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PREPARATION OF CHLORINATED RUBBER FROM EPOXIDIZED NATURAL
RUBBER USING SODIUM HYPOCHLORITE/SODIUM CHLORIDE



Miss Kittima Wongtawatchai

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

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ยางคลอรีเนตสามารถเตรียมได้จากปฏิกิริยากลอรีเนชันระหว่างยางธรรมชาติอีพอกซิไดส์และโซเดียมไฮโปคลอไรต์/โซเดียมคลอไรต์ จากงานวิจัยนี้ ได้ศึกษาอิทธิพลของเวลา อัตราส่วนของสารตั้งต้น โซเดียมไฮโปคลอไรต์และโซเดียมคลอไรต์ อุณหภูมิและค่าความเป็นกรด-เบสของปฏิกิริยากลอรีเนชัน การตรวจสอบคุณลักษณะของยางคลอรีเนต อาศัยเทคนิคอินฟราเรดสเปกโตรสโคปี และ โปรตอนนิวเคลียร์แมกนีติกเรโซแนนซ์ สำหรับการวิเคราะห์หาปริมาณคลอรีนในยางคลอรีเนต อาศัยเทคนิคเอ็กซ์เรย์ฟลูออเรสเซนซ์ พบว่าในการเตรียมยางคลอรีเนตนั้น ใช้ยางธรรมชาติอีพอกซิไดส์ ทำปฏิกิริยากับ โซเดียมไฮโปคลอไรต์ และ โซเดียมคลอไรต์ ในอัตราส่วน 1:4 โดยโมล ในสถานะที่เป็นกรด มีค่าความเป็นกรด-เบสประมาณ 1 ในเวลา และ อุณหภูมิที่เหมาะสม ได้ยางคลอรีเนตที่มีคลอรีนเป็นองค์ประกอบสูง สมบัติทางความร้อนของยางคลอรีเนตศึกษาด้วยเทคนิคดิฟเฟอเรนเชียลสแกนนิ่งแคลอริเมทรี และ เทอมัลแกรวิเมทรี/เดริเวทีฟเทอมัลแกรวิเมทริกแอนนาไลซิส ยางคลอรีเนตที่เตรียมได้จากงานวิจัยนี้ สามารถเป็นประโยชน์ในการพัฒนาไปเป็นเม็ดสีในอุตสาหกรรมสีได้

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Chlorinated rubber could be prepared from chlorination reaction between epoxidized natural rubber and sodium hypochlorite/sodium chloride. In this research, effects of time, the ratio of substrate, sodium hypochlorite and sodium chloride, temperature and pH were studied. The chlorinated rubber was characterized by Fourier Transform Infrared and Proton Nuclear Magnetic Resonance spectroscopies. The %chlorine content was analyzed by X-Ray Fluorescence. Results showed that the optimum condition for preparing the chlorinated rubber was the use of epoxidized natural rubber and sodium hypochlorite/sodium chloride of 1:4 by mol. The chlorination reaction was taken in an acidic condition at pH of 1 at suitable reaction time and temperature. The thermal properties of chlorinated rubber were studied by Differential Scanning Calorimetry and Thermogravimetry/Derivative Thermogravimetric analysis. The chlorinated rubber that was prepared in this research could be useful to develop as pigments in painting industry.

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ABBREVIATIONS

NR	Natural Rubber
ENR	Epoxidized Natural Rubber
CR	Chlorinated Rubber
FT-IR	Fourier Transform Infrared Spectroscopy
¹ H-NMR	Proton Nuclear Magnetic Resonance Spectroscopy
XRF	X-Ray Fluorescence
DSC	Differential Scanning Calorimetry
TG/DTG	Thermogravimetry/ Derivative Thermogravimetric Analysis
NaOCl	Sodium Hypochlorite
NaCl	Sodium Chloride
d.r.c.	Dry Rubber Content
°C	Degree Celsius
g	Gram
mol	Mole
ml	Milliliter
T _g	Glass Transition Temperature
T _m	Crystalline Melting Temperature
min	Minute
cm ⁻¹	Wavenumber

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CHAPTER I

INTRODUCTION

1.1 Introduction

The development of Thailand's rubber industry has been quickly advanced because the natural rubber is an important raw material used to process the manufacture of various products. Natural rubber has good properties such as elasticity, insulator, good adherence, coating, fibre, etc. and is used to produce chlorinated rubber in painting and coating industries [1].

The chlorinated rubber is a kind of white powder product prepared by the chlorinated modification of natural rubber from solution or latex. Because of the properties such as good filming formation, unique acid-proof, alkali-proof, corrosion-resistance, anti-penetrability, inflame-resistance and thermal stability, the chlorinated rubber has been applied in the production of the raw materials for paints and adhesives, additive for ink, and acid-proof and alkali-proof products. For the preparation of chlorinated rubber, chlorine gas is used to perform the chlorination that causes environmental hazards and is harmful to the health of workers [2].

By chemical modification, natural rubber was used to prepare epoxidized natural rubber that the structure had oxygen ring on backbone chain called epoxide ring by epoxidation reaction. Then epoxidized natural rubber was reacted using sodium hypochlorite with/without sodium chloride (NaOCl/NaCl) by chlorination reaction because of convention and safety reaction from chlorine gas and low costs in the process. This research was developed to prepare chlorinated rubber from epoxidized natural rubber using NaOCl/NaCl and investigated on the effects of time, the ratio of substrate, NaOCl and NaCl, temperature and pH in chlorination reaction. Then the chlorinated rubber was determined chlorine content by X-Ray Fluorescence (XRF) and tested the thermal properties by Differential Scanning Calorimetry (DSC) and Thermogravimetry (TG)/Derivative Thermogravimetric analysis (DTG).

1.2 Objectives and Scope of the Research

1.2.1 Objectives

1. To develop the preparation of chlorinated rubber from epoxidized natural rubber using sodium hypochlorite with/without sodium chloride.
2. To study the thermal properties of chlorinated rubber.

1.2.2 Scope of the Research

In initial step, epoxidized natural rubber was prepared from natural rubber and peracetic acid. It was characterized by FT-IR and $^1\text{H-NMR}$. Then chlorinated rubber was prepared by using epoxidized natural rubber and sodium hypochlorite with/without sodium chloride. Effects of time, the ratio of substrate, sodium hypochlorite and sodium chloride, temperature and pH were investigated in chlorination reaction. The characterization of chlorinated rubber was studied by FT-IR, $^1\text{H-NMR}$ and XRF. Finally, the thermal properties of chlorinated rubber were studied by DSC and TG/DTG.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Natural Rubber

Natural rubber is obtained from the milky latex of various plants, but the only important commercial source of natural rubber is the tree *Hevea brasiliensis*. *Hevea brasiliensis* is a native of the tropical rain forest of the Amazon Basin in Brazil. Most of the world's natural rubber comes today from South-East Asia, mainly Thailand, Malaysia and Indonesia [3].

Natural rubber is a natural polymer that called polyisoprene (Figure 2.1).

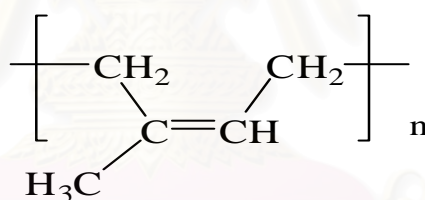


Figure 2.1 Structure of polyisoprene unit

Double bonds in the polymer chain can show *cis*- or *trans*-isomerism. The difference between the properties of the *cis*- and *trans*-isomers is apparent for naturally-occurring polyisoprene. *Gutta percha* is predominantly *trans*-1,4-polyisoprene, which has a regular structure that allows crystallization. As a result, *gutta percha* is hard and rigid. Natural rubber is *cis*-1,4-polyisoprene, which has a less symmetrical structure that does not allow easy crystallization. Natural rubber is an amorphous rubbery material (Figure 2.2) [4].

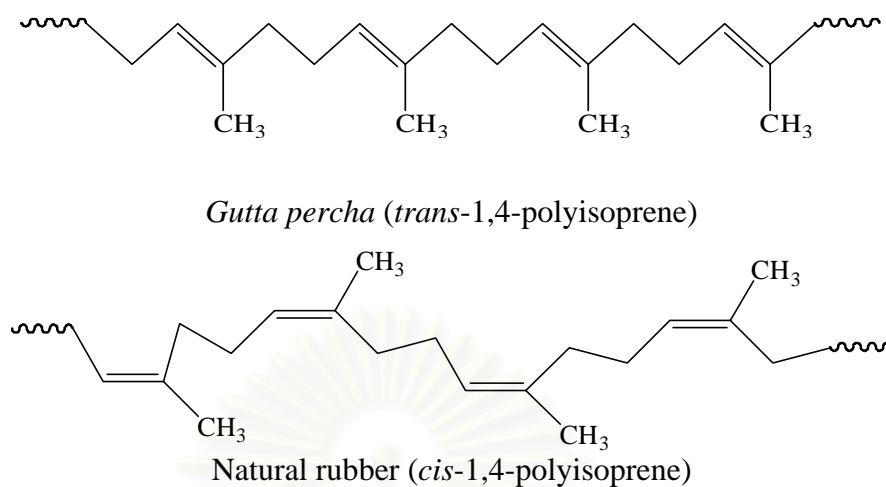


Figure 2.2 *Gutta percha* and natural rubber structures

Natural rubber latex, a milk-like liquid, comes from a layer of tiny tubes spiraling up the tree beneath the outer bark. Like milk, it is an emulsion particles suspended in water. Natural latex as it comes from the tree is known as field latex. Field latex is only about 36% rubber and 4% non-rubber substances. The non-rubber components include proteins, carbohydrates, liquids and inorganic salts. Its composition varies according to the clones of rubber, age of rubber tree and tapping method. The composition of typical field latex is presented in Table 2.1 [3,5].

Table 2.1 Composition of latex

Constituent	% Composition
Rubber particle	36.0
Proteinaceous substances	1.5
Sugar, Lipids, Resinous substances	2.5
Water	60.0

Natural rubber latex consists of hydrogen and carbon in the ratio expressed by C_5H_8 . It has a chemical structure of almost 100% *cis*-1,4-polyisoprene units. Physical properties of natural rubber may vary slightly due to the non-rubber constituents present and to the degree of crystallinity. When natural rubber is held

below 100°C, crystallization occurs, resulting in a change of density from 0.92 to about 0.95. Listed in Table 2.2 are some average physical properties [3].

Table 2.2 Physical properties of natural rubber

Physical property	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

2.2 Reactivity of Alkenes

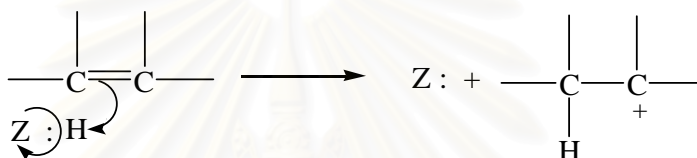
Before dealing with double bond reactivity in the particular environment of a long chain molecule it is worthwhile to summarize the general features of the reactivity of alkenes. The main point to be borne in mind are itemized below.

1. The peculiar reactions of alkenes stem entirely from the presence of the double bond although at points away from the double bond the alkene can also behave as an alkane.
2. The double bond consists of a strong σ bond and a weak π bond.
3. The π bond electrons, which lie in clouds above and below the plane of the atoms are less tightly held than the σ bond electron and may be considered as a source of electrons. In effect the double bond acts like a base.
4. These π bond electrons will tend to react with substances deficient in electrons, i. e. agents attracted to electrons (electrophilic agents, acids), by the process of electrophilic addition.

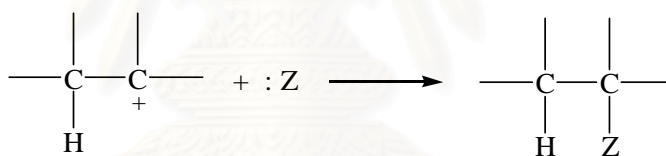
5. Free radicals are also attracted to electrons so that alkenes may also react with free radicals. Reactions affected by the presence of oxygen, peroxides, ultra-violet light and free-radical inhibitors such as hydroquinone, are indicative of being free radical reactions.

6. In the case of electrophilic addition (see 4 above) reaction is believed to proceed by two steps:

(a) Formation of a carbocation:



(b) Union of the carbocation with the nucleophile.



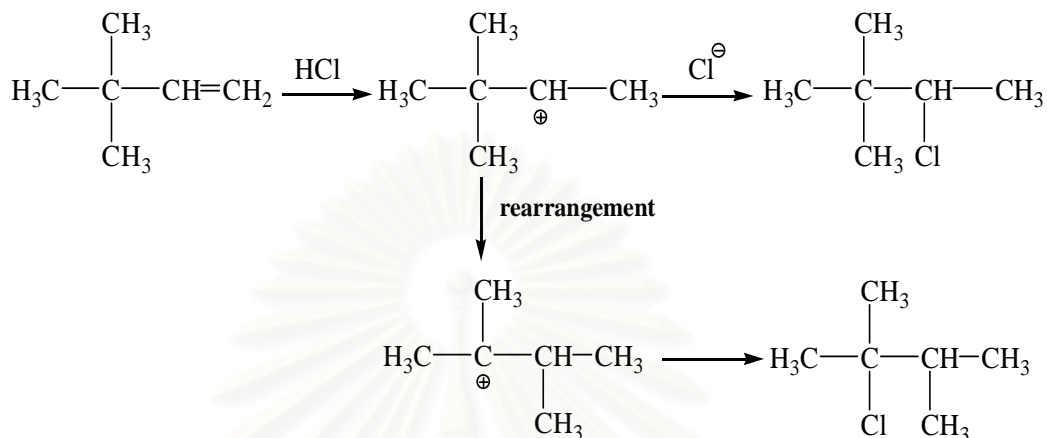
The first step is the most difficult and controls the overall rate of addition which need not only be the result of a Lowry-Brønsted acid transferring a proton but also the reaction of almost any kind of electron deficient molecule (Lewis Acid).

7. Tertiary cations are formed faster than secondary cations, which in turn are formed in preference to primary cations. (One may picture the alkyl groups as being able to push electrons to the far side of the double bond.)

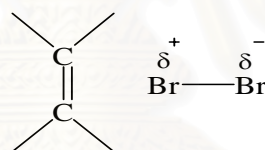
8. It is a direct consequence of 6 and 7 that a proton or other electrophile will add to the carbon with the most hydrogen atoms already attached (Markovnikov's Role).

9. Carbocations are liable to rearrangement. For example 3,3-dimethyl-1-butene yields not only 2-chloro-3,3-dimethyl butane but also 2-chloro-2,3-dimethyl

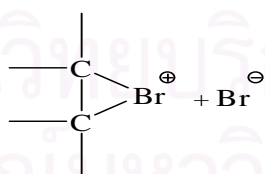
butane. Such a rearrangement can occur because the tertiary cation is more stable (as well as more reactive) than the secondary cation.



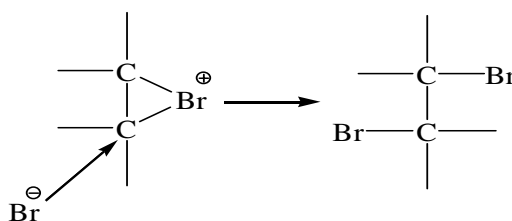
10. A halogen molecule may be polarized by the electric field of a double bond.



The more positive halogen is then abstracted by the alkene to form a cyclic halonium ion (rather than a carbonium ion) and a halide ion.



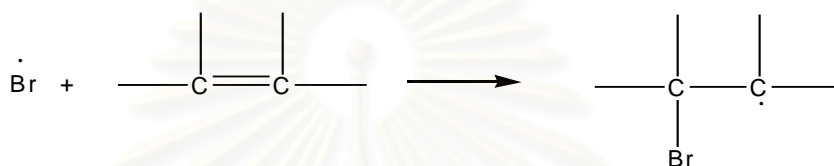
In the second step the halide ion attacks the halonium ion to yield the dihalide.



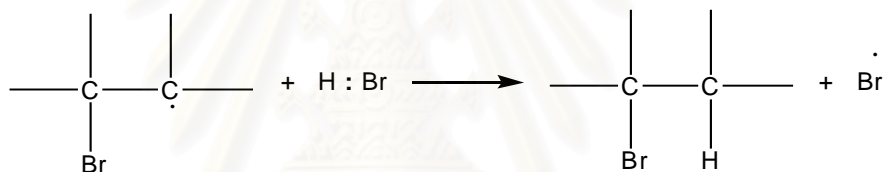
11. A number of alkene reactions involve free radicals (see 5 above). For example a free radical, produced by the decomposition of a peroxide will react with HBr to form bromine radicals.



This will react with the double bond to form a new radical



which then reacts with HBr.



It is interesting to note that, as with the carbocations, it is a tertiary radical which is in turn formed faster than a primary radical. However since in this case it is the free radical that adds on the hydrogen atom, then the hydrogen will go to the carbon containing the fewest hydrogen atoms (i. e. it will proceed by an anti-Markovnikov addition).

12. Whilst hydrogen atoms attached to double bond carbons (vinylic hydrogens) are difficult to abstract, those attached to the carbon atom adjacent to the double bond (allylic hydrogens) are very easy to abstract. It follows that the resulting allylic radicals are the most reactive and it is possible to build up a sequence of ease of abstraction of hydrogens from carbon atoms (and hence stability and reactivity of the resulting radical). Thus:



Since 1,4-polyisoprene has a secondary carbon atom at the double bond it follows that it is generally more reactive to both free radicals and to carbocations than 1,4-polybutadiene. The typical addition reactions associated with the double

bond suggest that the ultimate hydrogenated, halogenated, hydrohalogenated and isomerized diene polymers would have the same structure irrespective of the initial *cis-/trans-* ratio.

Those reactions of diene rubbers which show anti-Markovnikov addition, enhanced activity in the presence of peroxides and ultra-violet light, and inhibition by oxygen and chemicals such as hydroquinone, usually indicate that a free radical mechanism is operative.

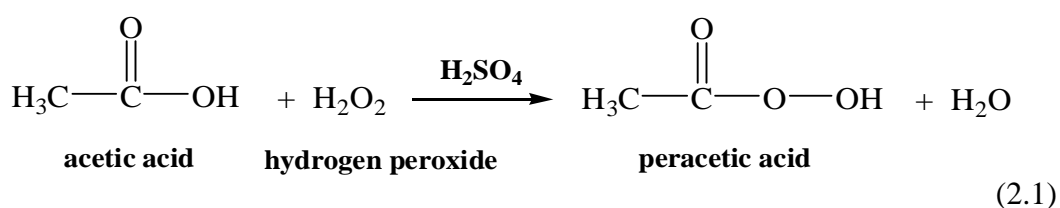
It is less easy to be certain that a mechanism is not free radical; many reactions at one time thought to be ionic have since been found to be of the free radical type. Indications may be obtained from a knowledge of the method of initiation, a Markovnikov addition and from a detailed analysis of the reaction kinetics.

The possibility that a reaction may involve movement of the double bond along the chain can usually be checked out by the use of deuterated compounds and a study of their spectra, or, perhaps less convincingly, by the use of model compounds [3].

2.3 Peracetic Acid

Peracetic acid is colourless liquid with a pungent, sour smell and is included in the chemical group of hydroperoxides. It is highly oxidant and corrosive and can explode at temperatures exceeding 110 °C. It is more fat-soluble than hydrogen peroxide.

Peracetic acid is produced by oxidation of acetaldehyde or by letting acetic acid react with hydrogen peroxide in the presence of a sulphuric acid catalyst that was showed in the Equation (2.1).



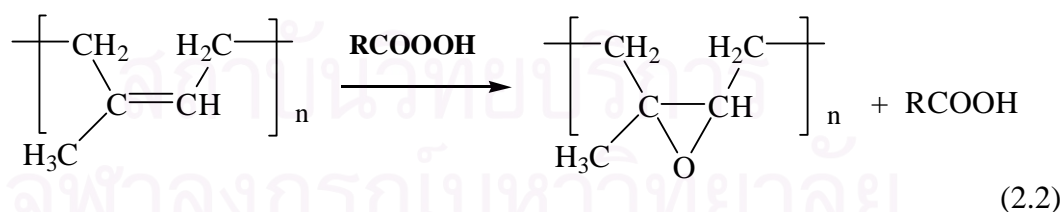
Peracetic acid is sold as a 40% solution in acetic acid. The mixture has to be stabilized with dipicoline acid, phytic acid or phosphates and a little hydrogen peroxide, to prevent the peracetic acid disintegrating too rapidly.

As a synthesis chemical, peracetic acid is used to add an oxygen atom to double bonds, e. g. in ethane and propene. In this way epoxides and alcohols can be formed and peracetic acid is used for production of synthetic glycerol (from propene). It is also used in nylon manufacturing.

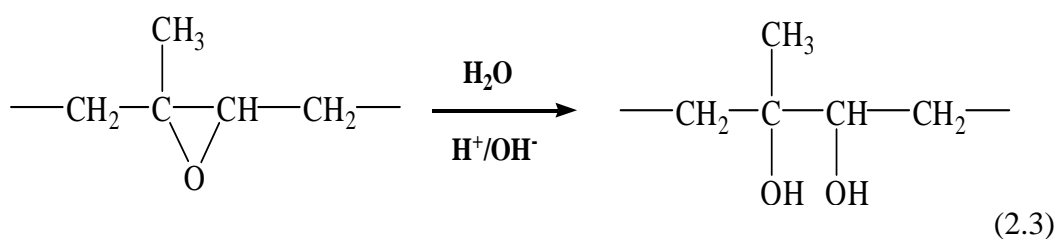
Peracetic acid can be used as a bleaching agent and for disinfection. Since it emits oxygen more readily and at lower temperatures than other bleaching agents, It is gentle on the material to be bleached or disinfected. It is broadly effective against micro organisms and is not deactivated by catalase and peroxidase, the enzymes which break down hydrogen peroxide. Peracetic acid is used especially in facilities for industrial handling of foodstuffs, because it acts at low temperature and low pH and the degradation product, acetic acid, seldom needs to be rinsed away [6].

2.4 Epoxidation Reaction and Ring Opening

Epoxidation is another typical modification reaction of unsaturated polymers. A variety of peroxides and peracids have been used to effect this transformation that were showed in the Equation (2.2).



It was found that the epoxidized natural rubber latex could be slightly hydrolysed under mildly acidic (pH 5) or alkaline (pH 11) conditions to diols by boiling the diluted latex for more than 30 min, when all the rubber coagulated out of the latex. It was showed in the Equation (2.3) [7].

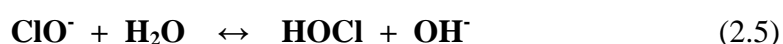
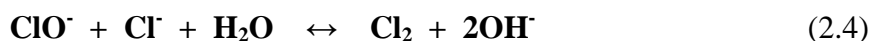


2.5 Chlorinated Natural Rubber

Chlorinated natural rubber is still nowadays an important industrial product. It is a thermoplastic powder that is nonflammable and resistant to chemical attack of both acid and basic solutions up to 100 °C. It is used mainly in the formulation of chemical- and heat-resistant paints and coatings by mixing in an opportune solvent at least 10% of chlorinated rubber with plasticizers and pigments. Chlorinated rubber is also used in the formulation of adhesives and printing inks [8].

2.6 Sodium Hypochlorite and Sodium Chloride

Sodium hypochlorite is a pale greenish liquid also known as soda bleach or liquid bleach. It can oxidize alcohols, aldehydes, electron deficient alkenes, amines and others. It is commercially available as aqueous solution with 5.25-12.5% available chlorine (w/v) (0.74-1.75 M). Concentration is expressed in % available chlorine, since half of chlorine in bleach is present as NaCl. The pH of commercial bleach is typically 11-12.5. The equilibrium composition of aqueous solutions of NaOCl is pH-dependent and so pH control can be a critical consideration in many oxidation and chlorination reaction. They were showed in the Equations (2.4) and (2.5).



Under strongly alkaline condition (pH > 12), OCl⁻ is the predominant form of positive chlorine. Because hypochlorite ion is insoluble in organic solvent, phase transfer catalysts are needed at this pH to effect oxidation reaction. Below pH 11, the

equilibrium amount of HOCl becomes significant and this form of positive chlorine is soluble in polar organic solvent such as CH₂Cl₂. No phase transfer catalysts is necessary to effect oxidation of substrates or catalysts dissolved in the pH range 10-11. Below pH 10, molecular chlorine becomes a significant component of aqueous bleach solutions and the reactivity of these solutions can be attributed to that of Cl₂ [9].

Sodium chloride or common salt is the chemical compound NaCl that composed of the elements sodium and chlorine. It forms in cubic crystals apparent even in table salt. It occurs commonly in the mineral form, halite, also called rocksalt. It can be formed by the acid-base reaction of hydrochloric acid sodium hydroxide that was showed in the Equation (2.6) below.



As a solid, sodium chloride is crystalline and forms a cubic lattice. The bonding of the sodium and chlorine atoms is one of the classic examples of ionic bonding. In aqueous solution it ionizes to Na⁺ and Cl⁻ ions and forms an electrically conducting solution. Sodium chloride exists on the earth in great abundance in sea water and is an important part of the fluid electrolytes of humans and other living organisms [10].

2.7 Literature Reviews

Epoxidation and chlorination reactions are widely used to modify natural rubber because they are simple, safe, cheap and easily available reaction. Therefore, a lot of approaches have been reported on various reactions which are listed as the following.

In 1984, Burfield, D. R. et al. [11] used high ammonia natural rubber latex, distilled water, glacial acetic acid, Vulcastab LW surfactant and peracetic acid in the epoxidation at 5 °C for 6 hours. They compared DSC, NMR, EA and direct titration methods for determining epoxide level of epoxidized natural rubber. They found that direct HBr titration gave fairly accurate information at low modification (<15 mol%).

Elemental analysis gave less satisfactory results. Tg data from DSC method related to epoxidation level through a calibration curve obtained from primary method such as NMR analysis. Both $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ provided the best results over the range of 20-75 mol% modification. The characteristic peaks of ENR were used in $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ analysis. In the $^1\text{H-NMR}$ analysis, the percentage of epoxidation modification was showed in Equation (2.7).

$$\text{Mol epoxidation (\%)} = 100 * \frac{A_{2.70}}{A_{5.14} + A_{2.70}} \quad (2.7)$$

$A_{2.70}$ = The integrated area of the proton adjacent to epoxide ring at 2.70 ppm

$A_{5.14}$ = The integrated area of the olefinic proton at 5.14 ppm

In 1984, Burfield, D. R. et al. [12] used high ammonia natural rubber latex (62% d.r.c.), Valcastab LW surfactant and 3 M peracetic acid to study in the epoxidation reaction. Investigated epoxidation routes include the use of bromohydrin intermediates, hydrogen-peroxide-catalyzed systems and preformed peracetic acid. The latter reagent allows almost quantitative epoxidation of natural rubber up to high modification levels with no detectable side reaction.

In 1985, Gelling, I. R. [13] used low ammonia natural rubber latex, Texofor A30 surfactant and 35% w/w peracetic acid in the epoxidation below 20 °C for 6 hours. He studied epoxidized natural rubber by IR spectroscopy and $^1\text{H-NMR}$. In the IR spectrum of ENR, there were absorptions at 870 and 1240 cm^{-1} . The $^1\text{H-NMR}$ spectrum revealed groups $\text{CH}_3\text{-CO}$ at 1.28 ppm, $\text{CH}_3\text{-C=C}$ at 1.65 ppm, CH-C-O at 2.70 ppm and CH=C at 5.05 ppm.

In 1991, Bac, N. V. et al. [14] used full ammonia natural rubber latex (57.7% d.r.c.), Verol S-15 surfactant, glacial acetic acid and peracetic acid in the 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 preformed peracetic acid. The epoxidation proceeded rapidly and effectively, leading to ENR products free of side ring-opening groups.

In 1991, Gelling, I. R. [1] used natural rubber latex and peroxyacetic acid to study epoxidation. A systematic study of the epoxidation of natural rubber latex with peroxyacetic acid solution revealed that high total acid concentrations and elevated temperatures favoured the formation of secondary ring-opened products. Two distinct types of ring-opened products were obtained depending principally on the level of epoxidation. At low levels of modification, the majority of epoxide groups are isolated and the main ring-opened products are those expected from simple epoxide chemistry (Figure 2.3).

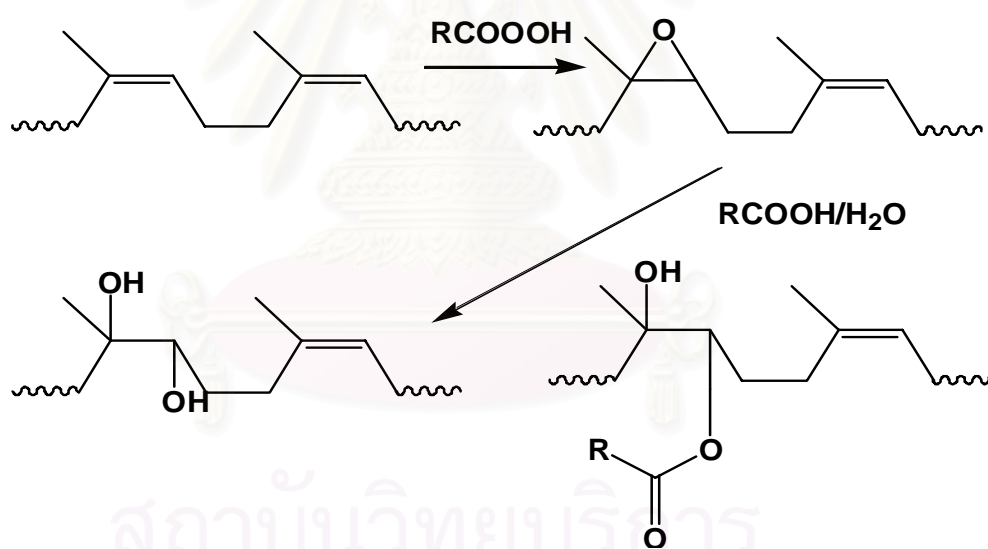


Figure 2.3 Epoxidation of natural rubber with a peroxyacid and secondary ring-opening of isolated epoxide groups

The final product is normally the trans diol, but dehydration of the tertiary alcohol can occur. As the level of modification is increased and hence, the number of adjacent epoxide groups, a five-membered cyclic ether becomes the major product. This arises from the attack of a ring-opened epoxide on the adjacent epoxide group

with the reaction proceeding along the rubber backbone until stopped by a non-epoxide group or steric considerations (Figure 2.4)

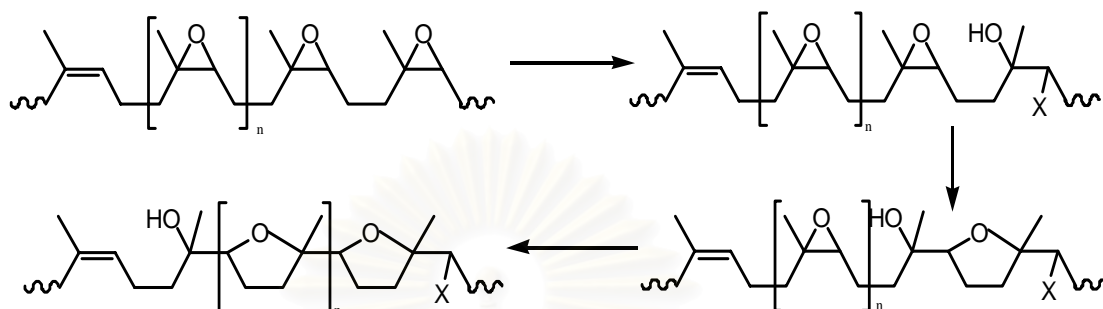


Figure 2.4 Ring-opening of adjacent epoxide groups to yield five-membered cyclic ethers

In 1985, Krentsel, L. B. et al. [15] used natural rubber and Cl_2/CCl_4 to prepare chlorinated natural rubber at room temperature. They studied the kinetics for the initial stage of CNR-1 (0.33 Cl/C₅) and CNR-2 (0.23 Cl/C₅). The products were chlorinated natural rubber and HCl that were showed chlorinated natural rubber unit in Figure 2.5.

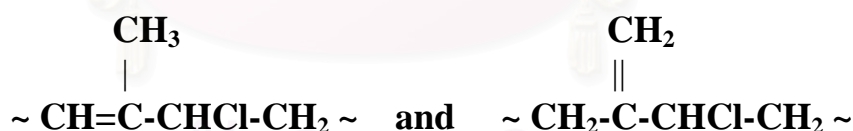


Figure 2.5 Structure of chlorinated natural rubber unit

In 1987, Kofman, V. L. et al. [16] used natural rubber and Cl_2/CCl_4 in chlorination at 20-50 °C that chlorinated natural rubber contained ≤ 1 Cl/C₅. They studied the initial stage of chlorinated natural rubber product structure. In IR spectrum, there were absorptions at 780 cm^{-1} of C-Cl and 910 cm^{-1} of $\text{CH}_2=\text{C}<$ that were increased but at 1378 cm^{-1} of $-\text{CH}_3$ was decreased when the Cl was increased in the chlorinated natural rubber.

In 1990, Eskina, M. V. et al. [17] used natural rubber and Cl_2/CCl_4 in chlorination. They studied the structure of chlorinated natural rubber by $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ data. In $^1\text{H-NMR}$ spectrum, the chlorinated natural rubber containing 0.6 Cl/C_5 were reported $-\underline{\text{C}}\text{H}$, $-\underline{\text{C}}\text{H}_2$, $-\underline{\text{C}}\text{H}_3$ at 1.5-2.8 ppm, $-\underline{\text{C}}\text{HCl}$ at 4.0-4.5 ppm and the olefinic proton at 4.8-5.6 ppm. In $^{13}\text{C-NMR}$ spectrum, the chlorinated natural rubber containing 0.4 Cl/C_5 were reported $-\underline{\text{C}}\text{H}_3$ at 23.6 ppm, $=\underline{\text{C}}\text{H}-\text{CH}_2-$ at 26.9 ppm, $-\underline{\text{C}}\text{H}_2-$ at 29.4 and 32.7 ppm, $=\underline{\text{C}}\text{H}-$ at 125.1 ppm and $>\underline{\text{C}}=$ at 135.2 ppm.

In 1992, Cataldo, F. [18] used 25 mol% epoxidized natural rubber and $\text{Cl}_2/\text{CH}_2\text{Cl}_2$ at room temperature for 2 hours to study the chlorination. The thermogravimetric analysis of chlorinated epoxidized natural rubber began to decompose between 90 and 130 °C and a plateau is reached with a weight loss of about 18%, probably due to first-stage dechlorination. The main decomposition starts at 260 °C with a weight loss in total of about 63%. The general formula of chlorinated epoxidized natural rubber was $\langle(\text{C}_5\text{H}_8\text{Cl}_{3.5})_{0.75n}(\text{C}_5\text{H}_8\text{O})_{0.25n}\rangle$. The DSC of chlorinated epoxidized natural rubber, two distinct endothermic peaks are found (one at 129 °C and the other at 158 °C) suggesting that this copolymer has a block type structure. Moreover, two distinct glass transitions have been detected. The first of these transitions, at -13 °C, has been assigned to the furanized portion of the chain, whereas that at 85 °C could be due to the chlorinated portion.

In 1995, Cataldo, F. [8] used liquid chlorine as chlorinating agent for preparation of chlorinated natural and synthetic rubbers. The FT-IR spectra of chlorinated natural and synthetic rubbers using liquid chlorine are indicated by the bands at 788, 706, 738, 668 and 640 cm^{-1} all for C-Cl stretching. Moreover, the strong band at 830 cm^{-1} present in the starting polymer and for *cis* =C-H bending has completely disappeared in the spectrum of the chlorinated product obtained.

In 1999, Zhong, J. P. et al. [19] used stabilized natural rubber latex, Cl_2 gas, concentrated chloric acid and distilled water to study the preparation of chlorinated natural rubber. The chlorination of natural rubber latex is carried out under the acidic

condition. The rate of chlorination is fast at early stage then slows down gradually.
The effect of temperature on the chlorination is not obvious.



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CHAPTER III

EXPERIMENTAL

3.1 Chemicals

1. Natural rubber latex : Revertex (Thailand) Ltd.
2. Tergitol NP10 : Union Carbide
3. Glacial acetic acid 100% : Carlo Erba Reagenti
4. Sulfuric acid 96% : Carlo Erba Reagenti
5. Hydrogen peroxide 50% : Merck
6. Sodium hypochlorite : Carlo Erba Reagenti
7. Sodium chloride : Merck
8. Sodium carbonate : Fluka
9. Methanol : Merck
10. Chloroform : 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 : Perkin Elmer, Nicolet (Impact 410)
4. Nuclear Magnetic Resonance Spectrometer : Bruker, ACF 400 MHz
5. X-Ray Fluorescence Spectrometer : Philips PW 2400
6. Differential Scanning Calorimeter : Mettler Toledo, DSC 822
7. Thermogravimetric analyzer : Perkin Elmer, Pyris Diamond

3.3 Experimental Procedure of Epoxidation

3.3.1 Preparation of Peracetic Acid [20]

The desired amounts of glacial acetic acid (90 g) and sulfuric acid (1.2 g) were added in a 500 ml round bottom flask. Then 50% hydrogen peroxide (153 g) was added dropwise and the mixture stirred at room temperature for 1 hour.

3.3.2 Preparation of Epoxidized Natural Rubber (ENR)

Natural rubber latex (60% d.r.c., 30 g) and distilled water (90 g) were added in a 600 ml beaker. The latex was stabilized with tergitol NP10 (5% by weight of natural rubber latex, 1.5 g) and the mixture stirred with a mechanical stirrer for 9 hours at room temperature. Then peracetic acid (200 ml, 3.31%) was added dropwise and the mixture stirred at 30-35°C for 30 minutes.

In the epoxidation, latex sample was taken at 30 minutes and isolated by pouring into methanol. The coagulum was washed to remove free acid by distilled water and then soaked in a 0.1 M Na₂CO₃ solution for 24 hours at room temperature. The resulting product was washed with distilled water until pH of 7 and then dried at 80°C to have constant weight before characterization.

3.4 Characterization of Epoxidized Natural Rubber

3.4.1 FT-IR Spectroscopy

Samples for FT-IR analysis were scanned on films of polymer cast on NaCl plate from chloroform solutions.

3.4.2 $^1\text{H-NMR}$ Spectroscopy

Samples for $^1\text{H-NMR}$ analysis were prepared by dissolving the material in deuterated chloroform. The epoxidation level of epoxidized natural rubber was calculated using the equation [11]:

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

$A_{2.70}$: The integrated area of the proton adjacent to epoxide ring at 2.70 ppm

$A_{5.14}$: The integrated area of the olefinic proton at 5.14 ppm

3.5 Experimental Procedure of Chlorination

3.5.1 Preparation of Chlorinated Rubber

ENR (80 g) and Tergitol NP10 (20 g) were added in a 500 ml round bottom flask. Then glacial acetic acid (160 ml) was added and the mixture was stirred. After stirring, the chlorinated rubber was poured into methanol. The coagulum was washed to remove free acid by distilled water and then soaked in a 0.1 M Na_2CO_3 solution for 24 hours at room temperature. The resulting product was washed with distilled water until pH of 7 and then dried at 80°C to have constant weight before characterization.

3.5.1.1 Effect of Time

The reaction time was studied for 1, 2, 4 and 6 hours at 30°C by varying the ratio of substrate, sodium hypochlorite and sodium chloride.

3.5.1.2 Effect of the Ratio of Substrate, Sodium Hypochlorite (NaOCl) and Sodium Chloride (NaCl)

The ratio of substrate, sodium hypochlorite (NaOCl) and sodium chloride (NaCl) were studied when the substrate (ENR) was constant weight of 80 g at 30°C. The ratio of NaOCl and NaCl (by mol) consist of 0:1, 1:0, 1:1, 1:2, 1:4, 2:1 and 4:1 were investigated.

3.5.1.3 Effect of Temperature

The reaction temperature was studied at 10, 20, 30 and 40°C for 6 hours using the highest chlorine content ratio.

3.5.1.4 Effect of pH

The pH of chlorination reaction was varied at 1, 2, 3 and 4 for 6 hours. The pH was adjusted by using glacial acetic acid and 0.1 M sodium carbonate. The highest chlorine content ratio was used to study pH at 30°C.

3.6 Characterization of Chlorinated Rubber

3.6.1 FT-IR Spectroscopy

Samples for FT-IR analysis were scanned on films of polymer cast on NaCl plate from chloroform solutions.

3.6.2 ¹H-NMR Spectroscopy

Samples for ¹H-NMR analysis were prepared by dissolving the material in deuterated chloroform.

3.6.3 X-Ray Fluorescence Spectroscopy

Samples for XRF analysis were a solid state. They were determined the chlorine content by Philips PW 2400 X-Ray Fluorescence Spectrometer.

3.7 Thermal Properties

3.7.1 Differential Scanning Calorimetry (DSC)

The 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 [21].

The DSC is used to measure the T_g , T_m , heats of crystallization and fusion, degree of cure of thermosets, heats of curing reactions, oxidative stability, heats of decomposition (dehydration), heats of vaporization and heats of solution [22].

In this research, the DSC used to evaluate the thermal properties of the natural rubber, epoxidized natural rubber and chlorinated rubber was a Mettler Toledo, DSC 822. The sample of 10 mg was placed in aluminum pan. The DSC was carried out under N_2 atmosphere at heating rate of $10^\circ C/min$ from $-100^\circ C$ to $200^\circ C$.

3.7.2 Thermogravimetry (TG)/Derivative Thermogravimetric Analysis (DTG)

Thermogravimetry (TG)/ Derivative Thermogravimetric analysis (DTG) dealt specifically with the change in mass of a sample as a function of temperature [23].

Thermogravimetry (TG)/Derivative Thermogravimetric analysis (DTG) was performed on Thermogravimetric analyzer (Perkin Elmer, Pyris Diamond). The

TG/DTG of the natural rubber, epoxidized natural rubber and chlorinated rubber was carried out under N₂ atmosphere at heating rate of 10°C/min from 30°C to 700°C.



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CHAPTER IV

RESULTS AND DISCUSSION

In this research, chlorinated rubber was prepared by chlorination reaction of epoxidized natural rubber using sodium hypochlorite with/without sodium chloride (NaOCl/NaCl). The compatibility of reaction time, the ratio of substrate, NaOCl and NaCl, reaction temperature and pH were determined. Then the thermal properties of the chlorinated rubber was determined by Differential Scanning Calorimetry (DSC) and Thermogravimetry (TG)/Derivative Thermogravimetric analysis (DTG).

4.1 Preparation and Characterization of Epoxidized Natural Rubber

Epoxidized natural rubber was obtained from epoxidation reaction between stabilized natural rubber (NR) and peracetic acid (200 ml, 3.31%). Reaction temperature of 30-35 °C was maintained for 30 minutes. The important factor on epoxidation reaction was suitable time, temperature and quantity of peracetic acid. The %yield of epoxidized natural rubber product was obtained to be 89.72%.The mechanism of the epoxidation reaction is showed in Figure 4.1 [24]. From the mechanism, the peracetic acid transfers an oxygen atom to the natural rubber in a cyclic, single-step mechanism. The resulting product are epoxidized natural rubber and acetic acid.

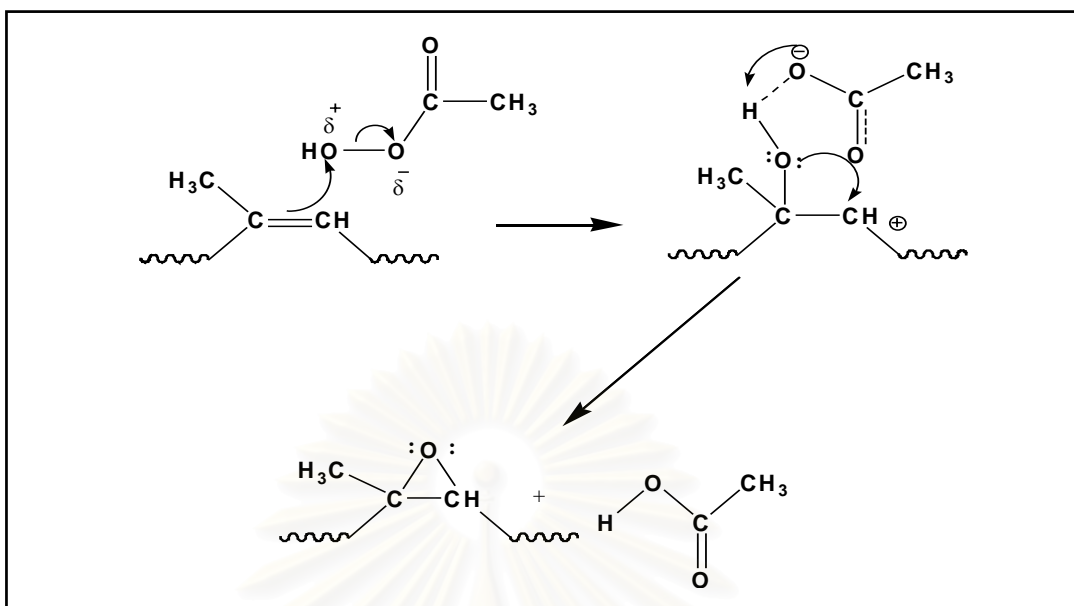


Figure 4.1 The mechanism of epoxidation reaction [24]

ENR was characterized by FT-IR and $^1\text{H-NMR}$ spectroscopies. The epoxidation level of ENR was calculated from $^1\text{H-NMR}$.

4.1.1 FT-IR Spectra

Samples for FT-IR analysis were scanned on films of polymer cast on NaCl plate from chloroform solutions. The FT-IR spectra of NR and ENR are shown in Figures 4.2-4.3, and the important peaks and their assignments are given in Table 4.1. The FT-IR spectrum of NR (Figure 4.2) showed the bands at 3434 cm^{-1} for OH stretching, 2959 cm^{-1} for CH-aliphatic, 1658 cm^{-1} for C=C stretching and 1375 and 1448 cm^{-1} all for CH_2 , CH_3 . The FT-IR spectrum of ENR (Figure 4.3) showed the bands at 3462 cm^{-1} for OH stretching, 2963 cm^{-1} for CH-aliphatic, 1660 cm^{-1} for C=C stretching, 1378 and 1452 cm^{-1} all for CH_2 , CH_3 and 875 cm^{-1} for epoxide rings. In comparison with the FT-IR spectrum of NR, the FT-IR of ENR with NR indicated the presence of a specific epoxide rings band at 875 cm^{-1} . In addition, the OH stretching of ENR at 3462 cm^{-1} was observed, while the C=C stretching of ENR at approximately 1660 cm^{-1} was decreased.

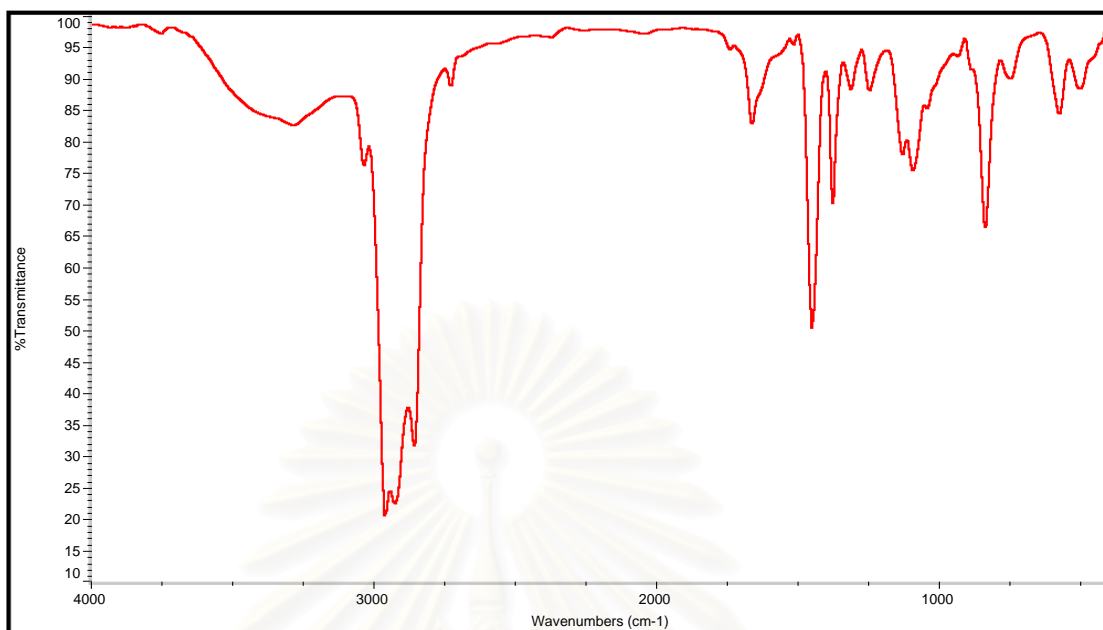


Figure 4.2 FT-IR spectrum of NR



Figure 4.3 FT-IR spectrum of ENR

Table 4.1 FT-IR spectral data of NR and ENR

Vibration assignments	Wavenumber (cm ⁻¹)	
	NR	ENR
OH stretching	3434	3462
CH-aliphatic	2959	2963
C=C stretching	1658	1660
CH ₂ , CH ₃	1375,1448	1378,1452
C-O epoxy ring	-	875

4.1.2 ¹H-NMR Spectra

The ¹H-NMR spectra of NR and ENR in deuterated chloroform were determined as showed in Figures 4.4-4.5. The important proton signals and their assignments are listed in table 4.2. The epoxidation level of ENR was calculated using Equation 2.7 (page 13). The ¹H-NMR spectrum of NR consisted of protons of methyl group adjacent to double bond (CH₃-C=C) at δ 1.68 ppm, -CH₂- at δ 2.10 ppm and a proton of the double bond (CH=C) at δ 5.14 ppm. The ¹H-NMR spectrum of ENR consisted of protons of methyl group adjacent to epoxide group (CH₃-CO) at δ 1.28 ppm, protons of methyl group adjacent to double bond (CH₃-C=C) at δ 1.68 ppm, -CH₂- at δ 2.10 ppm, the proton of the epoxide group (CH-C-O) at δ 2.70 ppm and a proton of the double bond (CH=C) at δ 5.14 ppm.

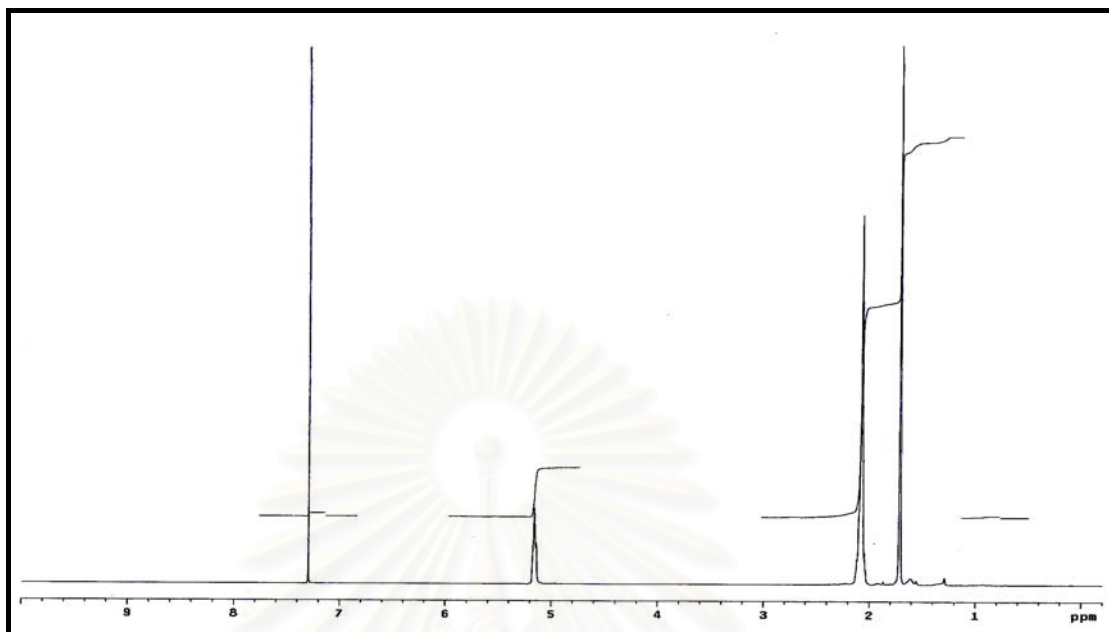


Figure 4.4 $^1\text{H-NMR}$ spectrum of NR

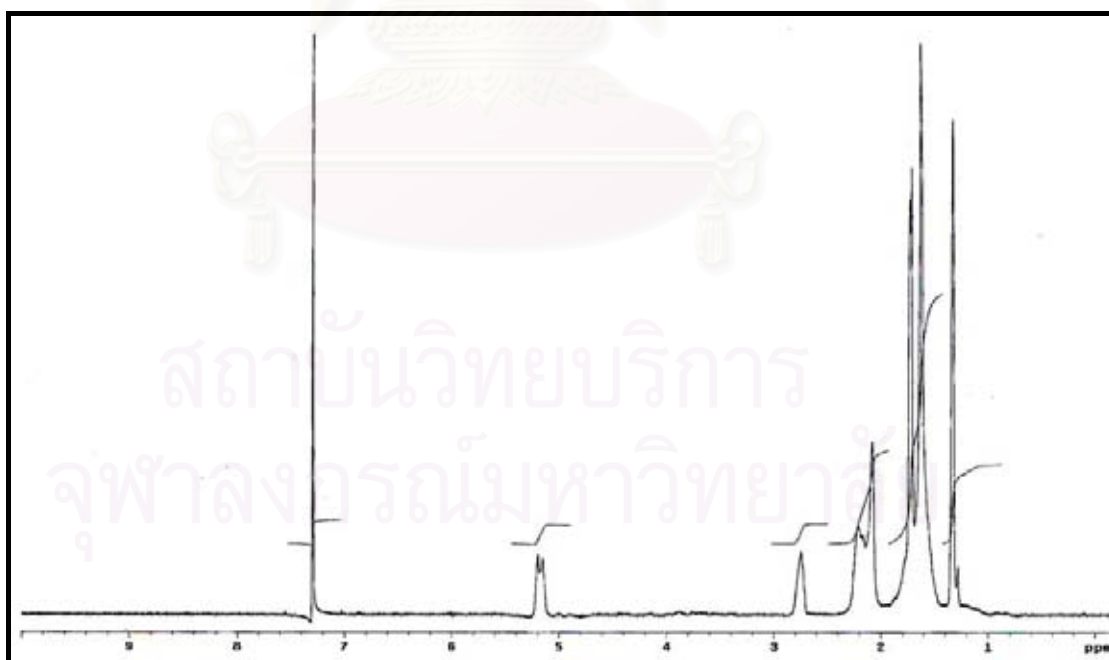


Figure 4.5 $^1\text{H-NMR}$ spectrum of ENR

Table 4.2 $^1\text{H-NMR}$ signal data of NR and ENR

A type of proton atom	Chemical shift (ppm)	
	NR	ENR
$\underline{\text{C}}\text{H}_3\text{-CO}$	-	1.28
$\underline{\text{C}}\text{H}_3\text{-C=C}$	1.68	1.68
$\text{-}\underline{\text{C}}\text{H}_2\text{-}$	2.10	2.10
$\underline{\text{C}}\text{H-C-O}$	-	2.70
$\underline{\text{C}}\text{H=C}$	5.14	5.14

The calculation of Mol epoxidation (%) as showed below:

$$\text{Mol epoxidation (\%), } A_{2.70} = 11.41$$

$$A_{5.14} = 9.37$$

$$\begin{aligned} \text{Mol epoxidation (\%)} &= 100 * \frac{11.41}{9.37+11.41} \\ &= 55\% \end{aligned}$$

4.2 Preparation and Characterization of Chlorinated Rubber

Chlorinated rubber (CR) was prepared from chlorination reaction by using ENR (80 g), Tergitol NP10 (20 g), glacial acetic acid (160 ml) and sodium hypochlorite/sodium chloride. The %yield of chlorinated rubber product is presented in Table 4.3. Effects of time, the ratio of substrate, sodium hypochlorite and sodium chloride, temperature and pH were studied. The mechanism of the chlorination reaction is presented in Figure 4.6 [15, 25, 26] :

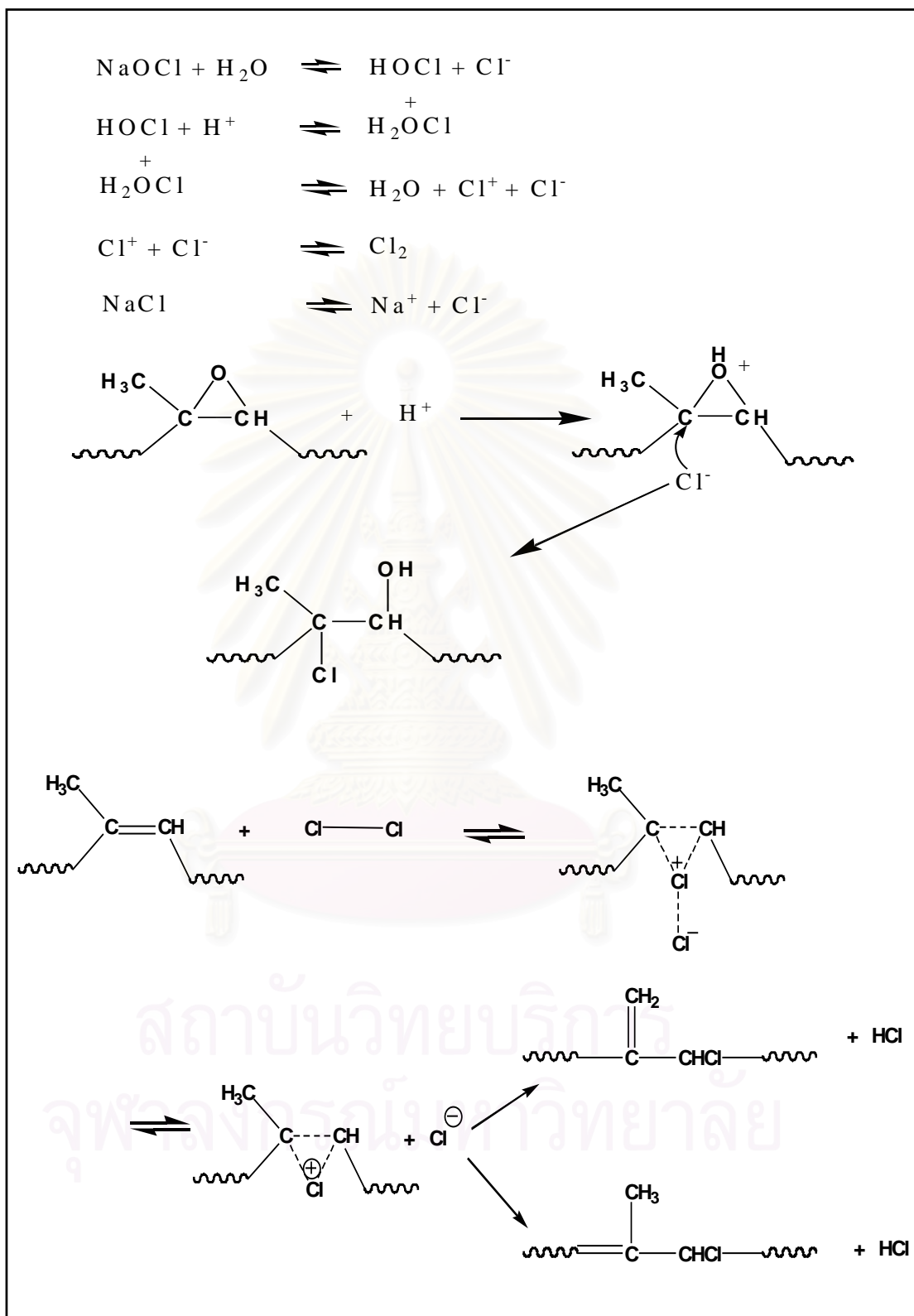


Figure 4.6 The mechanism of chlorination reaction

Table 4.3 %yield of CR

NaOCl:NaCl (by mol)	Temperature (°C)	pH	%yield (%)			
			Time (hours)			
			1	2	4	6
0:1	30	1	175.00	235.79	293.68	314.21
1:0	30	1	276.05	288.16	310.79	321.58
1:1	30	1	178.68	210.53	242.37	275.79
1:2	30	1	162.89	218.16	340.00	368.16
1:4	30	1	136.05	250.53	280.00	411.84
2:1	30	1	161.05	206.32	238.16	289.21
4:1	30	1	149.47	166.32	184.21	245.79
1:4	10	1	-	-	-	337.12
1:4	20	1	-	-	-	369.11
1:4	30	1	-	-	-	428.65
1:4	40	1	-	-	-	378.74
1:4	30	1	-	-	-	399.18
1:4	30	2	-	-	-	358.53
1:4	30	3	-	-	-	310.27
1:4	30	4	-	-	-	120.41

CR was characterized by FT-IR, ¹H-NMR and XRF spectroscopies.

4.2.1 FT-IR Spectra

Samples for FT-IR analysis were scanned on films of polymer cast on NaCl plate from chloroform solutions. The FT-IR spectra of CR given in Appendix A showed the bands at 3350-3480 cm⁻¹ for OH stretching, 2960-2975 cm⁻¹ for CH-aliphatic, 1365-1456 cm⁻¹ for CH₂, CH₃, 1070-1080 cm⁻¹ for C-O stretching and 740-760 cm⁻¹ for C-Cl stretching. Effects of time and the ratio of substrate, sodium hypochlorite and sodium chloride were presented in Figures A1-A7. The FT-IR of CR were showed the important band at 740-760 cm⁻¹ for C-Cl stretching. Effect of

temperature of FT-IR spectra of CR showed in Figure A8. It was found that the C-Cl stretching band was weak band as low temperature. Effect of pH is shown in Figure A9. The C-Cl stretching band was strong band at low pH. Table 4.4 provides the important peaks and their assignments.

Table 4.4 FT-IR spectral data of CR

Figure	Wavenumber (cm ⁻¹)				
	OH stretching	CH-aliphatic	CH ₂ , CH ₃	C-O stretching	C-Cl stretching
A1 (a)	3428	2965	1377,1453	1073	758
A1 (b)	3433	2964	1375,1453	1071	758
A1 (c)	3416	2967	1368,1455	1074	757
A1 (d)	3411	2968	1374,1454	1072	755
A2 (a)	3418	2962	1375,1454	1074	758
A2 (b)	3437	2964	1368,1448	1073	765
A2 (c)	3436	2964	1376,1453	1074	756
A2 (d)	3425	2967	1368,1454	1076	758
A3 (a)	3428	2960	1368,1441	1072	745
A3 (b)	3440	2967	1375,1453	1072	756
A3 (c)	3447	2969	1375,1454	1072	755
A3 (d)	3440	2967	1375,1448	1072	754
A4 (a)	3433	2963	1368,1454	1073	756
A4 (b)	3440	2964	1368,1454	1071	756
A4 (c)	3418	2964	1375,1448	1074	751
A4 (d)	3411	2968	1375,1454	1073	756

Table 4.4 (continued) FT-IR spectral data of CR

Figure	Wavenumber (cm ⁻¹)				
	OH stretching	CH-aliphatic	CH ₂ , CH ₃	C-O stretching	C-Cl stretching
A5 (a)	3433	2964	1368,1448	1072	751
A5 (b)	3433	2960	1381,1441	1073	755
A5 (c)	3433	2968	1368,1455	1072	756
A5 (d)	3425	2966	1368,1454	1072	755
A6 (a)	3425	2967	1368,1447	1071	751
A6 (b)	3433	2969	1368,1454	1071	755
A6 (c)	3476	2969	1375,1454	1071	754
A6 (d)	3469	2972	1368,1454	1070	755
A7 (a)	3353	2960	1368,1448	1072	752
A7 (b)	3382	2964	1368,1448	1073	751
A7 (c)	3382	297	1381,1454	1072	745
A7 (d)	3396	2967	1375,1448	1073	745
A8 (a)	3426	2971	1378,1455	1076	775
A8 (b)	3433	2960	1374,1454	1076	755
A8 (c)	3411	2971	1378,1455	1079	754
A8 (d)	3418	2970	1375,1456	1076	755
A9 (a)	3418	2971	1375,1456	1072	755
A9 (b)	3418	2969	1373,1455	1076	755
A9 (c)	3418	2964	1374,1456	1071	776
A9 (d)	3411	2963	1378,1452	1072	748

4.2.2 ¹H-NMR Spectra

The ¹H-NMR spectra of CR in deuterated chloroform were determined, as shown in Appendix B. The ¹H-NMR spectra of CR consisted of protons of methyl group adjacent to epoxide group ($\text{CH}_3\text{-CO}$) at δ 0.50-1.20 ppm, protons of methyl group adjacent to double bond ($\text{CH}_3\text{-C=C}$) at δ 1.20-1.70 ppm, $\text{-CH}_2\text{-}$ at δ 1.80-2.10 ppm, C-OH at δ 3.40-3.42 ppm, CH-Cl at δ 3.30-4.20 ppm and a proton of the double bond (CH=C) at δ 5.14 ppm. Effects of time and the ratio of substrate, sodium hypochlorite and sodium chloride are presented in Figures B1-B7. Effect of temperature is shown in Figure B8, and effect of pH is shown in Figure B9. The ¹H-NMR spectra of CR showed the important signal of CH-Cl at δ 3.30-4.20 ppm. Table 4.5 provides the important proton signals and their assignments.

Table 4.5 ¹H-NMR signal data of CR

Figure	Chemical shift (ppm)					
	$\text{CH}_3\text{-CO}$	$\text{CH}_3\text{-C=C}$	$\text{-CH}_2\text{-}$	C-OH	CH-Cl	CH=C
B1 (a)	1.18	1.65	2.10	3.40	3.50-4.20	5.14
B1 (b)	1.18	1.65	2.10	3.40	3.50-4.20	5.14
B1 (c)	1.18	1.65	2.10	3.40	3.60-4.20	5.14
B1 (d)	1.18	1.65	2.10	3.40	3.60-4.20	5.14
B2 (a)	1.18	1.65	2.10	3.40	3.50-4.20	5.14
B2 (b)	1.18	1.65	2.10	3.40	3.50-4.20	5.14
B2 (c)	1.18	1.65	2.10	3.40	3.50-4.20	5.14
B2 (d)	1.18	1.65	2.10	3.40	3.60-4.20	5.14
B3 (a)	1.18	1.68	2.10	3.40	3.50-4.18	5.14
B3 (b)	1.18	1.68	2.10	3.40	3.50-4.18	5.14
B3 (c)	1.18	1.68	2.10	3.40	3.50-4.18	5.14
B3 (d)	1.18	1.68	2.10	3.40	3.50-4.18	5.14

Table 4.5 (continued) $^1\text{H-NMR}$ signal data of CR

Figure	Chemical shift (ppm)					
	$\text{CH}_3\text{-CO}$	$\text{CH}_3\text{-C=C}$	$\text{-CH}_2\text{-}$	C-OH	CH-Cl	CH=C
B4 (a)	1.18	1.70	2.10	3.40	3.50-4.18	5.14
B4 (b)	1.18	1.70	2.10	3.40	3.50-4.18	5.14
B4 (c)	1.18	1.70	2.10	3.40	3.50-4.18	5.14
B4 (d)	1.18	1.70	2.10	3.40	3.50-4.18	5.14
B5 (a)	1.18	1.68	2.10	3.40	3.50-4.20	5.14
B5 (b)	1.18	1.68	2.10	3.40	3.50-4.20	5.14
B5 (c)	1.18	1.68	2.10	3.40	3.50-4.20	5.14
B5 (d)	1.18	1.68	2.10	3.40	3.50-4.20	5.14
B6 (a)	1.18	1.68	2.10	3.40	3.60-4.20	5.14
B6 (b)	1.18	1.68	2.10	3.40	3.60-4.20	5.14
B6 (c)	1.18	1.68	2.10	3.40	3.60-4.20	5.14
B6 (d)	1.18	1.68	2.10	3.40	3.60-4.20	5.14
B7 (a)	1.18	1.68	1.90	3.40	3.60-4.20	5.14
B7 (b)	1.18	1.68	1.90	3.40	3.60-4.20	5.14
B7 (c)	1.18	1.68	1.90	3.40	3.60-4.20	5.14
B7 (d)	1.18	1.68	1.90	3.40	3.50-4.20	5.14
B8 (a)	1.18	1.65	1.90	-	3.50-4.18	5.14
B8 (b)	0.80	1.25	1.90	-	3.60-4.20	5.14
B8 (c)	1.18	1.65	1.90	3.42	3.50-4.20	5.14
B8 (d)	1.18	1.65	1.90	3.42	3.50-4.20	5.14
B9 (a)	1.15	1.65	2.10	3.40	3.60-4.20	5.14
B9 (b)	1.15	1.65	2.10	3.42	3.50-4.20	5.14
B9 (c)	1.15	1.65	2.10	3.42	3.50-4.20	5.14
B9 (d)	1.35	1.65	2.10	-	3.50-4.20	5.14

4.2.3 XRF spectra

The %chlorine content was determined and calculated by XRF using Philips PW 2400 X-Ray Fluorescence Spectrometer. Samples for XRF analysis were a solid state. The XRF spectra of CR are shown in Appendix C. Table 4.6 shown chlorine content in CR. Effects of time and the ratio of substrate, sodium hypochlorite and sodium chloride presented in Figures C1-C7. The %chlorine content increased when the reaction time was increased. At high ratio of NaOCl, the %chlorine content decreased because amount of the NaOCl was excessed for chlorination reaction. Results are shown in Table 4.7 and Figure 4.7. At high ratio of NaCl, the %chlorine content was increased, as shown in Table 4.8 and Figure 4.8 . Effect of temperature is shown in Figure C8. The chlorination of ENR latex and NaOCl/NaCl that was carried out at middle temperature such as 30-40°C gave the high %chlorine content. Results are shown in Table 4.9 and Figure 4.9. Effect of pH is shown in Figure C9. The chlorination reaction was taken in an acidic condition at pH of 1. The results are shown in Table 4.10 and Figure 4.10.

Table 4.6 Chlorine content in CR

NaOCl:NaCl (by mol)	Figure	Temperature (°C)	pH	Chlorine content (%)			
				Time (hours)			
				1	2	4	6
0:1	C1 (a)-(d)	30	1	0.38±0.10	1.79±0.10	3.58±0.15	5.13±0.15
1:0	C2 (a)-(d)	30	1	4.44±0.10	8.59±0.10	12.54±0.15	15.31±0.15
1:1	C3 (a)-(d)	30	1	1.09±0.10	2.52±0.10	4.66±0.15	8.13±0.15
1:2	C4 (a)-(d)	30	1	1.52±0.10	3.28±0.10	6.82±0.15	11.32±0.15
1:4	C5 (a)-(d)	30	1	4.59±0.10	7.87±0.10	16.05±0.15	19.09±0.15
2:1	C6 (a)-(d)	30	1	0.97±0.10	1.64±0.10	3.36±0.15	6.45±0.15
4:1	C7 (a)-(d)	30	1	0.35±0.10	1.09±0.10	2.04±0.15	3.66±0.15
1:4	C8 (a)	10	1	-	-	-	6.25±0.10
1:4	C8 (b)	20	1	-	-	-	7.03±0.10
1:4	C8 (c)	30	1	-	-	-	19.06±0.10
1:4	C8 (d)	40	1	-	-	-	18.98±0.10
1:4	C9 (a)	30	1	-	-	-	19.02±0.15
1:4	C9 (b)	30	2	-	-	-	17.10±0.15
1:4	C9 (c)	30	3	-	-	-	5.11±0.15
1:4	C9 (d)	30	4	-	-	-	0.34±0.15

Table 4.7 Chlorine content in CR derived various ratio of NaOCl

NaOCl:NaCl (by mol)	Figure	Chlorine content (%)			
		Time (hours)			
		1	2	4	6
1:1	C3 (a)-(d)	1.09	2.52	4.66	8.13
2:1	C6 (a)-(d)	0.97	1.64	3.36	6.45
4:1	C7 (a)-(d)	0.35	1.09	2.04	3.66

Table 4.8 Chlorine content in CR derived various ratio of NaCl

NaOCl:Na Cl (by mol)	Figure	Chlorine content (%)			
		Time (hours)			
		1	2	4	6
1:1	C3 (a)-(d)	1.09	2.52	4.66	8.13
1:2	C4 (a)-(d)	1.52	3.28	6.82	11.32
1:4	C5 (a)-(d)	4.59	7.87	16.05	19.09

Table 4.9 Chlorine content in CR derived various temperature

Temperature (°C)	Figure	Chlorine content (%)
10	C8 (a)	6.25
20	C8 (b)	7.03
30	C8 (c)	19.06
40	C8 (d)	18.98

Table 4.10 Chlorine content in CR derived various pH

pH	Figure	Chlorine content (%)
1	C9 (a)	6.25
2	C9 (b)	7.03
3	C9 (c)	19.06
4	C9 (d)	18.98

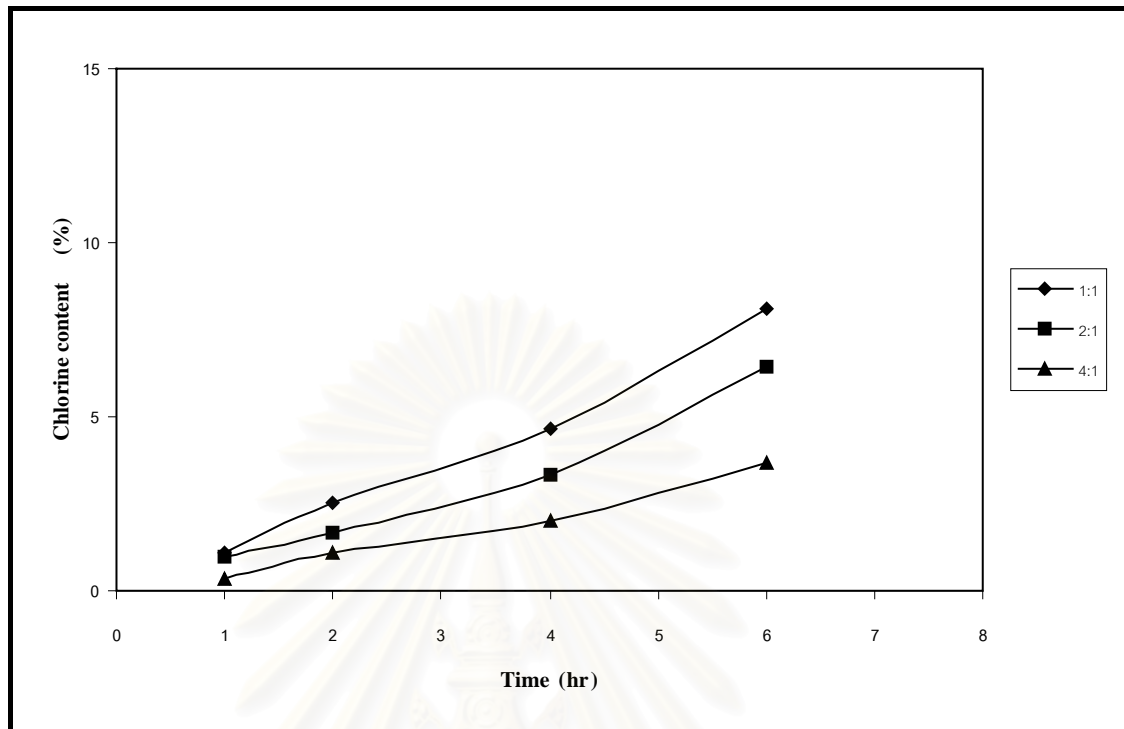


Figure 4.7 Chlorine content in CR derived various ratio of NaOCl

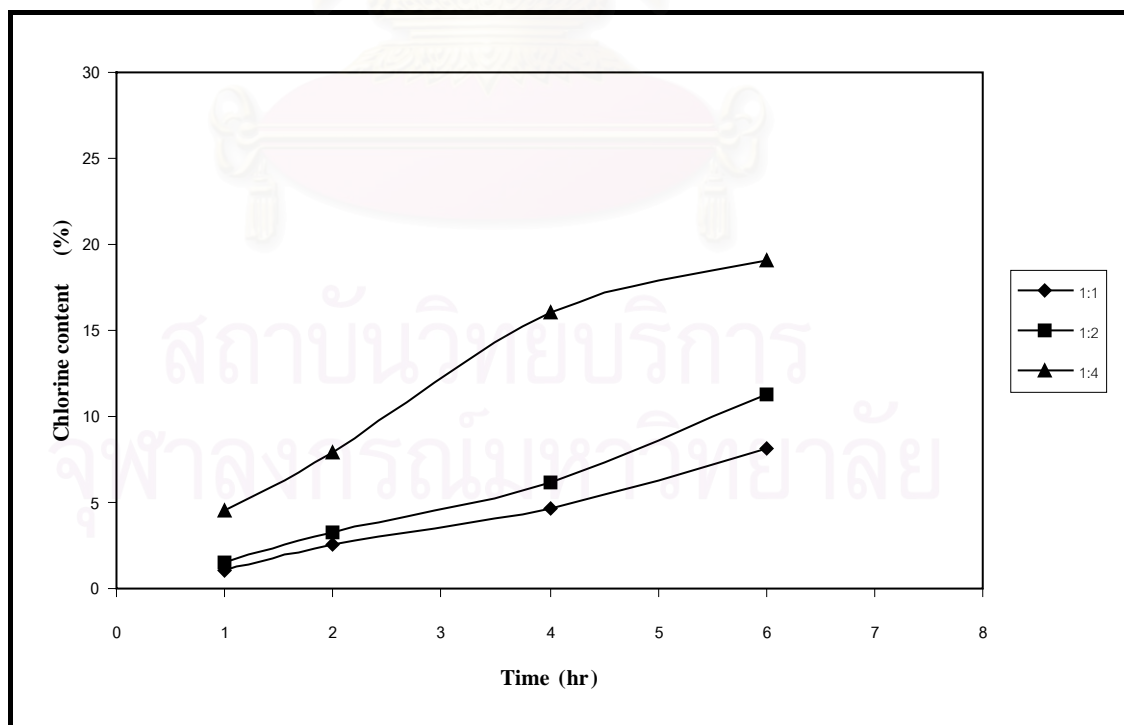


Figure 4.8 Chlorine content in CR derived various ratio of NaCl

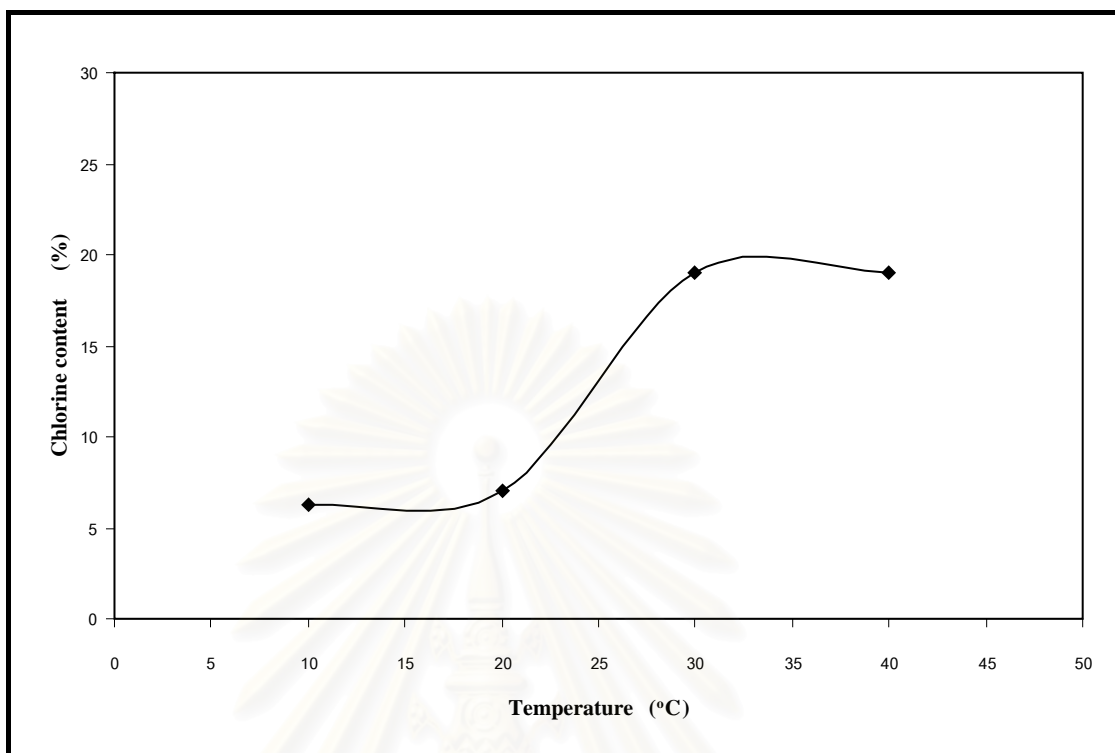


Figure 4.9 Chlorine content in CR derived various temperature

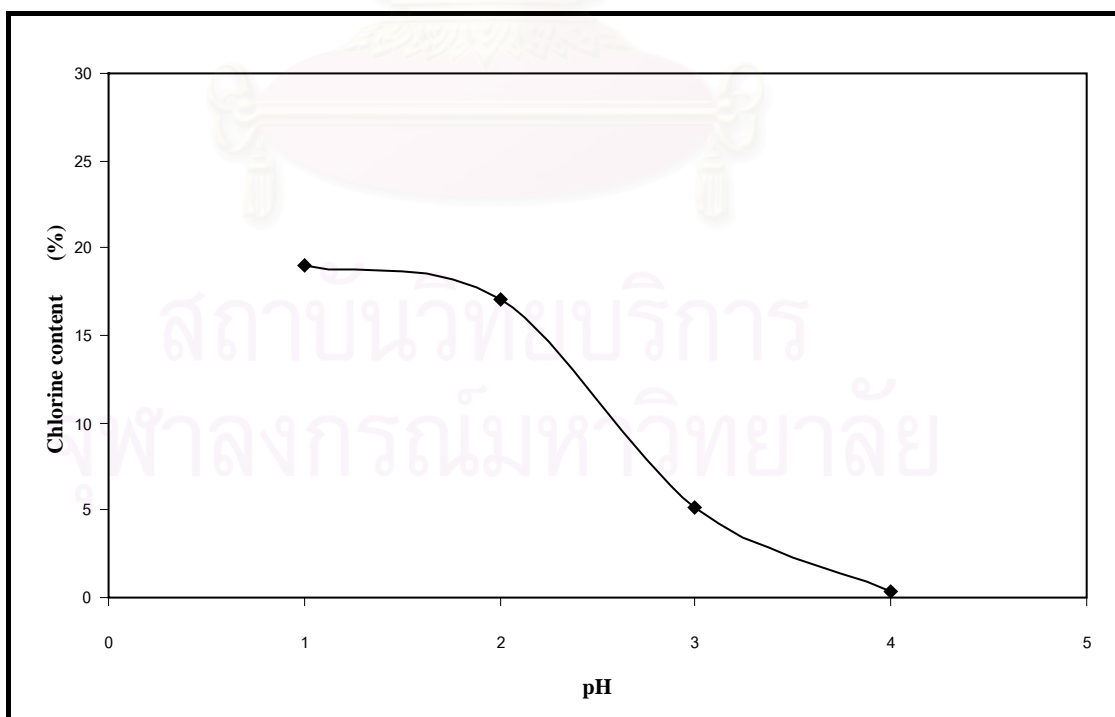


Figure 4.10 Chlorine content in CR derived various pH

4.3 Thermal Properties

4.3.1 Differential Scanning Calorimetry (DSC)

The DSC thermogram of NR as shown in Figure 4.11 indicated T_{g1} at -62.07°C , T_{g2} at 62.24°C and T_{m1} at 178.14°C . The DSC thermogram of ENR as shown in Figure 4.12 indicated T_{g1} at -14.89°C and T_{g2} at 32.37°C . The DSC thermogram of CR that as shown in Figure 4.13 indicated T_{m1} at -0.59°C , T_{g1} at 46.97°C and T_{m2} at 145.37°C . As results from DSC thermograms indicated that the flexibility of NR and ENR was higher than that of CR. This is because T_g of NR and ENR was lower than T_g of CR as compared in Table 4.11.

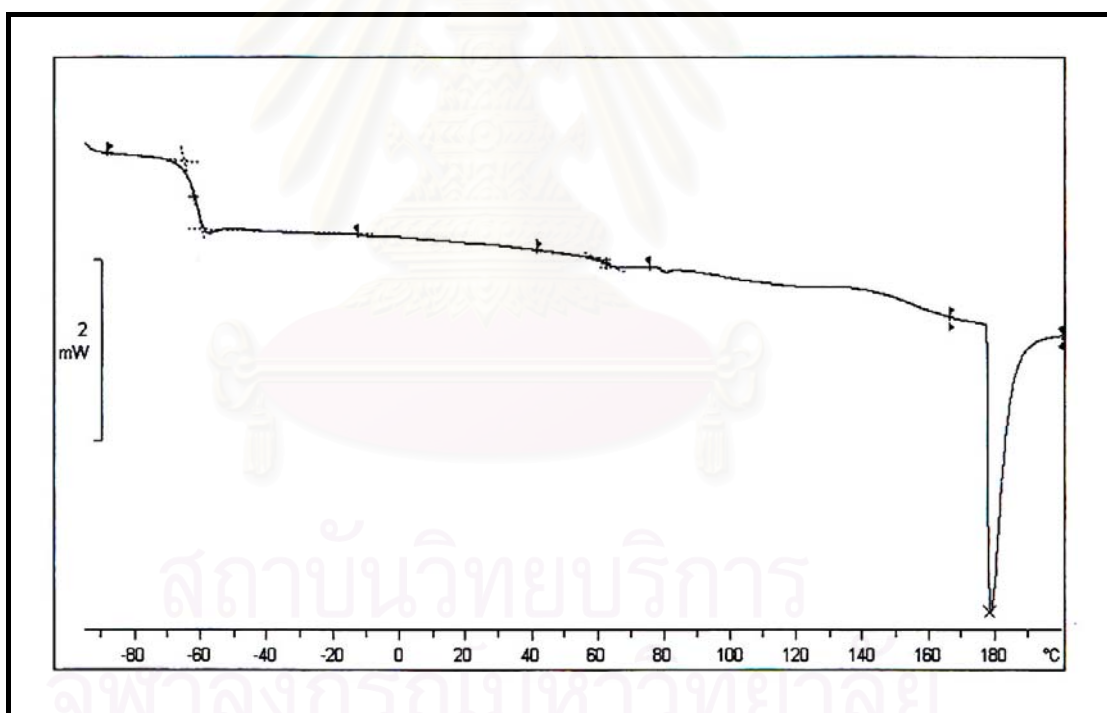


Figure 4.11 DSC thermogram of NR

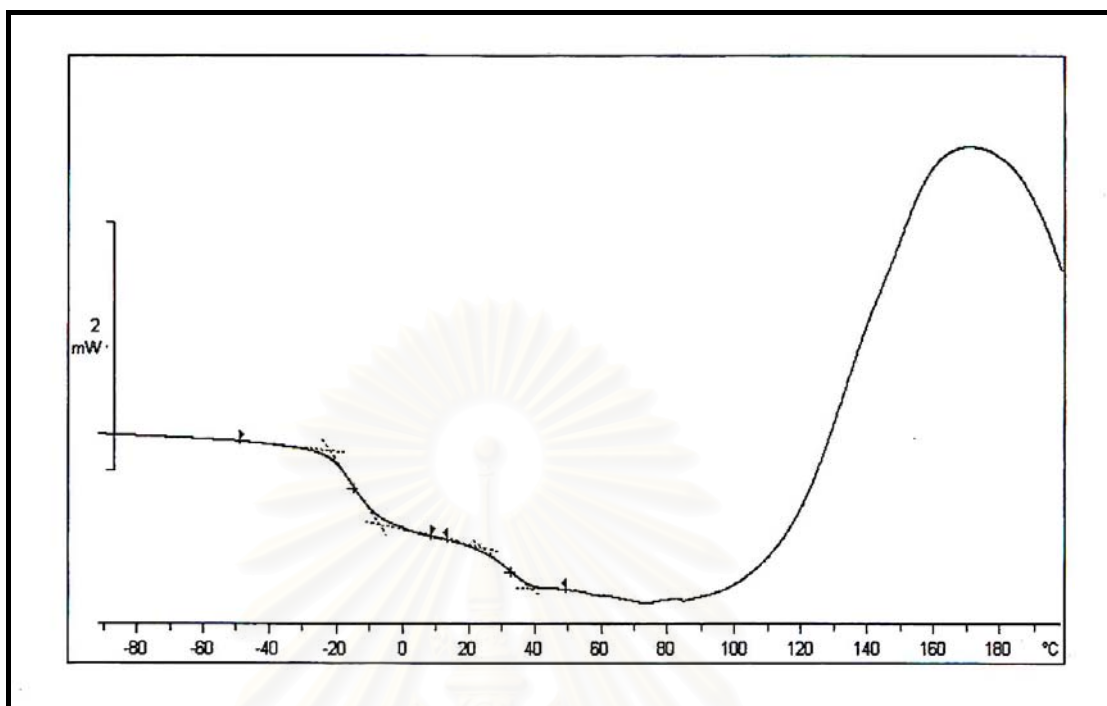


Figure 4.12 DSC thermogram of ENR

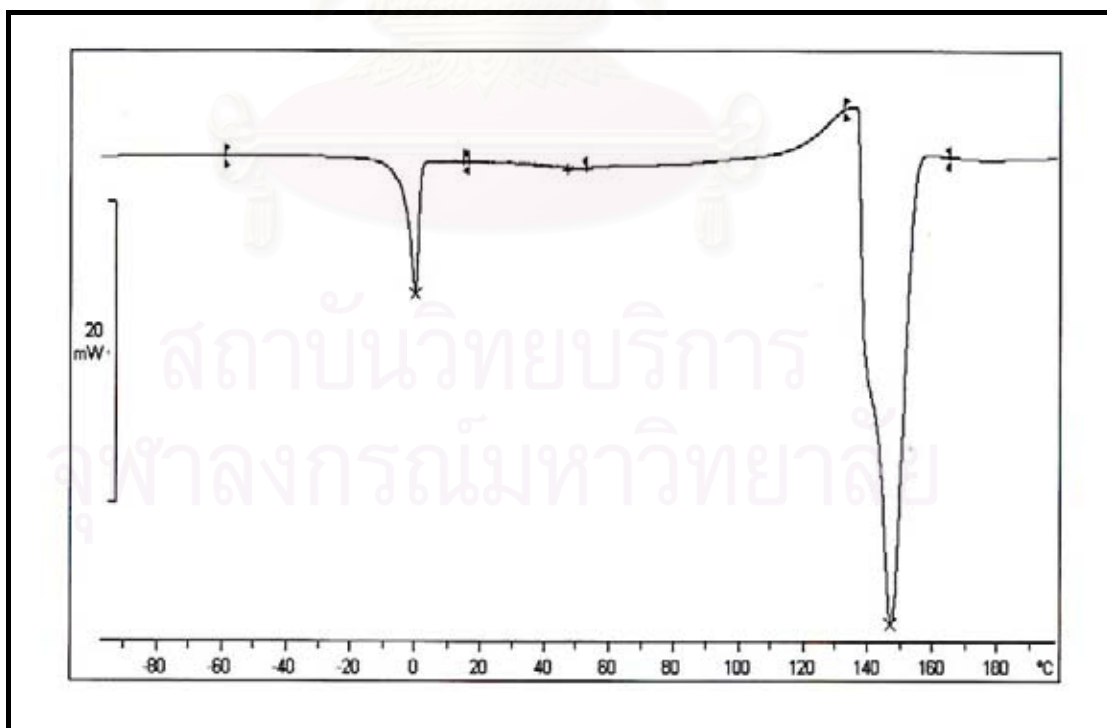


Figure 4.13 DSC thermogram of CR

Table 4.11 The T_g and T_m of NR, ENR and CR

Samples	T_g (°C)	ΔC_p (Jg ⁻¹ K ⁻¹)	T_m (°C)	H_f (mJ)
NR	$T_{g1} = -62.07$ $T_{g2} = 62.24$	0.426 0.054	$T_{m1} = 178.14$	106.87
ENR	$T_{g1} = -62.07$ $T_{g2} = 62.24$	0.335 0.172	-	-
CR	$T_{g1} = 46.97$	0.517	$T_{m1} = -0.59$ $T_{m2} = 145.37$	0.335 2084.84

4.3.2 Thermogravimetry (TG)/Derivative Thermogravimetric Analysis (DTG)

The TG and DTG curves of degradation of NR under nitrogen atmosphere are shown in Figure 4.14. From the DTG curve of NR, a peak at 378.20°C was appeared. This indicated that the degradation of NR was a one step reaction. From TG curve of NR, the first weight loss was 1.3% from 54.17 to 154.17°C of water, while the second weight loss was 99.5% from 183.33 to 493.75°C of rubber unit. The TG and DTG curves of degradation of ENR under nitrogen atmosphere are shown in Figure 4.15. From the DTG curve of ENR, a peak at 425.40°C was appeared. This indicated that the degradation of ENR was also a one step reaction. From TG curve of ENR, the first weight loss that was 5.5% from 83.33 to 304.17°C of water, while the second weight loss was 93.9% from 304.17 to 479.17°C of rubber unit. The TG and DTG curves of degradation of CR under nitrogen atmosphere are shown in Figure 4.16. From the DTG curve of CR, a peak at 191.00 and 405.40°C were appeared. It indicated that the degradation of CR was two steps reaction. In TG curve of CR, the first weight loss that was 2.7% from 37.50 to 89.58°C of water, the second weight loss was 10.2% from 104.17 to 247.92°C of hydrochloric acid. Finally, the third weight loss was about 80.3% from 247.92 to 560.42°C of dechlorination. Table 4.12 shows the %weight loss of NR, ENR and CR.

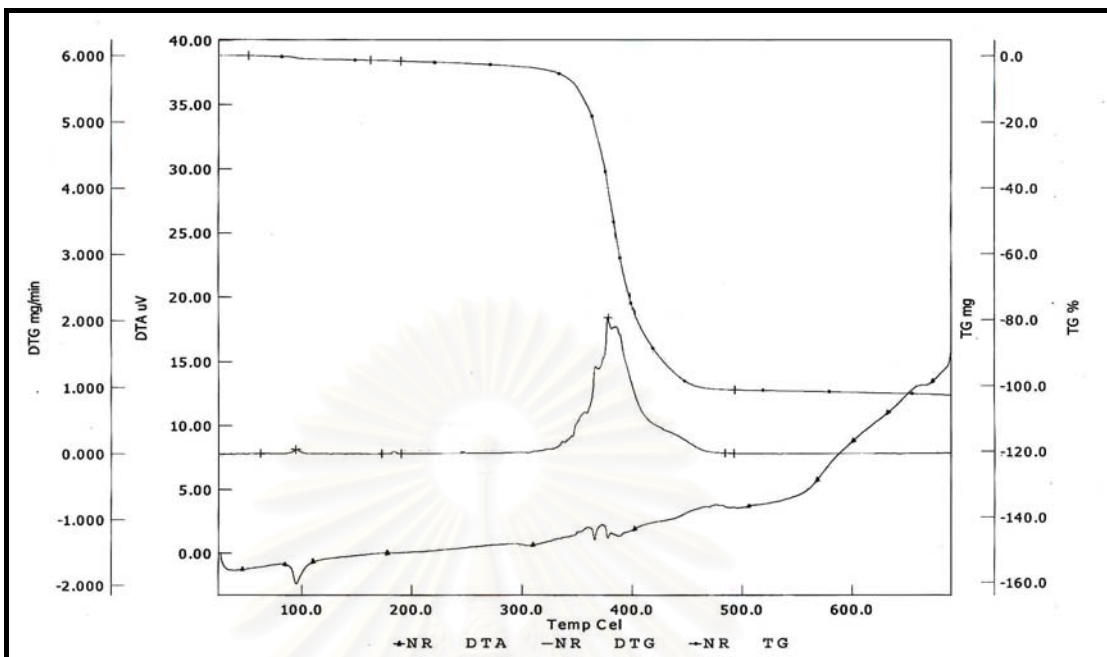


Figure 4.14 TG/DTG curves of NR

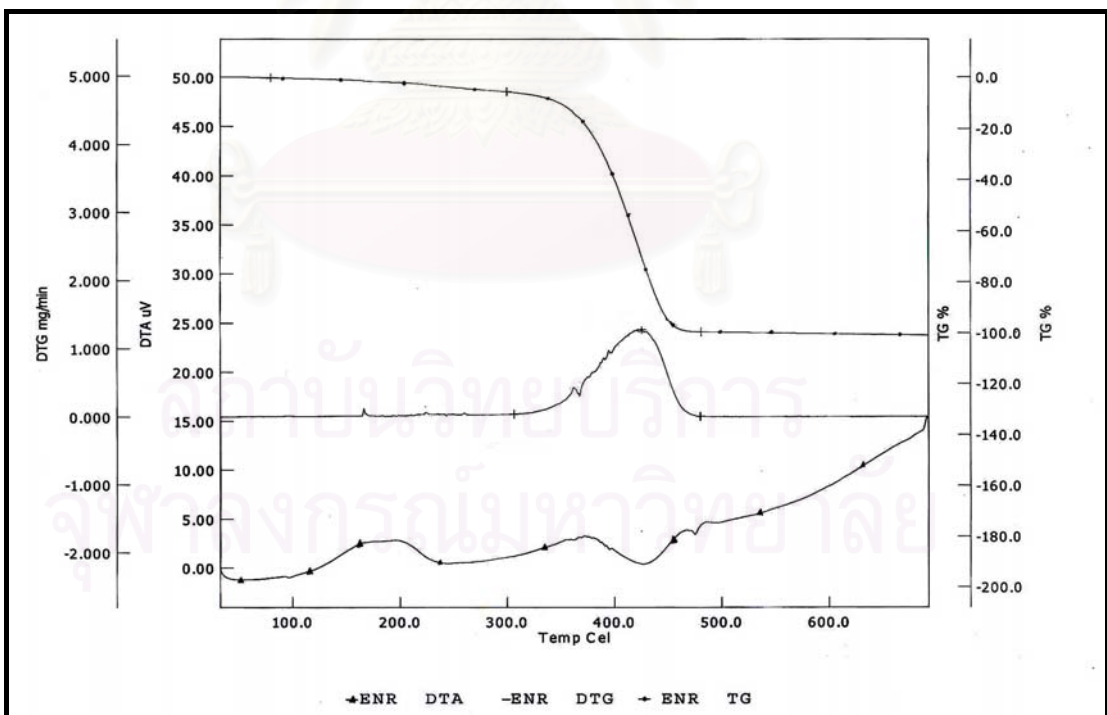


Figure 4.15 TG/DTG curves of ENR

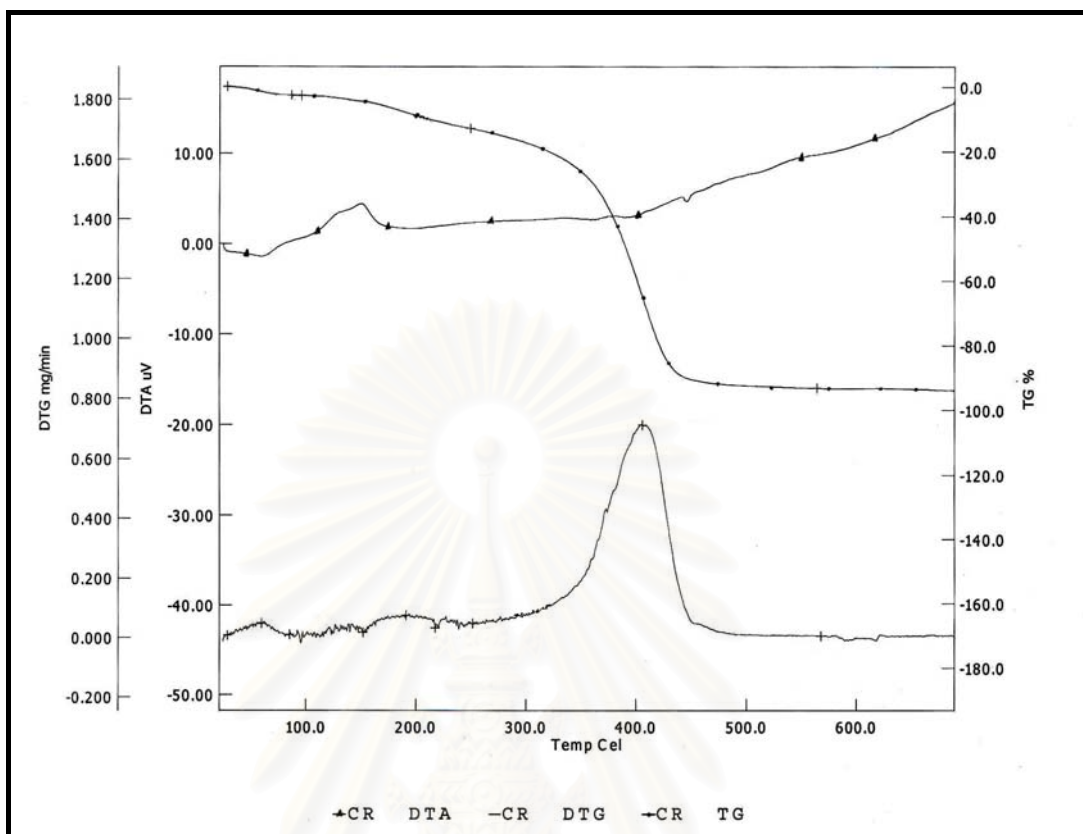


Figure 4.16 TG/DTG curves of CR

Table 4.12 The % weight loss of NR, ENR and CR

Samples	% Weight loss (%)	Temperature (°C)
NR	1.3	54.17-154.17
	99.5	1833.33-493.75
ENR	5.5	83.33-304.17
	93.9	304.17-479.17
CR	2.7	37.50-89.58
	10.7	104.17-247.92
	80.3	247.92-560.42

In comparison of CR using NaOCl/NaCl with commercial CR, the chlorine content in commercial CR was higher than that in CR using NaOCl/NaCl. This is because commercial CR had two chlorine atoms on the unit of rubber structure, while CR using NaOCl/NaCl had one chlorine atom and an OH group on the unit of rubber structure that called chlorohydrin. General physical properties were similar both CR using NaOCl/NaCl and commercial CR as presented in Table 4.13.

Table 4.13 The comparing physical properties of CR using NaOCl/NaCl and commercial CR

Samples	Chlorine content (%)	Melting point (°C)	Physical form	Color	Odor	Solubility in water
CR using NaOCl/NaCl	19.09	145	powder	white	odorless	insoluble
Commercial CR	64.50	200	powder	white	odorless	insoluble

CHAPTER V

CONCLUSION AND SUGGESTION

5.1 Conclusion

In this research, epoxidized natural rubber was prepared by epoxidation reaction of stabilized natural rubber latex with 3.31% of peracetic acid. The appropriate condition for the preparation of epoxidized natural rubber was at 30-35°C for 30 minutes. The 55 mol% epoxidation of epoxidized natural rubber was obtained.

The chlorinated rubber (CR) was prepared by chlorination reaction of epoxidized natural rubber using sodium hypochlorite and sodium chloride. The 19.09% chlorine content of CR was obtained.

The optimum condition for preparing the appropriate chlorinated rubber is presented in Table 5.1.

Table 5.1 The optimum condition for preparing the CR

ENR (g)	Ratio of NaOCl:NaCl (by mol)	Temperature (°C)	Time (hours)	pH
80	1:4	30	6	1

DSC thermogram of CR showed T_{m1} at -0.59°C , T_{g1} at 46.97°C and T_{m2} at 145.37°C . The flexibility of NR and ENR was higher than that of CR because T_g value of NR and ENR were lower than T_g value of CR.

From the DTG curve of CR, a peak at 191.00 and 405.40°C was appeared. This indicated that the degradation of CR was two steps reaction. From TG curve of CR, the first weight loss was 2.7% from 37.50 to 89.58°C of water. The second

weight loss was 10.2% from 104.17 to 247.92°C of hydrochloric acid. Finally, the third weight loss was 80.3% from 247.92 to 560.42°C of dechlorination.

5.2 Suggestion for Future Work

1. The chlorinated rubber should be further studied by chlorination reaction the epoxidized natural rubber using alkyl hypohalite/ sodium chloride.
2. The chlorinated rubber in this research could be possibly usal in painting industrial applications as a white pigments.



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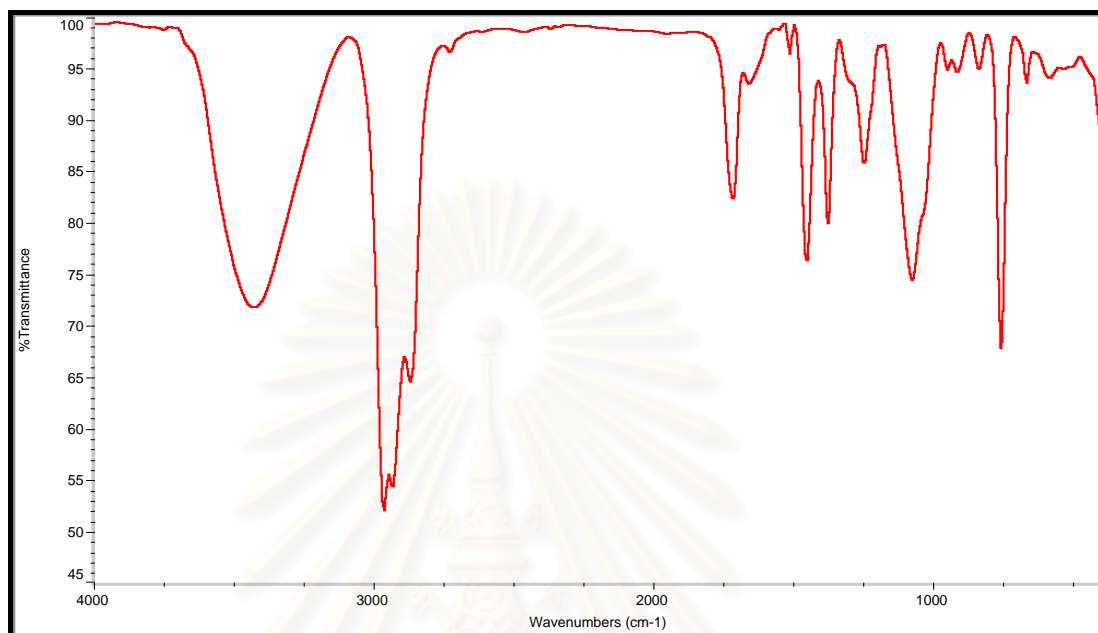
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APPENDICES

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APPENDIX A

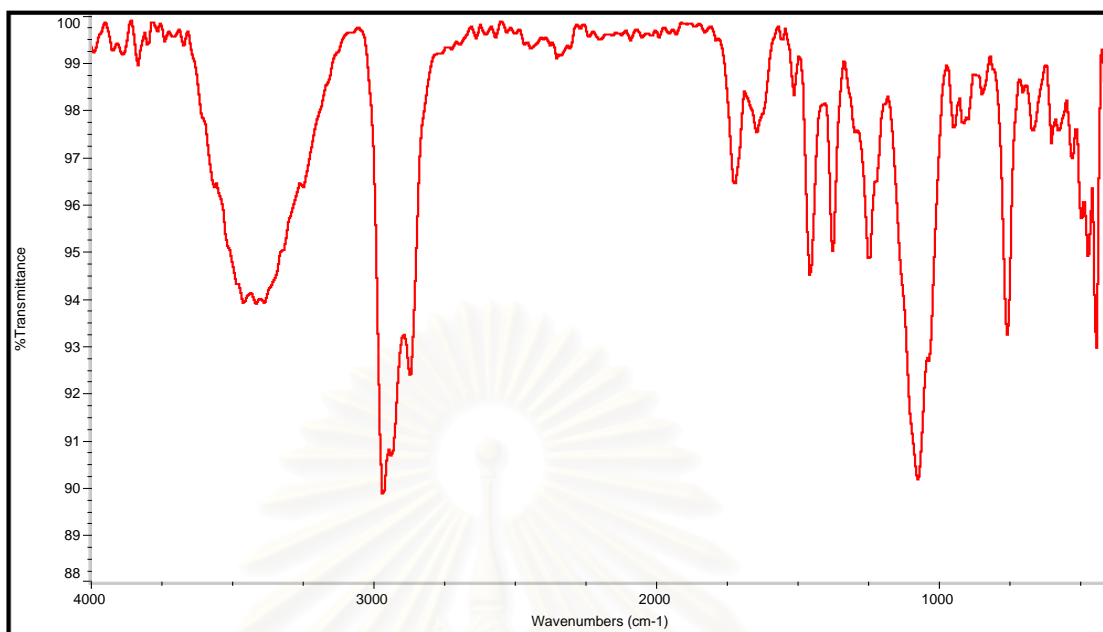


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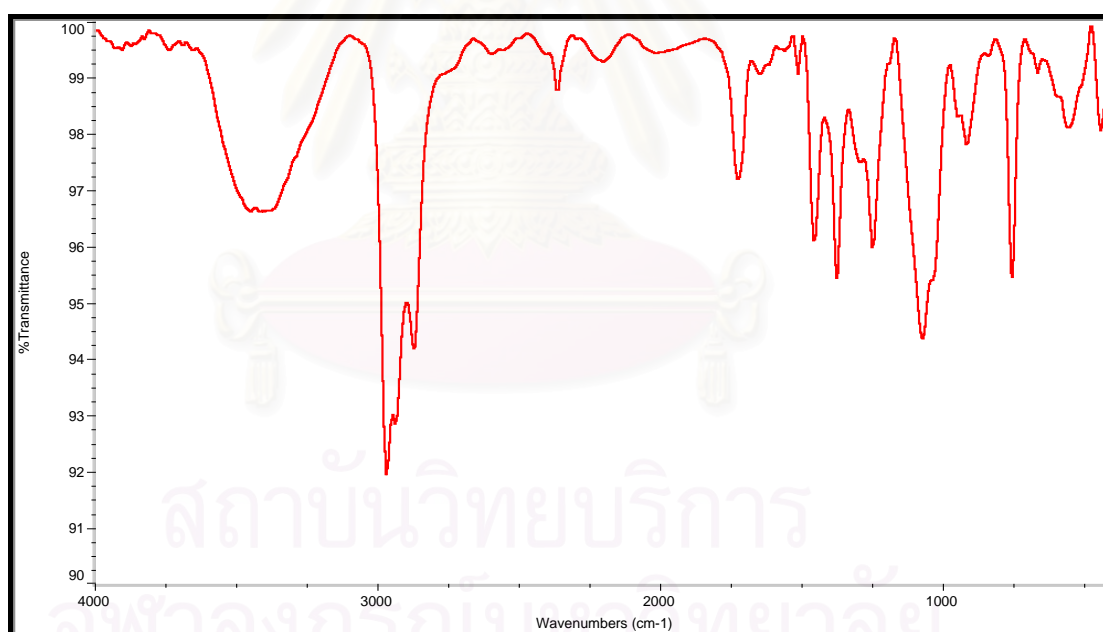


(b)

Figure A1 FT-IR spectra of CR derived effect of ratio of NaOCl:NaCl = 0:1 (by mol) for (a) 1 (b) 2 (c) 4 and (d) 6 hours

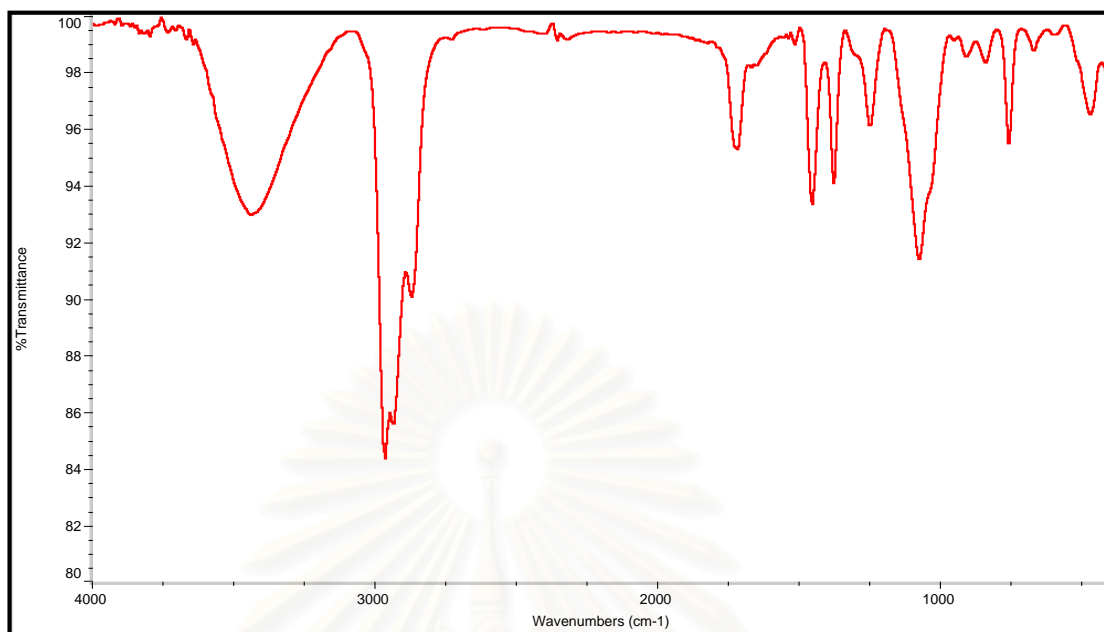


(c)

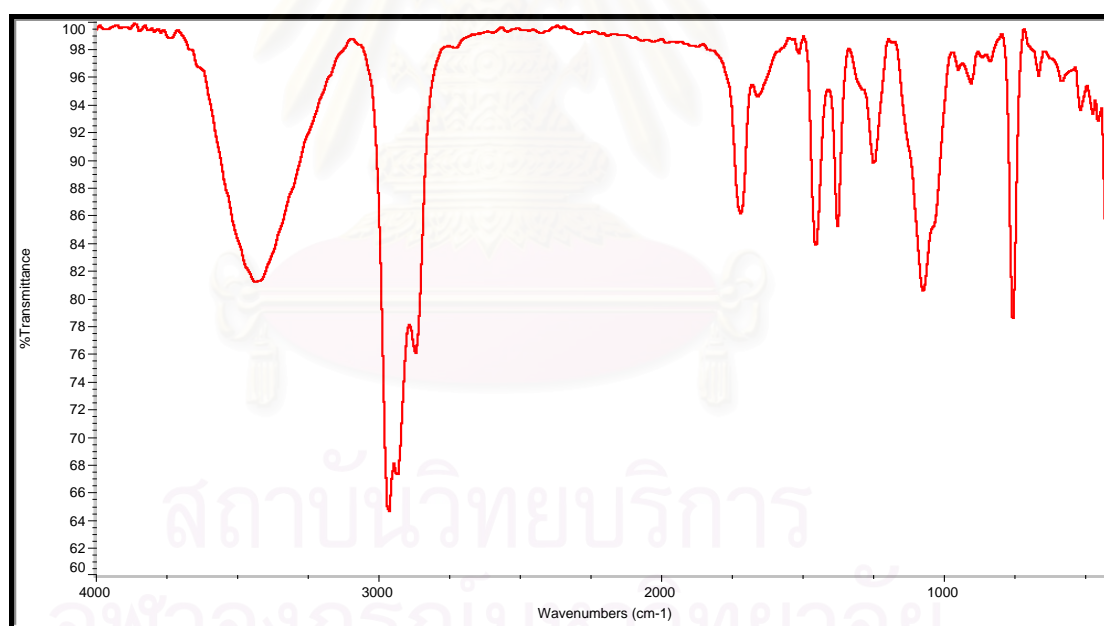


(d)

Figure A1 (continued) FT-IR spectra of CR derived effect of ratio of
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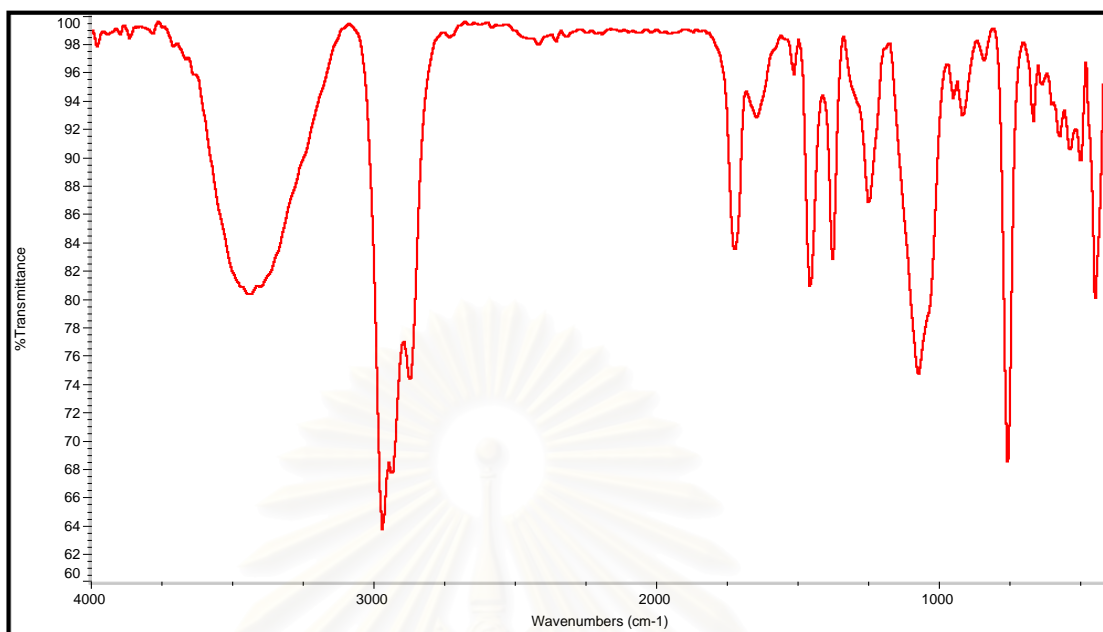


(a)



(b)

Figure A2 FT-IR spectra of CR derived effect of ratio of NaOCl:NaCl = 1:0
(by mol) for (a) 1 (b) 2 (c) 4 and (d) 6 hours

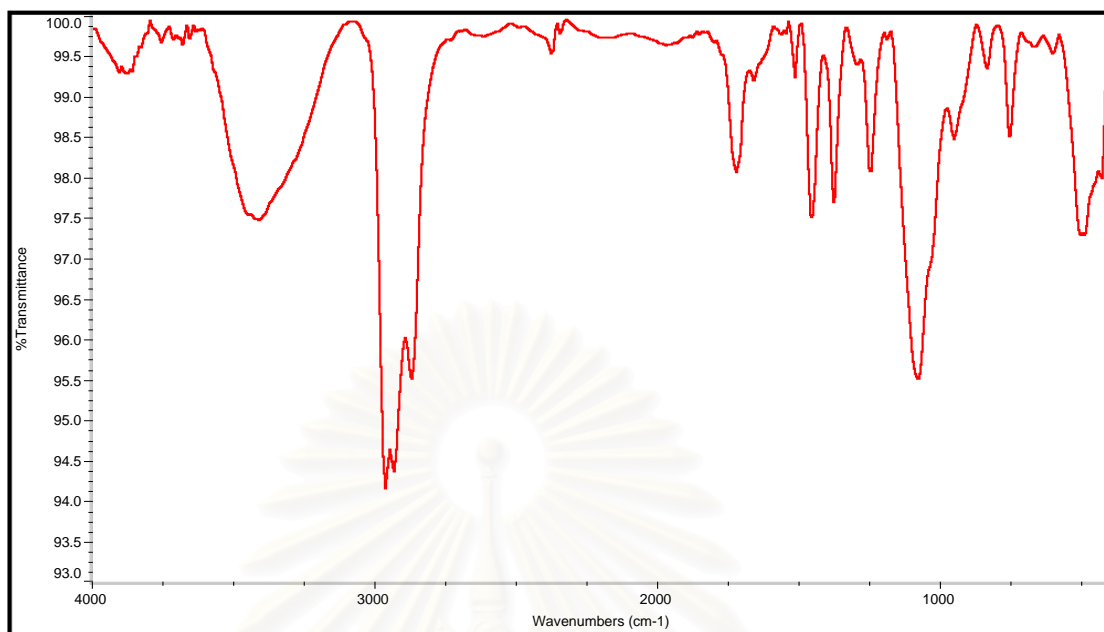


(c)

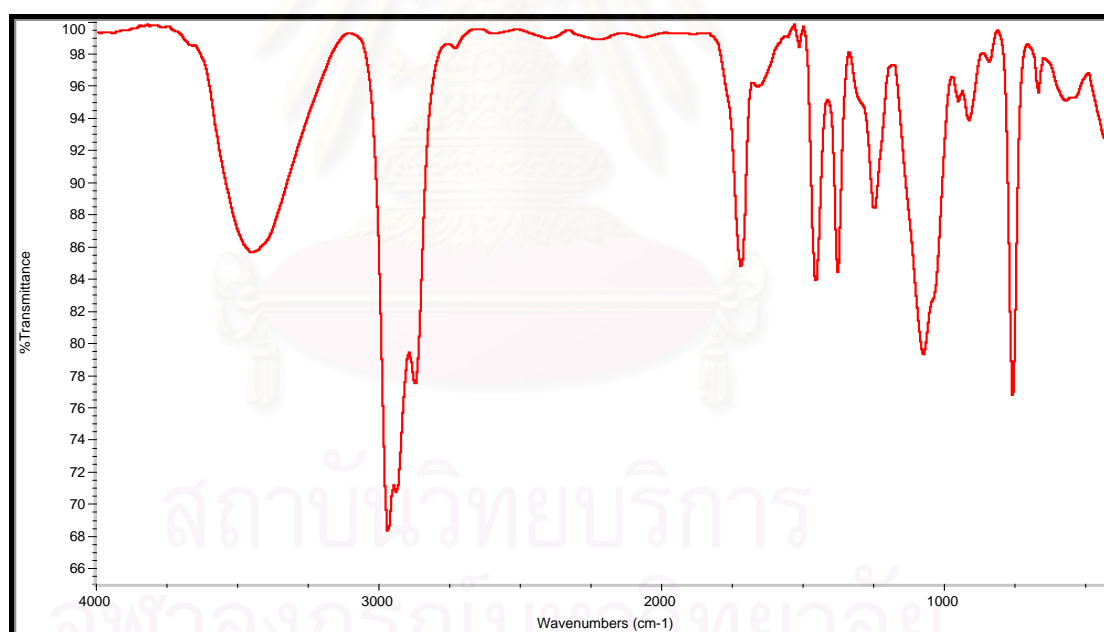


(d)

Figure A2 (continued) FT-IR spectra of CR derived effect of ratio of NaOCl:NaCl = 1:0 (by mol)

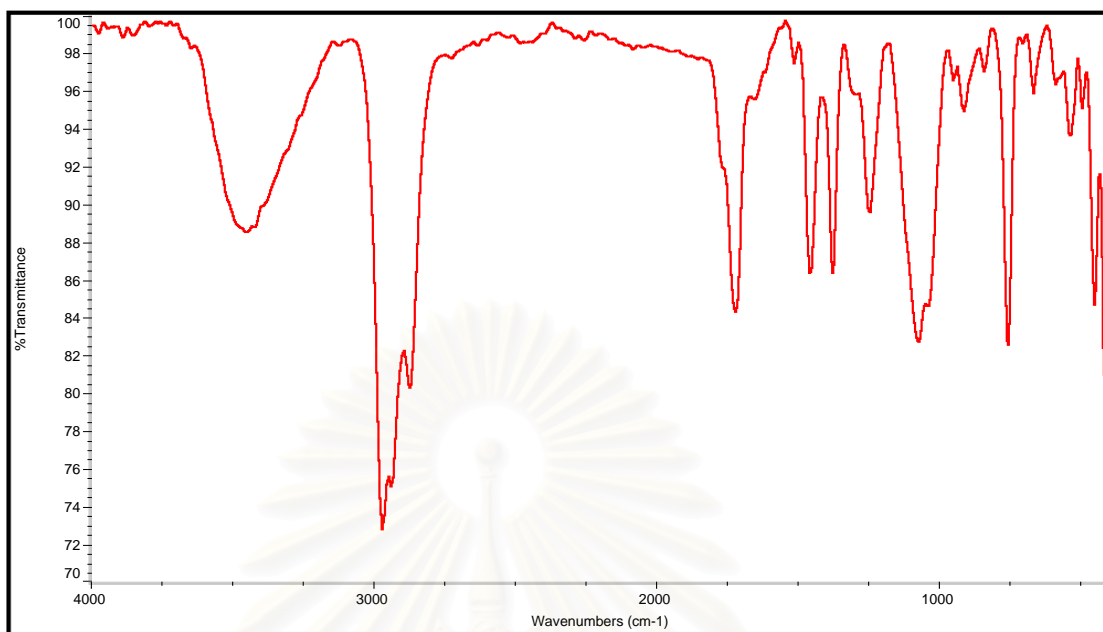


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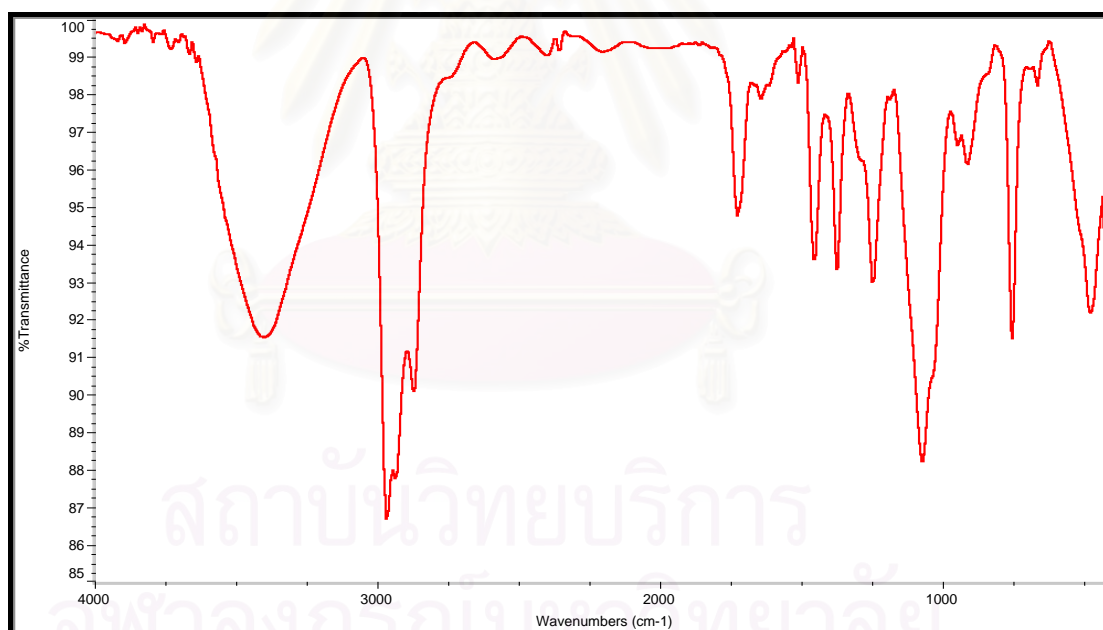


(b)

Figure A3 FT-IR spectra of CR derived effect of ratio of NaOCl:NaCl = 1:1 (by mol) for (a) 1 (b) 2 (c) 4 and (d) 6 hours

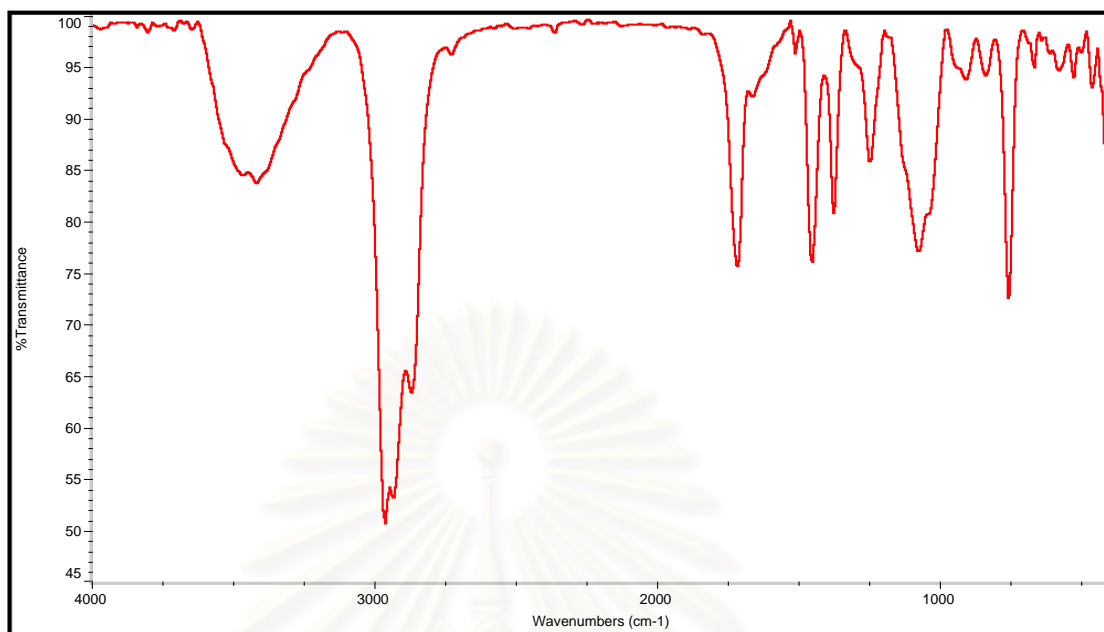


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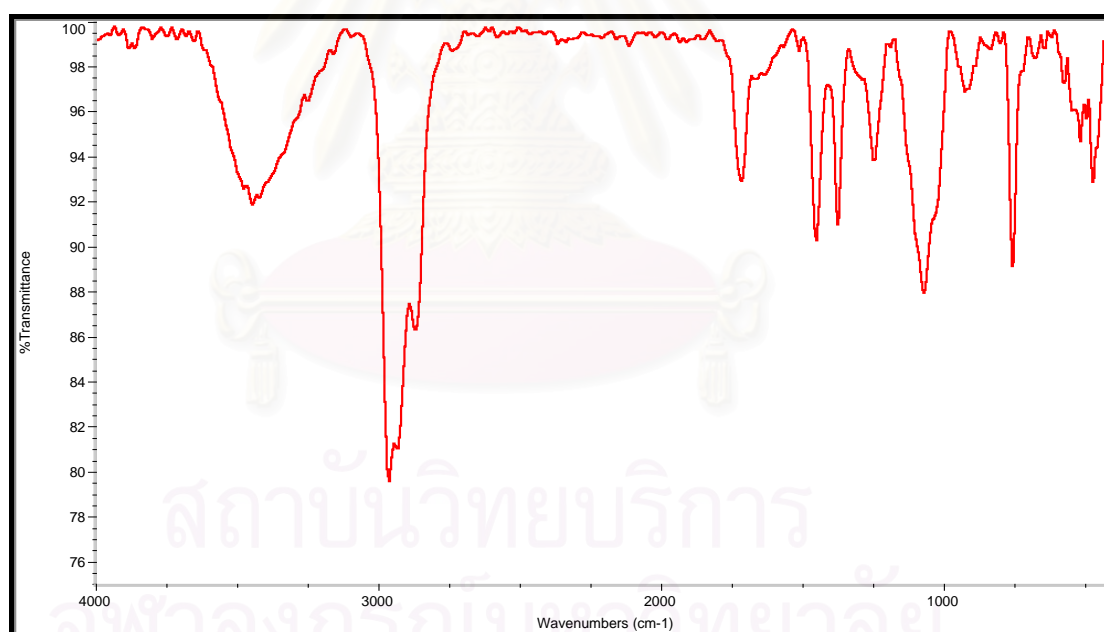


(d)

Figure A3 (continued) FT-IR spectra of CR derived effect of ratio of
NaOCl:NaCl = 1:1 (by mol)

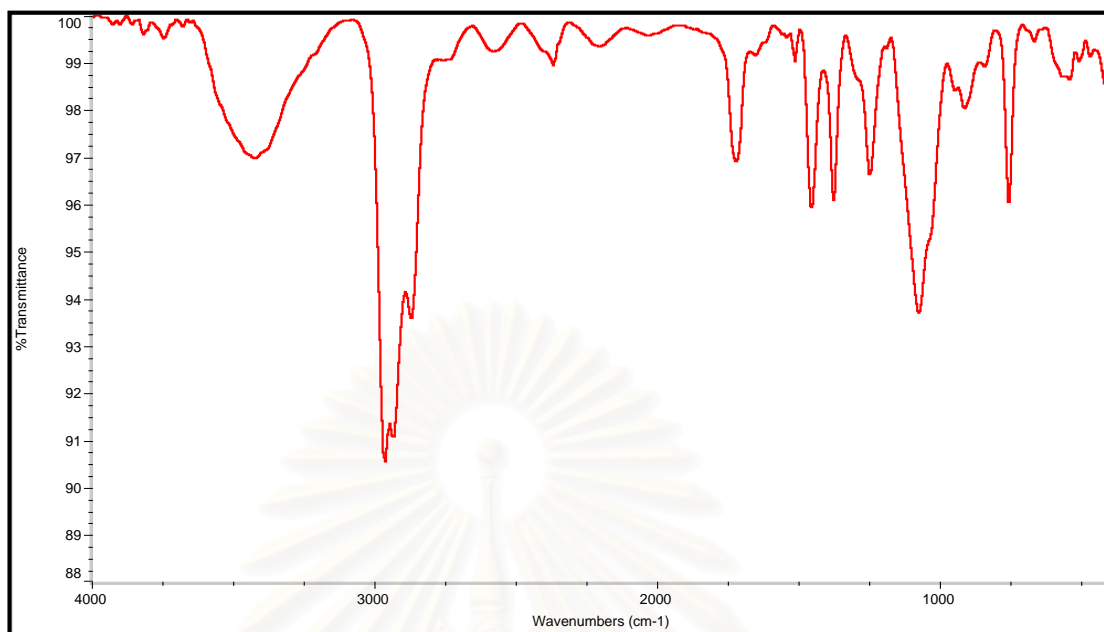


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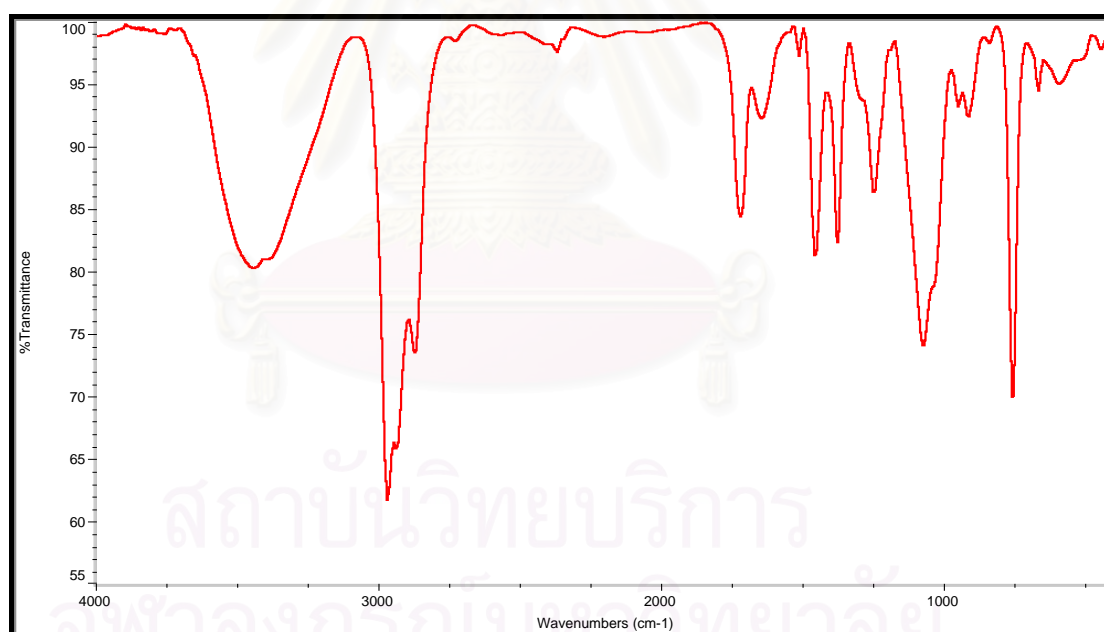


(b)

Figure A4 FT-IR spectra of CR derived effect of ratio of NaOCl:NaCl = 1:2 (by mol) for (a) 1 (b) 2 (c) 4 and (d) 6 hours

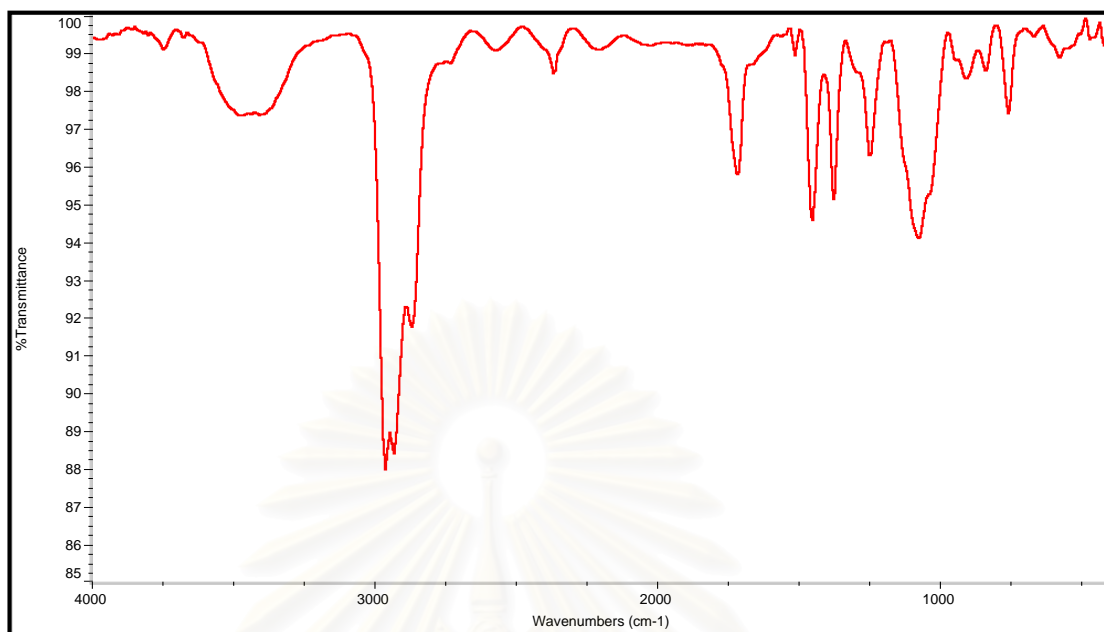


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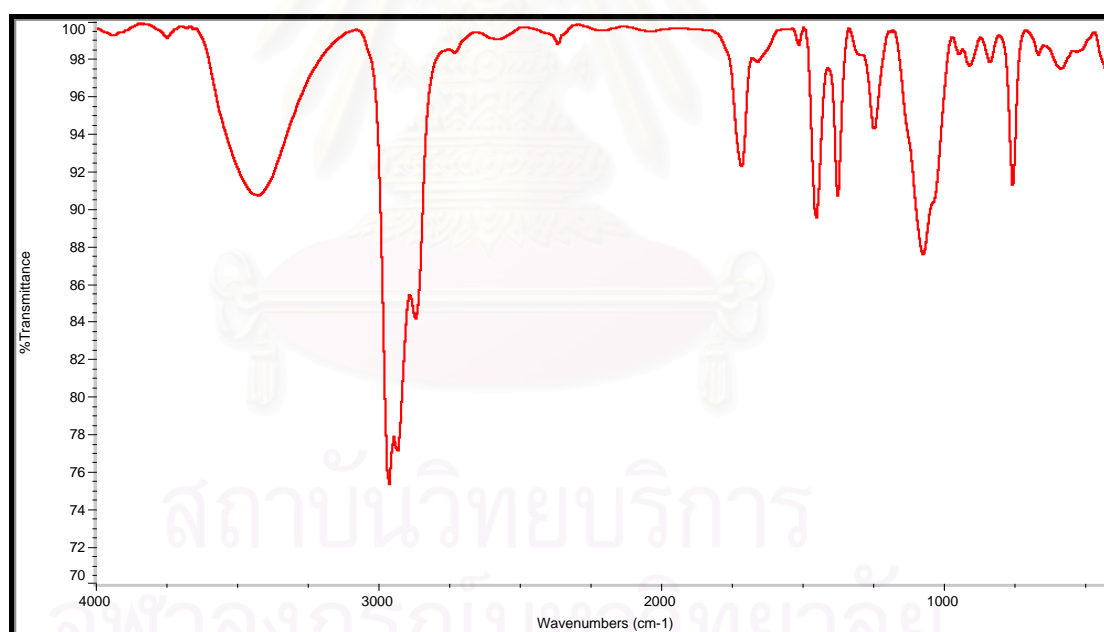


(d)

Figure A4 (continued) FT-IR spectra of CR derived effect of ratio of
NaOCl:NaCl = 1:2 (by mol)

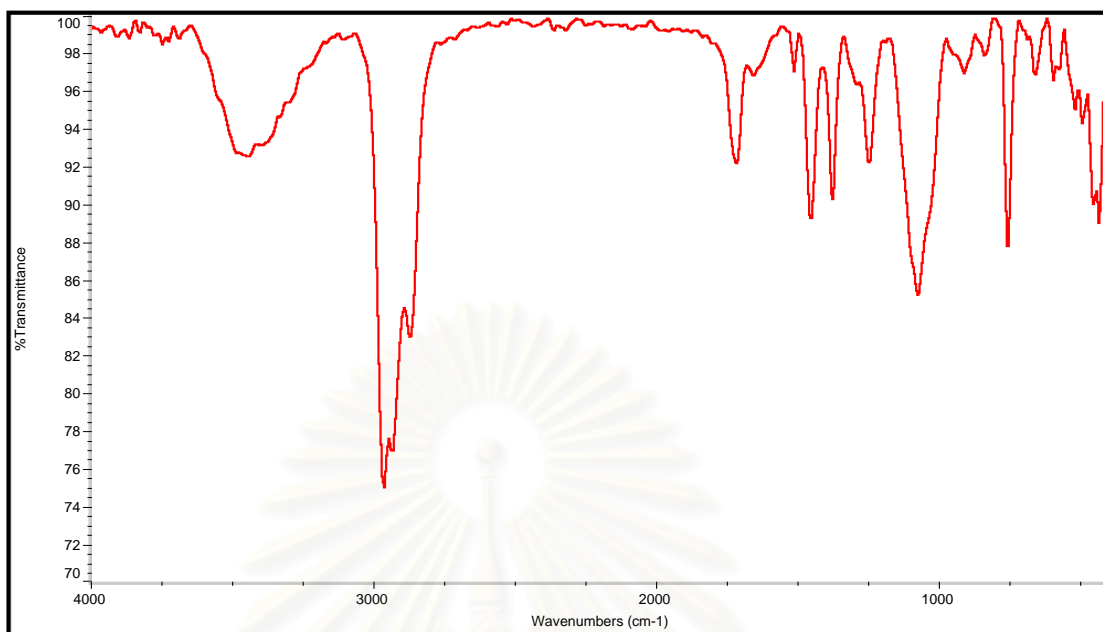


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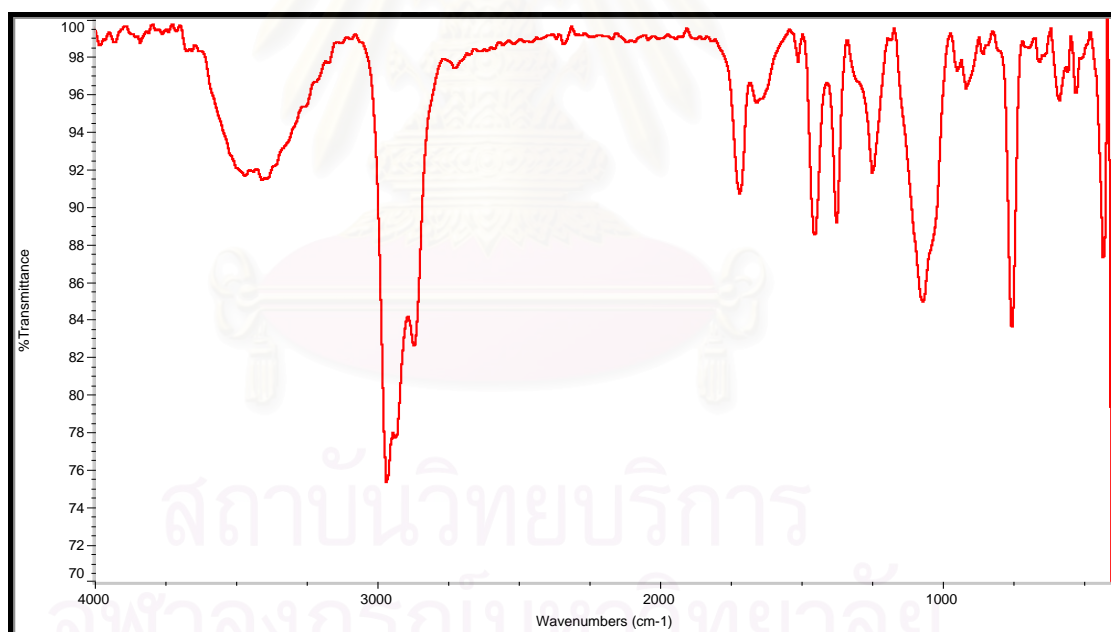


(b)

Figure A5 FT-IR spectra of CR derived effect of ratio of NaOCl:NaCl = 1:4 (by mol) for (a) 1 (b) 2 (c) 4 and (d) 6 hours

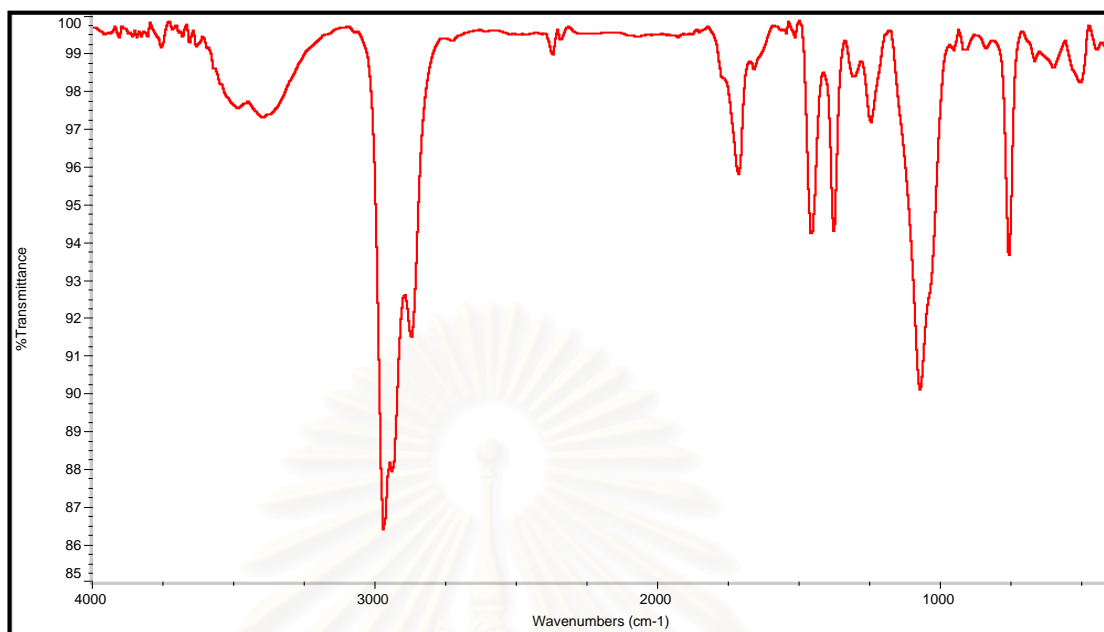


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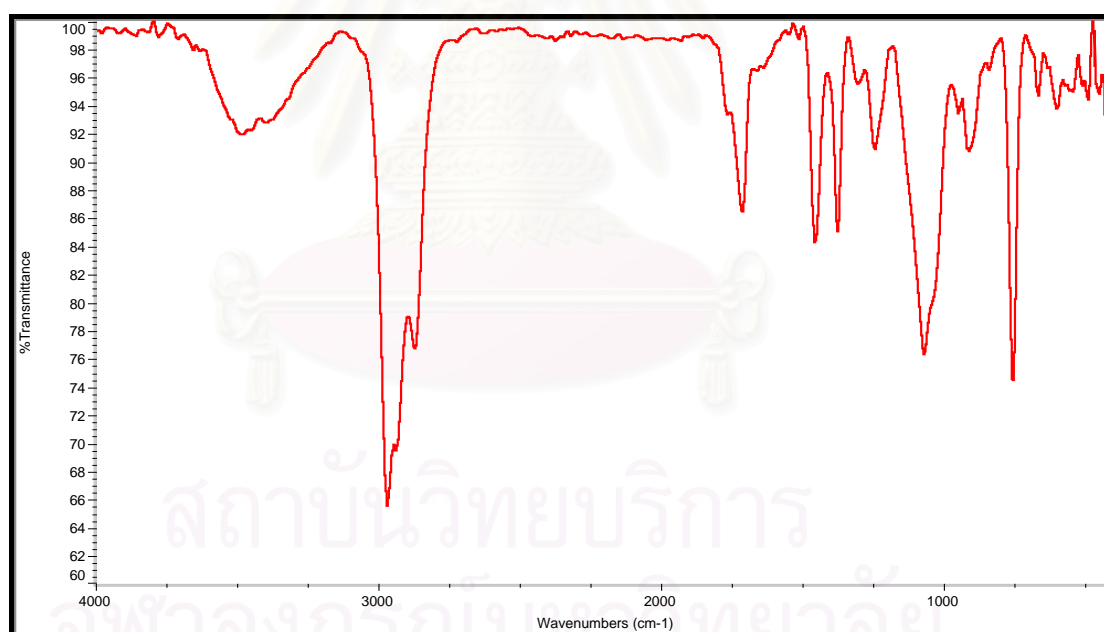


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Figure A5 (continued) FT-IR spectra of CR derived effect of ratio of
NaOCl:NaCl = 1:4 (by mol)

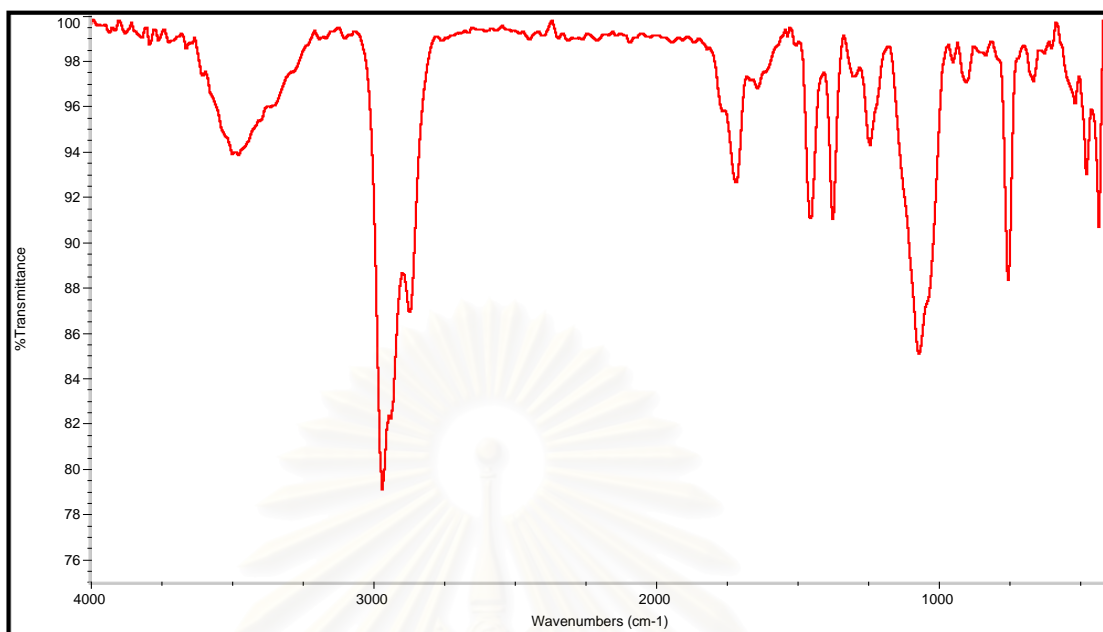


(a)

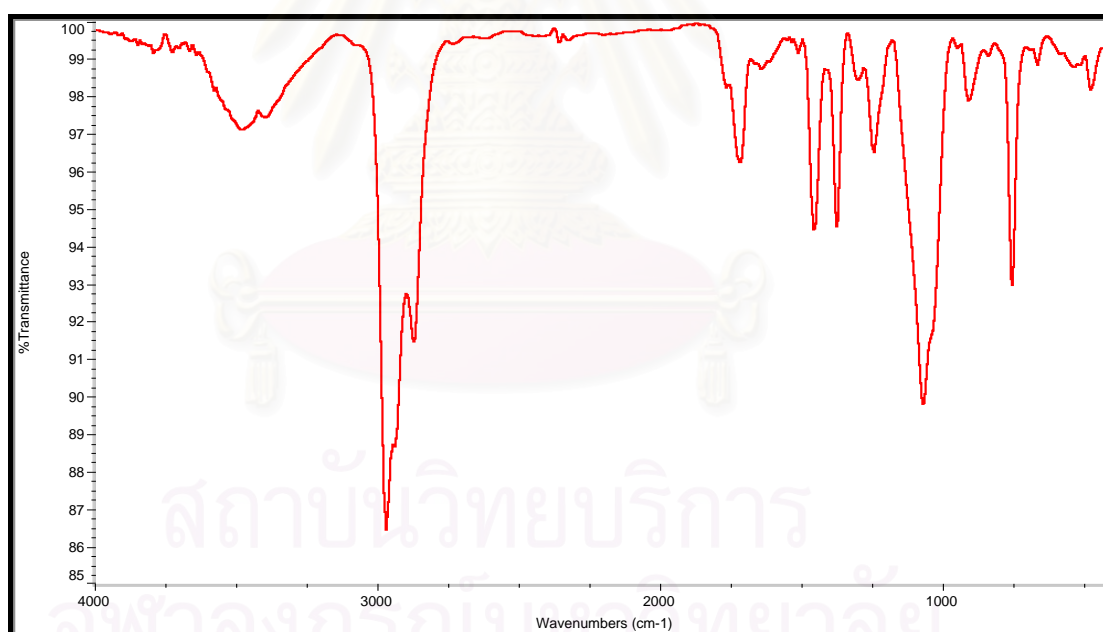


(b)

Figure A6 FT-IR spectra of CR derived effect of ratio of NaOCl:NaCl = 2:1 (by mol) for (a) 1 (b) 2 (c) 4 and (d) 6 hours

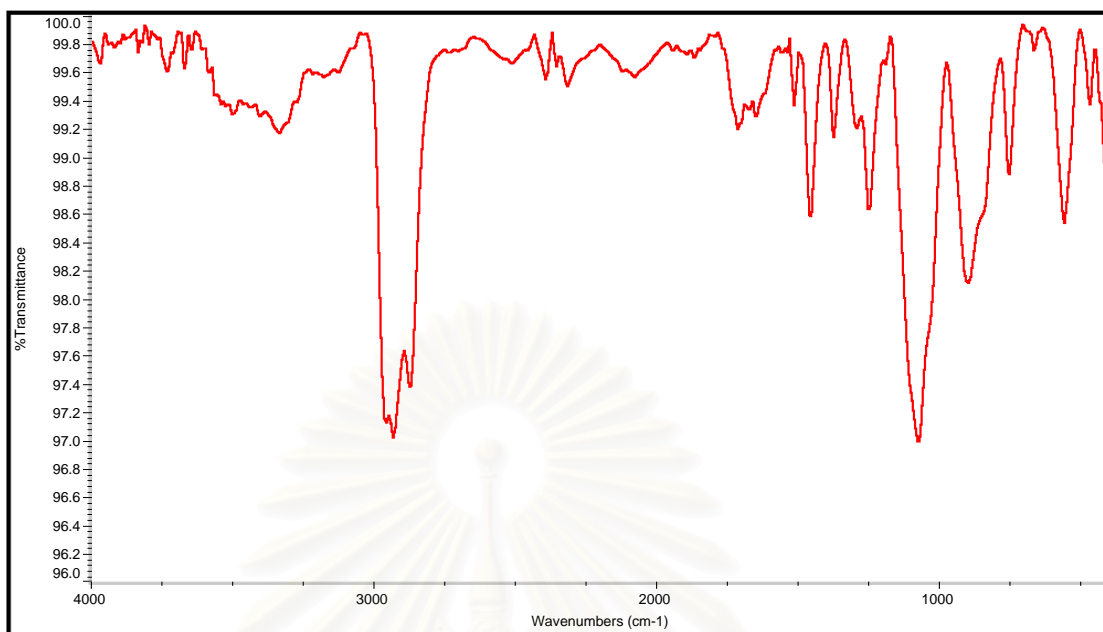


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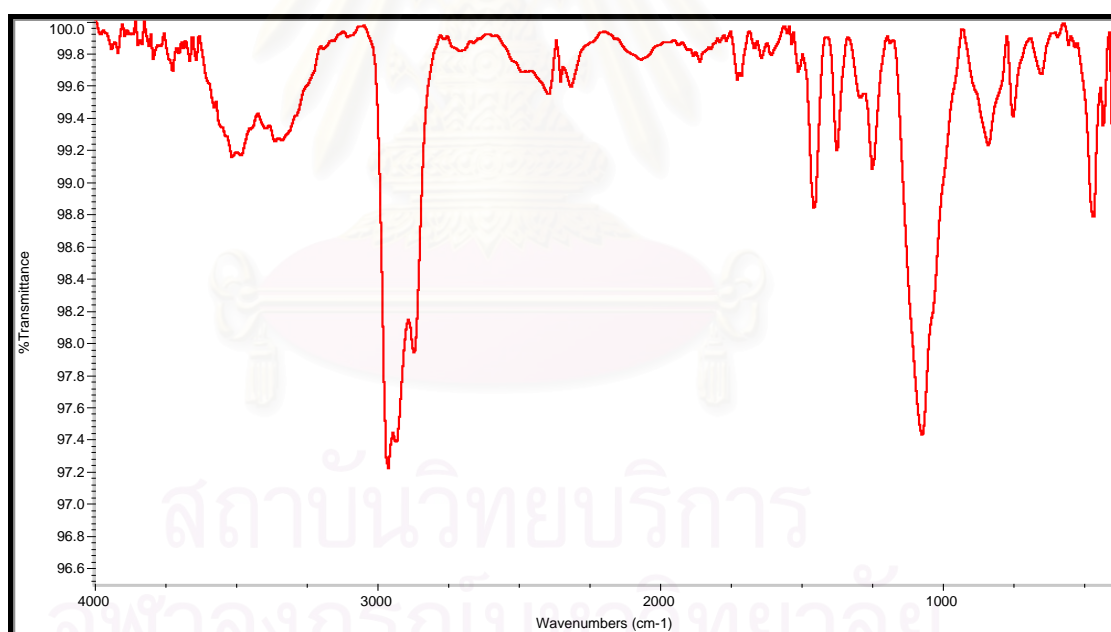


(d)

Figure A6 (continued) FT-IR spectra of CR derived effect of ratio of
NaOCl:NaCl = 2:1 (by mol)

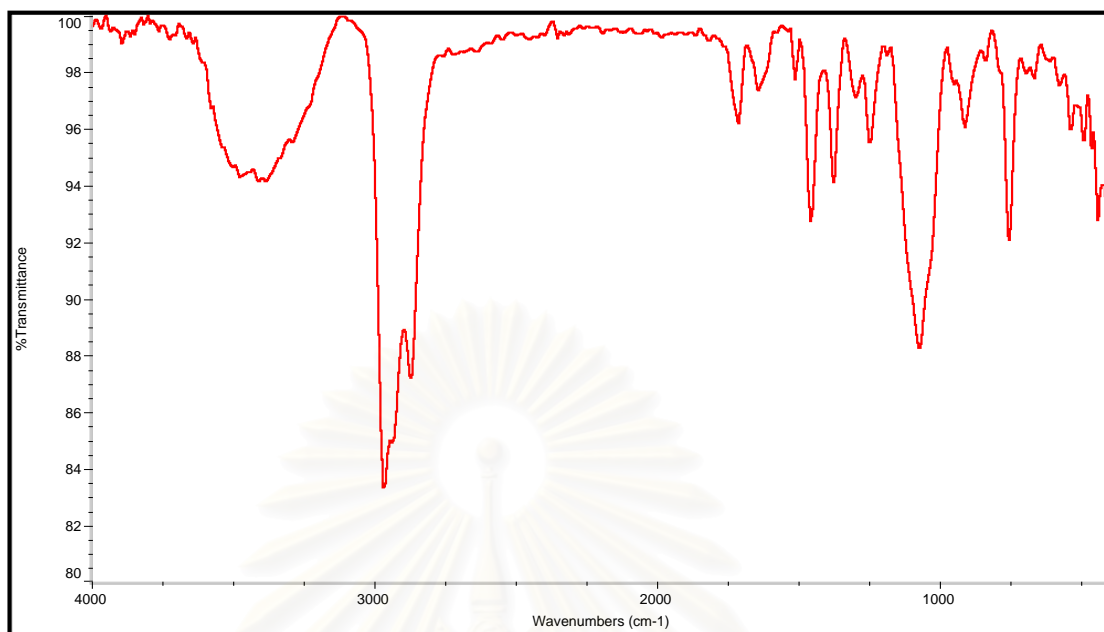


(a)

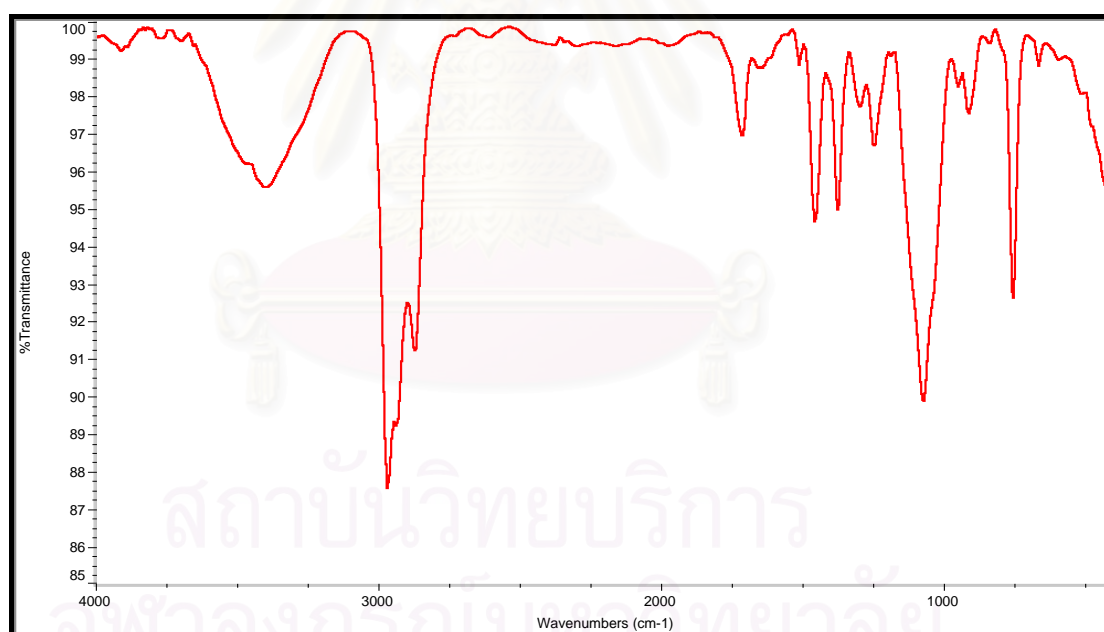


(b)

Figure A7 FT-IR spectra of CR derived effect of ratio of NaOCl:NaCl = 4:1 (by mol) for (a) 1 (b) 2 (c) 4 and (d) 6 hours

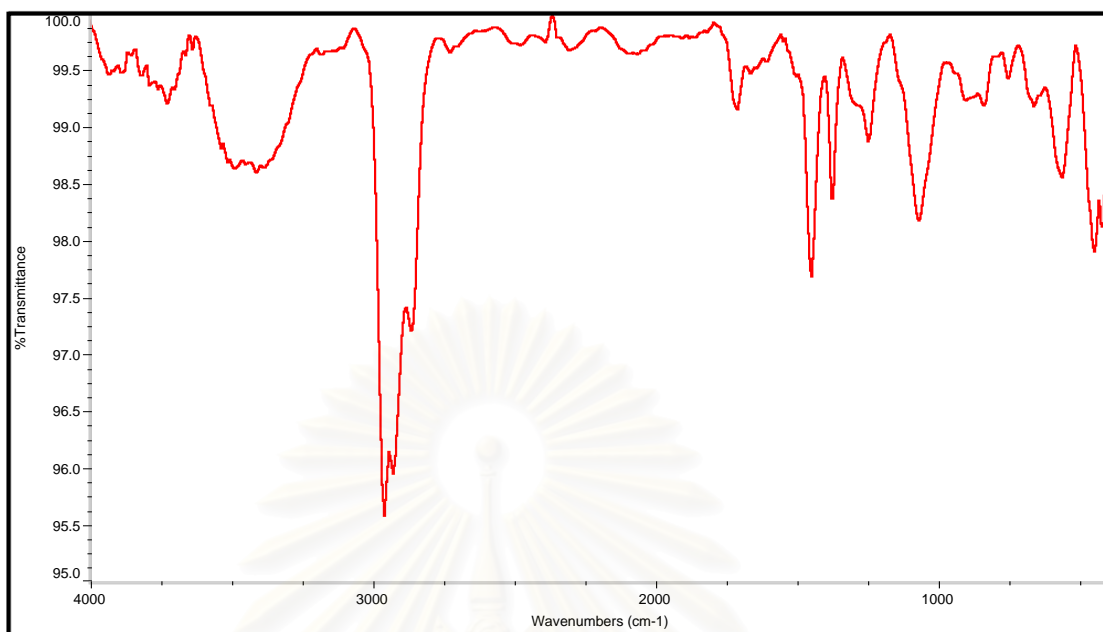


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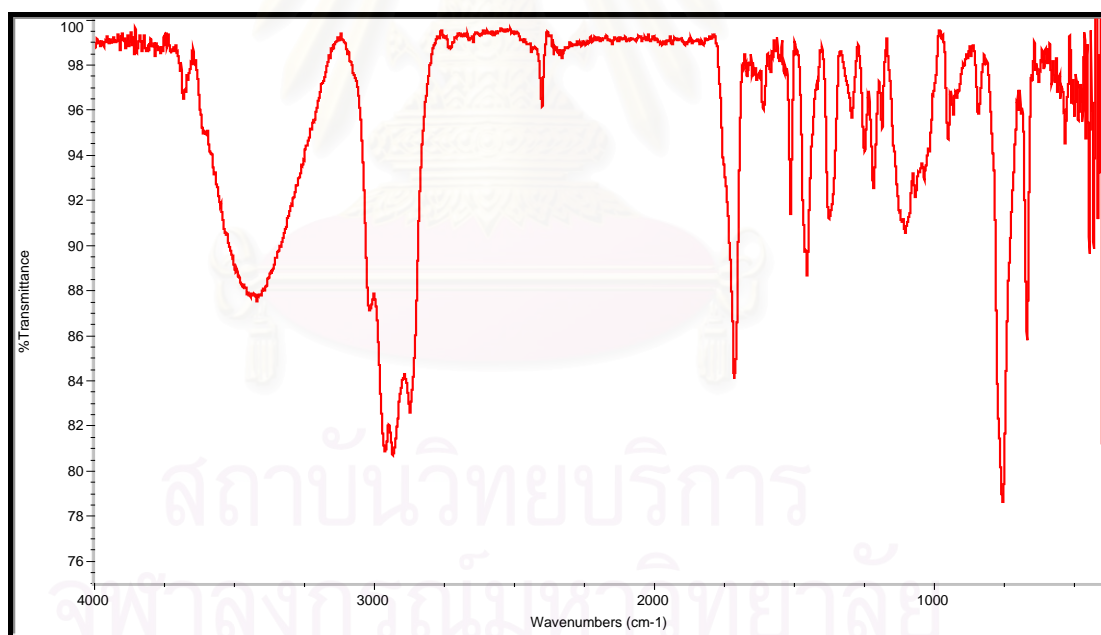


(d)

Figure A7 (continued) FT-IR spectra of CR derived effect of ratio of
 $\text{NaOCl}:\text{NaCl} = 4:1$ (by mol)

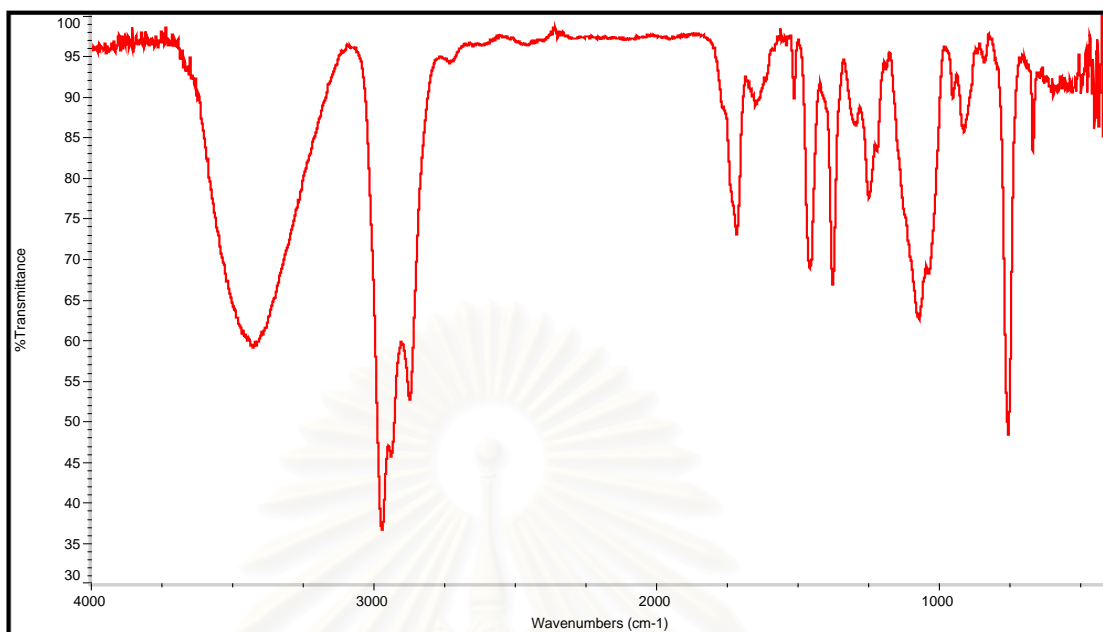


(a)



(b)

Figure A8 FT-IR spectra of CR derived effect of temperature at (a) 10 (b) 20 (c) 30 and (d) 40°C

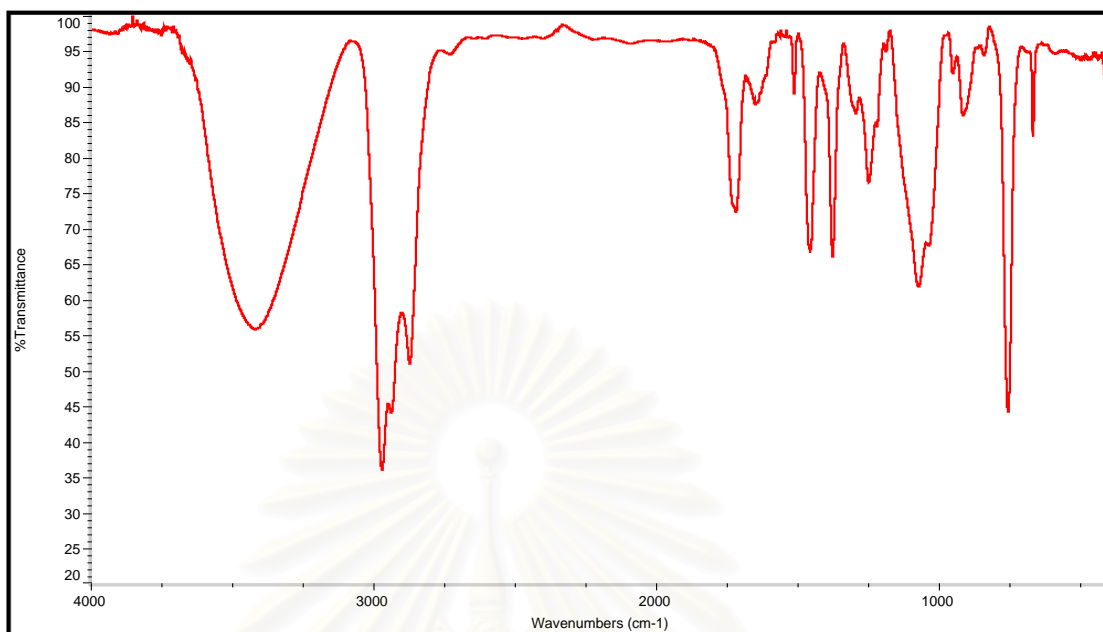


(c)



(d)

Figure A8 (continued) FT-IR spectra of CR derived effect of temperature

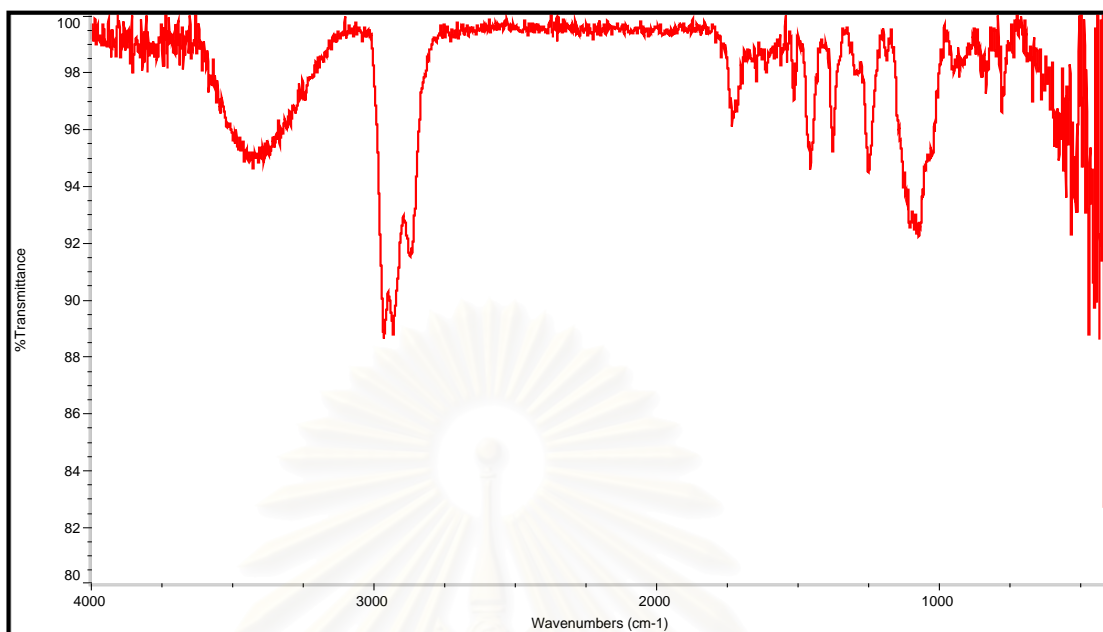


(a)

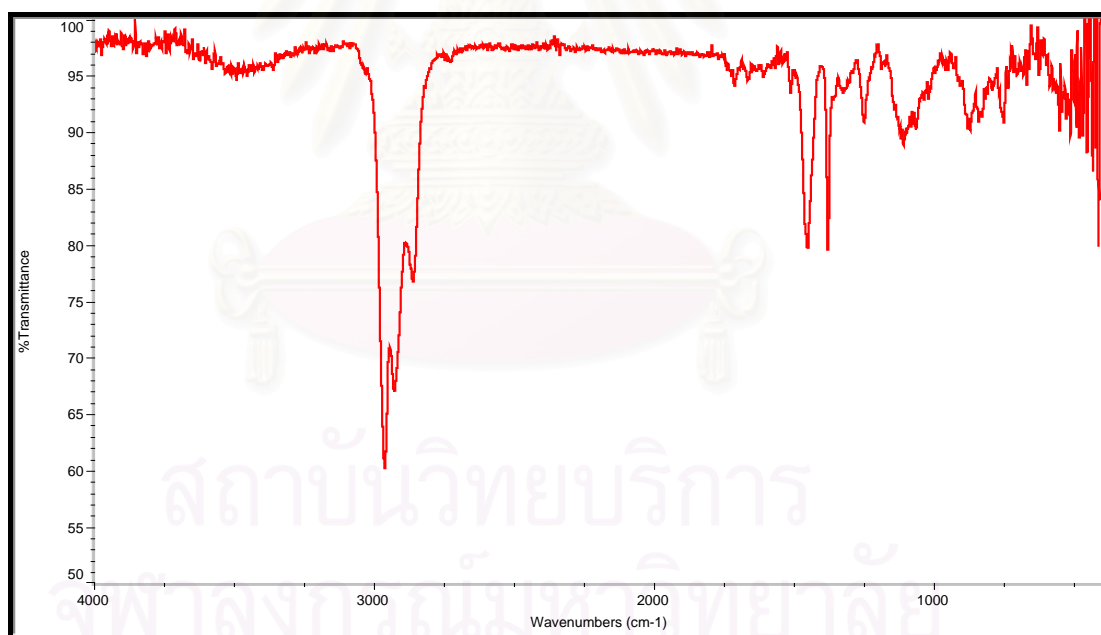


(b)

Figure A9 FT-IR spectra of CR derived effect of pH at (a) 1 (b) 2 (c) 3 and (d) 4



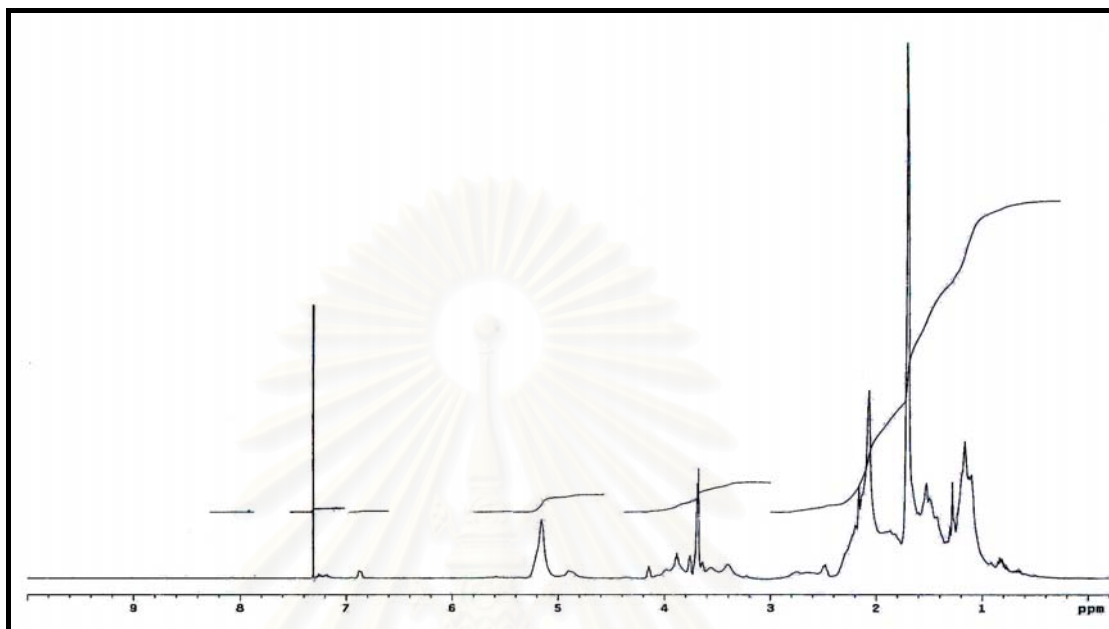
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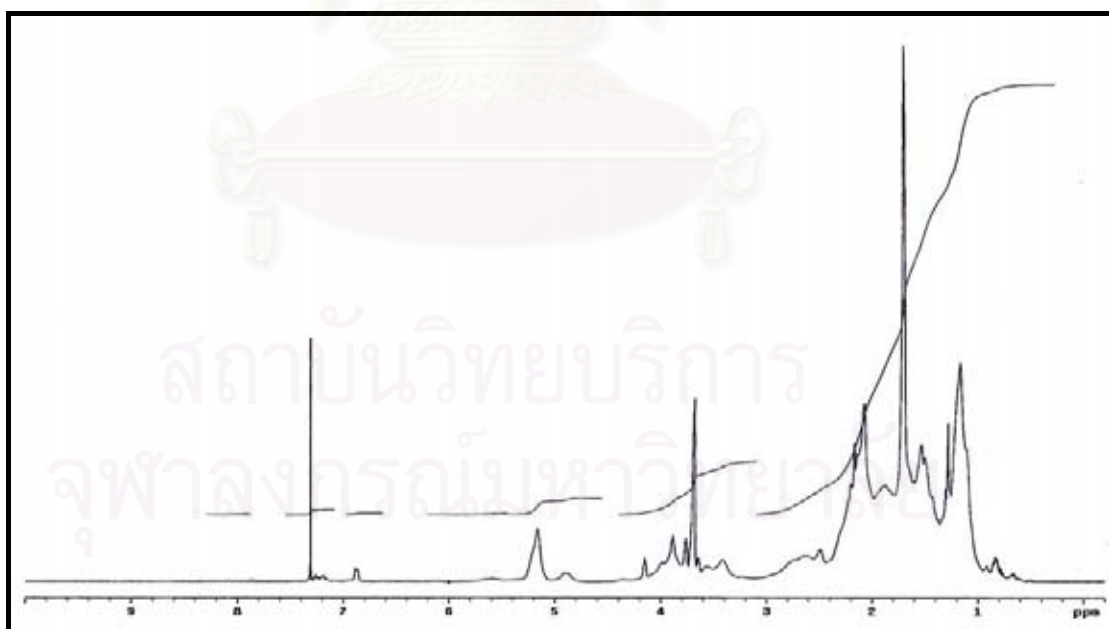
(d)

Figure A9 (continued) FT-IR spectra of CR derived effect of pH

APPENDIX B

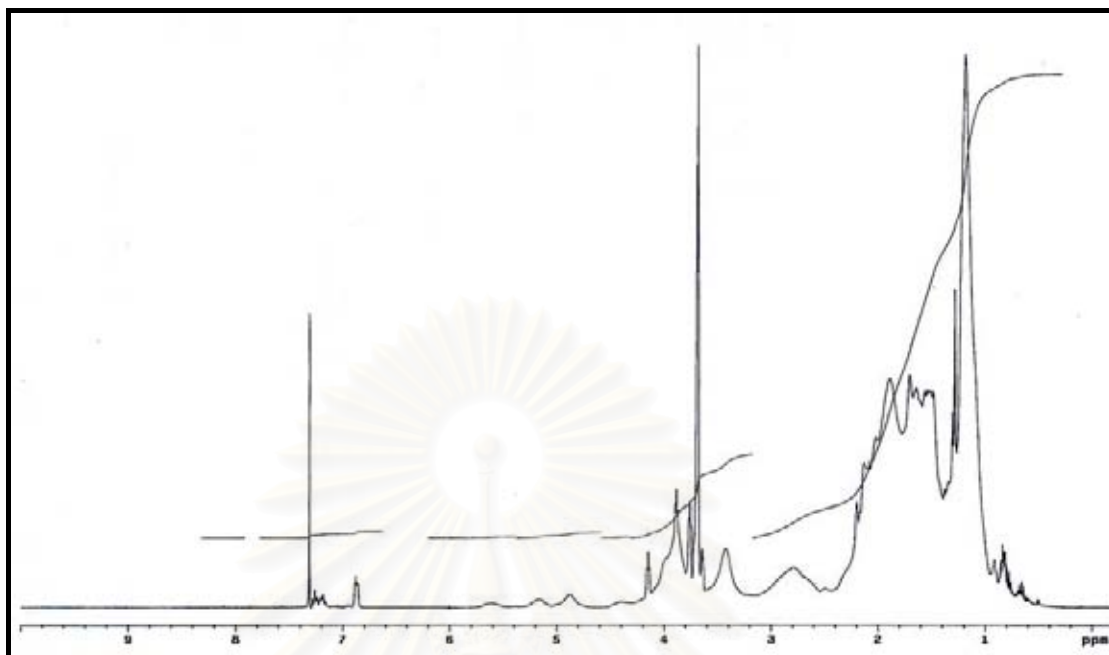


(a)

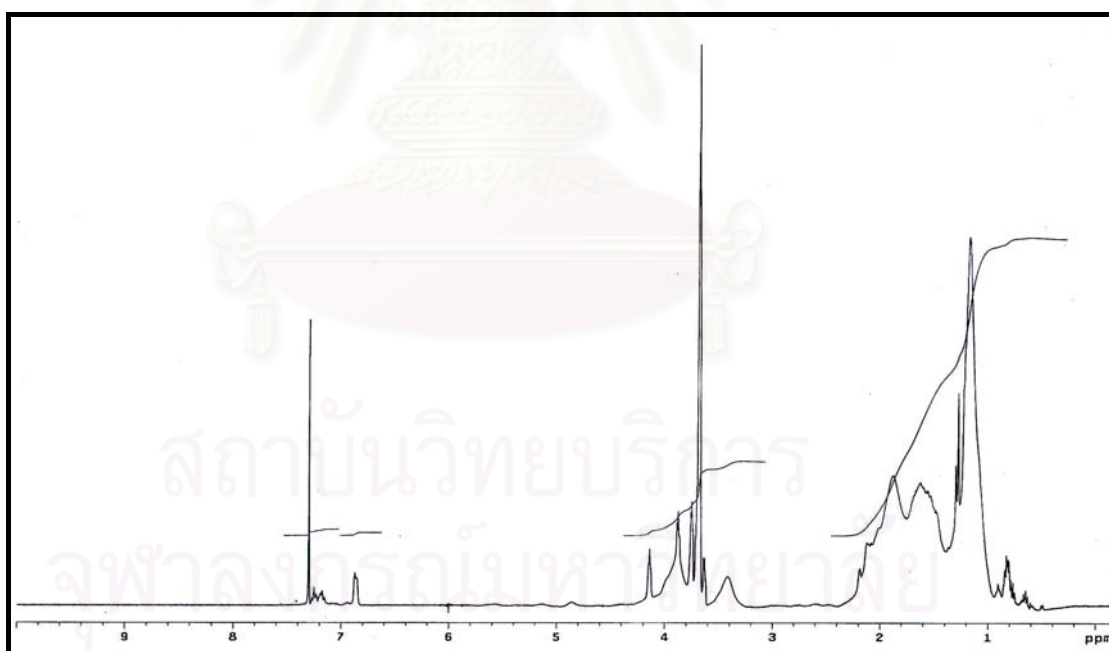


(b)

Figure B1 $^1\text{H-NMR}$ spectra of CR derived effect of ratio of $\text{NaOCl}:\text{NaCl} = 0:1$ (by mol) for (a) 1 (b) 2 (c) 4 and (d) 6 hours

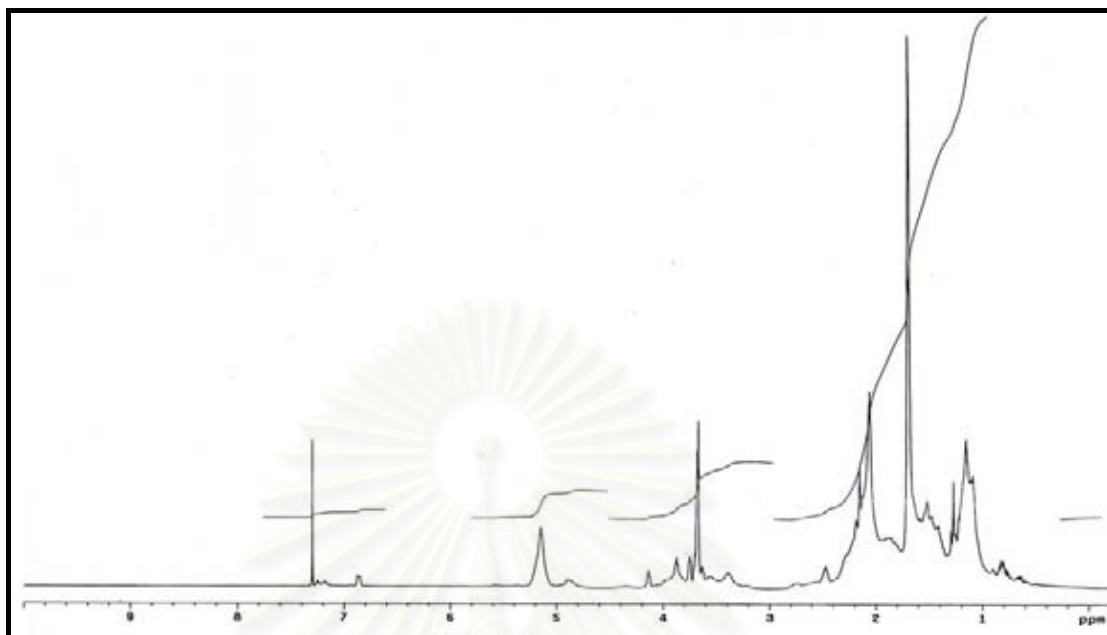


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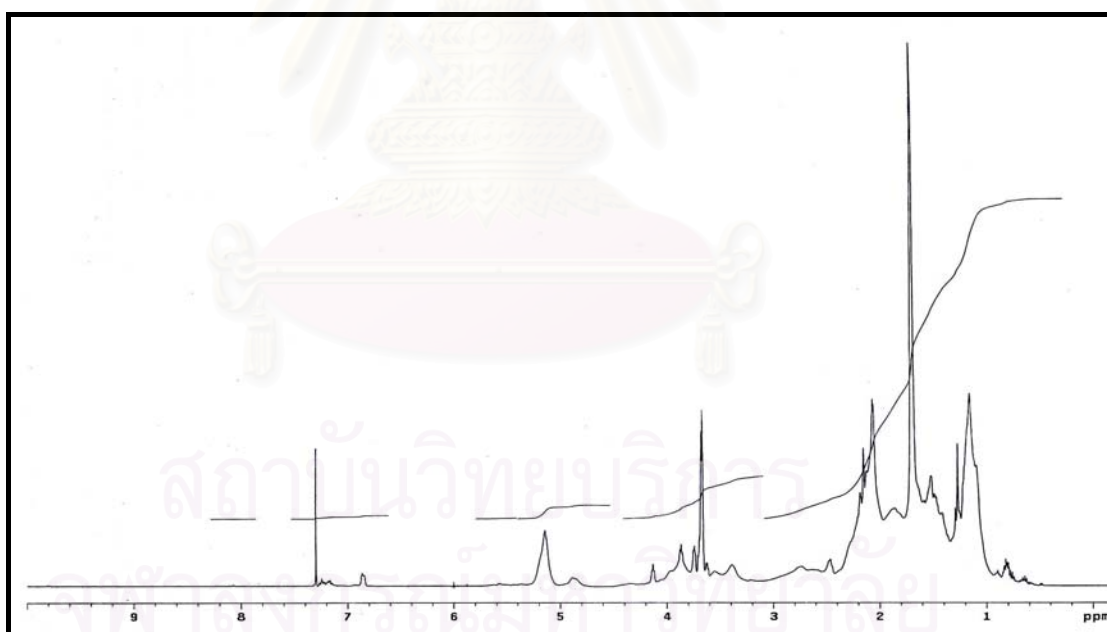


(d)

Figure B1 (continued) ^1H -NMR spectra of CR derived effect of ratio of
NaOCl:NaCl = 0:1 (by mol)

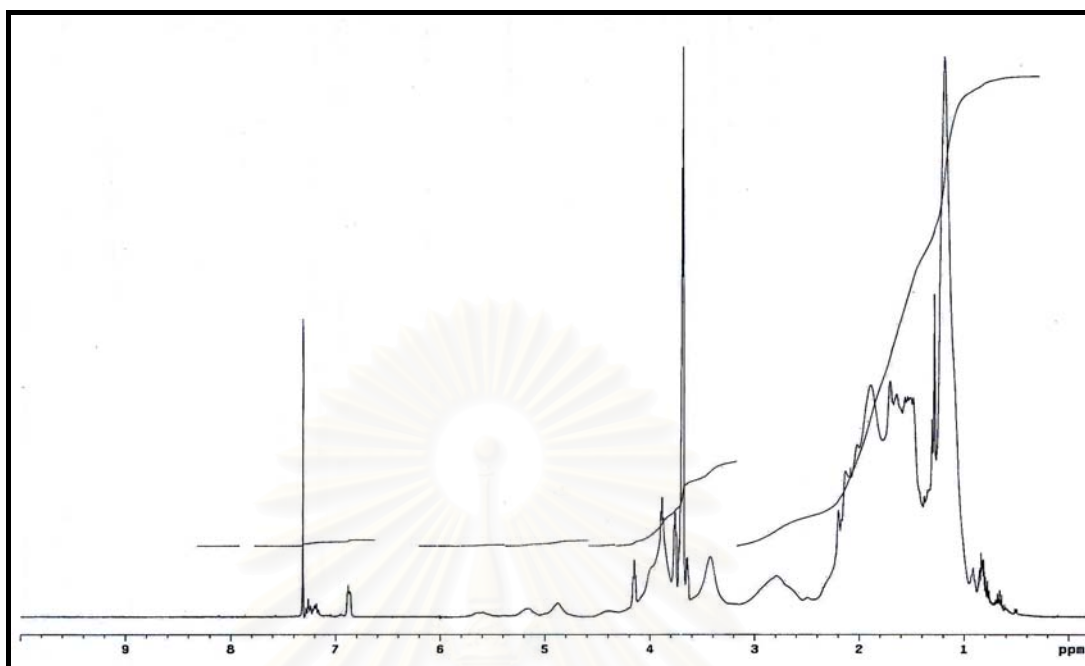


(a)

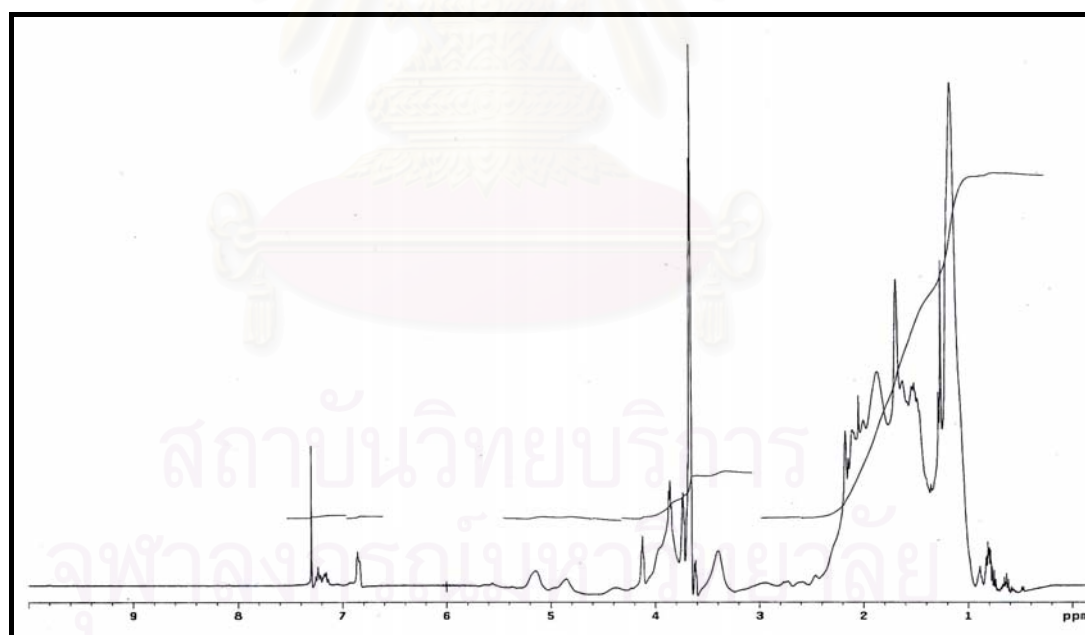


(b)

Figure B2 $^1\text{H-NMR}$ spectra of CR derived effect of ratio of $\text{NaOCl}:\text{NaCl} = 1:0$
(by mol) for (a) 1 (b) 2 (c) 4 and (d) 6 hours

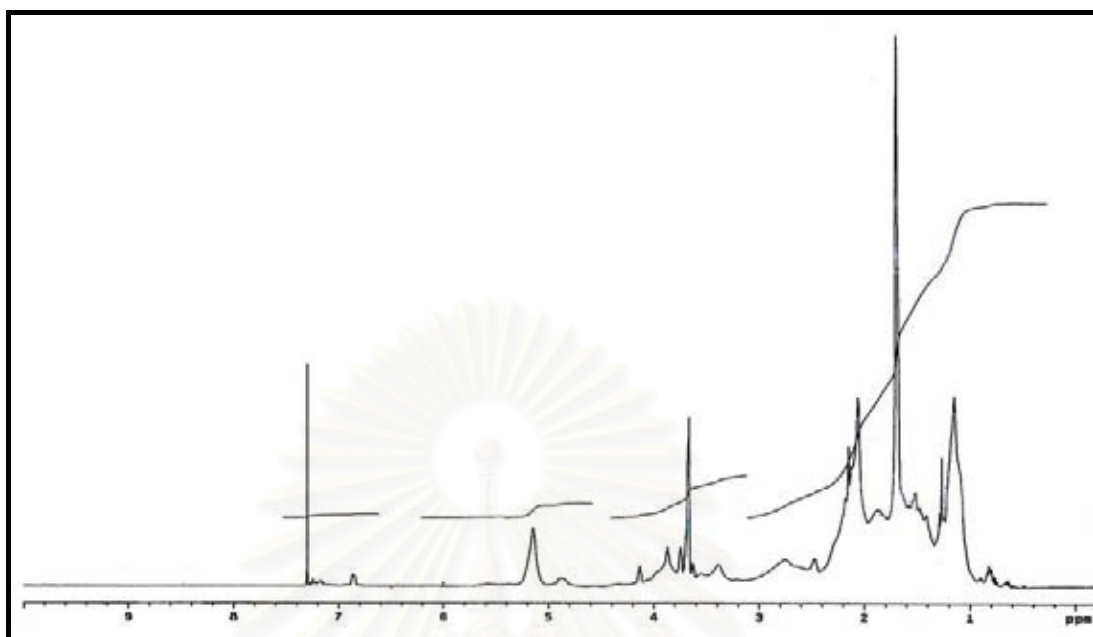


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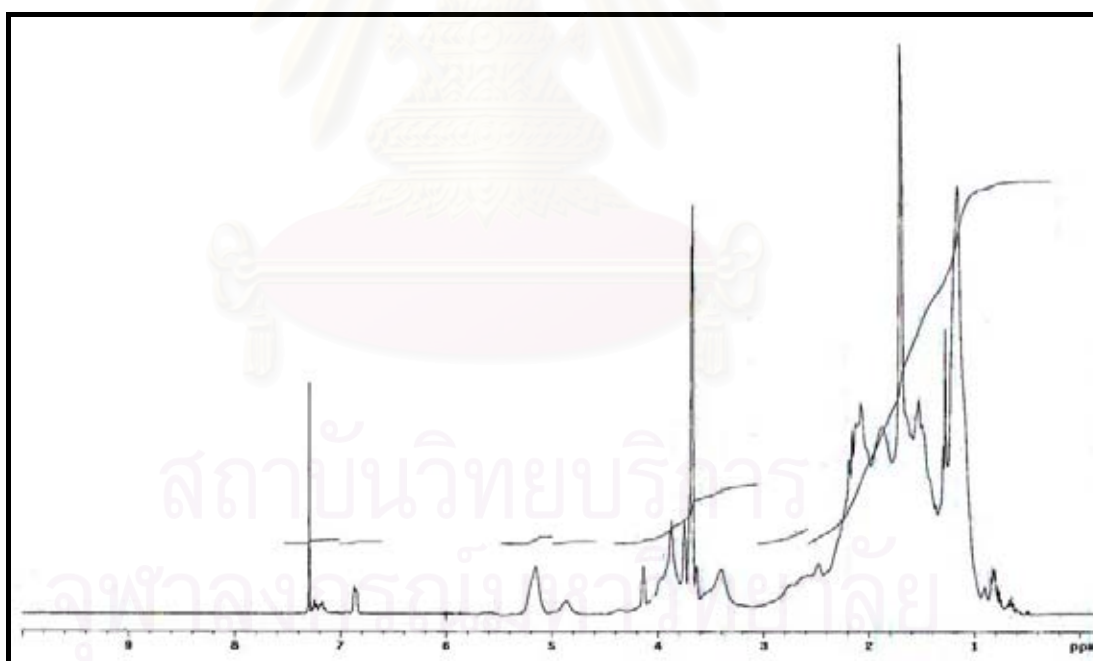


(d)

Figure B2 (continued) ^1H -NMR spectra of CR derived effect of ratio of $\text{NaOCl}:\text{NaCl} = 1:0$ (by mol)

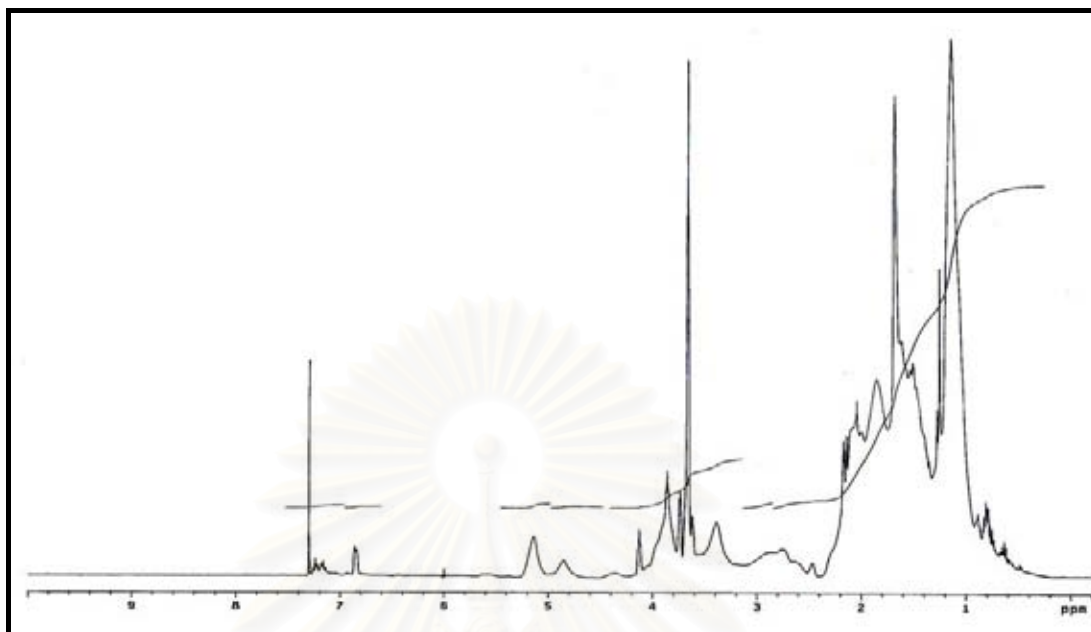


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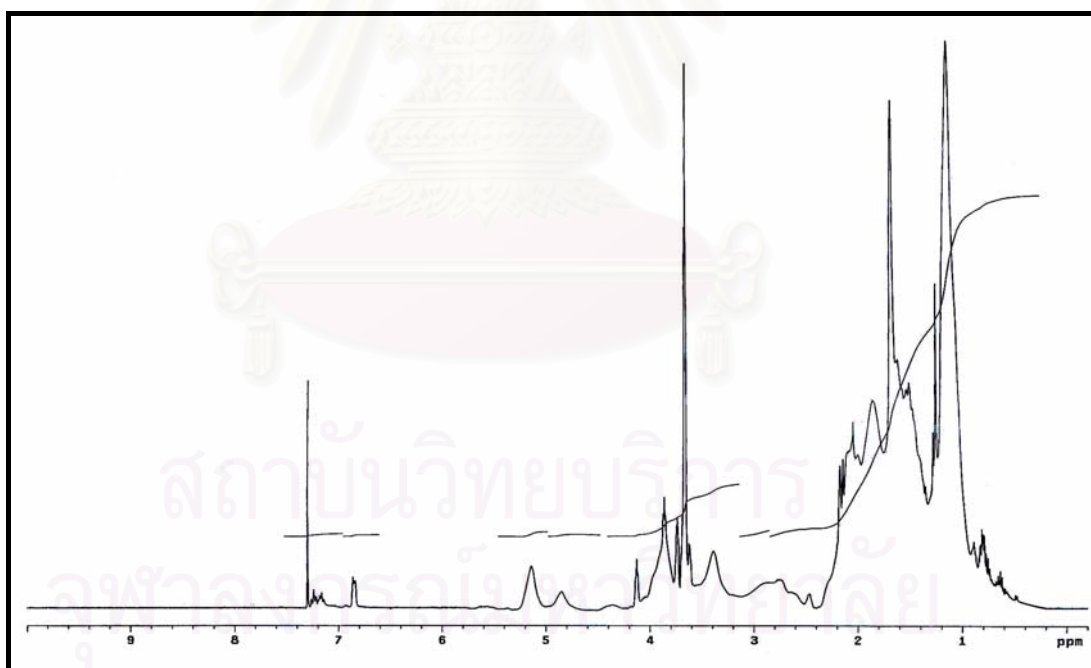


(b)

Figure B3 $^1\text{H-NMR}$ spectra of CR derived effect of ratio of $\text{NaOCl}:\text{NaCl} = 1:1$
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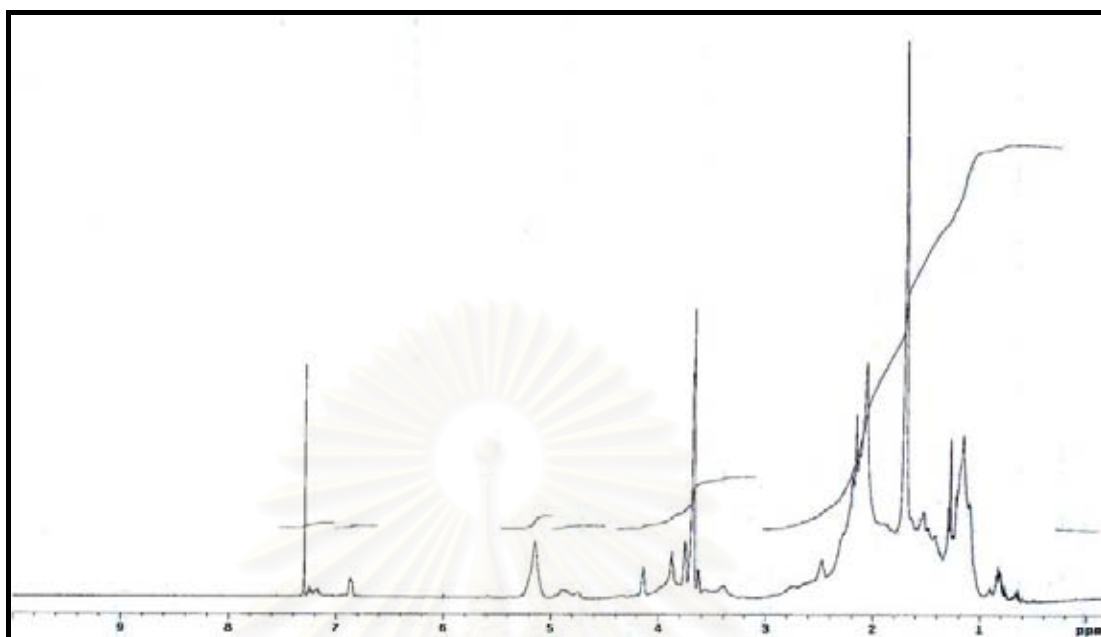


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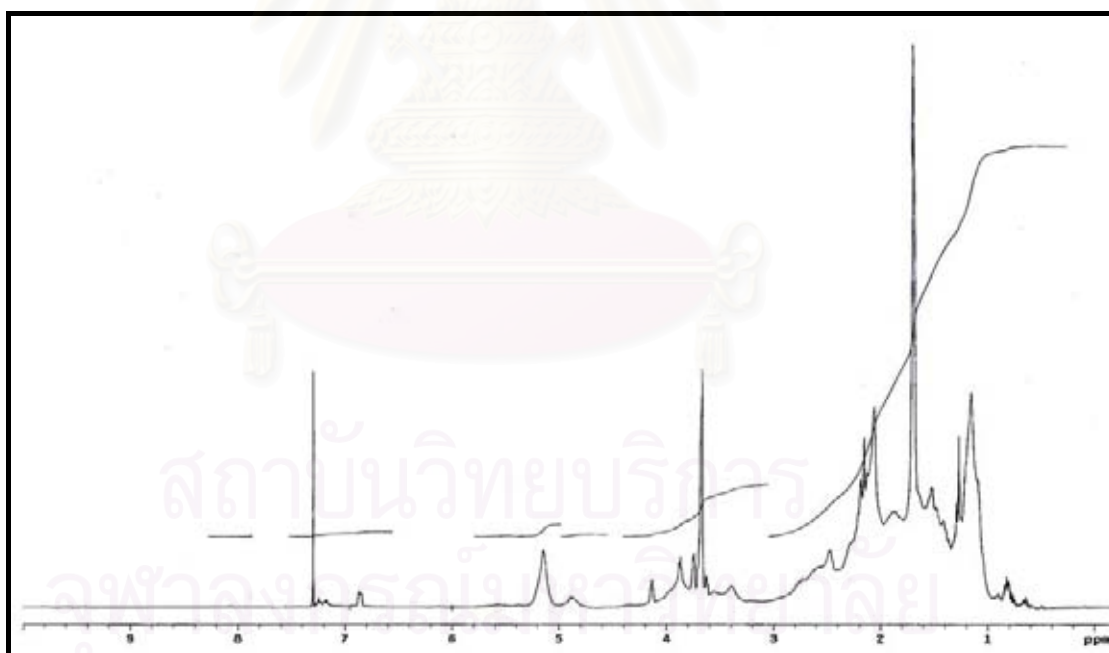


(d)

Figure B3 (continued) $^1\text{H-NMR}$ spectra of CR derived effect of ratio of $\text{NaOCl}:\text{NaCl} = 1:1$ (by mol)

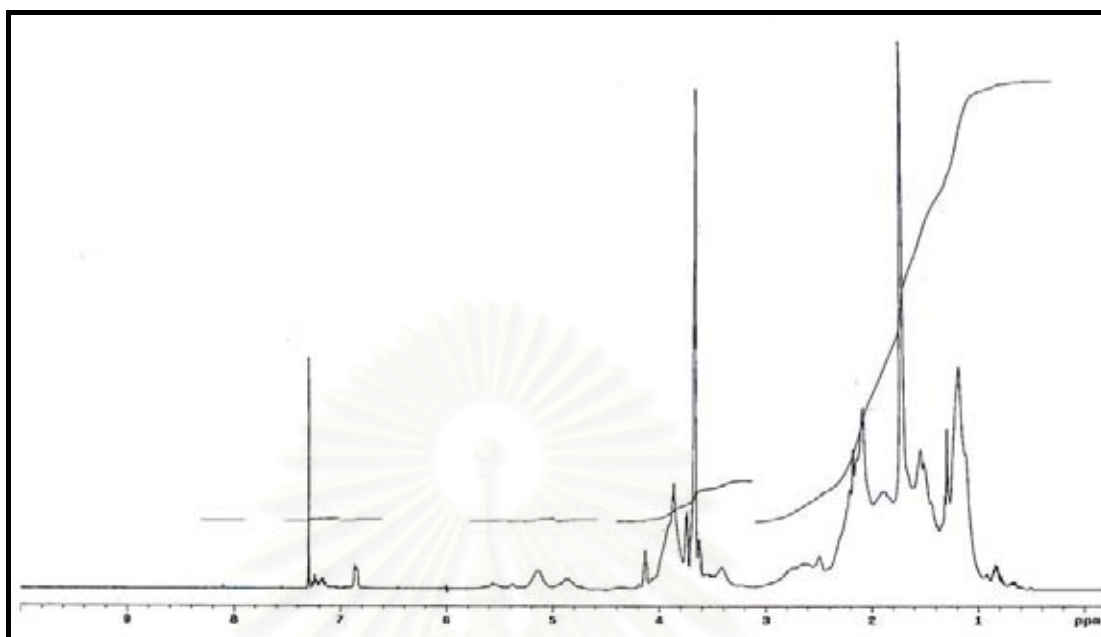


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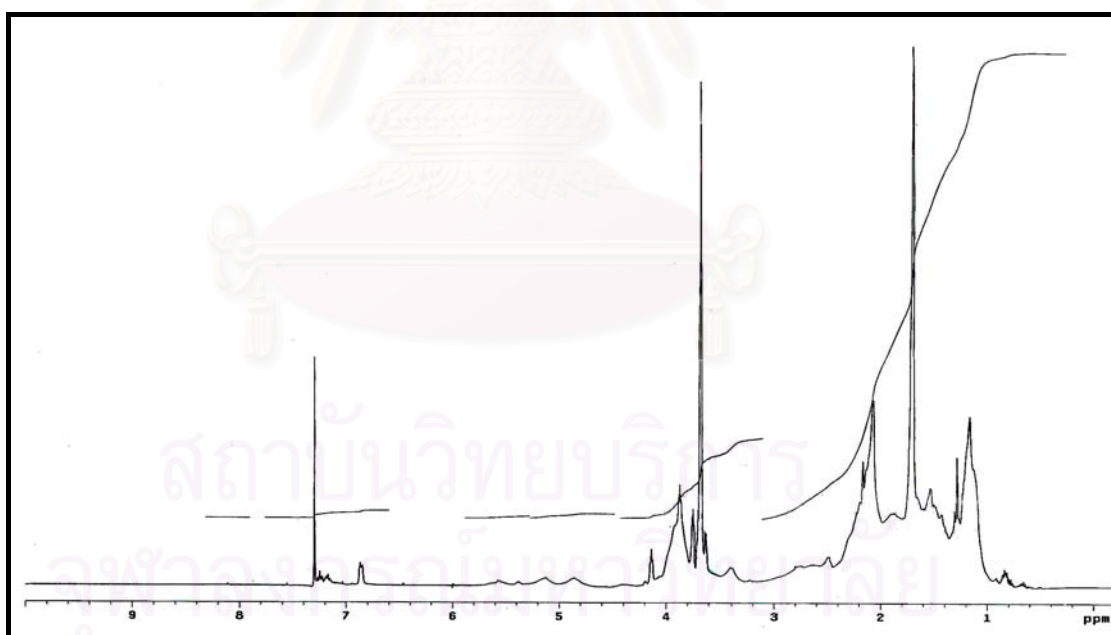


(b)

Figure B4 $^1\text{H-NMR}$ spectra of CR derived effect of ratio of $\text{NaOCl}:\text{NaCl} = 1:2$ (by mol) for (a) 1 (b) 2 (c) 4 and (d) 6 hours

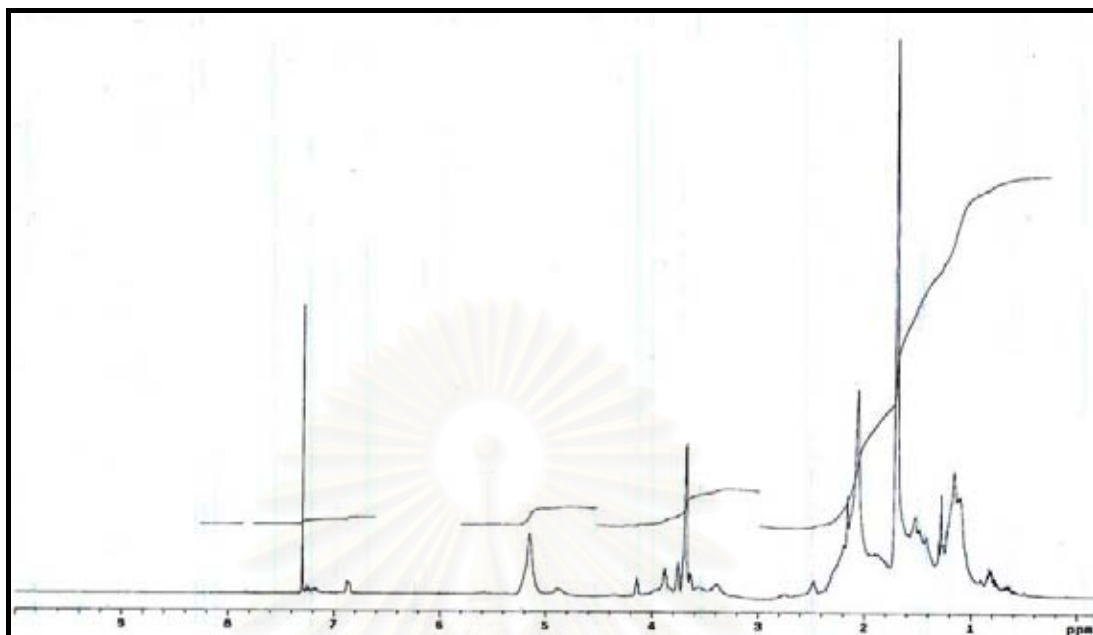


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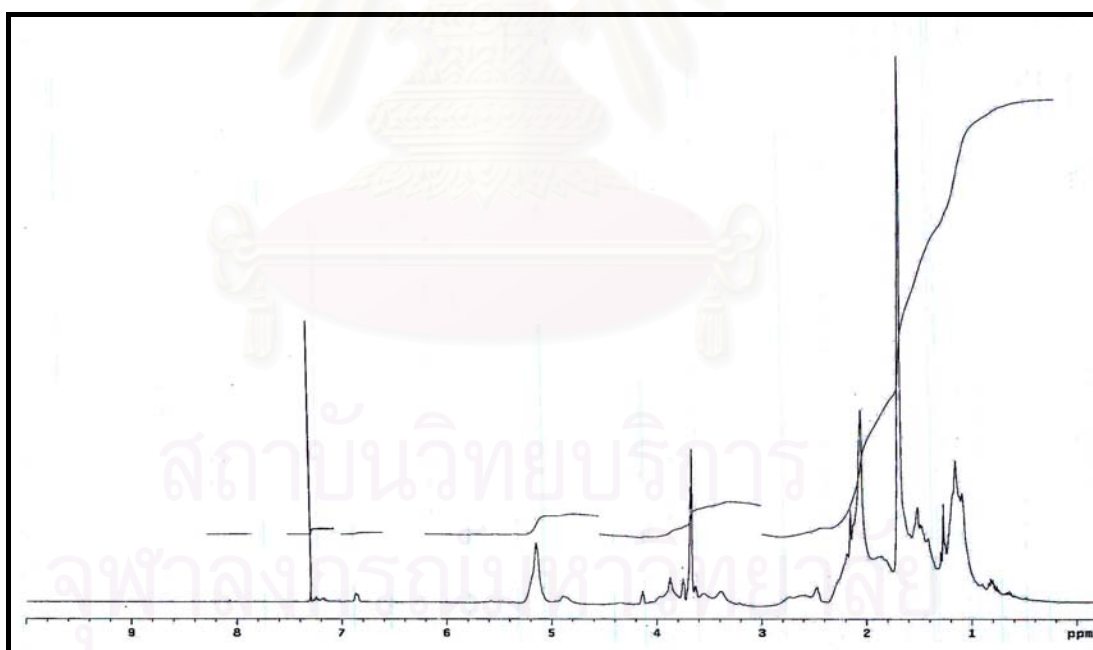


(d)

Figure B4 (continued) ^1H -NMR spectra of CR derived effect of ratio of
NaOCl:NaCl = 1:2 (by mol)

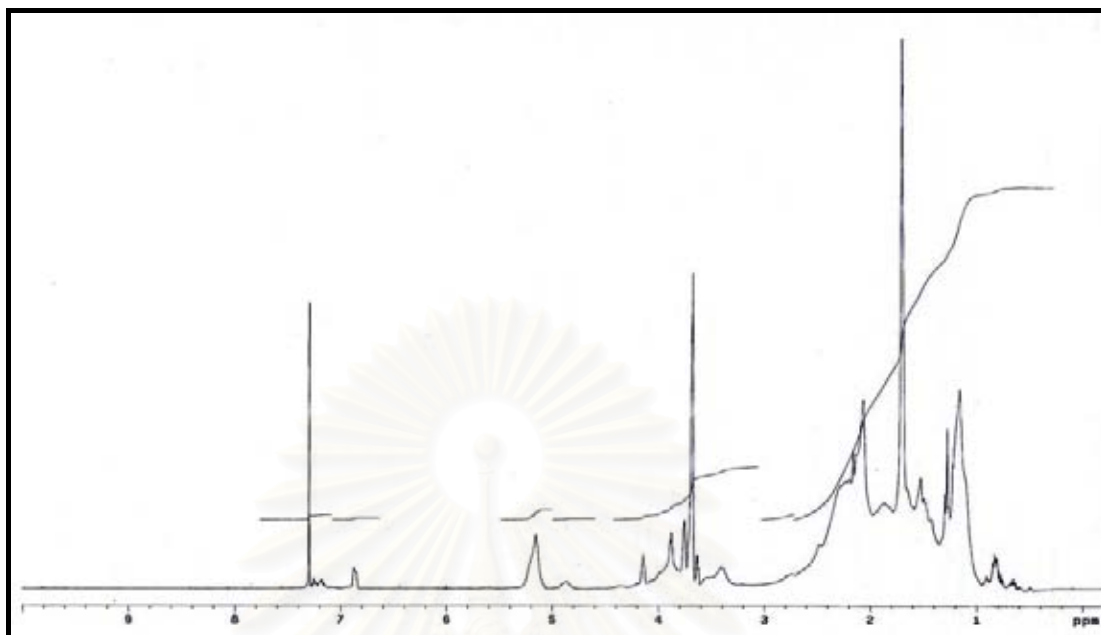


(a)

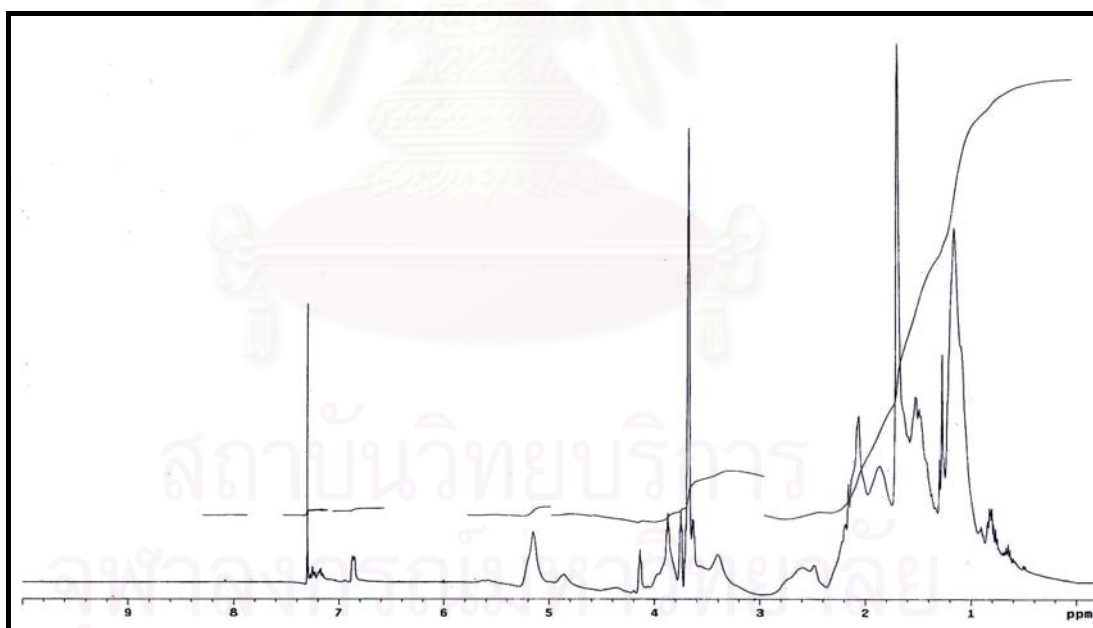


(b)

Figure B5 $^1\text{H-NMR}$ spectra of CR derived effect of ratio of $\text{NaOCl}:\text{NaCl} = 1:4$ (by mol) for (a) 1 (b) 2 (c) 4 and (d) 6 hours

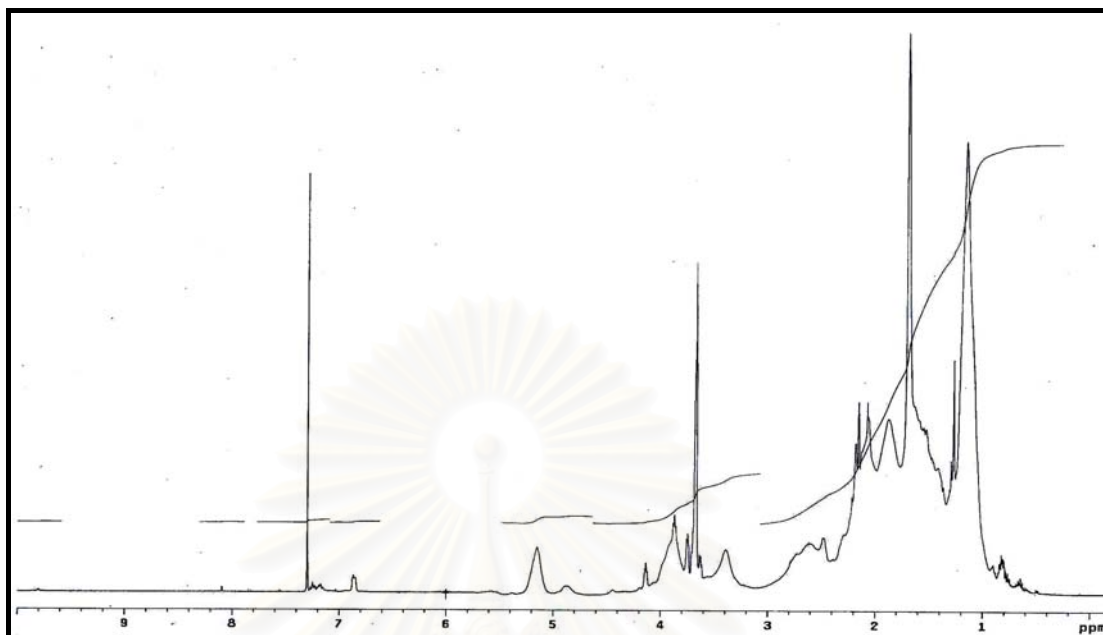


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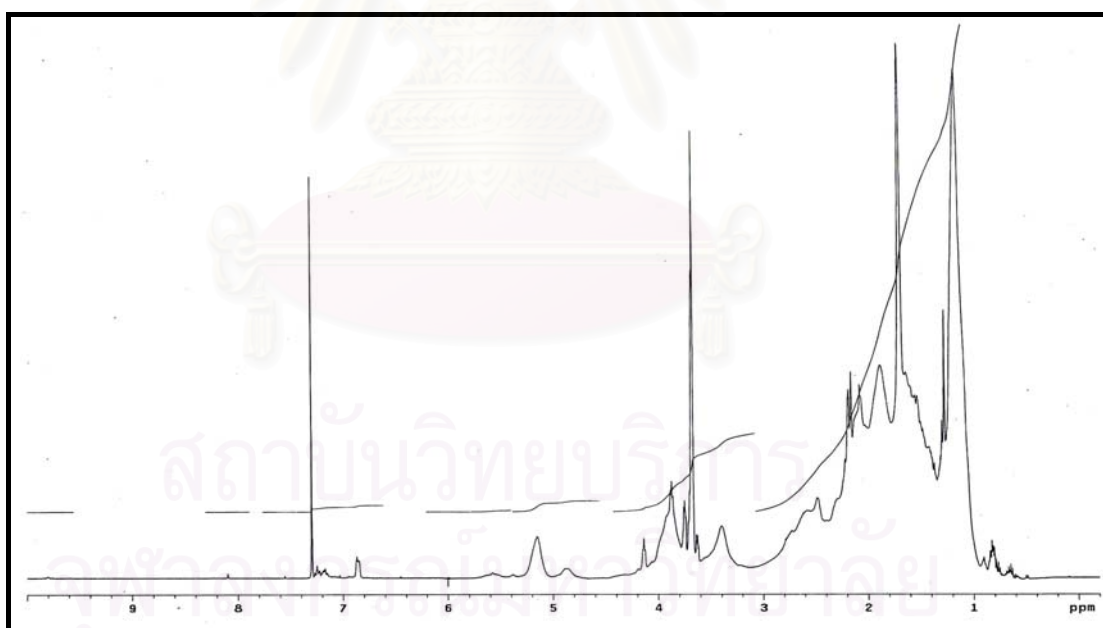


(d)

Figure B5 (continued) $^1\text{H-NMR}$ spectra of CR derived effect of ratio of
 $\text{NaOCl}:\text{NaCl} = 1:4$ (by mol)

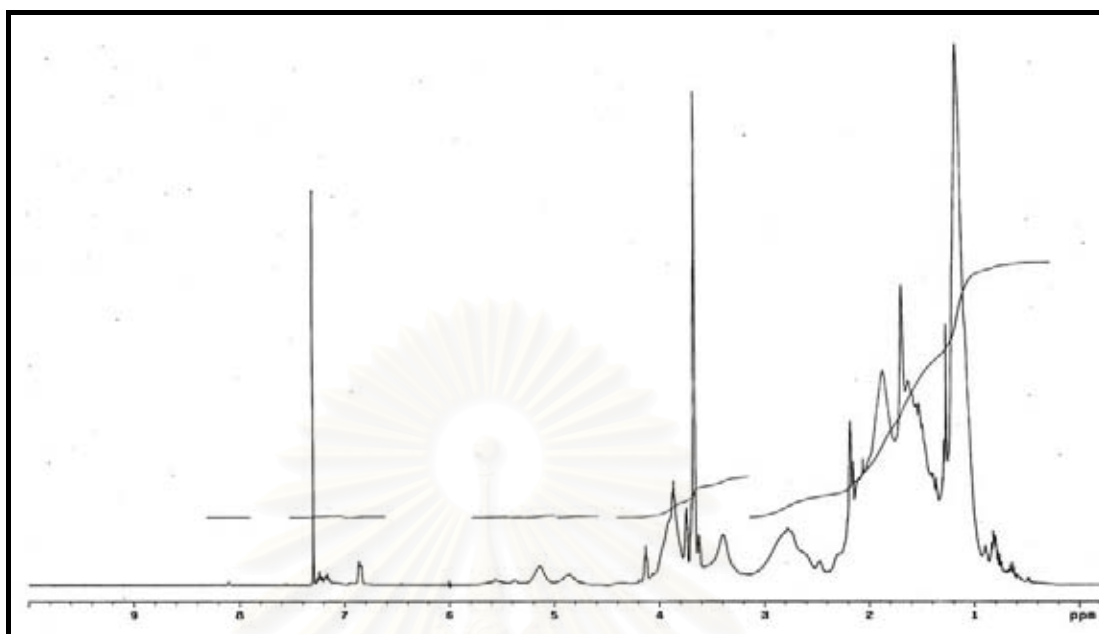


(a)

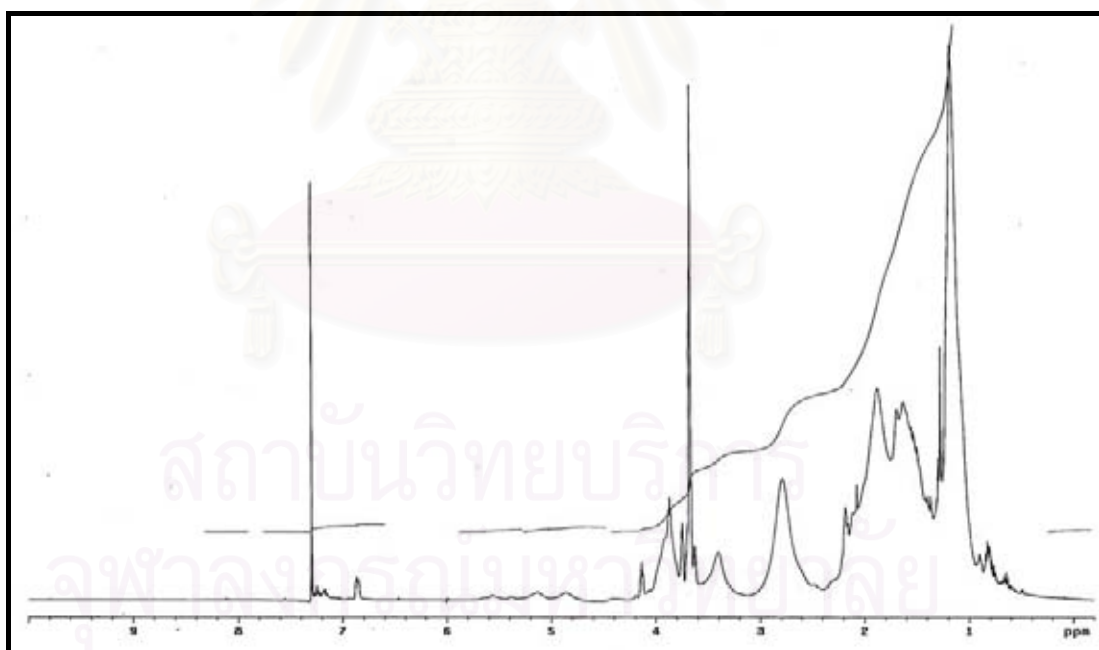


(b)

Figure B6 $^1\text{H-NMR}$ spectra of CR derived effect of ratio of $\text{NaOCl}:\text{NaCl} = 2:1$ (by mol) for (a) 1 (b) 2 (c) 4 and (d) 6 hours

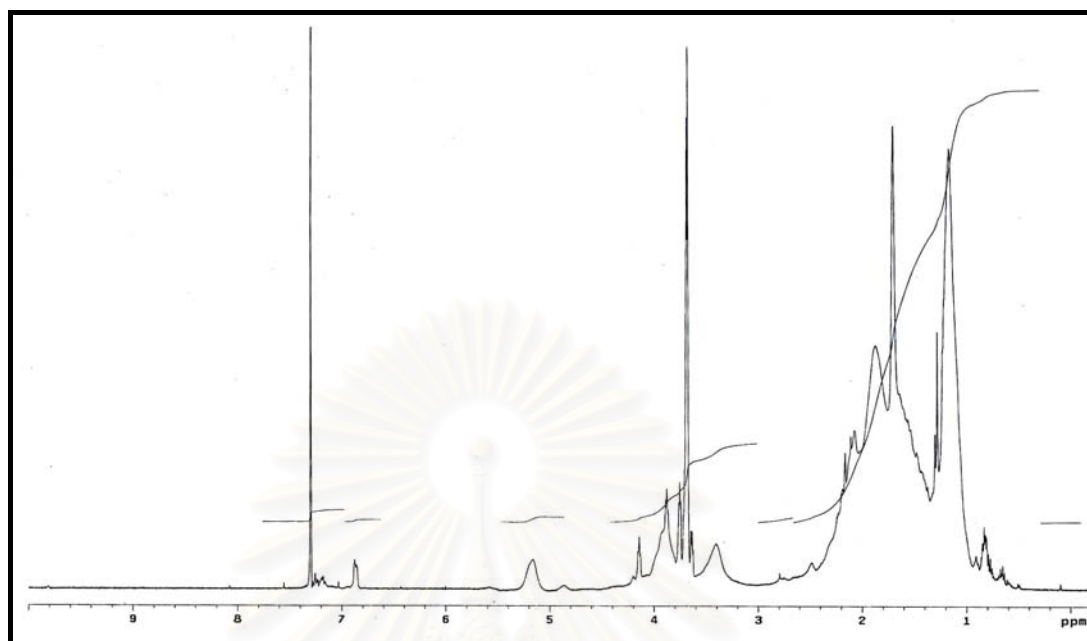


(c)

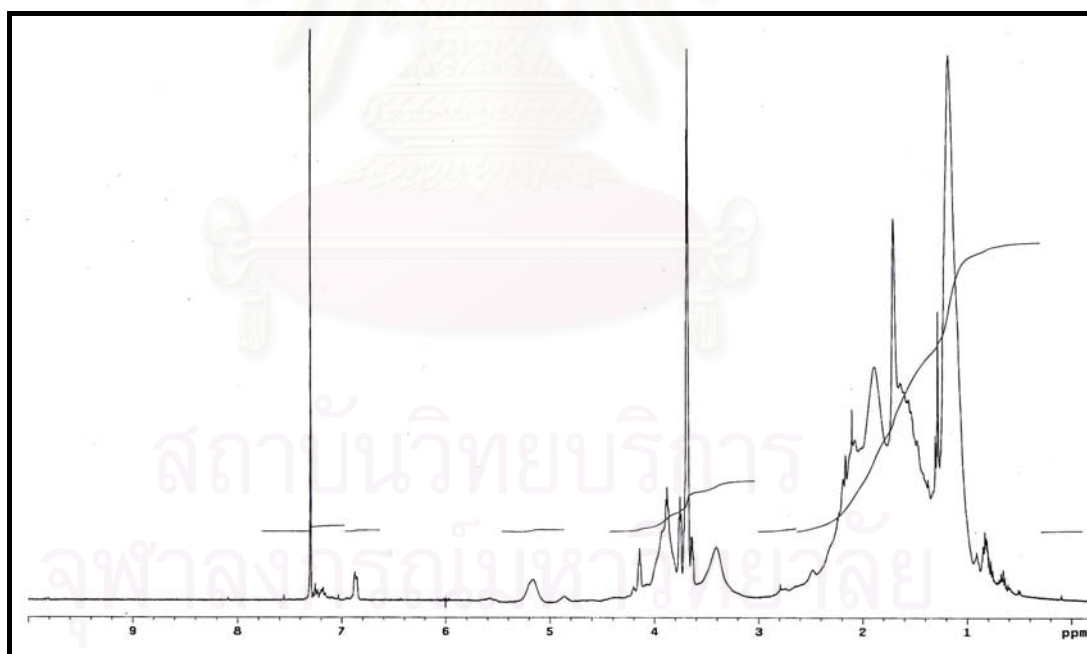


(d)

Figure B6 (continued) $^1\text{H-NMR}$ spectra of CR derived effect of ratio of $\text{NaOCl}:\text{NaCl} = 2:1$ (by mol)

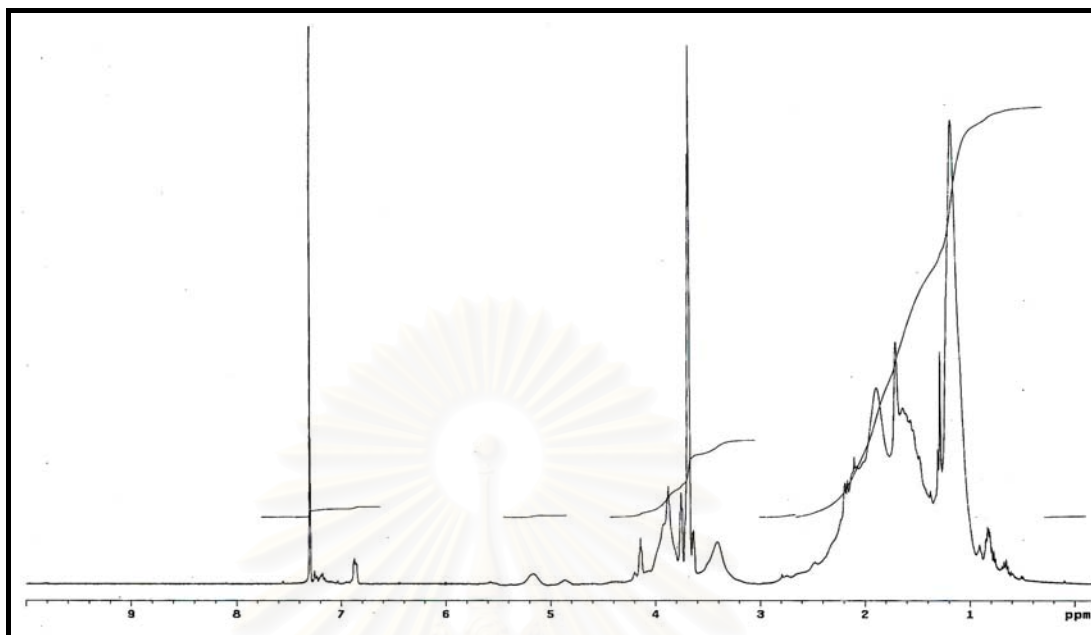


(a)

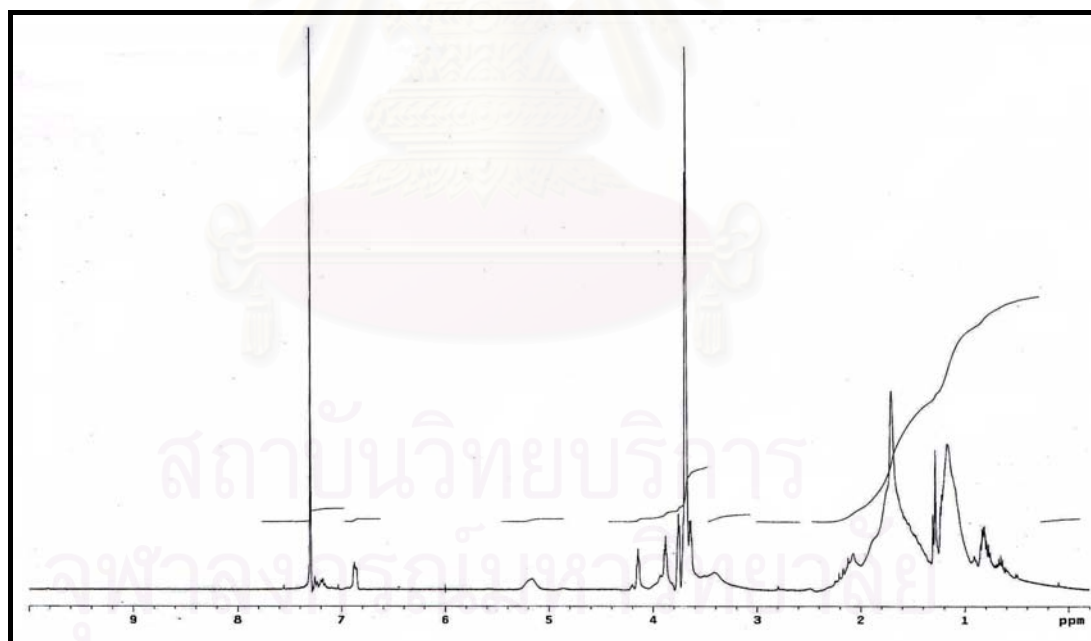


(b)

Figure B7 ^1H -NMR spectra of CR derived effect of ratio of $\text{NaOCl}:\text{NaCl} = 4:1$ (by mol) for (a) 1 (b) 2 (c) 4 and (d) 6 hours

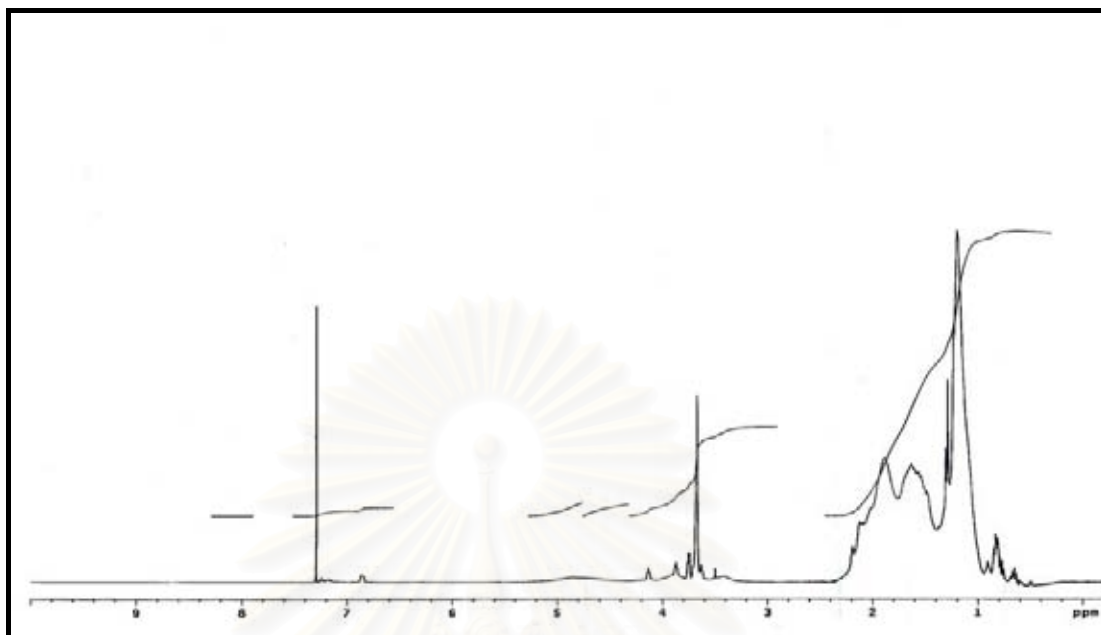


(c)

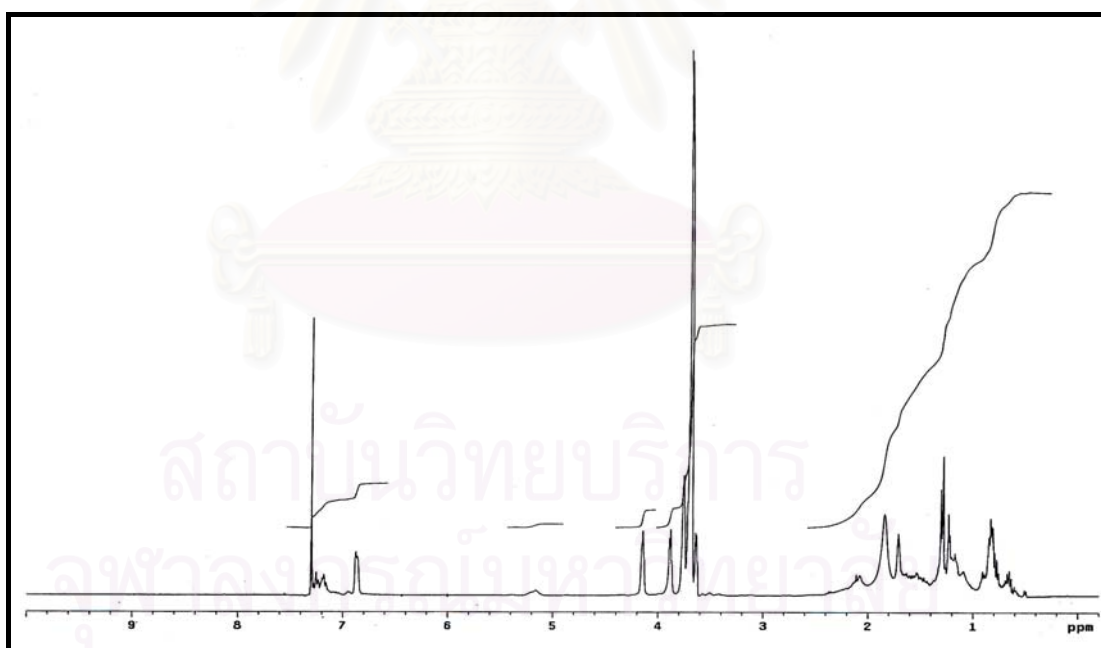


(d)

Figure B7 (continued) ^1H -NMR spectra of CR derived effect of ratio of
NaOCl:NaCl = 4:1 (by mol)

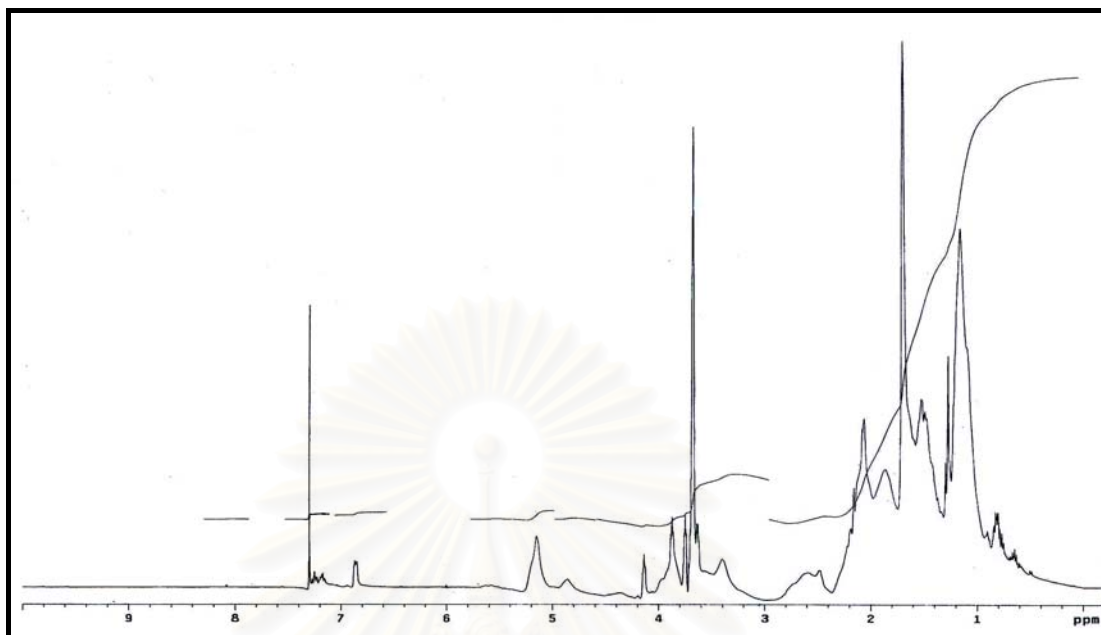


(a)

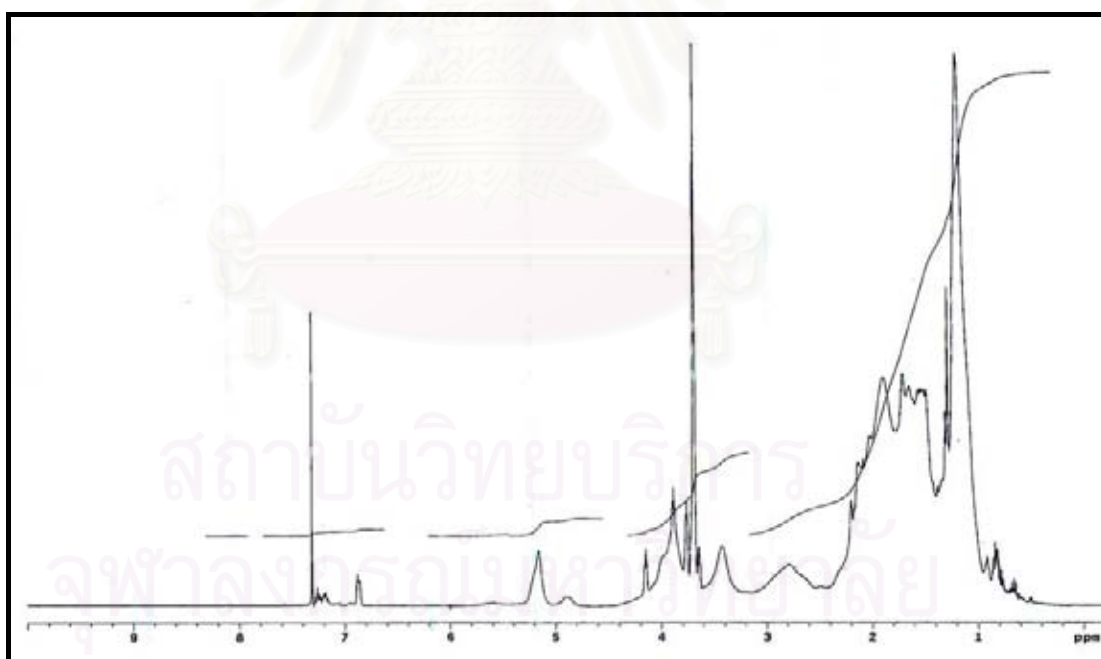


(b)

Figure B8 $^1\text{H-NMR}$ spectra of CR derived effect of temperature at (a) 10 (b) 20 (c) 30 and (d) 40°C

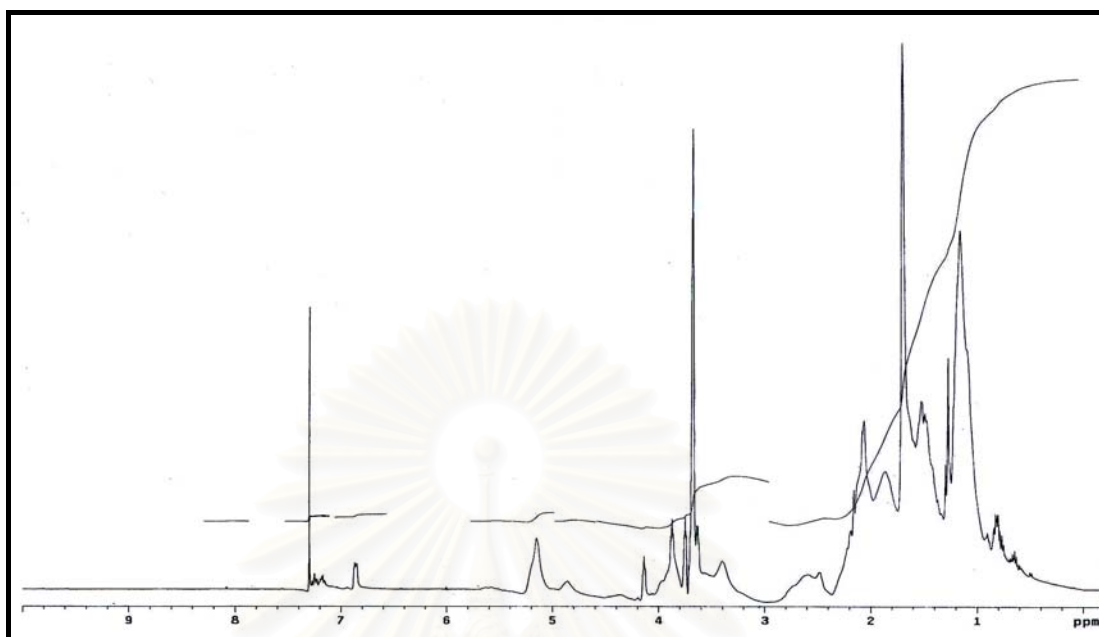


(c)

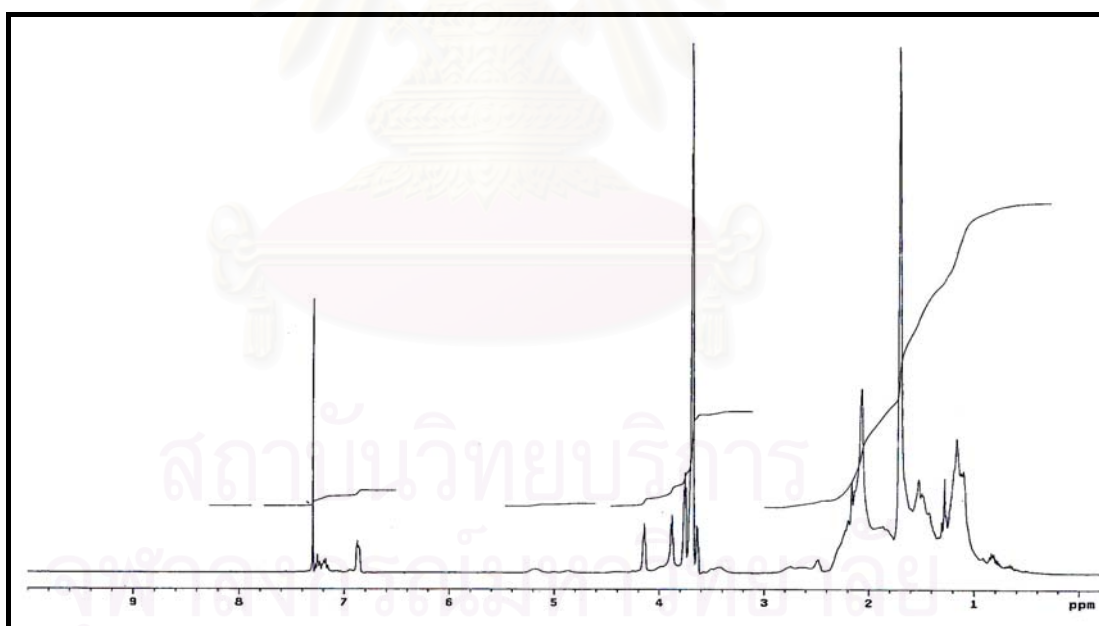


(d)

Figure B8 (continued) ^1H -NMR spectra of CR derived effect of temperature

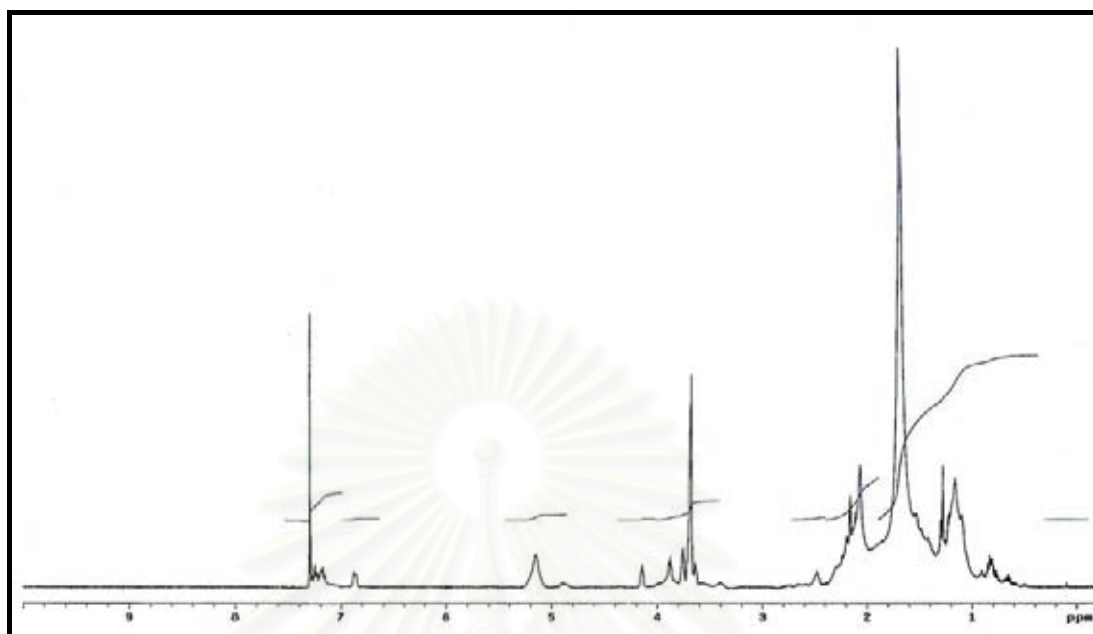


(a)

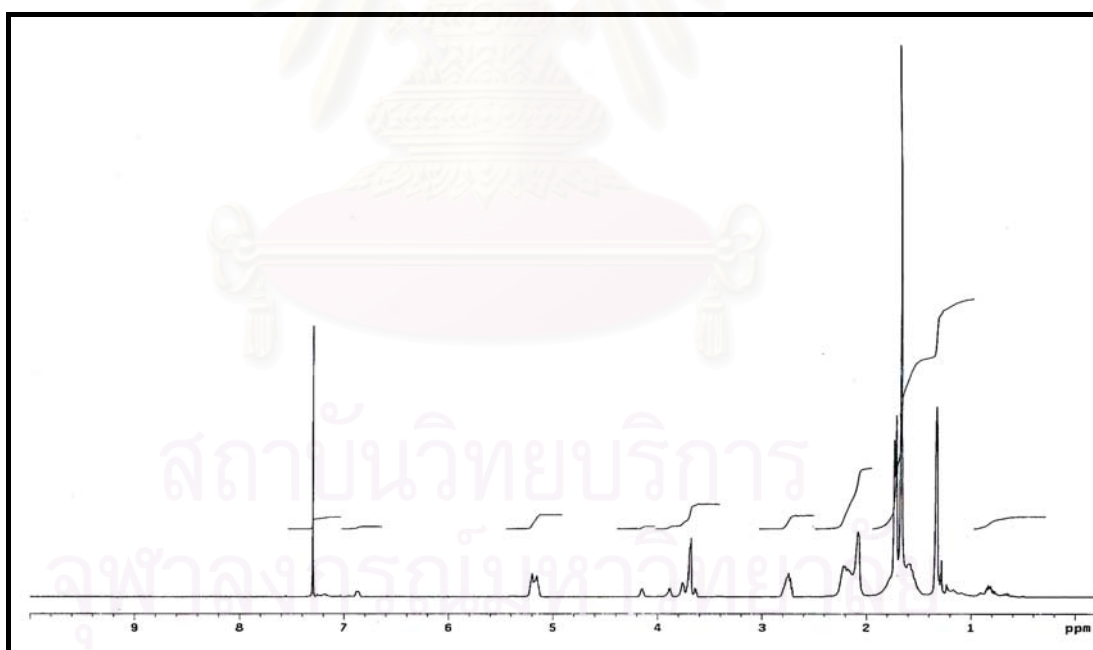


(b)

Figure B9 ^1H -NMR spectra of CR derived effect of pH at (a) 1 (b) 2 (c) 3 and (d) 4



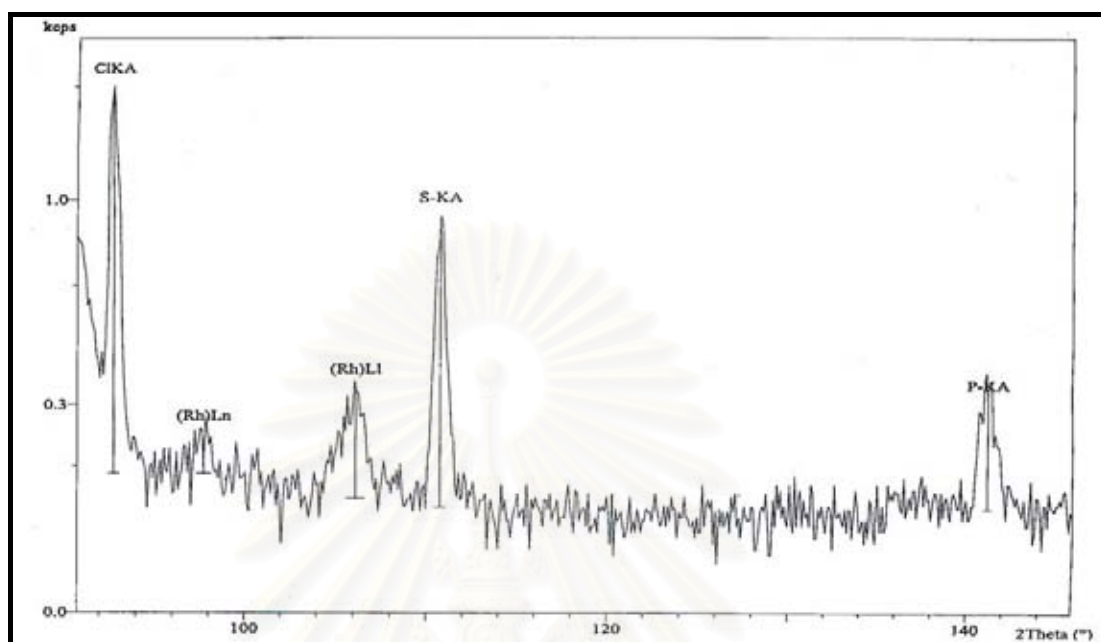
(c)



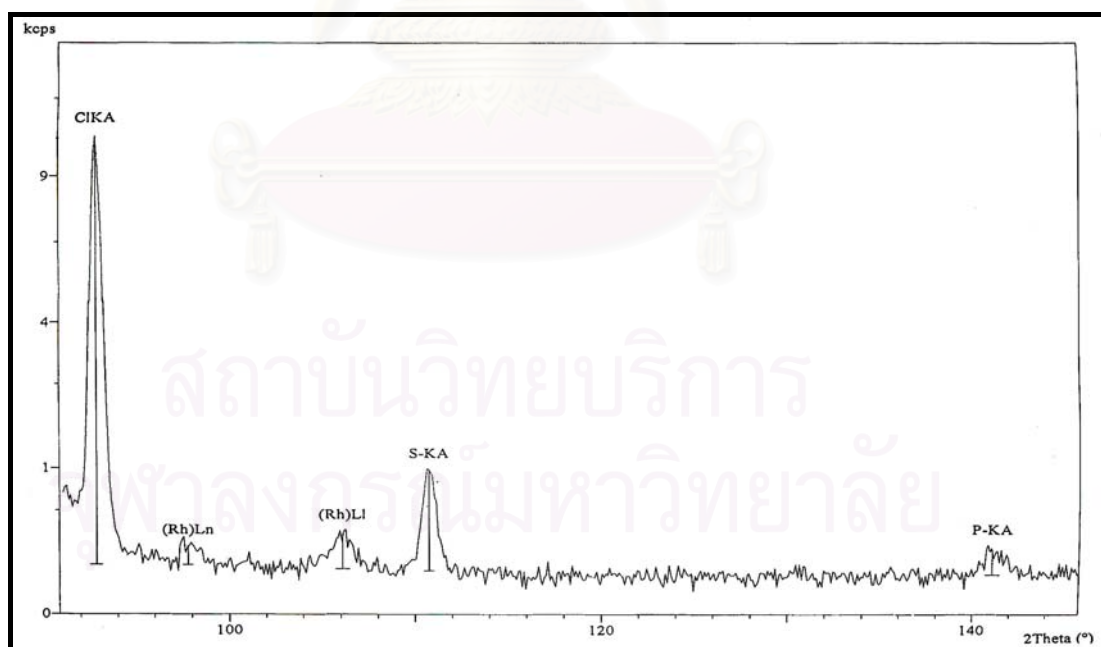
(d)

Figure B9 (continued) $^1\text{H-NMR}$ spectra of CR derived effect of pH

APPENDIX C

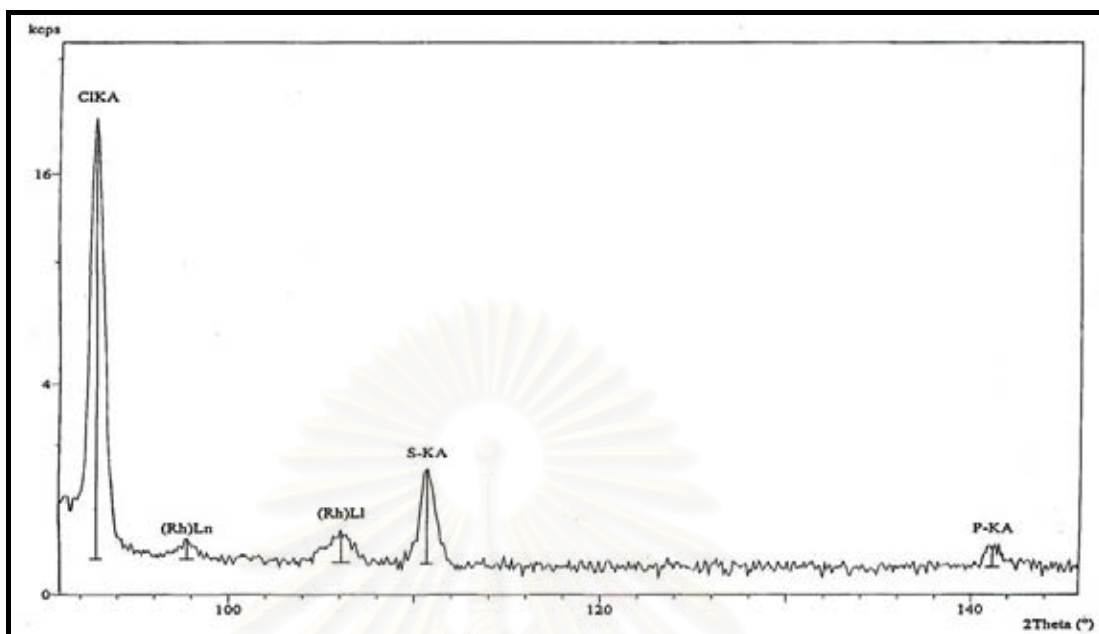


(a)

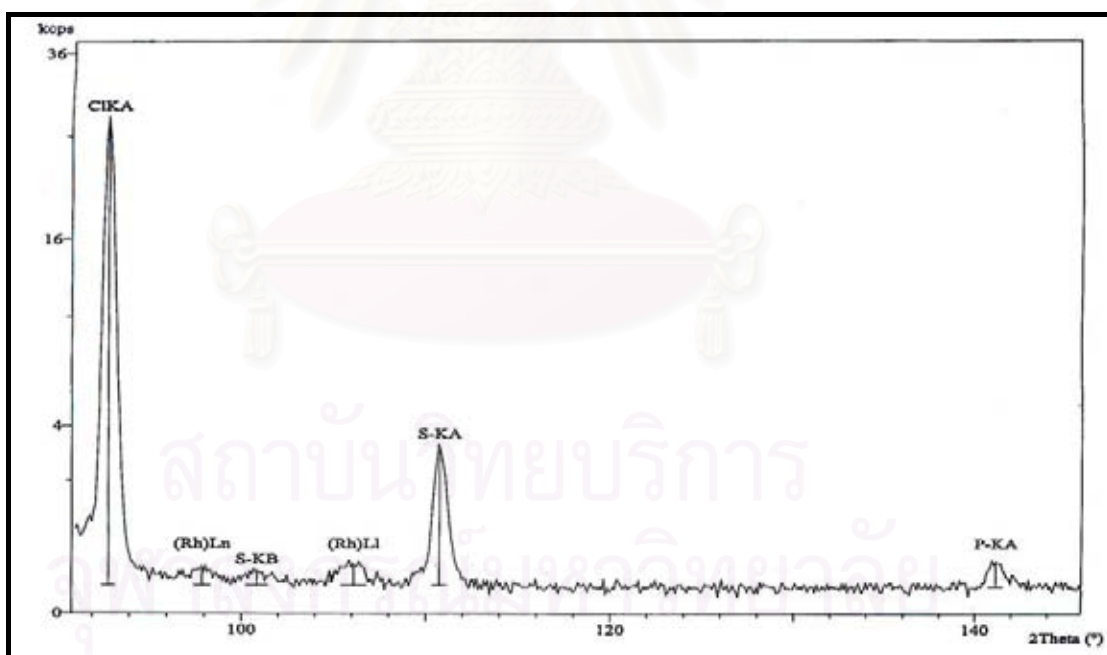


(b)

Figure C1 XRF spectra of CR derived effect of ratio of NaOCl:NaCl = 0:1
(by mol) for (a) 1 (b) 2 (c) 4 and (d) 6 hours

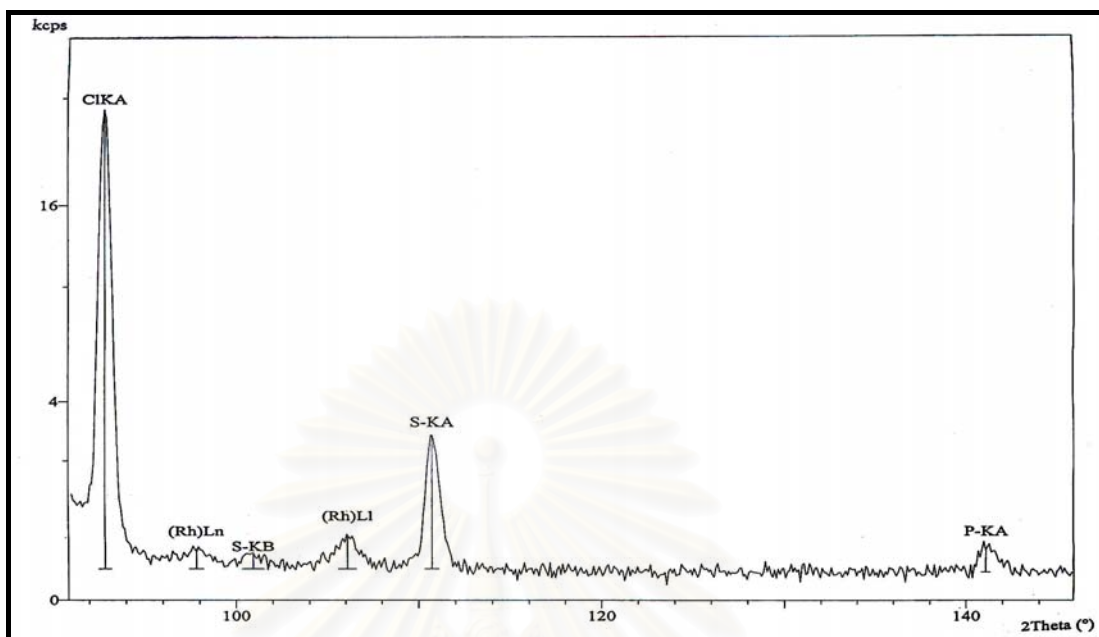


(c)

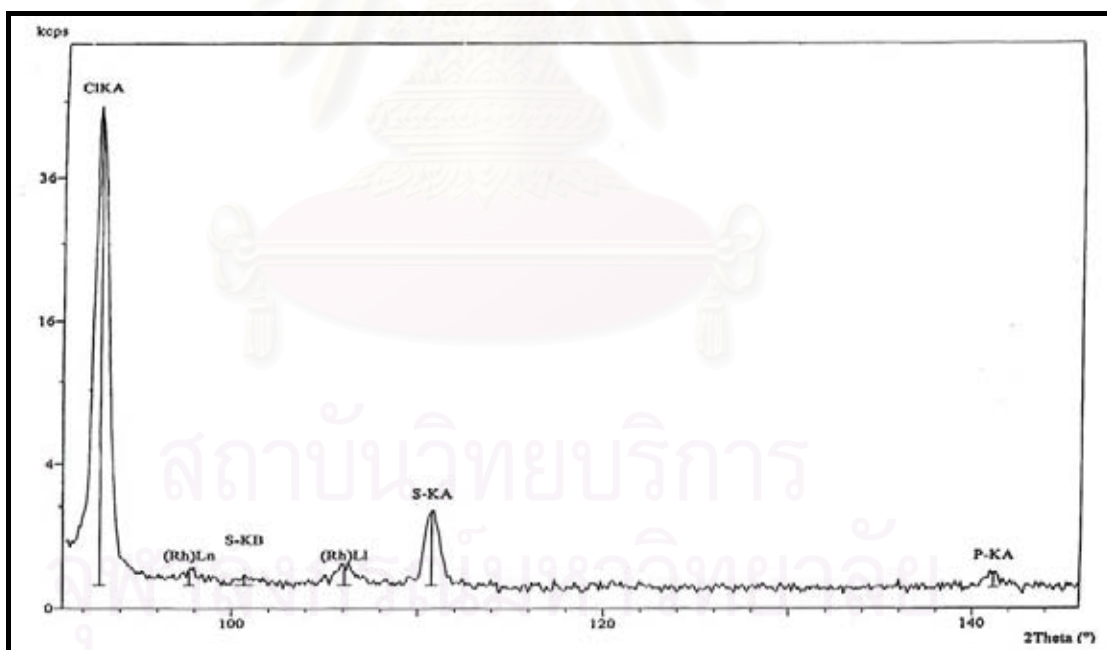


(d)

Figure C1 (continued) XRF spectra of CR derived effect of ratio of NaOCl:NaCl = 0:1 (by mol)

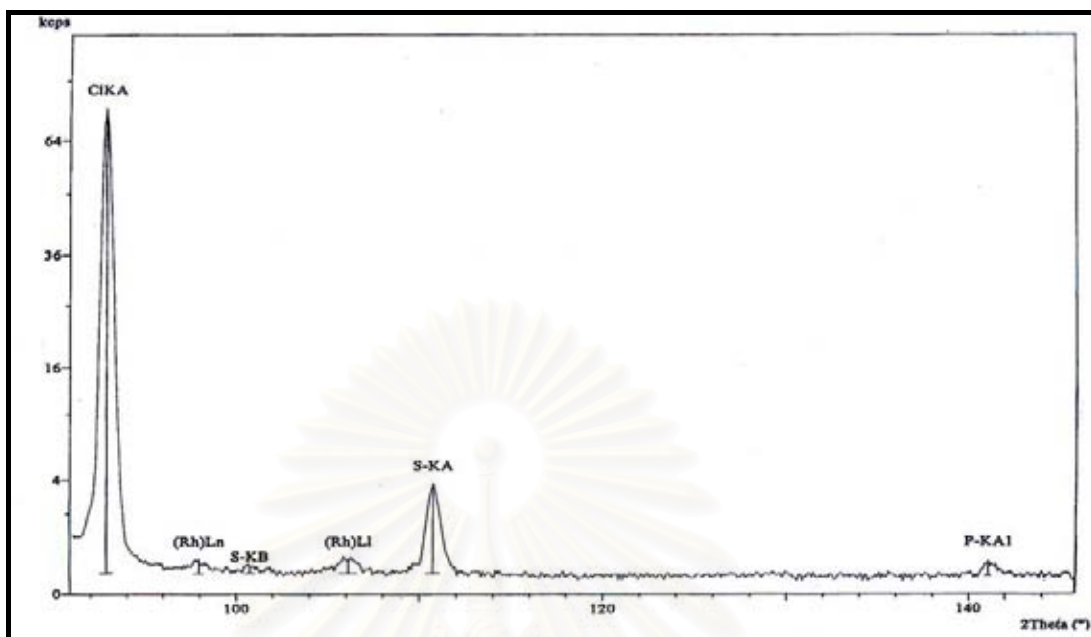


(a)

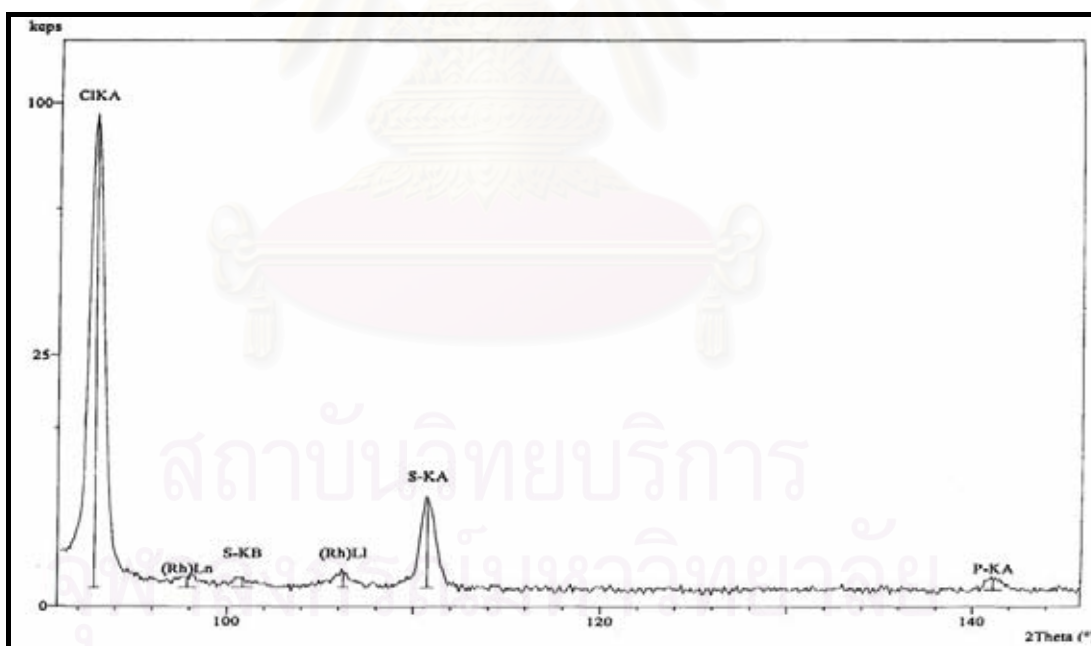


(b)

Figure C2 XRF spectra of CR derived effect of ratio of NaOCl:NaCl = 1:0 (by mol) for (a) 1 (b) 2 (c) 4 and (d) 6 hours

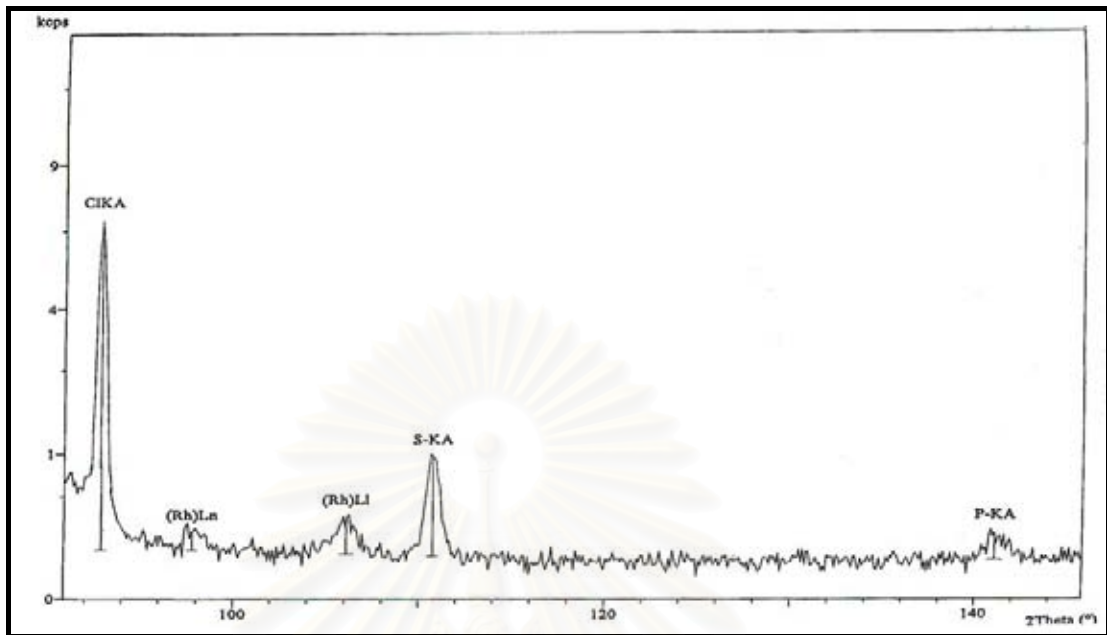


(c)

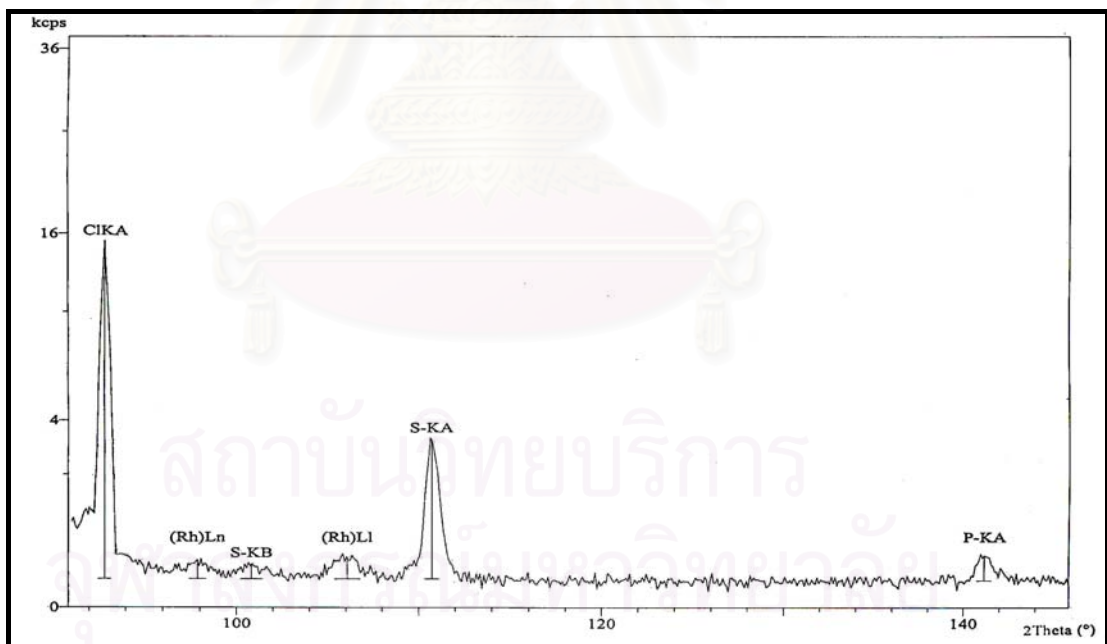


(d)

Figure C2 (continued) XRF spectra of CR derived effect of ratio of NaOCl:NaCl = 1:0 (by mol)

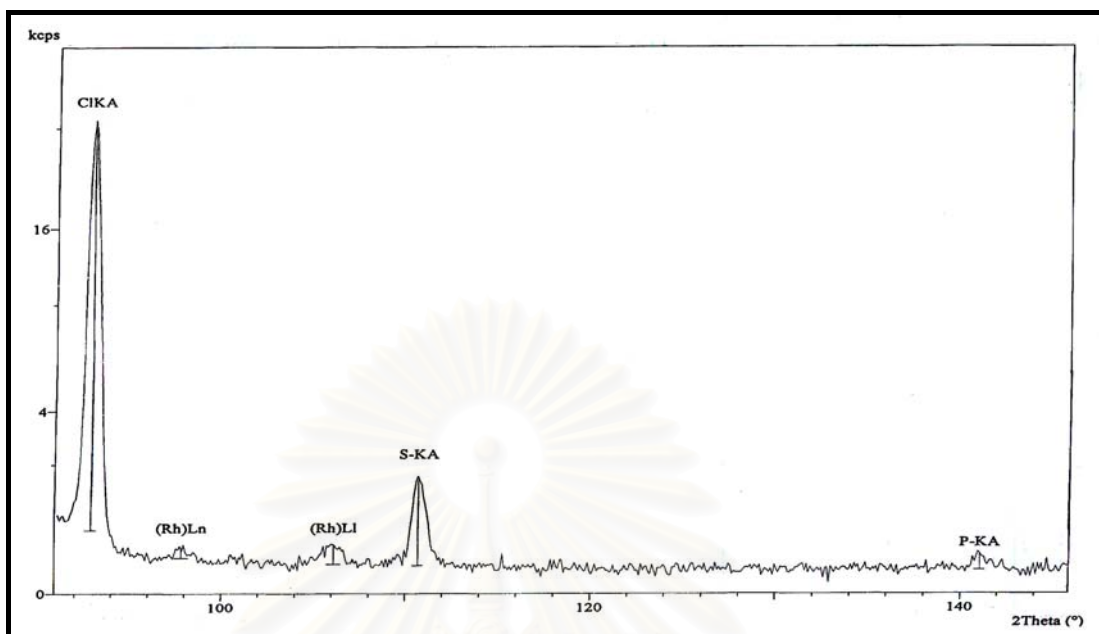


(a)

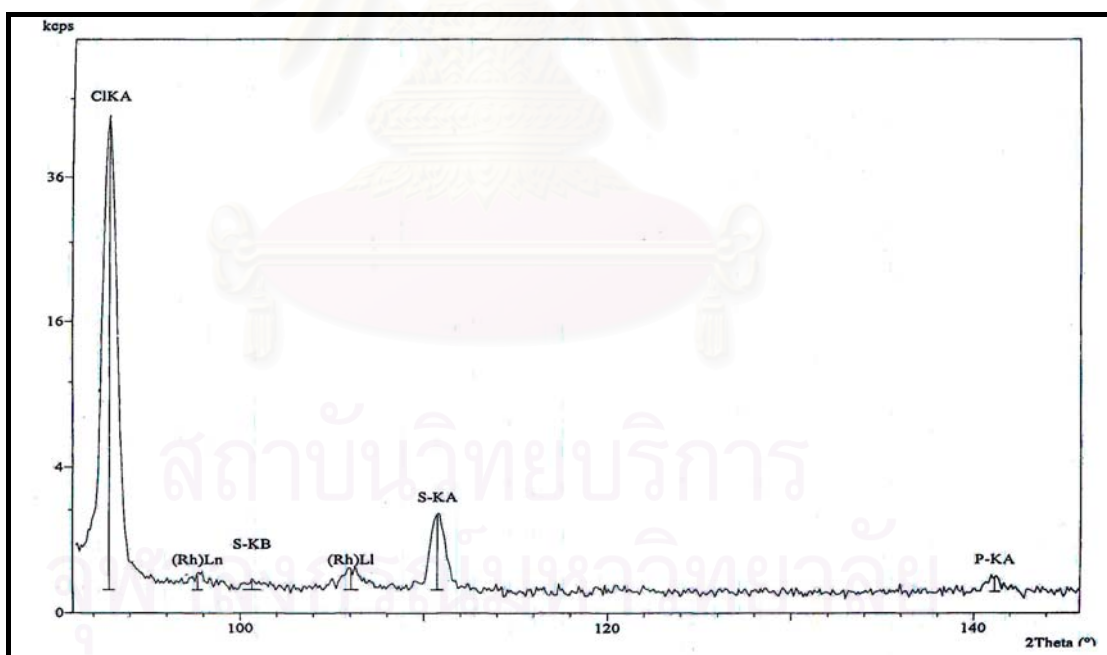


(b)

Figure C3 XRF spectra of CR derived effect of ratio of NaOCl:NaCl = 1:1
 (by mol) for (a) 1 (b) 2 (c) 4 and (d) 6 hours

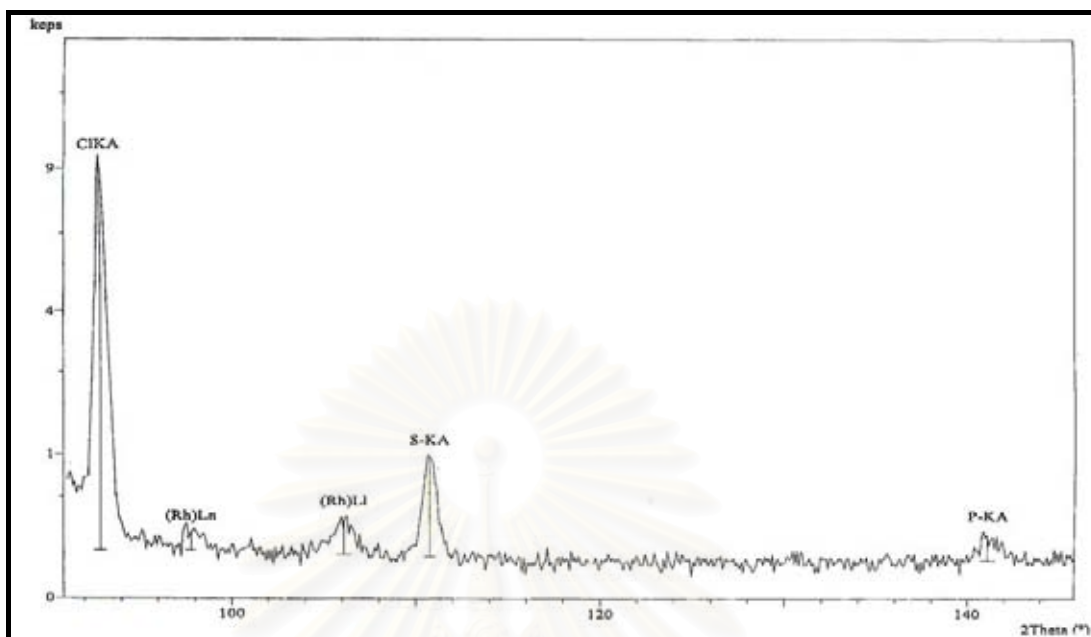


(c)

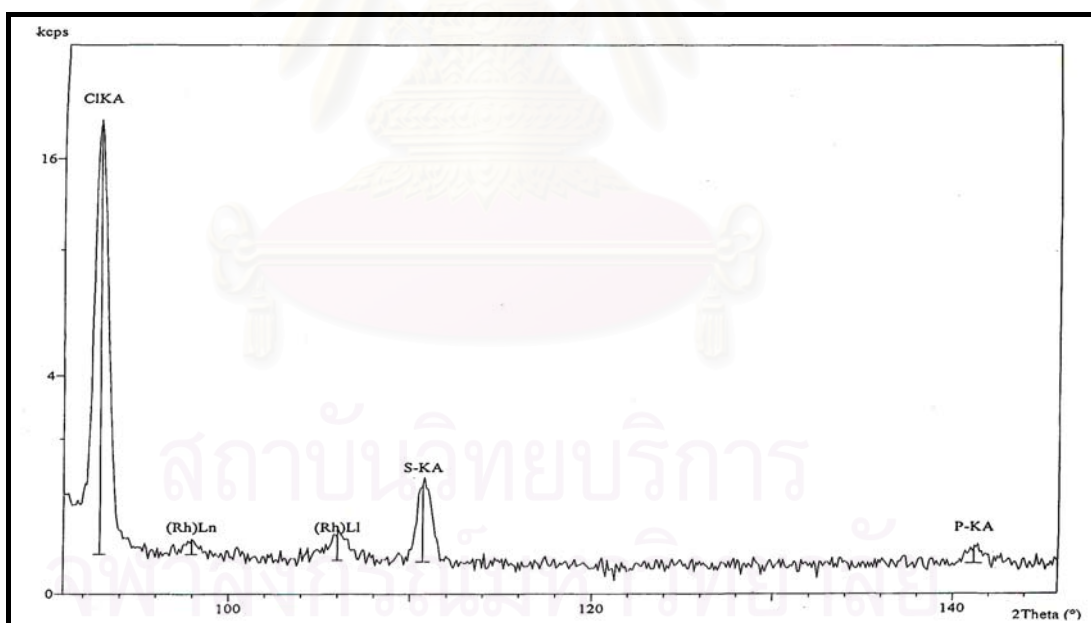


(d)

Figure C3 (continued) XRF spectra of CR derived effect of ratio of
 $\text{NaOCl}:\text{NaCl} = 1:1$ (by mol)

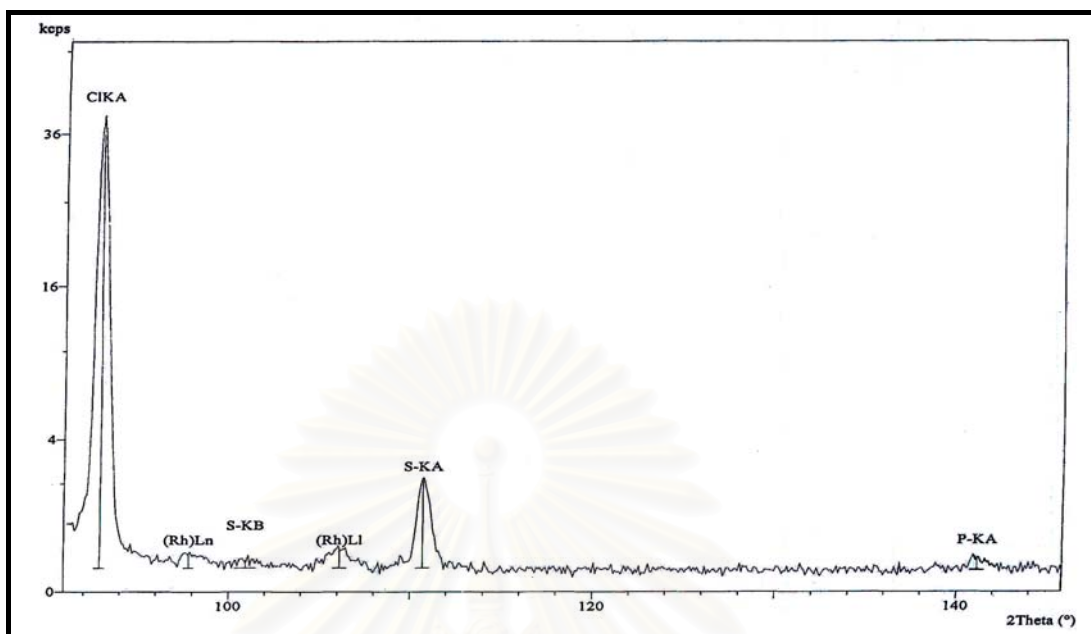


(a)

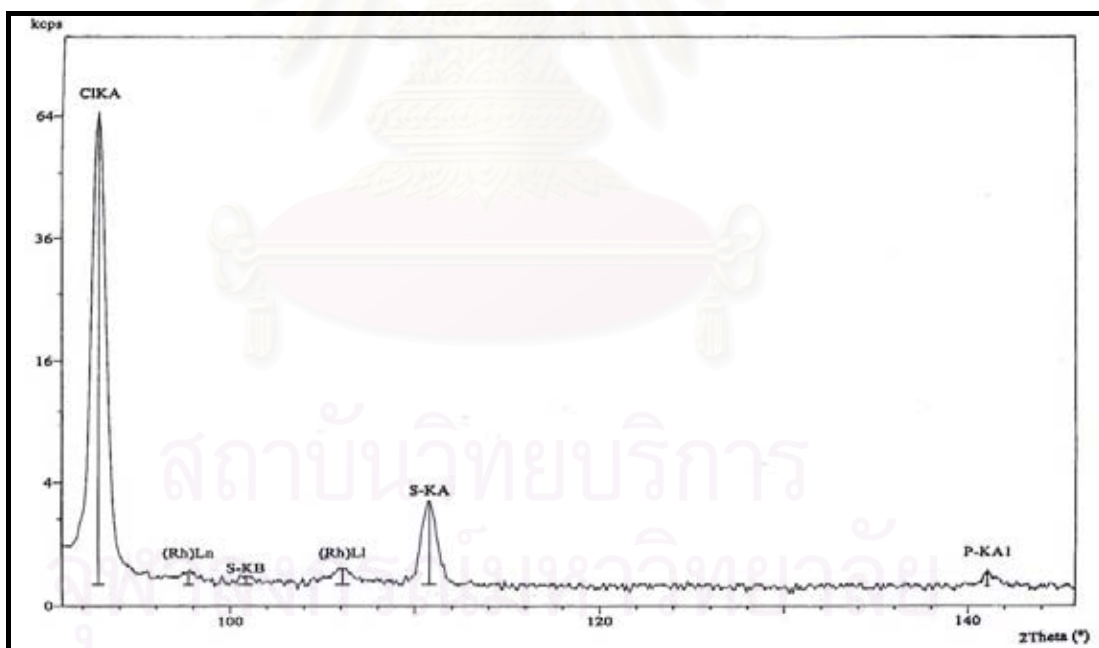


(b)

Figure C4 XRF spectra of CR derived effect of ratio of NaOCl:NaCl = 1:2 (by mol) for (a) 1 (b) 2 (c) 4 and (d) 6 hours

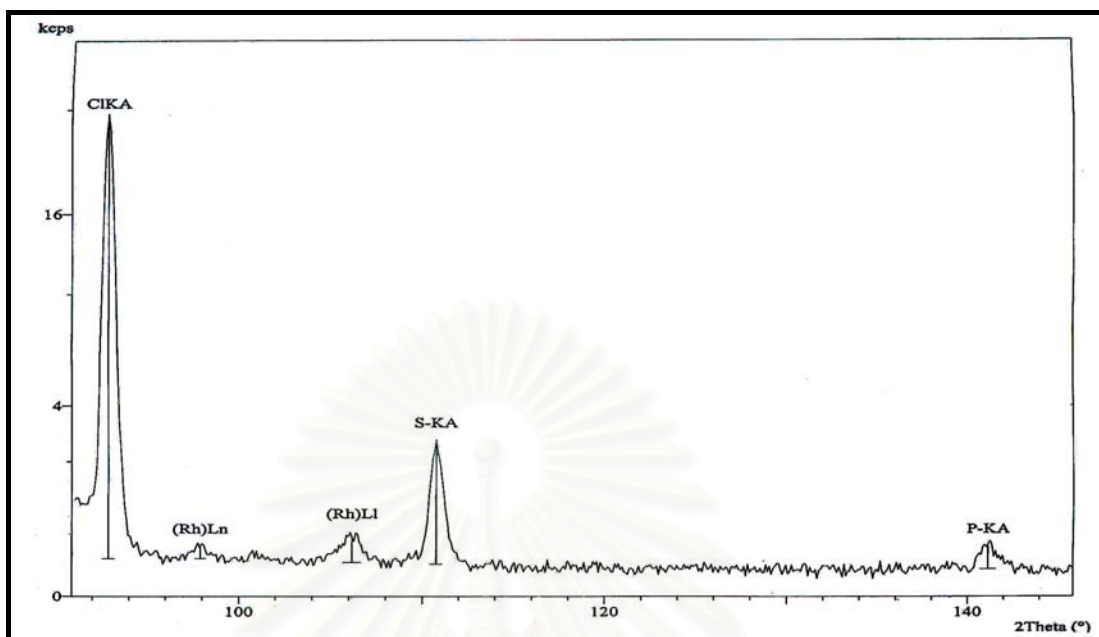


(c)

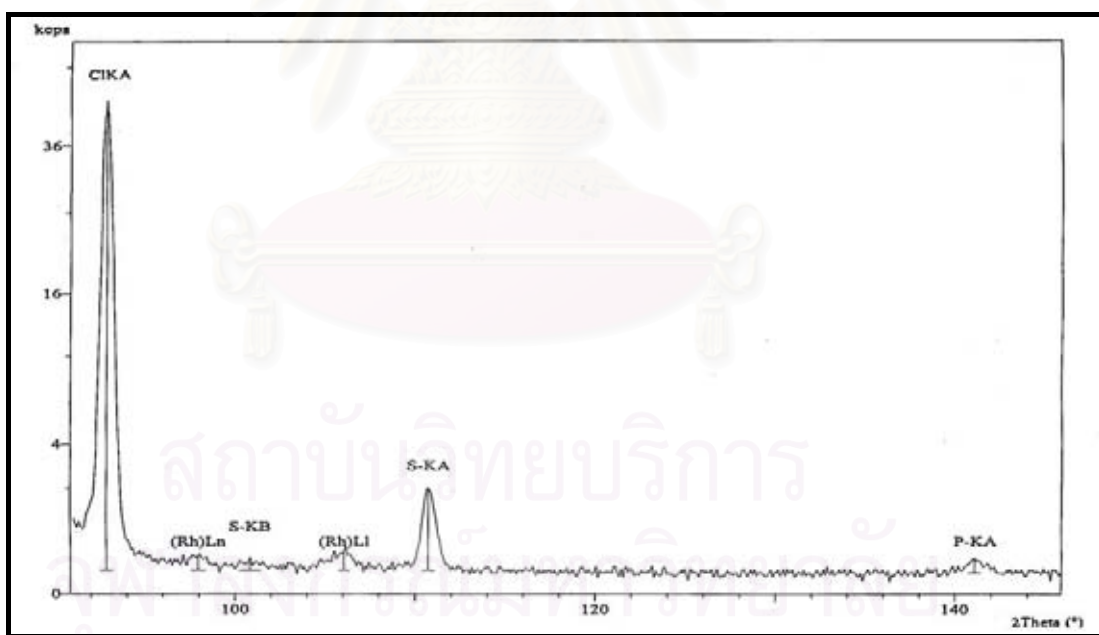


(d)

Figure C4 (continued) XRF spectra of CR derived effect of ratio of
NaOCl:NaCl = 1:2 (by mol)

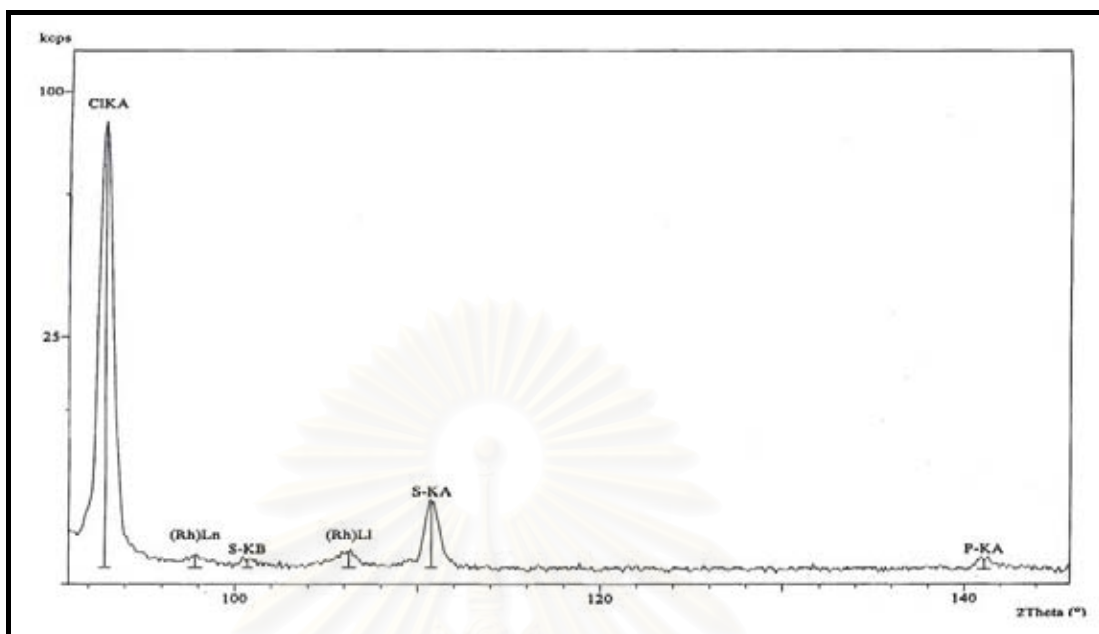


(a)

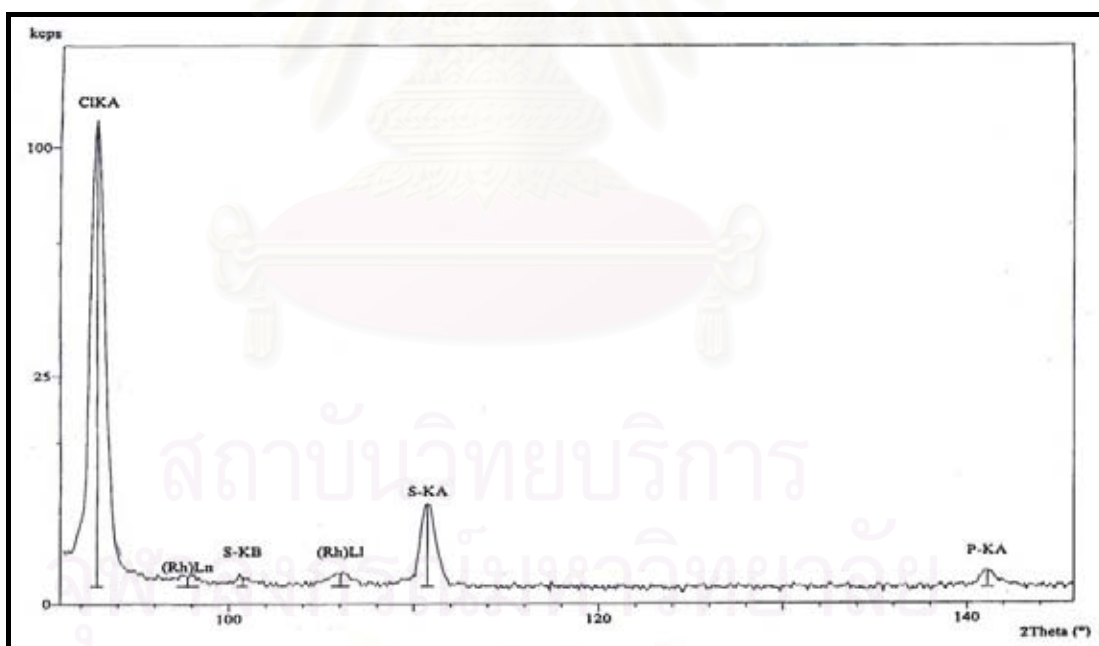


(b)

Figure C5 XRF spectra of CR derived effect of ratio of NaOCl:NaCl = 1:4 (by mol) for (a) 1 (b) 2 (c) 4 and (d) 6 hours

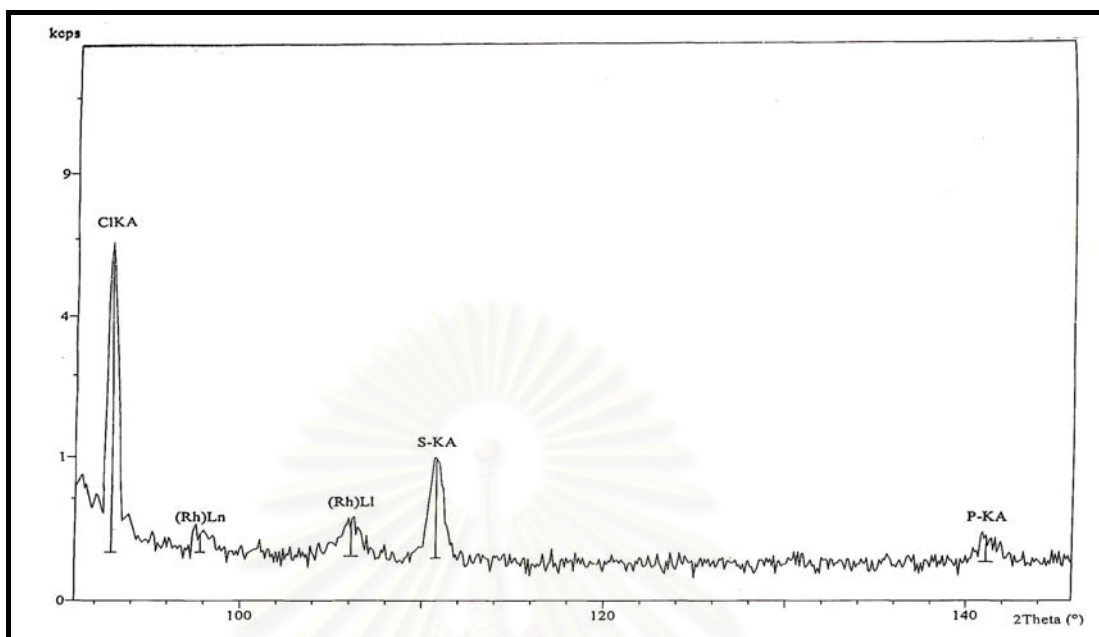


(c)

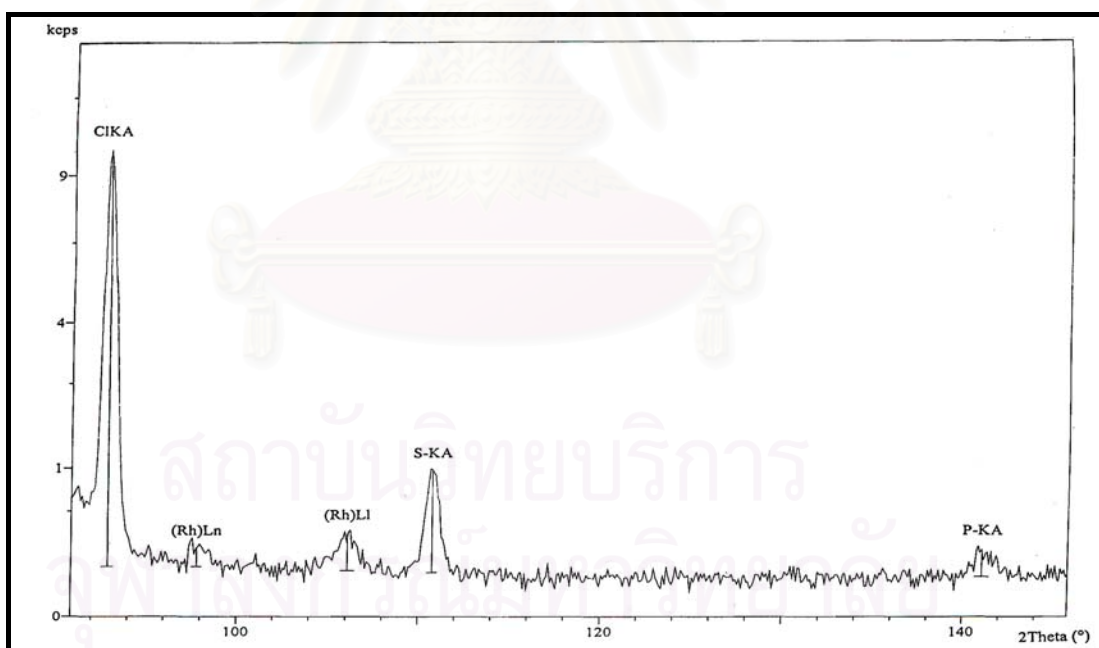


(d)

Figure C5 (continued) XRF spectra of CR derived effect of ratio of
NaOCl:NaCl = 1:4 (by mol)



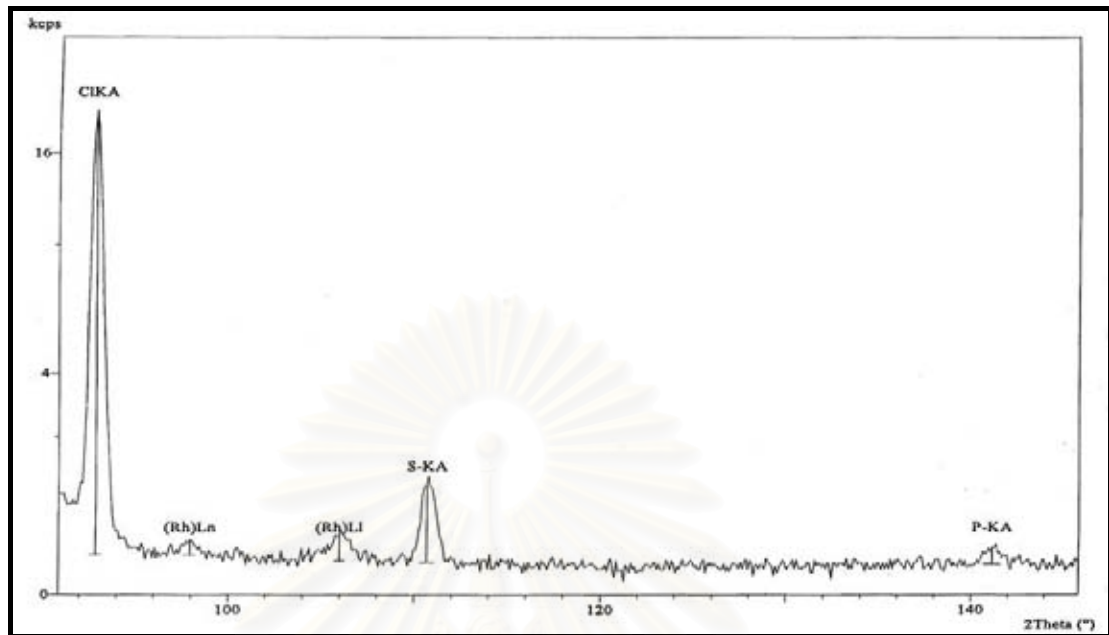
(a)



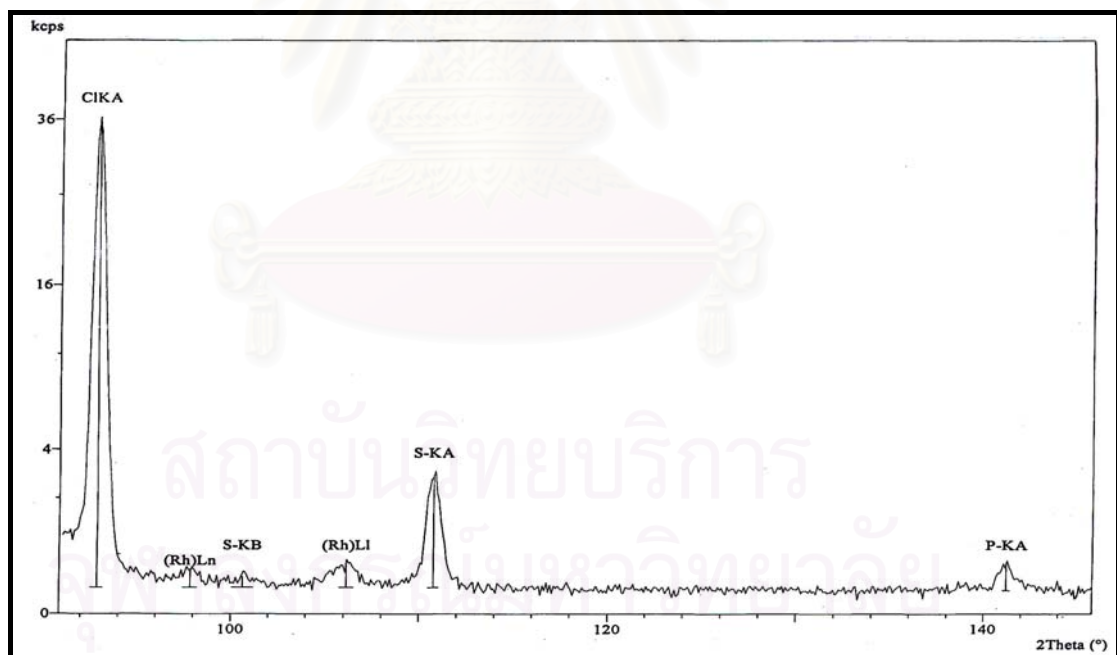
(b)

Figure C6 XRF spectra of CR derived effect of ratio of NaOCl:NaCl = 2:1

(by mol) for (a) 1 (b) 2 (c) 4 and (d) 6 hours

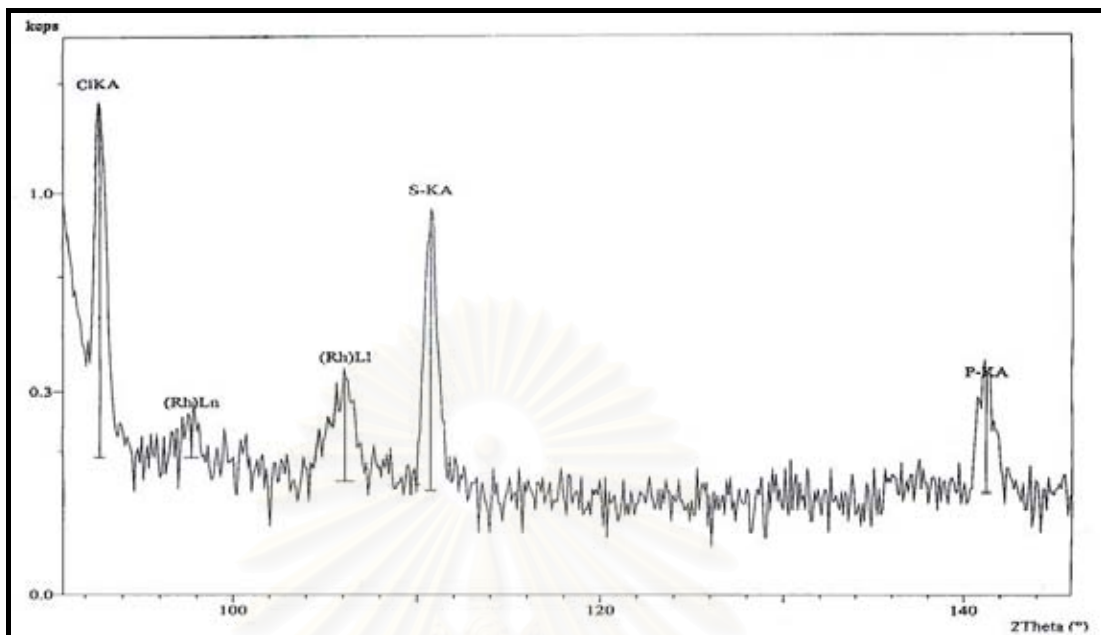


(c)

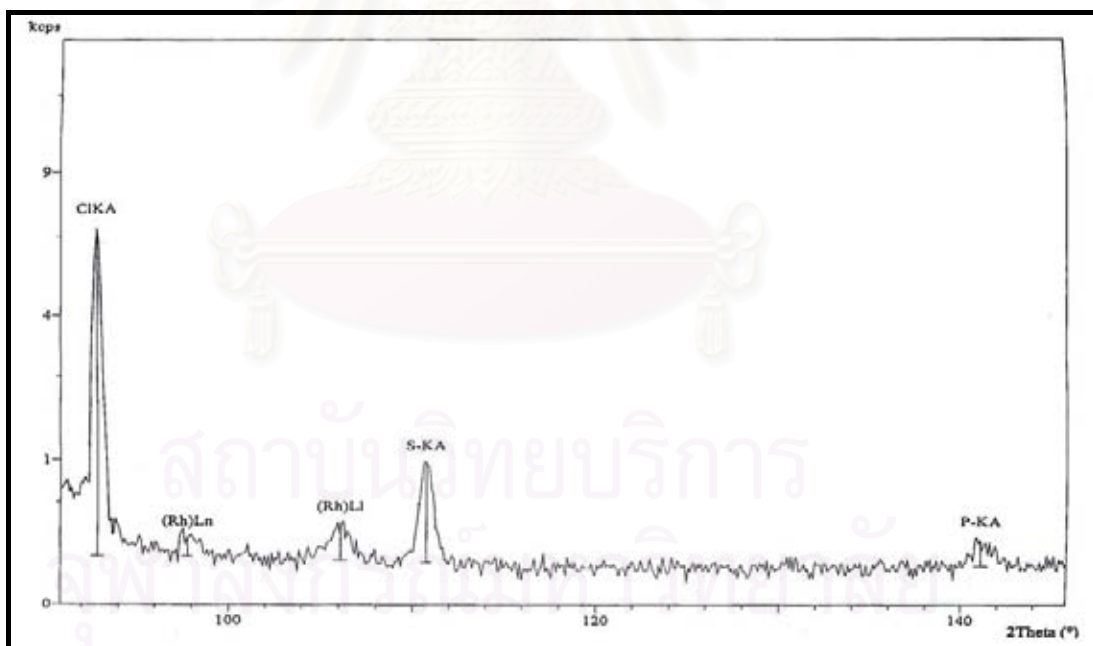


(d)

Figure C6 (continued) XRF spectra of CR derived effect of ratio of
NaOCl:NaCl = 2:1 (by mol)

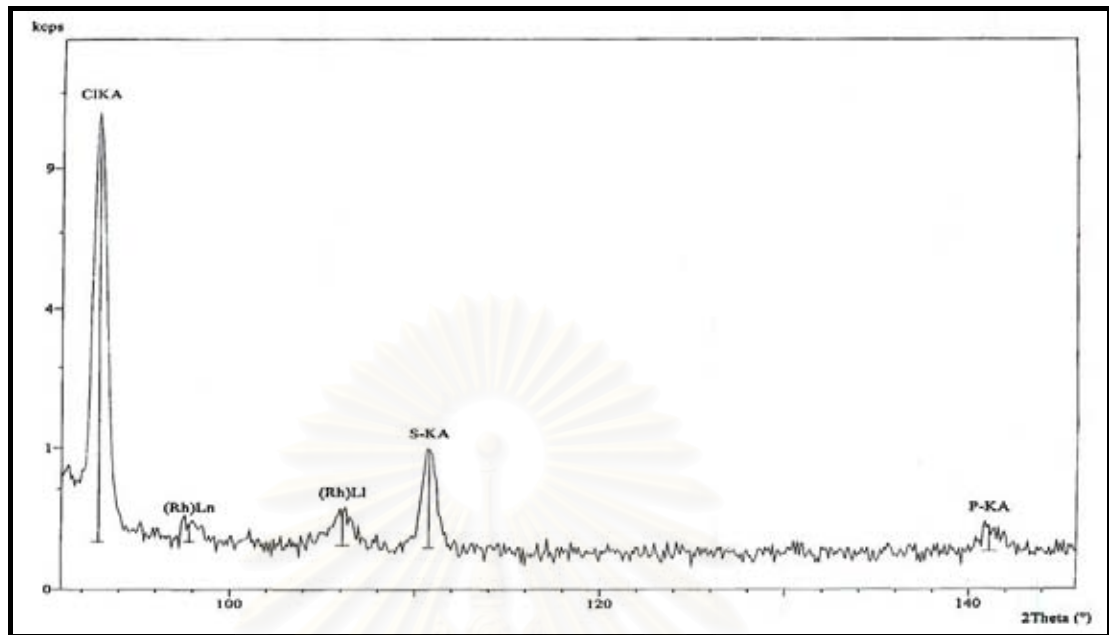


(a)

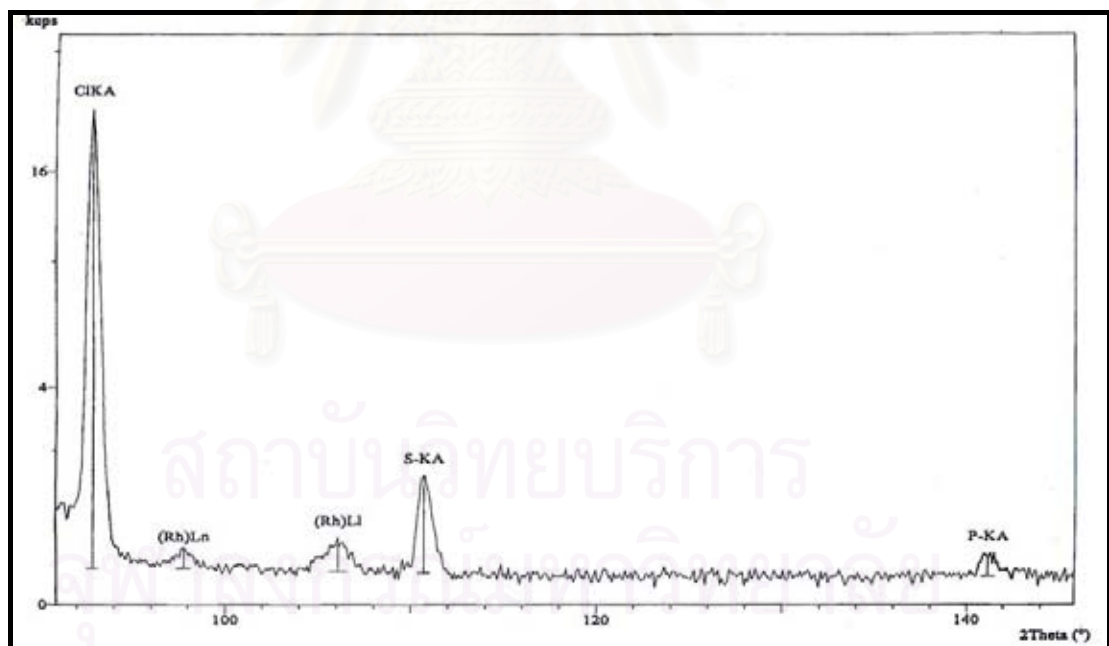


(b)

Figure C7 XRF spectra of CR derived effect of ratio of NaOCl:NaCl = 4:1 (by mol) for (a) 1 (b) 2 (c) 4 and (d) 6 hours

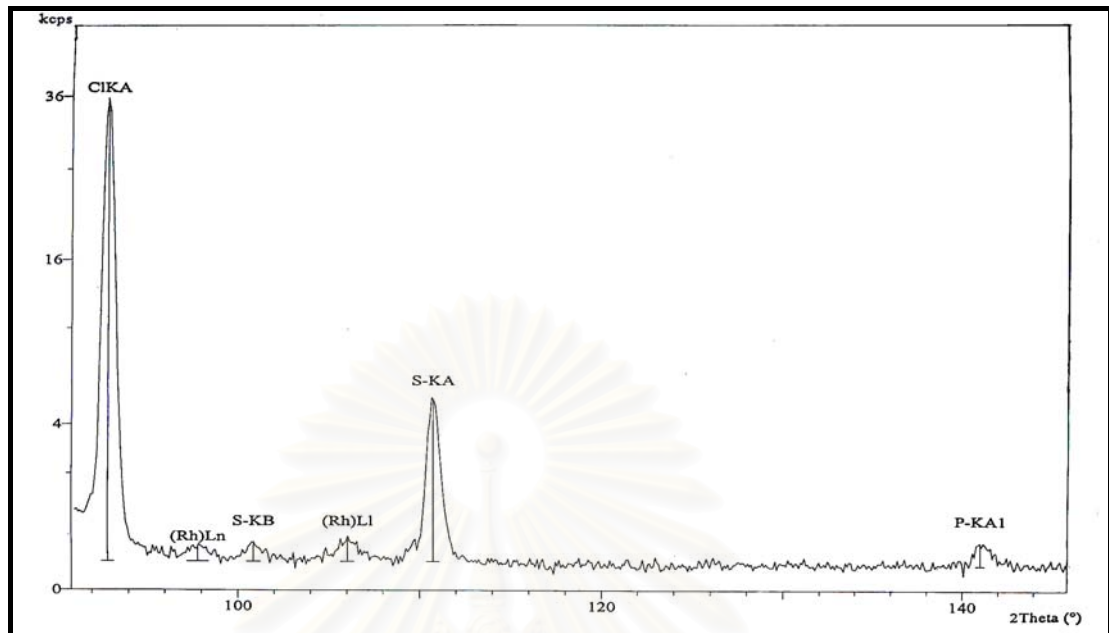


(c)

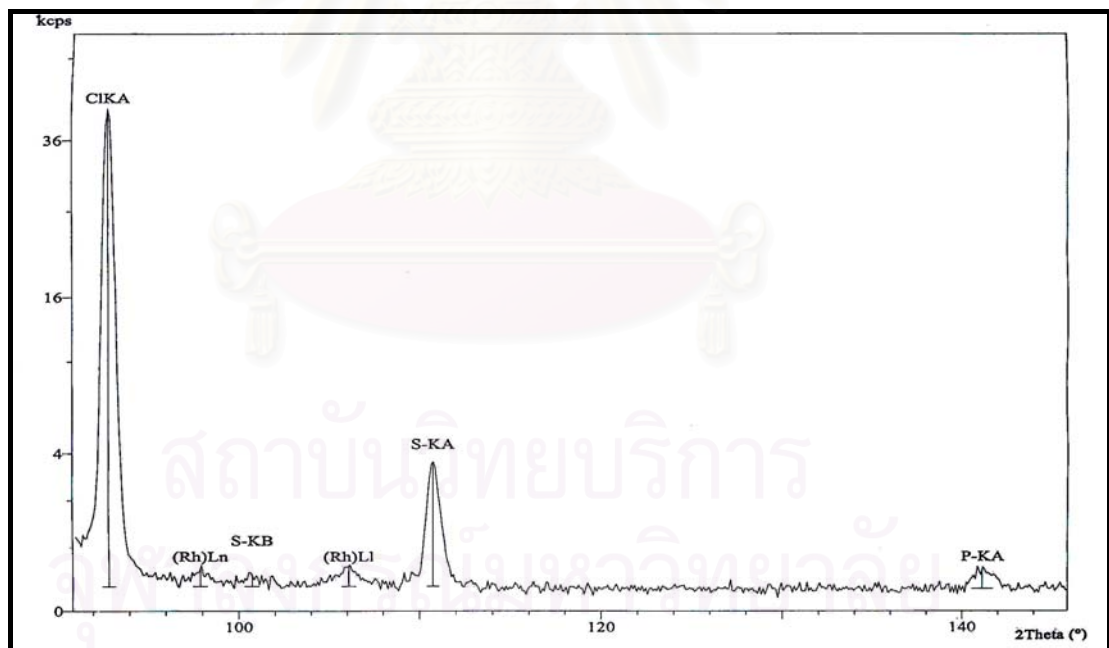


(d)

Figure C7 (continued) XRF spectra of CR derived effect of ratio of NaOCl:NaCl = 4:1 (by mol)

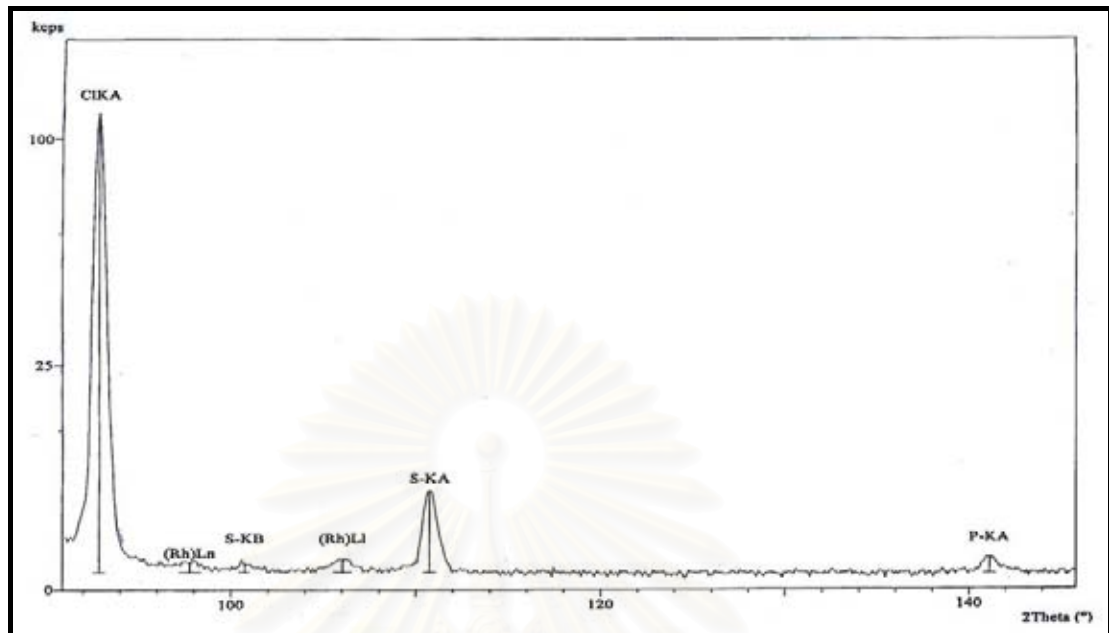


(a)

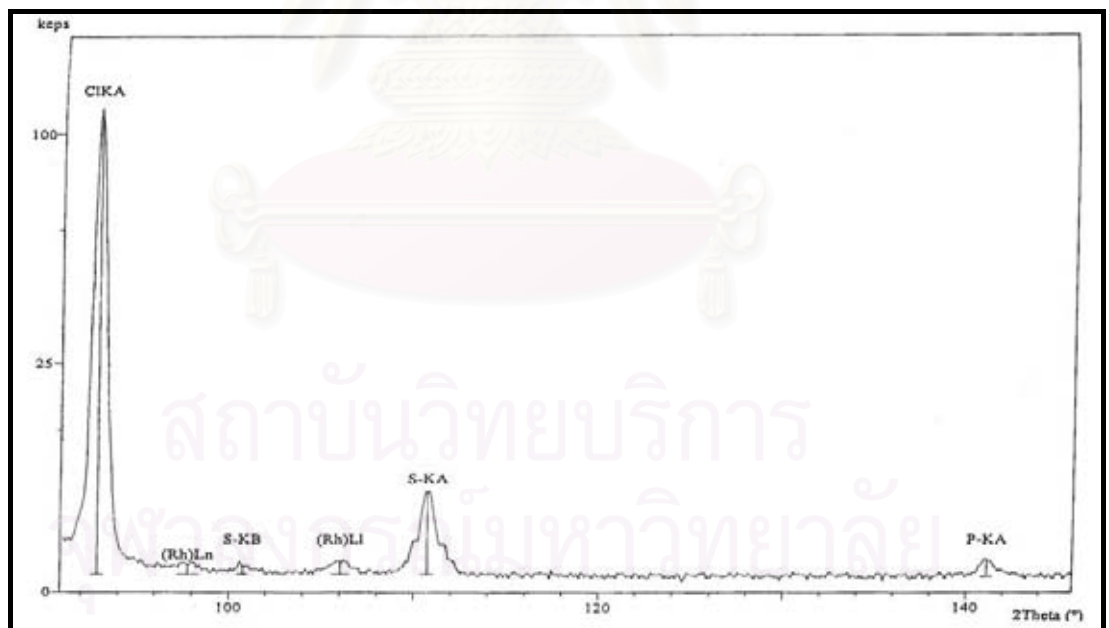


(b)

Figure C8 XRF spectra of CR derived effect of temperature at (a) 10 (b) 20 (c) 30 and (d) 40°C

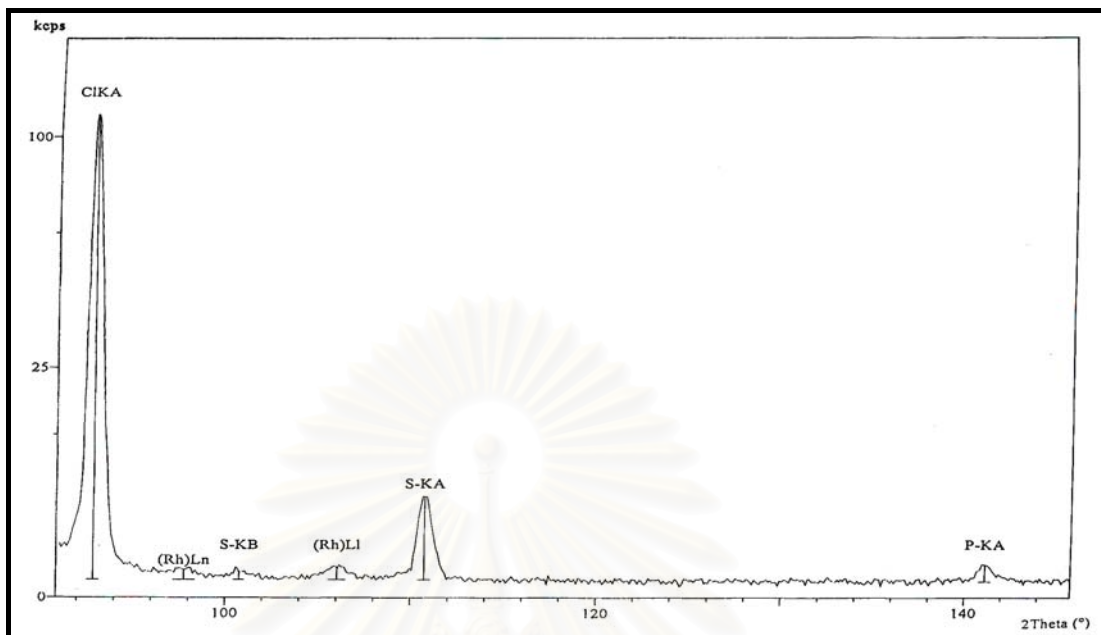


(c)

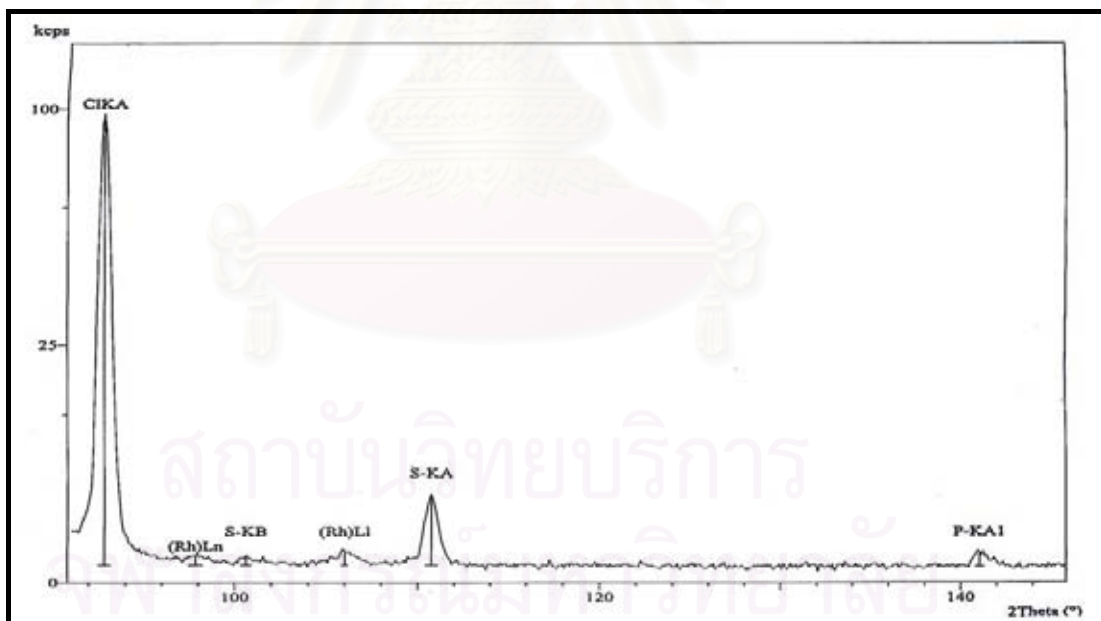


(d)

Figure C8 (continued) XRF spectra of CR derived effect of temperature

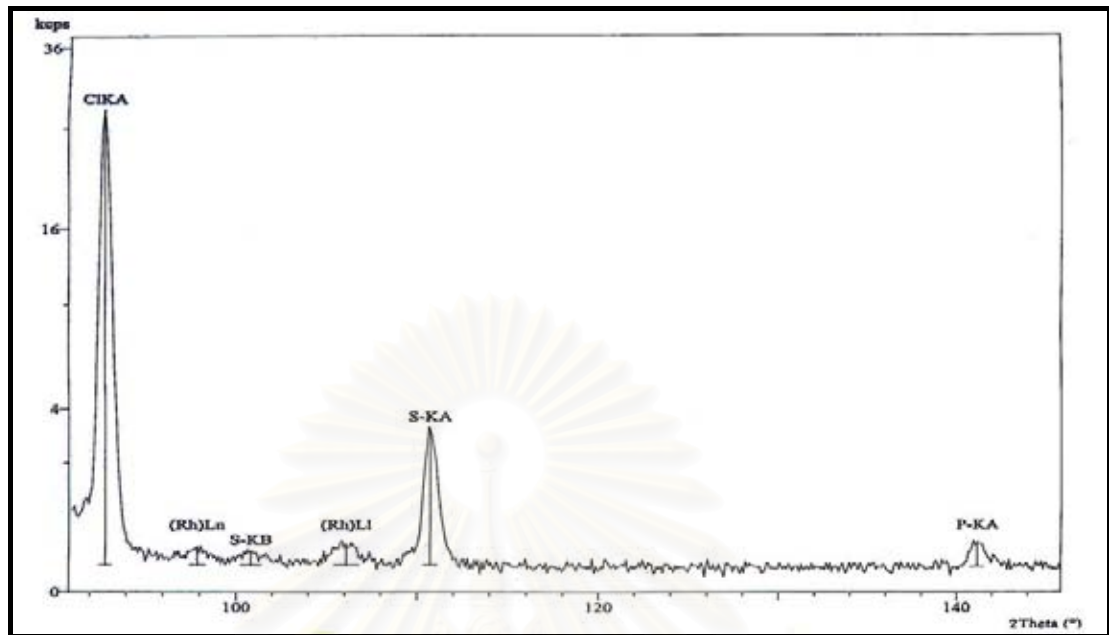


(a)

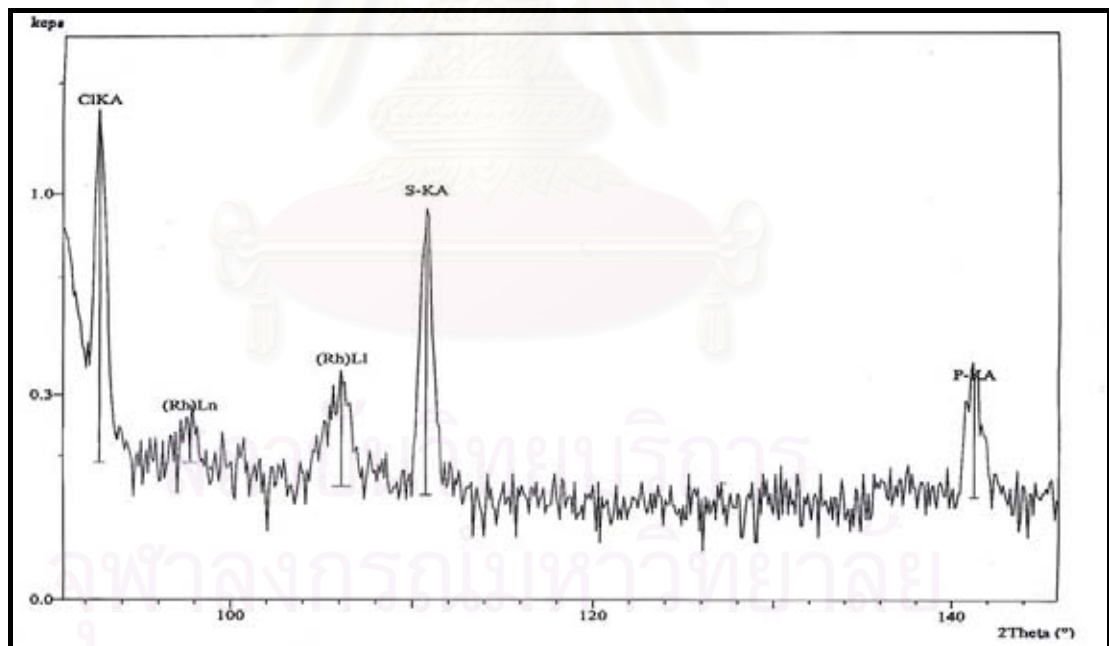


(b)

Figure C9 XRF spectra of CR derived effect of pH at (a) 1 (b) 2 (c) 3 and (d) 4



(c)



(d)

Figure C9 (continued) XRF spectra of CR derived effect of pH

VITA

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