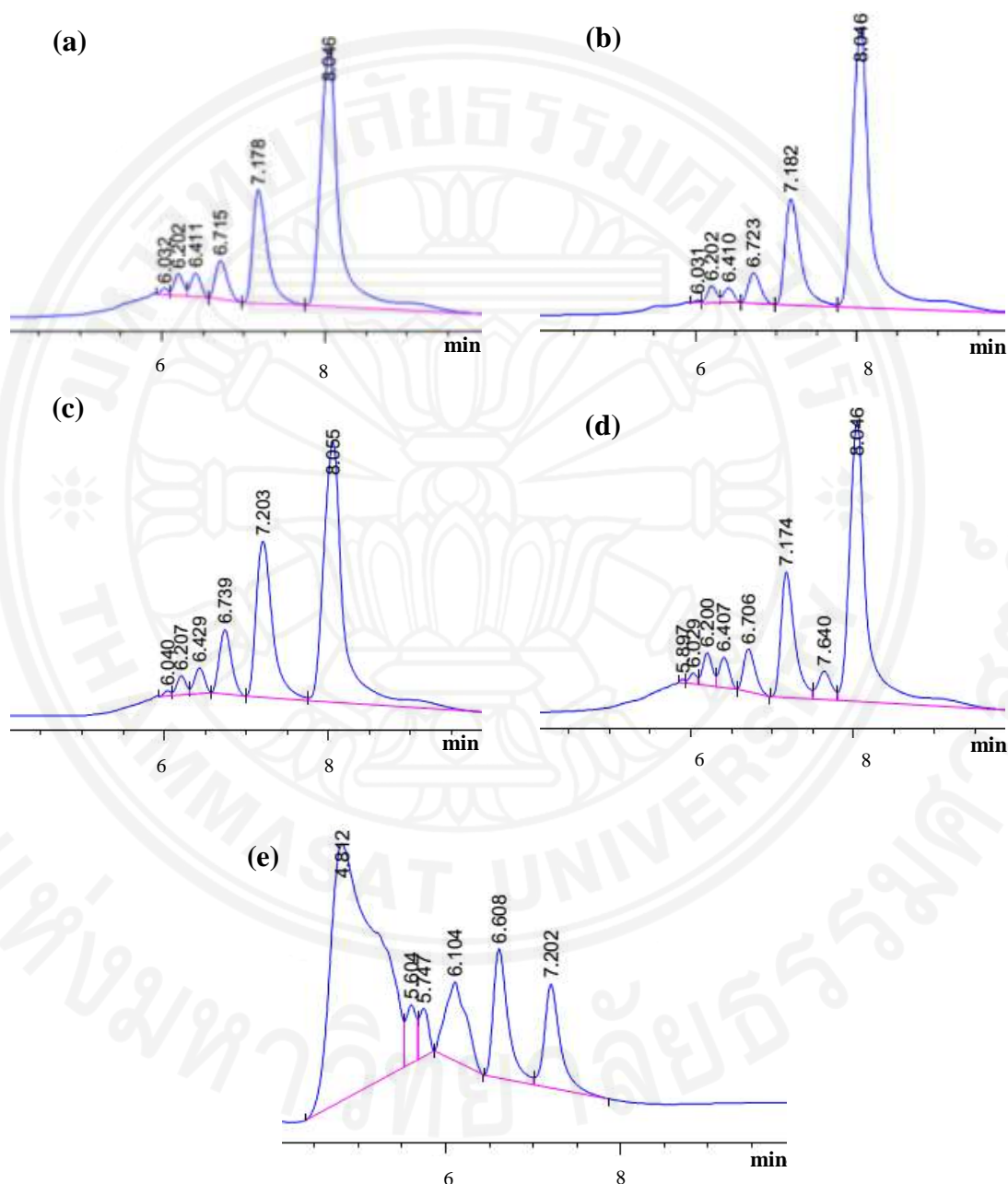

Figure 4.5 HPLC chromatogram of GlyPLA from different glycolysis conditions: a) B1, b) B2, c) B4, d) B5, and e) PLA.

Table 4.3 HPLC peak area of GlyPLA components from different glycolysis conditions.

Retention time (min)	Proportion of peak area (%)			
	B1	**B2**	**B4**	**B5**
6	0.55	0.21	0.36	0.96
6.2	2.64	2.03	1.93	3.76
6.4	3.07	1.87	2.83	3.57
6.7	6.22	4.74	8.63	5.96
7.2	22.32	21.37	28.37	20.86
8.0	65.20	69.78	57.87	60.10

HPLC chromatogram of PLA raw material is different from those of GlyPLA. The chromatogram consists of six significant peaks, but located at different retention times compared to those GlyPLA. The components of PLA are observed at the retention time ranging from 4 to 7.2 minutes. Almost all of the individual peaks of PLA chromatogram are different from the GlyPLA chromatograms, except the peak at 7.2 minute, as shown in figure 4.6. The major component appears at the retention time 4.8 minutes, with peak area of around 64.57%. This is shorter than that of GlyPLA. The shorter retention time of component implies that PLA components show higher hydrophobicity or have longer chain lengths than GlyPLA. Therefore, it is concluded that the introduction of MNPs and microwave irradiation in glycolysis reactions can break down PLA chains into shorter chain lengths which has higher polarity. The components of GlyPLA will have higher affinity than PLA raw material, which results in the differences in retention time of PLA and GlyPLA components.
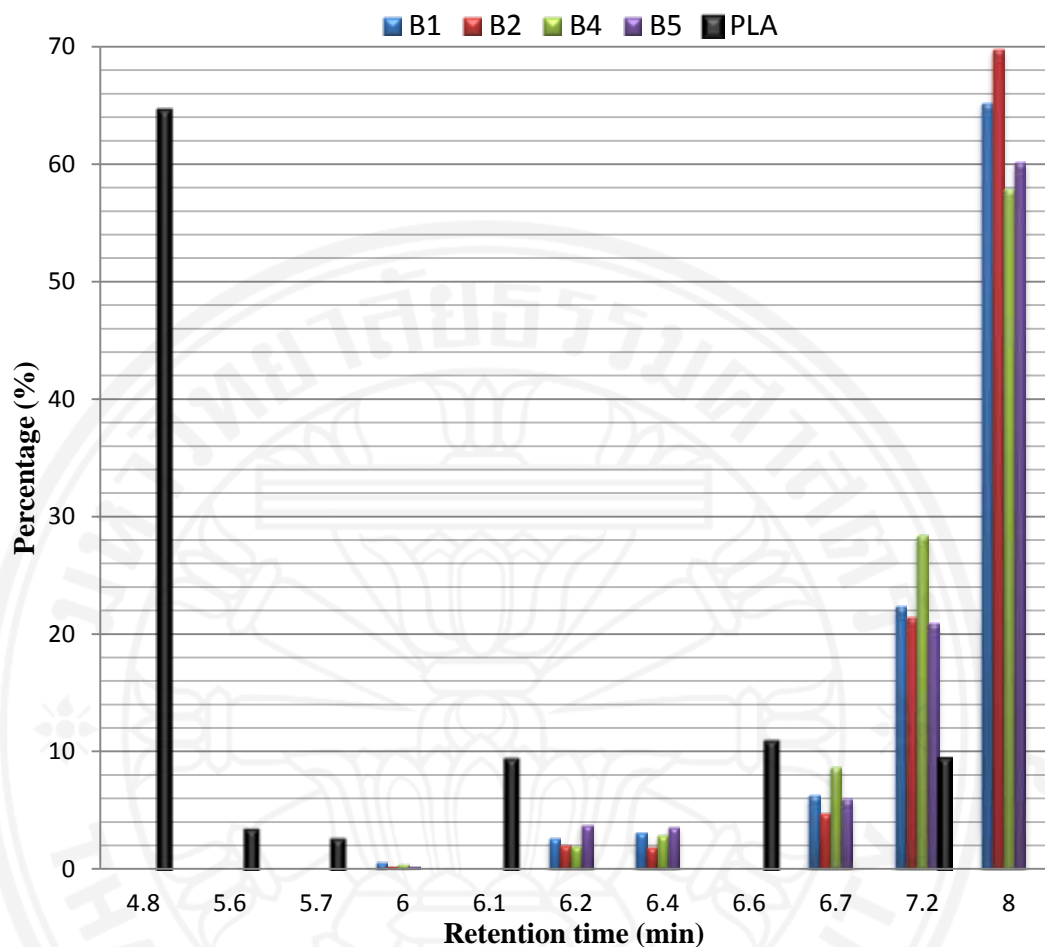
Figure 4.6 The compositions of component of PLA and GlyPLA products obtained from reaction conditions B1, B2, B4 and B5.

4.1.2.2 Effect of glycolysis reaction with MNPs

GlyPLA products from glycolysis reactions with microwave irradiation and MNPs catalyst cannot be re-precipitated. It is also observed that the amount of MNPs is a significant factor in glycolysis reaction. The result from condition B3 reveals that the content of MNPs catalyst is a significant factor that effect to GlyPLA chain lengths. It is found that 0.1 g of MNPs or PLA: MNPs ratio 100:1 is not sufficient to depolymerize polymer chain into oligomer because the products from condition B3 can be recovered by re-precipitation, similar to the GlyPLA from conditions A1-A6. However, when amount of MNPs is increased to 0.5 g (PLA: MNPs 20:1), a significant difference in properties of GlyPLA products can be clearly seen. In

addition, the products from all glycolysis conditions that employ the content of MNPs more than 0.5 g cannot be re-precipitated, as the products remain in liquid form. Therefore, the ratio between PLA: MNPs is the significant factor to decrease chain lengths of polymers.

Another aspect that can be seen clearly is the difference of the effect of the EG content. Without MNPs, the EG content is a significant factor in the proportion of short polymer chains in products. Shorter chain lengths of GlyPLA are achieved when the EG content is increased. On the other hand, EG content is not the key factor to control the proportion of short chain lengths when sufficient amount of MNPs catalyst is employed. HPLC results of B1with B4, which employ PLA: MNPs 10:1, can confirm this hypothesis. Additionally, considering the results from condition B2 and B5 reveals that the same trend of the effect of EG content on short polymer chains can be found although the ratio between PLA:MNPs is increased to 20:1.

In the present study, a conversion of PLA from conditions B1, B2, B4, and B5 is calculated in order to evaluate the performance of the catalyst and compare the efficiency of MNPs catalyst with other catalysts. The percentages of PLA conversion (X) can be calculated by using equation 3(Viana et al., 2011)

$$X\ (\%) = \frac{W_i - W_f}{W_i} \times 100 \quad \dots\dots\dots\dots \quad Eq3$$

Where W_i refers to the initial weight of PLA added to glycolysis reaction and W_f refers to the remaining weight of solid PLA after glycolysis reaction. The results from this calculation reveal that 100% of PLA conversion can be achieved with PLA: MNPs weight ratio of 20: 1. The same conversion percentages of PLA are also found at PLA: MNPs weight ratio of 10:1. In this study, amount of EG is not influence to PLA conversion. Therefore, employing MNPs catalyst can enhance the efficiency of PLA glycolysis reaction. The details of this calculation are summarized in appendix C.

Compared the percentages of conversion with zinc acetate in PET glycolysis (R. López-Fonseca et al., 2011), higher percentages of polymer conversion is

achieved in this study. In addition, higher percentage of conversion is also found when compared with recycling PLA by employing zinc acetate in alcoholysis reaction (Carné Sánchez and Collinson, 2011). Interestingly, employing MNPs catalyst is not only enhance the efficiency of PLA glycolysis, but using MNPs catalyst is also more environment-friendly catalyst than metal acetates such as zinc acetate. Less difficulty in separation of catalyst and recovery process is another advantage of using MNPs catalyst.

Generally, glycolysis reaction of PLA process typically occurs in acidic conditions, which mean that this reaction has proton (H^+) act as self-catalyst. However, higher degree of reduction in the activation energy barrier can be achieved when catalyst is introduced. The lower activation energy leads to an increase in the reaction rate, so glycolysis PLA with MNPs can produce higher ratio of oligomer in GlyPLA, while without MNPs cannot achieve. As a result from literature, Lewis acids law can be employed to expand this catalyst reaction. Therefore, Fe^{2+} and Fe^{3+} tends to pull the bond-pair of electrons at carbonyl group of ester towards itself. Thus, more electrophilic at carbonyl groups are formed, subsequently nucleophile group, which is diol group in EG, can attack easier. Proposed mechanism of PLA glycolysis with MNPs catalyst is illustrated in figure 4.7. To confirm this hypothesis, DP calculation is required.

SEM results reveal morphology of MNPs before and after glycolysis reactions, as illustrated in figures 4.8a, and 4.8b. It is observed that MNPs before reaction is coagulated in non-geometric shape. After glycolysis reaction, however, MNPs show spherical shape with rough surface morphology. Moreover, results from SEM backscattered mode reveal that MNPs after glycolysis might have polymer coat on the particles surface. Therefore, it is likely to conclude that MNPs partly dissolve into liquid phase which mean that all of amount of MNPs cannot be separated from the product. To confirm this hypothesis, ICP-OES was introduced to analyze the concentration of iron in GlyPLA solution. The result show that 140 mg/l of iron ion present in GlyPLA, obtained from condition B1. Therefore, this result confirms that

some MNPs remain in organic phase, which results in surface corrosion of the MNP particles.
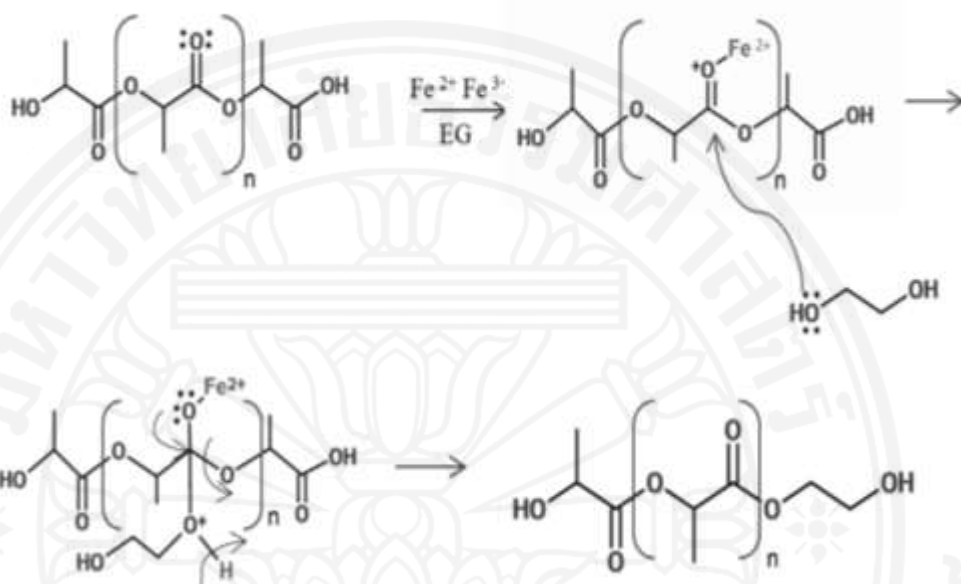

Figure 4.7 Proposed mechanism of PLA glycolysis with MNPs catalyst
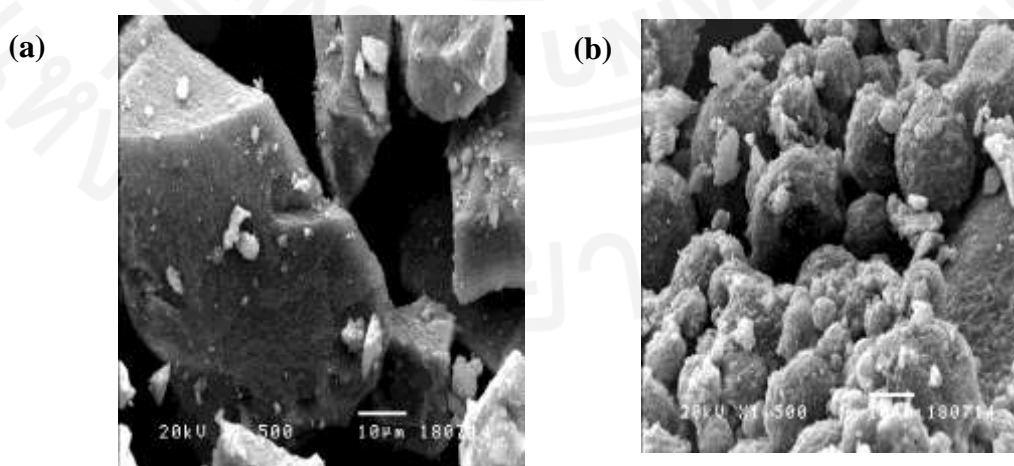

Figure 4.8 Scanning Electron Microscopy (SEM) images of Fe_3O_4 nanoparticles (MNPs): a) before, and b) after glycolysis reaction condition B1.

4.2 Separation of GlyPLA components by column chromatography

Glycolysis is an important chemical recycling process because the products can be used as a starting material in many applications. However, as the components of GlyPLA products contain different chain lengths mixed together. Therefore, separation of these components is essential process to fractionate each component. It is apparent that GlyPLA from glycolysis with microwave irradiation, and MNPs catalyst cannot be recovered by methanol sedimentation. Therefore, a new method for separation and recovery is developed. Column chromatography is a selected method to achieve this purpose. ^{1}H-NMR was then introduced to investigate the chemical structures of each separated component. Due to the results from HPLC reveal that GlyPLA components from glycolysis conditions B1, B2, B4 and B5 consist of the same components, so only GlyPLA from condition B1 was experimented.

Suitable mobile phase is one of the significant factors that influence the separation efficiency in column chromatography. In order to find a suitable solvent, three different solvents are employed, namely methanol (C1), THF (C2), and a mixed solvent of methanol and THF (C3), in the separation of the products from condition B1. Each fraction collected at different retention times is characterized by Fourier transforms infrared spectroscopy (FTIR).

4.2.1 Effect of solvent types

The results from FTIR reveal that the spectra of GlyPLA from all of separation processes are different from PLA raw material, which was reported by V. Krikorian et al. This indicates that the depolymerization reaction breaks the polymer chain of PLA into a different chain length of GlyPLA products. Chemical structure of GlyPLA products can be referred to the amount of the ester group. The changing amount of this functional group is implicated with breaking ester bonds in polymer chain, as a result of glycolysis reaction. Therefore, changes of FTIR spectra in the region of at $1700 - 1760$ cm^{-1} are examined. FTIR spectra show differences in many points in each solvent, such as retention time, intensity, number of separation components, and position of absorbance. These differences indicate that type of solvent is an influential factor in this separation.

The efficiency of separation is different because of the difference in the distribution of GlyPLA components in the stationary phase, and the mobile phase due to the different adsorption behavior of substance by the adsorbent. The rate at which the components of a mixture are separated depends on the activity of the adsorbent and polarity of the solvent. The results on separation efficiency of each solvent are discussed below:

4.2.1.1 GlyPLA separation by methanol

Separation of GlyPLA by methanol (C1 condition) has total retention time around 55 minutes. FTIR spectra of the products from this condition are illustrated in figure 4.9. The FTIR spectra in the C=O stretching region of GlyPLA after the separation process are present during 15 to 30 minutes. All spectra display strong bands around 1744 cm^{-1} and 1707 cm^{-1}, which indicate the carbonyl stretching vibration in ester repeating units, and in the end groups, respectively. All spectra of the eluate sample show strong carbonyl band at 1744 cm^{-1}, and a weak shoulder peak located at 1707 cm^{-1}, except at 15 minute, in which the 1707 cm^{-1} band is stronger. This indicates the shorter chain length. Additional band is also observed at 1655 cm^{-1}, corresponding to O-H bonding of remaining EG in the sample. The relative intensity of the 1744/1707 mode indicated the length of the GlyPLA products.

From FTIR, therefore, the chemical structures of all GlyPLA components after passing through the column chromatography with methanol consist of the ester group in the polymer chain. Even though using C1 separation condition can separate four components, due to the same position of band illustrates that only one component is separated by using methanol as an elution solvent. Compared with HPLC chromatogram, at least four components are included in this GlyPLA, so methanol is not a suitable solvent for separating components in this GlyPLA.
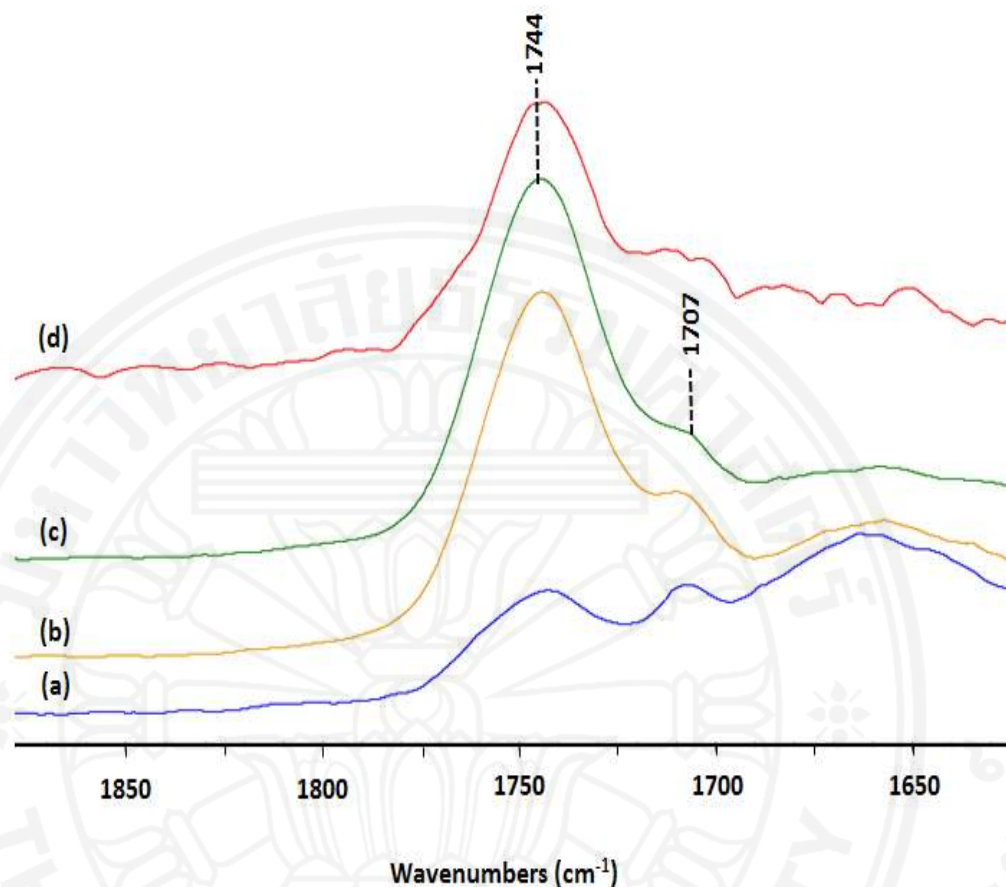
Figure 4.9 Infrared spectra from separation process condition C1 (methanol); (a) 15 minutes, (b) 20 minutes, (c) 25 minutes, and (d) 30 minutes.

4.2.1.2 GlyPLA separation by THF solvent

Compared with other separation conditions, C2 has the shortest retention time; around 25 minutes. Furthermore, the significant IR chromatogram appears from 10 to 18 minutes, as shown in figure 4.10. Two significant bands at 1744 cm^{-1} and 1752 cm^{-1} are investigated in this condition. The last two peaks at 16 and 18 minutes show the weak band of carbonyl region. After 18 minute, carbonyl bands are not appeared, so this result can be implied that GlyPLA do not remain in this separation process. Therefore, components of GlyPLA after separation from condition C2 have ester group as a significant component in polymer chain as the same as condition C1.

40

The remarkable difference between C1 and C2 condition is the shoulder band at 1707 cm^{-1}. This peak does not appear in C2 separation condition. Owing to the short retention time, this separation condition has low efficiency in order to separate the components in the GlyPLA products.

As discussed already in figure 4.9 and 4.10, the results can imply that components in GlyPLA compose of more than one component. Furthermore, both of methanol and THF are not appropriate elution solvent for separation component in GlyPLA, so C3 condition was introduced.
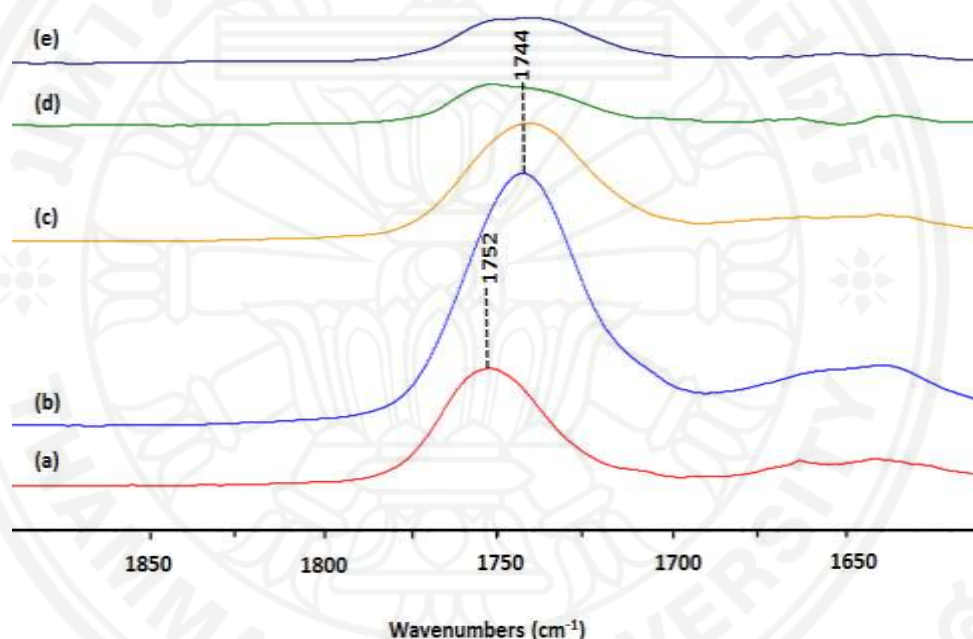

Figure 4.10 Infrared spectra from separation process condition C2 (THF); (a) 10 minutes, (b) 12 minutes, (c) 14 minutes, (d) 16 minutes, and (e) 18 minutes.

4.2.1.3 GlyPLA separation by mixed solvent

IR spectra from condition C3 show dramatic different points when compared with the previous separation conditions. Firstly, compared with the previous separation, using mixed solvent has the longest retention time (around 170 minutes). Another different point is that the spectra of C=O stretching vibration region are displayed after 30 minutes, while other separation processes show the significant IR spectra within the first 30 minutes. This change suggests to better efficiency of separation condition.

The significant spectra from C3 separation condition appear during 35 to 90 minutes, as shown in figure 4.11. At 35 minutes, only the infrared peak at 1757 cm^{-1} is present. This peak correlates to the ester functional group in repeating unit of GlyPLA, which refer to long chain lengths components. Furthermore, during 40 to 50 minutes, the peak of O-H bonding of remaining EG, which is located around 1655 cm^{-1}, is investigated. IR spectra from 40 to 90 minutes split into two frequencies; 1756 cm^{-1} and 1748 cm^{-1}. The ratios between these peaks illustrate the different interaction between GlyPLA components, stationary phase, and mobile phase. The shoulder of acid peak is investigated when retention time increases. Interestingly, distinguished acid peaks, around 1739 cm^{-1}, appear at retention time 55, 60, and 90 minutes. Additionally, this peak illustrates in C3 separation condition only.

Therefore, all of 12 separated samples from C3 condition illustrate three significant peaks around 1739, 1748, and 1757 cm-1, which correspond to acid peak and C=O stretching of ester groups, respectively. Furthermore, four patterns of IR spectra indicate that the chemical structures of the components in GlyPLA can be separated into four groups by using mixed solvent condition. These separated components consist of GlyPLA products with different chain lengths. Longer polymer chains should be separated and come out faster than shorter chain lengths because the influence of hydrogen bond from OH- group at the end of polymer chains affects polarity of products. This hydrogen bond has more influence to shorter polymer chains than the longer chain, so shorter chain lengths require longer retention time because of higher polarity. Furthermore, the results from C3 separation have good corresponding relation with HPLC result, in which four majorities of components can be separated. The present study raises the possibility that C3 condition might be better separation process for GlyPLA from glycolysis reaction with magnetic nano particle when compared with C1 and C2 separation conditions.
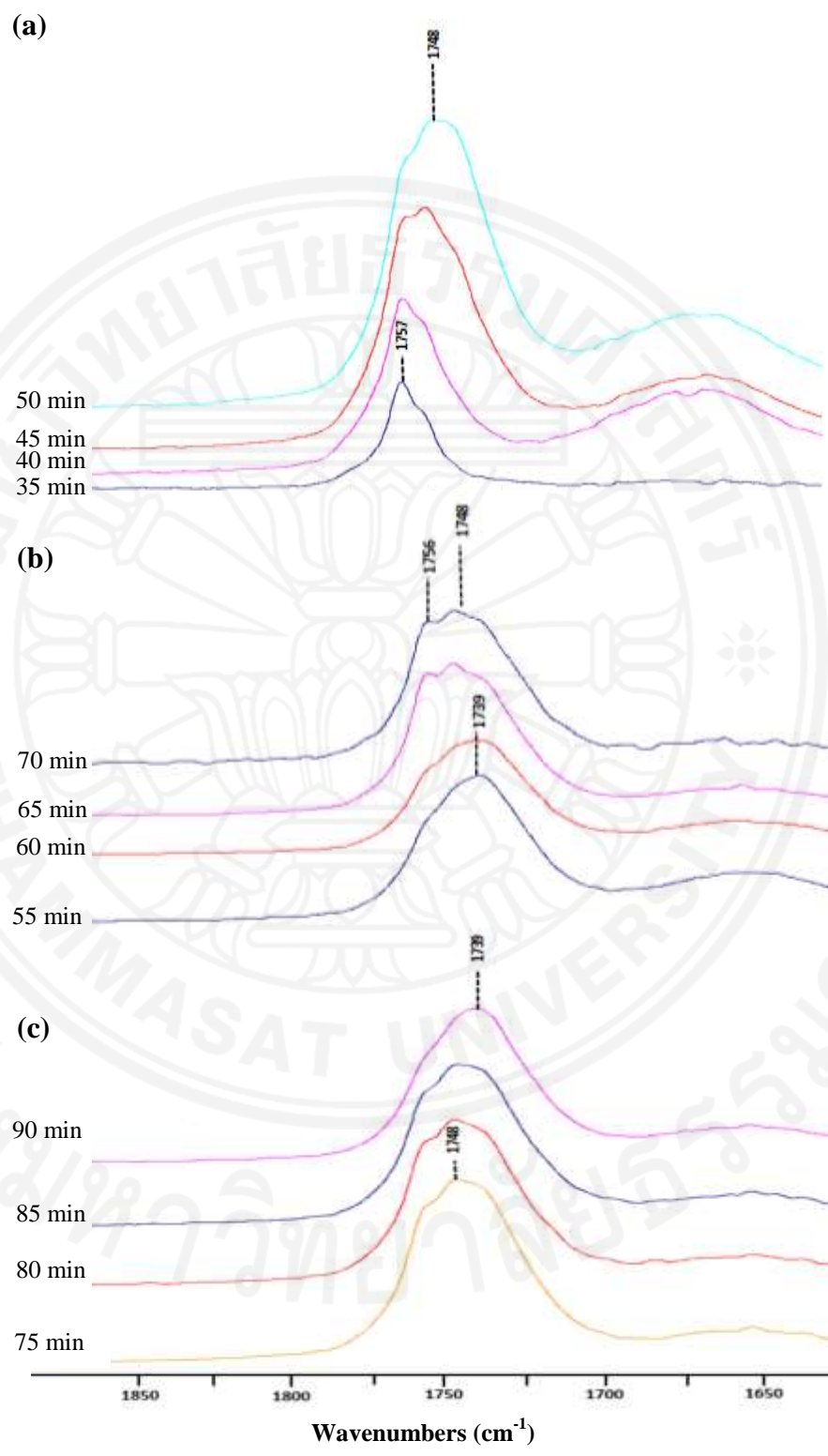
Figure 4.11 Infrared spectra from separation process condition C3 (Mixed solvent) :
(a) 35 to 50 minutes, (b) 55 to 70 minutes, and (c) 75 to 90 minutes.

In order to examine chemical structure of each component, which is obtained from the separation process, ^{1}H-NMR spectroscopy was introduced. The results are discussed, as follows:

4.2.2 Characterization of GlyPLA products from glycolysis reaction with microwave irradiation and magnetic nano particle

^{1}H-NMR was carried out in order to validate and identify chemical structures in GlyPLA components. Condition C3 was introduced in order to separate components in GlyPLA from condition B1. As a result of FTIR spectra in section 4.2.1.3, four samples at 40, 65, 75, and 90 minutes were selected as a representative of chemical structures in GlyPLA. ^{1}H-NMR spectrum of GlyPLA from those selected retention times reveal the similar resonance (5.1, 4.2, 4.3 and 3.8 ppm) to those ^{1}H-NMR from conditions A1 to A6. However, there are different in detail, especially intensity ratio of each chemical shift.

4.2.2.1 Polymer chain length of GlyPLA product after glycolysis reaction with microwave irradiation and MNPs

Interestingly, intensity of every chemical shift (5.1, 4.2, 4.3, and 3.9 ppm) from every retention time is different from glycolysis condition A. Moreover, the most intensity signal is not located at 5.1 as the same as previous part, except 40 minutes retention time. These results directly connect to polymer chain lengths of GlyPLA components because this signal (5.1 ppm) corresponds to CH in repeating unit of GlyPLA chain. This assumption is proved by applied equation 1 in order to calculate DP. The calculation results of DP, as shown in table 4.4, reveal that all of DP is dramatically decreased when compared with condition A.

The highest DP from B1 glycolysis condition is investigated at elution time 40 minutes. Then there is not significant difference of DP during 65 – 90 minutes. As mention in previous part, this result is also corresponding with the principle of column chromatography. Although the highest of DP from condition B1 is around 1, this is must lower than DP from condition A3 (DP is 27), which is the lowest DP from

glycolysis reaction with microwave irradiation without MNPs catalyst. Interestingly, A3 glycolysis condition uses the same PLA: EG ratio, reaction temperature, and time with B1 condition. This decreasing of DP can confirm the impact of MNPs to glycolysis reaction as a catalyst. Therefore, DP results indicate that introduction of MNPs catalyst into glycolysis reactions increases de-polymerization rate and oligomer can be achieved by applied this catalyst.

Table 4.4 Results of DP from C3 separated GlyPLA products obtain from condition B1 (MNPs 1 g, PLA: EG 1:2, 10 minutes, 600 Watt).

Retention time (min.)	Intensity (ppm)					DP (a/e)	$\dfrac{e}{c/2}$	c/d
	5.1 (a)	4.9 (f)	4.3 (e)	4.2 (c)	3.8 (d)			
40	1.15	0.08	1.01	0.28	0.49	1.14	7.21	0.57
65	0.18	-	0.52	0.67	0.66	0.35	1.55	1.02
75	74.43	-	236.80	521.95	208.22	0.31	0.91	2.51
90	4.7	12.83	11.98	13.53	15.38	0.39	1.77	0.88

4.2.2.2 Chemical structures of GlyPLA products after glycolysis reaction with microwave irradiation and MNPs

This is clearly illustrated that ^{1}H-NMR of GlyPLA from the glycolysis reaction with magnetic nano particle are not the same as ^{1}H-NMR of GlyPLA from glycolysis reaction without magnetic nano particle, as shown in figure 4.12, and the chemical structures of GlyPLA from each retention time can be predicted followed figure 4.13. ^{1}H-NMR from condition B1 clearly indicates that this ^{1}H-NMR exhibited higher signal than condition A. ^{1}H-NMR spectra in more details are presented in appendix D.
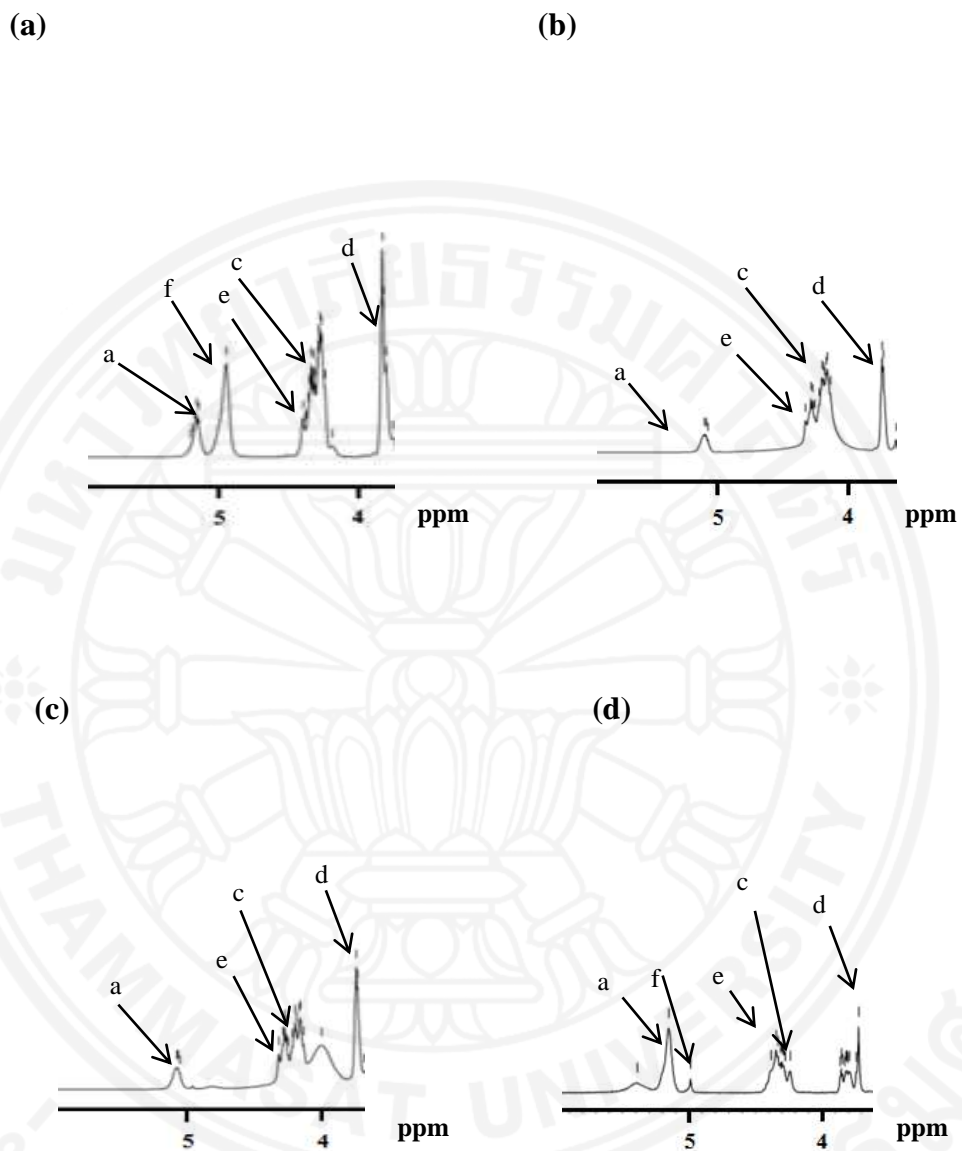
Figure 4.12 ^{1}H NMR spectra of C3 separated component of GlyPLA obtained by B1 glycolysis condition (MNPs 1 g, PLA: EG 1:2, 10 minutes, 600 Watt) a) 90 min. b) 75 min. c) 65 min. d) 40 min.
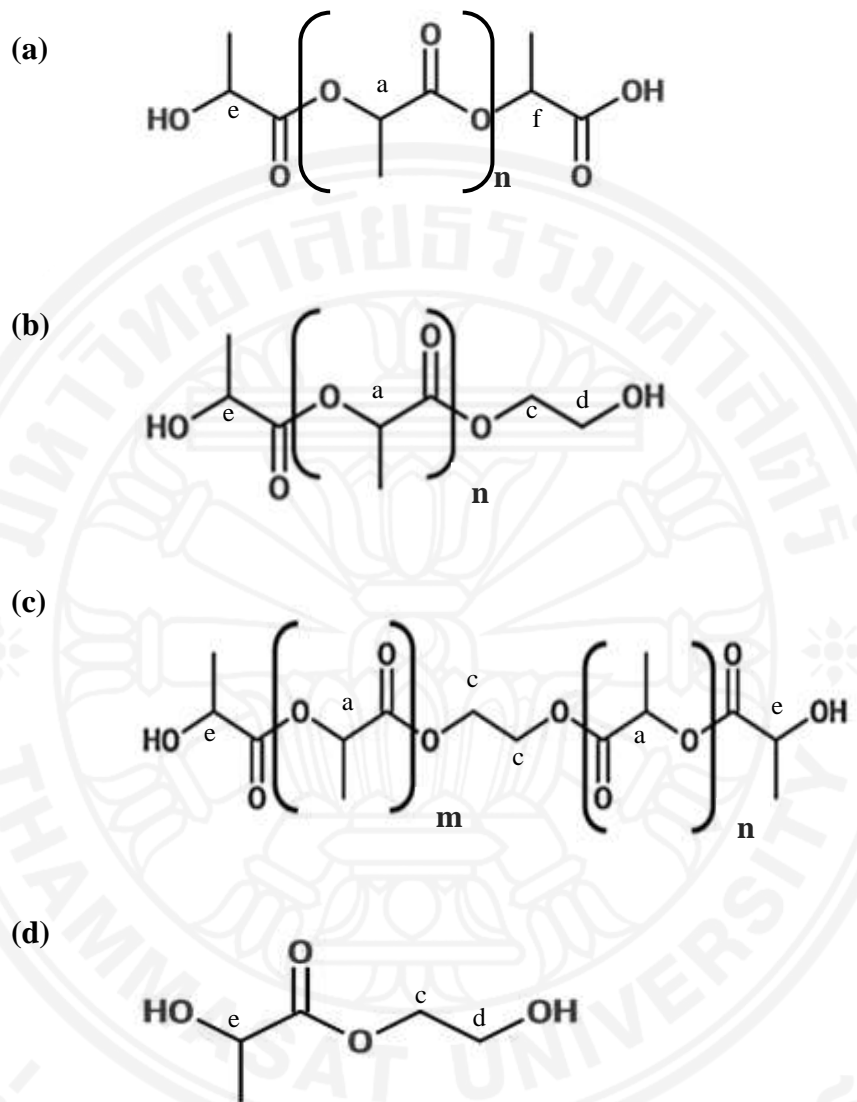
Figure 4.13 Proposed chemical structures of GlyPLA obtained from glycolysis reaction with microwave irradiation and MNPs.

As a result of ^{1}H-NMR and DP calculation, the proposed chemical structures of product for each retention time are illustrated in figure 4.13 (a) - 4.13 (b). However, the proportion of the chemical structures in each retention time is different. Due to the calculation results between chemical shifts 4.3 (e) and 4.2 (c), which refer to OHCH**CH**$_3$C=O and O=COC**H**$_2$CH$_2$OH, respectively, the highest proportion is observed at retention time 40 minutes. This proportion decreases when retention time increases. On the other hand, the calculation results between peaks 4.2 (c) and 3.8 (d), which refer to O=COC**H**$_2$CH$_2$OH and O=COCH$_2$C**H**$_2$OH, show the opposite trend. This indicates that oligomer of PLA followed figure 4.13 (a) should be the majority of the components at 40 minutes. Then, the proportion of PLA oligomer decreases when retention time increases. This hypothesis is a good correlation with the DP result at 40 minutes which has higher value than other retention times. Moreover, a significant chemical shift at 4.90 ppm is investigated in this retention time. This chemical shift refers to CH near acidity region (—COOH) at the end of polymer chain of PLA. Therefore, at retention time 40 minutes, oligomer of PLA is the major component of products.

At retention time 65 and 90 minutes, the ratio between peaks c and d is nearly 1. Thus, oligomer of GlyPLA which is illustrated in figure 4.13 (b) should be the majority of components in this retention time while the highest proportion of chemical structure 4.13 (c) is investigated at 75 minutes because of the highest ratio between peaks c and d. Interestingly, at 65 minutes and 90 minutes, the calculation results of $\frac{e}{c/2}$ and $\frac{c}{d}$ are nearly 1. This indicates that the components in products consist of higher proportion of a chemical structure followed figure 4.13 (d) than other retention times. Additionally, a significant chemical shift at 4.9 minutes is investigated at retention time 90 minutes as the same as retention time 40 minutes, so oligomer of PLA, as shown in figure 4.13 (a), should be another components of products at retention time 90 minutes. Although ^{1}H-NMR spectra of retention times 40 and 90 minutes illustrate the acid peak at 4.9 ppm, PLA oligomer from both retention times have different polymer chain lengths. The components of PLA oligomer at retention time 40 minutes have longer chain length than 90 minutes, which means that the components at 40 minutes have lower polarity. Therefore, it is reasonable that the

components at 40 minutes have shorter elution time when compare with components from other retention time.

Considered the result from HPLC, FTIR spectra, ^{1}H-NMR spectra, and DP calculation results indicated that, from 4 groups of FTIR pattern and HPLC, the components of products from glycolysis reaction with microwave irradiation and MNPs should consist of two groups of components. First group is oligomer of GlyPLA, which require longer time for separation in both separation technique; HPLC and column chromatography. In column chromatography, this component can be separated during retention time around 80 – 90 minutes. Furthermore, this oligomer might be the majority of component in GlyPLA products as revealed by higher percentage area of HPLC chromatogram in higher retention times. Another component is a short polymer chain length of PLA. This component can be separated during retention time around 35 – 50 minutes.

Chapter 5

Conclusion and Future works

5.1 Conclusion

Chemical-recycling process of polylactic acid (PLA) is developed by using a glycolysis reaction. Microwave irradiation is employed as heating source and MNPs is introduced as catalyst. The results show that a dramatic decreasing in the reaction time is achieved by applied microwave irradiation. Furthermore, decreasing of glycolysed PLA (GlyPLA) chain lengths is investigated when MNPs catalyst is employed to reaction, subsequently oligomer and monomer of GlyPLA can be achieved. The role of MNPs catalyst in PLA glycolysis can be explained by Lewis acid law. Chemical structures of the GlyPLA products are affected by glycolysis conditions, namely reaction temperature, reaction time, and EG: PLA feed ratios.

The significant advantage of this technique is more environmental friendly, as it requires lower energy consumption, when compared with conventional heating method. Additionally, lower energy consumption and shorter time for catalyst separation process is also the benefit from this technique. Shorter reaction time is also an advantage point from this technique because higher production rate can be achieved.

Separation and recovery GlyPLA can be done by two different approaches. GlyPLA from glycolysis reaction with microwave irradiation is recovered by re-precipitation in methanol, while GlyPLA from glycolysis reaction with microwave irradiation and MNPs can be separated by employed column chromatography technique. Mixed solvent between THF and methanol in the ratio 1:1 is the suitable solvent in this separation. Different chain lengths of each component can be separated. By using above separation method 12 rangs of components can be separated, in which can be classified into four significant groups. The insight into the reactions mechanisms and efficiency recovery process can be applied in the production of glycolized products for specific applications.

5.2 Future works

In order to improve future research, some aspects from this study should be considered. Firstly, although this study indicated that modified domestic microwave can be used as a reactor for PLA glycolysis reaction, employed microwave reactor should be considered in order to control power of irradiation more precisely and more stable of microwave irradiation during glycolysis reaction. Moreover, microwave reactor can measure temperature profile during glycolysis reaction, which can be used for study kinetic of the reaction.

Secondly, in order to confirm the proposed chemical structures of GlyPLA from glycolysis reaction. ^{12}C-NMR should be introduced, especial in GlyPLA from glycolysis reaction with microwave irradiation and MNPs.

Next, the study of mechanism of MNPs in glycolysis reaction should be concerned. In addition, the possibility of decreasing reaction temperature and EG concentration when MNPs catalyst is involved in reaction is also interesting and significant aspect. The reason is that saving energy will be achieved if reaction temperature decreases. This aspect clearly connects to more environmentally friendly recycling process development. Moreover, the study of reuse MNPs catalyst in reaction should be study in the future work.

Lastly, although separation of GlyPLA components, which obtain from glycolysis reaction with microwave irradiation and MNPs catalyst, can be achieved by column chromatography, this technique requires long separation time. In addition, this is not suitable for scale up for industrial scale. Therefore, searching other separation techniques is another aspect that should be developed in future work.

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Appendices

Appendix A

Table A The summary comparison of the synthetic methods of MNP.

method	Reaction	Temp [°C]	period	Solvent	agent	Size distribution	Shape control	Yield
co-precipitation	very simple, ambient conditions	20–90	minutes	Water	needed, added during or after reaction	relatively narrow	not good	high/ scalable
Thermal decomposition	complicated, inert atmosphere	100–320	hours–days	organic compound	needed, added during reaction	very narrow	very good	high/ scalable
Micro emulsion	Complicated, ambient conditions	20–50	hours	organic compound	needed, added during reaction	relatively narrow	good	low
Hydrothermal synthesis	simple, high pressure	220	hours ca. days	water-ethanol	needed, added during reaction	very narrow	very good	medium

Appendix B ^{1}H-NMR from conditions A1 –A6
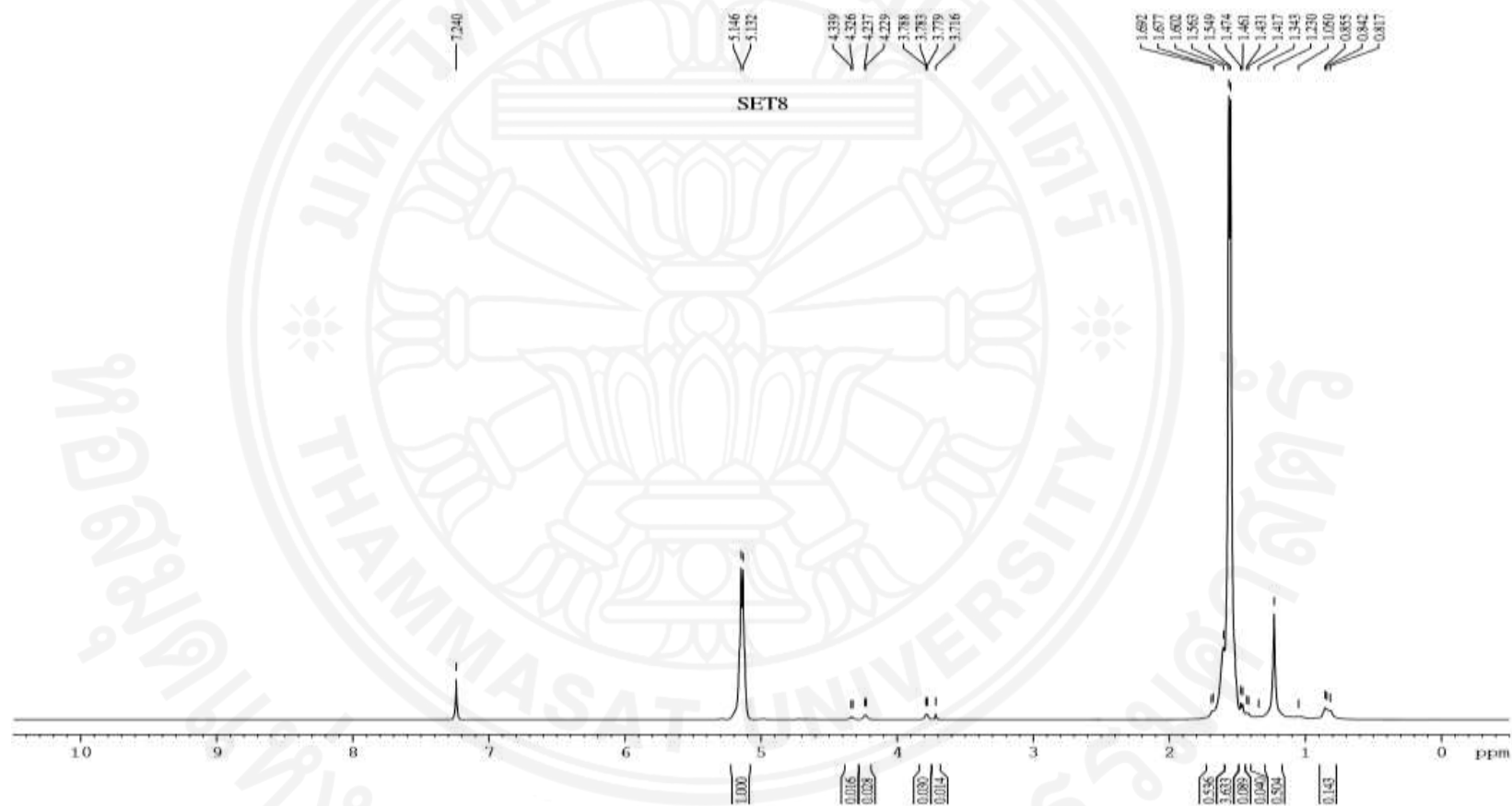
Figure B1 ^{1}H-NMR spectra from condition A1
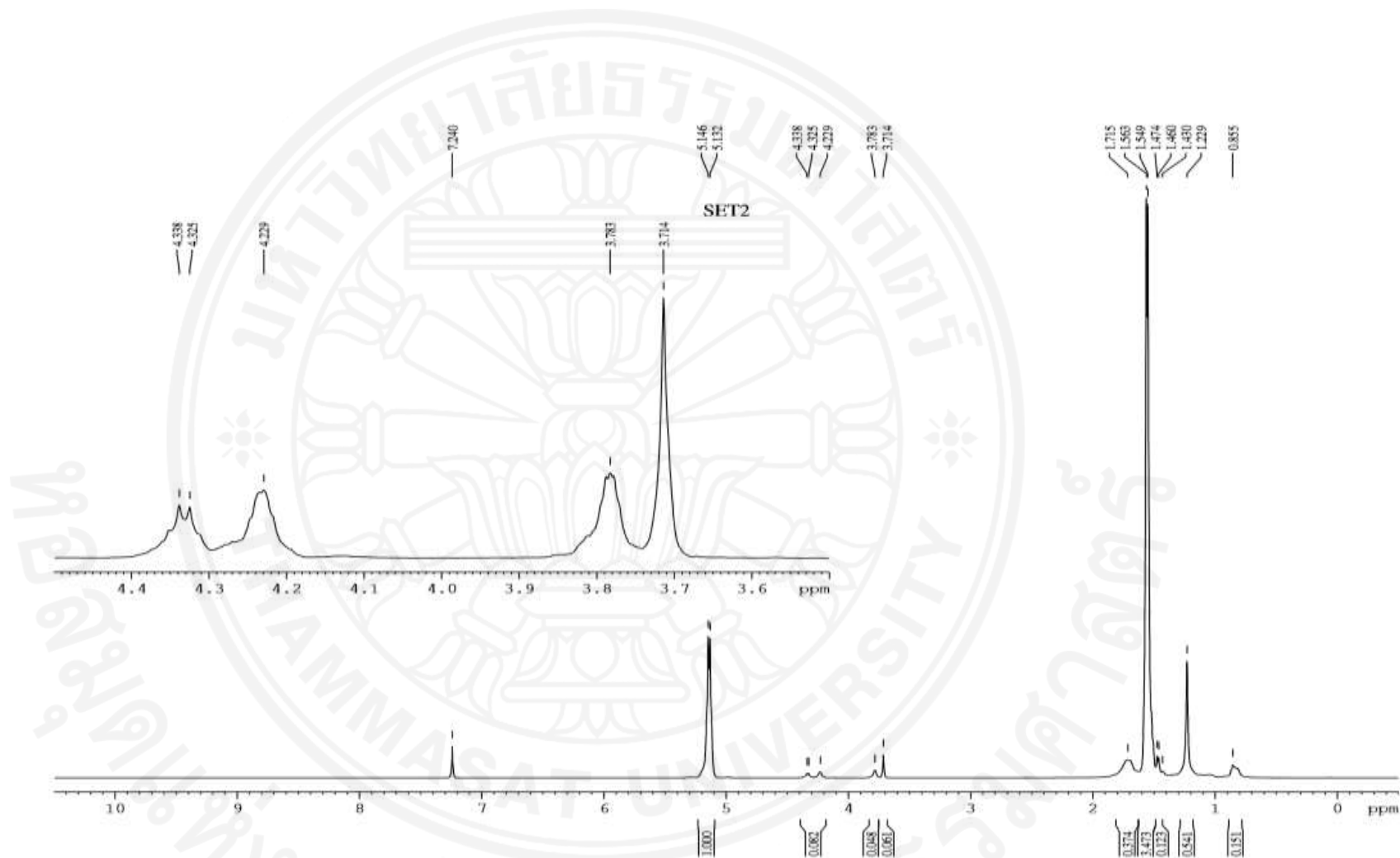
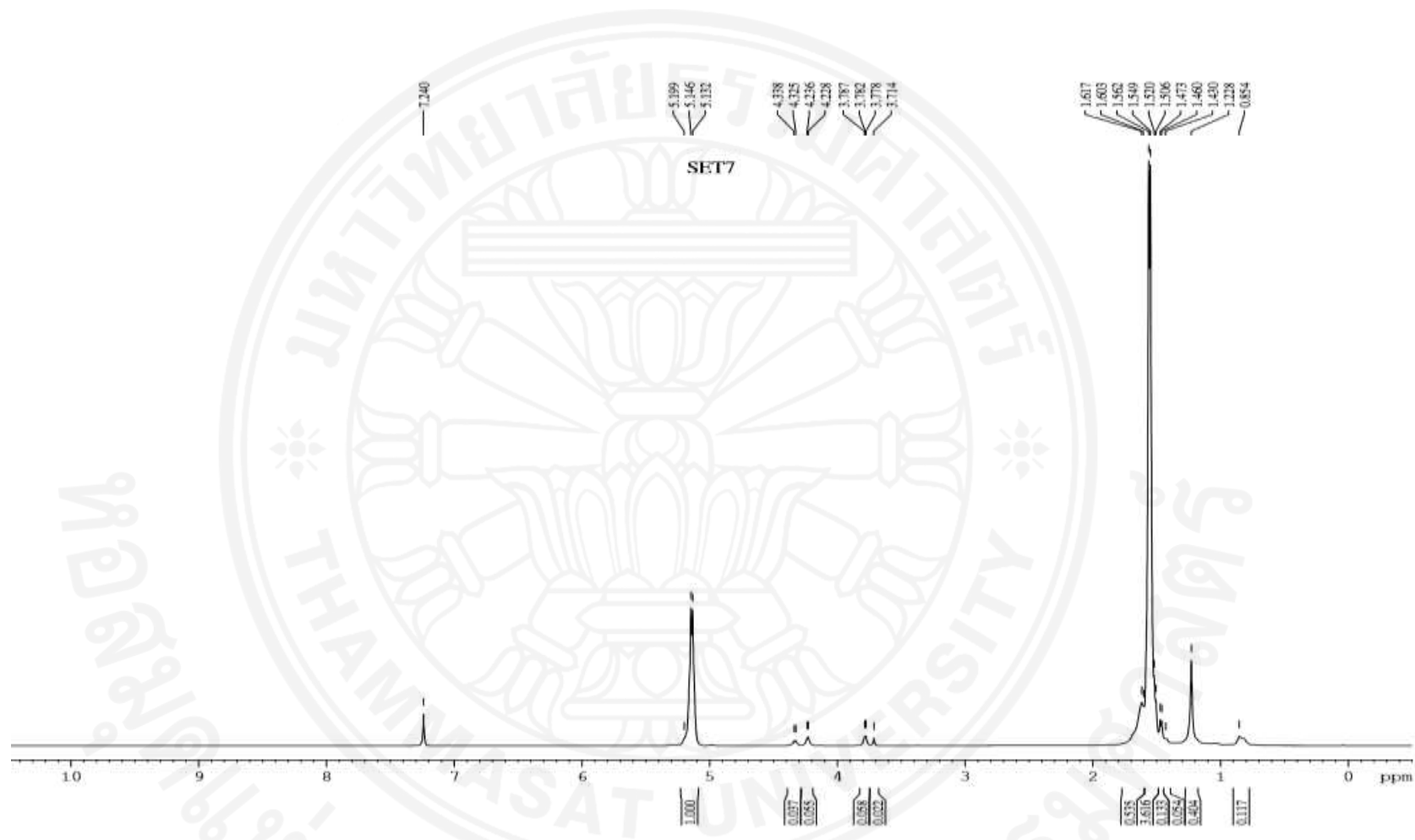**Figure B2** ^{1}H-NMR spectra from condition A2

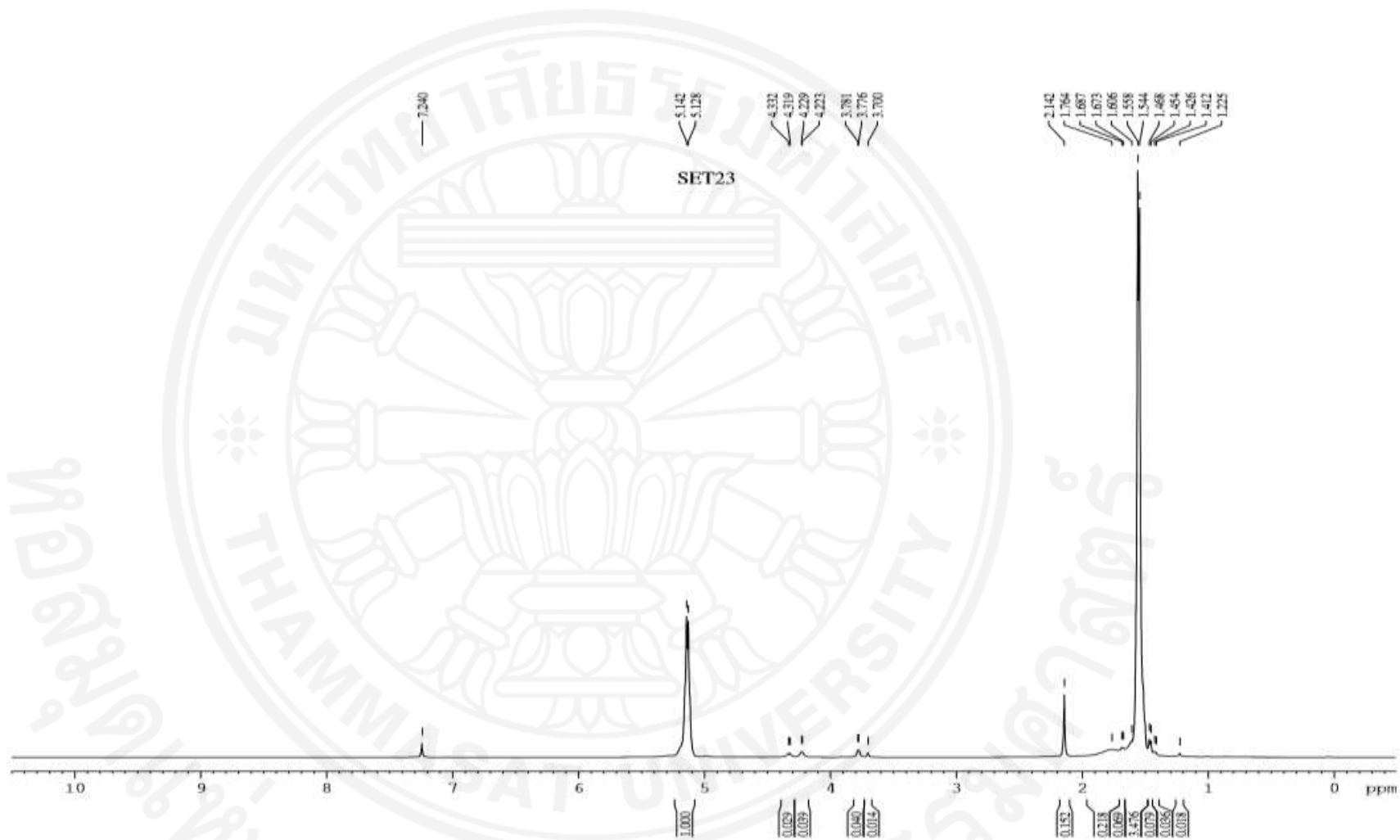**Figure B3** ^{1}H-NMR spectra from condition A3

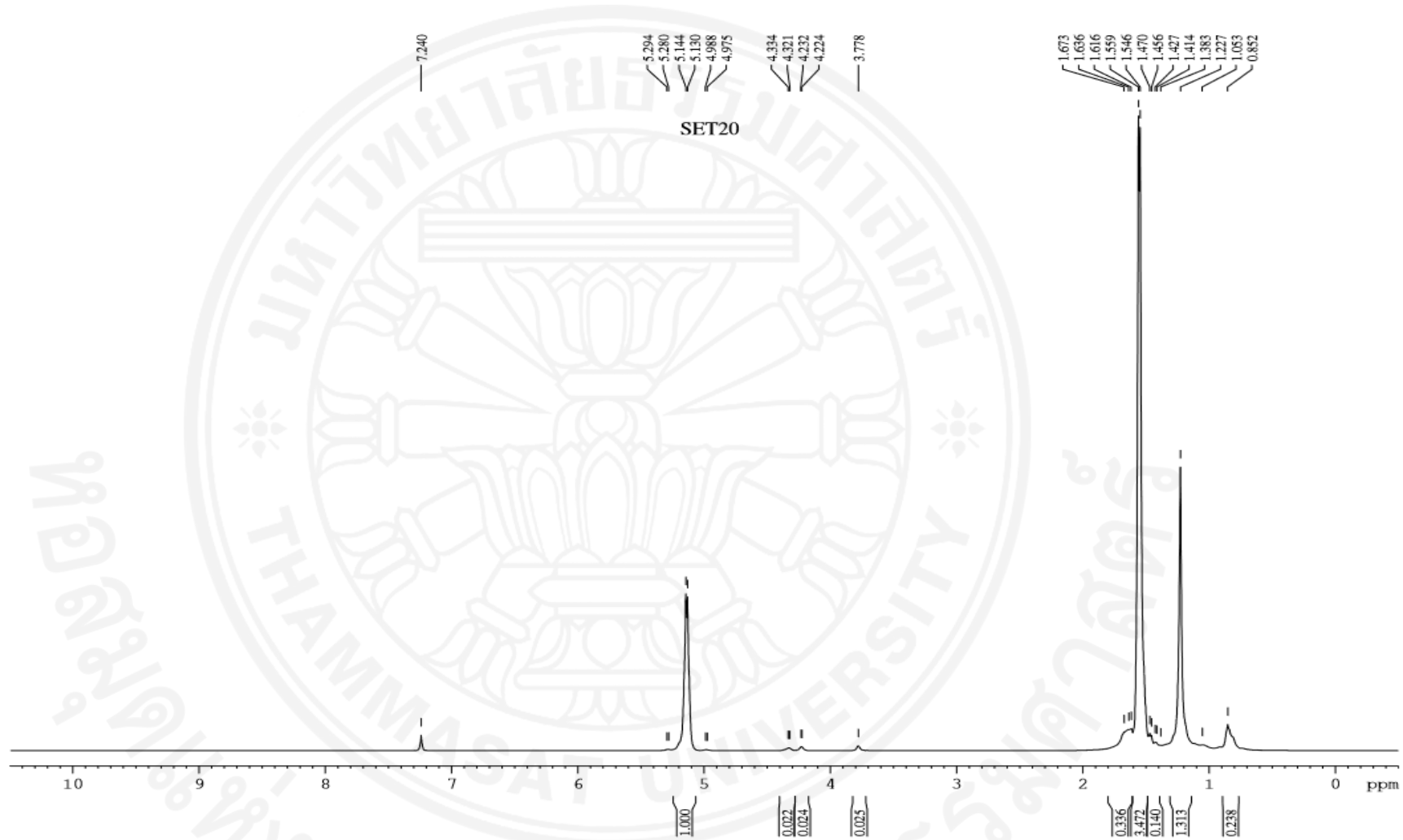**Figure B4** ¹H-NMR spectra from condition A4

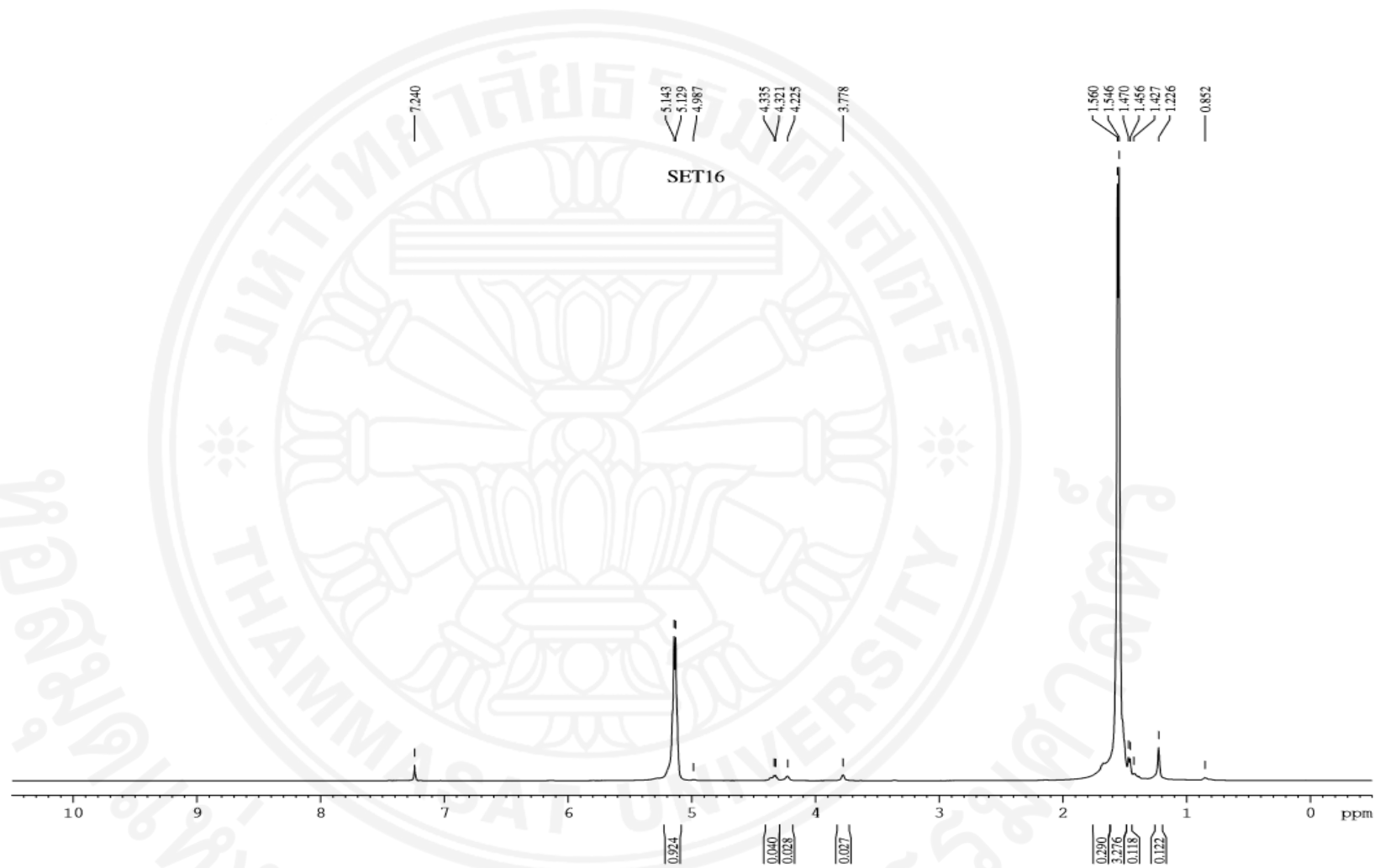**Figure B5** ^{1}H-NMR spectra from condition A5

Figure B6 ^{1}H-NMR spectra from condition A6

Appendix C

Table C The summary of calculation results of PLA conversion percentages (X)

No.	Reaction Conditions		Initial weight of PLA, W_i (g)	Remaining weight of solid PLA after glycolysis reaction, W_f (g)	Percentage of PLA conversion, X (%)
	PLA: MNPs (wt. %)	PLA: EG (wt. %)			
B1	10:1	1:2	10	0	100
B2	20:1	1:2	10	0	100
B4	10:1	1:1	10	0	100
B5	20:1	1:1	10	0	100

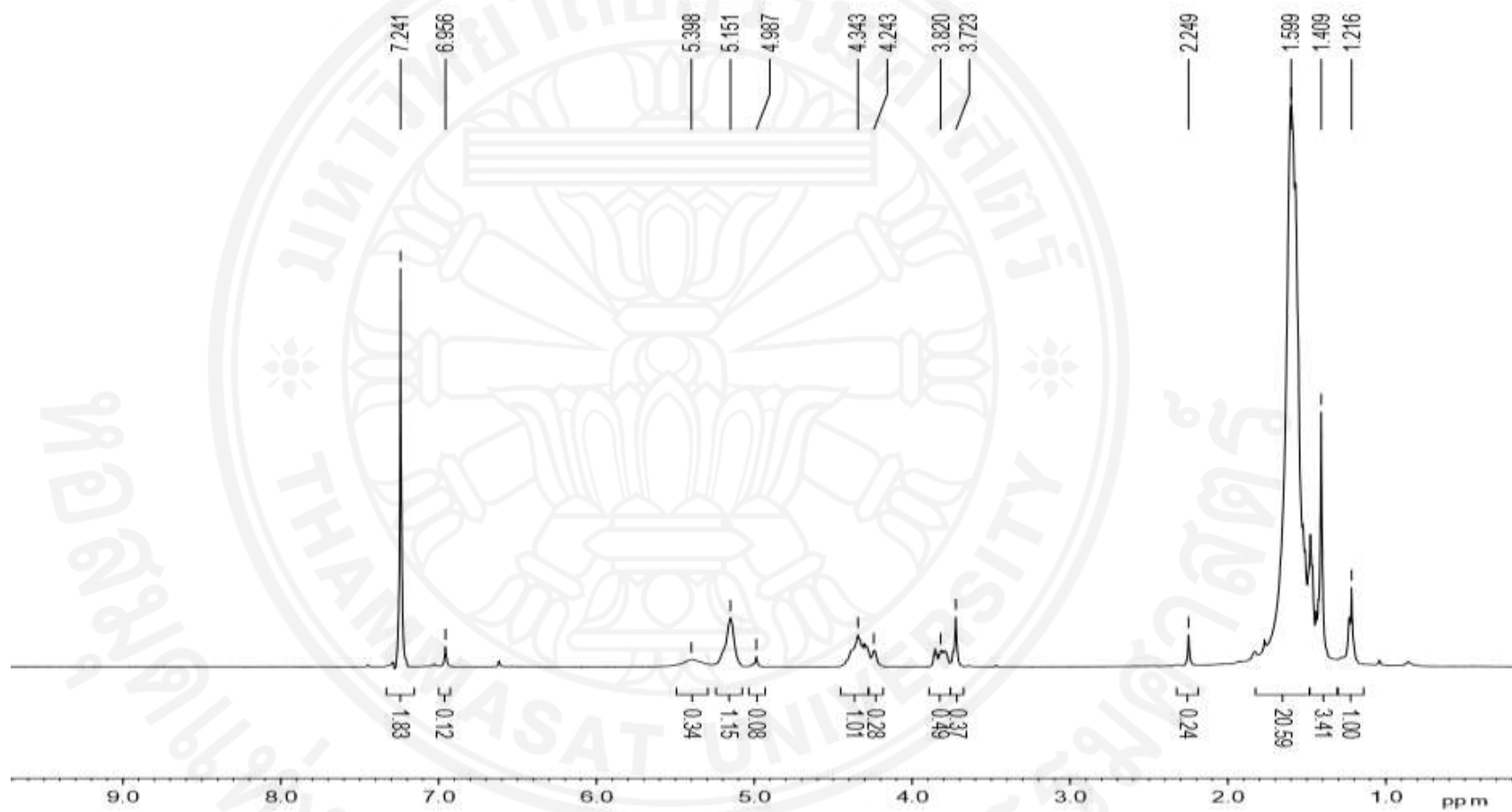**Appendix D** ^{1}H-NMR of separated ClyPLA obtained from condition C3

Figure D1 ^{1}H-NMR spectra of separated GlyPLA at 40 min.

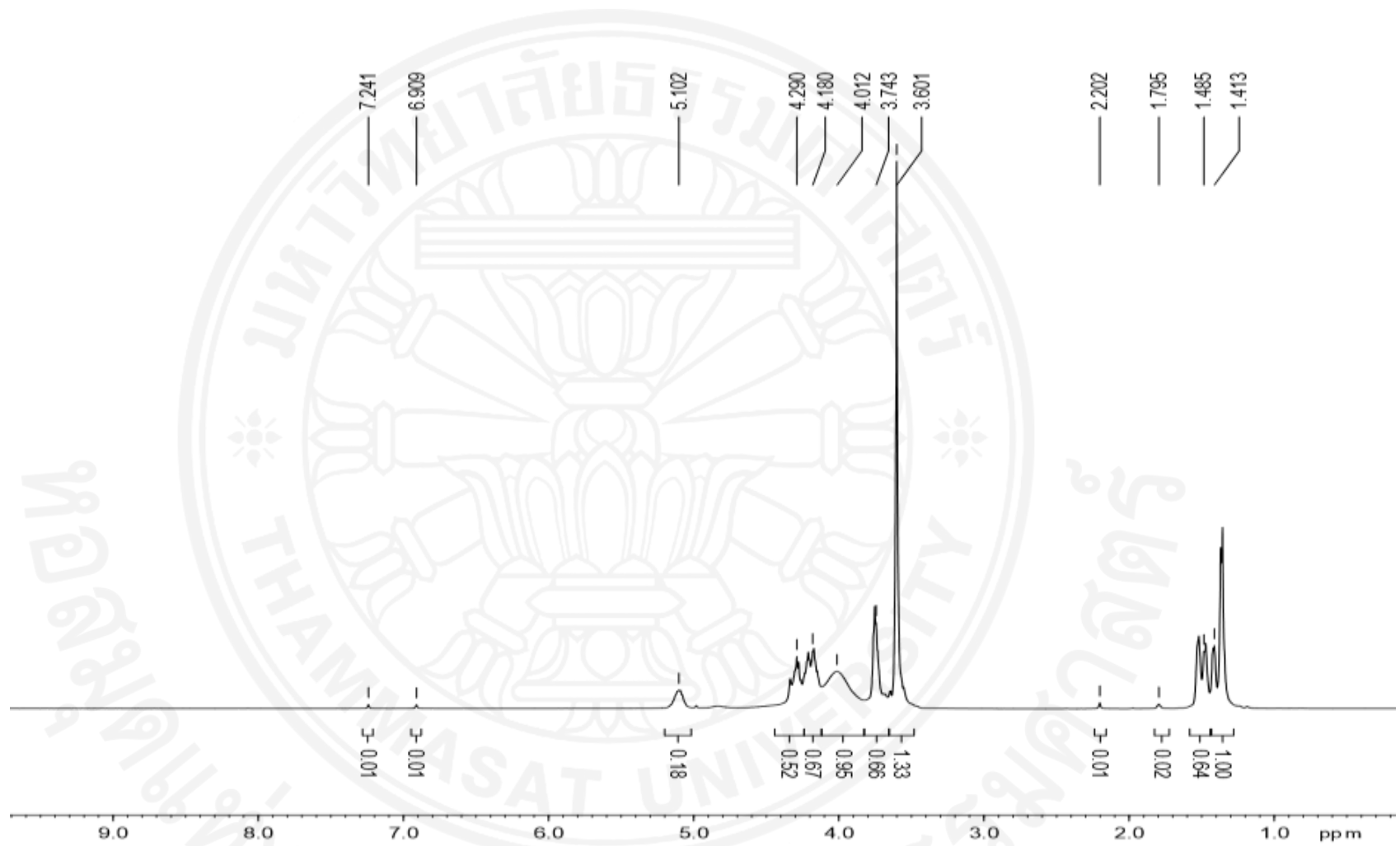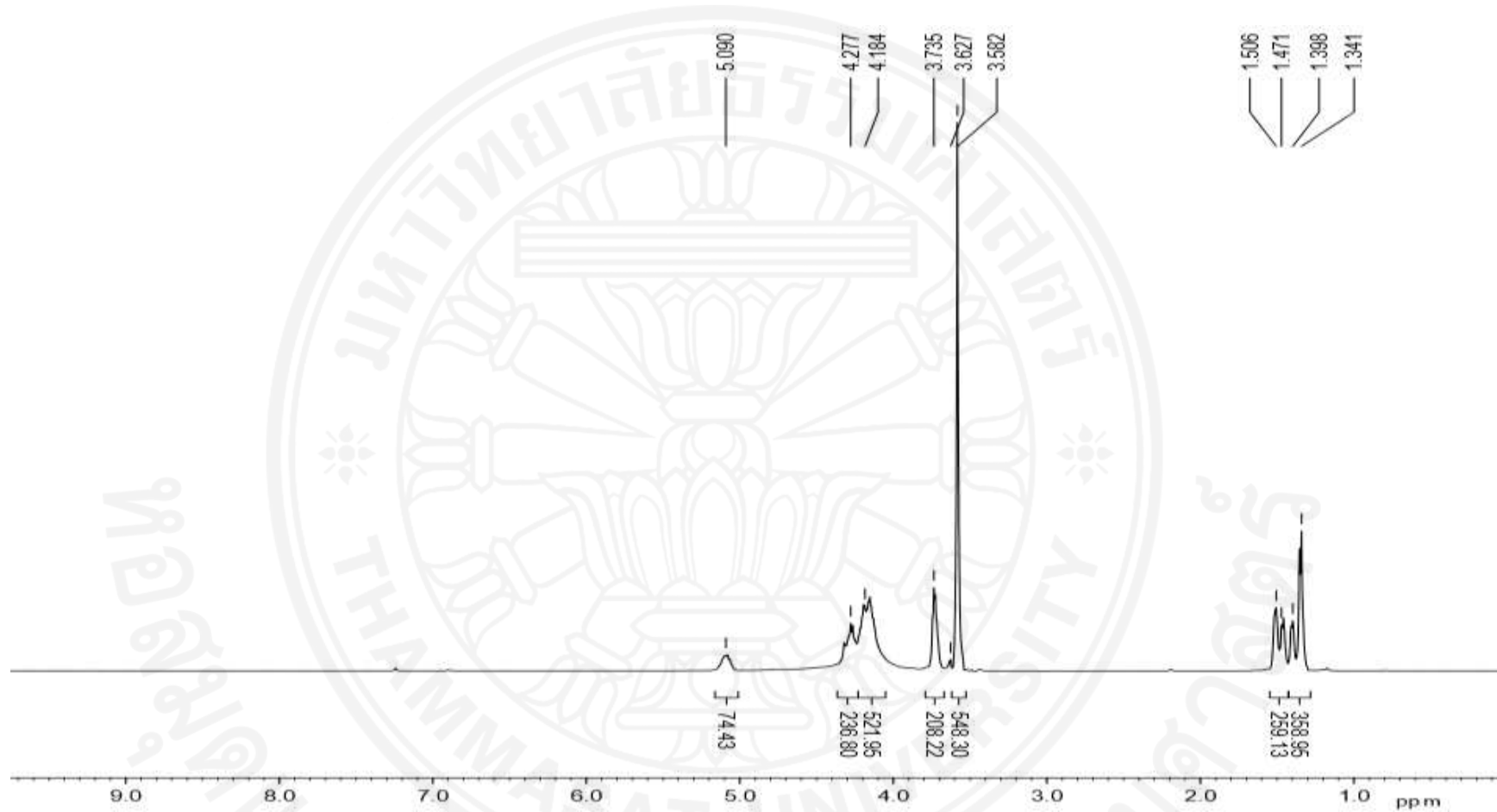**Figure D2** ^{1}H-NMR spectra of separated GlyPLA at 65 min.

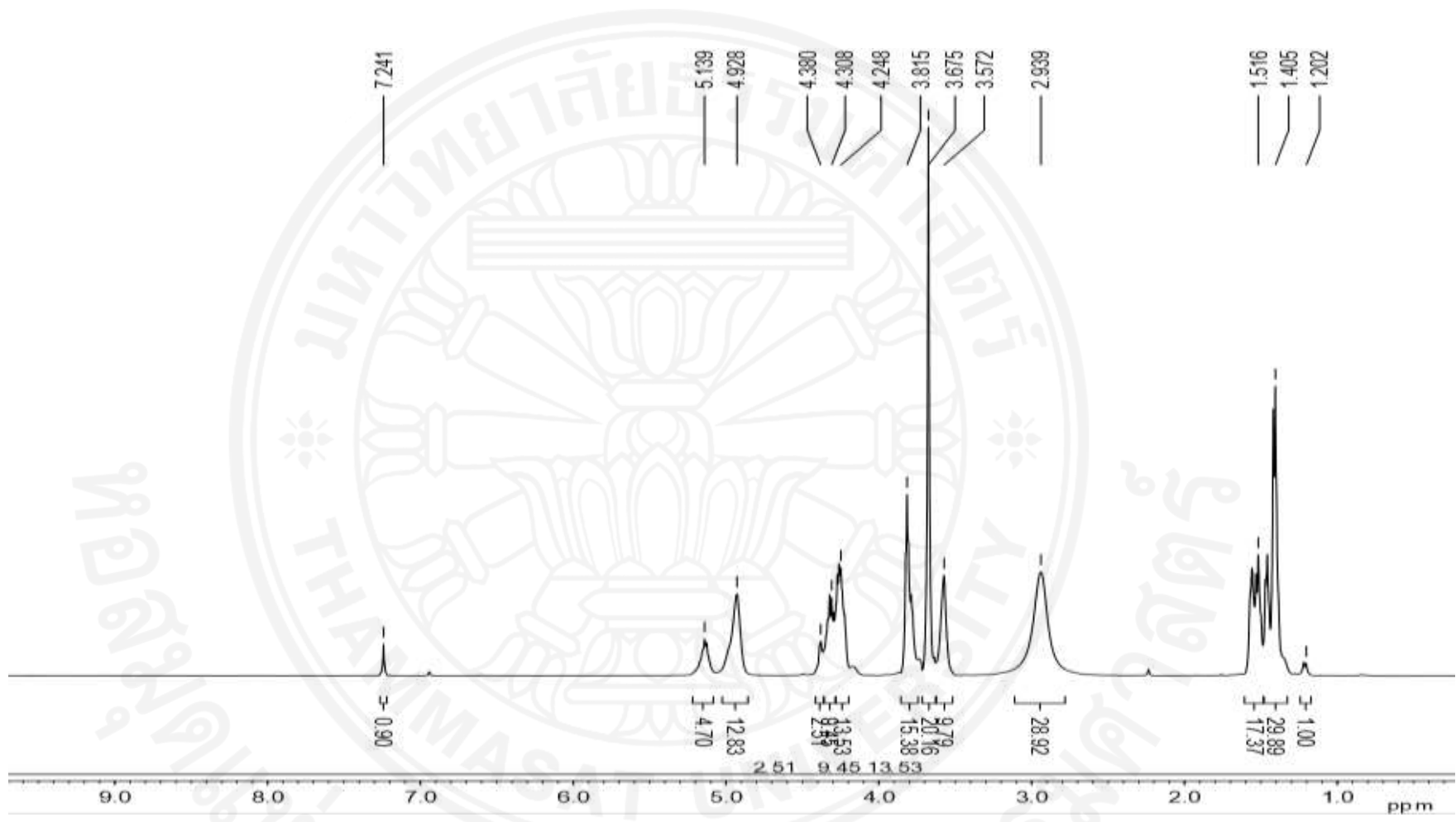**Figure D3** ^{1}H-NMR spectra of separated GlyPLA at 75 min.

Figure D4 ^{1}H-NMR spectra of separated GlyPLA at 90 min.