การเตรียมยางคลอริเนตจากยางอิพอกไซด์และโซเดียมคลอไรด์

นางสาวพัฒนาภรณ์ ผลพิบูลย์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2550

PREPARATION OF CHLORINATED RUBBER FROM EPOXIDIZED NATURAL RUBBER AND SODIUM CHLORIDE

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
Faculty of Science
Chulalongkorn University
Academic Year 2007

Thesis Title PREPARATION OF CHLORINATED RUBBER FROM EPOXIDIZED NATURAL RUBBER AND SODIUM CHLORIDE
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Field of Study Petrochemistry and Polymer Science
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Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master 's Degree

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งานวิจัยนี้เป็นการพัฒนาวิธีการเตรียมยางคลอริเนตในสภาวะอิมัลชัน ยางคลอริเนตเตรียมได้จากยางอิพอกไซด์โดยใช้กรดไฮโดรคลอริกและโซเดียมคลอไรด์ ศึกษาอิทธิพลของความเข้มข้นของกรดไฮโดรคลอริก ความเข้มข้นของโซเดียมคลอไรด์ อุณหภูมิและเวลาในการทำปฏิกิริยา ภาวะที่เหมาะสมในการสังเคราะห์ คือ 2% โดยน้ำหนักของกรดไฮโดรคลอริก 50% โดยน้ำหนักของโซเดียมคลอไรด์ ที่อุณหภูมิ 30 องศาเซลเซียส เป็นเวลา 4 ชั่วโมง พิสูจน์เอกลักษณ์ของยางคลอริเนตด้วย เทคนิคอินฟราเรดสเปกโตรสโกปีและโปรตอนนิวเคลียร์แมกเนติกเรโซแนนซ์สเปกโตรสโกปี และวิเคราะห์หาปริมาณคลอรีนในยางคลอริเนตด้วยเทคนิคเอ็กซ์เรย์ฟลูออเรสเซนซ์ พบว่ามีปริมาณคลอรีน 17.88% ในยางคลอริเนต รวมทั้งศึกษาสมบัติทางความร้อนของยางคลอริเนตด้วยเทคนิคดิฟเฟอร์เรนเชียลสแกนนิงแคลอริเมทรี และเทอมัลแกรวิเมทรี/เดริเวทีฟเทอมัลแกรวิเมทริกแอนาไลซีส พบค่าอุณหภูมิกลาสทรานซิชันเท่ากับ 56.56 องศาเซลเซียส การสลายตัวของยางคลอริเนต พบว่ามี 2 ขั้นตอน ในขั้นตอนแรกการสลายตัวเกิดขึ้นระหว่างอุณหภูมิ 141 ถึง 244 องศาเซลเซียส และในขั้นตอนที่สองการสลายตัวเกิดขึ้นระหว่างอุณหภูมิ 244 ถึง 478 องศาเซลเซียส โครงสร้างของยางคลอริเนตที่พบในงานวิจัยนี้ คาดว่ามีองค์ประกอบสามส่วนคือ หน่วยของยางธรรมชาติที่ไม่ทำปฏิกิริยา หน่วยของยางคลอโรไฮดรินและหน่วยของยางไดคลอริเนต

สาขาวิชา ...ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์... ลายมือชื่อนิสิต......พัฒนาภรณ์ ผลพิบูลย์......
ปีการศึกษา ....2550................................ ลายมือชื่ออาจารย์ที่ปรึกษา..................................

4872386023 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE

KEY WORD: CHLORINATED RUBBER/ EPOXIDIZED NATURAL RUBBER/ SODIUM CHLORIDE/ HYDROCHLORIC ACID

PATTANAPORN PHONPIBOON: PREPARATION OF CHLORINATED RUBBER FROM EPOXIDIZED NATURAL RUBBER AND SODIUM CHLORIDE. THESIS ADVISOR: PROF. SOPHON ROENGSUMRAN, Ph.D, 100 pp.

This research involves the preparation of chlorinated rubber in emulsion state. The chlorinated rubber was prepared from epoxidized natural rubber using hydrochloric acid and sodium chloride. The effect of hydrochloric acid concentration, sodium chloride concentration, reaction temperature and reaction time were studied. The optimal condition for the chlorination reaction of epoxidized natural rubber was carried out with 2% wt hydrochloric acid and 50% wt sodium chloride for 4 hours at 30°C. The chlorinated rubber was characterized by Fourier Transform Infrared and Proton Nuclear Magnetic Resonance Spectroscopies. The %chlorine content was analyzed by X-Ray Fluorescence. It was found that chlorine content in chlorinated rubber was 17.88%. The thermal properties of chlorinated rubber were studied by Differential Scanning Calorimetry and Thermogravimetry/Derivative Thermogravimetric Analysis. The result showed the glass transition temperature of the chlorinated rubber was 56.56°C. The chlorinated rubber degraded with two steps. The first step degradation range started at 141 to 244°C. The second step degradation range started at 244 to 478°C. The chlorinated rubber from this research might consist of three components which were unreacted natural rubber unit, chlorohydrin rubber unit and dichlorinated rubber unit.

Department : Petrochemistry and Polymer Science....Student's signature : Pattanaporn P.

Academic year : ....2007................................Advisor's signature : ....

ACKNOWLEDGEMENTS

I would like to express gratitude to my thesis advisor, Professor Dr. Sophon Reongsumran who not only originated this work, but also gave helpful suggestions, invaluable guidance, constant encouragement and kindness throughout this research. This thesis would not be completed without his advice and guidance.

I am also grateful to Associate Professor Dr. Sirirat Kokpol, Associate Professor Dr. Amorn Petsom, Associate Professor Dr. Somchai Pengprecha, Associate Professor Dr. Wimonrat Trakarnpruk, for serving as the chairman and members of my thesis committee, respectively, for their valuable suggestion and comment.

I gratefully thank to staffs of The Scientific and Technology Research Equipment Center (STREC), Chulalongkorn University and Department of Chemical Technology, Faculty of Science, Chulalongkorn University for assistance in using many instruments. I also thank Graduate School, Chulalongkorn University and Research Centre for Bioorganic Chemistry (RCBC) for welcoming me into their family, financial supports and giving the opportunity to study, laboratory facilities, chemicals and equipments. I feel blessed and very privileged to have joined a group with great members who supported me throughout this course.

I sincerely thank Mr. Jatupol Leangsakul, Miss Jumreang Tummatorn and Miss. Sunisa Suwancharoen for their tireless efforts in helping me with the NMR, suggestion, and comment. Special appreciation is also extended to Miss Saowanaporn Choksakulporn for her advice, helpfulness and kind gratitude of providing me the valuable information. Moreover, I express my appreciation to Kaewkan Wassanasuk for her sugguestion in English writing.

I gratefully thank to all my friends in RCBC group for help and friendship. Furthermore, I would like to express special thank to Miss Siriorn Puangmalee for her sharing happiness and troubles throughout my entire education.

Finally, I wish to express thankfulness to my family for the education, understanding, love, inspiration, encouragement and support throughout my study.

CONTENTS

Page

Page

Page

LIST OF TABLES

LIST OF FIGURES

Figure **Page**

Figure **Page**

Figure **Page**

Figure **Page**

LIST OF SCHEME

LIST OF ABBREVIATIONS

NR	Natural Rubber
ENR	Epoxidized natural rubber
CR	Chlorinated rubber
FT-IR	Fourier Transform Infrared Spectroscopy
^{1}H-NMR	Proton Nuclear Magnetic Spectroscopy
XRF	X-Ray Fluorescence
DSC	Differential Scanning Calorimetry
TG/DTG	Thermogravimetry/ Derivative Thermogravimetric Analysis
HCl	Hydrochloric acid
NaCl	Sodium chloride
d.r.c	Dry rubber content
°C	Degree celcius
g	Gram
wt	Weight
ml	Milliliter
T_g	Glass transition temperature
T_m	Crystalline melting temperature
Min	Minute
cm^{-1}	Wavenumber
%	Percent

CHAPTER I

INTRODUCTION

1.1 Introduction

Chlorinated natural rubber has been widely used as raw material for paint, coating, adhesive, and ink, etc. Because of its outstanding properties such as excellent filming-formation ability, abrasives resistance, quick-drying ability, corrosives resistance, flame retardancy, good insulation ability, and thermal stability, it has become one of the most important industrial derivatives of natural rubber [1].

Traditionally, the chlorinated rubber was prepared by dissolving the natural rubber in tetrachloromethane, and then chlorinating by passing gaseous chlorine through stabilized and strongly acidified Hevea latex. This method was proved to be a satisfactory method and commercially used for preparation of the chlorinated rubber [2]. However, this process produced the large amount of toxic solvent which might be easily leaked and caused environmental hazards and be harmful to human. In addition, carbon tetrachloride has recently banned in all industrial process since it was suspected that it can damage the layer of atmospheric ozone [3].

This research work, thus, developed the preparation of chlorinated rubber by synthesizing via epoxidized natural rubber (ENR). The epoxidation of rubber is a simple and effective method to introduce a new reactive group onto the polyisoprene backbone leading to new and useful properties. After reactive ENR was prepared, it was then chlorinated by using hydrochloric acid (HCl) and sodium chloride (NaCl) to obtain chlorinated rubber. This method avoids chlorine gas or tetrachloromethane which are extremely toxic. Moreover, it is very difficult to control the amount of chlorine gas on the reaction system. On the contrary, synthesizing chlorinated rubber with HCl and NaCl via epoxidized natural rubber has merits such as low price of raw materials and easier process than chlorinating by passing gaseous chlorine.

Conditions of chlorination reaction using sodium chloride and hydrochloric concentrated under the variation of time reaction and temperature were investigated in this research. The chlorine content in chlorinated rubber was analyzed by using Energy dispersive X-Ray Fluorescence spectrometer (EDXRF). The thermal properties of chlorinated rubber were analyzed by Differential Scanning Calorimetry (DSC) and Thermalgravimetry Analysis (TGA).

1.2 Objectives of the research

1. To find the optimum condition for preparation of chlorinated rubber by varying concentration of HCl and NaCl.
2. To study thermal properties of chlorinated rubber.
3. To analyze the chlorine content of preparation chlorinated rubber by X-Ray Fluorescence.

1.3 Scope of research work

In this research work, the chlorinated rubber was prepared from epoxidized natural rubber by reaction with NaCl under the variation of acid condition. The effect of NaCl and HCl concentration, reaction temperature and reaction time were also investigated.

The structure of the chlorinated rubber was analyzed using FT-IR and ^{1}H-NMR. The chlorine content of the product was determined by XRF. In addition, the thermal properties of chlorinated rubber were investigated by using DSC and TGA.

CHAPTER II

THEORETICAL AND LITERATURE REVIEWS

2.1 Natural rubber

Natural rubber can be obtained from nearly five-hundred different species of plants. The outstanding source is the tree Hevea brasiliensis, from which come name Hevea rubber [4]. Rubber is resulted from a latex that exudes from the stem bark of the Hevea tree when it is cut. More than 80% of natural rubber comes from Southeast Asia: production is about equal in Malaysia and Indonesia; Thailand accounts for much of the reminder in this area.

2.1.1 The chemical formula of natural rubber

The chemical structure, natural rubber is cis-1,4-polyisoprene, a linear long chain polymer with repeating isoprene unit (C_5H_8). The molecular unit structure of natural rubber is illustrated below [5].

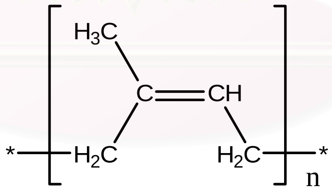


Figure 2.1 Structure of isoprene unit.

2.1.2 Composition of natural rubber [6]

The chemical composition of fresh *Heavea* latex is complex when compared to synthetic latex, which because fresh *Heavea* latex is a cycloplasm. It has been known for a long time that fresh *Heavea* latex contains, in addition to rubber hydrocarbon, a large number of non-rubber constituents (many proteinious and resinous substances, carbohydrates, inorganic matter, water, etc.) present in relatively small amounts. Many of these are dissolved in the aqueous serum of latex, the others are adsorbed at the surface of rubber particles and the non-rubber particles suspend in latex. The typical composition of field latex is shown in **Table 2.1**

Table 2.1 Composition of field latex [7]

Composition	% by weight
Water	55
Rubber hydrocarbon	35
Protein	4.5
Acetone extraction	3.9
Amino acid	0.2
Quebrachitol	1.0
Inorganic salts	0.4

2.1.3 Physical properties of natural rubber [8]

Physical properties of natural rubber may slightly be due to the non-rubber constituents present and to degree of crystallinity. When the natural rubber is held below 10˚C, crystallization occurs, resulting in the change of density from 0.92 to about 0.95. The average molecular weight natural rubber is in the range from 200,000-500,000. The average physical properties of natural rubber are shown in **Table 2.2**.

Table 2.2 The average physical properties of natural rubber

Properties	Value
Density	0.92
Refractive index (20˚C)	1.52
Coefficient of cubical expansion	0.00062˚C
Cohesive energy density	63.7 cal./c.c.
Heat of combustion	10,700 cal/g
Thermal conductivity	0.00032 cal./sec./cm^2/C˚
Dielectric constant	2.37
Power factor (1,000 cycles)	0.15-0.2
Volume resistivity	10^{15} ohms/c.c.
Dielectric strength	1,000 volts/mm^2

2.2 Modification of natural rubber

The modification of natural rubber has been performed in many ways. Modifications are not only directed towards the enhancement of certain properties characteristic of the respective polyisoprenes but also to introduce totally new properties not usually associated with these rubber, or to transform the natural rubber into new product used as high which added value for special applications. In particular, the method was extensively applied to polyisoprene rubbers, natural or synthetic, to prepare various new interesting rubbery material such as flame resistant [9] and thermoplastic NR [10] rubbers. Two chemical strategies are commonly delveloped to prepare polymer: by direct addition of electrophilic reagents onto carbon-carbon double bonds of the rubber chains or addition of nucleophilic reagents onto epoxidized units previously created on the polyisoprene backbone. The letter solution is of great interest because the oxirane group is epoxidized units can easily react in mild conditions with a large scale of nucleophillic reagent [11].

2.2.1 Epoxidized natural rubber [12]

Epoxidized natural rubber has been prepared in emulsion form or latex stage by reacting natural rubber emulsion with peroxide. During epoxidation of the rubber, gel fractions are formed due to formations of both physical crosslink point caused by protein present in natural rubber and chemical crosslink point caused by ring opening reaction of epoxide group. Epoxidation is another typical modification of reaction of unsaturated polymers. A variety of peroxides and peracids have been used to effect this transformation that were showed in the equation **(figure 2.2)**.

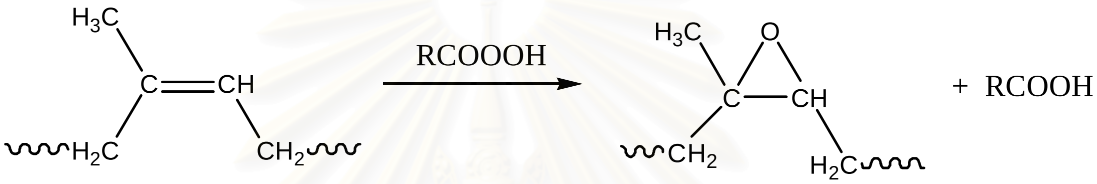


Figure 2.2 Epoxidation of natural rubber with a peroxyacid.

2.2.2 Epoxidation level determination [13]

The epoxidation level of epoxide was calculated using the equation:

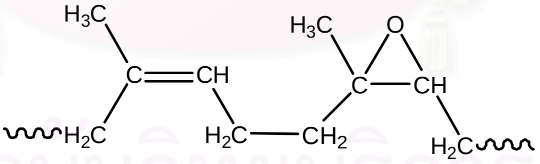


Figure 2.3 The formation of epoxidized natural rubber.

$$\text{Mol \% epoxidation} = 100 \times \frac{[A_{2.70}]}{A_{5.14} + A_{2.70}}$$

$A_{2.70}$ is the integrated area of the proton adjacent to epoxide ring at 2.70 ppm and $A_{5.14}$ is the integrated area of the olefinic proton at 5.14 ppm.

2.3 Hydrochloric acid [14]

Hydrochloric acid has the chemical formula HCl. It is an aqueous solution of hydrogen chloride, which when in a saturated form contains about 43% hydrogen chloride. Hydrogen chloride in aqueous solution is a strong electrolyte because it disassociates to form ions, H^+ and Cl^-. Hydrochloric acid is a proton donor, that is the hydrogen ion. When ionization occurs only one hydrogen ion is produced per molecule of HCl, which is an example of a monoprotic acid. Because ionization is complete with hydrochloric acid it is regarded as a strong acid and the maximum number of hydrogen ions are freed up per molecule. Hydrochloric acid is used in a wide range of chemical reactions and conversions of the chlorinated rubber.

2.4 Chlorinated rubber

In nineteenth century it had been found that chlorination of natural rubber gave products which had promising properties of film former. It was only during the 1930’s, however, that chlorinated rubber was first produced in qualities which were really suitable for lacquers, and the commercial importance of chlorinated rubber as a binder dates from that time [15].

Chlorinated rubber is a white powder forming hard film, fast drying and resistant to oxidation. It has fair resistance to acids, alkaline chemicals and miscellaneous salt solutions. Chlorinated rubber is compatible with the resins viz. coumarine indene resins, phenolic resins, aniline-formaldehyde and other types of various resins, which are used for manufacture of moulding powder as well as the paint forming composition [16]. The chlorinated rubber has been applied in the production of raw materials for paint and adhesives, additive for ink, and acid proof products [3].

Chlorinated rubber has become one of the most important industrial derivatives of natural rubber. There are mainly two kinds of methods for the production of CR. [1] In the traditional solution process, chlorination is carried out by passing chlorine gas into the rubber, which is first dissolved in CCl_4 and then chlorinating [2]. The advantage of solution process include the easy control of the reaction, and fast chlorination. However, the solution process needs expensive equipment and high cost. Moreover, it produces a huge amount of toxic solvent, which may be easily leaked and cause environmental hazards or be harmful to the health of workers [17]. In contrast, the preparation of CR from latex was reported that CNR with a chlorine content of 60% by Van Amerongen [2]. Through adding stabilizer, then adding concentrate hydrochloric acid or sulfuric acid to make the latex in positive state and then passing the chlorine gas into the latex to carry out the chlorination reaction.

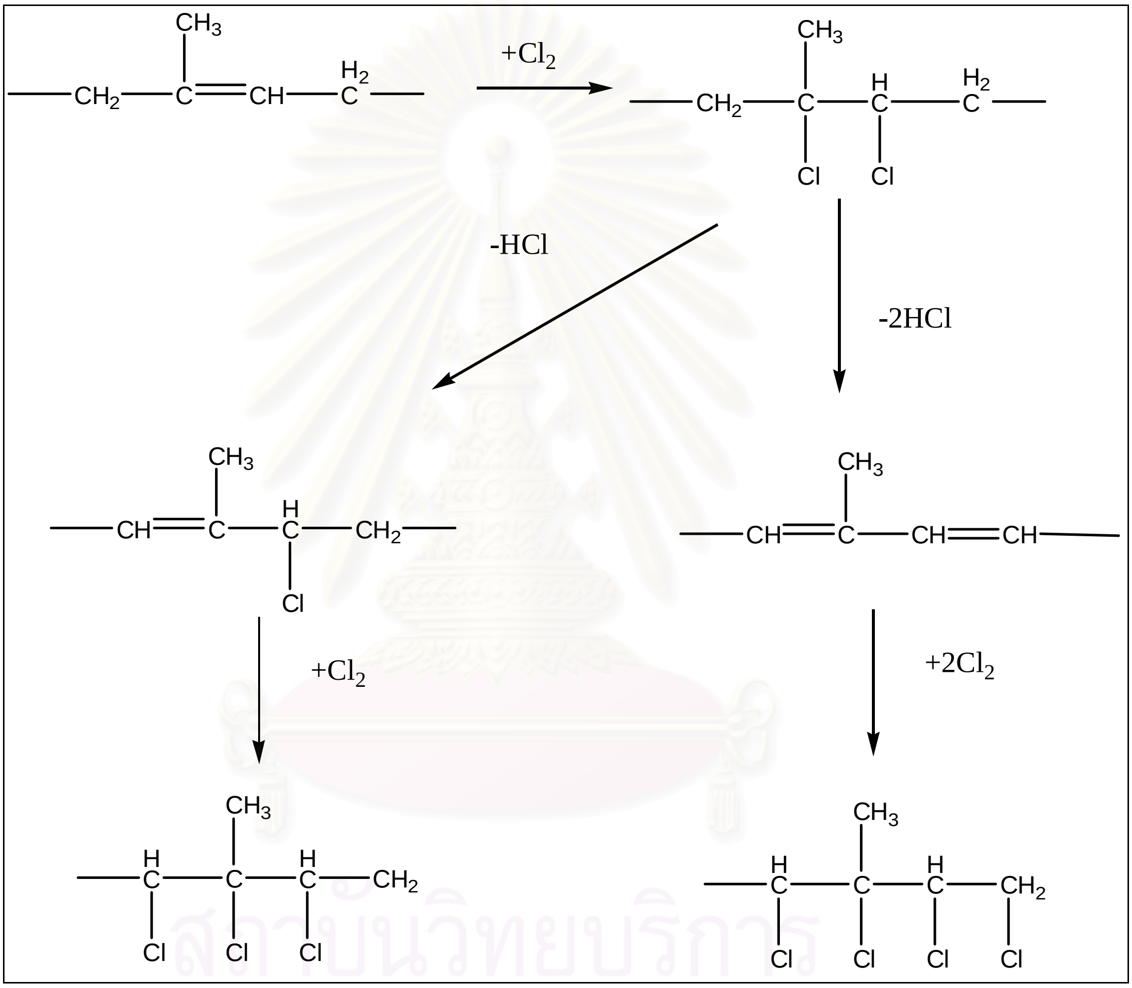


Figure 2.4 Mechanism of chlorination reaction.

Chlorinated rubber is sold under several trademarks, of which the principal are “Alloprene” (Imperial Chemical Industries Limited –I.C.I.) “Parlon” (Hercules Incoporated) and “Pergut” (Farbenfabriken Bayer). The chlorinated commercial product contains about 65% chlorine which is almost the stoichiometric proportion. There is evidence of some cyclization and substitution. According to Parker, the structure is considered to be that shown in **Figure 2.5**

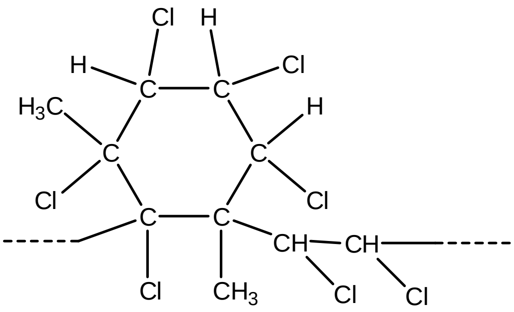


Figure 2.5 Structure of chlorinated rubber.

Chlorinated rubber is very soluble in toluene, xylene, esters, ketones, and other solvents. It is insoluble in hydrocarbons, alcohols and water. Chlorinated rubber finds use in following:

1. Where corrosion is to be prevented. It is used for outstanding resistance to corrosion caused by industrial fumes.
2. It is used in textile coatings, manufacture of paper coatings, adhesive, paints.
3. It is used in manufacture of the retardant paints having better and increased durability in addition to low water permeability, hard wearing, freedom from fontings and non-toxic nature. It is also used for joining in metal joints.

2.5 Application of chlorinated rubber paints [18]

2.5.1 Chemical and corrosive- resistant coating

The simplest type of chlorinated rubber paint, of brush consistency, is as follows:

	% by wt
Chlorinated rubber (20 cps)	20
Inert plasticizer	13
Inert pigment	16
Solvent	51

This type of coating will resist spillage even by a 98% H_2SO_4, concentrated nitric acid and sulfuric acid/ nitric acid 3:1 (nitration acid), as well as solution of caustic alkaline such as sodium and potassium hydroxide, or strongly alkaline oxidizing solutions such as sodium hypochlorite.

2.5.2 Building and swimming pool paints

The chlorinated rubber paint of conventional types were established early and are widely used for coating asbestos-cement sheeting. These coatings were shown to have excellent durability for period over 10 years. Use on concrete structures is also well established, with the object of giving long-lasting decoration to the building as well as preserving the surface from spalling. In some countries, this durability is attracting attention for the long-term decoration of the outside of brick houses. The formulation list in the **Table 2.3** has given excellent results over six years when used as a two-coat system on asbestos cement.

Table 2.3 Chlorinated rubber paint for asbestos cement and concrete

Components	% by wt
Chlorinated rubber (20 cps)	14.1
Chlorinated diphenyl (“Aroclor” 1254)	9.4
Titanium dioxide	15.0
China Cray (kaolin)	16.2
“Bentone” 34	0.5
Methanol	0.17
Aromatic solvent Mineral spirits	44.63
Pigment volume concentration, %	37.5
Viscosity, poise	5.6
Weight per gallon, lb	10

2.5.3 Road line paint

Traffic paints must be quick drying and must have a good durability and visibility. Paints with “no pickup” times of 10 to 20 minutes by the ASTM D-711-55 test can be formulated by using plasticized chlorinated rubber alone or in blends with alkyd or phenolic resins. Paints of this kind are in use in a number of countries of Europe, i.e. Sweden, Norway, Belgium and West Germany. A formulation based on the letter is shown in **Table 2.4**.

Table 2.4 Traffic paint based on chlorinated rubber and phenolic resin

	% by weight
Chlorinated rubber (10 cps)	6.60
Chlorinated paraffin (42% Cl)	3.18
20-gal tung oil phenolic varnish	18.90
Rutile titanium dioxide	5.15
Titanium calcium pigment (30% TiO_2)	25.70
Asbestine	4.64
Celite	7.30
Mica	5.15
Cobalt naphthenate	0.13
Epichlorohydrin	0.20
Mineral spirits	3.78
Toluene	19.27
Wt / gal / lb	12.0
ASTM D-711-55	
No pick-up time	20 min
Smear-free time	35 min

2.6 Thermal properties of polymers

2.6.1 Differential Scanning Calorimetry (DSC) [19]

Differential Scanning Calorimetry (DSC) is a technique for measuring the energy necessary to establish a nearly zero temperature difference between a substance and an inert reference material, as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate.

There are two types of DSC systems in common use **(Figure 2.6)**. In power compensation DSC the temperatures of the sample and reference are controlled independently using separate, identical furnaces. The temperatures of the sample and reference are made identically by varying the power input to the two furnaces; the energy required to do this is a measure of the enthalpy or heat capacity changes in the sample relative to the reference. In heat-flux DSC, the sample and reference are connected by a low resistance heat-flow path (a metal disc). The assembly is enclosed in a single furnace. Enthalpy or heat capacity changes in the sample cause a difference in its temperature relative to the reference; the resulting heat-flow is small compared with that in differential thermal analysis (and related to enthalpy change in the sample using calibration experiments.

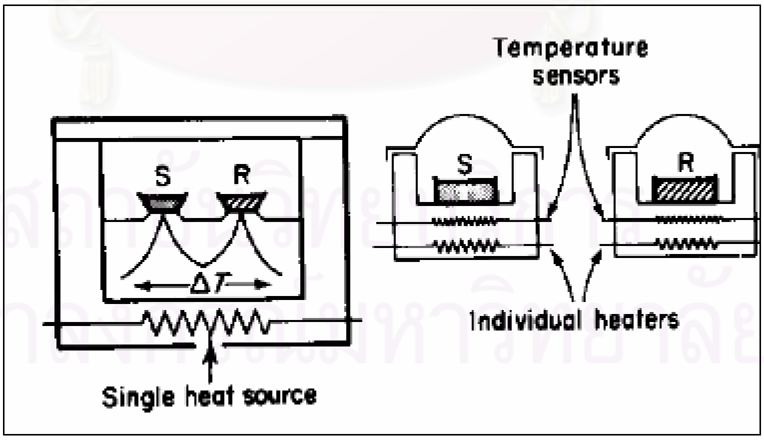


Figure 2.6 (a) Heat flux DSC; (b) power-compensation DSC.

Differential Scanning Calorimetry can be used to measure a number of characteristic properties of a sample. Using this technique it is possible to observe fusion and crystallization events as well as glass transition temperature (*Tg*). Glass transitions may occur as the temperature of an amorphous solid is increased. These transitions appear as step in the baseline of the recorded DSC signal. This is due to the sample undergoing a change in heat capacity; no formal phase change occurs.

As the temperature increases, an amorphous solid will become less viscous. At some point the molecules may obtain enough freedom of motion to spontaneously arrange themselves into a crystalline form. This is known as the crystallization temperature (*Tc*). This transition from amorphous solid to crystalline solid is an exothermic process, and results in a peak in the DSC signal. As the temperature increases the sample eventually reaches its melting temperature (*Tm*). The melting process results in an endothermic peak in the DSC curve. The ability to determine transition temperatures and enthalpies makes DSC an invaluable tool in producing phase diagrams for various chemical systems.

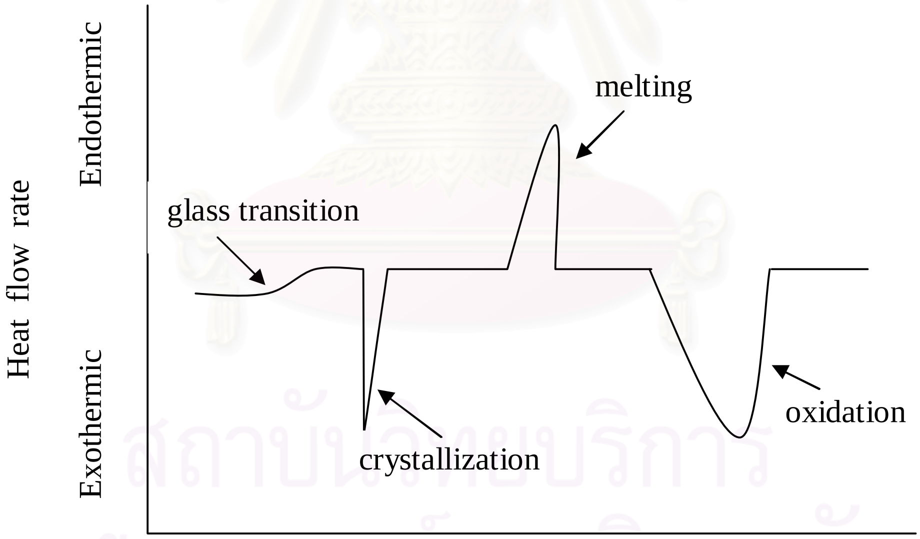


Figure 2.7 DSC curve for polymeric material in an air atmosphere [20].

2.6.2 Thermogravimetry analysis (TGA) [21]

Thermogravimetry is a technique in which the *mass* of the sample is monitored against time or temperature while the temperature of the sample, in specified atmosphere, is programmed. It should be recognized that several manufacturers and users prefer to call this technique *thermogravimetric analysis* (TGA). This avoids confusion with the glass transition temperature, T*g*. The apparatus is called a *thermobalance*, or less frequently, a thermogravimetric analyzer. In order to enhance the steps in the thermogravimetric curve, the *derivative thermogravimetric* (DTG) trace is frequently drawn. This is the plot of the rate of *mass change*, with *time*, d*m*/dt.

2.7 X-Ray Fluorescence (XRF) [22]

X-Ray Fluorescence analysis is a rapid, non destructive, qualitative and quantitative method of determining elements in solids and liquids. With the conventional instruments, it is base on the measurement of wavelengths and intensities of X-Rays emitted by a sample, when excited by the X-Ray from a primary X-Ray tube. It is essentially a surface technique, since the primary beam doesn’t penetrate very far into the specimen-typically a few micrometers for a heavy element such as gold to about half a millimeter for a lighter element such as aluminium.

An atom consisting of nucleus surrounded by a system of electrons contained in shells called K, L, M etc as shown in **Figure 2.8**. The electrons in K, L and M shells are the electrons with principal quantum numbers 1, 2 and 3 respectively. An electron bombarding the target may have sufficient energy to completely displace a K electron from the target atom. This produces an unstable ion, and 10^{-4} seconds later an electron from an outer shell drops into the vacant position. The transition is accompanied by the emission of a characteristic X-ray: a proton of definite wavelength. If the vacancy is filled by an M electron then the proton produced is called a Kb_1 X-ray. If the vacancy is filled by an L electron then a $K\alpha_1$ or $K\alpha_2$ is produced, depending on the subshell of the electron involved in the transition. The $K\alpha_1$ has a wavelength slightly shorter than $K\alpha_2$. Because $K\alpha_1$ and $K\alpha_2$ are so similar in wavelength, these two radiations have not been resolved. If L electrons are knocked out of a target atom, then electrons from outer M or N shells can drop into the vacancies to produce characteristic L radiations. Figure 2.8 shows the transitions that lead to the more important L lines, together with the names of the radiations. The removal of M electrons leads to the generation of M spectral lines, but the removal of electrons beyond this level does not give rise to any more characteristic X-ray line.

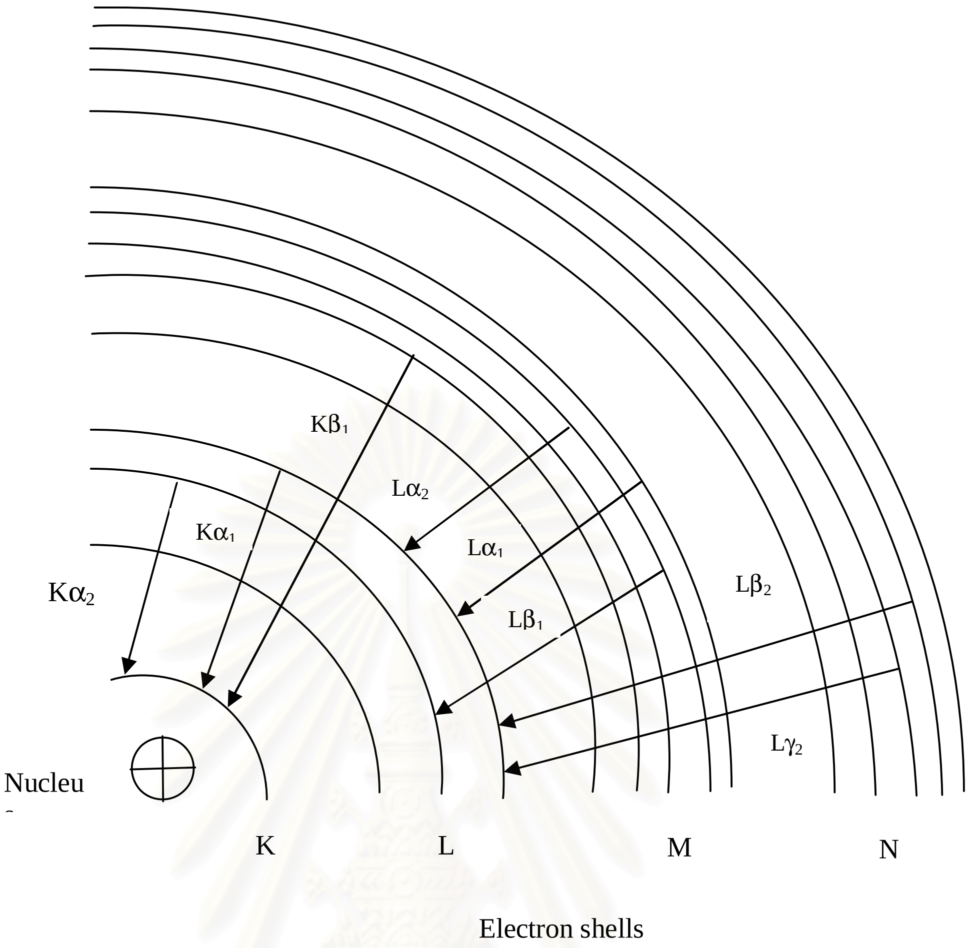


Figure 2.8 Schematic representation of the origin of some characteristic K and L lines.

2.7.1 Type of X-ray fluorescence [23]

A. Wavelength Dispersive

In wavelength dispersive spectrometers the diffracting property of a single crystal is used to separated the polychlomatic beam of radiation coming from the specimen.

1) Single crystal of fixed 2d acts as a spectrum analyzer.

2) Scanning 2θ range allows the completed spectrum to be acquired.

3) Selection of single wavelength is achieved by selection of equivalent 2θ value.

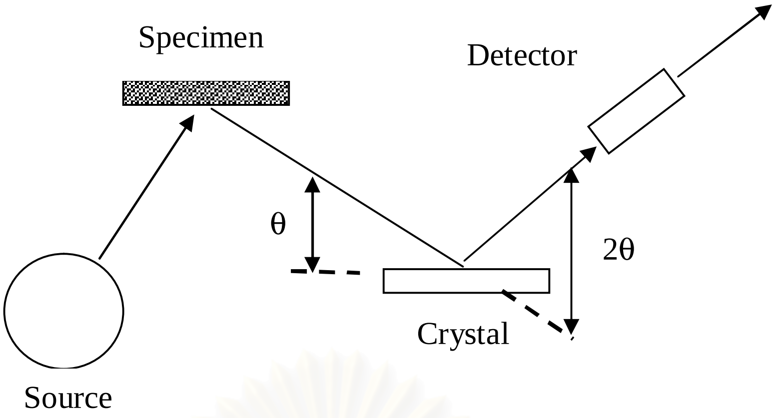


Figure 2.9 Wavelength dispersive spectrometer.

B. Energy Dispersive

In energy dispersive spectrometers a Si (Li) detector is utilized to give a spectrum of voltage pulses that is directly proportional to the spectrum of X-ray photon energies entering the detector. An electronic voltage level sorter, called a multichannel analyzer, is then use to separate and collected these voltage pulses and record them interm of their energies.

1) Proportional Si (Li) detector give a distribution of voltage pulses proportional to the spectrum of X-ray photons.

2) A multichannel analyzer is used to isolate the voltage pulse into discrete intervals. Consecutive output of the multichannel analyzer intervals allows completed spectrum to be displayed.

3) Selection a single energy interval is obtained by selection of appropriate voltage window (i.e. range of channels) on the multichannel analyzer.

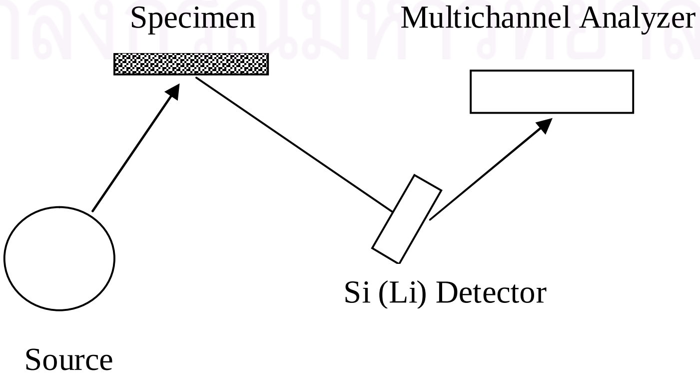


Figure 2.10 Energy dispersive spectrometer.

2.8 Literature reviews

- Epoxidation reaction

In 1984, Burfield [13] had compared DSC, NMR, elemental analysis and direct titration methods for determining epoxide ring of epoxidized natural rubber (ENR). They found that there are some limitation of methods. Direct titration with HBr in glacial acetic acid titration gave fairly accurate information at low modification (<15 mol %). Elemental analysis gave less satisfactory results. DSC analysis appeared to provide the highest precision of the methods examined but was subjected to independent calibration by a primary method. Both ^{1}H-NMR and ^{13}C-NMR analysis provided the best results over the range of 20-75 mol% modification.

In 1985, Gelling [24] used low ammonia natural rubber latex, Texofor A30 surfactant and 35% w/w peracetic acid in epoxidation below 20°C for 6 hours. The epoxidized natural rubber was studied by IR and ^{1}H-NMR spectroscopy. In the IR spectrum of ENR, there were absorptions at 870 and 1240 Cm^{-1}. The ^{1}H-NMR spectrum revealed $C\underline{H}_3$-CO at 1.28 ppm, $C\underline{H}_3$-C=C at 1.65 ppm, $C\underline{H}$-C-O at 2.70 ppm and $C\underline{H}$-C at 5.05 ppm.

In 1991, Bac et al. [25] used full ammonia natural rubber latex (57.7% d.r.c.), nonionic surfactant (fatty alcohol)/(ethylene oxide), glacial acetic acid and peracetic acid in epoxidation at 25°C for 30 min. They found that natural rubber latex was stabilized by 1.65-5.0 phr nonionic surfactant having up to 54% d.r.c. can be acidified by acetic acid to pH = 4, while retaining good aggregative stability. Stabilized latex of 25-48% d.r.c. could be successfully epoxidized at moderate temperature using performed peracetic acid. The epoxidation proceeded rapidly and effectively, leading to ENR products free of side ring opening groups.

In 2005, Chuayjuljit [26] prepared ENR via *in situ* epoxidation from high ammonia concentrate natural rubber latex with formic acid and hydrogen peroxide in the present surfactant at 50°C for 4, 8 and 12 hours. The obtained ENRs containing 20, 45, and 65 mol % of epoxide groups were denoted ENR20, ENR45, and ENR65, respectively. The DSC study revealed that there exhibited higher glass transition temperatures than that of natural rubber (-62.4°C), at -38.2°C for ENR20, -27.8°C for ENR45, and -19.7°C for ENR65, respectively.

In 2007, Takayuki [27] studied ENR by 2D NMR spectroscopy. The ENR was prepared by epoxidation of purified natural rubber with peracetic acid in latex stage followed by degradation with propanal and ammonium persulfate. The ENR was characterized by 1D and 2D-NMR spectroscopy such as two-dimensional heteronuclear shift correlation (HETCOR), two-dimensional homonuclear shift correlation (COSY) and heteronuclear long-range shift correlation (HMBC) measurement. The unknown signals at 1.55, 1.68, 2.05, 2.15 ppm in ^{1}H-NMR spectrum were assigned: that was, 1.55 ppm assigned to the methylene proton of the epoxidized isoprene unit, 1.68 ppm to the methylene proton of the isoprene unit as well as the methylene proton of the epoxidized isoprene unit, and 2.05 and 2.15 ppm to the methylene proton of isoprene unit. The assignment was proved with partially epoxidized squalene as a model compound.

- Chlorination reaction

1990, Eskina et al. [28] studied the structure of chlorinated natural rubber (CR) by ^{1}H-NMR and ^{13}C-NMR data. ^{1}H-NMR spectrum of CR containing 0.6 Cl/C_5 were reported at 1.5-2.8 ppm, aliphatic proton signal (from –CH, $-CH_2$, $-CH_3$ protons); 4.0-4.5 ppm –CHCl proton signals; 4.8-5.6 ppm olefinic proton resonance. ^{13}C-NMR spectrum of CR containing 0.4 Cl/C_5 were report intensity peak at 23.6, 26.9, 32.7, 135.2, 125.1 which were assigned to carbon C_5, C_4, C_1, C_2, C_3 of I unit, respectively.

1994, Tsuchiya et al [29] described the method of chlorinating rubber latex with chlorine gas in high-acidify aqueous dispersion of polyisoprene rubber. Nonionic and anionic surfactant is added to rubber latex and then large amount of acid is added to perform acidifying treatment of latex. Rubber latex is chlorinated up to at least not less than 30% chlorine content at a temperature of 10-20°C. Then raise the temperature to 40-70°C and irradiate with UV rays or use a radical initiator in the second step. The CR is a white solid.

1995, Cataldo [30] prepared CR from natural and synthetic rubber cis-1,4-polyisoprene using liquid chlorine, as solvent and chlorinating agent. The FT-IR spectrum was indicated by the bands at 788, 706, 738, 668, and 640 cm^{-1}, all due to C-Cl stretching.

1999, Zhong [31] studied CR, which is prepared by the chlorinated modification of NR from solution or latex. It has been found the chlorination of NR latex is carried out under the acidic condition, where the pH value is equal to or less than 1. The rate of chlorination was fast at early stage, then slowed down gradually. The effect of temperature on the chlorination is not obvious.

2004, Yu [3] studied thermooxidative degradation of CR from latex by use of the thermalgravimetric analysis TGA/FTIR coupling system. The compositions of gases evolved during the thermooxidative degradation of CR were identified and the *in situ* structure variation of CR during degradation were also analyzed. The CR from latex degrade in air with two distinct step of weight loss. The first step ranging from 160-390°C, mainly is a dehydrochlorination reaction with a little amount of carbon dioxide and the conjugated polyene sequences $(-[C{=}C]-)_{n=3,4}$ are formed on the molecule of CR. The second step ranging from 390-585°C, is an oxidative degradation reaction of the molecular backbones of CR and the evolved gas is only carbon dioxide.

2004, Kittima [32] prepared CR from chlorination reaction between ENR and sodium hypochlorite/sodium chloride (NaOCl/ NaCl). The optimal condition for preparing the CR was used ENR and sodium chloride of 1:4 by mol. The ENR combined with NaOCl/ NaCl of 1:4 by mole was used as optimal condition for preparation of the CR. The chlorination reaction was performed at 30° C, an optimal time of 6 hours, in an acidic condition at pH 1. The chlorine content of the chlorohydrin rubber of 19.06% was analyzed by X-Ray Fluorescence. The structure of CR was characterized by FT-IR and ^1H-NMR spectroscopies.

CHAPTER III

EXPERIMENTAL

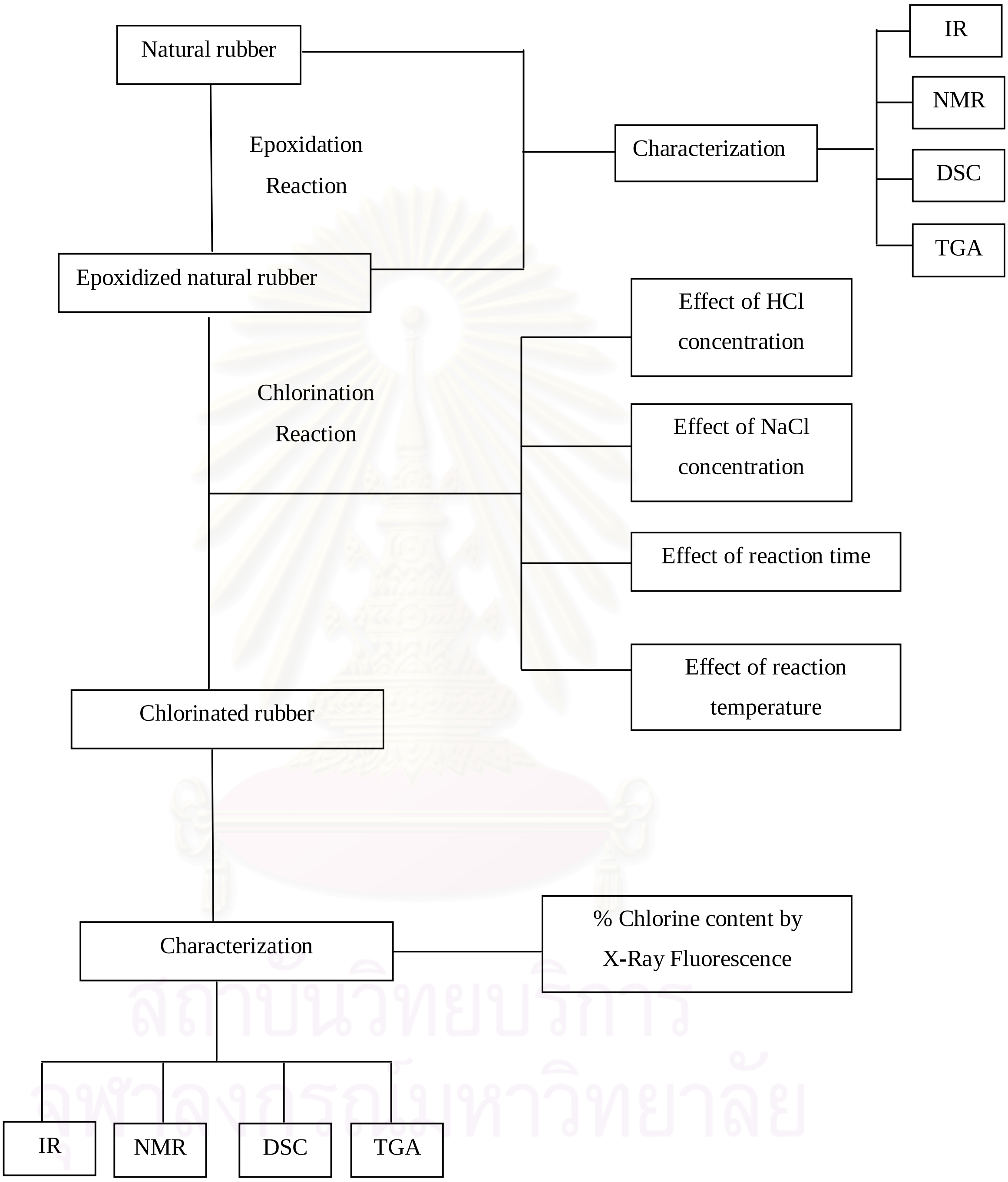
3.1 Chemicals

1. Natural rubber latex	: Thai Rubber Latex Corporation (Thailand) Public Co., Ltd
2. Tergitol NP 10	: Union Carbide
3. Glacial acetic acid 100%	: Carlo Erba
4. Hydrogen peroxide 50%	: Merck
5. Hydrochloric acid	: Merck
6. Sulfuric acid 96%	: Merck
7. Sodium hydrogen carbonate	: Fluka
8. Sodium chloride	: Fluka
9. Chloroform	: Merck
10. Methanol, AR grade	: Merck

3.2 Instruments and apparatus

1. Mechanical stirrer	: Janke & kunkel, RE 16
2. Magnetic stirrer	: Model 34532, Snijderes, CU
3. Fourier Transform Infrared Spectrophotometer (FT-IR)	: Perkin Elmer, Nicolet (Impact 410)
4. Proton Nuclear Magnetic Resonance Spectrometer (^{1}H-NMR)	: Varian Mercury spectrophotometer
5. Differential Scanning Calorimeter (DSC)	: Mettler Toledo, DSC 822
6. Thermogravimetric Analyzer (TGA)	: Perkin Elmer, Pyris Diamond
7. X-Ray Fluorescence (XRF)	: EDXRF 2000

3.3 Experiment procedure of epoxidized natural rubber (ENR) and chlorinated rubber (CR)



Scheme 3.1 Scope of preparation chlorinated rubber.

3.3.1 Preparation of peracetic acid [33]

Glacial acetic acid (90 g) and concentrated sulfuric acid (1.2 g) were mixed together and hydrogen peroxide 50% (153 g) was then added dropwise and allowed to stir at room temperature for 1 hour.

3.3.2 Preparation of epoxidized natural rubber and chlorinated rubber

Natural rubber latex (60% dry rubber content, 30 g) in distilled water (90 ml) was stabilized with tergitol NP 10 (3% by weight of natural rubber latex, 1.5 g) and stirred with a mechanical stirrer for 9 hours at room temperature. Peracetic acid (200 ml, 3.3%) was then added dropwise and stirred at 30°C. After 30 minutes, the white emulsion was poured into methanol to precipitate. The coagulum was washed with distilled water to remove free acid and soaked in 0.1M Na_2CO_3 aqueous solution for 24 hours at room temperature. It was then adjusted the pH until pH 7 with distilled water and dried at 80°C to obtained epoxidized natural rubber.

The obtained epoxidized natural rubber was used to synthesize chlorinated rubber. The emulsion of epoxidized natural rubber was stirred vigorously then the hydrochloric acid and sodium chloride solution were added slowly by dropwise. Reaction mixture was precipitated into methanol. The coagulum was washed with distilled water to remove free acid and then soaked in an aqueous solution of 0.1M Na_2CO_3 for 24 hours at room temperature. Then the coagulum was adjusted with distilled water until pH 7 and dried at 80°C.

During the chlorination process, the effects of concentration of sodium chloride solution and hydrochloric acid, reaction temperature and reaction time were observed.

3.3.2.1. Effect of hydrochloric acid and sodium chloride concentration

The prepared chlorinated rubber by variation of hydrochloric acid and sodium chloride concentration (% weight by weight) were demonstrated in **Table 3.1**

Table 3.1 Condition of CR were prepared by the variation of hydrochloric acid and sodium chloride concentration

Sample	Concentration of HCl (%wt)	Concentration NaCl (%wt)
A1	0.5	2
A2		4
A3		8
A4	1	2
A5		4
A6		8
A7	2	2
A8		4
A9		8
A10	3	2
A11		4
A12		8

From this condition, it was found that 2% hydrochloric acid concentration suitable for preparation of chlorinated rubber because the concentration of HCl was increased as high as 3% wt, the natural rubber was denatured. After that, the effect of NaCl concentrations was further studied to determine the optimal concentration of NaCl for preparation of chlorinated rubber, which were demonstrated in follow the **Table 3.2**

Table 3.2 Condition for preparation of chlorinated rubber under various sodium chloride concentrations at 2% hydrochloric acid concentration

Sample	NaCl (%wt)
B1	10
B2	20
B3	30
B4	40
B5	50
B6	60
B7	70

From this condition, it was found that the optimal concentration of sodium chloride was 50% which provided the maximum chlorine content for preparation of chlorinated rubber.

3.3.2.2 Effect of reaction time

The reactions were carried out at 30°C under the variation reaction times which of 1, 2, 4, 6 and 8 hours were demonstrated, respectively. From this condition, it was found that the optimal time was 4 hours for preparation of chlorinated rubber.

3.3.2.3. Effect of reaction temperature

This effect of reaction temperature was investigated by varying the reaction temperature at 10, 20, 30, 40°C, respectively for 4 hours.

3.4 Characterization of epoxidized natural rubber and chlorinated rubber

3.4.1 Proton Nuclear Magnetic Resonance Spectroscopy (^{1}H-NMR) [13]

Samples were dissolved in deuterated chloroform for ^{1}H-NMR analysis. The epoxidation level of epoxidized natural rubber was calculated using the equation:

$$\text{Mol \% epoxidation} = 100 \times \frac{[A_{2.70}]}{A_{5.14} + A_{2.70}}$$

where $A_{2.70}$ is the integrated area of the proton adjacent to epoxide ring at 2.70 ppm and $A_{5.14}$ is the integrated area of the olefinic proton at 5.14 ppm.

3.4.2 Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR analysis was obtained from Perkin Elmer system 200 FT-IR spectroscopy (Impact 410, Nicolet). The frequency range of 4000-400 cm^{-1} was observed using transmittance, Perkin Elmer, Nicolet (Impact 410) model.

- Natural rubber and epoxidized natural rubber were dissolved in chloroform and cast on NaCl plate for FT-IR analysis.
- Chlorinated rubber was mixed with potassium bromide in agate mortar and pestle. The mixture were then transferred to a hydraulic pressing machine and pressed into a thin disc for FT-IR analysis.

3.4.3 X-Ray Fluorescence (XRF)

Chlorine contents were analyzed by using a Energy Dispersive X-Ray Fluorescence spectrometer (EDXRF) serviced by the Scientific and Technology Research Equipment Center (STREC), Chulalongkorn University.

3.4.4 Differential Scanning Calorimetry (DSC)

The glass transition temperature (Tg) was investigated by using DSC-822 (Metter Toledo) with nitrogen flow and heating rate of 10 °C/min from -100°C to 220°C serviced by the Scientific and Technology Research Equipment Center (STREC), Chulalongkorn University.

3.4.5 Thermalgravimetry Analysis (TGA)

Thermalgravimetry (TG)/Derivative Thermalgravimetric Analysis (DTG) were investigated by using thermalgravimetric analyzer (Perkin Elmer, Pyris diamond) with nitrogen flow rate of 50 ml/min and a heating rate of 10°C/min from 40 to 800°C.

CHAPTER IV

RESULTS AND DISCUSSION

In this research, epoxidized natural rubber (ENR) was prepared by epoxidizing natural rubber (NR) with peracetic acid and then used ENR as starting material for chlorinated rubber (CR) preparation via reaction of CR with hydrochloric acid and sodium chloride. The optimal condition yielding the highest chlorination was determined by variation of the hydrochloric acid and sodium chloride concentrations, reaction temperature and reaction time. Structure of the product was characterized by using Fourier Transform Infrared spectroscopy (FT-IR) and Proton Nuclear Magnetic Resonance spectroscopy (^{1}H-NMR) techniques. Chlorine content of the CR was characterized by using X-Ray Fluorescence (XRF). Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) were used to study the thermal properties of NR, ENR and CR.

4.1 Synthesis and characterization of epoxidized natural rubber (ENR)

ENR was prepared by epoxidation of natural rubber latex with 3.3% peracetic acid in aqueous solution. A reaction was carried out at 30-35°C for 30 minutes. The product was then precipitated in methanol to obtain ENR. The chemical equation of the reaction was represented as follows:

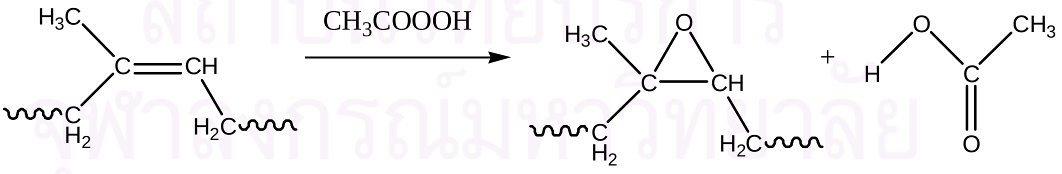


Figure 4.1 The natural rubber epoxidation.

ENR product was characterized by FT-IR spectroscopy. The percentage of epoxidation of ENR was calculated from ^{1}H-NMR.

4.1.1 Structural analysis by FT-IR and ^{1}H-NMR

Structural characterization of the product was done by using FT-IR spectroscopy. The FT-IR spectrum of NR and ENR are shown in Figure 4.2-4.3. From FT-IR spectrum **Figure 4.2**, NR showed characteristic peaks at 3356 cm^{-1} (OH stretching), 2961 cm^{-1} (C-H stretching), 1665 cm^{-1} (C=C stretching), 1376 and 1443 cm^{-1} (C-H bending) and 834 cm^{-1} (C=C cis). After reaction, a significant decrease of peak at 1668 cm^{-1} was identified and new peak at 883 cm^{-1} for epoxide ring was found as shown in **Figure 4.3** which implied the success of the reaction [24].

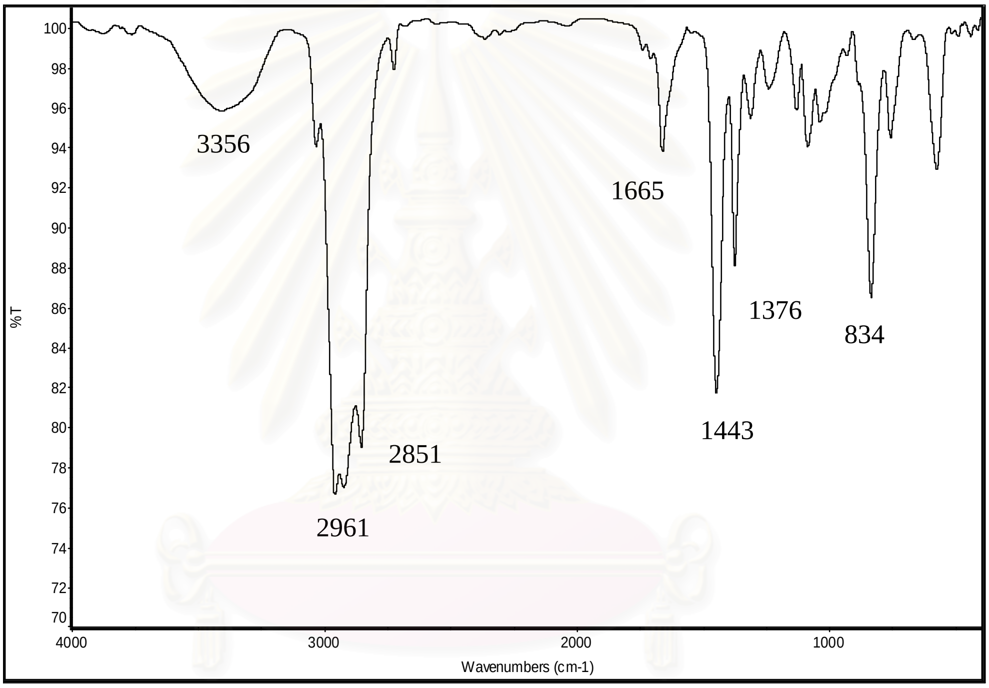


Figure 4.2 FT-IR spectrum of NR.

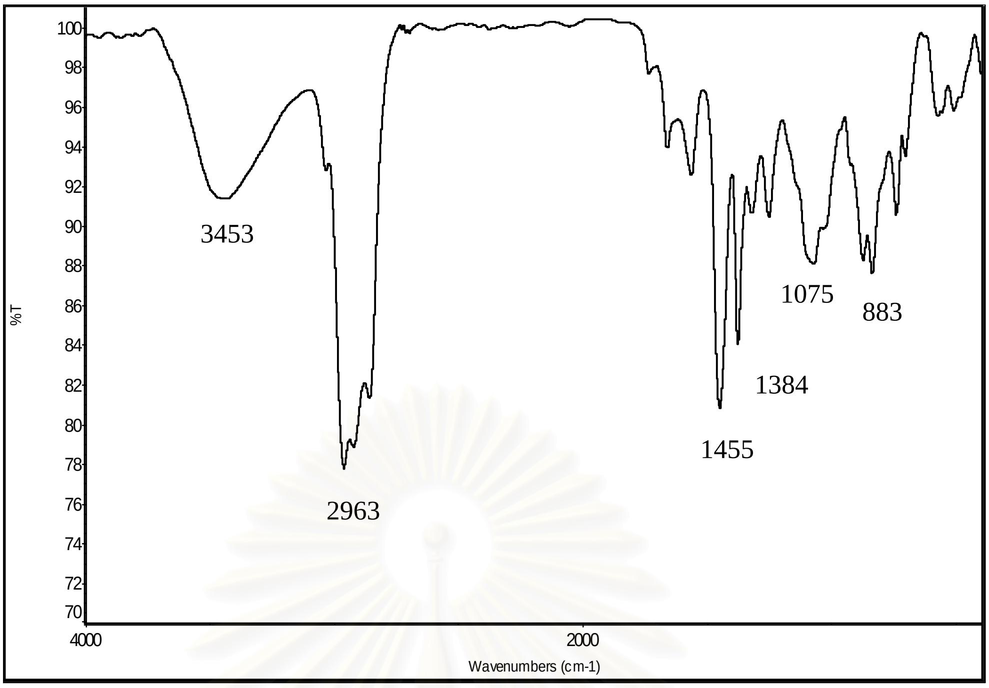


Figure 4.3 FT-IR spectrum of ENR.

The ^{1}H NMR operating at room temperature was used to confirm the structure of ENR and to determine the epoxidation level. **Figure 4.4** showed the chemical shift of NR in $CDCl_3$ with 1.68 ppm ($C\underline{H}_3$-C=C), 2.04 ppm (-$C\underline{H}_2$-), 5.12 ppm ($C\underline{H}$=C). After epoxidation, spectrum of ENR **(Figure 4.5)** showed the new peak at 1.28 ppm ($C\underline{H}_3$-CO) and 2.70 ppm ($C\underline{H}$-C-O). The ^{1}H NMR signals and their assignments are listed in **Table 4.1.**

Table 4.1 ^{1}H-NMR signal data of NR and ENR

A type of proton	Chemical shift(ppm)	
	NR	ENR
$C\underline{H}_3$-CO	-	1.28
$C\underline{H}_3$-C=C	1.68	1.67
-$C\underline{H}_2$-	2.04	2.06
$C\underline{H}$-C-O	-	2.70
$C\underline{H}$=C	5.12	5.12

The degree of epoxidation of ENR was calculated by using the integration of proton of double bond as the internal standard. The epoxidation level was found to be 45% based on the integration of epoxide group as demonstrated in the following equation.

$$\text{Mol \% epoxidation} = \frac{100 * [A_{2.70}]}{A_{5.14} + A_{2.70}}$$

$$\text{Mol \% epoxidation} = \frac{100 * [5.18]}{6.43 + 5.18}$$

$$\text{Mol \% epoxidation} = 45\%$$

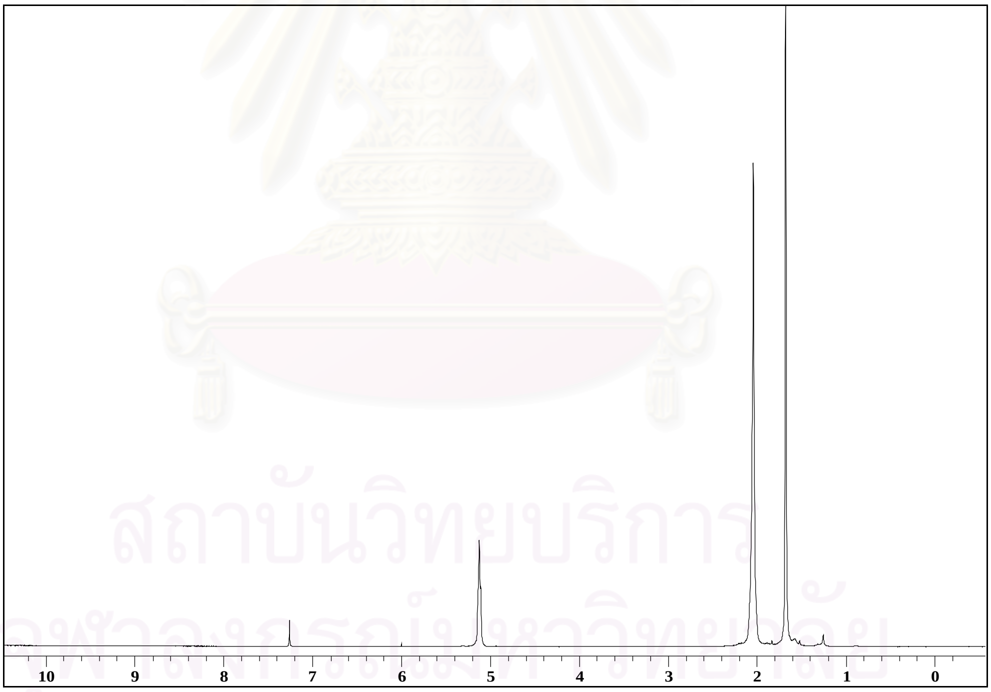


Figure 4.4 ^{1}H-NMR spectrum of NR.

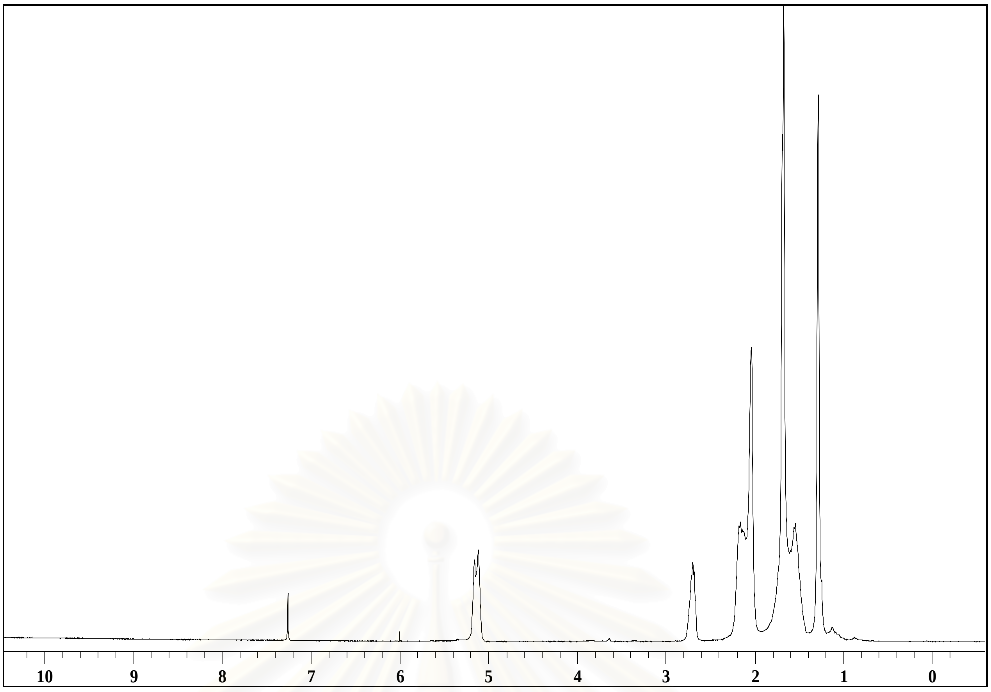
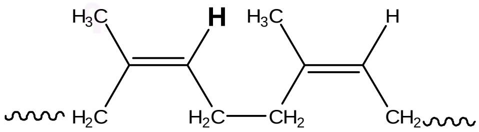
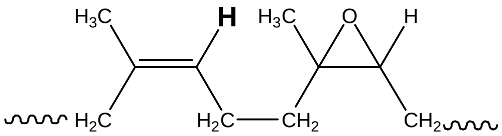


Figure 4.5 ^{1}H-NMR spectrum of ENR.

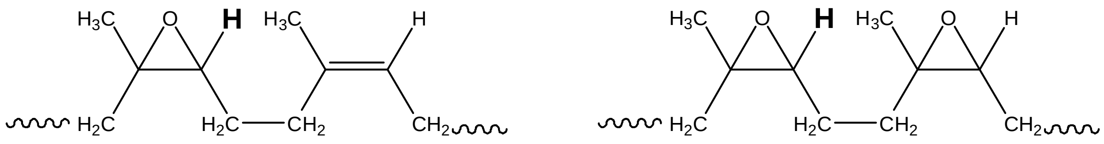
In the spectrum of ENR, the signal at 5.12 ppm was assigned to the olefinic protons of isoprene units which appearing two signals were overlapped. Two protons characteristic might be assigned due to environmental of these protons were different as showed in **Figure 4.5**. The structure (A) showed unreacted rubber unit that adjacent to other unreacted rubber unit while as the structure (B), unreacted rubber unit was adjacent to epoxide rubber unit. To consider, the signal at 2.70 ppm was assigned to proton of epoxide rubber unit. It was also found two signals overlap which might be two protons characteristic due to environmental of protons were different. The structure (C) showed epoxide rubber unit that adjacent to unreacted rubber unit. The structure (D) showed epoxide rubber unit that adjacent to epoxide rubber unit.



(A)



(B)



(C) (D)

Figure 4.6 Two protons characteristic of olefinic proton and epoxide proton of ENR.

4.1.2 Thermal properties

4.1.2.1 Differential scanning calorimetry (DSC)

Differential Scanning Calorimetry (DSC) was used to determine the changing in Tg when NR was processed to be ENR. The DSC thermogram of NR **(Figure 4.7)** indicated Tg of NR was at -64.6°C. (lit. -62.4°C, [26]). After epoxidation, ENR showed Tg at -26.5°C (lit. -27.8°C, [26]), (**Figure 4.8)** which was higher than that of NR. It might be explained that at room temperature NR was less tough than ENR.

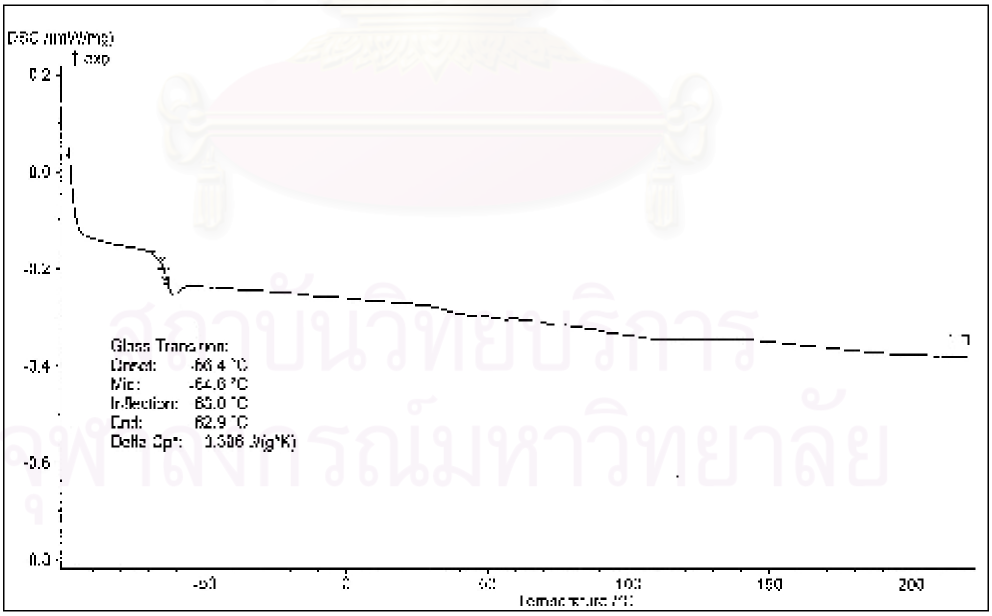


Figure 4.7 DSC thermogram of NR.

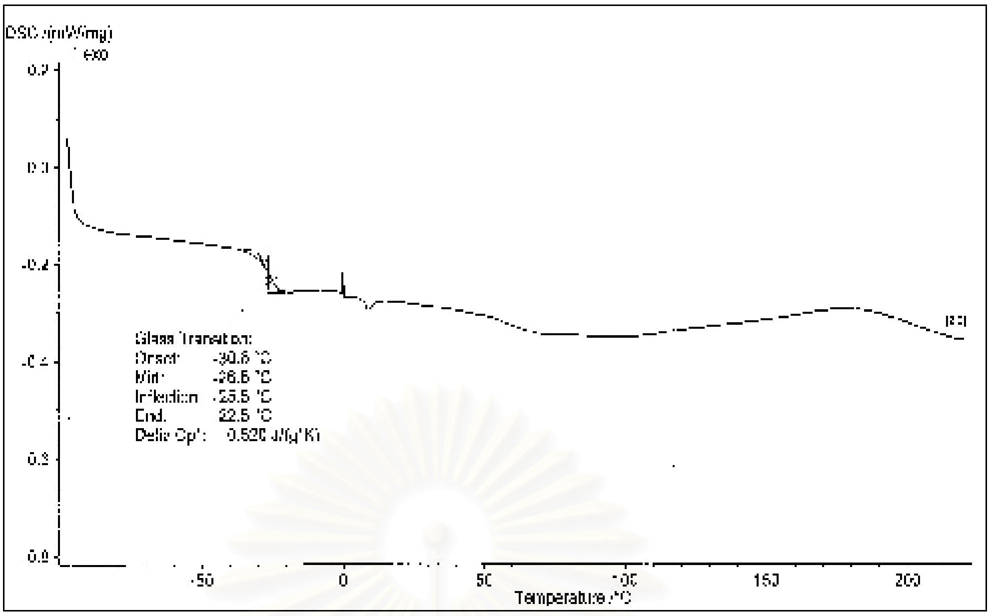


Figure 4.8 DSC thermogram of ENR.

4.1.2.2 Thermalgravimetry (TG) and Derivative Thermogravimetric Analysis (DTG)

Thermalgravimetry (TG) and Derivative Thermogravimetric Analysis (DTG) were also used to determine the thermal stability of NR and ENR. TG/DTG thermograms of NR and ENR are shown in **Figure 4.9** and **Figure 4.10**, respectively. Degradation of NR occurred in two steps. The first step degradation stated at about 208.1 and completed at 466.7°C. During this stage 90.9% weight loss of rubber unit was observed. The second step degradation started at 466.7 and completed at 550.2 °C. During this stage, the weight loss was 4.2%. In the DTG curve, the major peak was observed at 369°C. (lit. the first step degradation started at 267 to 460°C and weight loss was 85.88 %. The second step degradation started at 460 to 600°C and weight loss was 11.11 %. DTG curve showed that the major peak was observed at 373 °C, [34]). After epoxidation process, the degradation temperature of ENR increased a little bit. It started to degrade at 239.3°C and last until 471.2°C. In the DTG curve, the major peak was observed at 390°C. During this stage, the weight loss was 99.1% of rubber unit.

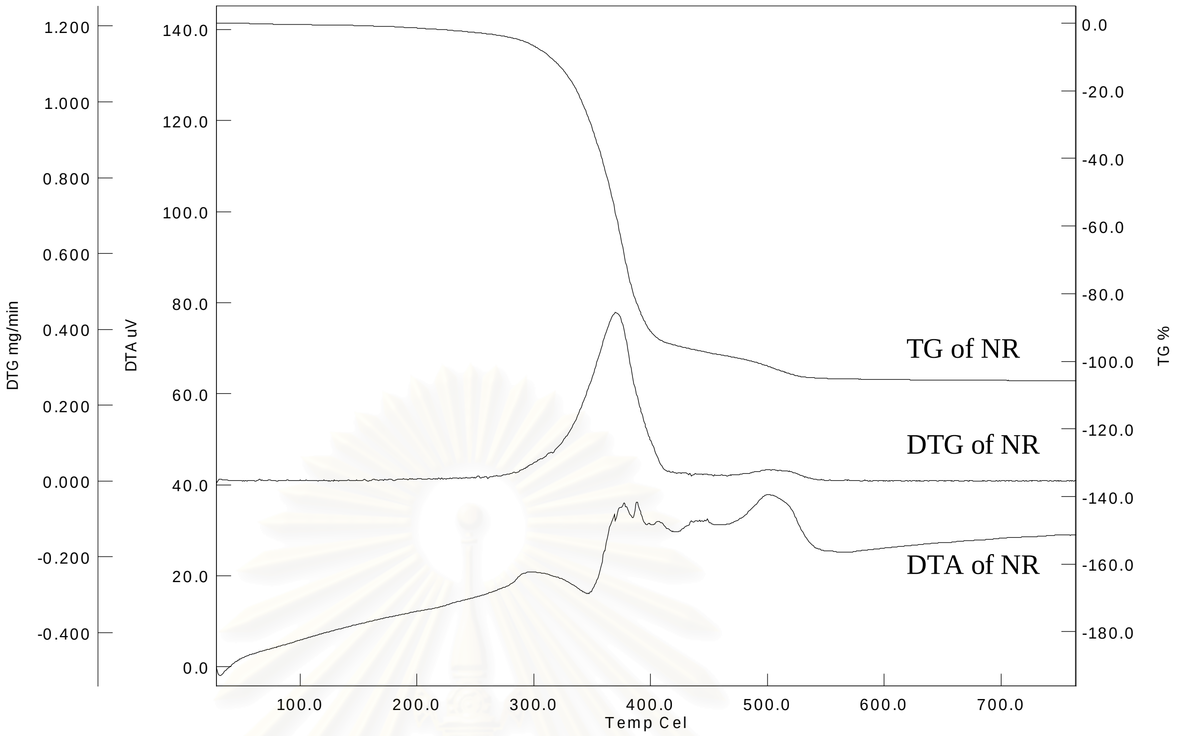


Figure 4.9 TG/DTG thermogram of NR.

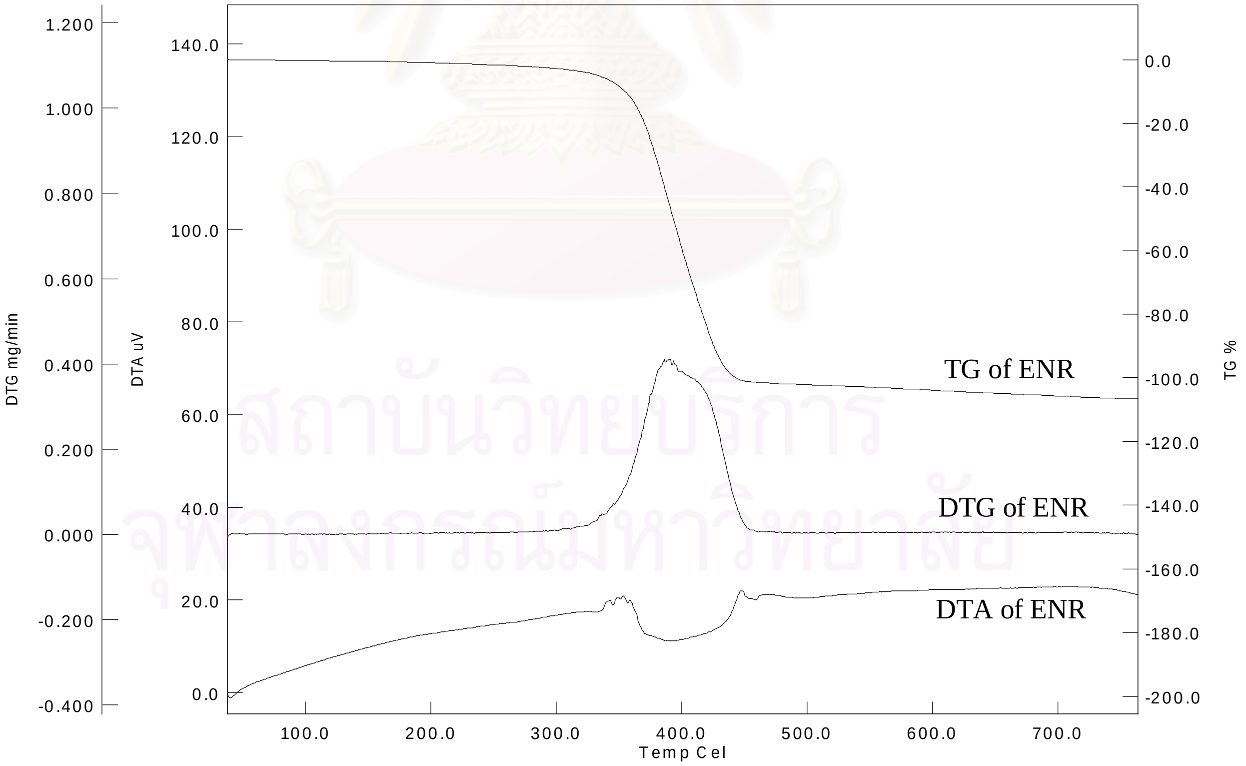


Figure 4.10 TG/DTG thermogram of ENR.

4.2 Synthesis and characterization of chlorinated rubber

CR was performed by chlorination of ENR with NaCl which acts as nucleophile under acid condition. The concentration of HCl and NaCl, reaction temperature and reaction time were varied to find the optimal condition. Qualitative and quantitative analysis of the CR were done by ^{1}H-NMR, FT-IR and XRF techniques.

4.2.1 Effect of hydrochloric acid and sodium chloride concentration

The effect of variation hydrochloric acid and sodium chloride concentrations was observed by varying the hydrochloric acid concentrations from 0.5, 1, 2 %wt and sodium chloride concentrations from 2, 4, 8 %wt to obtain A1 to A12 as shown in **Table 3.1**. The reaction temperature and reaction time were controlled at 30°C for 4 hours.

After the reaction, FT-IR technique was used to characterize the structure of the products. The FT-IR spectrum of the product A1 **Figure 4.11** showed peaks at 3454 cm^{-1} (O-H stretching), 2963 cm^{-1} (C-H stretching), 1638 cm^{-1} (C=C stretching), 1455 and 1376 cm^{-1} (C-H blending), 1072 cm^{-1} (C-O stretching) and 687 cm^{-1} (C-Cl stretching). ^{1}H-NMR technique was also used to confirm the structure. **Figure 4.12** showed the chemical shift of the product A1 in $CDCl_3$ with 1.24 ppm ($C\underline{H}_3$-CO), 1.67 ppm ($C\underline{H}_3$-C=C), 2.04 ppm (-$C\underline{H}_2$-), 3.40 ppm (C-O$\underline{H}$), and 5.12 ppm (C$\underline{H}$=C). The other products (A2-A9) also showed similar FT-IR and ^{1}H-NMR spectra. FT-IR spectra and ^{1}H-NMR spectra as shown in Appendix A (Figure A2-A9) and Appendix B (Figure B2-B9).

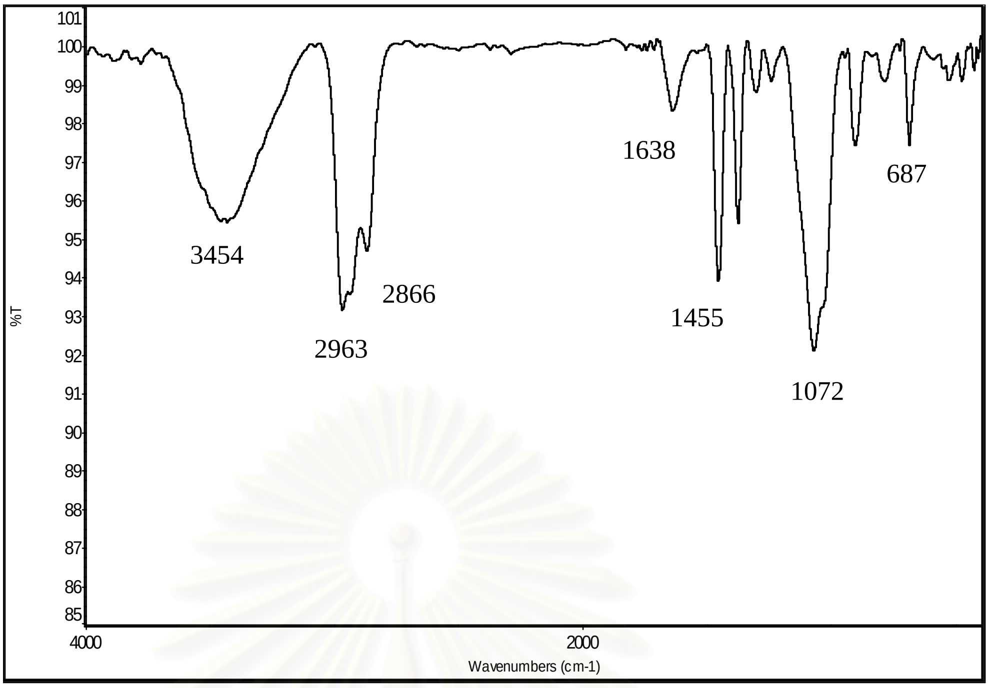


Figure 4.11 FT-IR spectrum of A1.

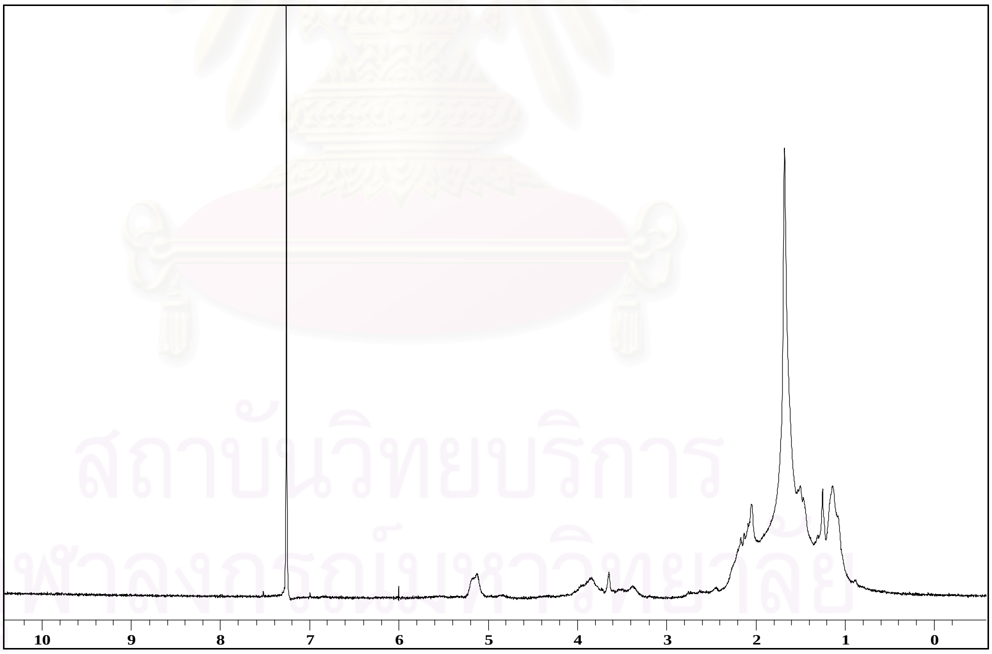


Figure 4.12 ^{1}H-NMR spectrum of A1.

Chlorine content of CR was determined and calculated by XRF technique. The chlorine content increased with the increase of hydrochloric acid concentration in the reaction system. The results (Table D1: Appendix D) showed that 2%wt hydrochloric acid concentration gave the highest chlorine content in the CR. From this condition, it was found that 2% hydrochloric acid concentration suitable for preparation of CR because the concentration of HCl was increased as high as 3% wt, the NR was denatured. The relationship between chlorine content and sodium chloride concentration is shown in **Figure 4.13**. The XRF spectra of CR are shown in Appendix C (Figures C1–C9). Therefore, in this research the effect of sodium chloride concentration with 2% wt hydrochloric acid concentration for increasing the chlorine content in ENR was investigated.

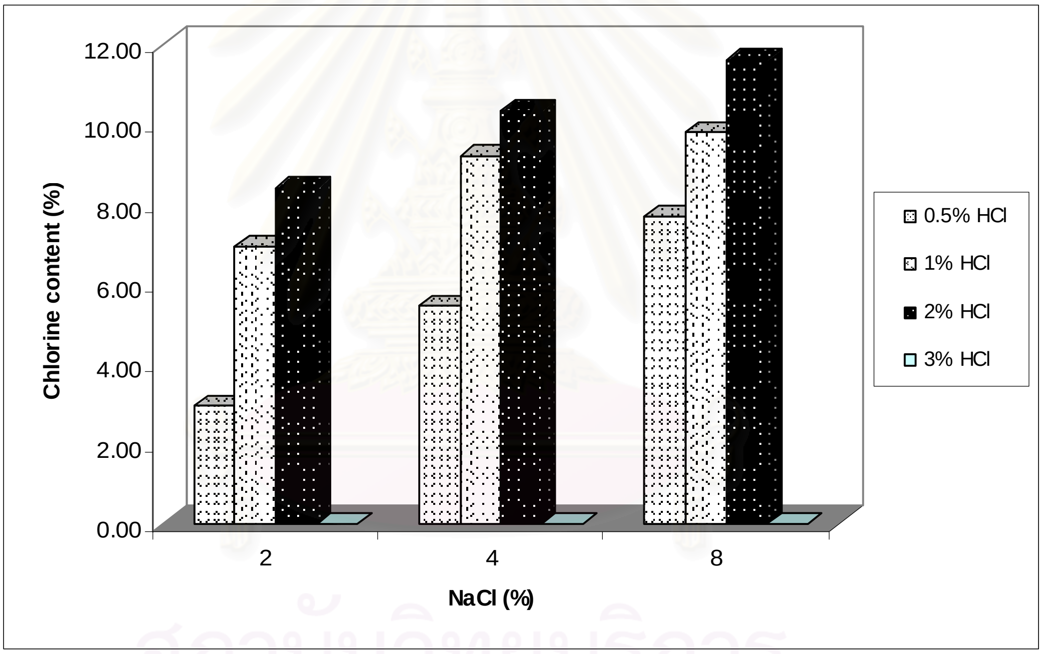


Figure 4.13 Chlorine content in CR derived by variation of hydrochloric acid concentration.

The effect of sodium chloride concentration was further investigated to determine the optimal sodium chloride concentration which gave the highest chlorine content in reaction product. The hydrochloric acid concentration was constant at 2% wt because this value gave the highest chlorine content. **Table D2** (Appendix D) showed that the chlorine content increased when the sodium chloride concentration was increased. The optimal sodium chloride concentration was 50% wt which provided 17.88% wt chlorine content for the chlorinated rubber preparation. On the contrary, when sodium chloride concentration was increased more than 50% wt, the chlorine content remained constant and tended to decrease after 70% sodium chloride concentration. Due to the excess of sodium chloride disturbed the equilibrium of the emulsion of ENR and partial ENR was then coagulated and finally caused the decrease of the chlorination of ENR. The relationship between the sodium chloride concentration and chlorine content is shown in **Figure 4.14**. The XRF spectra of CR are shown in Appendix C. (Figure C10-C16)

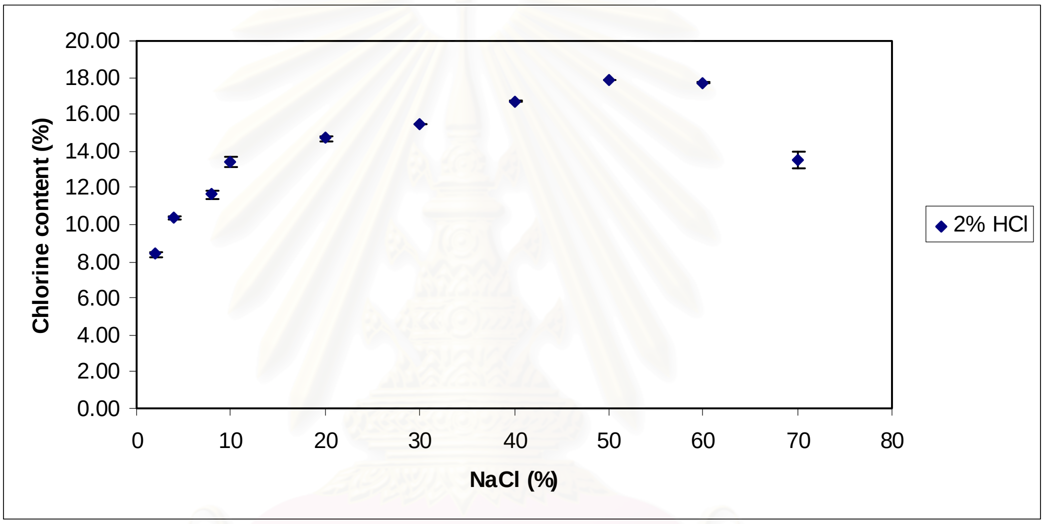


Figure 4.14 Chlorine content of CR at various sodium chloride concentrations with 2% hydrochloric acid concentration.

The value of chlorine content at 17.72% from reaction with 60% wt sodium chloride concentration was evaluated by using statistic method to compare with chlorine content at 50% weight of sodium chloride concentration. It was demonstrated that there is no difference in the chlorine content of CR at these two sodium chloride concentrations. Therefore the sodium chloride concentration at 50% was used to investigate the effect of reaction temperature and reaction time.

4.2.2 Effect of reaction time

The effect of reaction time for CR preparation was also observed by carried out each reaction in optimal condition (HCl 2% wt, NaCl 50% wt, at 30°C) for various period of time from 1, 2, 3, 4, 6 and 8 hours, respectively. After each reaction took place, each reaction product was analyzed by XRF in determining the chlorine content. The results are presented in **Table D3** (Appendix D). These results suggested that the chlorine content was gradually increased due to reaction time, and the chlorine content became steady after reaction was carried out for 4 hours. This result implied that the reaction was completed after 4 hours. The XRF spectra of CR are shown in Appendix C (Figure C17–C21). The relationship between the chlorine content and reaction time is shown in **Figure 4.15**.

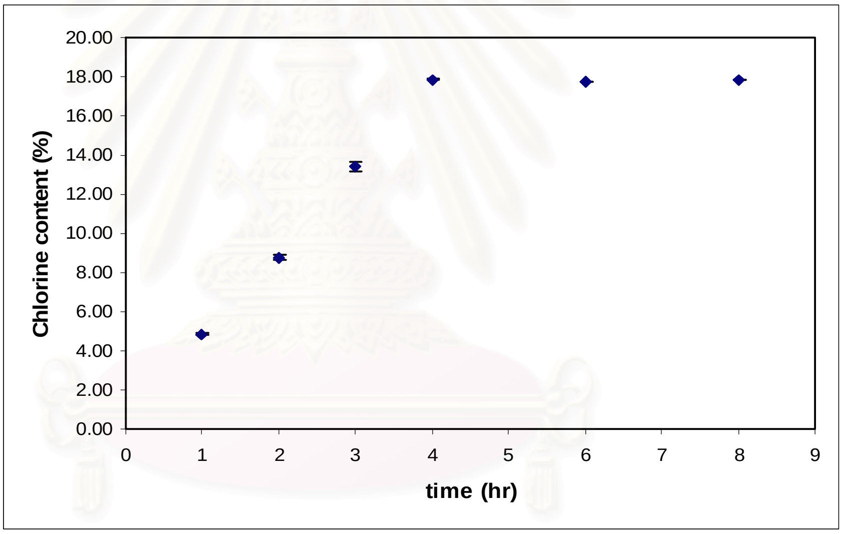


Figure 4.15 Chlorine content in CR at various reaction time.

4.2.3 Effect of temperature

After the optimal concentrations of HCl and NaCl were found, the variation of reaction temperature was also performed in this chlorination reaction which the purposed of finding an optimal reaction temperature for preparation of CR. The chlorination reaction of ENR was carried out with 2% wt hydrochloric acid and 50% sodium chloride concentration for 4 hours at various reaction temperatures of 10, 20, 30 and 40°C, respectively. After the reaction took place, the CR from each reaction product was analyzed for chlorine content by XRF. The results are presented in **Table D4**. These results indicated that when reaction temperature increased the chlorine content also increased until the reaction temperature reached 30°C, and was also found that the chlorine content of the product remained steady even if the reactions were performed at the temperature higher than 30°C. These results indicated that the optimal temperature for the chlorination reaction of ENR was 30°C. The XRF spectra of CR are shown in Appendix C (Figure C22–C24). The relationship between the chlorine content and reaction time is shown in **Figure 4.16**.

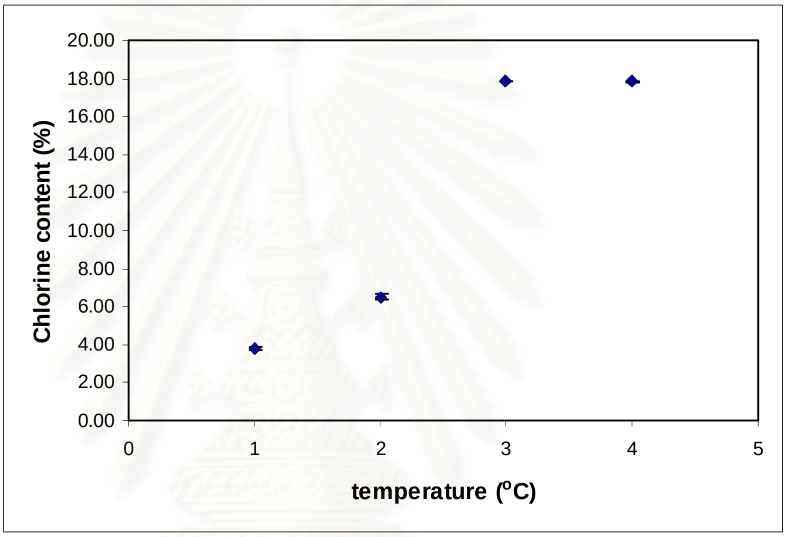


Figure 4.16 Chlorine content of CR at various reaction temperature.

In this research, ENR with 45% epoxide was obtained. The reaction mechanism was followed mechanism I as proposed in **Figure 4.17**.

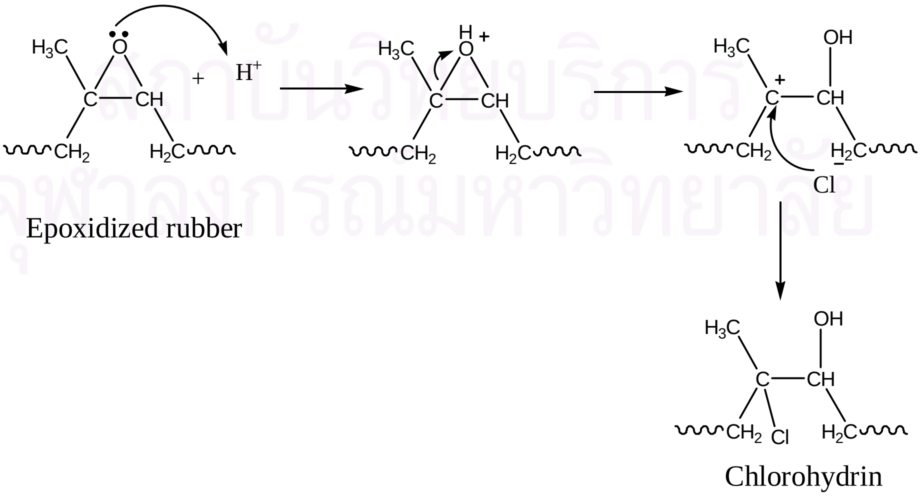


Figure 4.17 The mechanism I illustrated the chlorohydrin rubber formation from epoxidized natural rubber.

If 45% of ENR was used as starting material in this chlorination reaction the maximum chlorohydrin product which containing C-Cl or hydroxyl group would be only 13.27%. In this research, the chlorine content of 17.88% in chlorinated rubber which was proposed from ENR in the optimal condition (2% wt HCl, 50% wt NaCl, at 30°C, 4 hours) was higher than that from the calculation of 13.27%. This result suggested that the reaction was not stopped only in the chlorohydrin formation as proposed in mechanism I **(Figure 4.17)**. The chlorohydrin rubber unit was further reacted to give dichlorinated rubber unit as proposed in mechanism II **(Figure 4.18)**.

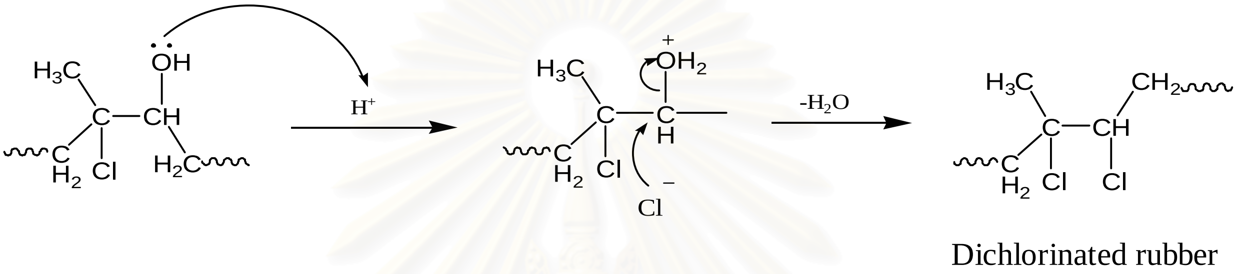


Figure 4.18 The mechanism II illustrated the chlorination of rubber.

The structure of dichlorinated rubber was also confirmed by FT-IR and ^{1}H-NMR spectroscopy. FT-IR spectrum of sample B5 **(Figure 4.19)** showed the significant intensity increased of the peak at 685-730 cm^{-1} due to C-Cl stretching [30]. Moreover the ^{1}H-NMR spectrum of sample B5 **(Figure 4.20)** showed the new peak at 4.34 ppm belonging to C<u>H</u>-Cl of dichlorinated rubber unit [28]. The FT-IR and ^{1}H-NMR spectra of the other products (B1-B7) are also presented in Appendix A (Figure A10-A16) and Appendix B (Figure B10-B16).

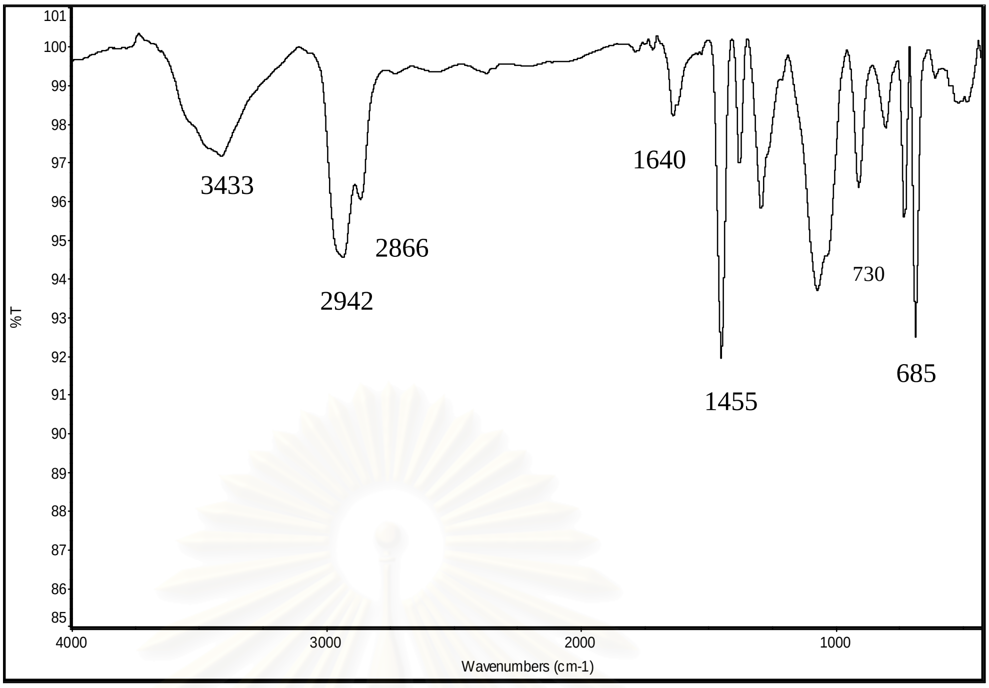


Figure 4.19 FT-IR spectrum of B5.

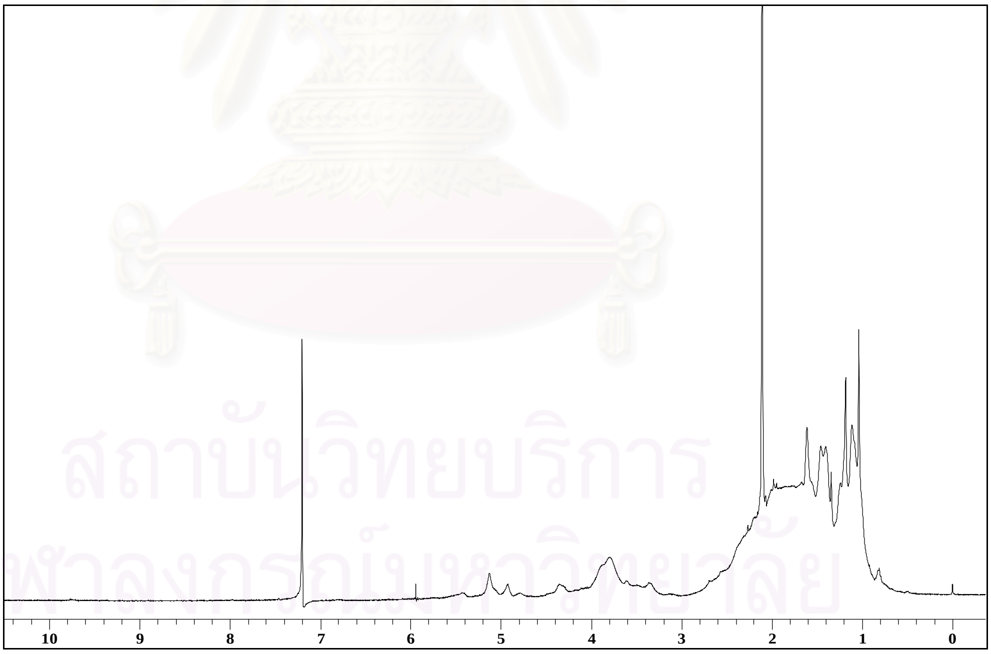


Figure 4.20 ^{1}H-NMR spectrum of B5.

To confirm the chlorination reaction was not reacted on double bond (C=C bond) in NR so the NR was directly reacted with optimal condition (2% wt HCl, 50% wt NaCl, at 30°C, 4 hours) and then the product was characterized with ^{1}H-NMR spectroscopy. The product was not found the proton signal CH-Cl at 4.34 ppm and not appeared any signal different from NR. ^{1}H-NMR spectrum **(figure 4.21)** showed the structure of product similar of NR.

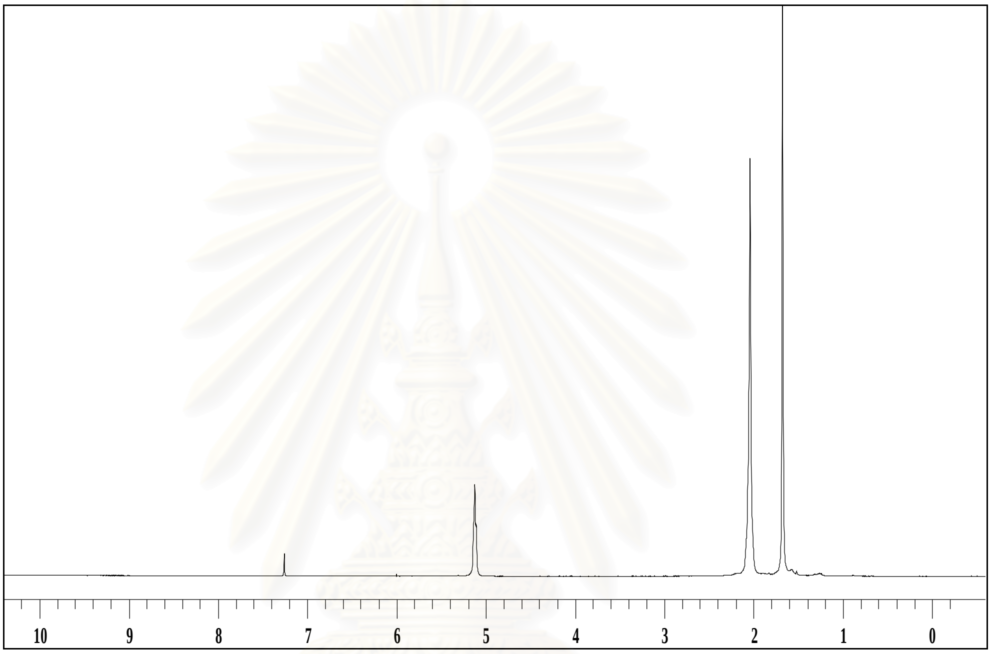


Figure 4.21 ^{1}H-NMR spectrum of NR was reacted with HCl/NaCl.

4.3 Thermal properties of CR

4.3.1 Differential Scanning Calorimetry (DSC)

The DSC thermogram of CR is shown in **Figure 4.22**. The temperature at 56.56°C was the glass transition temperature of CR which was higher than those of NR and ENR. This indicated that CR loss the rubbery property since Tg of CR was higher than that at room temperature.

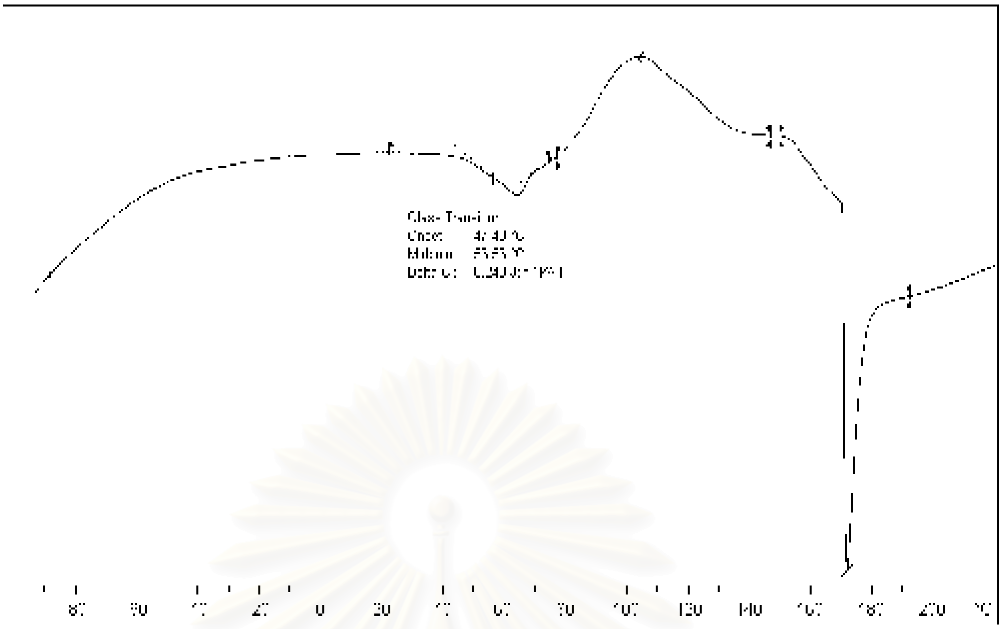


Figure 4.22 DSC thermogram of CR.

4.3.2 Thermalgravimetry (TG) and Derivative Thermogravimetric Analysis (DTG)

The TG and DTG thermograms of CR are shown in **Figure 4.23**. Two steps of degradation were observed. The first degradation started at 141.1°C and last until 244.0°C. During this stage, the weight loss was 11.1%, probably due to dehydrochlorination (hydrogen chloride was eliminated form the molecule of CR). The second degradation started at 244.0°C and last until to 478.9°C. During this stage, the weight loss was 63.7%, probably due to oxidative degradation reaction. In the DTG curve, the major peak was observed at 395°C. (lit. the first degradation started at 160.1°C and last until 390.0°C. The second degradation started at 390.0°C and last until to 598.0°C, [3]).

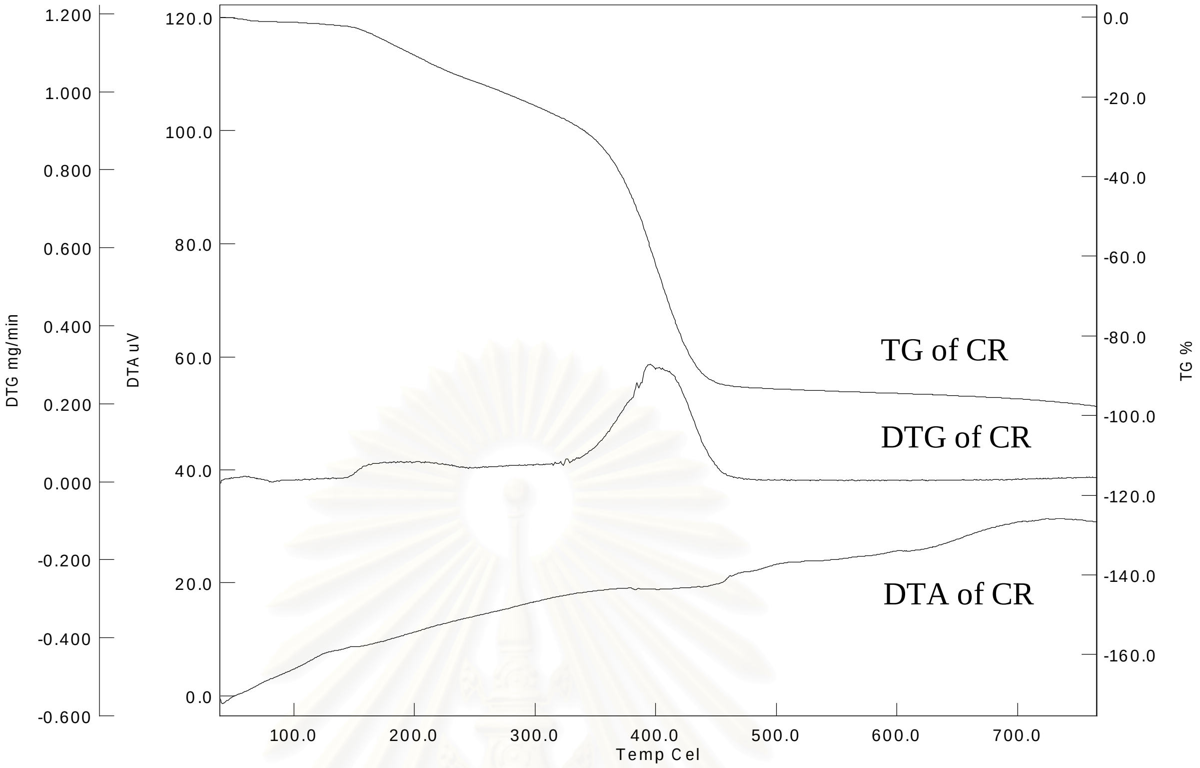


Figure 4.23 TG/DTG curve of CR.

The former CR was prepared on ENR with sodium hypochlorite and sodium chloride (NaOCl/ NaCl) [32]. That reaction was performed by reaction of ENR with NaOCl/ NaCl 1:4 by mol at 30°C for 6 hours as optimal condition. The structure of CR had one chlorine atom and OH group on the unit of rubber that called chlorohydrin rubber. The 19.06% chlorine content was obtained. The CR was prepared from this research by the reaction of ENR with HCl/ NaCl in the optimal condition (2% wt HCl, 50% wt NaCl, at 30°C, 4 hours). The 17.88% chlorine content was obtained. The structure of CR might consist of three components which were unreacted natural rubber unit, chlorohydrin rubber unit and dichlorinated rubber unit.

The commercial CR, the chlorine content, glass transition temperature and melting temperature (Appendix E: Figures E3-E4) were higher than CR from this research, this might be due to the difference in CR structure was different (the structure of commercial CR had only two components: unreacted natural rubber unit and dichlorinated rubber unit, Appendix E: Figures E1-E2). However general physical properties (such as color, odor and soluble in water) of commercial CR and CR from this research were similar as shown in **Table 4.2**.

Table 4.2 Comparing physical properties of CR using HCl/NaCl and commercial CR.

Samples	Chlorine Content (%)	Glass transition (°C)	Melting point (°C)	Physical form	Color	Odor	Solubility in water
CR using HCl/NaCl	17.88	56.56	171	powder	white	odorless	insoluble
Commercial CR [Appendix E]	50. 94	96.34	245	powder	white	odorless	insoluble

CHAPTER V

CONCLUSION AND SUGGESTION

5.1 Conclusion

In this research, the epoxidized natural rubber (ENR) was prepared by stabilizing natural rubber latex with 3.3 % peracetic acid in aqueous solution. A reaction was carried out at 30- 35°C for 30 minutes. The 45 mol% epoxidation of ENR was obtained. The ENR was used as starting material for chlorinated rubber (CR) preparation via reaction with hydrochloric acid and sodium chloride. CR was investigated for the hydrochloric acid and sodium chloride concentrations, reaction time and reaction temperature. The 17.88% chlorine content of CR was obtained. The optimal chlorination reaction was carried out with 2% wt hydrochloric and 50% wt sodium chloride for 4 hours at 30°C.

The DSC thermogram of CR showed T*g* at 56.56°C which was higher than those of NR and ENR. It might be explained that at room temperature NR and ENR was less tough than CR. From DTG thermogram, CR showed peaks at 395°C. Two steps of degradation were observed. The first degradation started at 141.1°C and last until 244.0°C and the second degradation started 244.0°C and last until 478.9°C.

The CR from this research (which was prepared from chlorination of epoxidized natural rubber with HCl/ NaCl) might consist of three components which were unreacted natural rubber unit, chlorohydrin rubber unit, and dichlorinated rubber unit as shown in **Figure 5.1**.

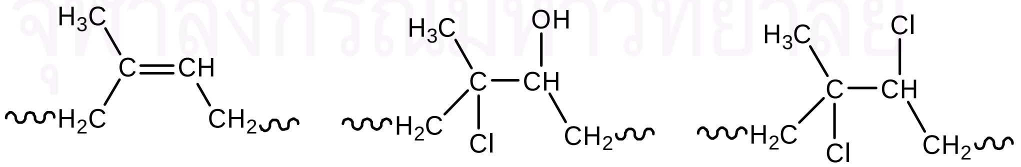


Figure 5.1 The proposed chlorinated rubber unit in this study: (a) unreacted natural rubber unit, (b) chlorohydrin rubber unit, (c) dichlorinated rubber unit.

5.2 Suggestion for future work

The application of chlorinated rubber in this research should be investigated as pigment in industrial applications.

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APPENDICES

APPENDIX A

APPENDIX A

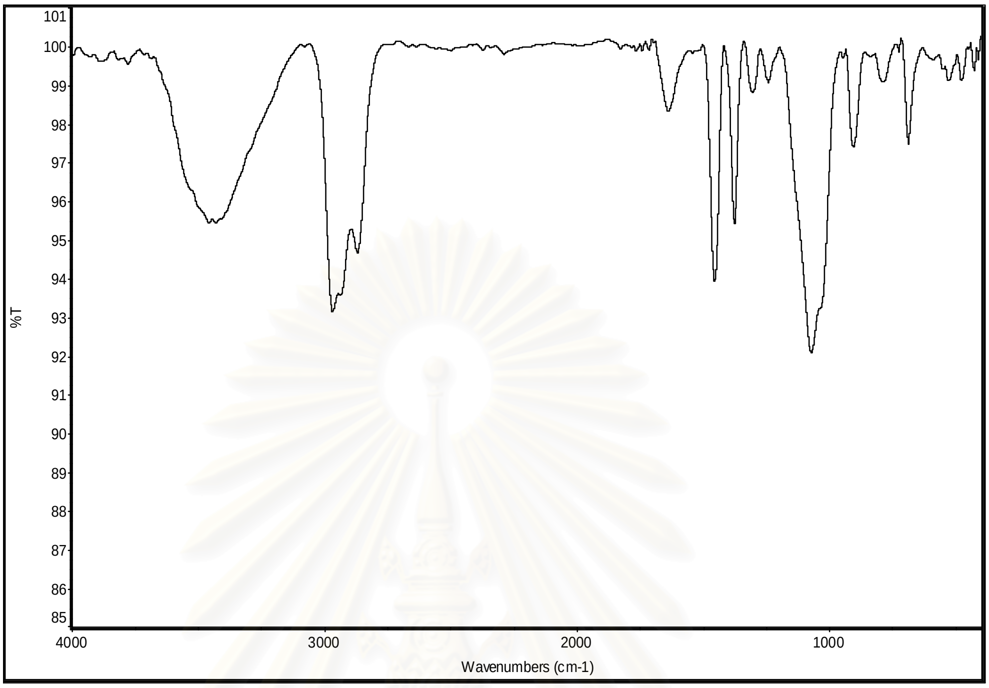

Figure A1 FT-IR spectrum of sample A1.

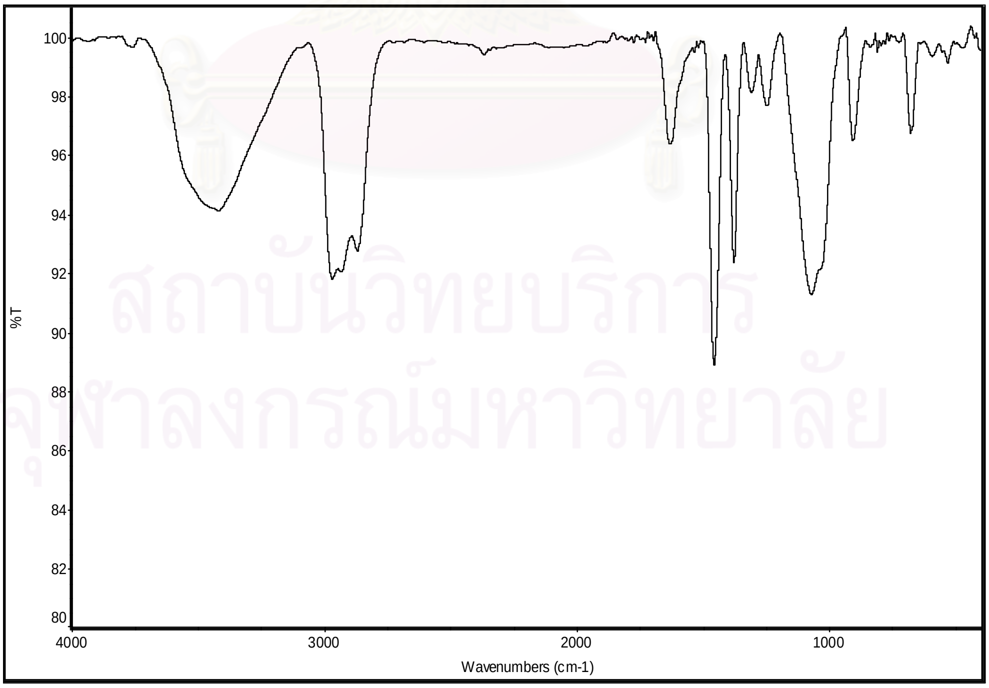

Figure A2 FT-IR spectrum of sample A2.

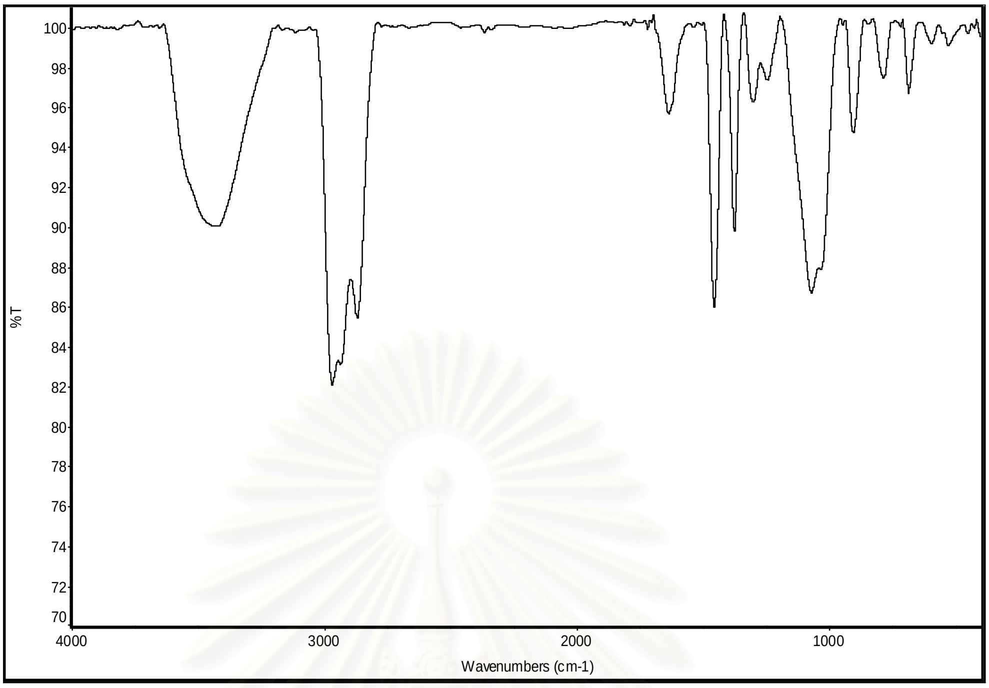

Figure A3 FT-IR spectrum of sample A3.

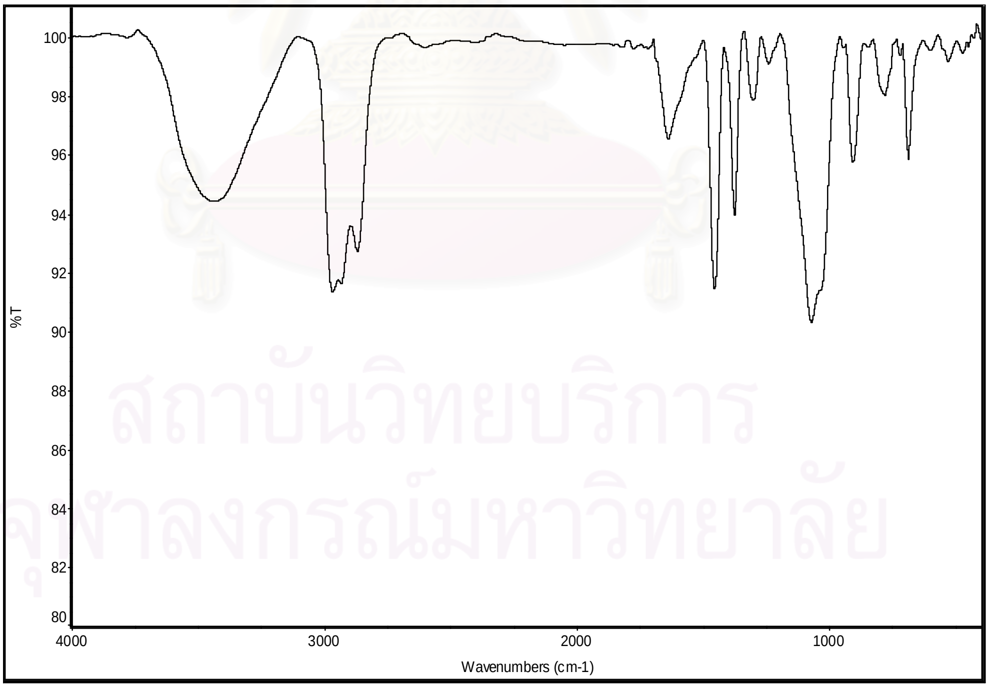

Figure A4 FT-IR spectrum of sample A4.

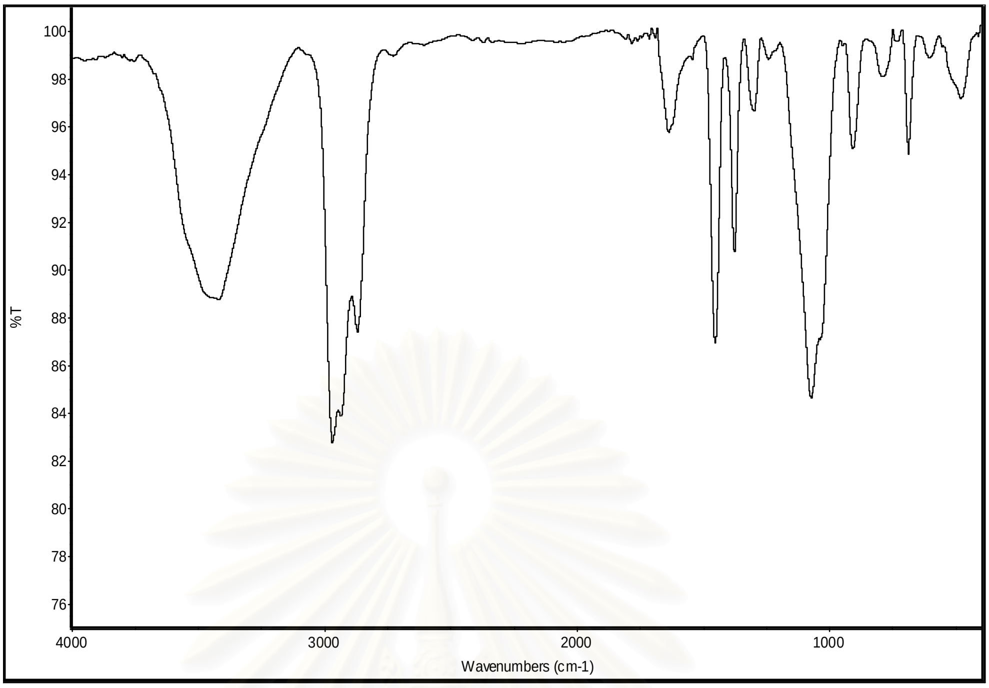

Figure A5 FT-IR spectrum of sample A5.

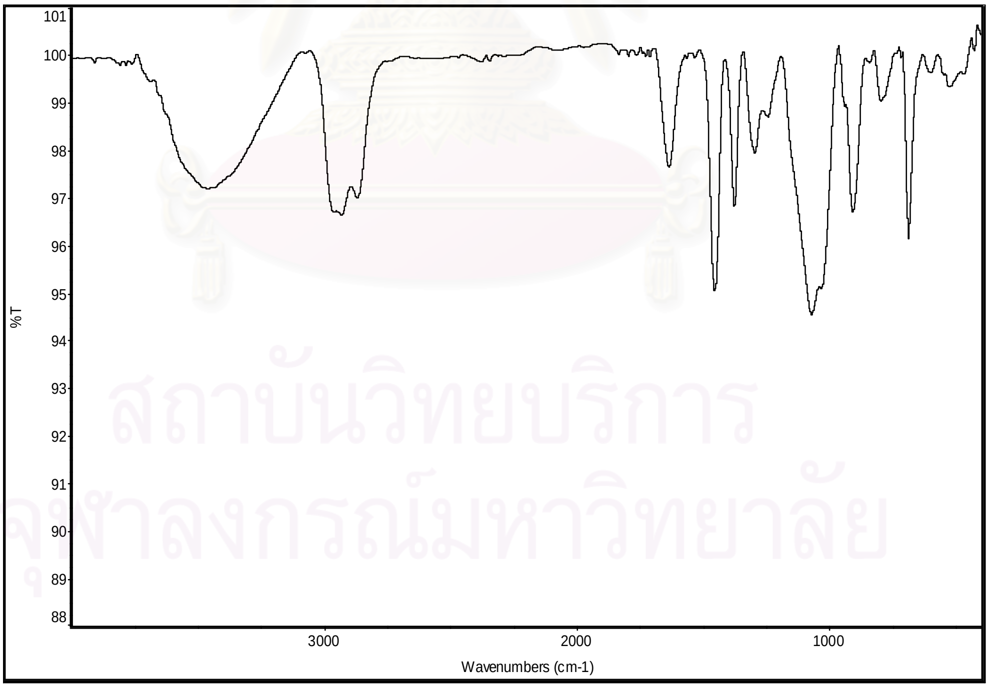

Figure A6 FT-IR spectrum of sample A6.

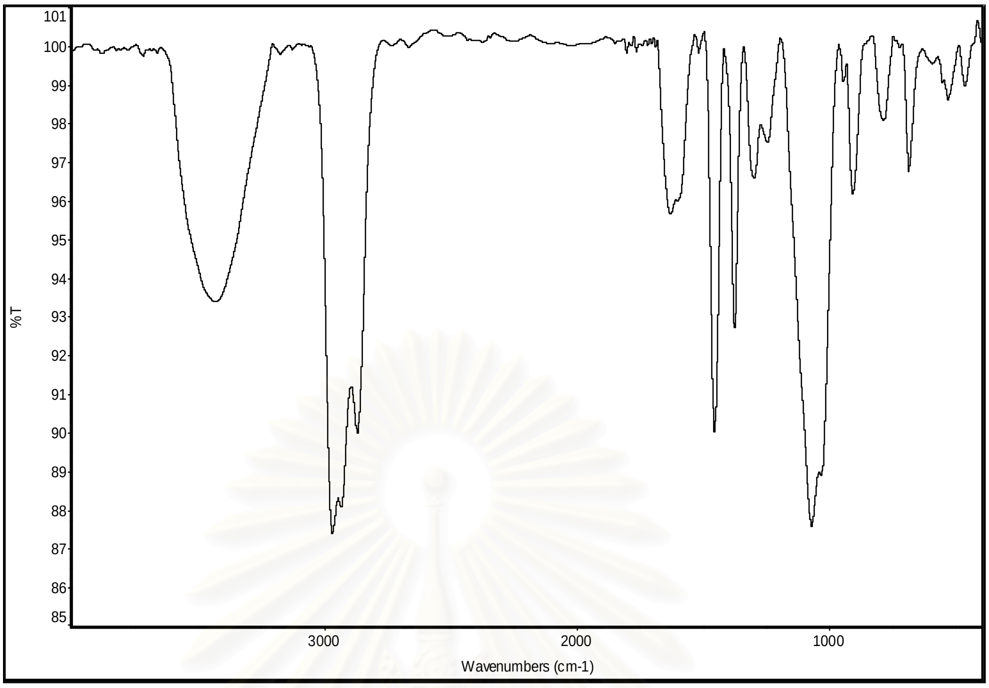

Figure A7 FT-IR spectrum of sample A7.

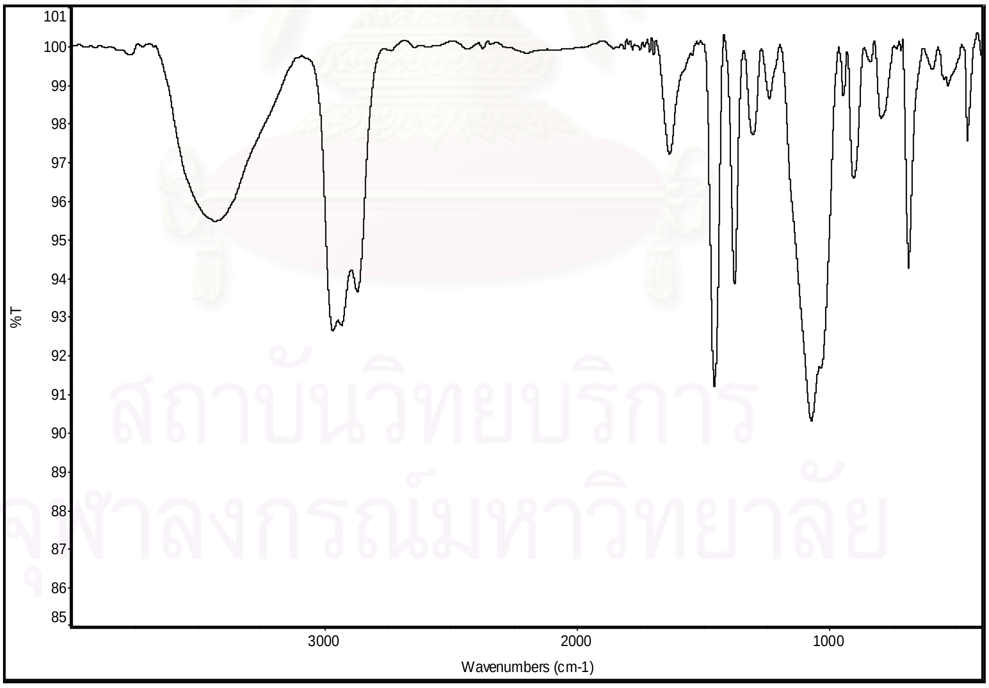

Figure A8 FT-IR spectrum of sample A8.

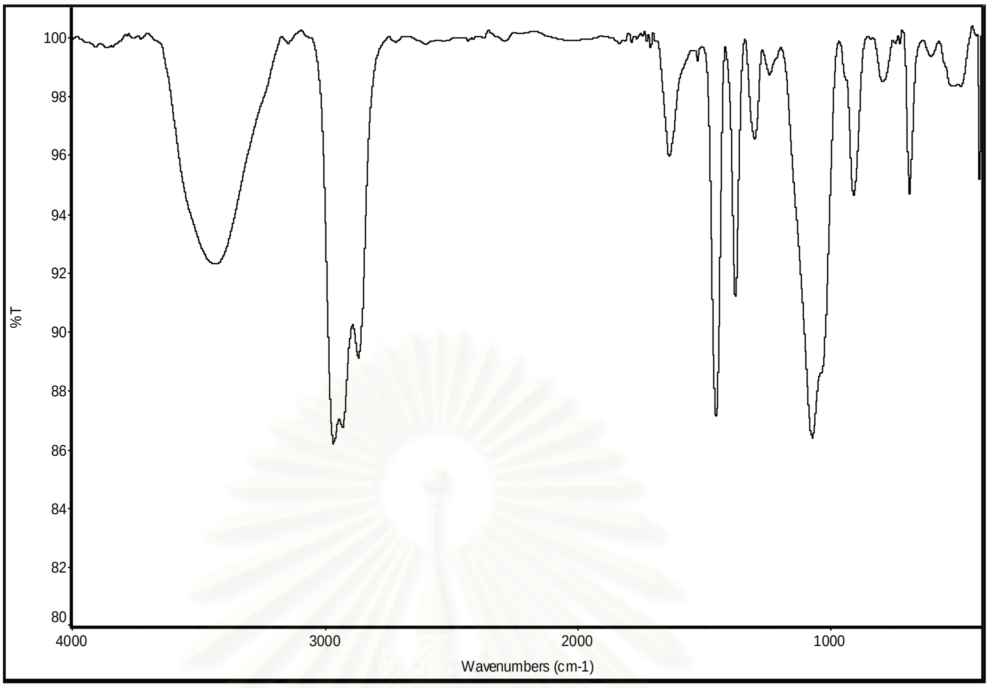

Figure A9 FT-IR spectrum of sample A9.

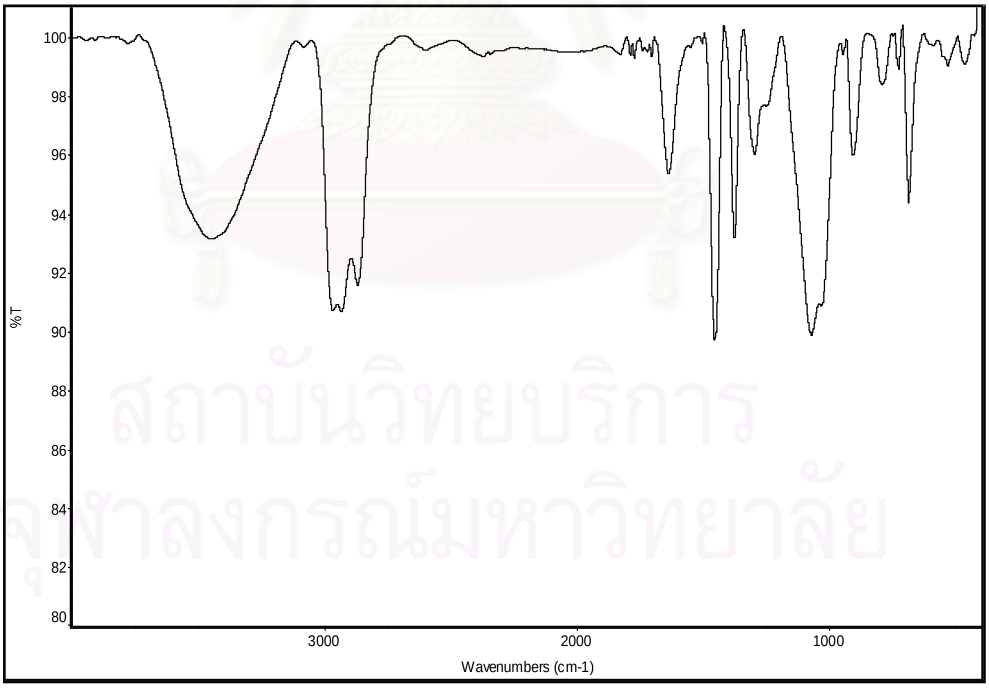

Figure A10 FT-IR spectrum of sample B1.

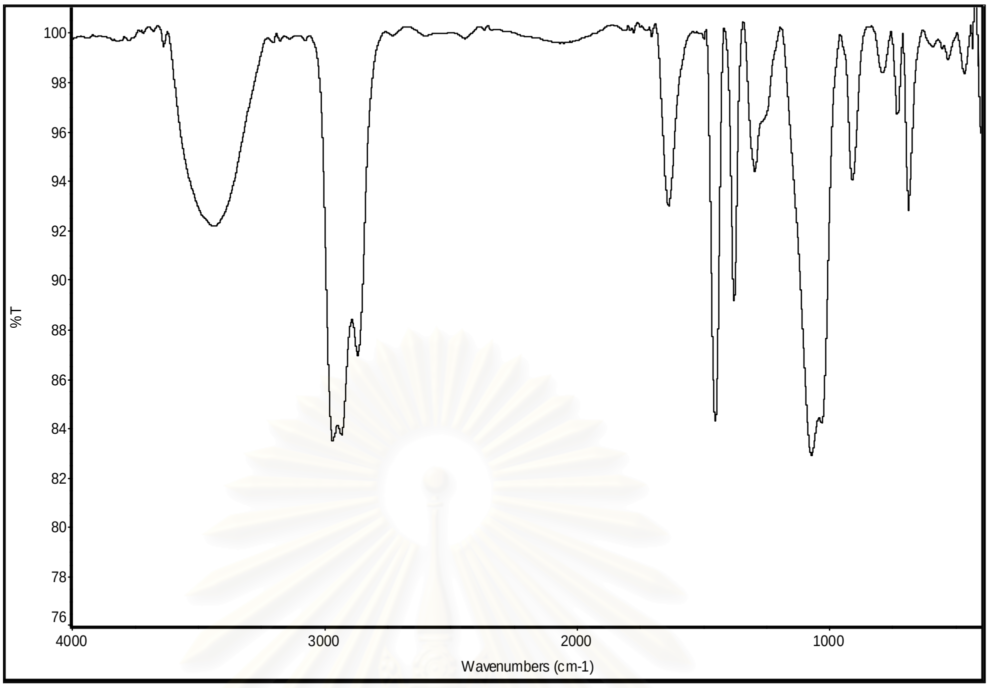

Figure A11 FT-IR spectrum of sample B2.

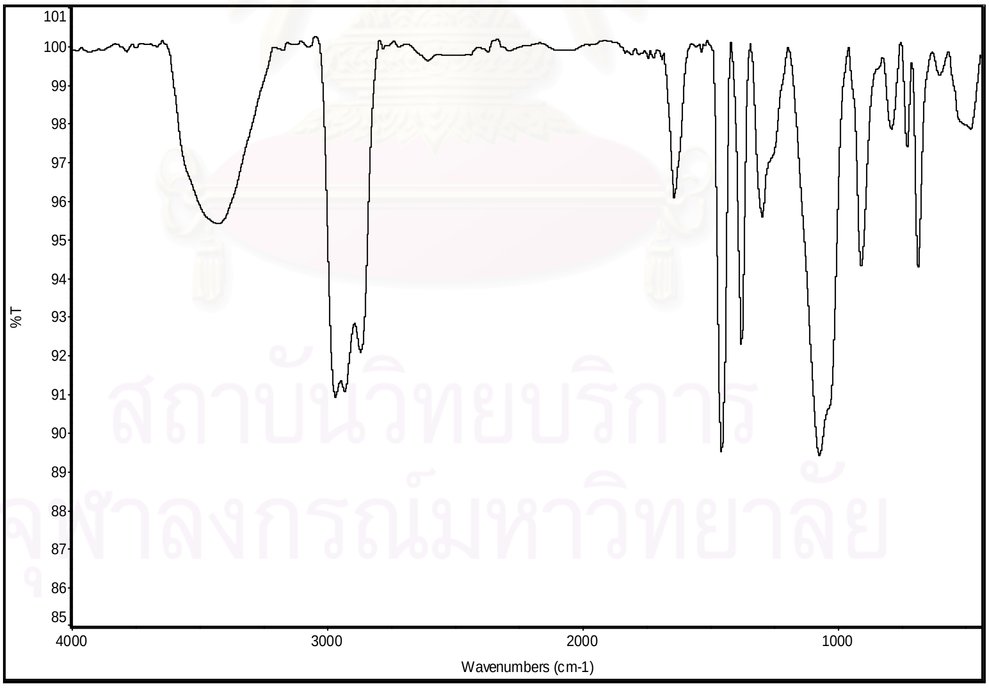

Figure A12 FT-IR spectrum of sample B3.

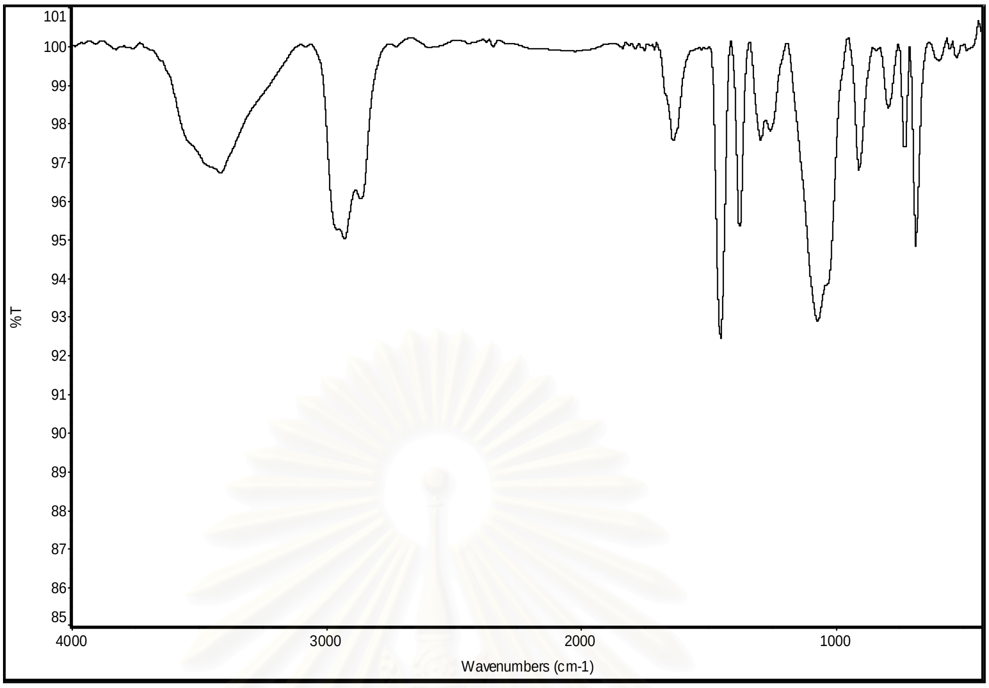

Figure A13 FT-IR spectrum of sample B4.

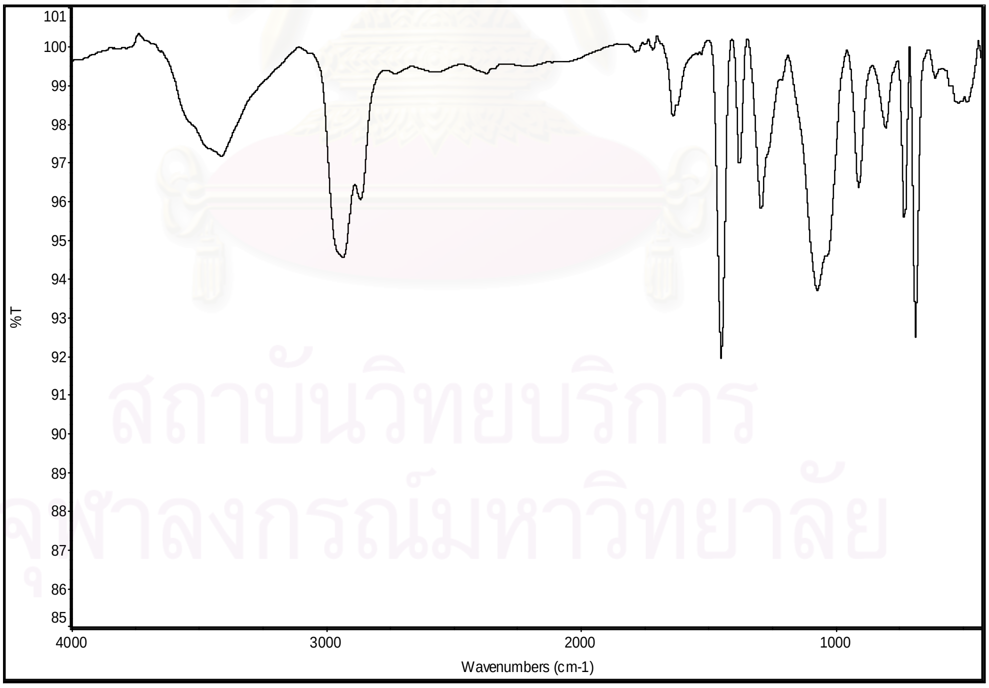

Figure A14 FT-IR spectrum of sample B5.

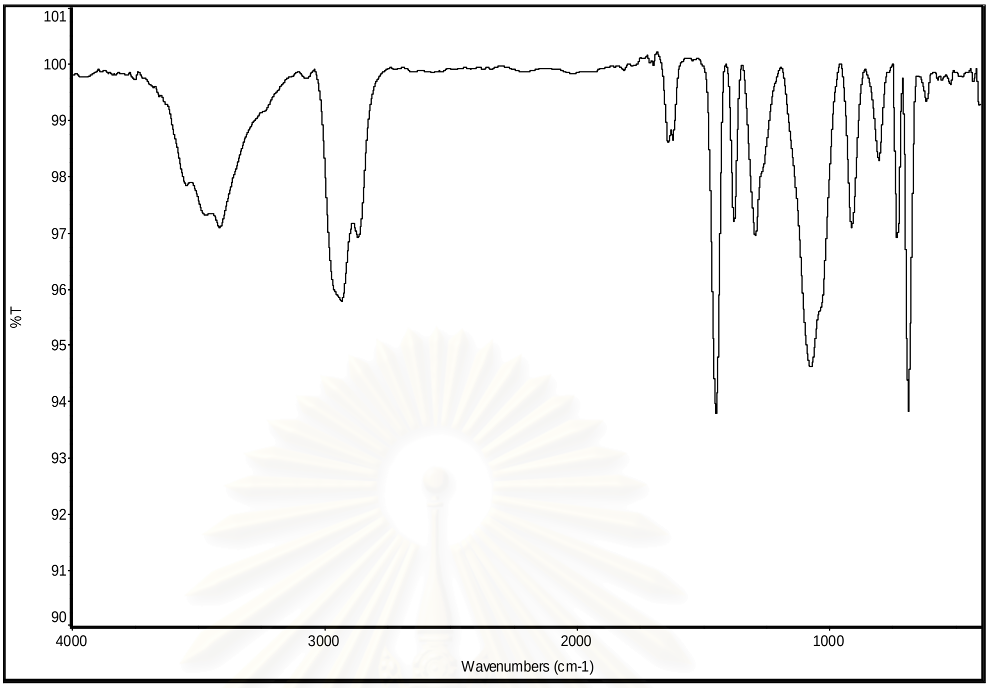

Figure A15 FT-IR spectrum of CR sample B6.

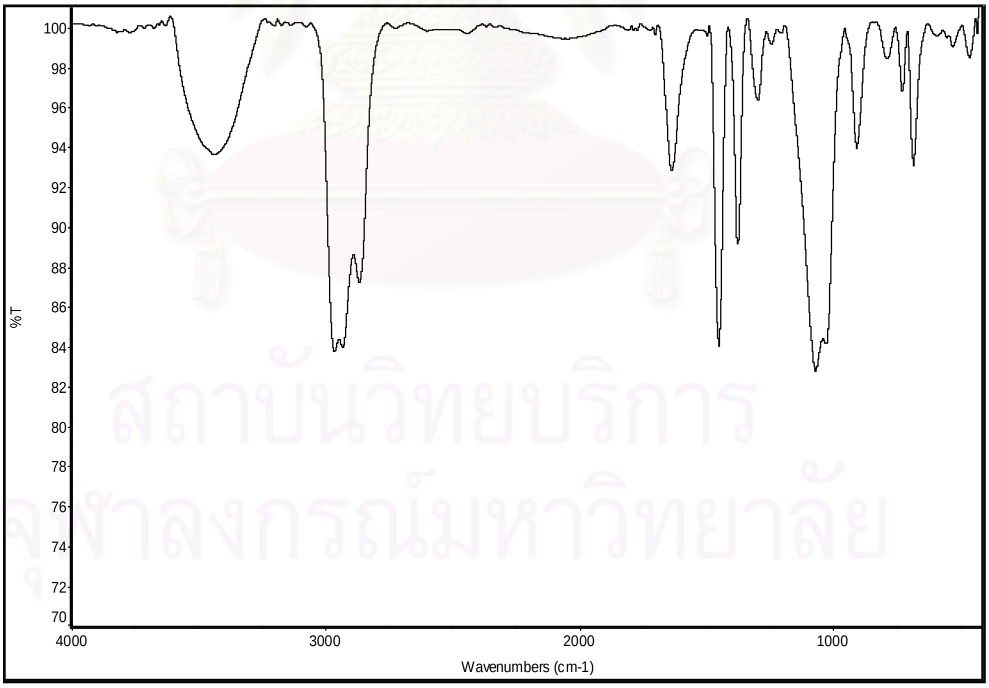

Figure A16 FT-IR spectrum of sample B7.

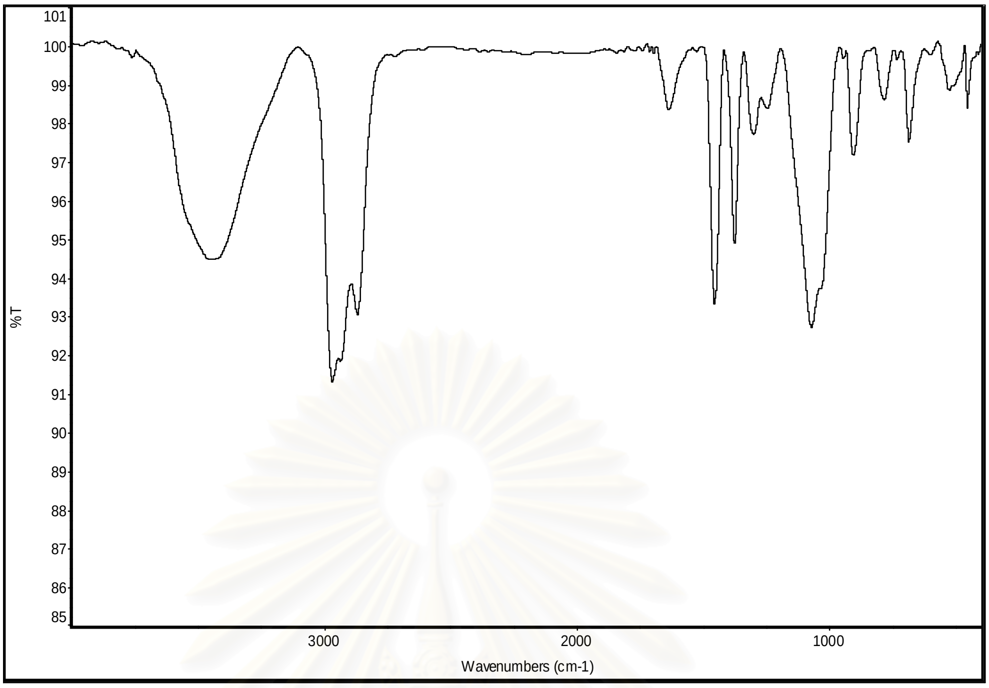

Figure A17 FT-IR spectrum of sample C1.

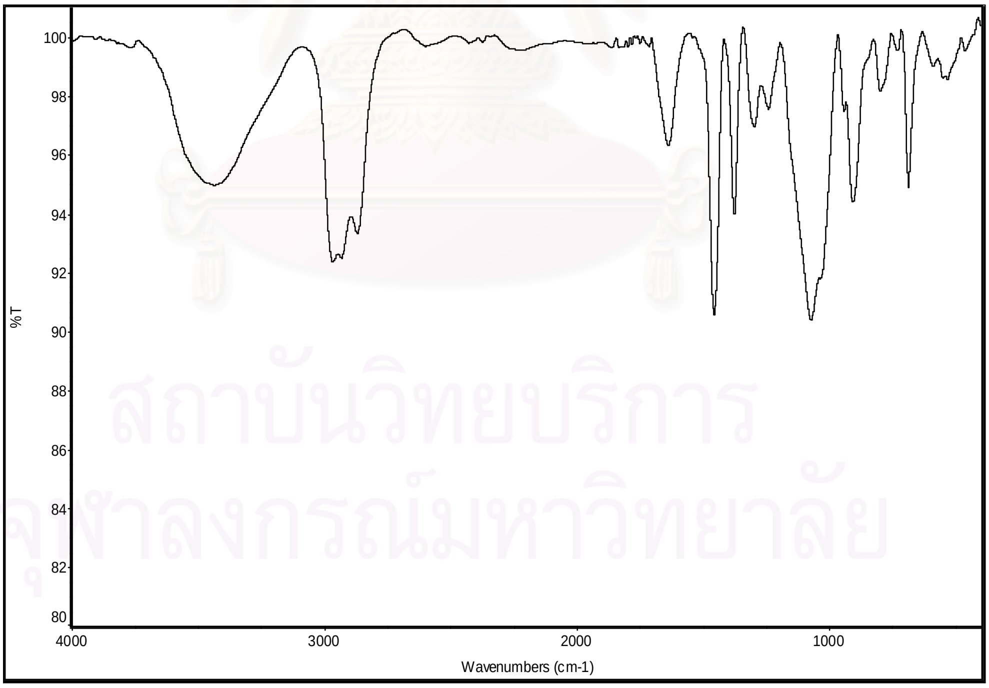

Figure A18 FT-IR spectrum of sample C2.

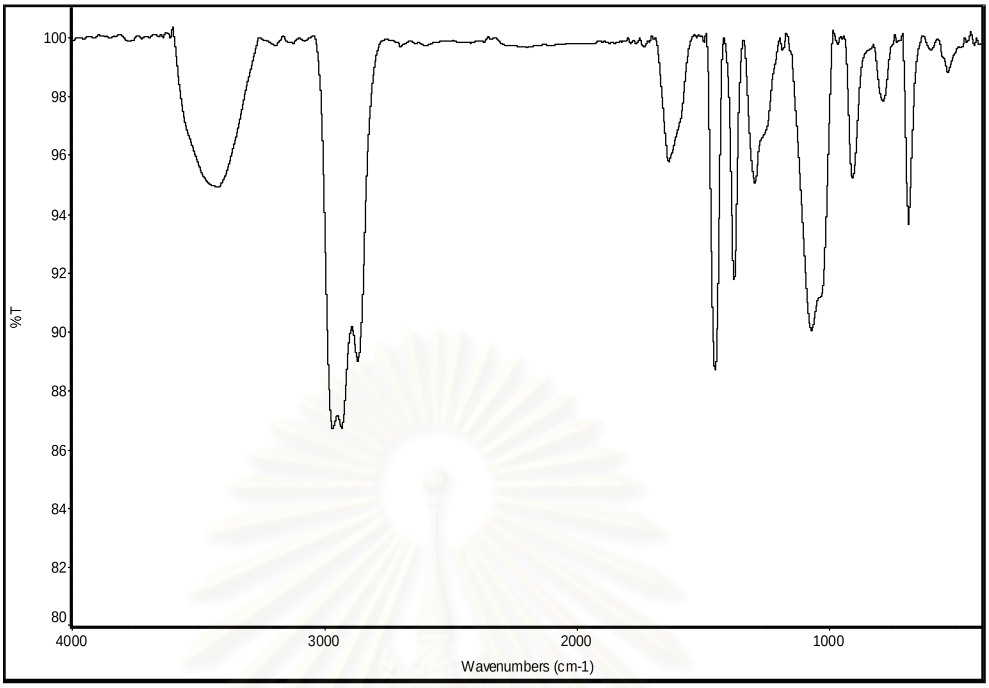

Figure A19 FT-IR spectrum of sample C3.

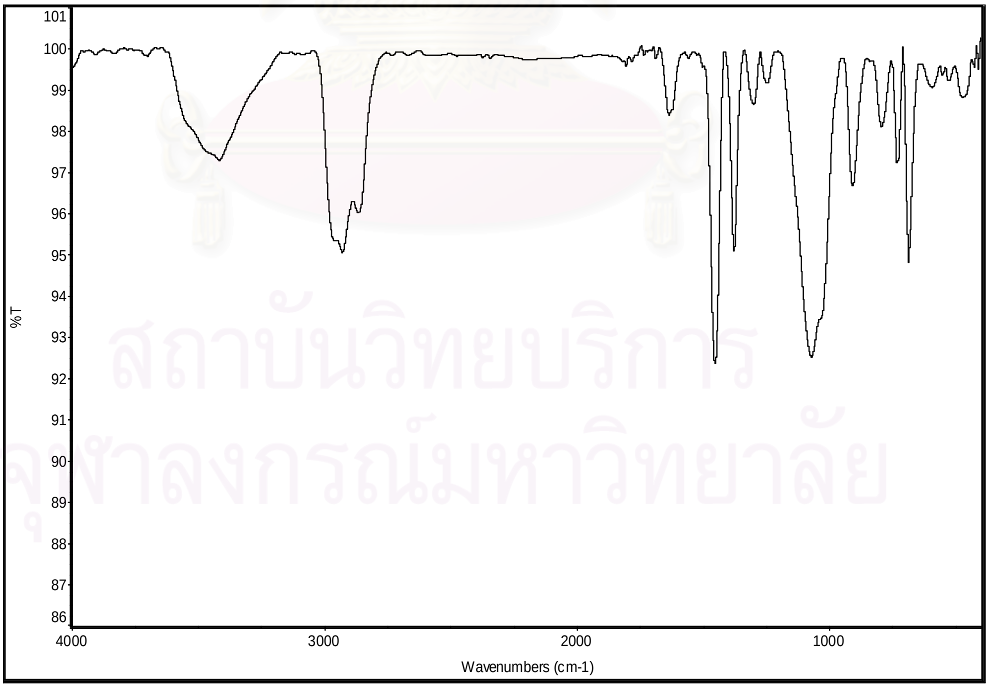

Figure A20 FT-IR spectrum of sample C4.

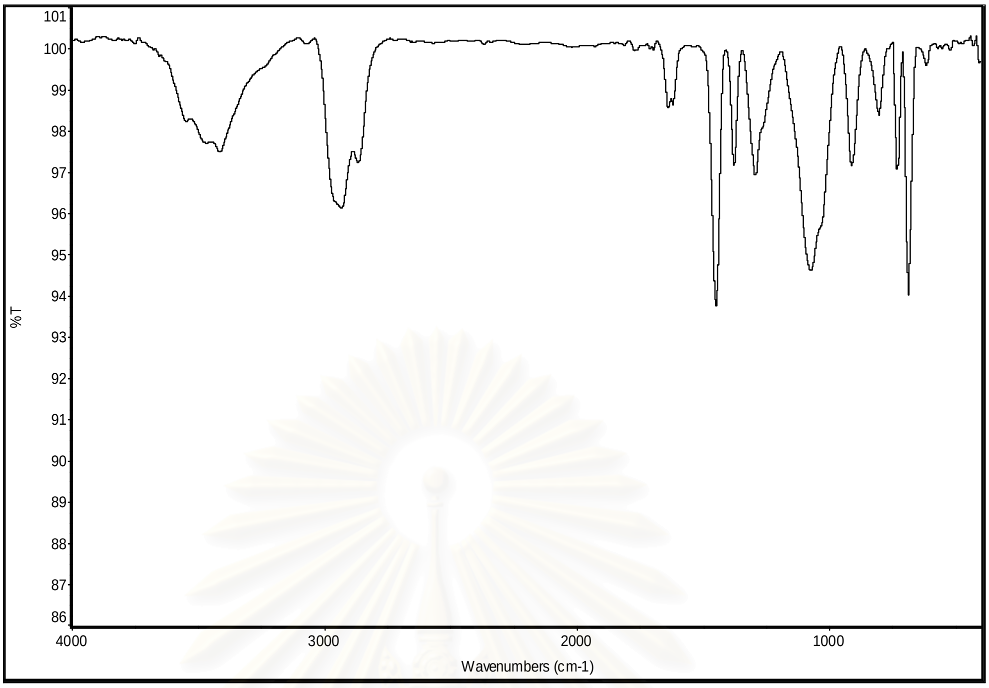

Figure A21 FT-IR spectrum of sample C5.

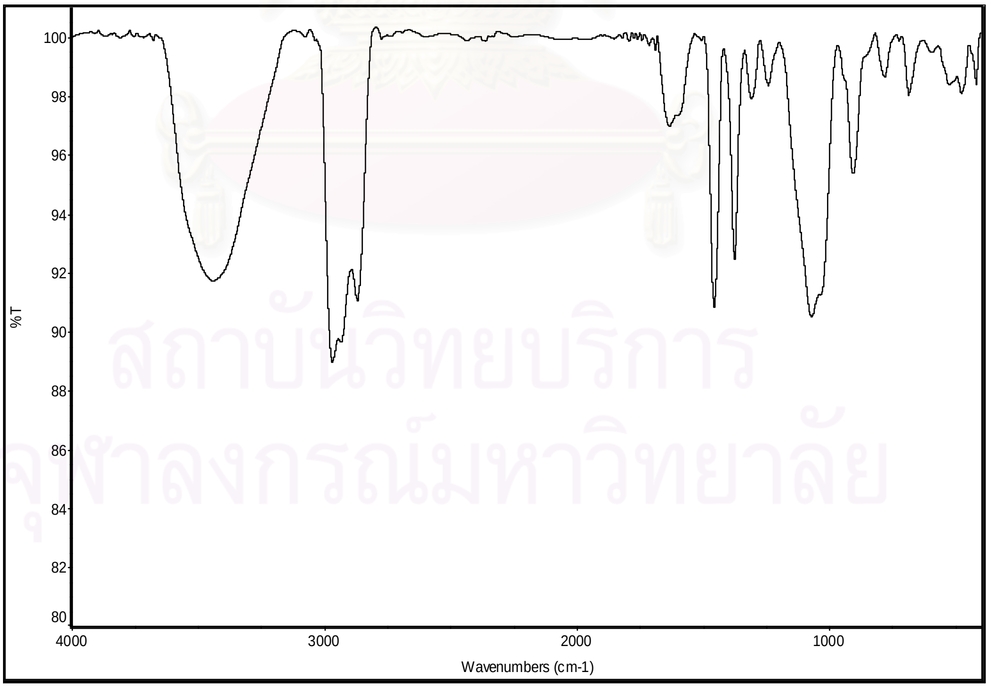

Figure A22 FT-IR spectrum of sample D1.

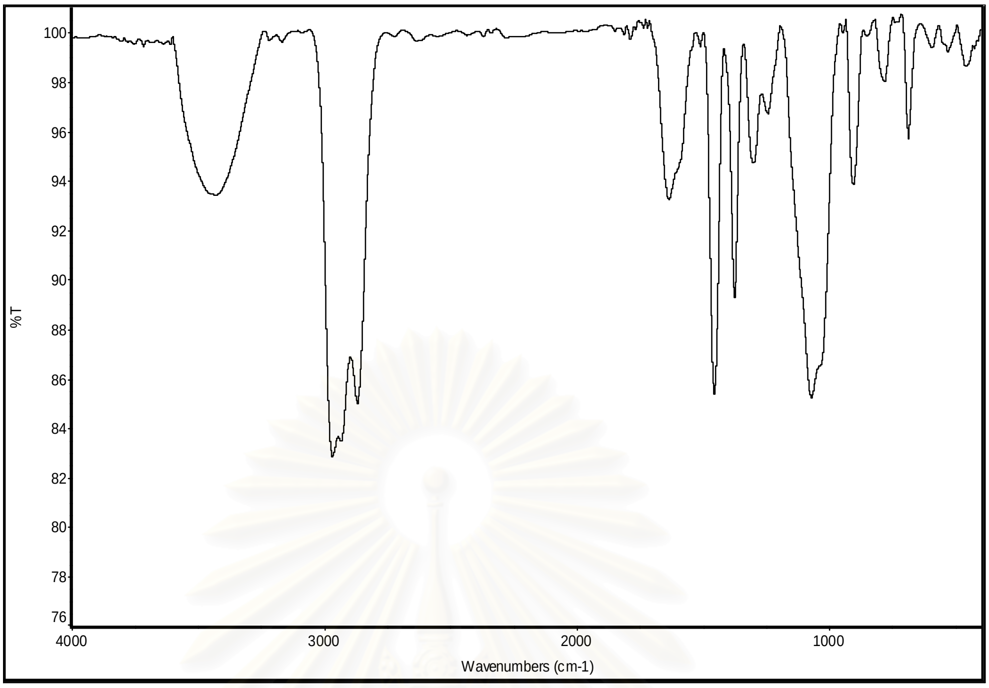

Figure A23 FT-IR spectrum of sample D2.

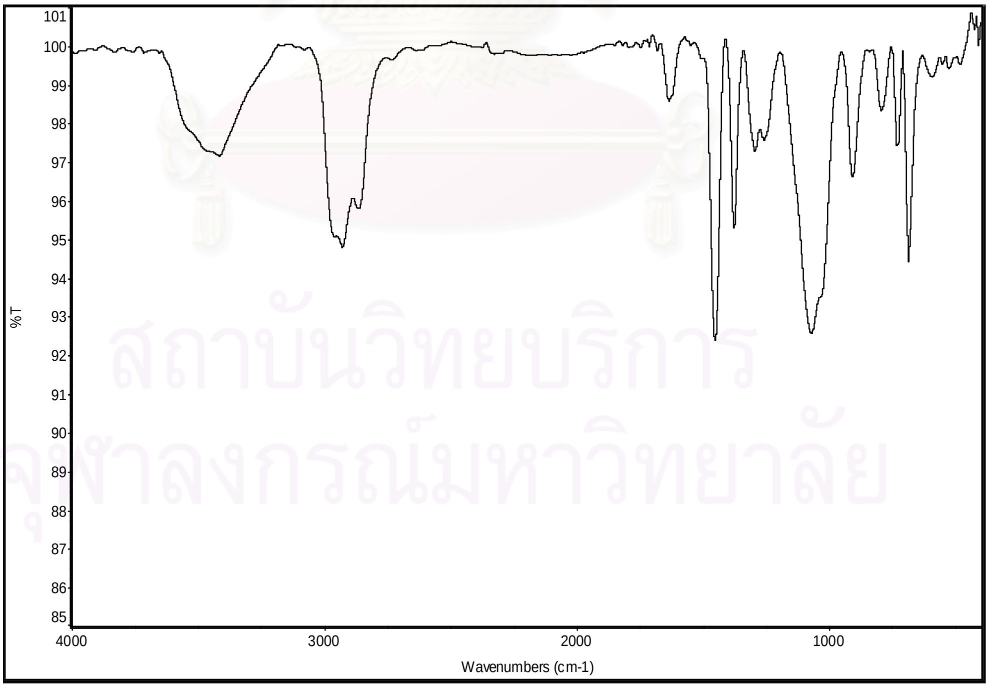

Figure A24 FT-IR spectrum of sample D3.

APPENDIX B

APPENDIX B

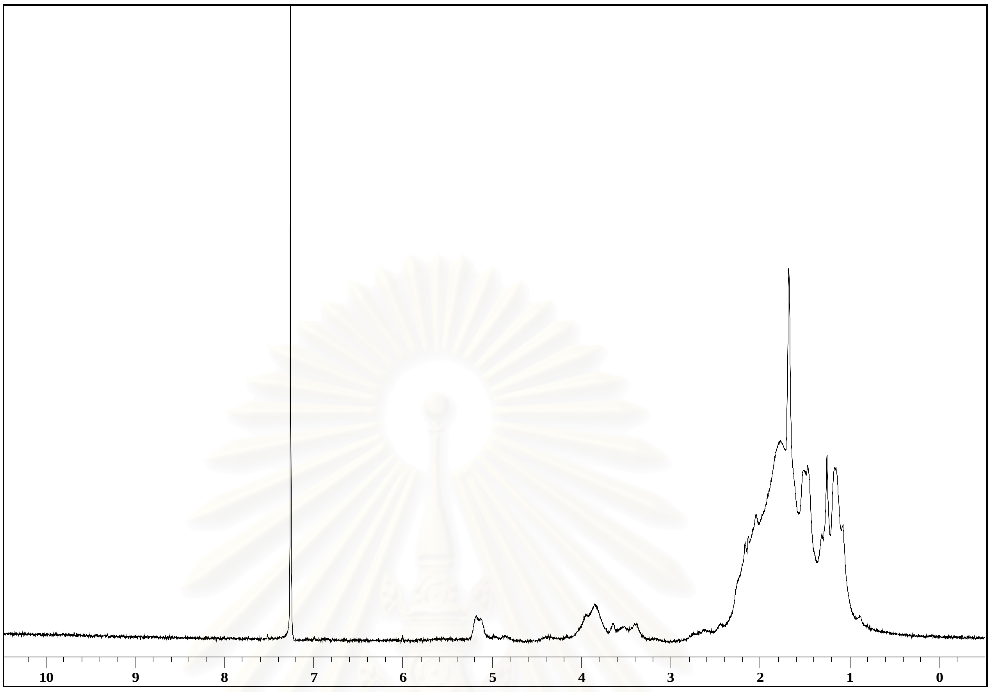

Figure B1 ^{1}H-NMR spectrum of sample A1.

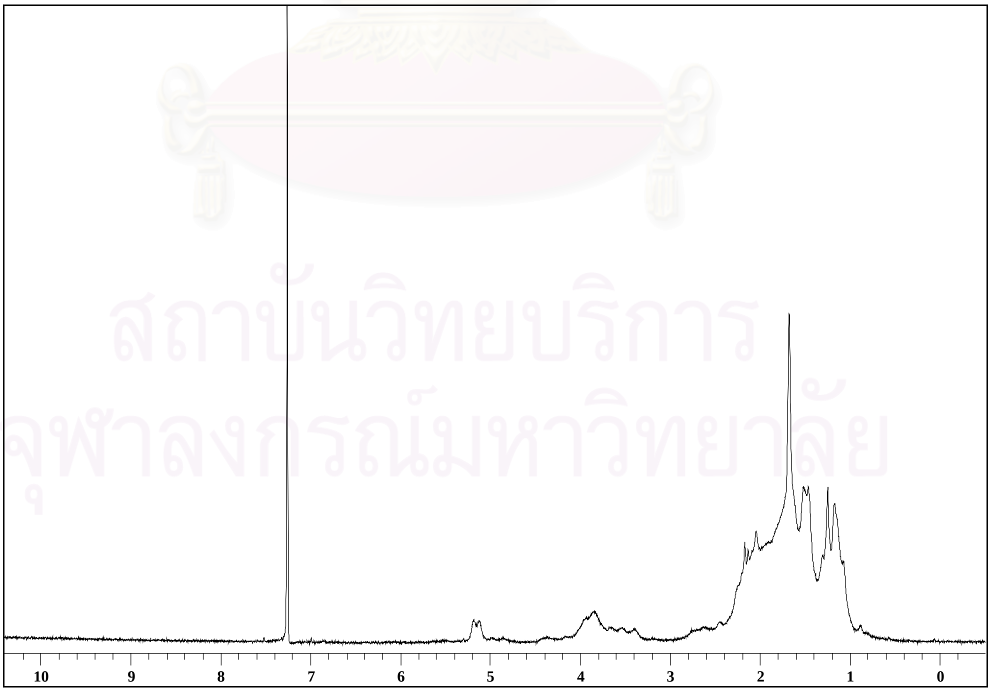

Figure B2 ^{1}H-NMR spectrum of sample A2.

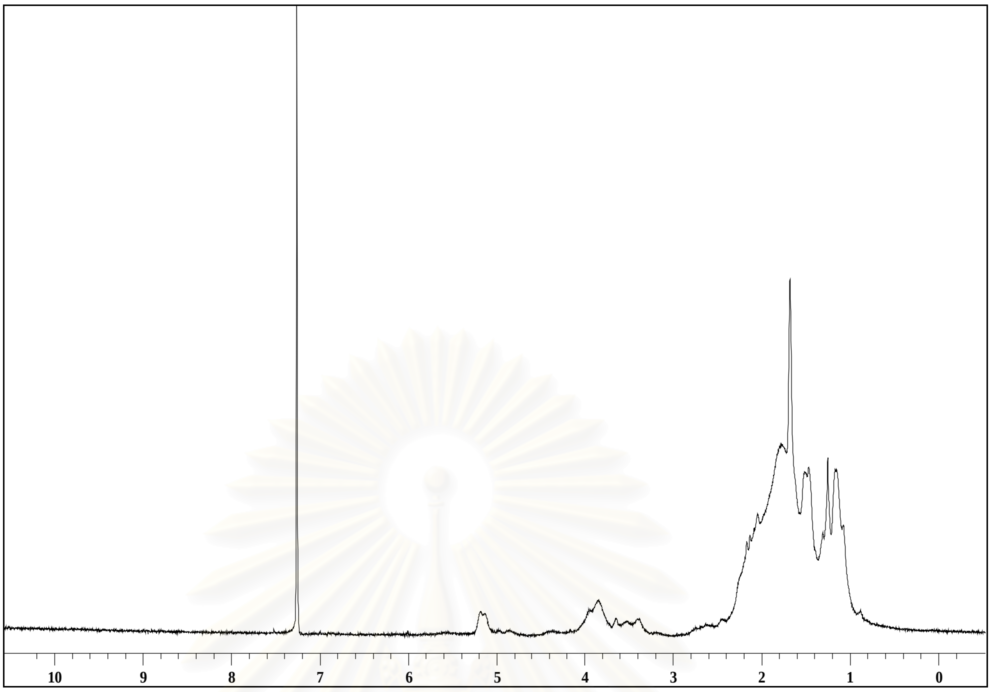

Figure B3 ^{1}H-NMR spectrum of sample A3.

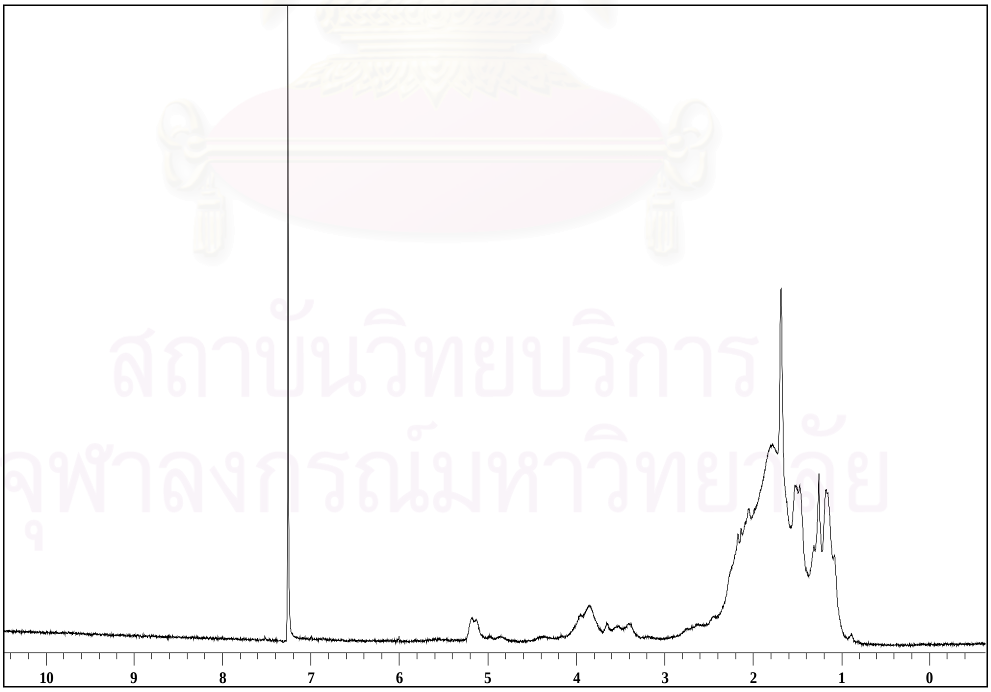

Figure B4 ^{1}H-NMR spectrum of sample A4.

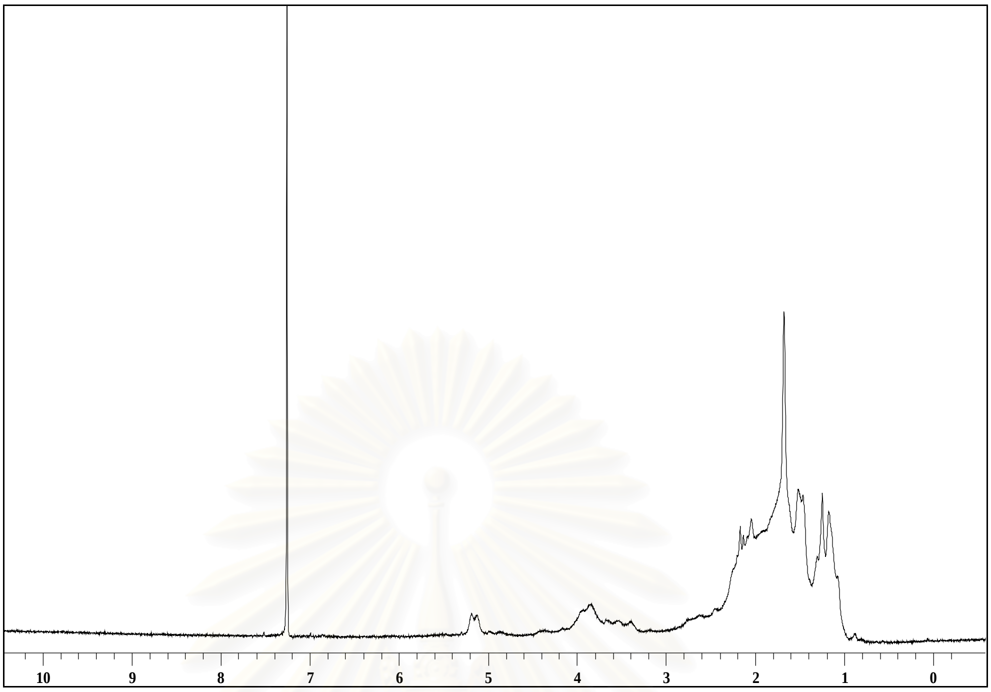

Figure B5 ^{1}H-NMR spectrum of sample A5.

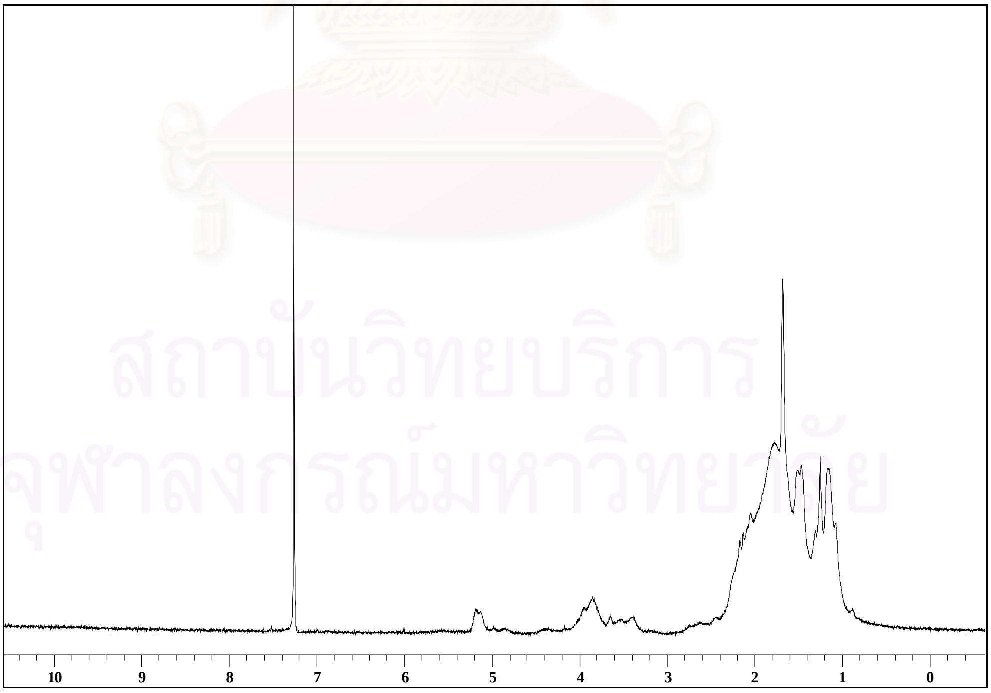

Figure B6 ^{1}H-NMR spectrum of sample A6.

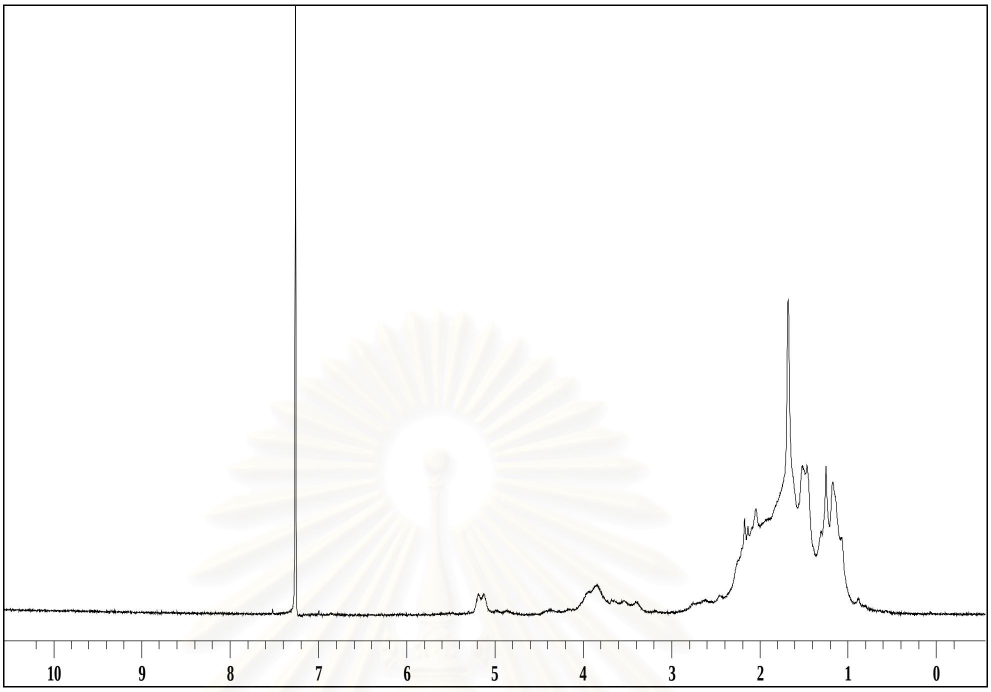

Figure B7 ^{1}H-NMR spectrum of sample A7.

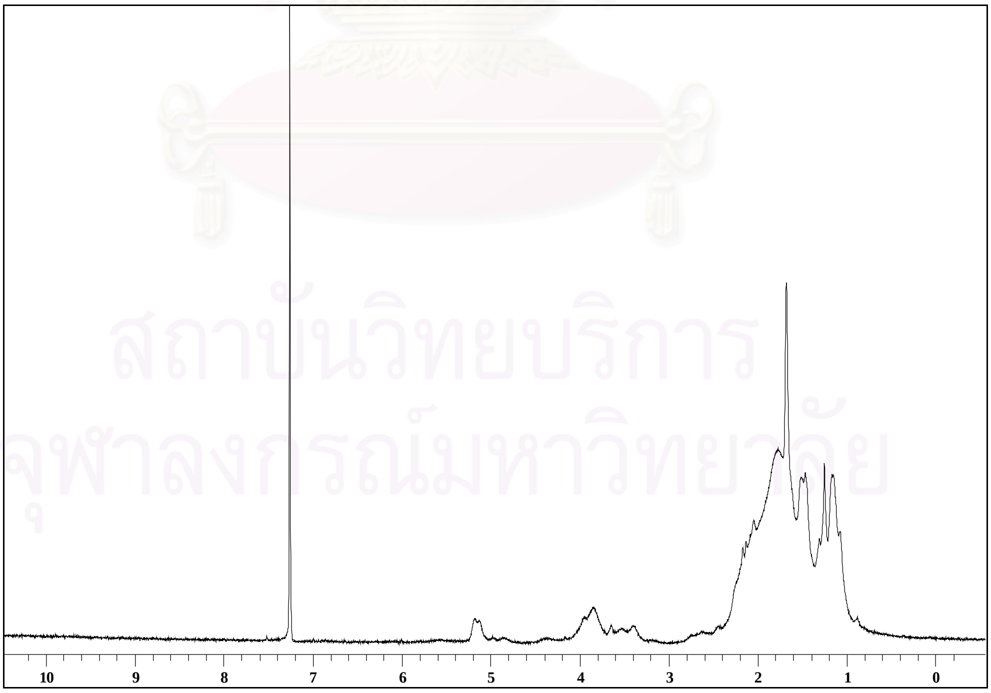

Figure B8 ^{1}H-NMR spectrum of sample A8.

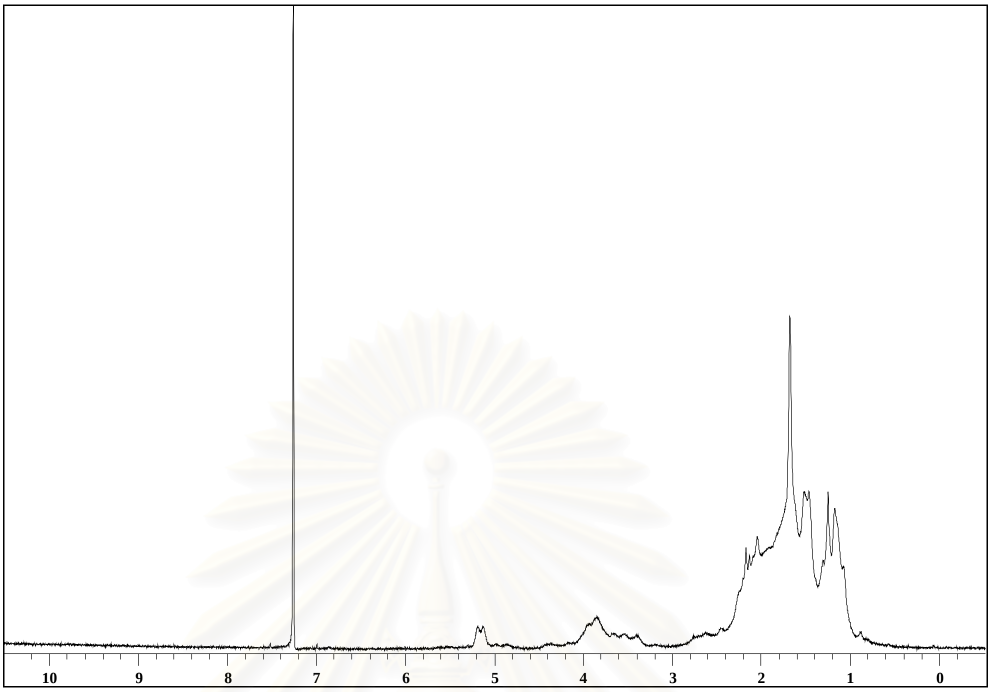

Figure B9 ^{1}H-NMR spectrum of sample A9.

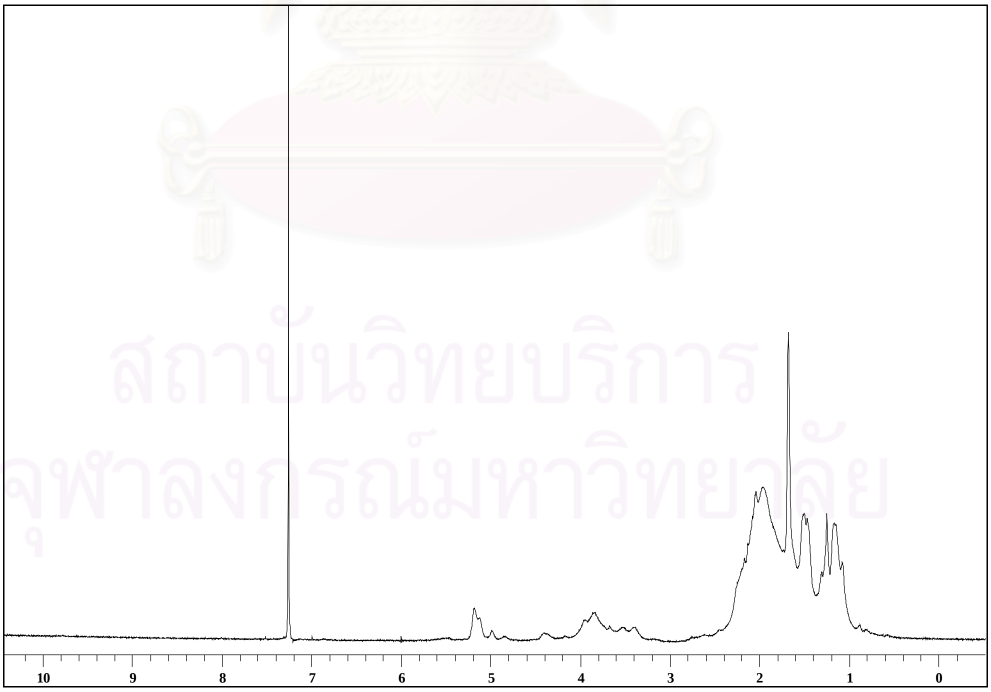

Figure B10 ^{1}H-NMR spectrum of sample B1.

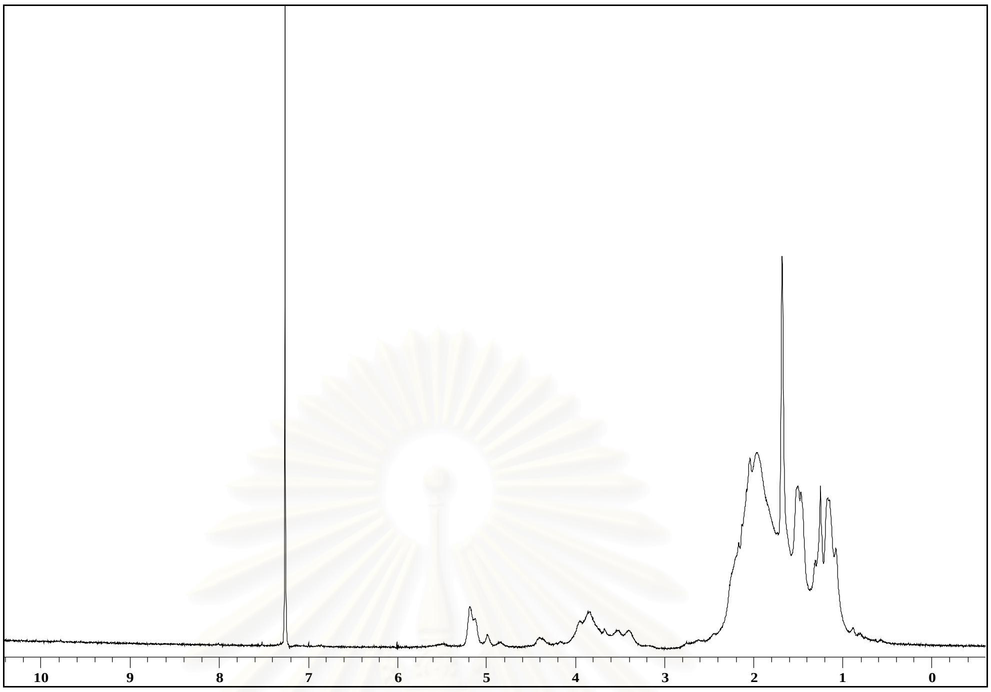

Figure B11 ^{1}H-NMR spectrum of sample B2.

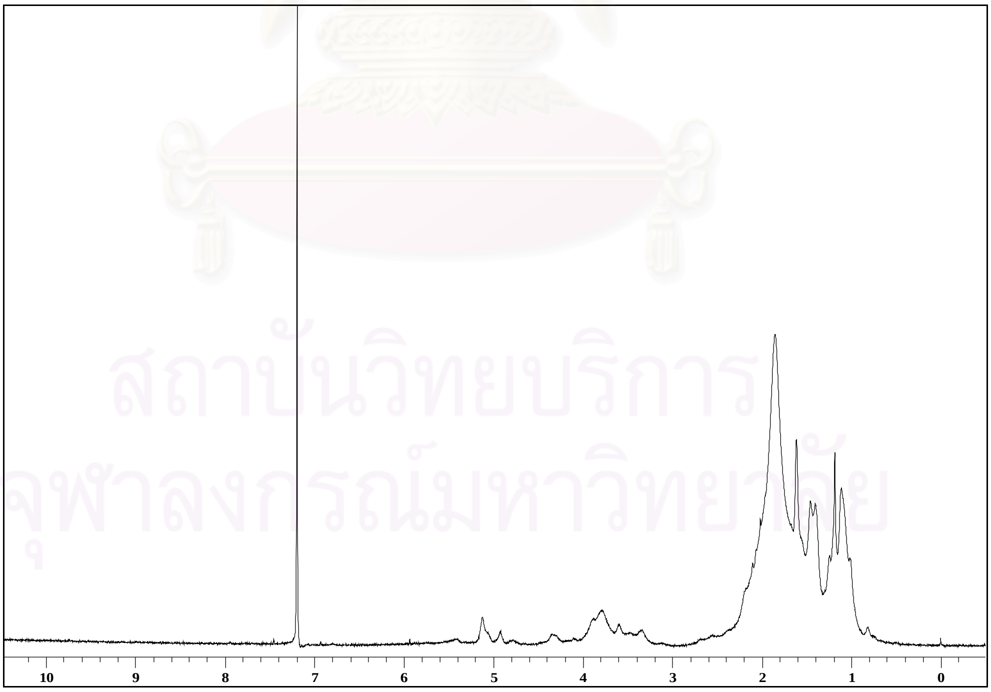

Figure B12 ^{1}H-NMR spectrum of sample B3.

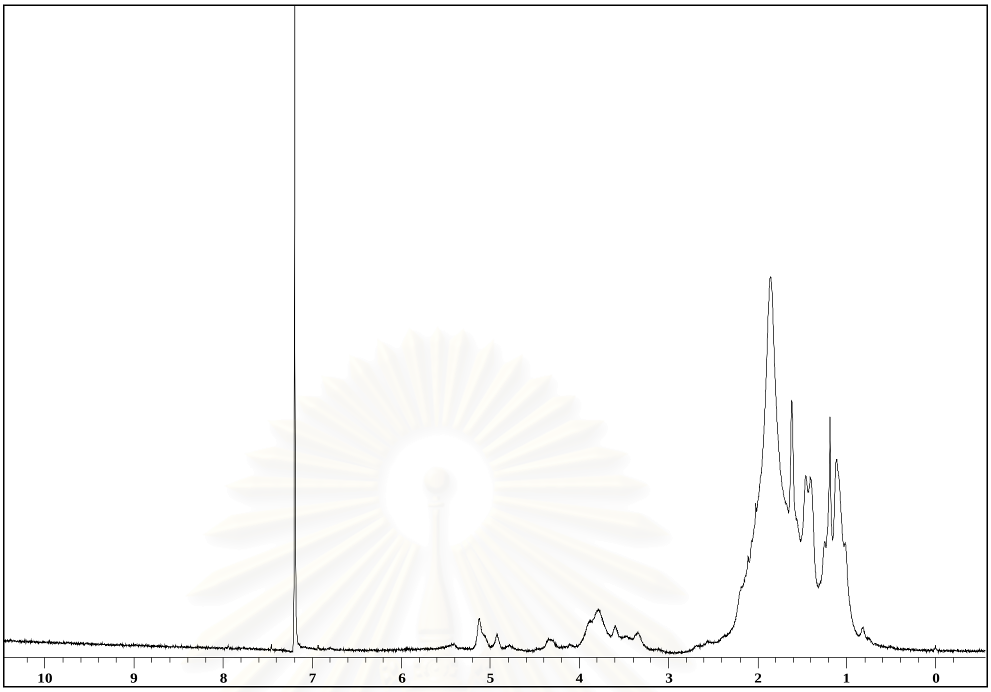

Figure B13 ^{1}H-NMR spectrum of sample B4.

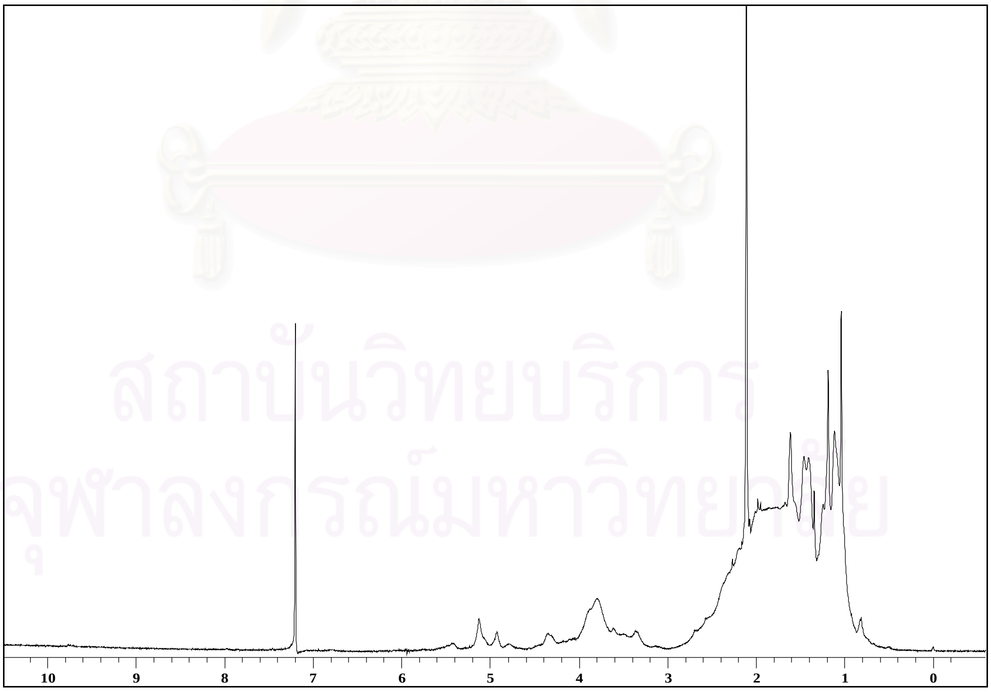

Figure B14 ^{1}H-NMR spectrum of sample B5.

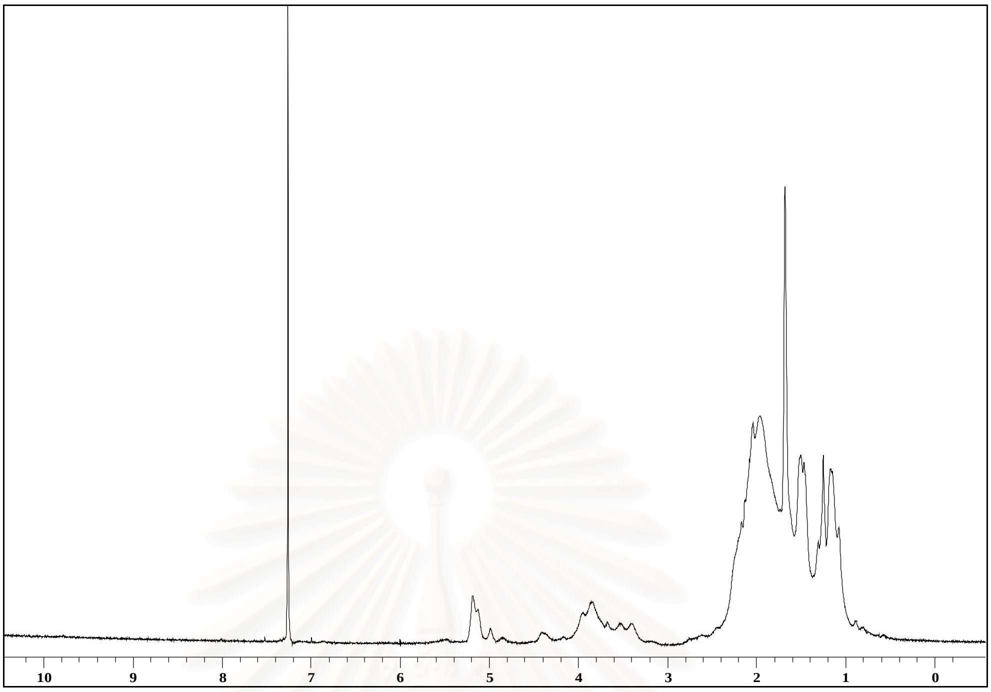

Figure B15 ^{1}H-NMR spectrum of sample B6.

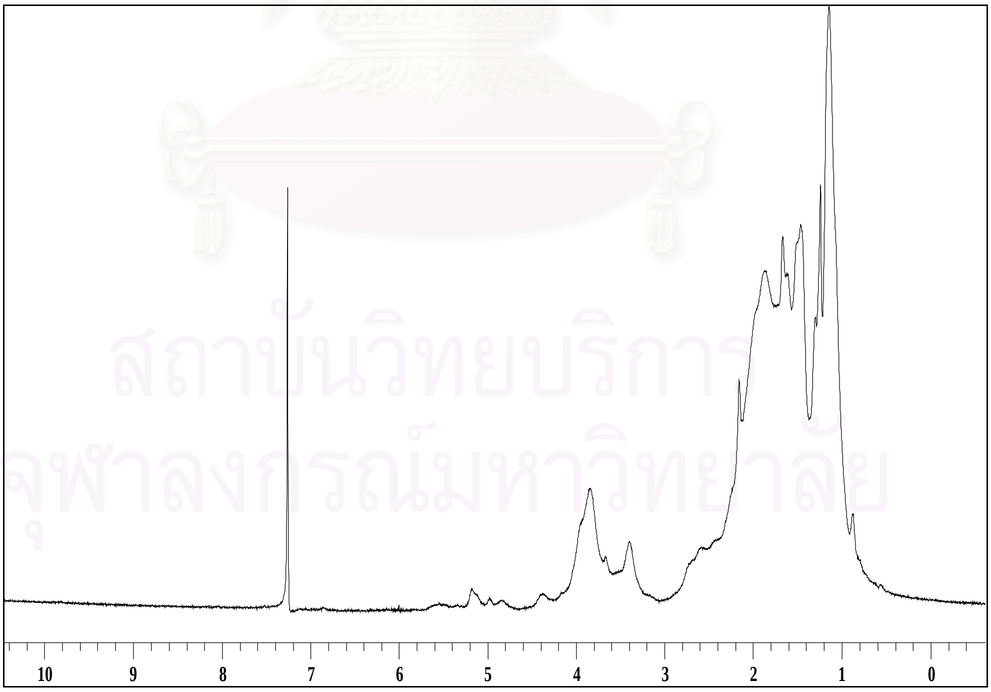

Figure B16 ^{1}H-NMR spectrum of sample B7.

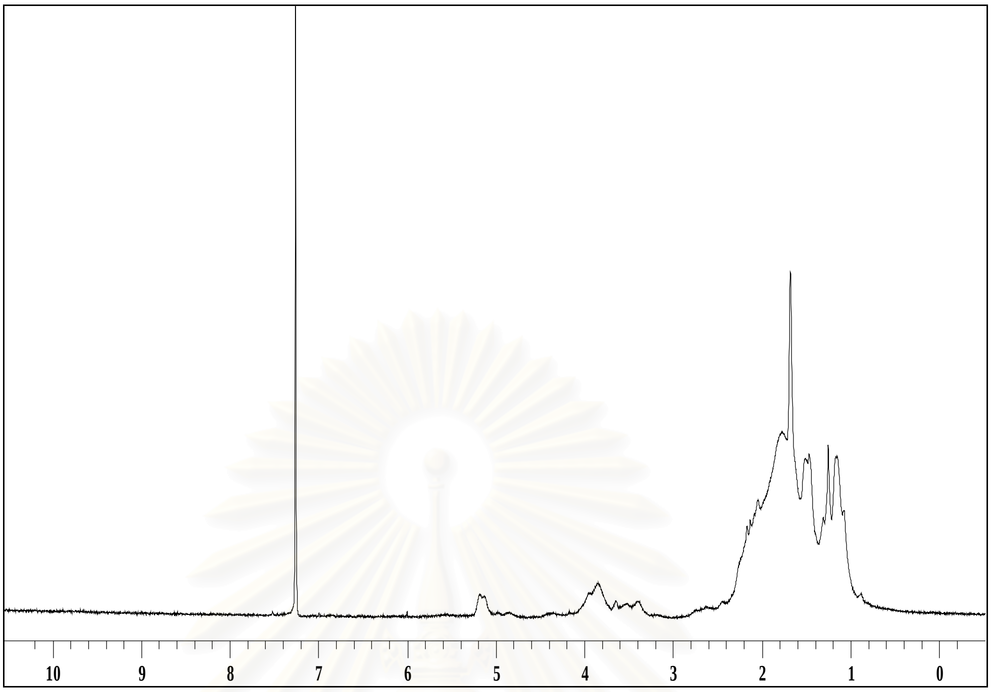

Figure B17 ^{1}H-NMR spectrum of sample C1.

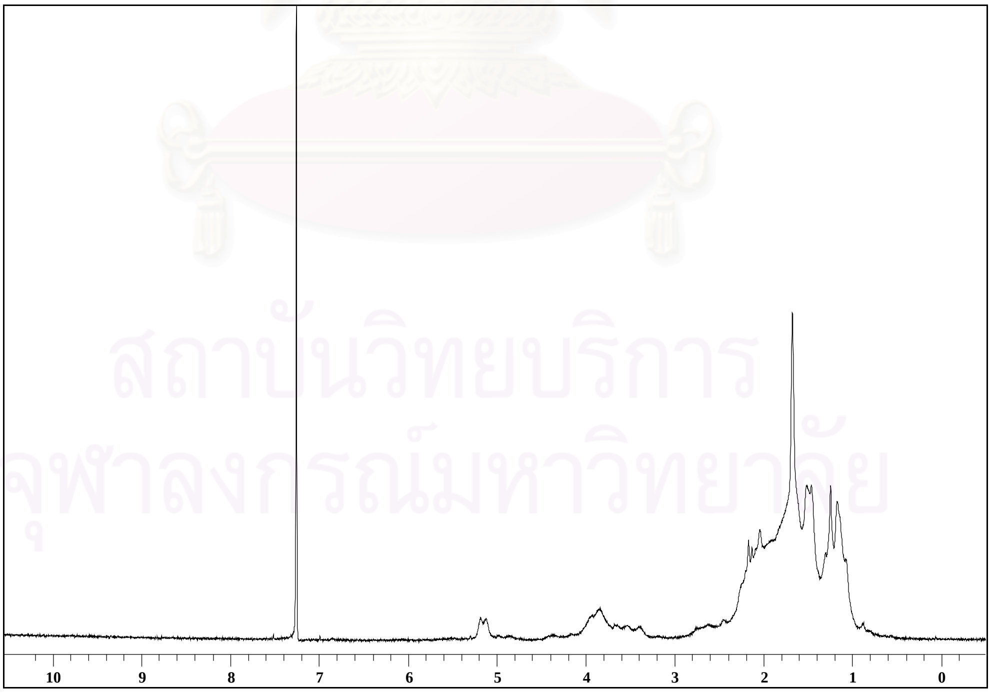

Figure B18 ^{1}H-NMR spectrum of sample C2.

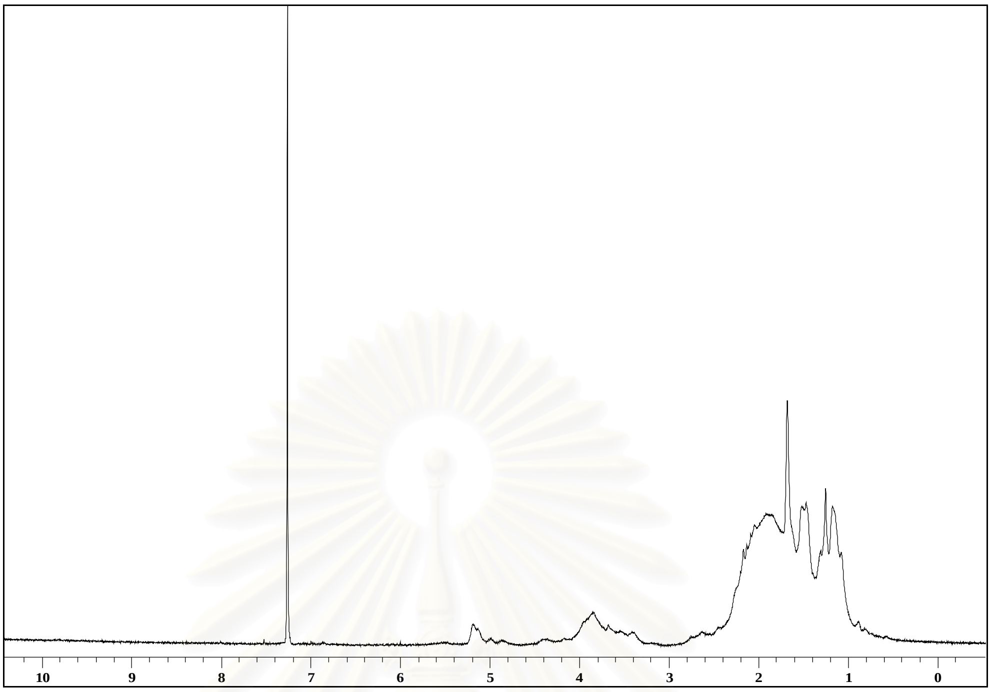

Figure B19 ^{1}H-NMR spectrum of sample C3.

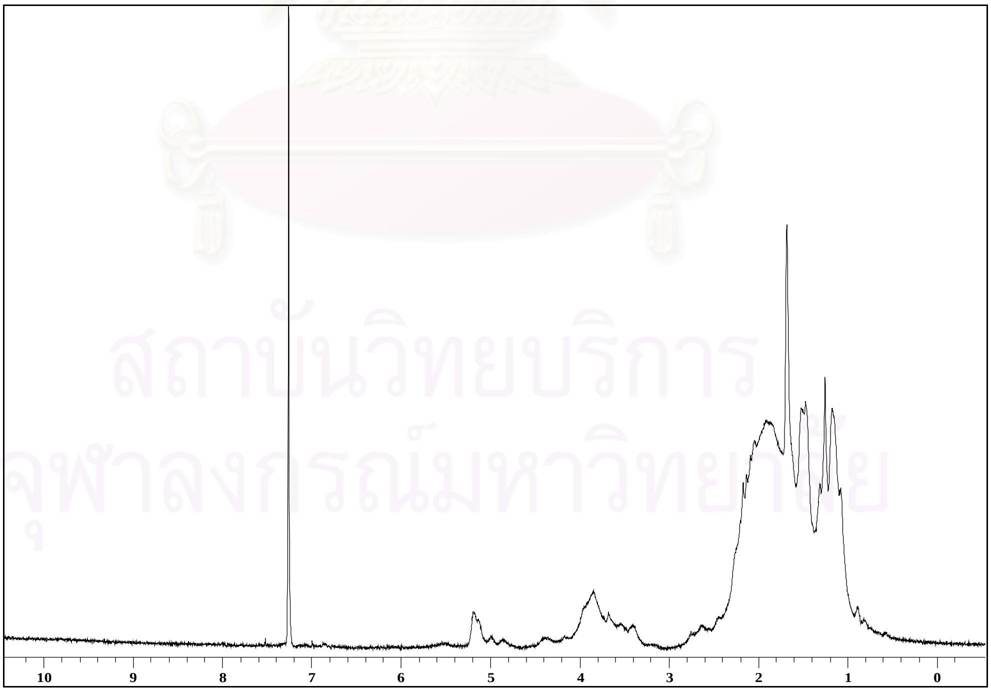

Figure B20 ^{1}H-NMR spectrum of sample C4.

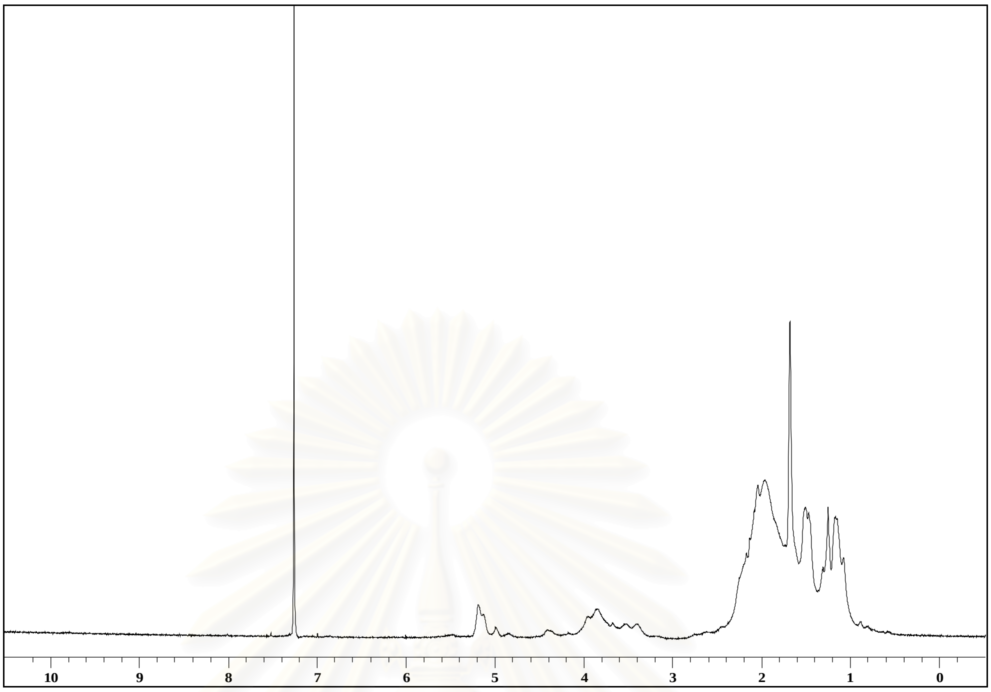

Figure B21 ^{1}H-NMR spectrum of sample C5.

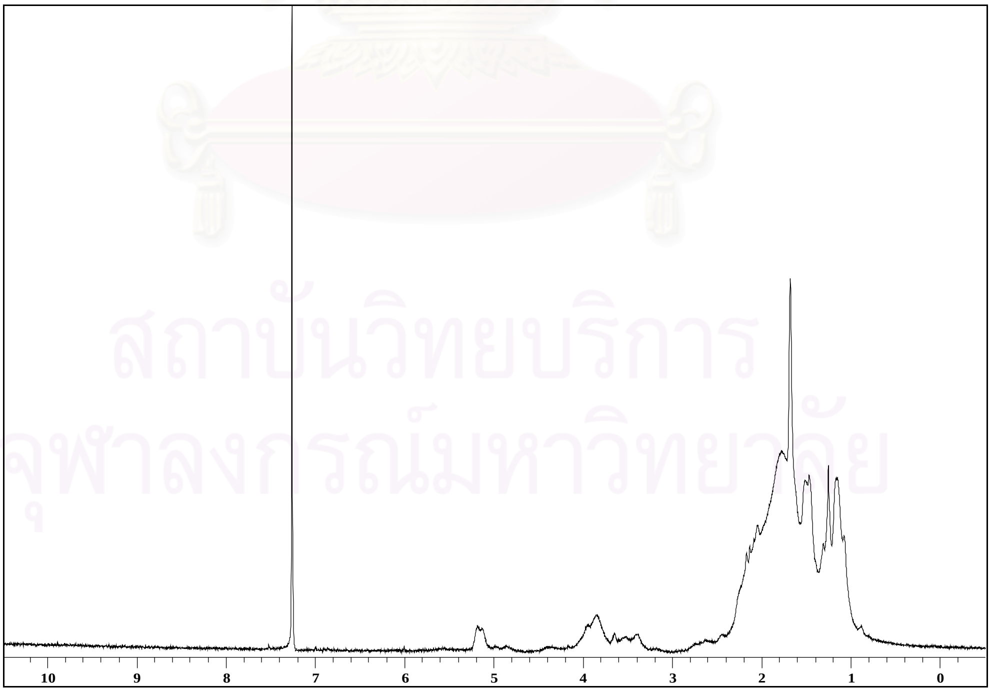

Figure B22 ^{1}H-NMR spectrum of sample D1.

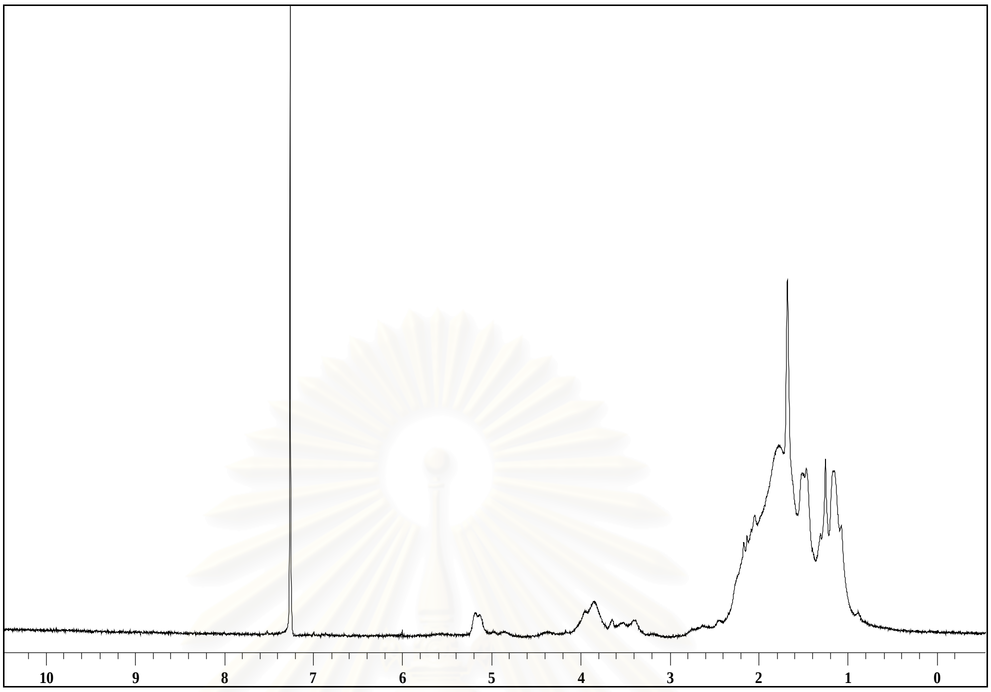

Figure B23 ^{1}H-NMR spectrum of sample D2.

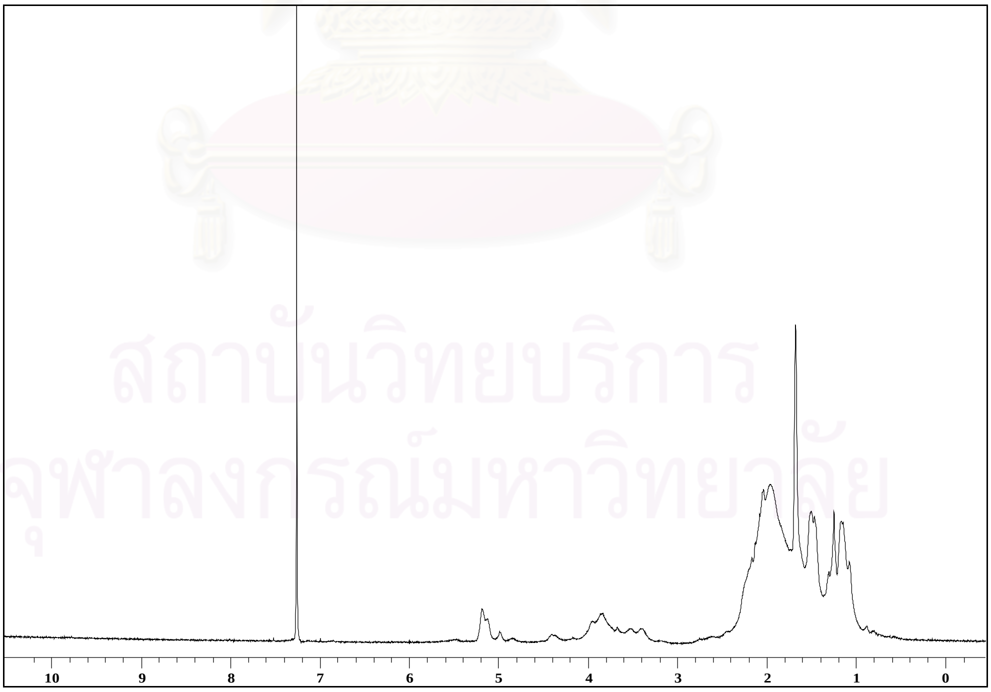

Figure B24 ^{1}H-NMR spectrum of sample D3.

APPENDIX C

APPENDIX C

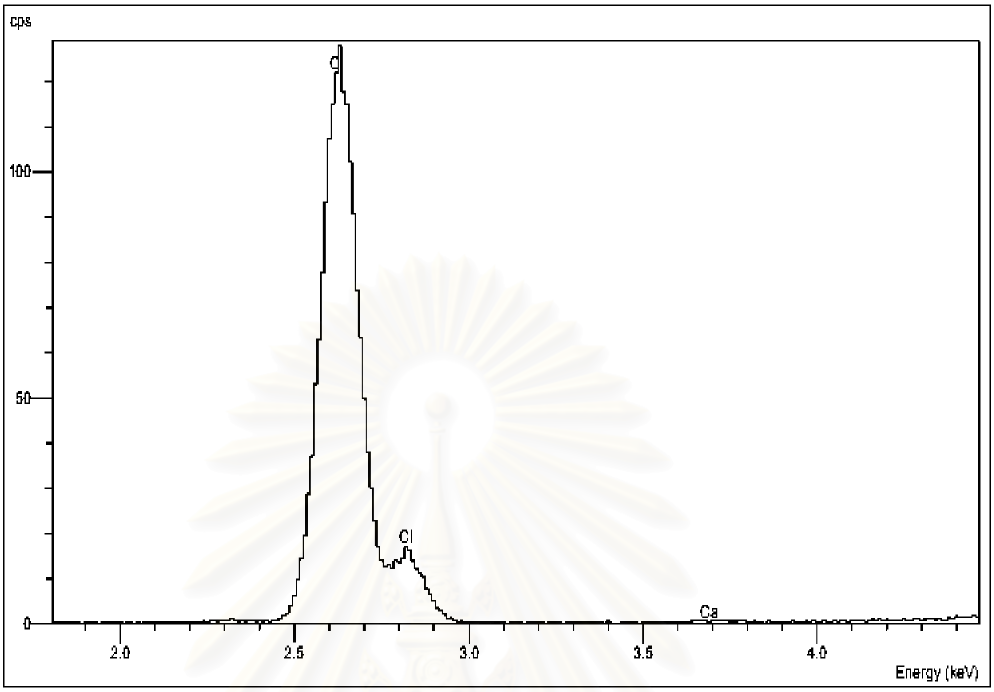

Figure C1 XRF spectrum of sample A1.

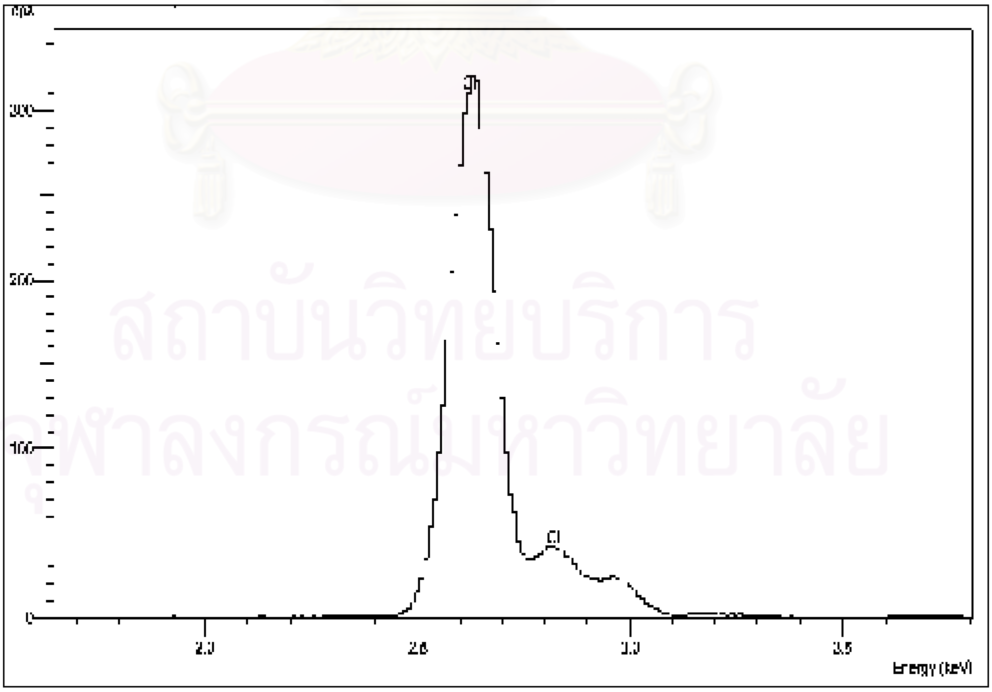

Figure C2 XRF spectrum of sample A2.

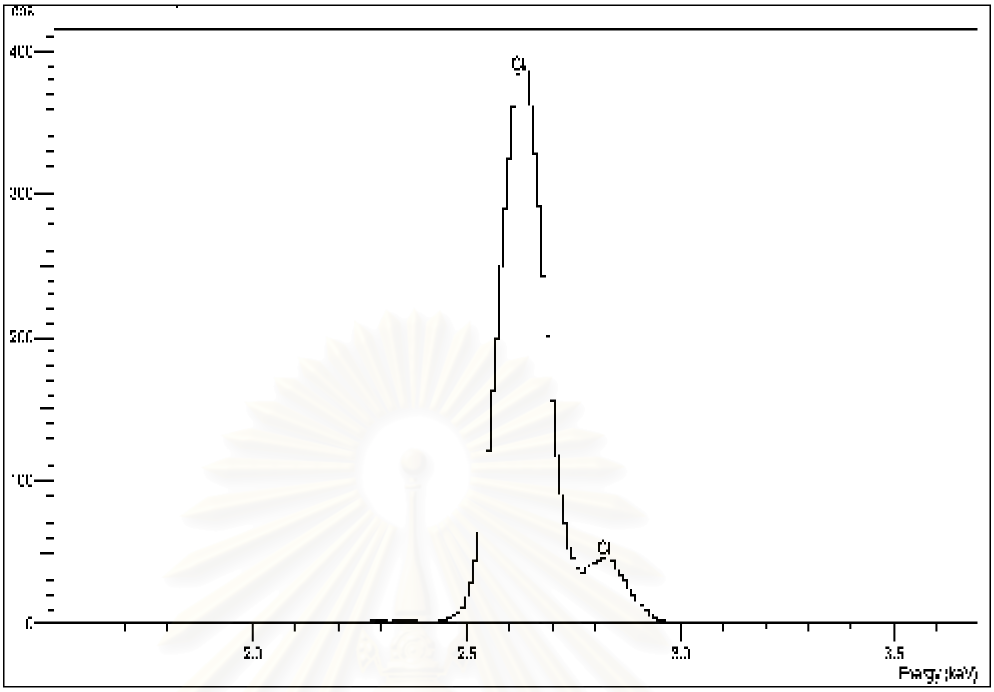

Figure C3 XRF spectrum of sample A3.

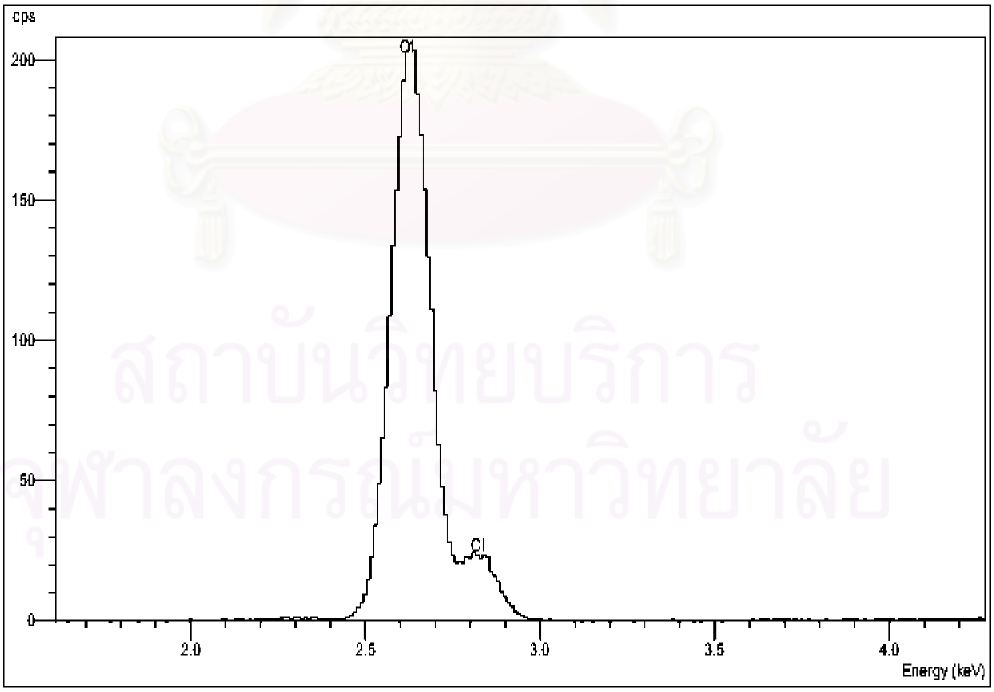

Figure C4 XRF spectrum of sample A4.

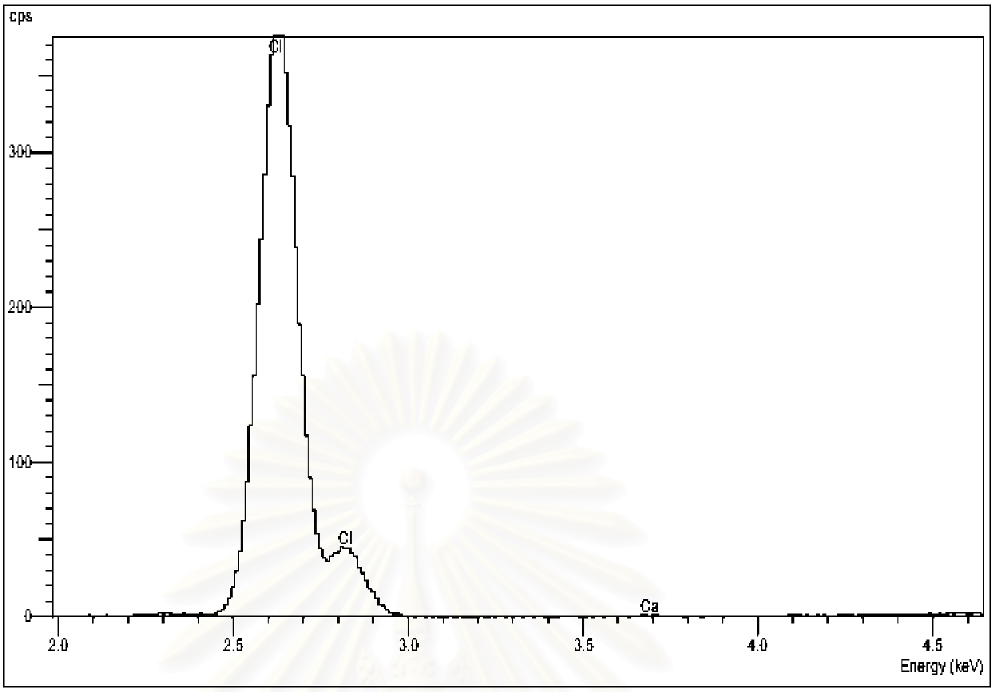

Figure C5 XRF spectrum of sample A5.

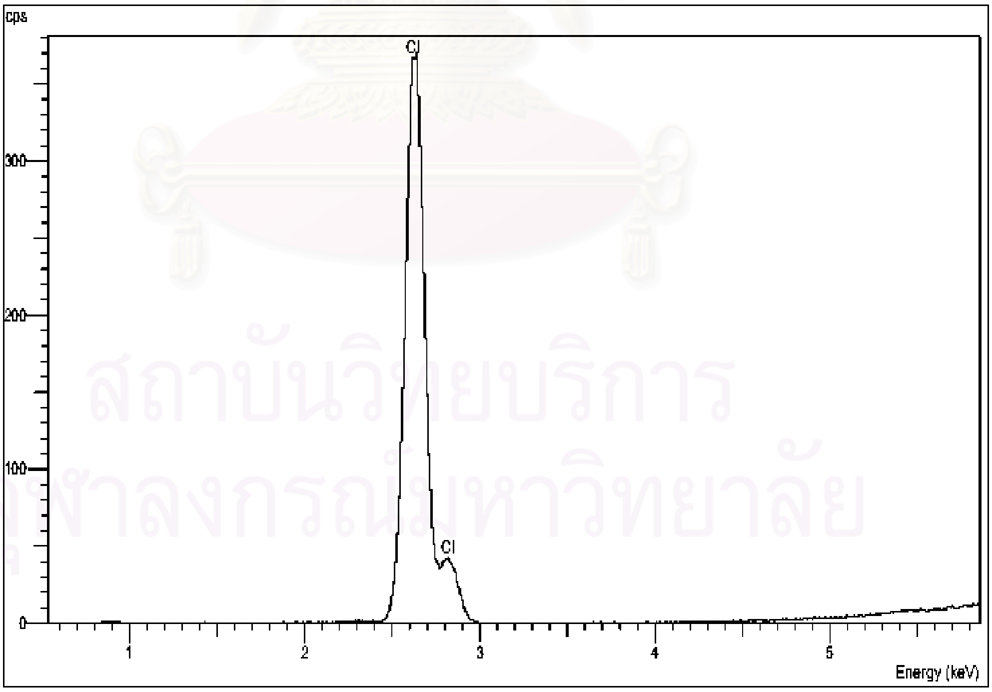

Figure C6 XRF spectrum of sample A6.

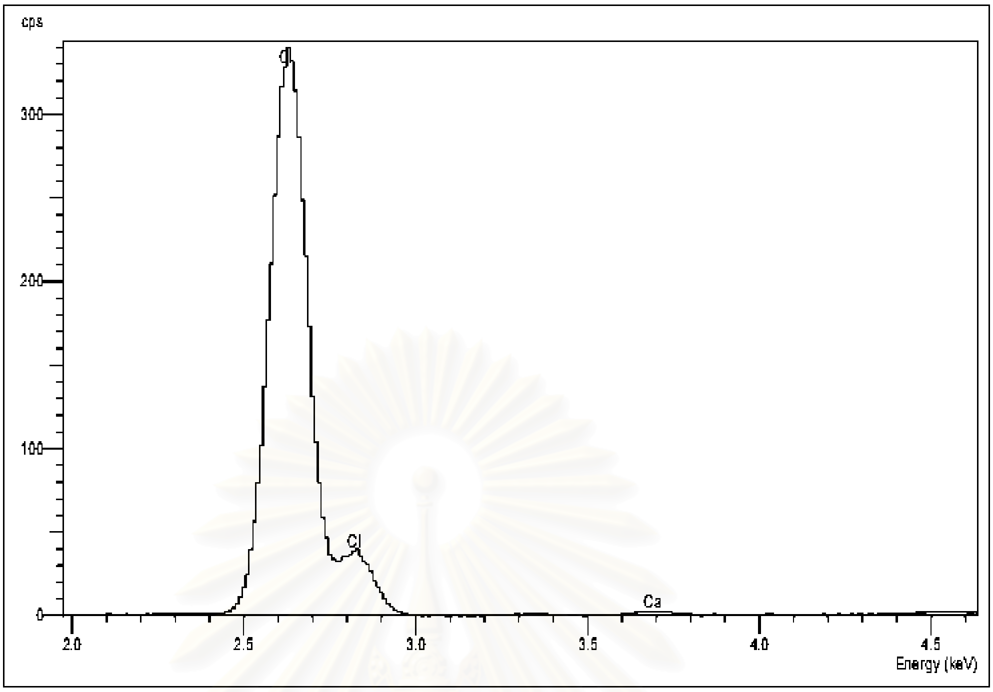

Figure C7 XRF spectrum of sample A7.

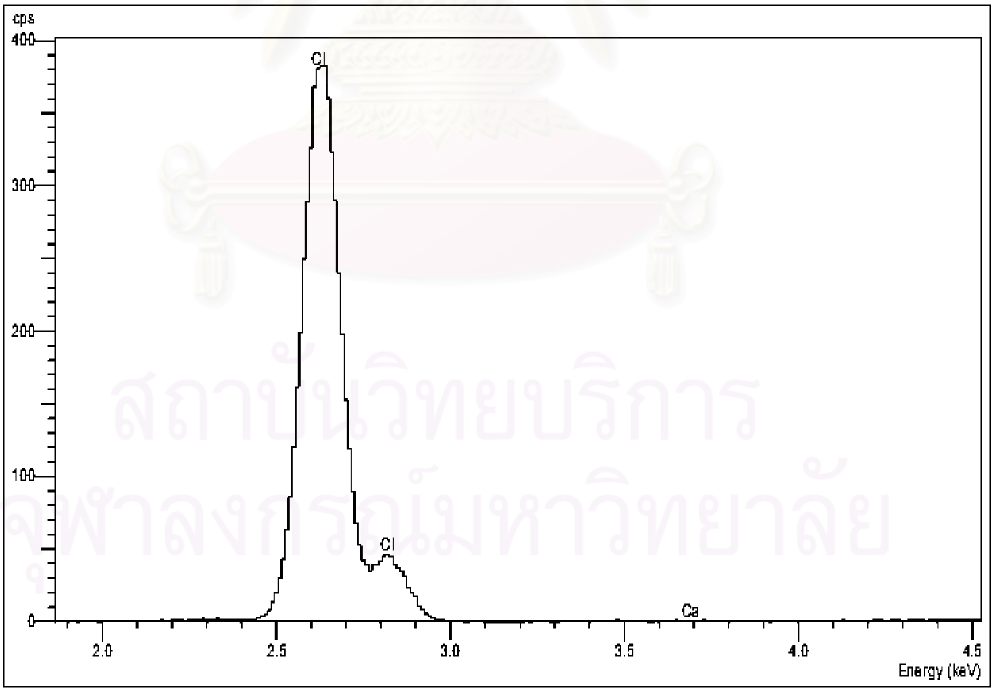

Figure C8 XRF spectrum of sample A8.

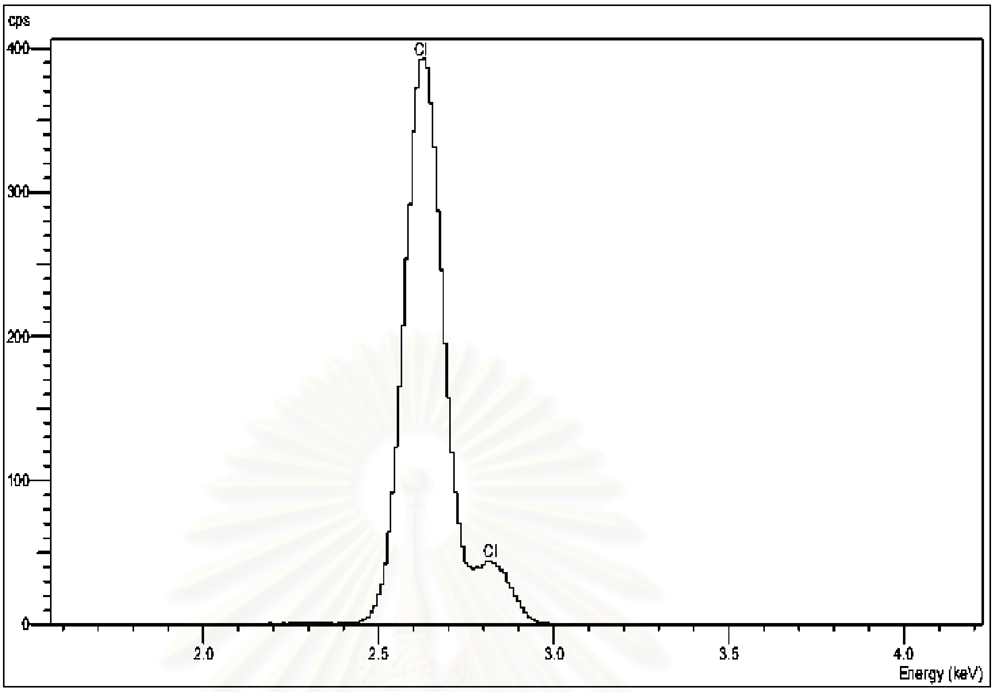

Figure C9 XRF spectrum of sample A9.

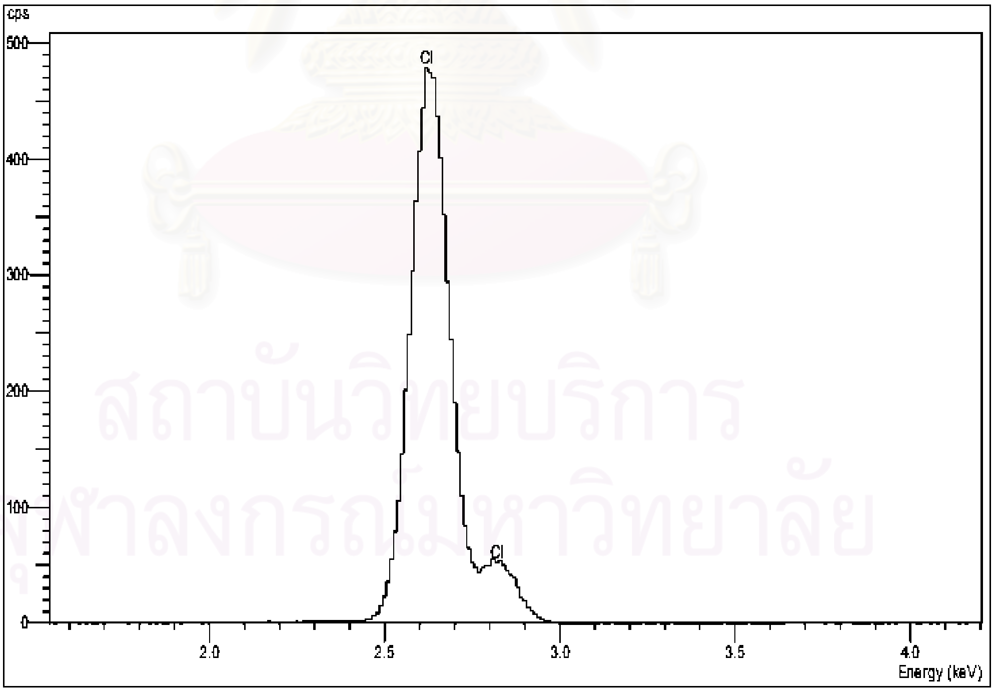

Figure C10 XRF spectrum of sample B1.

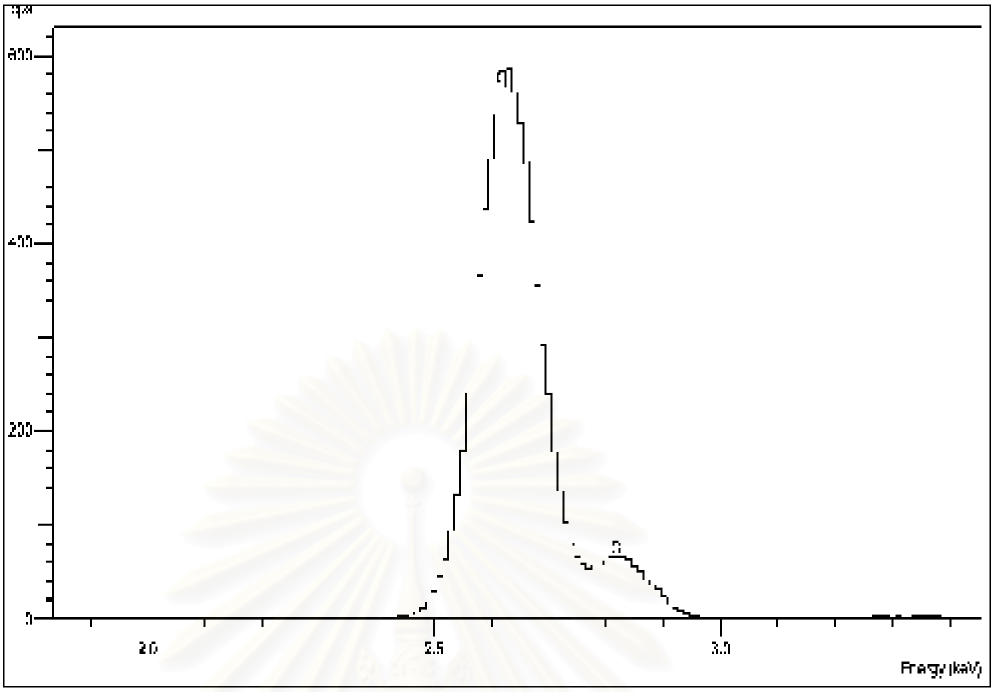

Figure C11 XRF spectrum of sample B2.

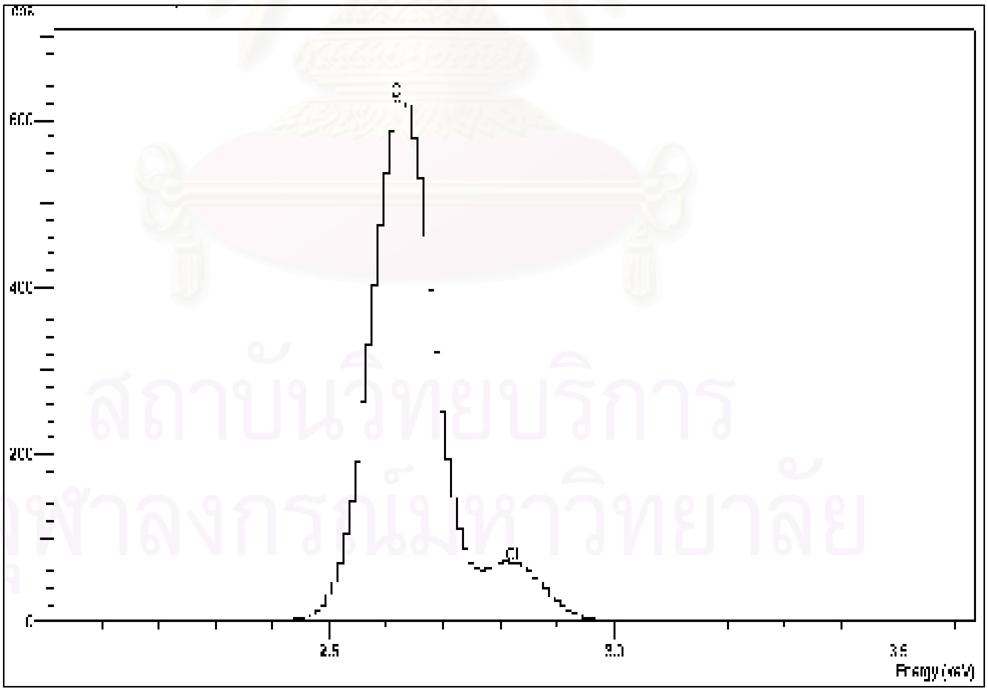

Figure C12 XRF spectrum of CR sample B3.

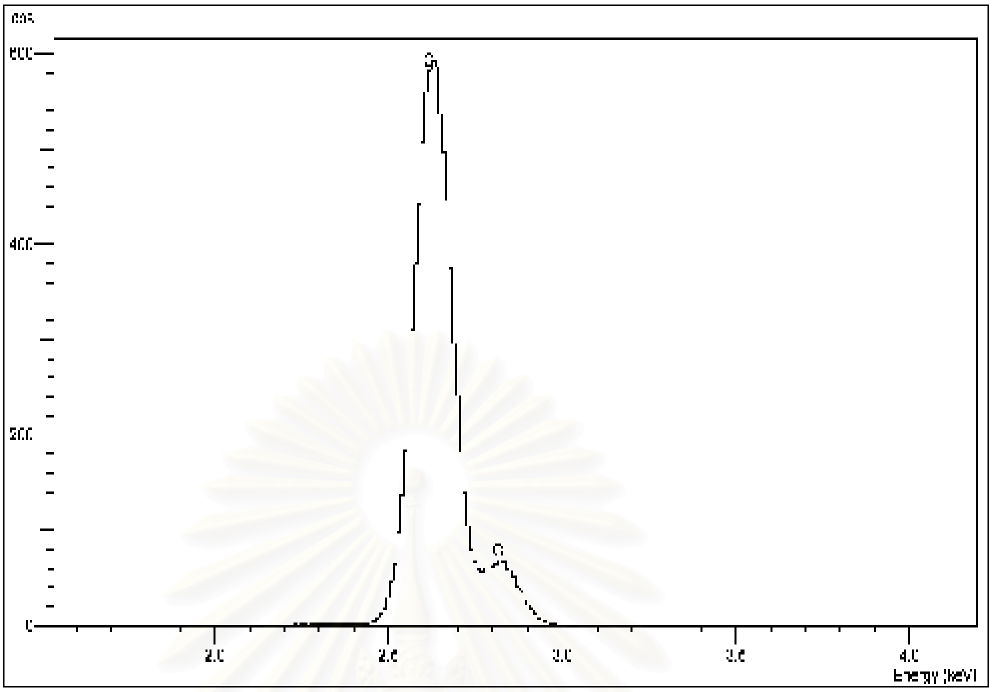

Figure **C13** XRF spectrum of sample B4.

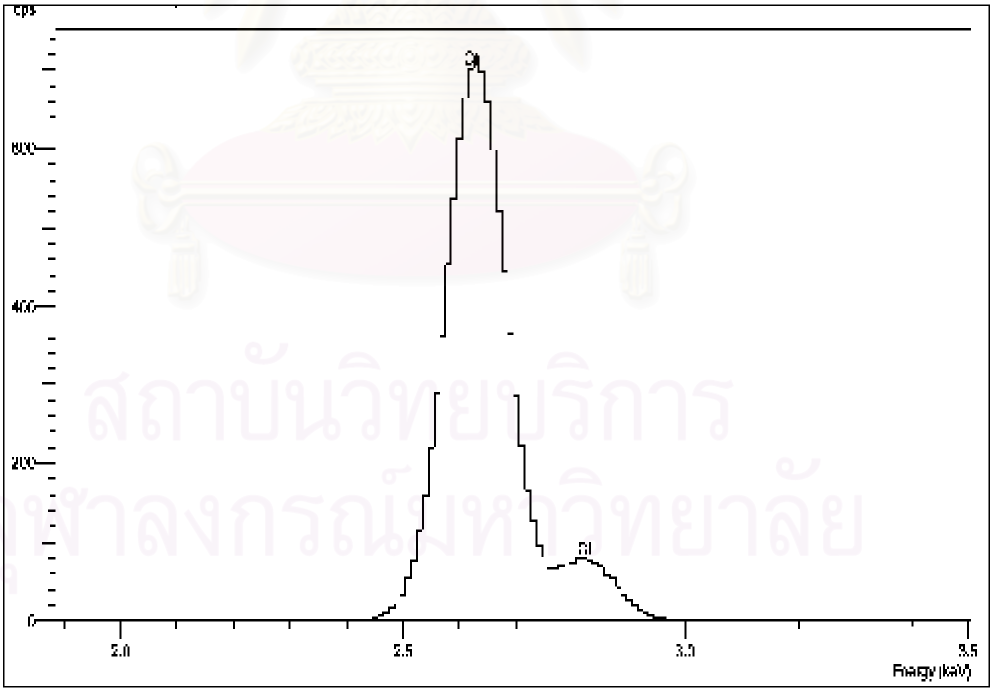

Figure C14 XRF spectrum of sample B5.

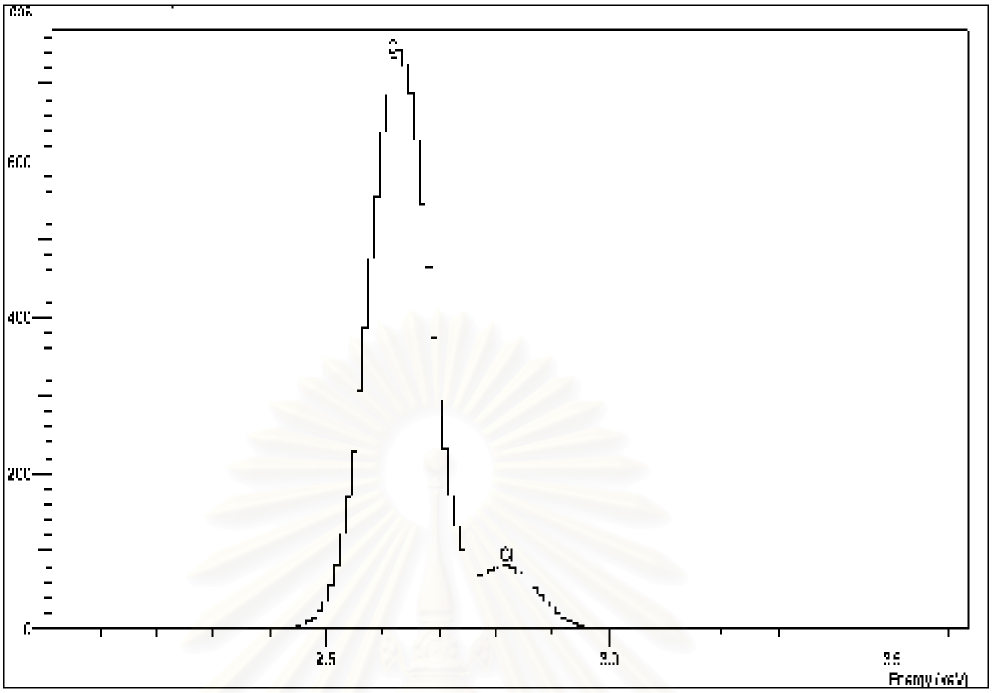

Figure C15 XRF spectrum of sample B6.

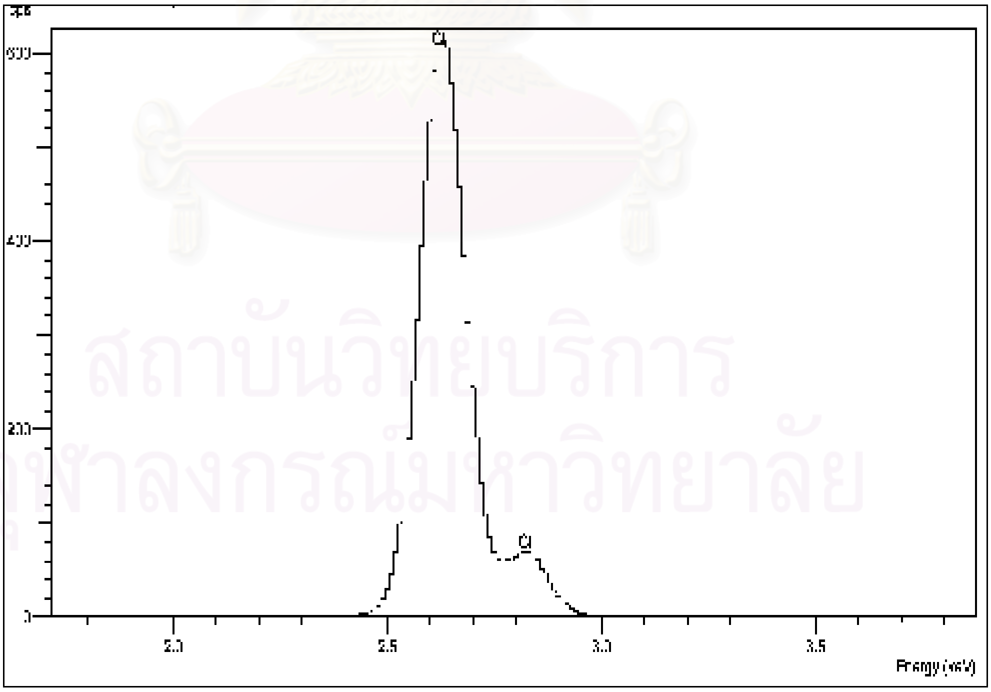

Figure C16 XRF spectrum of sample B7.

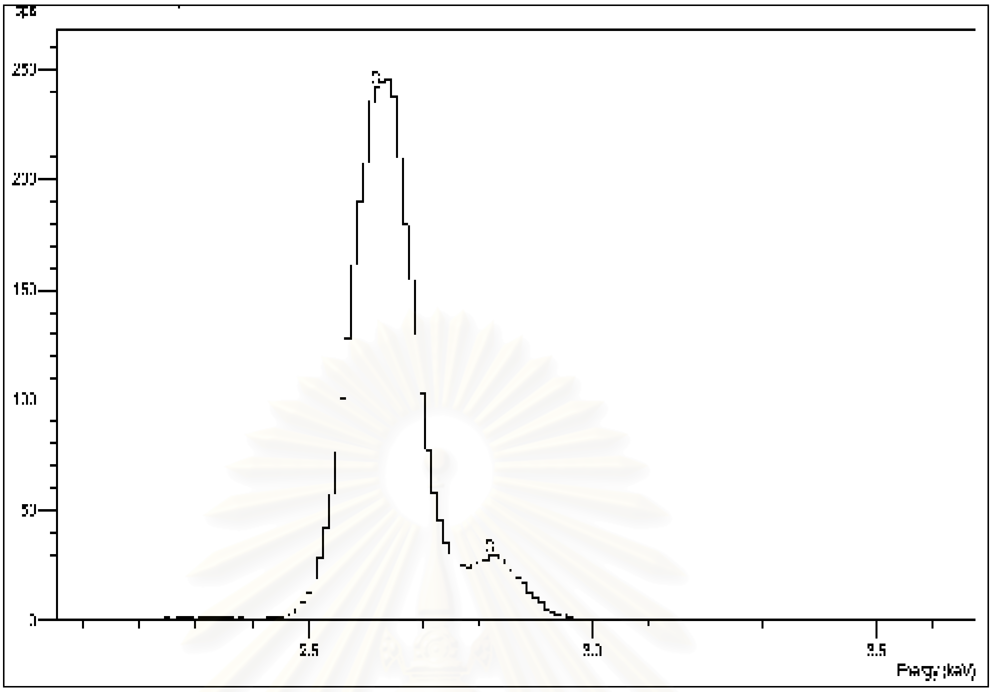

Figure C17 XRF spectrum of sample C1.

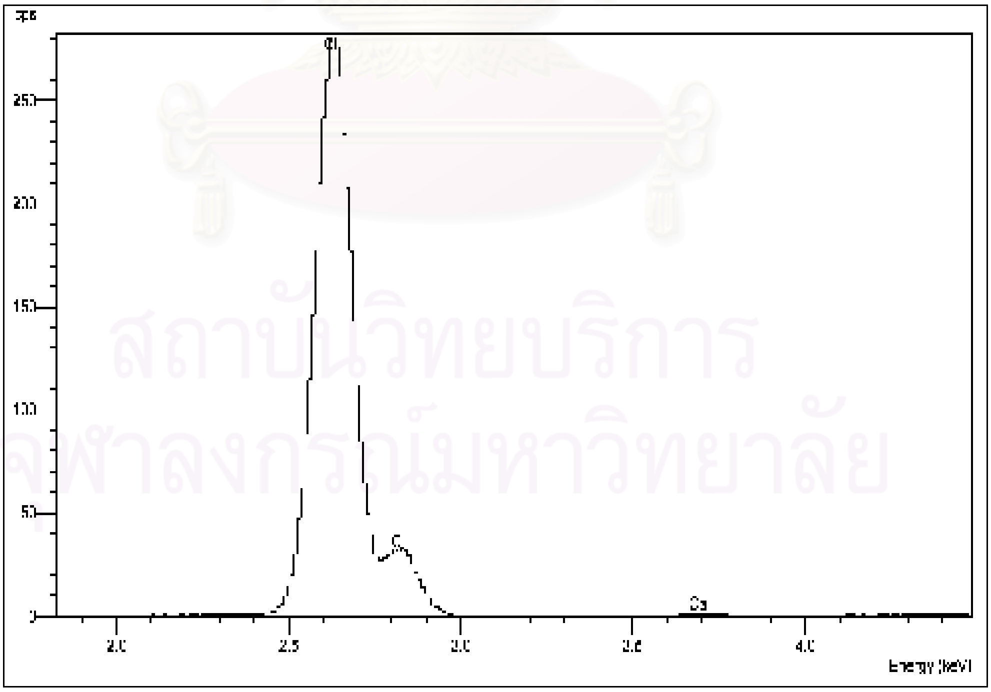

Figure C18 XRF spectrum of sample C2.

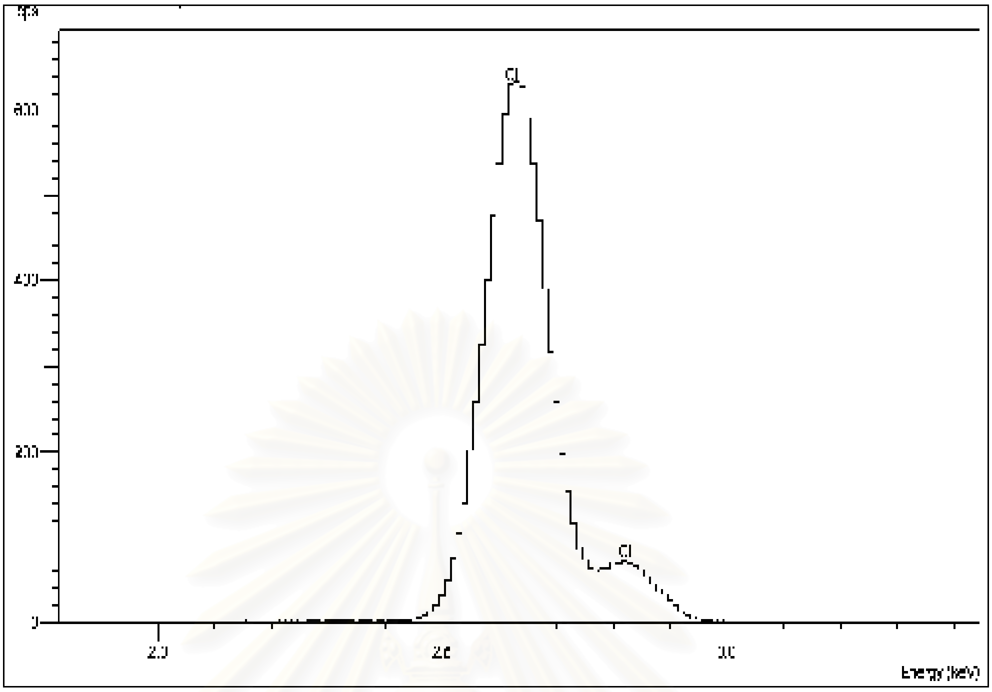

Figure C19 XRF spectrum of sample C3.

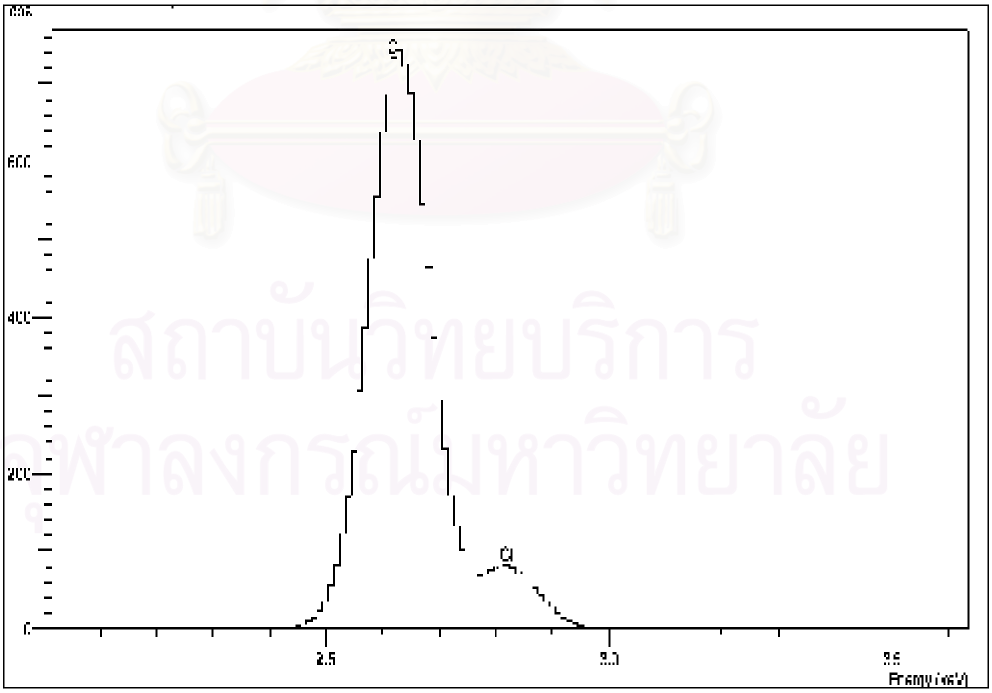

Figure C20 XRF spectrum of sample C4.

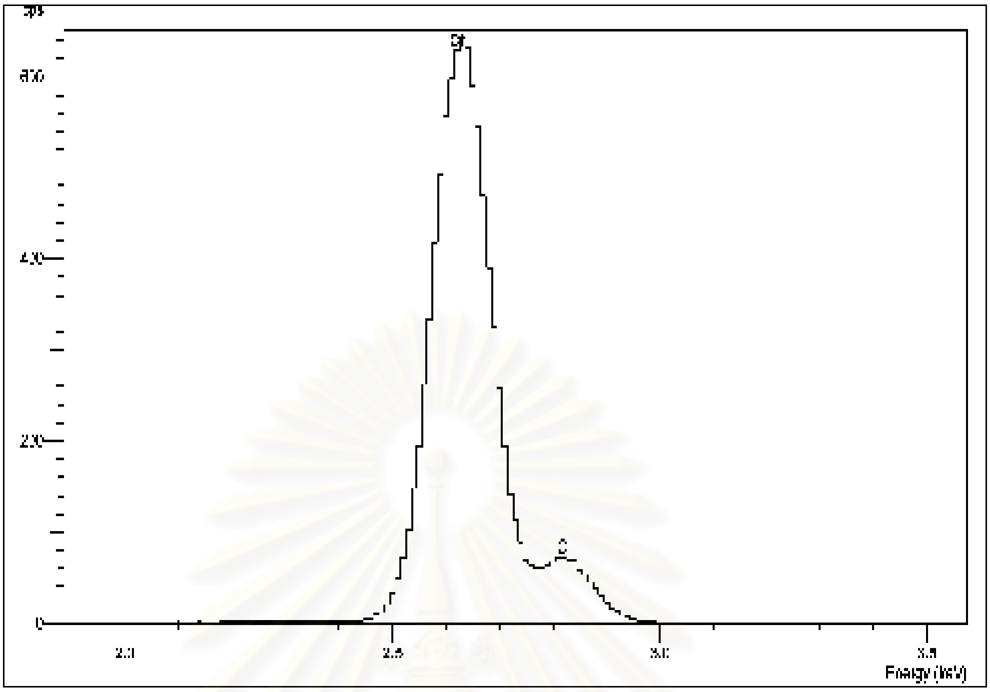

Figure C21 XRF spectrum of sample C5.

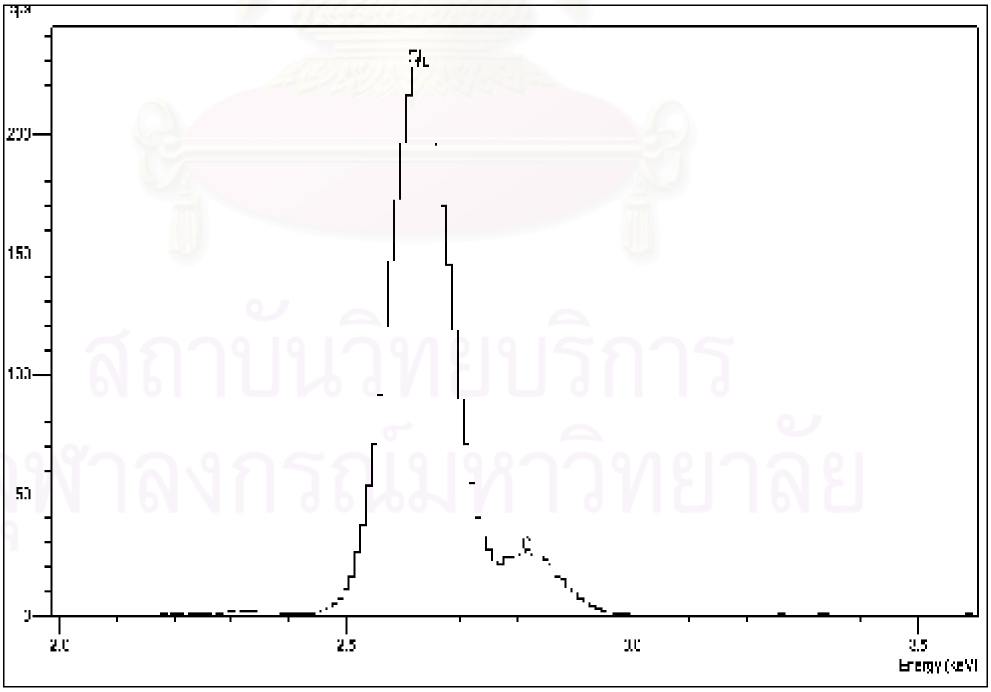

Figure C22 XRF spectrum of sample D1.

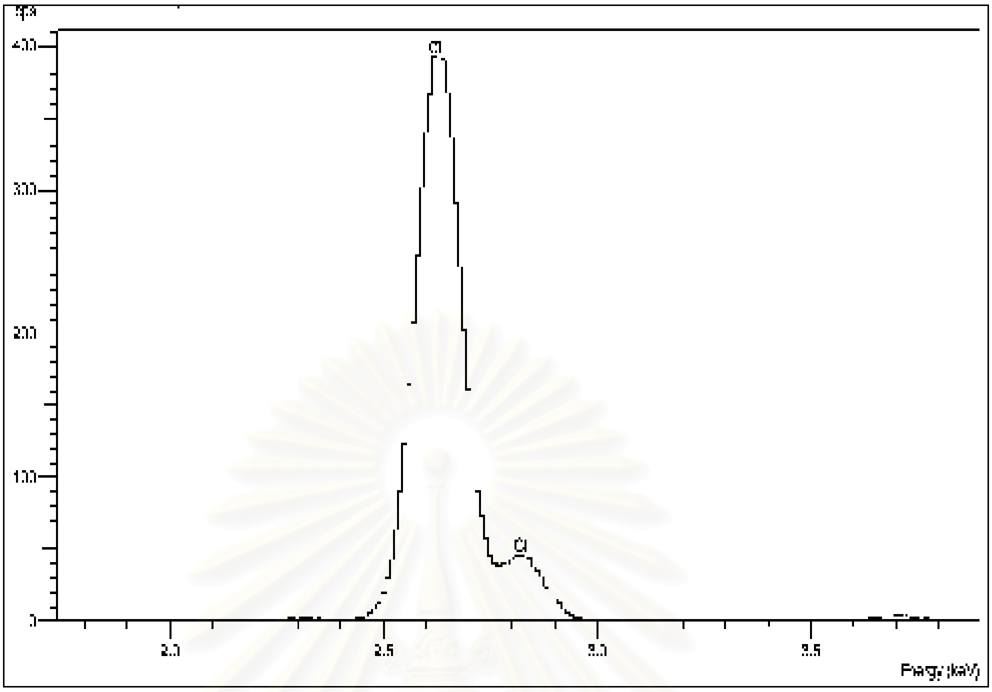

Figure C23 XRF spectrum of sample D2.

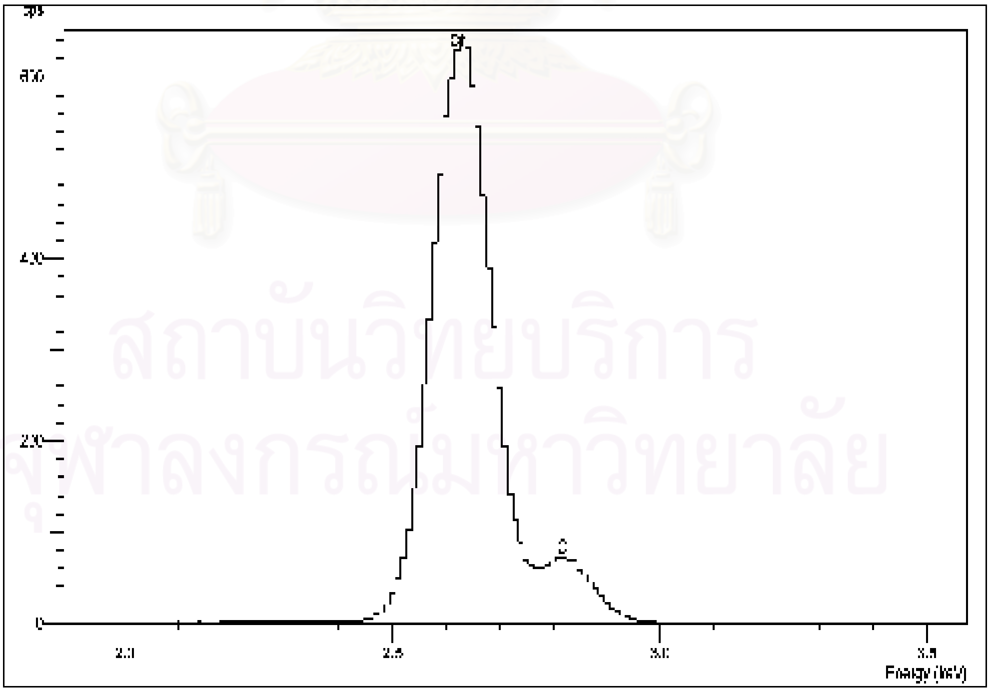

Figure C24 XRF spectrum of sample D3.

APPENDIX D

APPENDIX D

Table D1 Chlorine content of CR which were performed at various hydrochloric and sodium chloride concentrations

Sample	HCl Concentration (%wt)	NaCl Concentration (%wt)	Chlorine content (%wt)
A1	0.5	2	2.95 ± 0.58
A2		4	5.46± 0.18
A3		8	7.71 ± 0.11
A4	1	2	6.96 ± 0.65
A5		4	9.22 ± 0.01
A6		8	9.81 ±0.25
A7	2	2	8.41 ± 0.14
A8		4	10.35 ± 0.07
A9		8	11.63 ± 0.23
A10	3	2	Denature
A11		4	Denature
A12		8	Denature

Table D2 Chlorine content of CR at various concentrations of NaCl and 2% HCl

Sample	HCl Concentration (%wt)	NaCl Concentration (%wt)	Chlorine content (%wt)
A7	2	2	8.41 ± 0.14
A8		4	10.35 ± 0.07
A9		8	11.63 ± 0.23
B1		10	13.42 ± 0.28
B2		20	14.70 ± 0.13
B3		30	15.46 ± 0.01
B4		40	16.70 ± 0.03
B5		50	17.86 ± 0.02
B6		60	17.72 ± 0.04
B7		70	13.54 ± 0.47

Table D3 Chlorine content in CR derived various reaction time

Sample	Time (hr)	Chlorine content (%wt)
C1	1	4.86 ± 0.03
C2	2	8.79 ± 0.11
C3	3	13.39 ± 0.25
B5	4	17.86 ± 0.02
C4	6	17.76 ± 0.02
C5	8	17.84 ± 0.01

Table D4 Chlorine content in CR at derived various reaction temperatures

Sample	Temperature (°C)	(%) Chlorine content
D1	10	3.77 ± 0.08
D2	20	6.50 ± 0.14
B5	30	17.86 ± 0.02
D3	40	17.84± 0.02

APPENDIX E

APPENDIX E

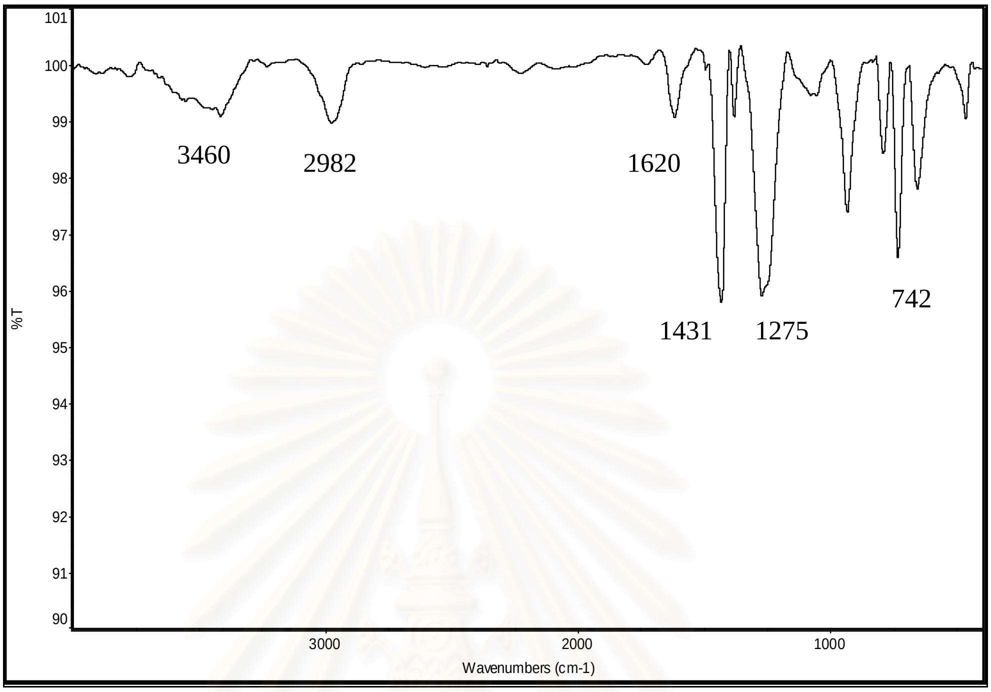

Figure E1 FT-IR spectrum of CR (commercial).

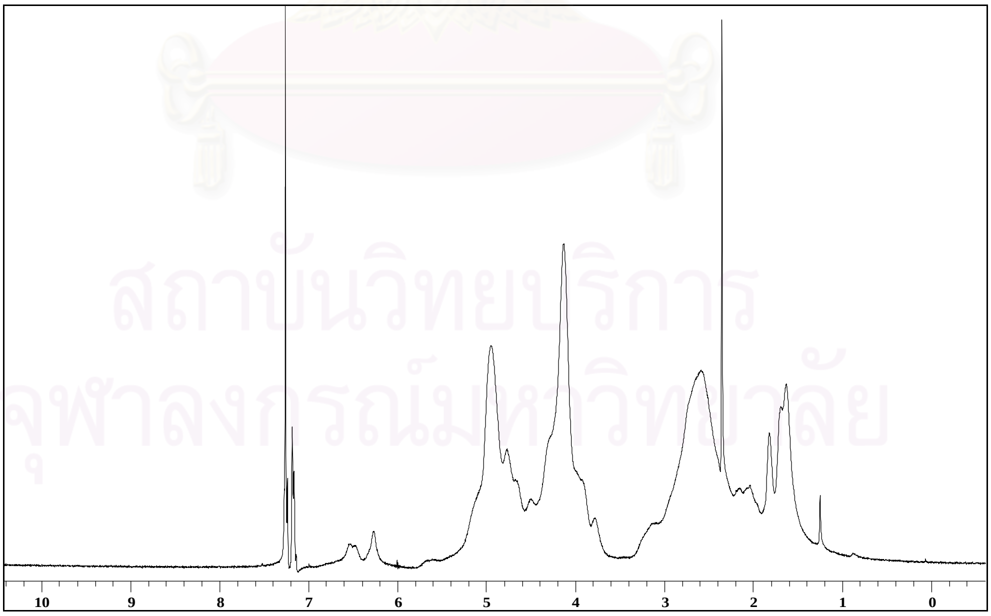

Figure E2 ^{1}H-NMR spectrum of CR (commercial).

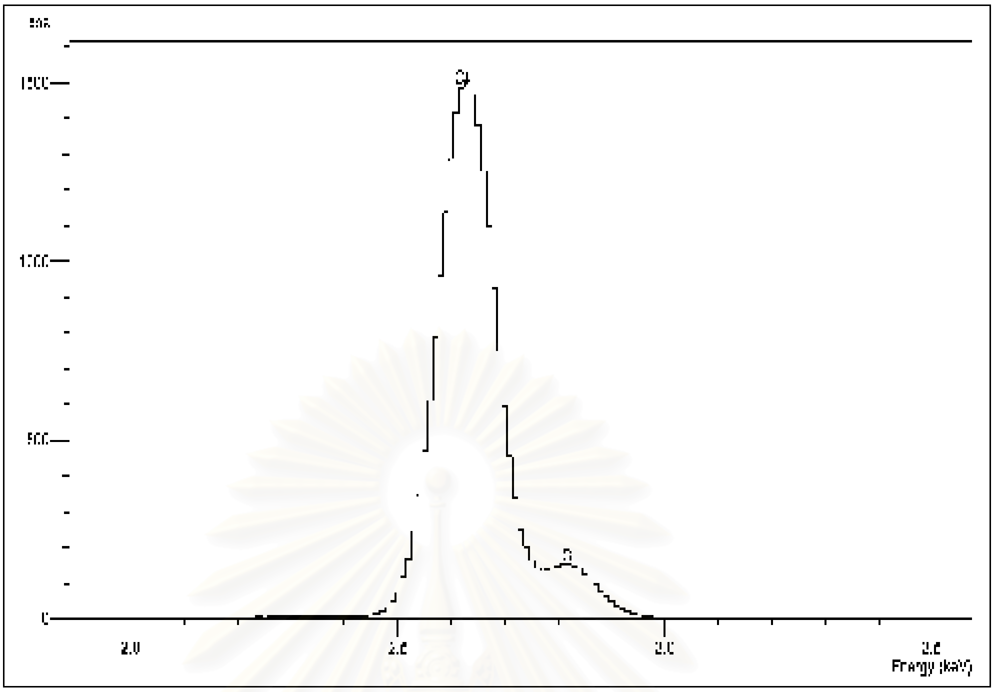

Figure E3 XRF spectrum of CR (commercial).

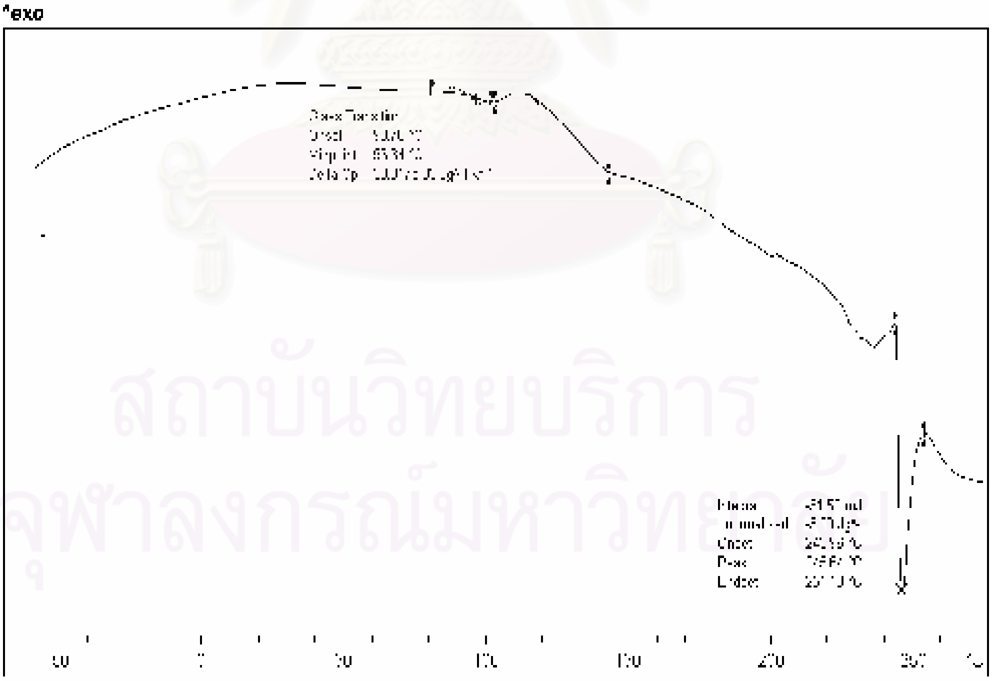

Figure E4 DSC Thermogram of CR (commercial).

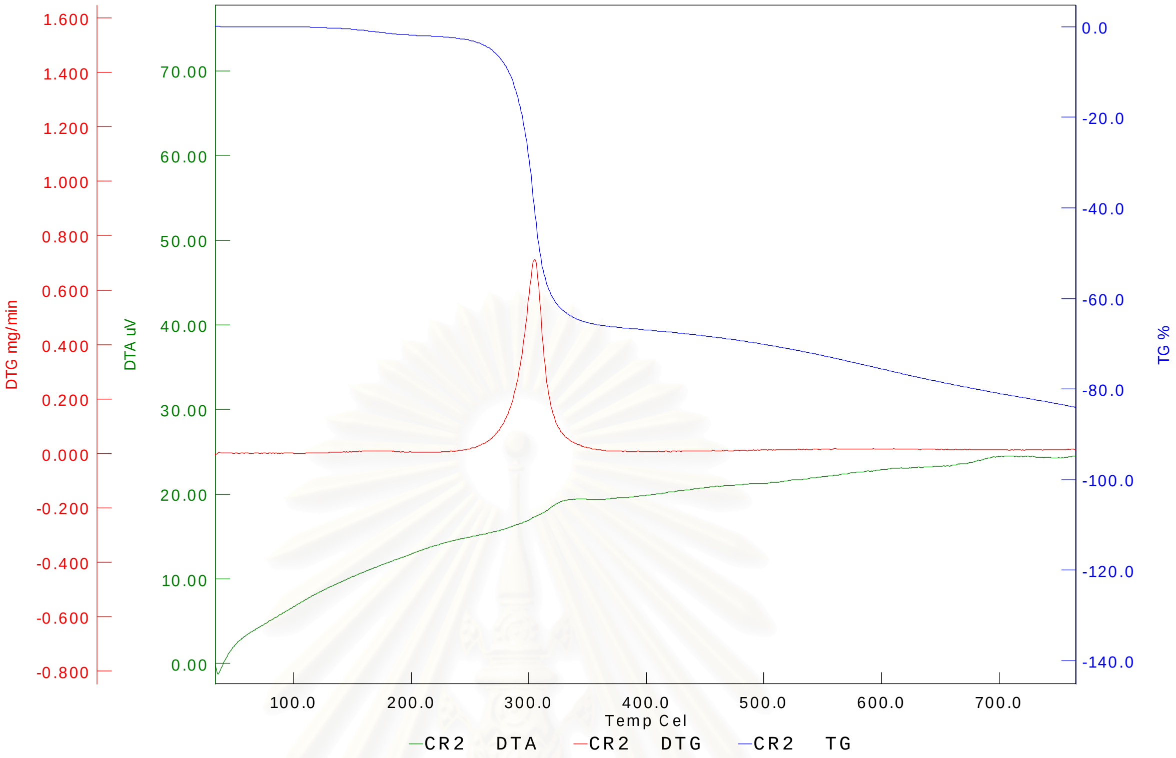

Figure E5 TG/ DTG curve of CR (commercial).

FT-IR spectrum of CR (commercial) showed peaks at 3460 cm^{-1} (O-H stretching), 2982 cm^{-1} (C-H stretching), 1620 cm^{-1} (C=C stretching), 1431 and 1381 cm^{-1} (C-H blending), and 663, 742, 794 cm^{-1} (C-Cl stretching) [31]. The^{1}H-NMR spectrum showed the chemical shift at 1.24 ppm ($C\underline{H}_3$-CO), 1.63 ppm ($C\underline{H}_3$-C=C), 2.06 ppm ($-C\underline{H}_2-$), 4.13 ppm (C-C$\underline{H}$Cl) and 4.94 ppm ($C=C\underline{H}_2$) [28]. The chlorine content was determined and calculated by XRF spectrometer. The 50.94% chlorine content of CR was obtained. DSC thermogram of CR showed Tg at 96.34°C and Tm at 245.64°C. The TG and DTG thermograms of CR showed two steps of degradation. The first degradation started at 171°C and last until 394°C. The second degradation started at 394°C and last until 615°C.

VITA

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