INDUSTRIAL PRODUCTION GRAFT COPOLYMERIZATION PROCESS OF VINYL MONOMERS ON NATURAL RUBBER

MR. PICHET TANGPANYARAT

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE
MASTER OF SCIENCE PROGRAMME IN APPLIED CHEMISTRY
GRADUATE SCHOOL
KING MONGKUT'S INSTITUTE OF TECHNOLOGY LADKRABANG
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หัวข้อวิทยานิพนธ์	กระบวนการผลิตกราฟท์โคโพลีเมอร์ของไวนิลโมโนเมอร์บนยางธรรมชาติในเชิงอุตสาหกรรม
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บทคัดย่อ

กราฟท์โคโพลีเมอร์ของไวนิลโมโนเมอร์บนยางธรรมชาติสามารถที่เตรียมได้โดยปฏิกิริยาโคโพลีเมอไรเซชันแบบอิมัลชัน โดยใช้น้ำยางข้นชนิดแอมโมเนียความเข้มข้นสูงปั่นกวนรวมกับตัวช่วยเสถียรและไวนิลโมโนเมอร์ภายใต้บรรยากาศของไนโตรเจน ที่อุณหภูมิ 25 องศาเซลเซียส เป็นเวลา 60 นาที หลังจากนั้นทำการเติมเทอเทียรีบิวทิวไฮโดรเปอร์ออกไซด์ 0.2 ส่วน และไดเอทิลีนไตรเอมีน 0.88 ส่วน แล้วทำการปั่นกวนต่อเป็นเวลา 15 นาที ตั้งให้ปฏิกิริยาเกิดสมบูรณ์เป็นเวลา 24 ชั่วโมง เปอร์เซนต์การเปลี่ยนแปลงของโมโนเมอร์ไปเป็นโพลีเมอร์มีค่าอยู่ในช่วง 81-90 เปอร์เซนต์ ในการตรวจสอบสมบัติใช้กราฟท์โคโพลีเมอร์ที่ผ่านการสกัดแล้ว การตรวจสอบสมบัติทางเชิงกลและทางฟิสิกส์ทำในรูปของลาเท็กซ์ และยางที่ไม่ได้วัลคาไนซ์ พบว่ายางธรรมชาติที่กราฟท์ด้วยเมทิลเมทาอะคริเลต 30 เปอร์เซนต์มีค่าความหนืดแบบ Mooney สูงสุด ยางธรรมชาติที่กราฟท์ด้วยเมทิลเมทาอะคริเลต 30 เปอร์เซนต์และกรดอะคริลิก 5 เปอร์เซนต์ มีค่าความต้านทานต่อแรงดึงสูงสุด และกราฟท์โคโพลีเมอร์ที่ผลิตได้มีความต้านทานต่อแรงดึงมากกว่ายางธรรมชาติ ยางธรรมชาติที่กราฟท์ด้วยเอทิลอะคริเลต 50 และ 70 เปอร์เซนต์ จะมีเปอร์เซนต์การยืดตัวได้มากที่สุดและมีค่ามากกว่ายางธรรมชาติ ยางธรรมชาติที่กราฟท์ด้วยอะคริลาไมด์ 70 เปอร์เซนต์ จะมีค่าความต้านทานต่อการฉีกขาดสูงสุด ยางธรรมชาติที่กราฟท์ด้วยเมทิลเมทาอะคริเลต 50 เปอร์เซนต์มีค่าความแข็งสูงสุด ยางธรรมชาติที่กราฟท์ด้วยไวนิลอะซิเทต 30 เปอร์เซนต์ มีค่าความต้านทานต่อการสึกหรอได้มากที่สุด ยางธรรมชาติที่กราฟท์มีค่าดรรชนีการไหลแบบพลาสติกมีค่าอยู่ในช่วง 90-99 เปอร์เซนต์ และมีค่ามากกว่ายางธรรมชาติ

Thesis Title	Industrial Production Graft Copolymerization Process of Vinyl Monomers on Natural Rubber
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Abstract

Graft copolymer of natural rubber with vinyl monomer was prepared by emulsion graft copolymerization. The high ammonia natural rubber latex was stirred in stabilizer with vinyl monomer in nitrogen blanket at 25 °C for 60 minutes. After that t-butyl hydroperoxide 0.2 phr and diethylene triamine 0.88 phr were added and continued to stir for 15 minutes. The reaction was stand for 24 hrs. Conversions of monomer to polymer were nearly quantitative. Graft copolymers were characterised with respect to extractable polymer. Mechanical and physical properties were tested in latex and solid unvulcanised forms. The Mooney vicosity of NR-g-MMA 30% was highest (142.2) . Tensile strength of NR-g-MMA30%+Acrylic acid 5% was the highest (50.00 kg/cm^2). When compaired with natural rubber, tensile strength of graft copolymers were higher than the natural rubber. Natural rubber was higher elongation at break than graft copolymer except NR-g-Ethyl acrylate 50% (700 %) and NR-g-Ethyl acrylate 70% (1060 %). Tear resistance of graft copolymers were higher than natural rubber, NR-g-Acrylamide 70% was the highest (45.15 kg/cm). Hardness of NR-g-MMA 50% was highest (68) and NR-g-Ethyl acrylate 30% was the lowest (7). Taber volume abrasion loss of NR-g-Vinyl acetate 30% was the lowest (17.20 mm^3) and NR-g-MMA 70% was the highest (60.00 mm^3). PRI of graft copolymer was nearly 99%, its higher than the natural rubber (62.32).

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Pichet Tangpanyarat

TABLE OF CONTENTS

CHAPTER TITLE PAGE

1 INTRODUCTION

LITERATURE REVIEW

2 Natural Rubber and Natural Rubber Latex

3 Graft Copolymer

4. Emulsion Polymerization

5 MATERIALS AND METHODS

6 RESULTS AND DISCUSSION

LIST OF TABLE

LIST OF TABLE (Continued)

LIST OF FIGURES

LIST OF FIGURES (Continued)

LIST OF FIGURES (Continued)

LIST OF FIGURES (Continued)

LIST OF FIGURES (Continued)

LIST OF FIGURES (Continued)

Chapter 1
Introduction

An important economic crop for Thailand is Para rubber because of their incomes. Now, the export of Thai Para is in the first priority of the world. Para rubber includes latex concentrate, thick pale crepes, ribbed smoked sheet, compound crepes, brown thick crepes, flat bark crepes production etc. In addition to that, Para rubber is modified to adhesive, soles, automobile parts etc. Although Thailand can export the Para rubber much in the first of the world, the price of Para rubber of the world market cannot be set by Thai. The reason is that natural rubber (Para rubber) modification on some counties which are the industrial leader of the world causing the price change with the situations. From the reason, the natural rubber was used as the material making a rubber modifying product and develop the technology of rubber production

1.1 Problems.

Nowadays, the economy and industry of natural rubber product has been developed. Although natural rubber is used widely, however it has several disadvantage e.g. abrasion loss, thermal degradation, oxidation, etc. All weak point give the limitation of product. The weak point can be modified by chemical and physical methods.

1.2 Modification.

Properties of natural rubber can be modified by chemical and physical methods. In chemical methods can be made by vulcanization , prevulcanization, epoxidation, chlorination, cyclization and graft copolymerization etc. In physical methods, blending are used for modification.

In this work natural rubber was modified by graft copolymerization and compounding with vinyl monomers, such as methyl methacrylate, 2-ethylhexyl acrylate, ethyl acrylate, butyl acrylate, vinyl acetate, acrylic acid and acrylamide.

1.3 Objective

The overall objective of this study is to produce the graft copolymer of vinyl monomers on natural rubber for testing the physical and mechanical properties and scale up to the production of graft copolymer in pilot plant.

The specific objectives of the study are as follow:

1. To synthesis graft copolymer by emulsion copolymerization system.
2. To test the above product properties in latex form such as total solid content, conversion, viscosity, pH, total alkalinity and mechanical stability.
3. To test the above product in physical and mechanical properties such as Mooney viscosity, tensile strength, elongation at break, tear resistance, hardness, abrasion resistance, plasticity retention index and density.
4. Scale up to the production of graft copolymer in 200 liters reactor pilot plant.

Chapter 2
Natural Rubber and Natural Rubber Latex

Natural rubber (NR) occurs in over 2,000 species of plants. The earliest written reference to natural rubber were made by Spaniards following the voyages of Columbus in the late 15th century. In 1770, the word rubber coined by Joseph Priestly when he observed the gum from the Hevea tree could be used to rub out pencil marks. Hevea tree is native of South America[1].

Because of the high price of rubber in the 1870 s some 2000 seeds were smuggled out of the Amazon basin and planted by Sir Joseph Hooker in Kew Garden, London, in 1873. The seedlings did not survive but a future consignment of 70000 seed was brought from Brazil by Sir Henry Wickhan and 2000 plants were raised at Kew. Some of these plants were then sent to what was then Ceylon, and it is from the servitors that the rubber plantation of the Far Eastern Malaysia, Indonesia, Thailand, Sri Lanka and else where have developed.

The significant event in the development of the rubber industry was the invention of the masticator in 1820 by Thomas Hancock. The masticator softened rubber and facilitated dissolution. In 1839, Charles Goodyear discover that rubber and sulfur combined in the presence of heat and white lead yielded a new substance with improved physical properties. This process became known as vulcanization.[23]

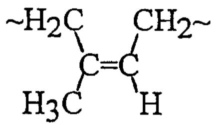
Now 80 percent of the natural rubber market produced from four countries in Far East. Thailand alone is responsible for over one third of the world ' s natural rubber.

2.1 Structure of natural rubber

Natural rubber field latex following may be considered as typical [2]

Total solid content	~30%
Proteineous substance	~1-1.5%
Resineous substance	~1-1.5%
Ash	<1%
Sugars	~1%
Water	~60%

The natural rubber molecules consist virtually entirely of cis-1,4-Polyisoprene



cis-1,4-Polyisoprene

The molecular weight of the natural rubber is very high but varies between lattices from different clones. In one study (Nair, 1970) the number average molecular weight (M_n) was found to range from $2.5x10^5$ to $2.71x10^6$ and weight average molecular weight (M_w) from $3.4x10^6$ to $1.073x10^7$.

2.2 Properties of natural rubber

The pure natural rubber is colorless, odorless, elastic and transparent. The natural rubber has softening point of about 120 °C and dissolves in naphthalene, toluene, benzene, carbon disulfide and petrol etc. Its specific gravity varies from 0.915 to 0.930.

Its very flexible chain backbone leads to a very low T_g of about -73 °Cand crystalline melting point (T_m) of about +25 °C.

2.3 Grade of natural rubber[2]

International recognized market grades of natural rubber are given in Table 2.1

Table 2.1 International recognized market grades of natural rubber[2]

Type	Grade
Ribbed Smoked Sheets	1XRSS,RSS Nos.1-5
Thick Pale Crepes	1X,1,2,3
Thin Pale Crepes	1X,1,2,3
Estate Brown Thick Crepes	1X,2X,3X
Estate Brown Thin Crepes	1X,2X,3X
Compound Crepes	1,2,3
Thin Brown Crepes (Remills)	1,2,3,4
Thick Brown Crepes (Ambers)	1,2,3,4
Flat Bark Crepes	Standard, Hard
Pure Smoked Blanket Crepe	Standard

Natural Rubber Latex[10]

Latex is an emulsion of rubber obtained from the rubber tree. It is trapped from the bark by making a special type of cut throughout the bark.

On tapping the Hevea brasiliensis tree, natural rubber latex exude, which has a rubber content between 25 and 40 percent by weight. This latex is normally called **field latex** and its average rubber contents 30 percent by weight. This material is not utilized in its original form due to its high water content and susceptibility to bacterial attack. It is necessary to preserve and concentrate it, so that then product is stable and contains 60 percent or more of rubber. The latex that has rubber content average 60 percent is called **Concentrated latex.**

2.4 Latex concentration

Concentrated latex is differentiated by the method of concentration and type of preservative used. In addition to the general purpose type of latex, then are specialty forms such as double centrifuged latex, creamed/centrifuged latex(sub-stage latex) and modified types such as prevulcanized latex.

Three methods of concentration are employed creaming, centrifugation and evaporation etc.

2.4.1 *Creaming*

Creaming was the first method to modify latex. In this method the latex of 60 to 70% solid can be obtained with a heavy creamy viscosity.

2.4.2 *Centrifugation*

Latex can be concentrated by using a special centrifuge. The latex concentrate by centrifugation has total solid content about 58 to 62% and dry rubber content about 60%.

The ISO 2004 requirements for centrifuged and creamed latex concentrates in table 2.2 .

2.4.3 *Evaporation*

In this method, latex is concentrated by heating with or without vacuum. It is necessary to use a stabilizer such as soap or fixed alkali. The main difficulty of this method is the formation of a dry surface resin and local heating.

By this methods latex paste is obtained containing about 75% dry rubber as it is required in ISO 2027 for evaporation concentrated latex (Table 2.3).

Table 2.2 The ISO 2004 requirements for centrifuged and creamed latex concentrate[10]

	Contrifuged latex		Creamed latex	
	HA	LA	HA	LA
Total solid content (%) (min)	61.5	61.5	66.00	66.00
Dry rubber content (%) (min)	60.00	60.00	64.00	64.00
Non-rubber solid (%) (max)	2.00	2.00	2.00	2.00
Alkalinity (as NH_3)	0.6	0.29	0.55	0.35
(on latex)	(min)	(max)	(min)	(min)
Mechanical stability (s) (min)	650	650	650	650
Coagulum content (%)(max)	0.05	0.05	0.05	0.05
Copper content (mg/kg of solid)(max)	8	8	8	8
Manganese content (mg/kg of solid)(max)	8	8	8	8
Slug content (%) (max)	0.10	0.10	0.10	0.10
Volatile fatty acid number	>0.20	>0.20	>0.20	>0.20
Potassium hydroxide number	>1.0	>1.0	>1.0	>1.0

Color on visual inspection	No pronounced blue or gray.
Odor after neutralization with boric acid	No pronounced odor of putrefaction

Table 2.3 The ISO 2027 requirements for evaporation concentrated latex[10]

	Type HA	Type KHA	Type KLS
Total solid content (%) (min)	61.5	72.0	67.0
Non-rubber solid (%() (max)	5.5	8.0	7.5
Alkalinity,as NH_3 (% on latex)(min)	0.6	-	-
Alkslinity,as KOH (% on latex)(min)	-	0.75	0.80
Mechanical stability (sec)(min)	540	-	-
Coagulum content (%)(max)	0.50	0.05	0.05
Copper content(mg/kg of solid)(max)	8	8	8
Manganese content (mg/kg of solid) (max)	8	8	8
sludge content (%) (max)	0.40	0.40	0.40
Volatile fatty acid number	> 0.20	> 0.20	> 0.20

Color on visual inspection	No pronounced blue or gray
Odor after neuterization with boric acid	No pronounced odor of putrefaction

*HA = High Ammonia.

*LA = Low Ammonia.

2.5 Composition of latex

2.5.1 *Dispersed phase*

The rubber in natural latex is cis-1,4-polyisoprene. The molecular weight is in the region of 1,000,000. The molecular weight cannot be determined precisely because there is always a proportion of the rubber which is insoluble. The molecular weight of the sole fraction of the rubber in mature concentrated latex can be determined by gel permeation chromatography. The type of molecular weight by this method is weight average molecular weight (M_W).

2.5.2 *Non-rubber materials in the serum*

The major constituents of non rubber material in the serum are known to be proteins and their decomposition products, fatty acid soap , organic and inorganic salts.

The overall composition of both HA and LA-TZ lattices are summarized in Table 2.3 for both latex and total solids film.

2.5.3 *Absorbed non-rubber materials*

When in the tree, the particles in natural latex are presumed to possess an adsorbed layer of a protein-lipid complex. As a consequence of the addition of ammonia to preserve the latex concentrate, the lipid materials are believed to hydrolyze slowly, releasing fatty acid soaps which themselves become adsorbed on to the particle surface. The adsorption of these soaps is thought to account for the spontaneous rise in mechanical stability when ammoniated concentrate is stored.

2.6 Materials affecting liquid properties

2.6.1 *Stabilizers*

Stabilizers are added to protect the latex from the shock of subsequent ingredients. The more common stabilizers are alkaline, alkali soap, synthetic detergents and protective colloids. Example of alkalis are ammonia, dimethylamine, monoethylamine, morpholine, caustic soda, caustic potash, TSP, TSPP, mono and di-triethanoamine. Soaps are reaction products of the alkali mentioned with oleic, staric, lauric and palmitic acids etc. Synthetic detergents include salts of sulfate monoesters of higher alcohol, alkyl aryl sulphonates and polyethylene ethers of a fatty alcohol and glycol etc. Protective colloids include casein, glue, shellac, alginates, starch, methylcelluose, sodium polyacrylate and polyvinyl alcohol. Stabilizers may serve the function of dispersing agent as well.

2.6.2 *Preservatives*

Preservatives also contribute towards latex stability by preventing putrefaction and the action of bacteria. Ammonia or some other preservatives are already present but due to the incorporation of other ingredients some dilution takes place, thus further quantities of preservatives are required. Preservatives such as sodium pentachlorophenate, sodium phenyl phenate, p-dichlorometacresol, etc. are used for this purpose. The disadvantage of this kind of preservatives is their toxicity.

2.6.3 *Wetting agents*

Various stabilizers reduce the surface tension and aid the latex particles in penetrating the surface pores. Thus saturation of fabrics or paper is facilitated. Stabilizers which do not increase viscosity and which give the lowest surface tension are more effective . Anionic synthetic detergents are most effective in this case.

2.6.4 *Chelating agents*

Special stabilizers are used to protect against calcium and magnesium ions present in hard water, which may have effection the latex stability. They ensure stability by sequestering bivalent ions; if these non-ionic materials cannot be used effectively then chelating agents are used, one of the most commonly used is ethylene diaminotetracetic acid (EDTA) .

2.6.5 *Coagulants*

Coagulants modify the stability of the latex. Coagulants are not a part of the rubber. They are employed to break the latex emulsion locally, e.g. adjacent the surface of a dipping form so that a dense layer of wet coagulum is deposited. Certain compounds called heat sensitizers when added with zinc oxide make the compound heat sensitive i.e. when a heated former is dipped into the latex, a layer of coagulum deposits on it. Such heat sensitizers are diphenyl guanidine(DPG), 1-nitropropane, and polyvinyl methyl ether .

2.5.6 *Gelling agents*

Gelling agents cause coagulation to take place at low temperatures, even at room temperature. They are offen used in foam rubber products. Sodium silicofluoride is very popular gelling agent as it has a more delayed effect than, for example, ammonium nitrate. Potassium silicofluoride is sometimes used in place of sodium silicofluoride to give a slower rate of gelation.

2.5.7 *Antifoams*

Antifoams are used to promote foam collapse and prevent web formation. In latex processing, other than in the manufacture of latex foam sponge, foam is undesirable and intolerable. Pine oil and octyl alcohol are quite popular and efficient antifoams. Silicones are and very efficient (0.1% in sufficient) antifoams and can be used with latex.

2.5.8 *Dispersing agents*

Dispersing agents and stabilizers have rather similar functions and many chemicals serve as both. Effective dispersing agents allow the production of free flowing grinds of many solids compounding ingredients with a relatively small amount of water; they also prevent the formation of agglomerates. Karaya gum, gum arabic and sodium alkyl naphthalene sulphonate are examples of the dispersing agents.

2.5.9 *Thickeners*

In some applications e.g. coating and spreading, a viscous compound is desirable so that excessive penetration does not take place. High solid compounds pose processing difficulties; hence low solid compounds are used and to increase the viscosity, thickeners are added. Sodium silicate, methyl cellulose, CMC, sodium polyacrylate, alginates, karaya gum, bentonite clay, etc. are the most common thickeners used in latex compounds.

2.7 Graft copolymerization on polymer molecule.

Graft copolymerization was one of the method for modified natural rubber and recently developed many different techniques. In 1982, the natural rubber was grafted with methyl acrylate using radical initiators such as benzoyl peroxide(BPO), azobisisobutylronitrile(AIBN) and potassium persulphate in benzene-water medium.

The graft copolymerization with some hydrophilic vinyl monomers such as 2-hydroxyethyl methacrylate, N-vinyl pyrollidone and methyl acrylate onto natural rubber had studied in 1986 by Erbil, M.Y.. The system of hydroperoxide-polyamine and ammonium persulphate-sodium metal bisulphate were introduced as initiators.

Lenka, S., Nayak, P.L. and Brsak, A.(1986) prepared graft copolymer of methyl methacrylate onto natural rubber using dimethyl aniline-cupric ion redox system. The concentration of N,N-dimethylaniline was varied within the range of $0.59x10^{-3}$ to $1.57x10^{-3}$ mol/L. at low temperature.

Hoursten D.J. and Momaine, J. (1990) developed the properties of natural rubber by graft copolymerization with methyl methacrylate using an amine-activated hydroperoxide. The morphology of materials was determined both by transmission electron microscopy and by dynamic mechanical analysis.

Razzak, M.T., Tabata, Y. and Otsuhata, K.(1993) synthesized graft copolymer of N,N-dimethyl acrylamide onto natural rubber using simultaneous, pre-oxidation and preirradiation techniques. The degree of grafting was studied.

Mizzadeh, H., Katbab, A.A., Kharasani, M.T. and Burfard, R.R.(1994) introduced the hydrophilic site onto the surface of ethylene-propylene rubber (EPR) by grafting 2-hydroxyethyl methacrylate (HEMA) and N-vinyl pyrolidone (NVP) onto the EPR surface using CO_2-plused laser as excitation source. The effect of benzophenone and azoisobutylronitrile as photosensitizer was studied upon the graft level.

Coutinho, F.M.B. and Ferreira, M.P. (1994) studied bulk functionalisation of EPDM rubber with maleic anhydride using aromatic peroxides initiator.

Natural rubber can be chemically modified e.g. by epoxidation, prevulcanization and graft copolymerization, etc. In this work graft copolymerization, was used to modify the natural rubber.

Chapter 3
Graft Copolymer

3.1 Graft copolymer

Graft copolymer is a polymer comprising molecules with one or more species of block connected to the main chain. The simplest case of graft copolymer can be represented by this structure.

AAAAAAAAAAAAAAAAAAAA
B
B
B
B
B

Graft copolymer

Where a sequence of monomer A is chain or backbone and monomer B is side chain or graft.

The graft copolymers, the backbone and side chains may both be homopolymeric, the backbone may be homopolymeric and side chains copolymeric, the backbone may be copolymeric and side chains homopolymeric or both backbone and side chains are copolymeric.

Graft copolymerization is common method to modifying polymer. The product from graft copolymerization is graft copolymer. Properties of graft copolymer are combined between backbone and side chain polymers.

Graft copolymers have been prepared by polymerization of a monomer in the presence of preformed backbone polymer. The monomer can be polymerized by any of the traditional mode of polymerization. The free-radical polymerization is the one method used in graft copolymerization. Backbone polymer for free-radical graft copolymerization required the presence of an atom or group that can be abstracted or displaced by another radical, by chemicals or mechanical degradation or radiation. Free-radical polymerization is most widely used to produce graft copolymer because they are relative by simple.

3.2 Free-radical polymerization

Free-radical grafting procedures involve radical chain transfer and/or addition reaction to the polymer backbone in the presence of polymerizing monomer.

3.2.1 Free radical

A free radical may be defined as an unsaturated molecular fragment that can be considered to have been formed by the homolytic fission of a covalent bond, in which the resulting unpaired electron takes no part in bonding. The unpaired electron, which characterizes free radical, does not impart any charge to the species and many radicals are electrically neutral.

Free radical can be produced by a varity of techniques. It may be divided into two mains categories.

a. Fission of covalent bond

b. Transfer process

a. *Fission of covalent bond*

The fission of covalent bond may be achieved by thermal or photochemical reaction, or high energy irradiation, or mechanical processes. The position of the thermal dissociation occurred at the weak bond in the molecule e.g. the oxygen-oxygen bond (3.1).

$$CH_3\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}OOH \longrightarrow CH_3\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}O\cdot + \cdot OH$$

(3.1)

Thermal decompositions are normally associated with an activation energy of about 30 kcal/mol.

b. *Transfer process*

Free radical in this method occurred in redox reaction, that occurred by one electron transfer process involving the transfer of an electron to form an ion or molecule with the subsequent formation of radicals, for example, ferrous ion is oxidized to ferric ion by hydrogen peroxide with the formation of free radical (3.2).

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + \cdot OH \qquad (3.2)$$

Redox process is usually of 10 kcal/mol activation energy. Reaction of radicals with substrates may occur by three reactions as following

(1) Addition to molecule containing multiple bond (3.3).

$$R\cdot + C{=}C \longrightarrow R\text{-}C\text{-}C\cdot \qquad (3.3)$$

(2) Transfer reaction of atom or functional group (3.4).

$$R\cdot + X\text{-}R \longrightarrow R\text{-}X + \cdot R \qquad (3.4)$$

(3) Electron transfer in redox reaction (3.5).

$$RO\cdot + Fe^{3+} \longrightarrow RO^- + Fe^{2+} \qquad (3.5)$$

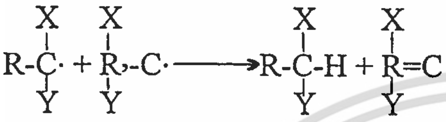
Reactions 1 and 2 are no change in overall concentration of radicals, since a new radical is produced in the reaction. In the reaction 3, radical is destroyed.

Destruction of free radicals occur by two reactions.

(1) Interaction between two radicals or combination (3.6).

$$R\cdot + R\cdot \longrightarrow R\text{-}R \qquad (3.6)$$

(2) Disproportionation (3.7).



$$R\text{-}\overset{X}{\underset{Y}{C}}\cdot + \overset{X}{\underset{Y}{R'}}\text{-}C\cdot \longrightarrow R\text{-}\overset{X}{\underset{Y}{C}}\text{-}H + \overset{X}{\underset{Y}{R}}=C$$

(3.7)

3.2.2 Special features of free-radical polymerization

(a) High molecular weight of the polymer produced from the reaction.

(b) Concentration of the monomer decrease only slowly with time.

(c) Molecular weight of the polymer is uneffected by long reaction time.

3.3 Mechanism and kinetic of free-radical polymerization

The mechanism of free-radical polymerization can be divided into three steps.

(3.3.1) Initiation
(3.3.2) Propagation
(3.3.3) Termination

3.3.1 Initiation

Initiation is the first step for beginning in polymerization. In this step involves creation of the free radical active center. The first is formation of free radicals from initiator and the second is the addition of one of these free radicals to monomers (3.8),(3.9).

$$I_2 \xrightarrow{K_d} 2I\cdot \qquad (3.8)$$

where; I_2 = Initiator

$$\text{Rate} = K_d[I_2]x2$$

This first step is called dissociation and k_d is called dissociation constant.

$$I\cdot + M \xrightarrow{K_i} IM\cdot \qquad (3.9)$$

$$\text{Rate} = K_i[I\cdot][M]$$

This second step is called initiation and K_i is called initiation constant.

So excess of free radicals produced by the initiator then rate of production of excess free radicals is:

$$\frac{d[I\cdot]}{dt} = 2K_d[I_2]-K_i[I\cdot][M]$$

In steady state:

$$\frac{d[I\cdot]}{dt} = 0$$

Then

$$2K_d[I_2] = k_i[I\cdot][M]$$

But the reaction of dissociation is slowly than the rate of initiation, then the rate of initiation is:

$$\text{Rate} = 2K_d[I_2]$$

The efficiency of the initiator(f) defined as:

$$f = \frac{\text{rate of initiation of propagation chains}}{2(\text{rate of decomposition of the initiator})}$$

3.3.2 Propagation

This step is involved growth of the polymer chain by rapid sequential addition of monomers to the active center (3.10).

$$
\begin{array}{l}
M\cdot + M \xrightarrow{K_p} M_2\cdot \\
M_2\cdot + M \xrightarrow{K_p} M_3\cdot \\
\cdot \quad \cdot \qquad\qquad \cdot \\
\cdot \quad \cdot \quad K_p \quad \cdot \\
M_n\cdot + M \xrightarrow{} M_{n+1}\cdot
\end{array}
\qquad (3.10)
$$

where, K_p = Propagation constant

Rate of propagation step is:

$$\text{Rate} = k_p[M.][M]$$

3.3.3 Termination

In this step, the polymer chain growth are terminated. The two most common mechanisms of termination involved the bimolecular reaction of growing polymer chains. It can be devided into two step i.e.

a. Combination reaction (3.11)
b. Disproportionation reaction (3.12)

$$M_i\cdot + M_j\cdot \xrightarrow{K_t} M_{i+j} \qquad (3.11)$$

$$M_i\cdot + M_j\cdot \xrightarrow{K_t} M_i + M_j \qquad (3.12)$$

Rate of termination is:

$$\text{Rate} = K_t[M_i.]^2 x2$$

But the growing chain can be transfer its free radical to another substrate in reaction mode.

1.Transfer to monomer (3.12).

$$M_i\cdot + M \xrightarrow{K_{ttm}} M_i + M\cdot \qquad (3.12)$$

$$\text{Rate} = K_{ttm}[M_i.][M]$$

2.Transfer to solvent (3.13).

$$M_i\cdot + S \xrightarrow{K_{tts}} M_i + S \qquad (3.13)$$

$$\text{Rate} = K_{tts}[M_i\cdot][S]$$

The Rate of polymerisation(P) is equal to the rate of disproportion of monoer.

$$P = \frac{-d[M]}{dt}$$

Monomer is consumed in the propagation reaction and the growing chain radical is transfer to monomer in the termination step. Then.

$$\frac{-d[M]}{dt} = \sum_{i=1} K_p[M_i\cdot][M] + \sum_{i=1} K_{ttm}[M_i\cdot][M]$$

$$P = K_p[M] + K_{ttm}[M] \underset{i=1}{} [M_i\cdot]$$

$$P = K_p[M]\left[1 + \frac{K_{ttm}}{K_p} \sum_{i=1} [M_i\cdot]\right]$$

But $\frac{K_{ttr}}{K_p} = \mathcal{E}_n$ (transfer to monomer constant).

$$P = K_p[M]\ 1 + \mathcal{E}_n \sum_{i=1} [M_i \cdot]$$

In the experiment, it is difficult to evaluate value of $[M_i.]$, then the solution to this problem is to make use of the steady state assumption, i.e. rate of initiation = rate of termination.

$$2K_d[I_2] = \sum_{i=1} K_t[M_i \cdot]^2 x2$$

$$\sum_{i=1} [M_i \cdot]^2 = \frac{2K_d\ [I_2]}{2K_t}$$

$$\sum_{i=1} [Mi \cdot] = \frac{K_d\ [I_2]}{K_t}$$

Then, $P = \frac{K_d\ [I^2]}{K_t}$

The rate of free-radical polymerization is:

$$P = \frac{K_d\ [I_2]}{K_t}$$

3.4 Copolymerisation

Consider a reaction mixture consisting of two different types of monomers M_1 and M_2, there will be four different types of propagation reaction. i.e.

1. $M_1\cdot + M_1 \xrightarrow{K_{11}} M_1\cdot$ (3.14)

$$\text{Rate} = K_{11}[M_1\cdot][M_1]$$

2. $M_1\cdot + M_2 \xrightarrow{K_{12}} M_2\cdot$ (3.15)

$$\text{Rate} = K_{12}[M_1\cdot][M_2]$$

3. $M_2\cdot + M_1 \xrightarrow{K_{21}} M_1\cdot$ (3.16)

$$\text{Rate} = K_{21}[M_2\cdot][M_1]$$

4. $M_2. + M_2 \xrightarrow{K_{22}} M_2.$ (3.17)

$$\text{Rate} = K_{22}[M_2.][M_2]$$

Rate of disappearance of M_1 will be:

$$\frac{-d[M_1]}{dt} = K_{11}[M_1.][M_1] + K_{21}[M_2.][M_1]$$

$$\frac{-d[M_1]}{dt} = [M_1](K_{11}[M_1\cdot]+K_{21}[M_2\cdot])$$

Rate of disappearance of M_2 will be:

$$\frac{-d[M_2]}{dt} = K_{21}[M_1\cdot][M_2] + K_{22}[M_2\cdot][M_2]$$

$$\frac{-d[M_2]}{dt} = [M_2](K_{21}[M_1\cdot]+K_{22}[M_2\cdot])$$

Then, the relative rate of additions of monomer type 1 and monomer type 2 to the growing chain will be:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]\left(K_{11}\frac{[M_1\cdot]}{[M_2\cdot]} + K_{21}\right)}{[M_2]\left(K_{21}\frac{[M_1\cdot]}{[M_2\cdot]} + K_{22}\right)}$$

In the experiment can not be determined concentration of growing radicals $[M_1.]$ and $[M_2.]$ then we are make use the "steady state" i.e.

$$\frac{-d[M_1\cdot]}{dt} = 0$$

then, $$K_{12}[M_1\cdot][M_2] - K_{21}[M_2\cdot][M_1] = 0$$

$$K_{12}[M_1\cdot][M_2] = K_{21}[M_2\cdot][M_1]$$

$$\frac{[M_1\cdot]}{[M_2\cdot]} = \frac{K_{21}[M_1]}{K_{12}[M_2]}$$

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\left[\frac{K_{11}\frac{K_{21}[M_1]}{K_{12}[M_2]} + K_{21}}{K_{12}\frac{K_{21}[M_1]}{K_{12}[M_2]} + K_{22}}\right]$$

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\left[\frac{\frac{K_{11}\cdot[M_1]}{K_{12}\ [M_2]} + 1}{\frac{[M_1]}{[M_2]} + \frac{K_{22}}{K_{21}}}\right]$$

$$r_1 = \frac{K_{11}}{K_{12}} , \quad r_2 = \frac{K_{22}}{K_{21}}$$

where , r_1 and r_2 are the monomer reactivity ratio

Then the copolymer equation is:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\left[\frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]}\right]$$

If the value of $r_1 = 1$ we would get a random addition of M_1 or M_2 monomers on to the end of $M_1\cdot$ and $r_2 = 1$ we would get a random addition of M_1 or M_2 monomers on to the end of $M_2\cdot$ The overall result will be a "Random Copolymer".

Where, $r_1 \rightarrow 0$ and $r_2 \rightarrow 0$, the result of this case is "Alternating Copolymer".

If the r_1 and $r_2 \rightarrow \infty$, the result of this case is "Homopolymer", i.e. copolymer not formed.

Now, we know about the graft copolymer, graft copolymerization technique for the synthesis graft copolymer and free-radical polymerization. Graft copolymerization can be produced in bulk polymerization , solution polymerization, suspension polymerization and emulsion polymerization. In this work use to "Emulsion Polymerization Technique" for the synthesis of graft copolymer.

Chapter 4

Emulsion Polymerization

Emulsion polymerization is one of the process used for production of graft copolymer. It is heterogeneous reaction process in which unsaturated monomers or monomers solutions are dispersed in continuous phase with the aid of an emulsifier system and polymerized with free-radical initiators.

Monomers polymerized by this way include styrene, butadiene, acrylic, chloroprene, vinyl acetate, acrylonitrile, ethylene, and many others. Emulsion polymerization was first produced during World War II. It was used for producing styrene-butadiene (Synthetic rubber) in United States rubber industry.

Emulsion polymerization refers to a unique process employed for some radical chain polymerization. The form of monomer is emulsion i.e. colloidal dispersion e.g. latex. The size of particle about 0.05-1.0 μm. Emulsion polymerization process has several distinct advantages. The physical state of emulsion(colloidal) system makes it easy to control the process. Thermal and viscosity are less significant than in bulk polymerization. Product of emulsion polymerization can be used directly with out further separation. Such application include coating, adhesive, paints etc.

4.1 Monomer

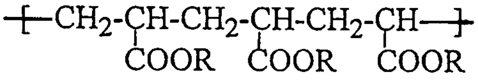
The most commonly monomer used are substituted ethylene $CH_2=CHX$ (eg.styrene, vinyl acetate, vinyl chloride, acrylic acid, acrylonitrile, acrylamide, or acrylic esters) and $CH_2=CXY$ (eg. 2-methylstyrene, vinylidene chloride, or methacrylic acid and its derivative).

In this work was use acrylic esters (i.e. ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate), methyl methacrylate, vinyl acetate, acrylic acid and acrylamide grafting on natural rubber (<u>cis</u>-1,4-polyisoprene).

4.1.1 *Structure and Properties of monomer*

Structure and molecule formula of monomers are given in table 4.1. Acrylate and methacrylate esters are derivatives of the corresponding acid, the respective structures are $CH_2=CHCOOR$ and $CH_2=C(CH_3)COOR$. The polyacrylates obtained by head-to-tail addition process consist of a hydrocarbon backbone with a pendant ester group; the polymethacrylates also have a pendant methyl group on same carbon atom.

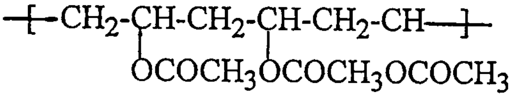
Polyacrylates have a general form i.e.



$$-\!\left[CH_2\text{-}\underset{COOR}{CH}\text{-}CH_2\text{-}\underset{COOR}{CH}\text{-}CH_2\text{-}\underset{COOR}{CH}\right]\!-$$

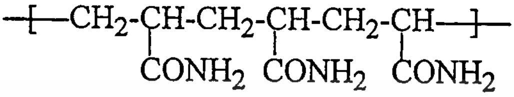
If the polymers are poly(ethyl acrylate); $R = -C_2H_5$, poly(butyl acrylate); $R=C_4H_9$, poly(2-ethylhexyl acrylate); $R = -CH_2CH(CH_3)C_4H_9$, poly(acrylic acid); $R = H$

Poly(vinyl acetate) has a general form i.e.



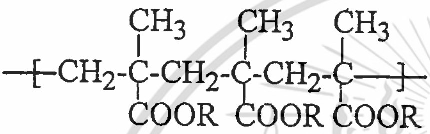
$$-\!\!\left[-\mathrm{CH_2}-\underset{\mathrm{OCOCH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{OCOCH_3}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{OCOCH_3}}{\mathrm{CH}}-\right]\!\!-$$

Polyacrylamide has a general form i.e.



$$-\!\!\left[-\mathrm{CH_2}-\underset{\mathrm{CONH_2}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{CONH_2}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{CONH_2}}{\mathrm{CH}}-\right]\!\!-$$

Polymethacrylates also have a general structure i.e.



$$-\!\!\left[-\mathrm{CH_2}-\underset{\mathrm{COOR}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{CH_2}-\underset{\mathrm{COOR}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{CH_2}-\underset{\mathrm{COOR}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\right]\!\!-$$

If the polymer is methyl methacrylate; R = CH_3

Table 4.1 Structure and molecule formula of monomers

Monomer	Formular	Structure
Ethyl acrylate	$C_5H_8O_2$	$CH_2{=}CHCOOC_2H_5$
Butyl acrylate	$C_7H_{12}O_2$	$CH_2{=}CHCOOC_4H_9$
2-Ethylhexyl acrylate	$C_{11}H_{20}O_2$	$CH_2{=}CH\ COOCH_2CH(C_2H_5)C_4H_9$
Methyl methacrylate	$C_5H_8O_2$	$CH_2{=}C(CH_3)COOCH_3$
Vinyl acetate	$C_4H_5O_2$	$CH_2{=}CHOCOCH_3$
Acrylic acid	$C_3H_4O_2$	$CH_2{=}CHCOOH$
Acrylamide	C_3H_5ON	$CH_2{=}CHCONH_2$

Physical properties of monomers are shown in Table 4.2, 4.3. Rate and heat of polymerization of monomers are given in Table 4.4 and physical properties of polymer are shown in table 4.5.

Table 4.2 Physical properties of acrylate monomers and methacrylate monomer.[12]

Physical properties	Ethyl acrylate	Butyl acrylate	2-Ethylhexyl acrylate	Methyl methacrylate
boiling range (°C)	98-100	145-149	130	100-101
density (g/cm3)	0.917	0.894	0.881	0.939
n^{25}_{D}	1.4037	1.4106	1.4332	1.4119
flash point (°F)	50a	120a	195b	55a
solubility at 25 °C				
-in water,parts/100	1.5	0.2	0.01	0.015
-parts/100 monomers	1.5	0.7	0.15	-
heat of vaporization (cal/g)	83	46	61	86
specific heat (cal/g °C)	0.47	0.46	0.46	0.45

a= Tagliabue open cup
b=Cleveland open cup

Table 4.3 Physical properties of acrylamide[12], acrylic acid[12] and vinyl acetate[15] monomer.

Physical properties	Acrylamide	Acrylic acid	Vinyl acetate
molecular weight	71.08	72.06	86.091
melting point (°C)	84.5±0.3	13.5	-93
vapor pressure (mmHg)			
at 40 °C	0.029	-	-
at 25 °C	-	0.57	-
at 20 °C	-	-	92
density (g/cm^3)	1.122	1.045	0.9342
refractive index			
n_x	1.460	-	-
n_y	1.550±0.003	-	-
n_z	1.581±0.003	-	-
n^{25}_{D}	-	1.4185	1.3953
solubility(g/100ml)			
water	-	miscible	-
at 25 °C	204	-	2.1
at 50 °C	426	-	-

Table 4.4 Rate and heat of polymerization.[12,13]

Monomer	$Kp/Kt^{-1/2}$ 44.1 (°C)	 60(°C)	Ka 44.1(°C)	 60 (°C)	ΔH kgcal/mole
Ethyl acrylate	123^b	2.27^b	313^b	1730^a	18.6
Butyl acrylate	-	-	-	-	18.5
2--Ethylhexyl acrylate	-	-	-	-	14.5
Methyl methacrylate	0.105^a	1.161^a	27^a	123^a	13.8
Acrylic acid	-	-	-	-	76.99
Vinyl acetate	-	-	-	-	21±0.5

a = Measured in the bulk
b = Measured in the solution

Table 4.5 Physical properties of polymer.[25]

Monomers	Density 25 C (g/cm3)	Tg (°C)	Brittle point (°C)	Softening point (°C)
Ethyl acrylate	1.095	-22	-24	-17
Butyl acrylate	-	-54	-44	-
2-Ethylhexyl acrylate	-	-55	34	-
Methyl methacrylate	1.190	105	92	113
Acrylamide	1.122	106	-	-
Acrylic acid	1.045	165	-	-
Vinyl acetate	1.11	32	-	-

4.2 Reaction[21]

The typical system of emulsion polymerization include the continuous phase, normally water, monomer, monomer mixture, or monomer solution, emulsifiers and stabilizers; initiator system; and less important ingredients such as chain-transfer agent, buffers and sometimes a seed latex, swollen agent, and solvent.

In conventional emulsion polymerization, a hydrophobic monomer is dispersed in continuous phase with an emulsifier. The polymerization is usually carried out with a water soluble initiator system. The size of the polymer particles in the final latex is generally much smaller than the droplets formed when the monomer is emulsified at the beginning of the reaction.

4.2.1 *Particle formation mechanism*

The Harkins model of emulsion polymerization for a batch reaction is described in terms of three Intervals.

Interval 1

In this interval is a beginning step, consists of a continuous water phase and a dispersion of monomer droplets 1-10μm. In the water phase contains the initiator, buffer or other electrolytes, small quantities of dissolved monomer and other minor ingredients such as chain-transfer agent, and emulsifier.

Most of monomer is located in large droplets, but some is solubilized within the micelles and some dissolved in the water. The polymerization reaction starts when water-borne free radicals migrate into the monomer-swollen micelles. Polymerization within these micelles depletes the monomer and establishes a thermodynamic driving force which causes mass transfer from the monomer droplets through the water phase to the newly formed growing polymer particles (see Fig. 4.1).

Particle nucleation is normally completed early in course of a batch reaction, conversion of 2-3 percent are typical. The explanation of this phenomenon is based on the new surface area formed by the growing monomer-swollen polymer particles. Nucleation stops when the surface area of the previously formed particles plus of the monomer droplets is adequate for thead sorption of all emulsifier. This point in the reaction sequence constitutes the end of Interval 1.

Interval 2

When the Interval 1 end, The reaction mixture is comprised of monomer-swollen polymer particles and monomer droplets; 90 percent of the monomer is present in the droplets. The reaction proceeds by polymerization within the particles. Monomer is supplied by diffusion from the shrinking monomer droplets. The diffusion of free radicals into monomer droplets is usually not considered important. The particles grow during Interval 2, the total interfacial area increases, usually to values higher than can be saturated with the emulsifier used in the initial charge. The end of Interval 2 get when the monomer is depleted from the droplets.

Interval 3

Overall monomer conversion at beginning of Interval 3 varies considerably among different monomer system. Continuing polymerization during Interval 3 reduces the monomer concentration in the particles.

In Interval 3, polymerization take place with higher polymer concentrations at the reaction , and thus more branching and cross-linking reactions are expected.

The Harkins mechanism and three-interval reaction scheme are not consistent with all experimental data. Nevertheless, this model represents a useful basis for examining the influence of various reaction and reaction parameters on the course of the polymerization and the characteristics of the latex.

4.3 Rate of emulsion polymerization

An expression for the rate of polymerization can be obtained by considering first the rate in a single polymer particle in which propagation is occurring (i.e. a particle containing a radical, an then the number of such particles.

At the start of polymerization in a typical system where the concentration of micelles is 10^{18} per milliliter and the initiation rate 10^{13} radicals per milliliter-second, a radical diffuses into a micelle every 10^5 sec at the start of Interval 1. As the system progresses through Interval 1, this time period decreases sharply, since the concentration of micelles is decreasing. A radical enters each particle on an average of every 10 sec during Interval 2 and 3 (Different rate of Interval 1,2 and 3 shown in picture 4.2) where N is typical 10^{14} particles per milliliter. Inside the micelles or polymer particles r_p (rate of propagation)dependent on K_p and [M] in the particle.(Eq 4.1)

$$r_p = K_p[M] \qquad (4.1)$$

Now the particle has a radical inside. The radical concentration in polymer particle is 10^{-6} mol/liter or higher. This is a higher radical concentration than in homogeneous polymerization system. The entry of a second radical into the polymer particle, the polymer will have either one or zero radical because of two radicals can get termination. The particle is then dormant until another (the third) radical arrives. The particle is again activated and propagation proceeds until the next radical. The cycle of alternate growth and inactivity of the polymer particle continues until the monomer conversion is essentially complete.

The rate of polymerization, R_p , at any instant is given by product of the concentration of active particles [P·] and rate of propagation in the particle (Eq. 4.2).[3]

$$R_p = K_p[M][P\cdot] \tag{4.2}$$

[P·] conveniently express by Eq. 4.3

$$[P\cdot] = \frac{10^3 N n}{N_A} \tag{4.3}$$

where N is the concentration of micelles plus particles, n is the average number of radical per micelle plus particle, and N_A is Avogadro number. The use of $10^3/N_A$ in Eq.4.3 and in the subsequent equation express [P·] in moles/liter and Rp in mole/liter-sec. Combination of Eq. 4.2 and 4.3 yields of polymerization rate as (Eq. 4.4).

$$Rp = \frac{10^3 N n Kp[M]}{N_A} \tag{4.4}$$

4.4 Degree of polymerization

The number average degree of polymerization, an emulsion polymerization can be obtained by considering what occurs in single polymer particle. The degree of polymerization is then the rate of growth of polymer chain divided by the rate at which primary radicals enter the polymer particle (Eq. 4.5).

$$Xn = \frac{NKp[M]}{Ri} \tag{4.5}$$

Where, Xn = Degree of polymerization
Ri = Rate of initiation
[M] = Concentration of monomer

4.5 Other characteristic of emulsion polymerization

4.5.1 *Initiator*

The initiators used in emulsion polymerization are water-soluble such as potassium or aluminium persulfate and hydrogen peroxide. Partial water-soluble peroxides such as succinic acid peroxide, and t-butyl hydroperoxide and azo compounds such as 4,4-azobis(4-cyanopentanoic acid) have also been used. Redox systems such as persulfate with ferrous ion are commonly used.

Redox systems are advantageous in yielding desirable initiation rate at temperature below 50°C. Other useful redox include cumyl hydroperoxide or hydrogen peroxide with ferrous sulfite, or bisulfite ion.

4.5.2 *Surfactants*

Anionic surfactants are the most commonly used in emulsion polymerization. These include fatty acid soaps (sodium or potassium sterate, laurate, palmitate), sulfates, and sulfonates (sodium lauryl sulfate and sodium dodecylbenzene sulfonate). The sulfates and sulfonates are useful for polymerization in acidic medium.

Nonionic surfactants such as poly(ethylene oxide), poly(vinyl alcohol) and hydroxyethyl cellulose are sometimes used in conjunction with anionic surfactants for improving the freeze-thaw and shear stability of the polymer.

4.5.3 *Energetics*

The heat of emulsion polymerization is the same as that for corresponding bulk or solution polymerizations, since H is essentially the enthalpy change of the propagation step. Thus, the heats of emulsion polymerization for acrylic acid, methyl acrylate and methyl methacrylate are -67, -77 and -58 kJ/mole, respectively in excellent agreement with the ΔH value for the corresponding homogeneous polymerization (table 4.4).

The effect of temperature on the rate of emulsion polymerization, although not extensively studied, is generally similar to that on homogeneous polymerization with the few modification. The overall rate of polymerization increases with an increase in temperature. Temperatrue increases the rate by increasing both K_p and *N*. The increase in *N* is due to the increased rate of radical generation at high temperature. But, at high temperature, initiator can be get thermal decomposition (table 4.5).

Table 4.4 Enthalpy and Entropy of polymerization at 25 °C [a,b]

Monomer	$-\Delta H$	$-\Delta S$
Isoprene	75b	101b
Acrylic acid	67b	-
Ethyl acrylate	18.6	-
2-Ethylhexyl acrylate	14.5	-
Butyl acrylate	18.5	-
Methyl methacrylate	56b	117b
Vinyl acetate	88b	110b

[a] Data from Brandrup and Immergut[1989]; Sawada[1976]

[b] H refers to the conversion of liquid monomer to amorphous or (slightly) crystalline polymer. S refers to the conversion of monomer (at concentration of 0.1 M) to amorphous or slighly crystalline polymer.

Table 4.5 Thermal decomposition of initiator.[a,b,c]

Initiator	$K_d x10^5$	T(°C)	E_d
2,2,-Azo-bis-isobutyronitrile	0.845	60	23.4
Acetyl peroxide	2.39	70	136.0
Benzoyl peroxide	5.50	85	124.3
Cumyl peroxide	1.56	115	170.3
t-Butyl peroxide	3.00	130	146.9
t-Butyl hydroperoxide	0.429	155	170.7

[a] All data for decompositions in benzene solution.

[b] Data from Brandrup and Immergut[1989].

[c] The units of K_d are sec^{-1}; the units of E_d are kJ/mole.

4.6 Reactor

A wide variety of both laboratory and commercial-scale reactors have been designed for emulsion polymerization. They are classified as batch, semibatch, and continuous process reactors.

4.6.1 *Batch reactor*

Batch reactors are the simplest to operator. The ingredients are added near the start of the cycle, the polymerization is carried out and the latex is removed. A typical process includes a preemulsification tank in which all ingredients except a water solution of initiator or, in the case of redox initiation, of one initiator component, are emulsified before charging.

A standard batch cycle includes the following operations; the reactor is charged with an emulsion containing all recipe ingredients except initiator; the initiator is added and the batch is heated if the preemulsion was cold; cooling is started after the inhibitor has been consumed and the reaction exotherm begins; the temperature is controlled and the course of the reaction monitored; when the target conversion is reached, the reaction is terminated by cooling or adding a short stop; ingredients, such as a poststabiliser,are added if needed; the reactor is discharged into downstream processing units; and the reactor is cleaned if necessary and set up for the next batch.

Production rates are determined by total cycle times. Since the reaction part is usually fixed, production is increased by reducing the time required for other parts of the cycle.

Batch reactors are frequently used in preliminary research and development studies, especially with bottle polymerizes. Large numbers of experiments can be completed quickly. Heat transfer is rapid because of high surface-to-volume ratios, and reaction temperature is easily controlled.

Because of problems with heat transfer in large commercial reactors, batch operations employed in production systems are frequently modified. Difficulties in controlling or changing the course of the polymerization are another disadvantage of batch reactors; reaction manipulations are not possible. For the scale up in 200 liter in this work is used batch reactor for the production of graft copolymer. This reactor consists of cooling part and heating part for the controlling of the temperature.

4.6.2 *Semibatch reactor*

In semibatch reactors, the most commonly used process, a portion of the recipe is charged at the beginning of the reaction, followed by the controlled addition of the remaining charge. This permits close control of the reaction and product properties. Such processes are extremely versatile and permit the production of a wide variety of latex products in a single reactor.

Reaction cycles can be adjusted to the limit of heat release, control particle number and size, polymer composition, particle morphology, and other parameters. However, changes made to improve one parameter may adversely affect others. Therefore, reaction cycles planned for commercial systems should first be tested in the laboratory and product-development studies.

Semibatch processes offer more flexibility than batch or continuous systems. However, some disadvantages is high. Second, mixing in reactors with highly variable fluid levels is more difficult; a different agitator design, such as longer shafts with multiple impellers may be required. Third, the effective heat-transfer area in jacketed reactors is a linear function of fluid level. Last, but not least, reaction cycles may be longer, thus reducing productivity.

4.6.3 *Continuous reactor*

Continuous stirred-tank reactors (CSTRs) produce a wide variety of latex products. They are fed with one or more streams, and the product is removed from one location. They offer advantages when high production rates are required or when closely related products are manufactured. Products can be changed without shutdown. Material below specifications produced during formation changes can be minimized with proper operating procedures. Such materials can often be blend, in small amounts, into one or both of the two products involved in the transition.

Continuous reactors operating at steady state can perform differently than batch or semibatch reactors; therefore, the design of a continuous process based on batch or semibatch data is risky. Data from small-scale continuous reactors should be used for the design of commercial units.

Cyclic variations of conversion and particle concentrations are frequently encountered with CSTR systems, especially with the reactors near the feed end of the series. These cyclic variations are not very sensitive to scale and would probably be detected in pilot-size equipment. The success of commercial continuous systems depends mostly on the ability to eliminate or control the cyclic variations of the reactor and other variables. This potential problem area is the principle motivation for the utilization of continuous pilot plants early in product and process-development programs.

Limit-cycle-type variations are common in continuous systems involving particle-nucleation and growth phenomena. Emulsion polymerization, crystallization, and other heterogeneous reactions can oscillate for the same fundamental reasons; excessive nucleation rates followed by rapid growth of surface area.

Operations can be stabilized by several techniques. A tubular prereactor is used to nucleate particles which are fed directly into a CSTR. A seed prepared in a separate batch reactor is inserted in the feed stream. Start-up techniques also influence initial vacillations and may prevent cyclic variations. A careful selection of formulation parameters and reaction conditions results in stable operations.

4.7 Products

4.7.1 *Solid concentration.*

The difference between latices used for fundamental colloid and kinetics studies and those used for commercial application is the solids, dilute systems permit the application of less complex theories. Handing and coagulation problems encountered with concentrated systems are avoided.

High solids systems offer numerous advantages for most commercial applications, e.g.. low shipping costs and no need for removing water. High solids concentrations are used for coatings and adhesives and in many lattices and formulated products.

4.7.2 *Molecular weight.*

Emulsion polymerization produces high molecular weight polymer at high rates. This is possible in systems with out strong free radical transfer reaction, because free radicals in close proximity to one another but in separate particles cannot colloid and terminate. Bulk, solution, or suspension polymerization at high rates, obtained by increasing the initiator concentration, often yield lower molecular weight polymer. They can be avoided in emulsion polymerization by nucleating more particles and thereby providing more sites for polymerization. With systems following the Harkins model, more particles can be formed by increasing the initiation rate during Interval 1 or, more likely, by increasing the emulsifier concentration.

The environment at the polymerization site changes gradually from pure monomer to highly concentrated polymer solution in homogeneous bulk, solution, and suspension reactions. A polymer concentration increase, Chain-transfer to polymer, terminal double-bond propagation, and other branching and cross-linking mechanisms become more important. The termination reaction rate also slows because of reduced mobility of the radicals i.e. the gel effect. These reactions broaden the molecular weight distribution and affect molecular structure; molecular weight is usually increased.

4.7.3 *Particle-size distribution.*

Variations in process design can yield lattices with a broad range of size characteristics. Monodisperse lattices are usually chosen for studies of fundamental colloids and reaction phenomena. Lattices with very narrow size distributions are available with diameters of 50 nm to 50 μm. Colloids of size 50-500 nm can be produced by single step emulsion polymerization.

4.7.4 *Molecular structure.*

Cross-linking, branching, grafting are significant in emulsion polymerization. Because of the average polymer concentration at reaction site is higher over most of the reaction cycle. This is advantageous if polymer-radical reactions are desired, as is sometimes the case with grafting.

In copolymer systems, the sequence of polymerization is important for grafting reaction. If two polymers with different tendencies to participate in chain-transfer reactors are polymerized in two stages with the initial particles beginning formed from the low reactivity polymer, very little graft occurs. If the system is turned around and the seed particles are comprised of chain-transfer active polymer, significant grafting occurs.

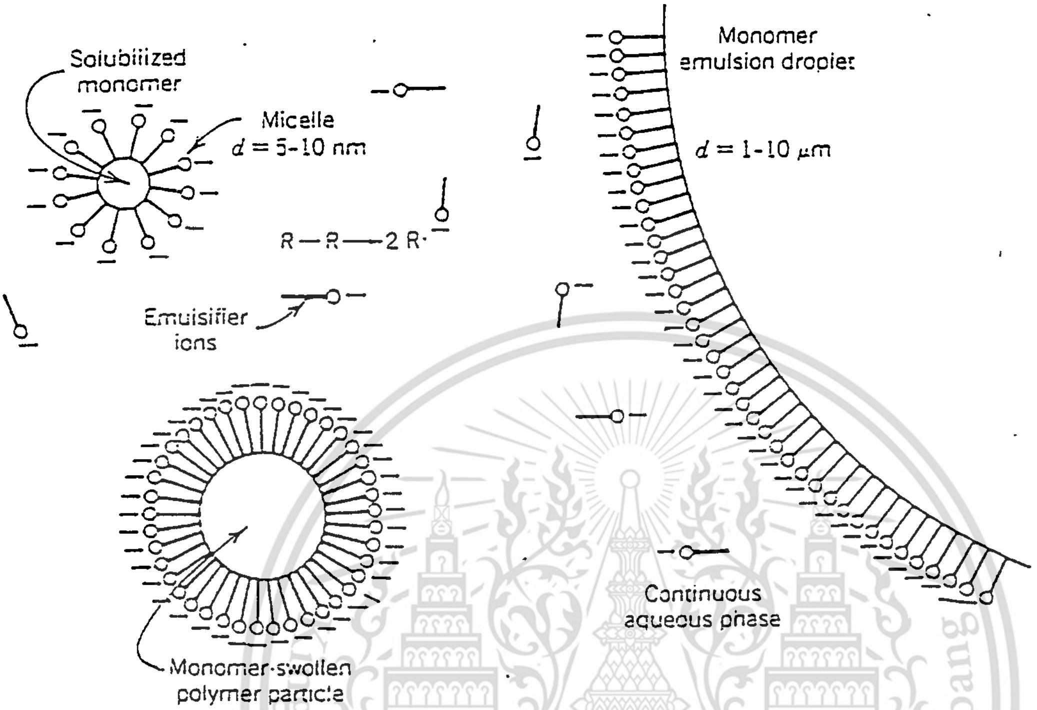


Fig. 4.1 The mechanism of emulsion polymerization.

Chapter 5
Materials and Methods

5.1 Apparatus

5.1.1 Synthesis and production of graft copolymer

Synthesis of graft copolymer with vinyl monomers was used 2 L. Pyrex glass reactor. The reactor was used in the reaction which consisting condenser, thermometer and agitator. Temperature was controlled by the cooling system Model CA-111, Toko Rikakikai Co.,Ltd. The production of graft copolymer was carried out in 200 L. size pilot plant reactor. The 200 L. plant reactor consisted condenser, agitator, thermometer and pressure gauges. The reaction temperature was controlled by two layers jacket connected with cooling water system. The drain valve of the pilot plant reactor was set at the bottom to let out the finished product. The agitator was paddle type and variable control the rotor speed. The 200 L. plant reactor was made from stainless steel. The 200 L. pilot plant reactor was made in Thailand by Supreme Stainless Steel WorksCO.,Ltd.

5.1.2 Latex properties testing.

Viscosity of latex was measured on Brookfield viscometer Model LVT (Brookfield Engineering Inc.,). Mechanical stability was obtained by mechanical stability tester Model K114S which purchased from Klaxon Co.,Ltd. pH value was determined by pH meter, Metrohm Model 654 and calibrated by buffer pH 4.

5.1.3 Characterization and identification of graft copolymer.

Extraction of graft copolymer was used by soxhlet extraction. The soxhlet dimension was 30x100 mm. and using 28x100 mm. of cellulose extraction timber. The reflux was effected with Heidolph Model MR 3001 heating mentle.

Fourier IR and Raman spectra waere recorded from Fourier IR and Raman spectrophotometer, Perkin-Elmer Model 2000. Measurements were carried out by laboratory of the National Metal and Materials Technology Center (METC) inwhich located at Faculty of Science Building, Mahidol University.

Pyrolysis chromatogram was carried out by pyrolysis gas chromatography at temperature 590 °C. The pyrolysis gas chromatograph was composed of pyrolyzer unit Model JHP-22, Japan Analytical Industry Co.,Ltd.and gas chromatography Model GC-9A connected with the recorder chromatopac CR-3A, Shimudzu Co.,Ltd.. The column was SE-30.

Thermogravimetric analysis was performed on a Du Pont Model TGA 51 thermogravimetric analyzer using samples that had been heated under nitrogen gas.

5.1.4 Physical and mechanical properties testing.

Graft copolymer in solid form was masticated using two rolls mill size 10 " diameter, Lab Tech Engineering Co.,Ltd.. The sheet forming was carried out by hot compression, Lab Tech Engineering Co.,Ltd., Model LP 20. Tensile strength, modulus 300%, elongation at break and tear resistance were measured on tensile testing machine Model S-100-C, Shimudzu Co.,Ltd.. Mooney viscosity was determined by Mooney viscometer Model MV-201, Shimudzu Co.,Ltd.Abrasion resistance was tested on Taber abrasor Model 5130. Plasticity Retention Index (PRI) was measured on Wallac plastimeter. Hardness testing was operated by Shore A type on hardness tester .

5.2 Reagent.

High ammonia natural rubber latex was purchased from Thai rubber latex Co.,Ltd.. Methyl methacrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, vinyl acetate, acrylic acid and acrylamide monomers were 97-99 % grade obtained from commercial sources and were used without further purification. NP 4000 was used as stabilizer in graft copolymerization. Diethylene triamine supplied from Dow chemical CO.,Ltd.. t-Butyl hydroperoxide was kindly donated from TOA Co.,Ltd.. Dionized water was produced from laboratory, Department of Chemistry. Light petroleum ether boiling rang 60-80 °C analytical grade selected from Ridel-de Haen AG. Acetone was purchased from Analar Co.,Ltd. (AR grade). Methyl alcohol supplied from J.T. Baker Analyzed Co.,Ltd. as analytical grade. Sodium hydroxide, laboratory grade was obtained from Merck Co.,Ltd.. Sulfuric acid, analytical grade was purchased from J.T. Baker Analyzed Co.,Ltd.

5.3 Experiment

5.3.1. Synthesis of graft copolymer

Procedure I

High ammonia natural rubber latex 500 g. was charged into the 2 L glass reactor. Added 90 ml. of 10% NP 4000 solution , the mixture was stirred in nitrogen blanket for 60 minutes at the rotor speed 165 rpm. Afterthat monomer 30% mole rubber was slowly dropped into the reactor and then stirred for 60 minutes at 200 rpm. of rotor speed. The temperature of reactor was controlled at 25 °C. Afterthat, t-butyl hydroperoxide initiator 1 g. and diethylene triamine catalyst 4.44 g. were added into the reactor. The mixture was stirred at rotor speed 165 rpm. for 15 minutes, and then the agitator was stopped. The reactor was stand at room temperature for 24 hrs.

For the system of 50% and 70% mole rubber of monomers, the conditions were the same as 30% mole rubber of monomer.

Procedure II

High ammonia natural rubber latex 500 g. and distilled water 500 g. were charged into the 2 L glass reactor. Added 90 ml. of 10% NP 4000 solution , the mixture was stirred in nitrogen blanket for 60 minutes at the rotor speed 165 rpm. Afterthat monomer 30% mole rubber was slowly dropped into the reactor and then stirred for 60 minutes at the rotor speed 200 rpm. The temperature of reactor was controlled at 25 °C. Afterthat, t-butyl hydroperoxide initiator 1 g. and diethylene triamine catalyst 4.44 g. were added into the reactor. The mixture was stirred at rotor speed 165 rpm. for 15 minutes, and then the agitator was stopped. The reactor was stand at room temperature for 24 hrs.

For the system of 50% and 70% mole rubber of monomers, the conditions were the same as 30% mole rubber of monomer.

Procedure III

High ammonia natural rubber latex 500 g. and distilled water 500 g. were charged into the 2 L glass reactor. Added 90 ml. of 10% NP 4000 solution, the mixture was stirred in nitrogen blanket for 60 minutes at the rotor speed 165 rpm. Afterthat the monomer 300 g. was slowly dropped into the reactor and then stirred for 60 minutes at rotor speed 200 rpm.. The temperature of reaction was controlled at 25 °C. Afterthat, t-butyl hydroperoxide initiator 1 g. and diethylene triamine catalyst 4.44 g. were added into the reactor. The mixture was stirred at rotor speed 165 rpm. for 15 minutes, and then the agitator was stopped. The reactor was stand at room temperature for 24 hrs.

5.3.2. Characteriation of graft copolymer.

Extraction technique.

Percent ungrafted free polymer of acrylate (i.e. ethyl acrylate, butyl acrylate and 2-ethylhexyl acrylate), methyl methacrylate and vinyl acetate in the graft copolymer were determined by acetone extraction and ungrafted free polymer of acrylic acid and acrylamide were examined by water extraction. Percent ungrafted free rubber in the graft copolymer was found by light petroleum ether extraction.

Two grams of each sample was extracted with 300 ml. of light petroleum ether (bp. 60-80 °C) for 24 hrs and then dried in the air oven at 50 °C for 24 hrs. Afterthat, the sample was extracted with 300 ml. of acetone for poly(ethyl acrylate), poly(2-ethylhexyl acrylate), poly(butyl acrylate), poly(methyl methacrylate),poly(vinyl acetate) and with 300 ml. of water for poly(acrylic acid) and poly(acylamide) for 24 hrs., dried in air oven at 50 °C for 24 hrs and weight.

The percent graft copolymer was calculated as:

$$\text{graft copolymer (\%)} = \frac{W}{W_0} \times 100 \qquad (5.1)$$

where,
W_0 = initial weight of sample, g.
W = final weight from extraction, g.

Identification of graft copolymer.

The identification of graft copolymer was performed by Fourier infrared spectrophotometer, Raman spectrophotometer and pyrolysis gas chromatography.

Fourier Infrared Spectrophotometer.

The Fourier IR was determined the functional group natural rubber and graft copolymer. The sample was prepared in thin film on NaCl cell by dissolved in chloroform (A.R. grade) and casting on the NaCl cell.

The measurement was operated between 4000-600 cm^{-1} wavenumber and the functional group was identified in Fourier IR spectrum.

Raman Spectrophotometer.

The extracted graft copolymer and natural rubber were in the solid form. The measurement was operated between 3600-200 cm^{-1} wavenumber and the functional group was identified in Raman Spectrum.

Pyrolysis gas chromatography

The pyrolysis gas chromatography was carried out to identify structure of polymer by using the temperature at Curie point to crack the polymer molecule into fragment. The fragment was passed to the column of gas chromatography. The retention time was selected to identify the polymer structure. The pyrolysis temperature at Curie point was operated at 590 °C.

The temperature of gas chromatography was operated at 50 °C for initial column temperature, 220 °C for final column temperature and 200 °C for injection port. The column temperature was increased for 15 °C/min.. The pyrolyzer unit was carried out at 150 °C for pipe and 200 °C for oven temperature.

Ten mg. of sample was packed in pyrofoil. The pyrofoil was used to induce the temperature to Curie point. The pyrofoil was put into the tube and then put into the pyrolyzer.

The recorder was operated attenuation at 5 and slope below 30. The retention time was shown in chromatogram which could be identified the polymer structure.

The natural rubber and extracted graft copolymer were identified by using SE-30 column of gas chromatography for separated the fragment product.

5.3.3. Latex testing.

1) Total solid content. (TSC)

The total solid content was determined by weight 2 g. of sample into the dish and dried the sample in the vent air oven for 24 hrs., at 50 °C. Afterthat the sample was cooled down in the desicator to room temperature and weight. Repeat drying and weighing until the mass of sample was constant.

$$\text{TSC (\%)} = \frac{(C-A)}{(B-A)} \times 100 \qquad (5.2)$$

where,

A = mass of the weighing dish, g.
B = mass of dish plus the original sample, g.
C = mass of the dish plus the dried sample, g.

2) Conversion.

The conversion of monomer was determined by TSC. The TSC of experiment was calculated in:

$$\text{Conversion (\%)} = \frac{X}{Y} \times 100 \qquad (5.3)$$

where,

X = TSC from the experiment.
Y = TSC from the theory.

3) Viscosity.

The sample of latex at the original TSC was determined the viscosity by Brookfield viscometer. The sample was put into 250 ml beaker. The rotor spindle number 2 and 50 rpm rotor speed were used to measure the viscosity. The value of viscosity was read from the Brookfield viscometer scale. Repeated to measure twice and the unit of viscosity was centipoise (cps).

4) Total alkalinity.

Weight 10 g. of sample at original TSC and then was diluted with 300 ml. of distilled water. Methyl red indicator was dropped in the sample. The mixture was titrate with 0.1 N. sulfuric acid until the colour was changed. The volume of sulfuric acid was recorded and the total alkalinity was calculated.

$$\text{Total alkalinity } (\%NH_3/100 \text{ g. water}) = \frac{170 \cdot N \cdot V}{W \cdot (100 - TSC)} \quad (5.4)$$

where, N = nomality of sulfuric acid.
V = volume of sulfuric acid, cm^3.
W = original mass of sample, g.

5) pH value.

The pH meter was calibrated with the buffer at pH 4. The temperature of sample was adjusted to 25 °C and then measured.

6 Mechanical stability.

Weight the sample at original TSC 100 g. into the glass and the temperature of sample was adjusted to 30 °C. The sample was stirred by mechanical stability tester at 14,000 rpm. until end point. The time at the end point was reported.

5.3.4. Physical and mechanical properties testing.

The sample for physical and mechanical properties testing was an unvalcanized solid form. The latex sample was air dried at room temperature for 5 days. The solid sample was masticated to be the sheet form for the determining of mechanical properties. The sheet form sample was placed on the standard sheet-shaped compression mould. The hot compression was set a heater temperature at 110 °C and 85 kg/cm^2 of pressure. The sheet-shaped compression moulding was done for 10 minutes. The sheet sample was used to determine the tensile strength, elongation at break, modulus 300%, tear resistance and abrasion resistance properties. The test specimen was recommened in ASTM-D 412 for tensile strength, elongation at break, modulus 300% and ASTM-D 624 for tear resistance testing. The condition for testing was used at 50 kg of load cell and crosshead speed at 50 mm/min.

1) Tensile strength.

The tensile strength was determined by load at break (kg) per cross-sectional area of gage length (cm^2).

$$TS = \frac{F}{A} \qquad (5.5)$$

Where,
TS = tensile strength at break, (kg/cm^2)
F = load at break, kg.
A = cross-sectional area of gage length, cm^2.

2) Elongation at beak.

For elongation at break was calculated as follow.

$$E\,(\%) = \frac{L-L_0}{L_0} \times 100 \qquad (5.6)$$

where,
E = Elongation at break, (%)
L = stretch length at break.
L_0 = original length of specimen (gage length).

3) Modulus 300%.

The modulus 300% was selected the value of load at length of specimen stretch three folds from the original gage length. The modulus 300% was calculated as following.

$$\text{Modulus } 300\%\ (kg/cm^2) = \frac{F_1}{A} \qquad (5.7)$$

where,
F_1 = load at the specimen was stretch three folds from original, kg.
A = cross-sectional area of gage length, cm^2.

4) Tear resistance.

The specimen for tear resistance testing was measured the thickness. The tear resistance was determined and calculated as:

$$\text{Tear resistance } (kg/cm) = \frac{F}{A} \qquad (5.8)$$

where,
F = load at break, kg.
A = thickness value, cm.

5) Mooney viscosity.

The Mooney viscocity testing was recommended in ASTM-D 1646 . The Mooney viscosity was determined by Mooney viscometer. The condition for Mooney viscosity testing was 100 °C of temperature, 1 minute for preheat and large rotor. The Mooney viscosity value was measured at 4 minutes. The solid rubber was used to measure the Mooney viscosity. The specimen was cut in the round form and put on top and down of the rotor. The rotor was put into the hold of the Mooney viscometer and measured the Mooney viscosity.

6) Hardness.

The hardness value was measured from hardness tester in Shore A type. The sample was laid down on the stand at hardness tester and pressed the specimen for 3 sec. under 5 kg. of load. The value was read from the dial.

7) Abrasion resistance

The abrasion resistance was reported on abrasion loss value, mm^3. The specimen for testing was prepared in round sheet and rubbed at 1000 rounds. The weight loss of specimen was determined. If the specimen had high volume loss then the specimen was low abrasion resistance.

8) Plasticity retention index.(PRI)

The PRI was measured on Wallac plastimeter. The top and down platen of Wallac plastimeter was set the temperature at 100 °C. The specimen was used in compound form. The specimen for testing was cut by cutter and put the specimen into the hold of the apparatus. The apparatus was closed for 15 sec. and measured the plasticity original (P_0). For plasticity aged (P_{30}) was determined by aged the specimen at 140 °C for 30 minutes and cooled to room temperature. The measurement of P_{30} was the same as P_0. The PRI was calculated as:

$$PRI = \frac{P_0 \times 100}{P_{30}} \qquad (5.9)$$

where,

PRI = plasticity retention index.

P_0 = plasticity original.

P_{30} = plasticity aged.

9) Density.

The density value of sample was determined by the liquid displacement method. Methanol was used as immersion liquid to remove any adhering to the specimen. The density was calculated as:

$$D = \frac{(AxD)}{(B+A-M)} x\ 0.9975 \qquad (5.10)$$

where, D = density of specimen, (g/cm^3).
A = weight of specimen, g.
B = weight of pycnometer filled with methanol, g.
D = density of methanol, $(0.79\ g/cm^3)$.
m = weight of pycnometer containing the specimen and filled with methanol, g.

5.3.5 Thermal properties.

Thermogravimetric analysis was used to determine thermal property of polymer. Thermal property was measured by thermogravimetric analyzer. The condition for testing was set at 50 °C for starting temperature and 850 °C for finish temperature. The temperature was increased about 15 °C/min. The 1 mg. of sample was put on the sample pan on the beam. The glass tube was closed and set the condition. At the end, the thermogram was reported. The thermogram was shown between degradation temperature and weight loss .

5.3.6. Production of graft copolymer.

The methyl methacrylate (MMA) 30% mole rubber and acrylic acid 5% mole of MMA were used as monomers to produce the graft copolymer on the natural rubber in the 200 L. pilot plant reactor. The pilot plant reactor consists of condensor, agitator and thermometer. The pilot plant reactor had the jacket for control temperature. The water temperature was controlled the temperature by external cooling water. The water temperature cooling was set at 5 °C for control the reaction mixture inside the reactor at 25 °C.

The 50 kg. natural rubber latex was charged into the reactor. Added 10% NP 4000 solution 9 kg., the mixture was stirred in nitrogen blanket for 60 minutes at 165 rpm. of rotor speed. MMA 13.24 kg. and acrylic acid 95 g. were slowly added into the reactor and stirred for 60 minutes at the rotor speed 200 rpm. After that added 1 kg. of t-butyl hydroperoxide initiator and diethylene triamine catalyst 4.44 kg., the reactor mixture was continued stir for 15 minutes at 165 rpm. and then stopped the agitator. The reaction mixture was stand for 24 hrs.

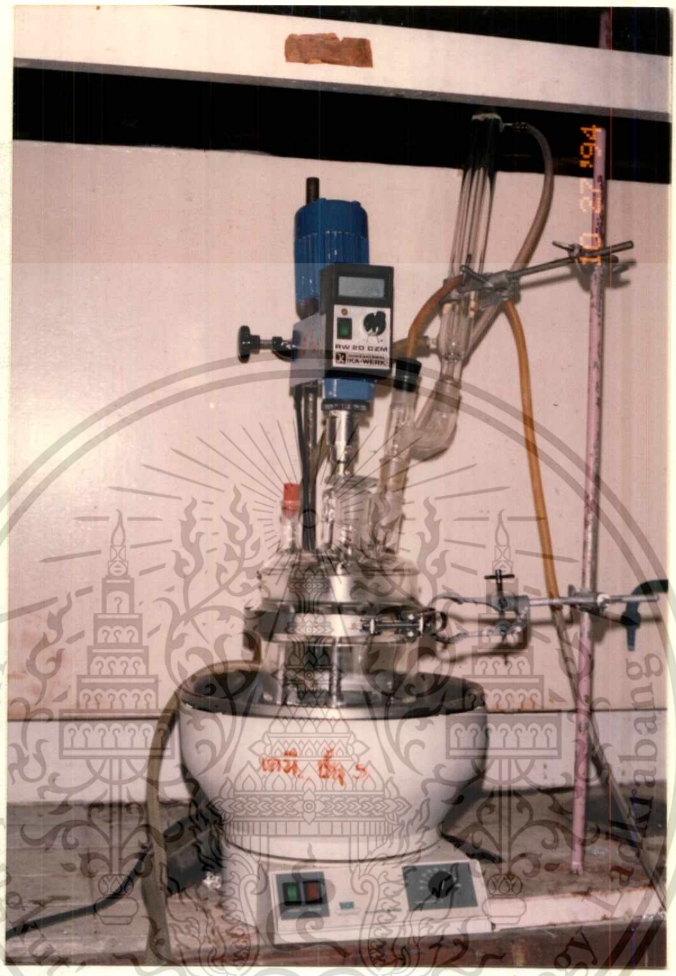


Fig. 5.1 The reactor(2 L) for the synthesis of graft copolymer.

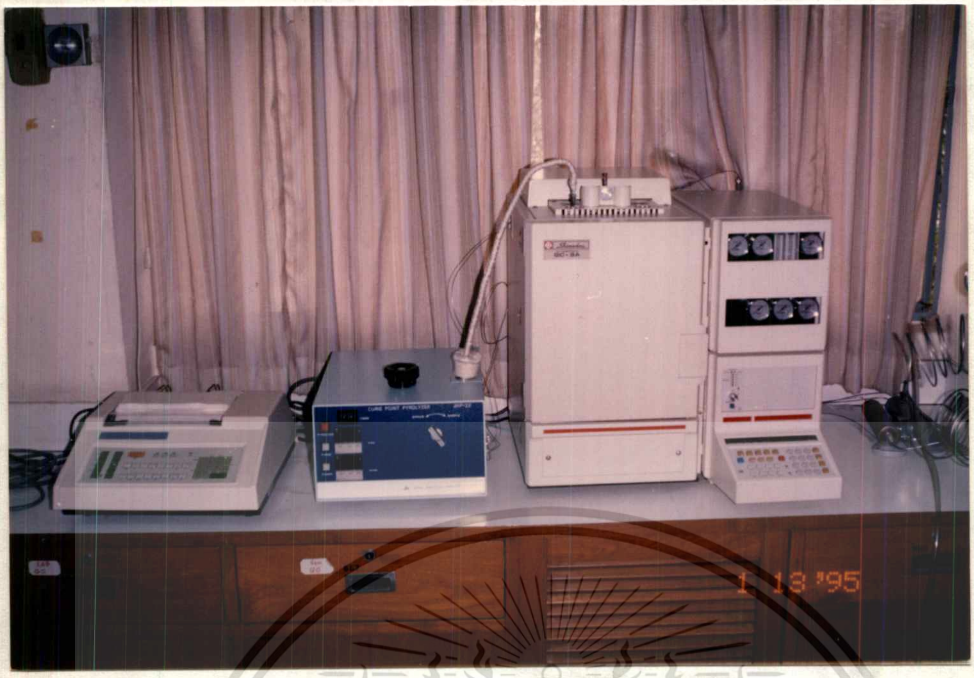


Fig. 5.3 The pyrolysis gas chromatography.

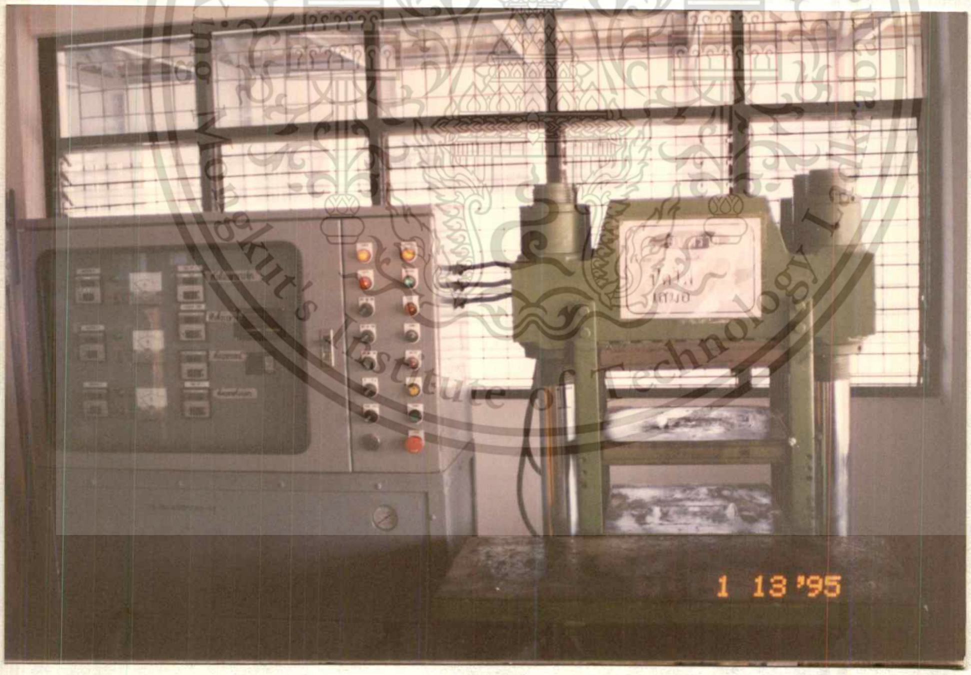


Fig. 5.4 The hot compression machine.

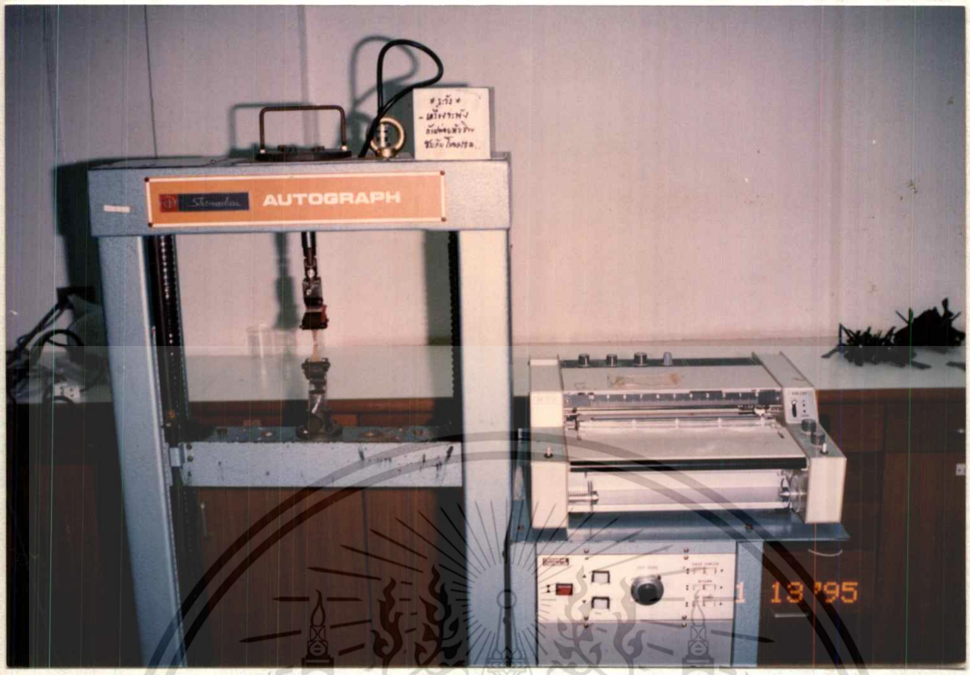


Fig. 5.5 The tensile testing machine.

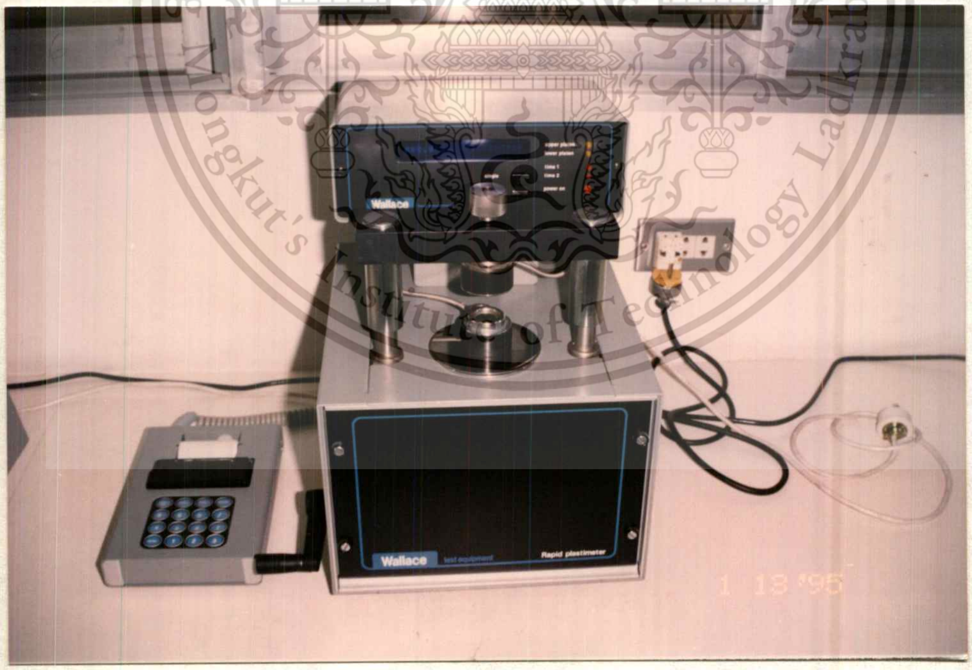


Fig. 5.8 The Wallac plastimeter

Fig. 5.6 The hardness tester.

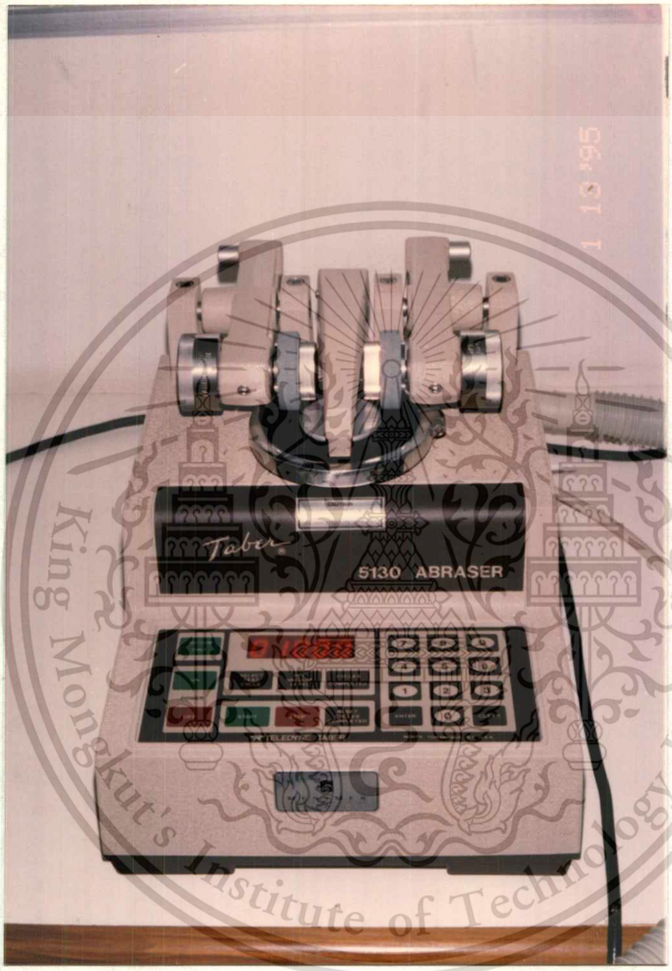


Fig. 5.7 The abrasion tester (Taber).

Fig. 5.9 The Mooney viscometer.

Fig. 5.10 The thermogravimetric analyzer (TGA).

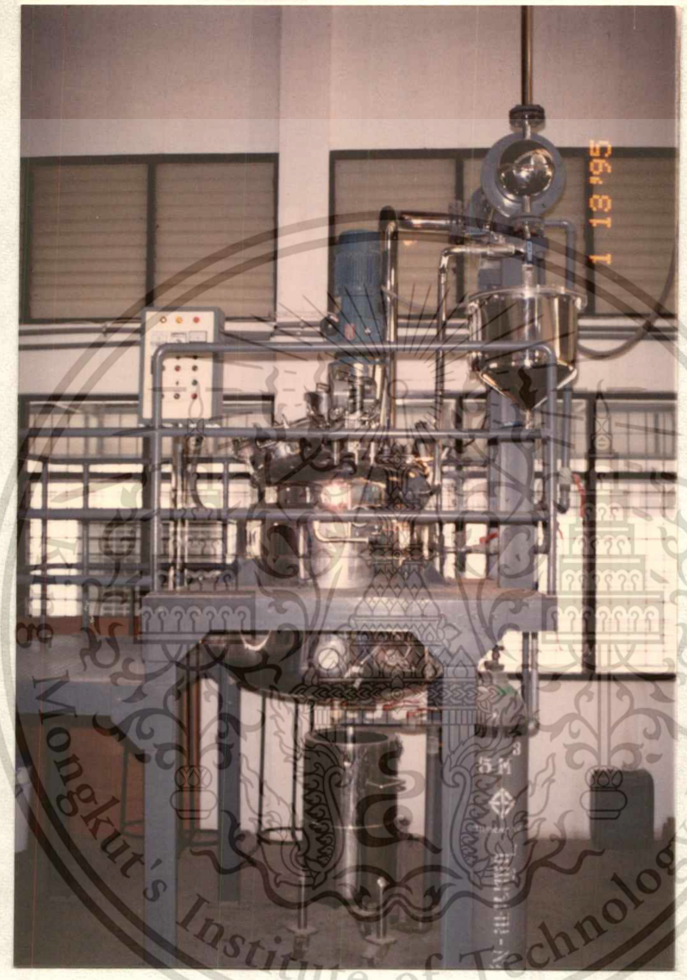


Fig. 5.11 The pilot plant reactor (200 L)

Chapter 6
Results and Discussion

Synthesis of graft copolymer with vinyl monomers on natural rubber latex by emulsion polymerization technique was carried out using t-butyl hydroperoxide as initiator and diethylene triamine as catalyst. The temperature was controlled at 25 °C in nitrogen blanket. The natural rubber in latex form should be grafted with vinyl monomers i.e. ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, acrylic acid. acrylamide and vinyl acetate monomers. The appearance of natural rubber latex grafted with acrylate monomers such as NR-g-MMA, NR-g-EA, NR-g-BA, NR-g-2-EHA were milky white latex forms except NR-g-Acrylic acid and NR-g-Acrtylamide inwhich they seem to be solidified. The NR-g-VA emulsion was become yellowish after storage in normal temperature.

6.1 Latex properties.

6.1.1 Total solid content. (TSC)

For the preparation of graft copolymer the emulsion polymerization was performed up to a high polymerization conversion. Base on this synthesis, TSC of graft copolymer was lower than the natural rubber latex. This has been confirmed to be correct by another two preparation methods. TSC of graft copolymers was shown in figure A-2 indicate the amount of the polymers formed by emulsion graft copolymerization, as relate to the monomers contents. When the monomer content was increased, the TSC was increased too.

Moreover the figures show that the TSC of graft copolymer is in good agreement with the theoretical value for the respective conversion. However, the graft copolymerization with hydrophilic monomers such as acrylic acid and acrylamide is formed to be similarly conversion with hydrophobic monomers (i.e. ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, vinyl acetate).

The vinyl monomers were successfully grafted onto the natural rubber form. The results of the conversion for the samples synthesized by three different procedures are given in table 6.1. It is clear that % conversion of monomer to polymer gave to be corresponding with TSC.

For the preparation of NR-g-MMA 30%+acrylic acid system, the conversion increased with the increased extent of acrylic acid in the polymerization reaction system.

The results of conversion are increased considerably relative to negative charge on rubber particles.

For the preparation NR-g-2-EHA system, The percent conversion was decreased at higher monomer concentration. The effect of monomer concentration on the polymerization conversion is due to the sterric effect of 2-EHA monomer.

Table 6.1 The conversion of graft copolymer by three different methods.

Graft copolymer	Conversion (%)		
	Procedure I	Procedure II	ProcedureIII
NR-g-MMA 30%	85.02	85.00	84.70
NR-g-MMA 50%	86.71	86.69	-
NR-g-MMA 70%	87.79	87.80	-
NR-g-MMA 30%+Acrylic acid 5%	88.15	88.00	90.00
NR-g-MMA 30%+Acrylic acid 10%	89.79	89.00	90.00
NR-g-MMA 30%+Acrylic acid 20%	89.20	89.10	90.00
NR-g-MMA 30%+Acrylic acid 30%	90.14	90.10	90.00
NR-g-EA 30%	81.00	80.00	90.00
NR-g-EA 50%	89.00	88.15	-
NR-g-EA 70%	90.00	89.53	-
NR-g-2-EHA 30%	89.00	89.00	85.00
NR-g-2-EHA 50%	85.00	86.10	-
NR-g-2-EHA 70%	85.00	85.57	-
NR-g-BA 30%	90.00	90.00	90.00
NR-g-BA 50%	85.00	85.00	-
NR-g-BA 70%	89.00	88.72	-
NR-g-VA 30%	89.00	88.15	86.90
NR-g-Acrylic acid 30%	82.00	82.00	73.00
NR-g-Acrylic acid 50%	84.30	84.00	-
NR-g-acrylic acid 70%	85.47	85.00	-
NR-g-Acrylamide 30%	85.00	86.75	70.00
NR-g-Acrylamide 50%	86.50	87.14	-
NR-g-Acrylamide 70%	87.20	87.50	-

6.1.2 Viscosity of graft copolymer latex.

The viscosity of NR-g-MMA was highest due to the NR-g-MMA has very high backbone molecular weight.

For the synthesis of NR-g-MMA 30% + Acrylic acid % system, the viscosity decreased with the increased extent of acrylic acid in the polymerization reaction system. The results are shown in table 6.2. The influence of the acrylic acid content in the monomer mixture on the residual of natural rubber particle contained in the graft copolymer latex as an important viscosity of this latex.

The viscosity of graft copolymers were nearly the viscosity of natural rubber except the graft copolymer with MMA and vinyl acetate. The viscosity of graft copolymers were increased when MMA 50-70% content were between 50-70% mole rubber.

For the preparation of NR-g-acrylic acid and NR-g-acrylamide , the result products were found to be solidified during stand in room temperature. Therefore, their viscosity could not be measured the same as others.

Table 6.2 Properties of NR and graft copolymer[a] in latex form.

	TSC (%)	Conversion (%)	Viscosity (30 °C) (cps.)	pH	Total Alkalinity (%)	Mechanical stability (sec)
Natural rubber (NR)	61.54	-	68.17	10.48	0.72	1040
NR-g-MMA 30%	45.92	85.02	69.00	9.98	0.54	735
NR-g-MMA 50%	47.30	86.71	375.00	10.12	0.58	752
NR-g-MMA 70%	49.95	87.79	610.00	10.74	0.67	770
NR-g-MMA30%+Acrylic acid 5%	46.30	88.15	78.40	9.72	0.32	720
NR-g-MMA30%+Acrylic acid 10%	47.18	89.79	70.68	9.27	0.19	713
NR-g-MMA30%+Acrylic acid 20%	46.90	89.20	60.40	9.28	0.19	700
NR-g-MMA30%+Acrylic acid 30%	47.42	90.14	47.85	6.85	0.02	560
NR-g-MMA30%+Acrylic acid 5% [b]	46.25	86.40	79.80	9.98	0.54	715
NR-g-2-Ethylhexyl acrylate 30%	48.56	89.00	51.50	9.65	0.27	120
NR-g-2-Ethylhexyl acrylate 50%	47.38	85.00	52.00	9.39	0.14	90
NR-g-2-Ethylhexyl acrylate 70%	48.01	85.00	51.60	8.74	0.06	70
NR-g-Ethyl acrylate 30%	43.21	81.00	64.00	4.60	-	40
NR-g-Ethyl acrylate 50%	48.38	89.00	66.00	4.67	-	20
NR-g-Ethyl acrylate 70%	49.60	90.00	64.30	4.73	-	12
NR-g-Butyl acrylate 30%	44.62	85.00	43.80	6.31	0.01	330
NR-g-Butyl acrylate 50%	49.28	89.76	45.20	6.43	0.01	130
NR-g-Butyl acrylate 70%	47.39	86.00	48.00	6.35	0.01	65
NR-g-Vinyl acetate 30%	47.23	89.00	312.00	3.92	-	392
NR-g-Acrylic acid 30%	37.50	85.00	-	9.86	0.47	-
NR-g-Acrylic acid 50%	40.96	86.50	-	9.62	0.40	-
NR-g-Acrylic acid 70%	42.88	87.20	-	10.24	0.62	-
NR-g-Acrylamide 30%	43.26	82.00	-	8.93	0.19	-
NR-g-Acrylamide 50%	43.94	84.30	-	9.28	0.20	-
NR-g-Acrylamide 70%	45.27	85.47	-	9.23	0.19	-

(a) Synthesis in reactor (2 L).
(b) Production in pilot plant reactor (200 L).
TSC = Total solid content

6.1.3 pH value.

The pH values of graft copolymer are shown in table 6.2. They found to be lower than the natural rubber (10.48) except NR-g-MMA 70% (10.74). The pH value was related to the total alkalinity. When the pH of graft copolymer was in acid range then the total alkalinity could not be measured.

6.1.4 Total alkalinity.

The total alkalinity was varied similar to the pH value. In case the graft copolymer was in acid range then the total alkalinity could not be obtained.

In this work, the latex of NR-g-EA and NR-g-VA could not be determined and the total alkalinity was the same as pH value of the product.

The NR-g-MMA 70% latex provided the highest value of total alkalinity (0.67%) due to the high pH value. In system of NR-g-MMA 30% + acrylic acid % system, the total alkalinity increased with the extent of acrylic acid concentration in the monomer mixture.

The overall total alkalinity of graft copolymers were lower than the total alkalinity of the natural rubber except NR-g-MMA 70%.

6.1.5 Mechanical stability.

The mechanical stability was measured for testing latex stability of the product. The NR-g-MMA system had the high value of mechanical stability due to the natural rubber particles formed the negative charge on the surface particles. Therefore the latex could be good stabilized with the negative charge on the natural rubber particle.

The NR-g-EA was the lowest value of mechanical stability (12 sec) because of this latex has pH in the acid range. Then the natural rubber particles could not be stabilized in the acid media.

6.2 Characterization of graft copolymer.

6.2.1 Extraction technique.

The extraction technique is determined percent grafted polymer. The free rubber was extracted by light petroleum ether (bp. 60-80 °C). The free polymer of poly(ethyl acrylate), poly(2-ethylhexyl acrylate), poly(butyl acrylate), poly(methyl methacrylate) and poly(vinyl acetate) was extracted by acetone and poly(acrylic acid), poly(acrylamide) was extracted by water.

From the synthesis, the free polymer was increased when the monomer content was increased. But the grafted polymer was decreased when the monomer content was increased.

The graft copolymer with vinyl acetate or ethyl acrylate is easily to be grafting on natural rubber. (see table 6.3) For the system of natural rubber grafted with acrylic acid or acrylamide was low percent of grafted polymer. The molecule of acrylic acid and acrylamide were hydrophilic but the natural rubber was hydrophobic then, the rubber molecule is not swollen by acrylic acid and acrylamide monomers.

In system of natural rubber grafted with MMA and acrylic acid, the percent grafted polymer decreased when the acrylic acid content is increased. The expression is the same as the natural rubber grafted with acrylic acid.

Table 6.3 Characterization by extraction technique of graft copolymer[a].

	Free rubber(c) (%)	Free polymer(d) (%)	Graft copolymer(e) (%)
NR-g-MMA 30%	15.37	13.21	71.42
NR-g-MMA 50%	13.21	17.08	69.71
NR-g-MMA 70%	12.12	26.08	61.08
NR-g-MMA30%+Acrylic acid 5%	13.03	19.09	67.88
NR-g-MMA30%+Acrylic acid 10%	14.04	21.05	64.10
NR-g-MMA30%+Acrylic acid 20%	13.52	27.69	58.79
NR-g-MMA30%+Acrylic acid 30%	2.92	48.20	49.50
NR-g-MMA30%+Acrylic acid 5%[b]	15.58	20.08	64.37
NR-g-2-Ethylhexyl acrylate 30%	11.92	13.96	74.12
NR-g-2-Ethylhexyl acrylate 50%	10.72	16.88	72.36
NR-g-2-Ethylhexyl acrylate 70%	9.89	21.04	69.07
NR-g-Ethyl acrylate 30%	10.93	29.07	60.00
NR-g-Ethyl acrylate 50%	10.09	31.83	58.08
NR-g-Ethyl acrylate 70%	9.65	33.30	57.05
NR-g-Butyl acrylate 30%	15.37	10.89	73.74
NR-g-Butyl acrylate 50%	11.87	16.61	71.52
NR-g-Butyl acrylate 70%	11.16	22.16	66.66
NR-g-Vinyl acetate 30%	16.63	7.95	75.42
NR-g-Acrylic acid 30%	28.81	31.90	39.29
NR-g-Acrylic acid 50%	29.12	35.79	29.09
NR-g-Acrylic acid 70%	27.51	54.36	18.13
NR-g-Acrylamide 30%	25.67	21.81	52.52
NR-g-Acrylamide 50%	17.39	32.16	50.45
NR-g-Acrylamide 70%	17.68	35.09	47..23

(a) Synthesis in reactor (2 L.)
(b) Production in pilot plant reactor (200 L)
(c) Extraction by light petroleum ether bp.60-80 ° C
(d) Extraction by acetone for acrylate and methacrylate,water for acrylic acid and acrylamide.
(e) see calculation method in 5.3.2

The identification of graft copolymer was performed by Fourier IR spectrophotometer, Raman spectrophotometer and pyrolysis gas chomatography.

6.2.2 Fourier IR spectrum.

The Fourier IR spectra are shown in appendix C. The fourier IR spectrum of natural rubber, the main absorption peak is shown at 760 cm^{-1} for cis isomer, 836 cm^{-1} as CH=C (out of plane) and 2850 cm^{-1} as C-H ($-CH_2-$, $-CH_3$). The Fourier IR spectra of graft copolymer with ethyl acrylate, 2-ethylhexyl acrylate, butyl acrylate and methyl methacrylate give the extra peak between 1731-1733 cm^{-1}. These peaks are identified as carbonyl group of acrylate polymer. The graft copolymer with acrylic acid had the extra peak at 1211 cm^{-1}. The NR-g-acrylamide gives the extra peak at 1449 cm^{-1}.

6.2.3 Raman spectrum.

The Raman spectra are shown in appendix D. The natural rubber gives absorption at 1315 cm^{-1}, 2912 cm^{-1}. The natural rubber grafted with ethyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, acrylic acid and vinyl acetate give the extra peak at 211 cm^{-1}. For the natural rubber grafted with acrylamide provides the extra peak at 1374 cm^{-1}.

6.2.4 Pyrolysis gas chromatography.

The pyrolysis chromatogram of natural rubber and natural rubber graft copolymer are shown in appendix F.

The natural rubber gives the retention time of the fragment products at 1.47 and 7.57 minutes. The two peaks are identified as isoprene and dipentene. The systems of natural rubber grafted with methyl methacrylate show the MMA retention time at 3.27 minutes. The systems of natural rubber grafted with ethyl acrylate provide the extra retention time at 0.62 minutes. This retention time is identified as ethyl acrylate. The systems of natural rubber grafted with butyl acrylate show the butyl acrylate retention time at 0.93 minutes. The systems of natural rubber grafted with 2-ethylhexyl acrylate give the retention time of 2-ethylhexyl acrylate at 4.45 minutes.

For the system of natural rubber grafted with acrylic acid, acrylamide and vinyl acetate, The SE-30 column is not appropriated to identify the natural rubber grafted with acrylic acid, acrylamide and vinyl acetate. Because of acrylic acid, acrylamide and vinyl acetate are polar structure.

6.3 Physical and mechanical properties of graft copolymer.

The physical and mechanical properties of natural rubber and graft copolymers were tested in unvalcanized solid form.

6.3.1 Compression forming of natural rubber and graft copolymers.

The ability of natural rubber and graft copolymers in compression thermoforming is illustrated in table 6.4.

Table 6.4 The result of compression thermoforming of natural rubber and graft copolymers.

Sample	Physical characteristics	Result
Natural rubber (NR)	opaque,brown-yellow colour,soft,smooth surface	P
NR-g-MMA 30%	opaque,pale brown colour,rigid,smooth surface	P
NR-g-MMA 50%	opaque,pale brown colour,rigid,smooth surface	P
NR-g-MMA 70%	opaque,pale brown colour,rigid, brittle,smooth surface	P
NR-g-MMA 30%+acrylic acid 5%	opaque,pale brown colour,rigid,smooth surface	P
NR-g-MMA 30%+acrylic acid 10%	opaque,pale brown colour,rigid,smooth surface	P
NR-g-MMA 30%+acrylic acid 20%	opaque,pale brown colour,soft,smooth surface	P
NR-g-MMA 30%+acrylic acid 30%	opaque,pale brown colour,soft,smooth surface	P
NR-g-MMA 30%+acrylic acid 5%(200 L,)	opaque,pale brown colour,rigid,smooth surface	P
NR-g-EA 30%	opaque,yellow colour,grind,soft	F
NR-g-EA 50%	opaque,yellow colour,grind,smooth surface	P
NR-g-EA 70%	opaque,yellow colour,grind,smooth surface	P
NR-g-2-EHA 30%	opaque,pale yellow light,ground form,soft	F
NR-g-2-EHA 50%	opaque,pale yellow light,ground form,soft	F
NR-g-2-EHA 70%	opaque,pale yellow light,smooth surface	P
NR-g-BA 30%	opaque,pale yellow light,ground form,soft	F
NR-g-BA 50%	opaque,pale yellow light,ground form,soft	F
NR-g-BA 70%	opaque,pale yellow light,ground form,soft	F
NR-g-VA 30%	opaque,dark brown colour,soft,smooth surface	P
NR-g-acrylic acid 30%	opaque,yellow-brown,soft,smooth surface	P
NR-g-acrylic acid 50%	opaque,yellow-brown,rigid,smooth surface	P
NR-g-acrylic acid 70%	opaque,yellow-brown,rigid, brittle,smooth surface	P
NR-g-acrylamide 30%	opaque,light-yellow,rigid,brittle,smooth surface	P
NR-g-acrylamide 50%	opaque,light-yellow,rigid,brittle,smooth surface	P
NR-g-acrylamide 70%	opaque,light-yellow,rigid, brittle,smooth surface	P

P = could be formed; F = could not be formed

6.3.2 Mooney viscosity

The Mooney viscosity is measured on Mooney viscometer at 100 °C, 4 minutes by large rotor, the results are shown in table 6.5. The Mooney viscosity of natural rubber was 53.23. In system of natural rubber grafted with MMA or vinyl acetate give high value of the Mooney viscosity. The results are clearly seen that the MMA and VA produce high Tg polymers (see table 4.5). The MMA and VA polymers introduce the hard segment in graft copolymer. In this hard segment is against the rotor to rotate then increasing the torque value.

The natural rubber grafted with acrylic acid and acrylamide are shown to be lower Mooney viscosity when compared with NR-g-MMA although the acrylic acid and acrylamide polymers are high Tg polymer. These results should be explained by the lower percent grafted polymer of NR-g-acrylic acid and NR-g-acrylamide. The another graft copolymers are lower Mooney viscosity value than natural rubber.

6.3.3 Tensile strength.

The tensile strength was measured at 50 kg. of load and calculated by equation 5.5. Form the result, the tensile strength of natural rubber was lower than the tensile strength of graft copolymer. (see Fig. A-6) The tensile strength value of natural rubber grafted with the high Tg polymer i.e. poly(methyl methacrylate), poly(acrylic acid) and poly(acrylamide) are high tensile strength value. In system of natural grafted with MMA, the tensile strength value decreased when the monomer content was increased. The cause of that was the MMA 30% mole rubber could be grafted on the natural rubber more than MMA 50% and 70% mole rubber. The natural rubber grafted with MMA and acrylic acid 5% from the production is the highest value of tensile strength (50 kg/cm^2).

In system of natural rubber grafted with ethyl acrylate, butyl acrylate, acrylic acid or acrylamide, the tensile strength value were increased to the extent of monomer content i.e. when the monomer content increased, the tensile strength was increased. The tensile strength property is inverse proportion of the elongation at break.

6.3.4 Elongation at break.

The elongation at break was measured on tensile testing machine. The condition of testing was the same as the tensile strength testing.

The result from testing was obtained that the elongation at break of graft copolymer was lower than the natural rubber except natural rubber grafted with ethyl acrylate. The natural rubber grafted with ethyl acrylate is the highest value of elongation at break (1060%). The assumption of that is chain entanglements of graft copolymer molecule.

The elongation at break value is inverse proportion of tensile strength. Then, the natural rubber grafted with high Tg polymer produces low elongation at break value. (see table 6.5 and Fig. A-7)

6.3.5 Modulus 300%.

The modulus 300% value was selected the load at the length of specimen stretch three folds from original gage length.

The result found that, the graft copolymers give higher than natural rubber (3.17 kg/cm^2). (see Fig. A-8) The modulus 300% of natural rubber grafted with MMA was the highest value (39.0 kg/cm^2) due to the MMA produces the high Tg polymer. Therefore the natural rubber grafted with MMA is rigid. For the system of natural rubber grafted with acrylic acid or acrylamide are the same as the natural rubber grafted with MMA. The modulus 300% of natural rubber grafted with acrylic acid or acrylamide is high value.

6.3.6 Tear resistance.

The tear resistance value are shown the resistance of materials to tear. The tear resistance of natural rubber grafted with MMA, acrylic acid or acrylamide are high value. These graft copolymers are effected by MMA, acrylic acid and acrylamide which produce high Tg polymers. Therefore the graft copolymers of MMA, acrylic acid and acrylamide were hard and the segment was against tear force.

For the natural rubber grafted with low Tg polymer, their tear resistance are low value e.g. the natural rubber grafted with ethyl acrylate, 2-ethylhexyl acrylate or butyl acrylate. The polymer which produce from ethyl acrylate, 2-ethylhexyl acrylate and butyl acrylate are low Tg polymer. Therefore, the products are soft segment in graft copolymer.

6.3.7 Hardness.

The hardness value was measured on hardness tester Shore A type. The high hardness value is obtained with natural rubber grafted with MMA, acrylic acid and acrylamide. (see Fig.A-10) This may be caused by the hard segment polymer of MMA, acrylic acid and acrylamide in the graft copolymer molecule. The hard segment in the graft copolymer of MMA, acrylic acid or acrylamide polymers are high Tg polymer, therefore they produce high hardness value.

For the system of natural rubber grafted with ethyl acrylate, 2-ethylhexyl acrylate or butyl acrylate are low hardness value because of the graft copolymer with ethyl acrylate, 2-ethylhexyl acrylate and butyl acrylate are soft polymer.

6.3.8 Abrasion resistance.

Abrasion resistance is reported in abrasion loss value i.e. the high value of abrasion loss, the abrasion resistance is low.

From the results are shown in Fig. A-11, the natural rubber grafted with the high Tg polymers and the natural rubber grafted with the low Tg value polymers give low abrasion resistance. The graft copolymers with MMA or acrylic acid is high abrasion loss. The graft copolymer is effect by the use of various monomers. The graft copolymer with MMA or acrylic acid is hard graft copolymer therefore they are more easily to volume loss. The graft copolymer with ethyl acrylate and 2-ethylhexyl acrylate give high abrasion loss due to low Tg polymer. Therefore, the graft copolymers are soft and easy to loss.

6.3.9 Plasticity retention index (PRI).

The PRI is shown in the figure A-12 or table 6.6 which characterizes the plastic flow of rubber. The graft copolymer is combined with two segments i.e. hard and soft segments. The natural rubber is soft segment and vinyl monomers produce hard segment polymer.

From the results, the graft copolymers could be flow like plastic. The PRI of graft copolymers are nearly quantitative and higher than the natural rubber.

6.4 Thermal property of graft copolymer.

The thermal property is measured by thermogravimetric analyzer (TGA). The result is shown in TGA thremogram. (see appendix E) Form the results found that the thermogram of graft copolymer is the same as natural rubber. The degradation temperature of natural rubber and graft copolymer are about 400 °C. Weight loss of natural rubber is equal with graft copolymer. These could be explained that the chain breaking of graft copolymer is at natural rubber molecule.

Table 6.5 Physical and mechanical properties of natural rubber and graft copolymer [a].

	Mooney viscosity ML (1+4) 100 °C	Tensile strength[c] (kg/cm^2)	Elongation at break [d] (%)	Modulus 300% [e] (kg/cm^2)	Tear resistance[f] (kg/cm)
Natural rubber (NR)	53.23	5.25	600	3.17	3.85
NR-g-MMA 30%	142.20	46.00	395	39.90	22.00
NR-g-MMA 50%	129.47	44.70	387	37.10	39.15
NR-g-MMA 70%	100.10	42.00	377	35.40	39.93
NR-g-MMA30%+Acrylic acid 5%	72.36	45.01	387	33.00	19.32
NR-g-MMA30%+Acrylic acid 10%	70.60	40.42	382	31.79	17.79
NR-g-MMA30%+Acrylic acid 20%	65.17	34.29	381	33.70	19.05
NR-g-MMA30%+Acrylic acid 30%	54.10	8.02	299	-	9.15
NR-g-MMA30%+Acrylic acid 5%[b]	59.23	50.00	416	29.24	19.26
NR-g-2-Ethylhexyl acrylate 30% *	7.86	5.07	73	-	2.43
NR-g-2-Ethylhexyl acrylate 50% *	7.96	4.06	98	-	1.25
NR-g-2-Ethylhexyl acrylate 70%	36.83	6.15	510	3.78	3.86
NR-g-Ethyl acrylate 30% *	26.77	4.41	131	-	1.78
NR-g-Ethyl acrylate 50%	43.47	8.89	700	3.17	5.98
NR-g-Ethyl acrylate 70%	47.93	22.31	1060	3.78	10.37
NR-g-Butyl acrylate 30% *	25.20	2.87	73	-	1.20
NR-g-Butyl acrylate 50% *	24.67	5.32	120	-	1.34
NR-g-Butyl acrylate 70% *	24.47	6.72	169	-	2.80
NR-g-Vinyl acetate 30%	106.60	12.65	428	8.27	10.15
NR-g-Acrylic acid 30%	37.30	8.60	324	9.22	8.96
NR-g-Acrylic acid 50%	48.60	9.73	87	-	12.25
NR-g-Acrylic acid 70%	52.10	14.20	43	-	12.25
NR-g-Acrylamide 30%	34.90	9.54	430	8.31	4.84
NR-g-Acrylamide 50%	41.60	24.62	392	21.91	15.08
NR-g-Acrylamide 70%	77.40	29.81	104	-	45.15

(a) Synthesis in reactor (2 L)
(b) Production in pilot plant reactor (200 L)
(c) see the calculation in equation 5.5
(d) see the calculation in equation 5.6
(e) see the calculation in equation 5.7
(f) see the calculation in equation 5.8
* could not be fomed

Table 6.6 Physical and mechanical properties of natural rubber and graft copolymers[a].

	Hardness (ShoreA)	Abrasion loss[c] (mm^3)	Plasticity original (P_0)	Plasticity aged (P_{30})	PRI[d]	Density[e] (kg/cm^3)
Natural rubber (NR)	28	30.40	93.70	58.40	62.32	0.90
NR-g-MMA 30%	50	31.60	99.90	97.60	97.69	0.97
NR-g-MMA 50%	68	58.00	99.80	97.80	98.89	1.01
NR-g-MMA 70%	66	60.00	99.90	98.80	98.89	1.03
NR-g-MMA30%+Acrylic acid 5%	60	32.30	91.13	89.90	98.65	0.97
NR-g-MMA30%+Acrylic acid 10%	54	29.90	96.00	94.70	98.64	0.98
NR-g-MMA30%+Acrylic acid 20%	51	25.00	97.40	95.50	98.05	0.98
NR-g-MMA30%+Acrylic acid 30%	36	21.90	94.50	92.60	97.98	0.99
NR-g-MMA30%+Acrylic acid 5%[b]	43	31.70	99.00	97.80	98.78	0.97
NR-g-2-Ethylhexyl acrylate 30% *	37	-	86.70	86.20	99.42	1.00
NR-g-2-Ethylhexyl acrylate 50% *	28	-	73.70	73.10	99.18	1.02
NR-g-2-Ethylhexyl acrylate 70%	21	66.40	89.20	87.80	98.43	1.03
NR-g-Ethyl acrylate 30% *	7	-	79.80	78.40	98.24	0.93
NR-g-Ethyl acrylate 50%	16	57.30	89.00	86.60	97.30	0.96
NR-g-Ethyl acrylate 70%	24	67.20	92.60	85.20	92.00	0.98
NR-g-Butyl acrylate 30% *	22	-	75.10	74.70	99.46	0.95
NR-g-Butyl acrylate 50% *	17	-	69.80	68.70	98.42	0.97
NR-g-Butyl acrylate 70% *	10	-	67.00	65.20	97.31	1.02
NR-g-Vinyl acetate 30%	24	17.20	98.40	87.50	88.92	1.10
NR-g-Acrylic acid 30%	38	69.30	76.20	75.20	98.68	0.99
NR-g-Acrylic acid 50%	57	55.00	96.90	94.90	97.93	1.02
NR-g-Acrylic acid 70%	78	42.47	96.50	95.50	98.96	1.04
NR-g-Acrylamide 30%	22	12.30	87.40	79.10	90.50	1.02
NR-g-Acrylamide 50%	45	22.14	90.20	87.00	96.45	1.04
NR-g-Acrylamide 70%	63	21.93	96.10	92.43	96.18	1.18

(a) Synthesis in reactor (2 L).
(b) Production in pilot plant in reactor (200 L).
(c) Taber type
(d) see the calculation in equation 5.9
(e) see the calculation in equation 5.10
* could not be formed

6.5 Production of graft copolymer.

The natural rubber grafted with MMA 30% mole rubber and acrylic acid 5% mole of MMA could be produced in 200 L pilot plant reactor by emulsion polymerization system. The condition for the production of graft copolymer is the same as the synthesis in laboratory i.e. the temperature was controlled at 25 °C under nitrogen atmosphere. The t-butyl hydroperoxide, diethylene triamine and NP 4000 are used in the production.

The properties of graft copolymer by production is compared with graft copolymer by synthesis which shows in Table 6.7.

Table 6.7 The properties of graft copolymer by production and synthesis

Properties of graft copolymer	From the production with 200 L pilot plant reactor	From the synthesis with 2000 ml glass reactor
TSC (%)	46.25	46.30
Conversion (%)	86.40	88.15
Viscosity (cps.)	79.80	78.40
pH	9.98	9.72
Total alkalinity (%)	0.54	0.32
Mechanical stability (sec)	715	720
Grafted polymer (%)	64.37	67.88
Mooney viscosity	59.23	72.36
Tensile strength (kg/cm^2)	50.00	45.01
Elongation at break (%)	416	387
Modulus 300% (kg/cm^2)	29.24	33.00
Tear resistance (kg/cm)	19.26	19.32
Hardness (Shore A)	43	60
Abrasion loss (mm^3)	31.70	32.30
PRI	98.78	98.65
Density (g/cm^3)	0.97	0.97

From the result, the graft copolymer from the production is soften than the graft copolymer from the synthesis. The Mooney viscosity, modulus 300% and hardness of graft copolymer by production are lower than graft copolymer from synthesis. Percent grafted polymer of production is lower than synthesis. The assumption could be explained that the production of graft copolymer produces heat build-up more than the synthesis of graft copolymer in the laboratory. Whereas the reaction produces high heat build-up value, the grafted polymer reduces in the reaction. Therefore the percent grafted polymer by production is lower and the hard segment is less than the graft copolymer by synthesis respectively.

Chapter 7
Conclusion

The emulsion polymerization by free-radical using t-butyl hydroperoxide as initiator and diethylene triamine as catalyst could be prepared the graft copolymer of vinyl monomer i.e. ethyl acrylate, 2-ethylhexyl acrylate, butyl acrylate, acrylic acid, acrylamide and vinyl acetate on natural rubber.

The properties of graft copolymer are summarized as following. The total solid content of graft copolymer are lower than natural rubber and total solid content value are between of 45-49%. The conversion of monomer are nearly quantitative. The conversion increased similar to the TSC. The conversion of natural rubber grafted with MMA 30% mole rubber and acrylic acid 30% mole of MMA is the highest conversion (90.14%) and natural rubber grafted with ethyl acrylate 30% is the lowest conversion (81%).

The viscosity of graft copolymers are nearly the viscosity of natural rubber except the system of natural rubber grafted with MMA or vinyl acetate. The system of natural rubber grafted with acrylic acid or acrylamide could not be measured the viscosity value due to the latex product are solidified during stand for 24 hrs.

The mechanical stability of natural rubber grafted with MMA is high value of mechanical stability but lower than natural rubber (1040 sec). The natural rubber grafted with MMA 70% is the highest value of mechanical stability (770 sec). The system of natural rubber grafted with ethyl acrylate is low value of mechanical stability due to the latex is in acid pH.

The physical and mechanical properties of graft copolymer are summarized in table 7.1.

Table 7.1 The physical and mechanical properties of graft copolymer.

Physical and mechanical properties	The highest value	The lowest value
Mooney viscosity	NR-g-MMA 30%	NR-g-2-EHA 30%
Tensile strength (kg/cm^2)	NR-g-MMA30%+Acrylic acid 5%	NR-g-2-EHA 50%
Elongation at break (%)	NR-g-EA 70%	NR-g-Acrylic acid 30%
Tear resistance (kg/cm)	NR-g-Acrylamide 70%	NR-g-BA 30%
Modulus 300% (kg/cm^2)	NR-g-MA 30%	NR-g-2-EHA 30%
Hardness (Shore A)	NR-g-MA 70%	NR-g-EA 30%
Abrasion resistance (mm^3)	NR-g-Acrylamide 30%	NR-g-MMA 70%

The natural rubber graft copolymer with MMA gives high value of Mooney viscosity, modulus 300% and hardness value due to the hard segment of MMA branch polymer. The natural rubber grafted with 2-ethylhexyl acrylate shows low value of Mooney viscosity, tensile strenght and modulus 300%. Because of, the natural rubber grafted with 2-ethylhexyl acrylate is soft graft copolymer.

From the physical and mechanical properties, the graft copolymer of natural rubber with the high Tg polymer e.g. MMA produces the high value of Mooney viscosity, tensile strength, tear resistance and modulus 300%. The graft copolymer of natural rubber with the high Tg polymer are used for the development tensile strength, hardness, tear resistance modulus 300% of natural rubber. For the natural rubber grafted with ethyl acrylate could be used to introduce higher elongation at break.

For the production of graft copolymer in pilot plant reactor could be produced graft copolymer of vinyl monomers i.e. MMA 30% + acrylic acid on the natural rubber. The properties of graft copolymer from the production are similar to the synthesis but percent grafted polymer is less. The assumption is higher heat build-up produces in the production. This problem is in good reason when produces the graft copolymer in pilot plant scale. The control of heat build-up is problem for further study.

RECOMMENDATIONS FOR FURTURE STUDIES

1. A study should be made on mix monomers i.e. use the monomer more than one to graft on the natural rubber.
2. A study on grafting with another rubber.
3. A study on grafting with another monomer on the natural rubber.

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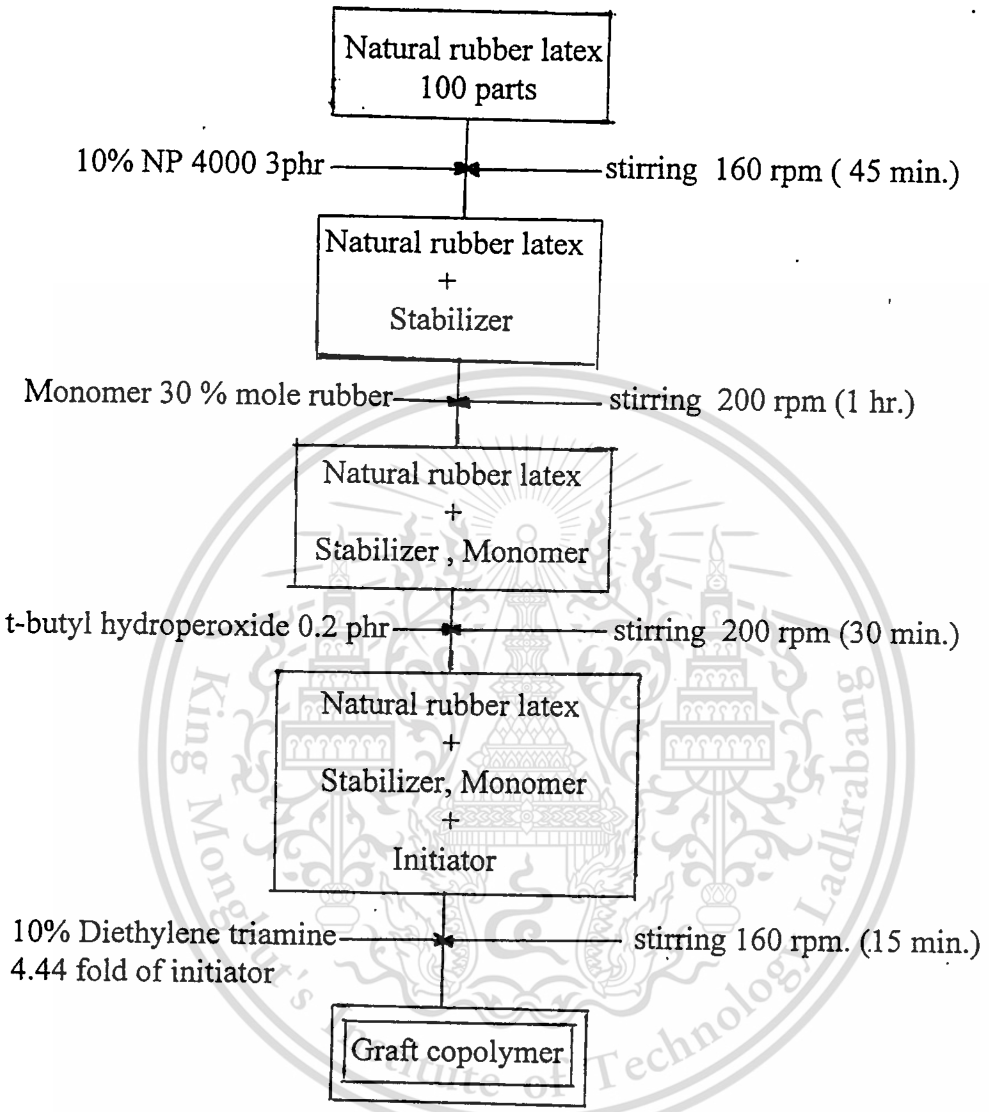
Appendix A

Flowchart for Synthesis graft copolymer



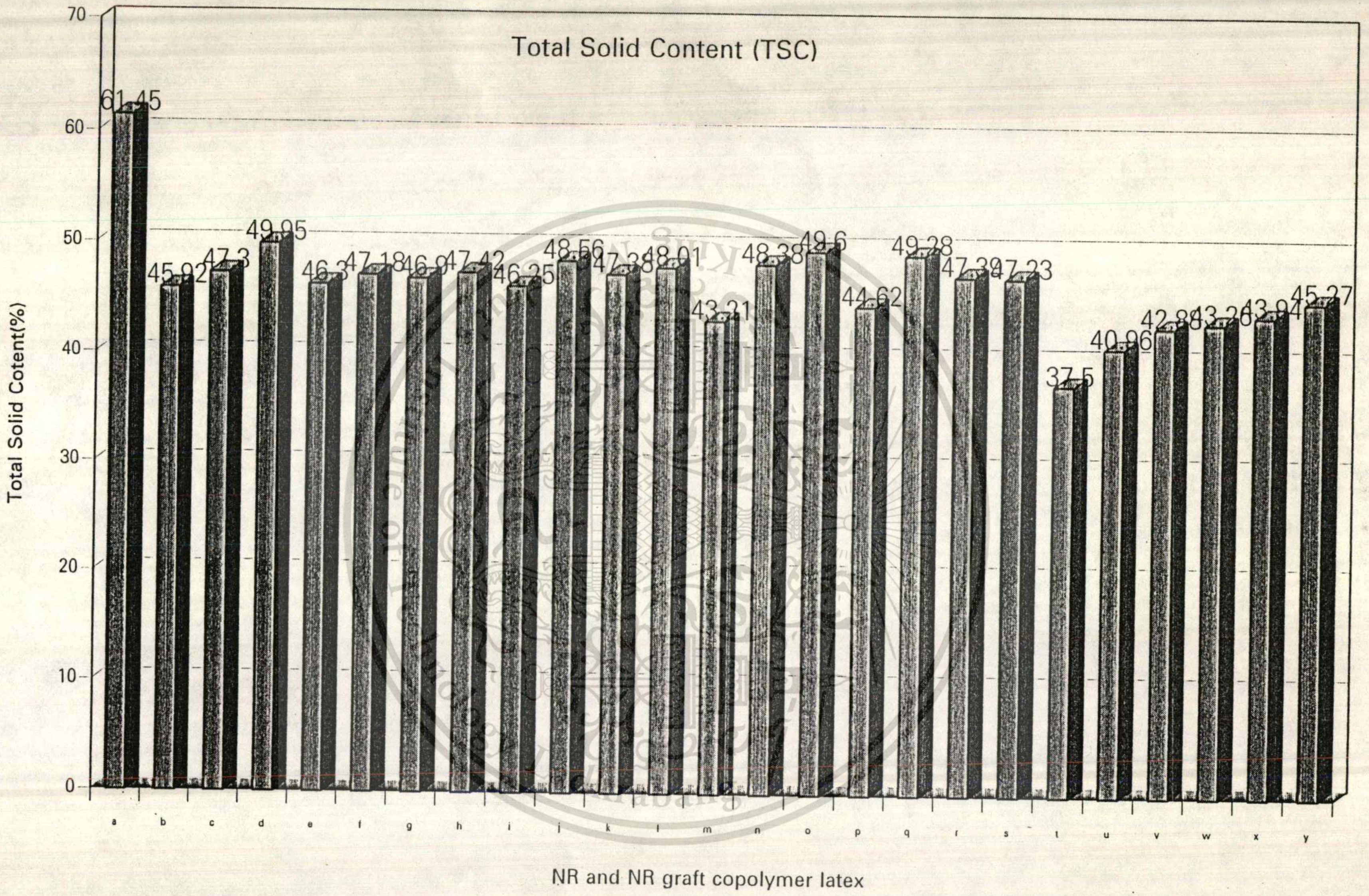

Total Solid Content (TSC)
Total Solid Cotent(%)
0
10
20
30
40
50
60
70
61.45
45.92
47.3
49.95
46.3
47.18
46.9
47.42
46.25
48.56
47.38
48.01
43.21
48.38
49.6
44.62
49.28
47.39
47.23
37.5
40.96
42.88
43.26
43.94
45.27
a
b
c
d
e
f
g
h
i
j
k
l
m
n
o
p
q
r
s
t
u
v
w
x
y
NR and NR graft copolymer latex

Fig. A-1

From the Fig. A-1

a = Natural rubber latex.
b = NR-g-MMA 30%
c = NR-g-MMA 50%
d = NR-g-MMA 70%
e = NR-g-MMA 30% + Acrylic acid 5%
f = NR-g-MMA 30% + Acrylic acid 10%
g = NR-g-MMA 30% + Acrylic acid 20%
h = NR-g-MMA 30% + Acrylic acid 30%
i = NR-g-MMA 30% + Acrylic acid 5% (200 L.)
j = NR-g-2-Ethylhexyl acrylate 30%
k = NR-g-2-ethylhexyl acrylate 50%
l = NR-g-2-Ethylhexyl acrylate 70%
m = NR-g-Ethyl acrylate 30%
n = NR-g-Ethyl acrylate 50%
o = NR-g-Ethyl acrylate 70%
p = NR-g-Butyl acrylate 30%
q = NR-g-Butyl acrylate 50%
r = NR-g-Butyl acrylate 70%
s = NR-g-Vinyl acetate 30%
t = NR-g-Acrylic acid 30%
u = NR-g-Acrylic acid 50%
v = NR-g-Acrylic acid 70%
w = NR-g-Acrylamide 30%
x = NR-g-Acrylamide 50%
y = NR-g-Acrylamide 70%

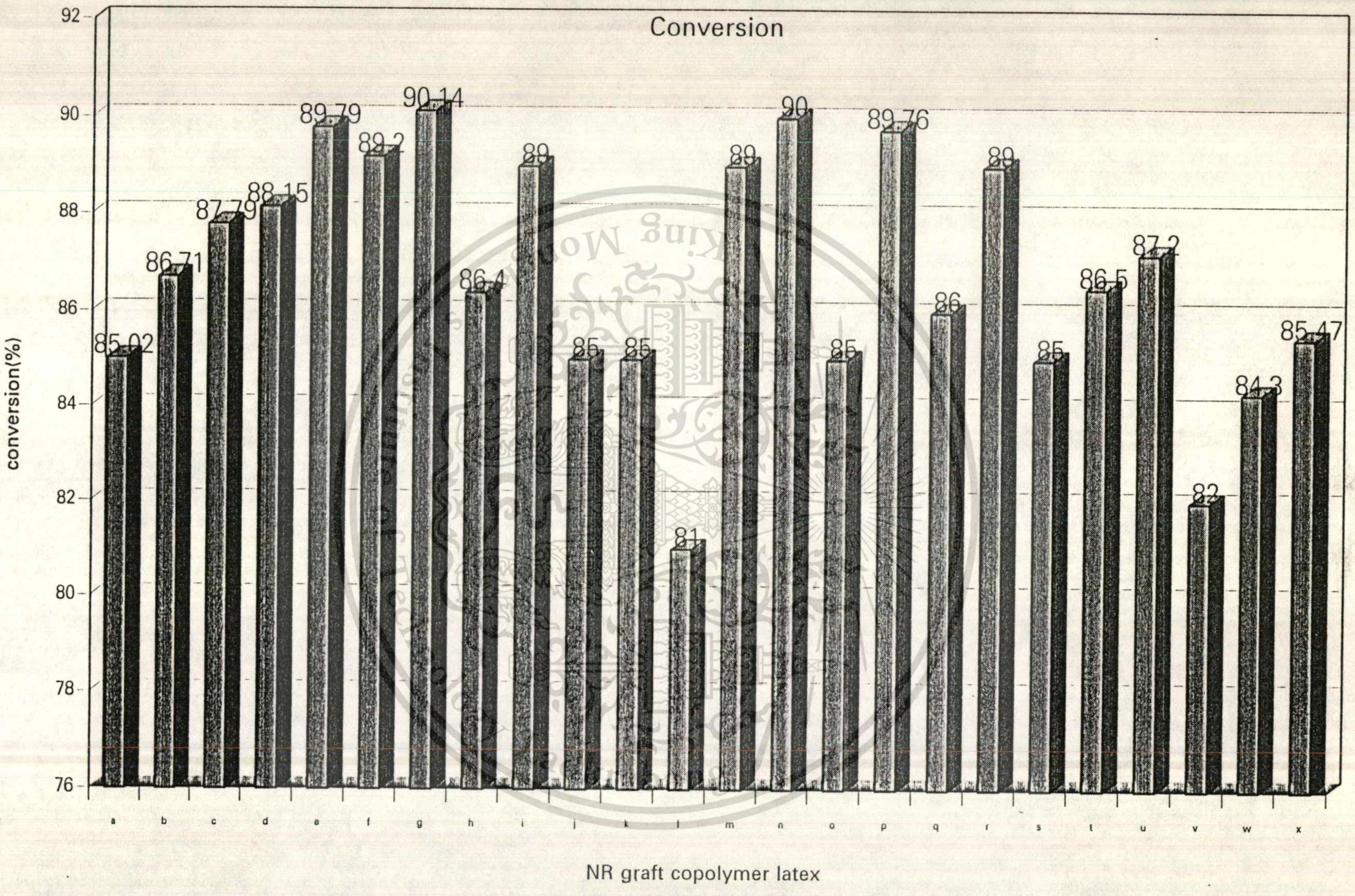

Conversion
conversion(%)
92
90
88
86
84
82
80
78
76
85.02
86.71
87.79
88.15
89.79
89.2
90.14
86.4
89
85
85
81
89
90
85
89.76
86
89
85
86.5
87.2
82
84.3
85.47
a
b
c
d
e
f
g
h
i
j
k
l
m
n
o
p
q
r
s
t
u
v
w
x
NR graft copolymer latex

Fig. A-2

From the Fig. A-2
a =NR-g-MMA 30%
b = NR-g-MMA 50%
c = NR-g-MMA 70%
d = NR-g-MMA 30% + Acrylic acid 5%
e= NR-g-MMA 30% + Acrylic acid 10%
f = NR-g-MMA 30% + Acrylic acid 20%
g = NR-g-MMA 30% + Acrylic acid 30%
h= NR-g-MMA 30% + Acrylic acid 5% (200 L.)
i = NR-g-2-Ethylhexyl acrylate 30%
j = NR-g-2-ethylhexyl acrylate 50%
k = NR-g-2-Ethylhexyl acrylate 70%
l = NR-g-Ethyl acrylate 30%
m = NR-g-Ethyl acrylate 50%
n= NR-g-Ethyl acrylate 70%
o = NR-g-Butyl acrylate 30%
p = NR-g-Butyl acrylate 50%
q = NR-g-Butyl acrylate 70%
r = NR-g-Vinyl acetate 30%
s = NR-g-Acrylic acid 30%
t = NR-g-Acrylic acid 50%
u = NR-g-Acrylic acid 70%
v = NR-g-Acrylamide 30%
w = NR-g-Acrylamide 50%
x = NR-g-Acrylamide 70%

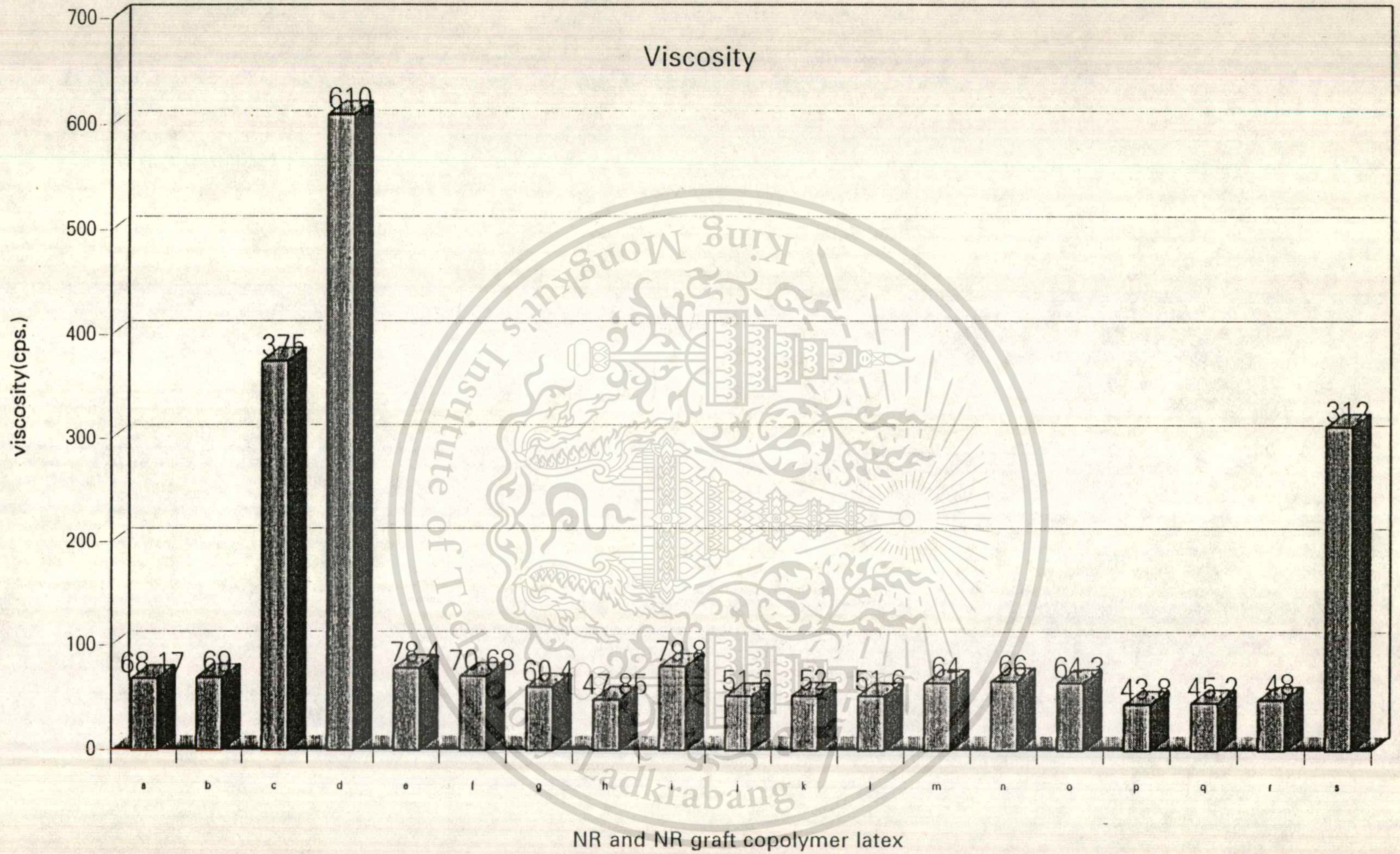

Viscosity
viscosity(cps.)
700
600
500
400
300
200
100
0
68.17
69
375
610
78.4
70.68
60.4
47.85
79.8
51.5
52
51.6
64
66
64.3
43.8
45.2
48
312
a
b
c
d
e
f
g
h
i
j
k
l
m
n
o
p
q
r
s
NR and NR graft copolymer latex

Fig. A-3

From the Fig. A-3

a = Natural rubber latex.
b = NR-g-MMA 30%
c = NR-g-MMA 50%
d = NR-g-MMA 70%
e = NR-g-MMA 30% + Acrylic acid 5%
f = NR-g-MMA 30% + Acrylic acid 10%
g = NR-g-MMA 30% + Acrylic acid 20%
h = NR-g-MMA 30% + Acrylic acid 30%
i = NR-g-MMA 30% + Acrylic acid 5% (200 L.)
j = NR-g-2-Ethylhexyl acrylate 30%
k = NR-g-2-ethylhexyl acrylate 50%
l = NR-g-2-Ethylhexyl acrylate 70%
m = NR-g-Ethyl acrylate 30%
n = NR-g-Ethyl acrylate 50%
o = NR-g-Ethyl acrylate 70%
p = NR-g-Butyl acrylate 30%
q = NR-g-Butyl acrylate 50%
r = NR-g-Butyl acrylate 70%
s = NR-g-Vinyl acetate 30%

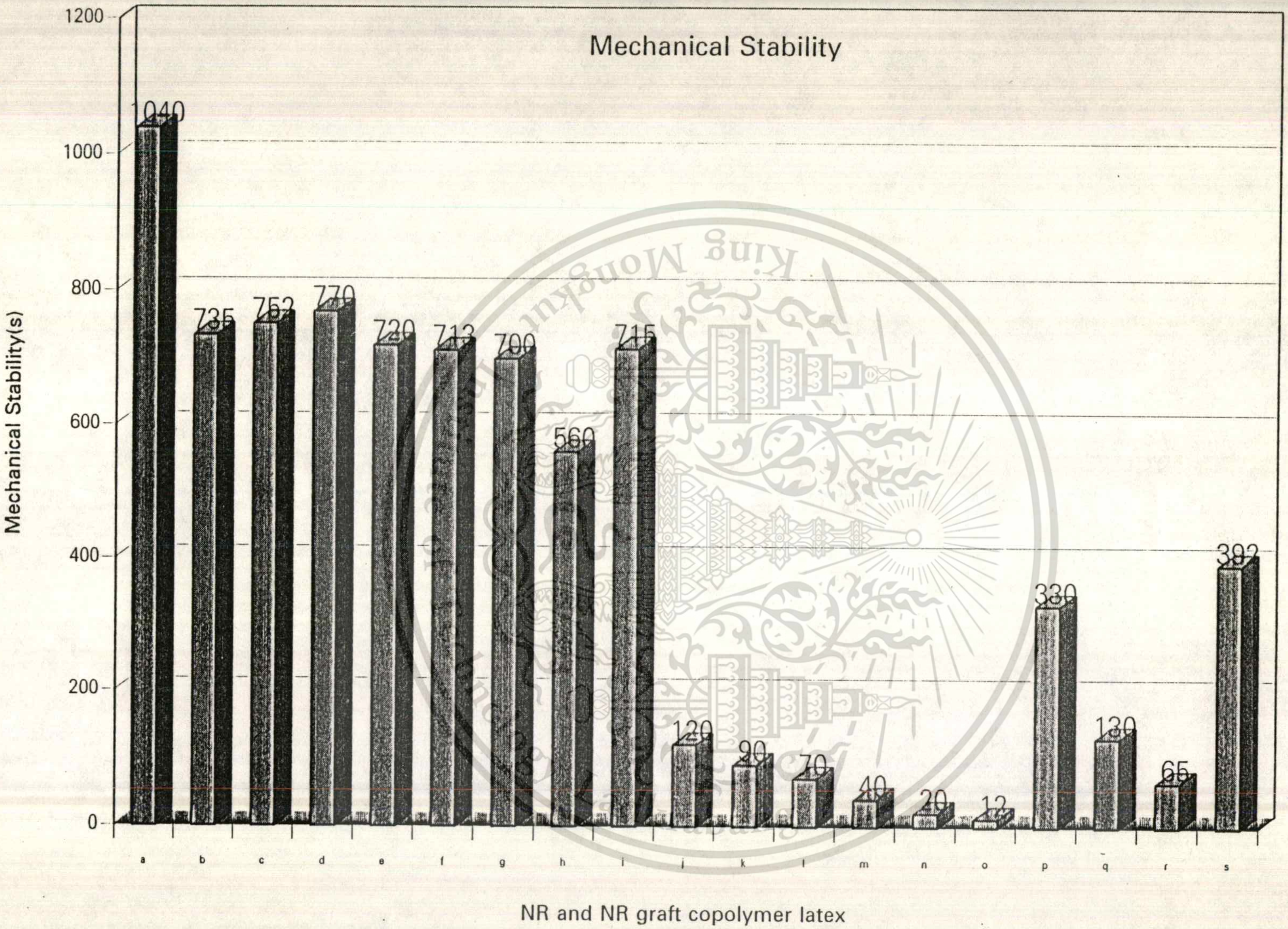

Mechanical Stability
Mechanical Stability(s)
1200
1000
800
600
400
200
0
1040
735
752
770
720
713
700
560
715
120
90
70
40
20
12
330
130
65
392
a
b
c
d
e
f
g
h
i
j
k
l
m
n
o
p
q
r
s
NR and NR graft copolymer latex

Fig. A-4

From the Fig. A-4

a = Natural rubber latex.
b = NR-g-MMA 30%
c = NR-g-MMA 50%
d = NR-g-MMA 70%
e = NR-g-MMA 30% + Acrylic acid 5%
f = NR-g-MMA 30% + Acrylic acid 10%
g = NR-g-MMA 30% + Acrylic acid 20%
h = NR-g-MMA 30% + Acrylic acid 30%
i = NR-g-MMA 30% + Acrylic acid 5% (200 L.)
j = NR-g-2-Ethylhexyl acrylate 30%
k = NR-g-2-ethylhexyl acrylate 50%
l = NR-g-2-Ethylhexyl acrylate 70%
m = NR-g-Ethyl acrylate 30%
n = NR-g-Ethyl acrylate 50%
o = NR-g-Ethyl acrylate 70%
p = NR-g-Butyl acrylate 30%
q = NR-g-Butyl acrylate 50%
r = NR-g-Butyl acrylate 70%
s = NR-g-Vinyl acetate 30%

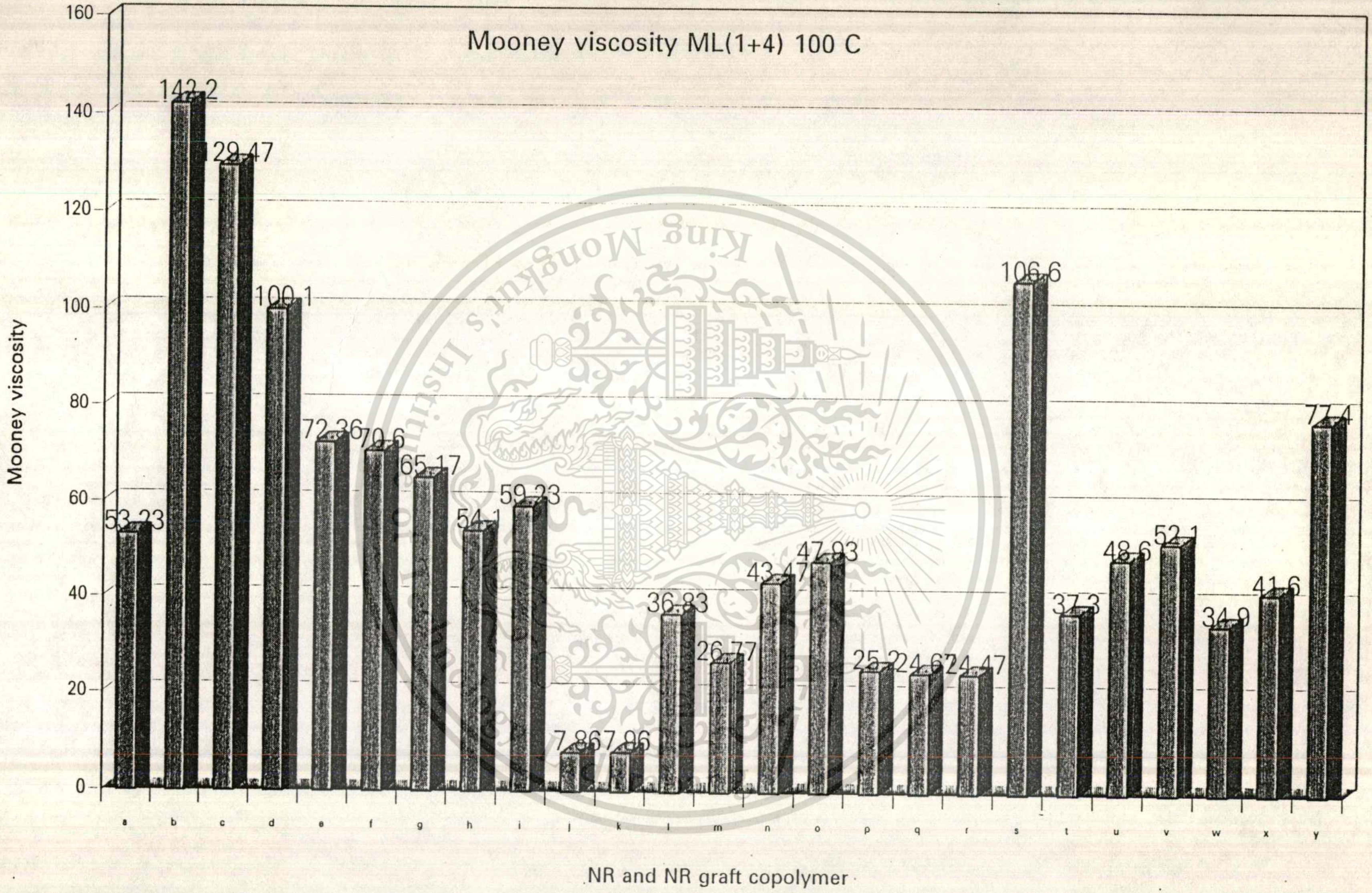

Mooney viscosity ML(1+4) 100 C
Mooney viscosity
160
140
120
100
80
60
40
20
0
53.23
142.2
129.47
100.1
72.36
70.6
65.17
54.1
59.23
7.86
7.96
36.83
26.77
43.47
47.93
25.2
24.67
24.47
106.6
37.3
48.6
52.1
34.9
41.6
77.4
a
b
c
d
e
f
g
h
i
j
k
l
m
n
o
p
q
r
s
t
u
v
w
x
y
NR and NR graft copolymer

Fig. A-5

From the Fig. A-5

a = Natural rubber .
b = NR-g-MMA 30%
c = NR-g-MMA 50%
d = NR-g-MMA 70%
e = NR-g-MMA 30% + Acrylic acid 5%
f = NR-g-MMA 30% + Acrylic acid 10%
g = NR-g-MMA 30% + Acrylic acid 20%
h = NR-g-MMA 30% + Acrylic acid 30%
i = NR-g-MMA 30% + Acrylic acid 5% (200 L.)
j = NR-g-2-Ethylhexyl acrylate 30%
k = NR-g-2-ethylhexyl acrylate 50%
l = NR-g-2-Ethylhexyl acrylate 70%
m = NR-g-Ethyl acrylate 30%
n = NR-g-Ethyl acrylate 50%
o = NR-g-Ethyl acrylate 70%
p = NR-g-Butyl acrylate 30%
q = NR-g-Butyl acrylate 50%
r = NR-g-Butyl acrylate 70%
s = NR-g-Vinyl acetate 30%
t = NR-g-Acrylic acid 30%
u = NR-g-Acrylic acid 50%
v = NR-g-Acrylic acid 70%
w = NR-g-Acrylamide 30%
x = NR-g-Acrylamide 50%
y = NR-g-Acrylamide 70%

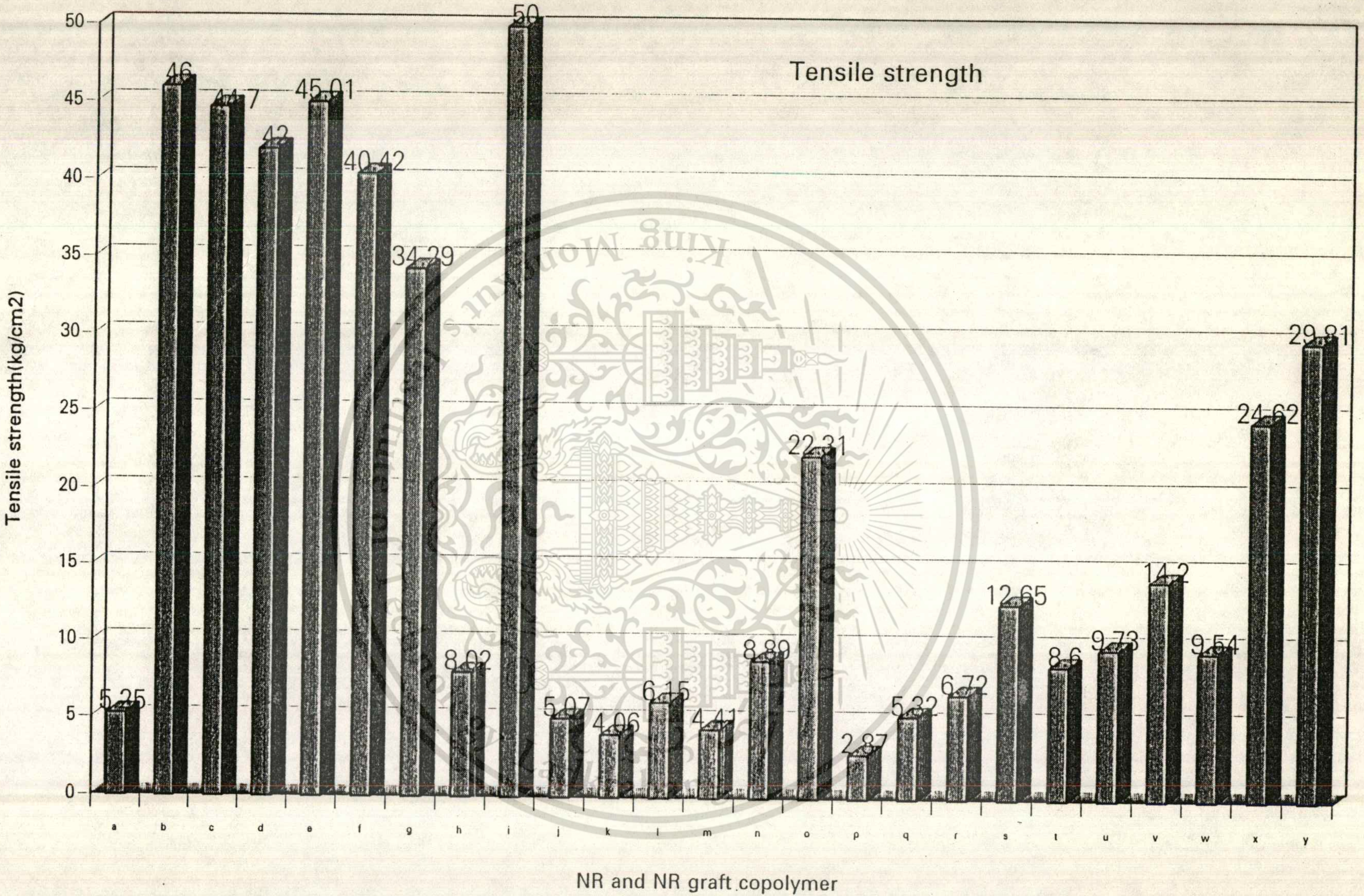

Tensile strength
Tensile strength(kg/cm2)
0
5
10
15
20
25
30
35
40
45
50
5.25
46
44.7
42
45.01
40.42
34.29
8.02
50
5.07
4.06
6.15
4.41
8.89
22.31
2.87
5.32
6.72
12.65
8.6
9.73
14.2
9.54
24.62
29.81
a
b
c
d
e
f
g
h
i
j
k
l
m
n
o
p
q
r
s
t
u
v
w
x
y
NR and NR graft copolymer

Fig. A-6

From the Fig. A-6

a = Natural rubber .
b = NR-g-MMA 30%
c = NR-g-MMA 50%
d = NR-g-MMA 70%
e = NR-g-MMA 30% + Acrylic acid 5%
f = NR-g-MMA 30% + Acrylic acid 10%
g = NR-g-MMA 30% + Acrylic acid 20%
h = NR-g-MMA 30% + Acrylic acid 30%
i = NR-g-MMA 30% + Acrylic acid 5% (200 L.)
j = NR-g-2-Ethylhexyl acrylate 30%
k = NR-g-2-ethylhexyl acrylate 50%
l = NR-g-2-Ethylhexyl acrylate 70%
m = NR-g-Ethyl acrylate 30%
n = NR-g-Ethyl acrylate 50%
o = NR-g-Ethyl acrylate 70%
p = NR-g-Butyl acrylate 30%
q = NR-g-Butyl acrylate 50%
r = NR-g-Butyl acrylate 70%
s = NR-g-Vinyl acetate 30%
t = NR-g-Acrylic acid 30%
u = NR-g-Acrylic acid 50%
v = NR-g-Acrylic acid 70%
w = NR-g-Acrylamide 30%
x = NR-g-Acrylamide 50%
y = NR-g-Acrylamide 70%

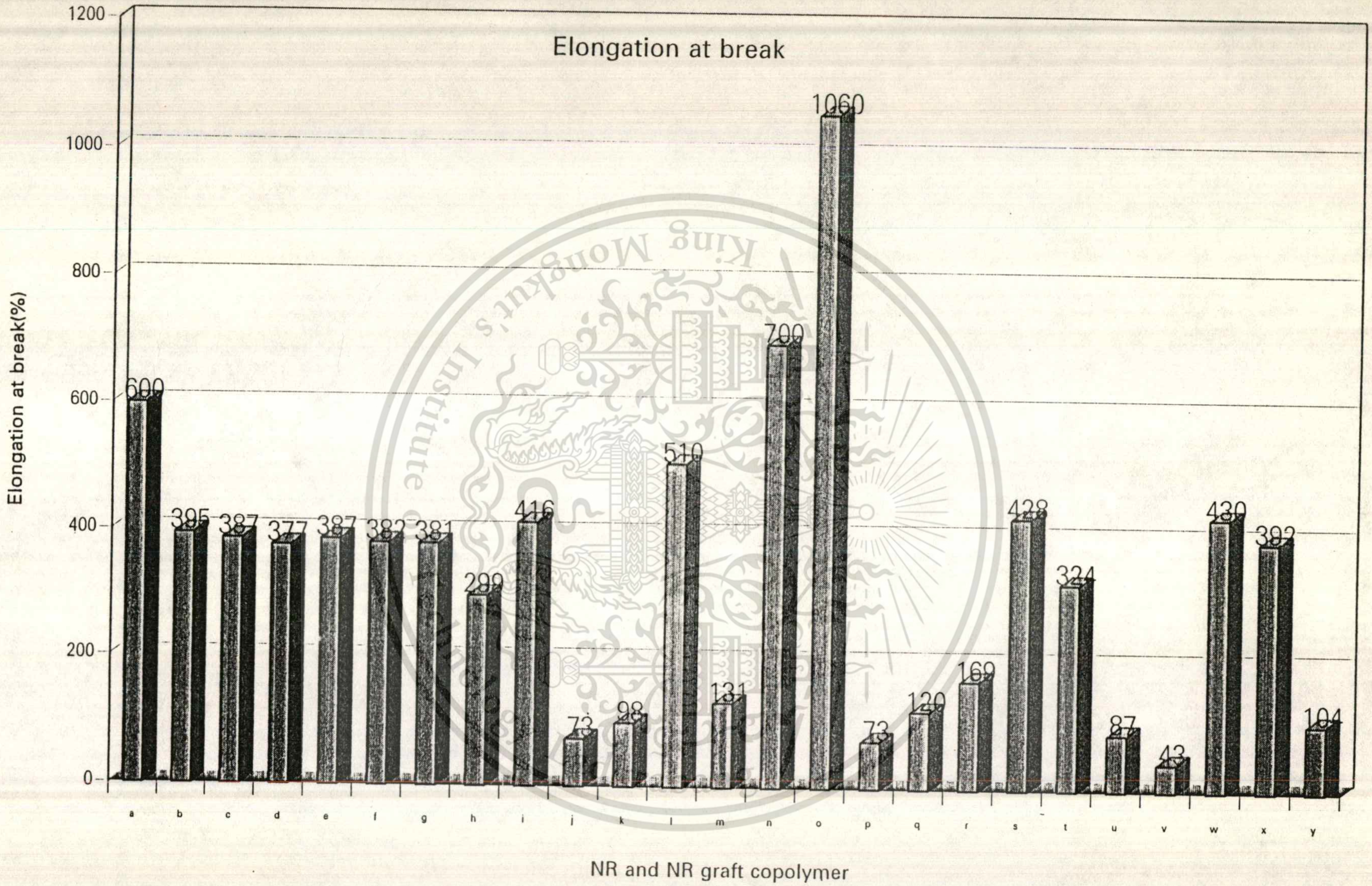

Elongation at break
Elongation at break(%)
1200
1000
800
600
400
200
0
600
395
387
377
387
382
381
299
416
73
98
510
131
700
1060
73
120
169
428
324
87
43
430
392
104
a
b
c
d
e
f
g
h
i
j
k
l
m
n
o
p
q
r
s
t
u
v
w
x
y
NR and NR graft copolymer

Fig. A-7

From the Fig. A-7
a = Natural rubber .
b = NR-g-MMA 30%
c = NR-g-MMA 50%
d = NR-g-MMA 70%
e = NR-g-MMA 30% + Acrylic acid 5%
f = NR-g-MMA 30% + Acrylic acid 10%
g = NR-g-MMA 30% + Acrylic acid 20%
h = NR-g-MMA 30% + Acrylic acid 30%
i = NR-g-MMA 30% + Acrylic acid 5% (200 L.)
j = NR-g-2-Ethylhexyl acrylate 30%
k = NR-g-2-ethylhexyl acrylate 50%
l = NR-g-2-Ethylhexyl acrylate 70%
m = NR-g-Ethyl acrylate 30%
n = NR-g-Ethyl acrylate 50%
o = NR-g-Ethyl acrylate 70%
p = NR-g-Butyl acrylate 30%
q = NR-g-Butyl acrylate 50%
r = NR-g-Butyl acrylate 70%
s = NR-g-Vinyl acetate 30%
t = NR-g-Acrylic acid 30%
u = NR-g-Acrylic acid 50%
v = NR-g-Acrylic acid 70%
w = NR-g-Acrylamide 30%
x = NR-g-Acrylamide 50%
y = NR-g-Acrylamide 70%

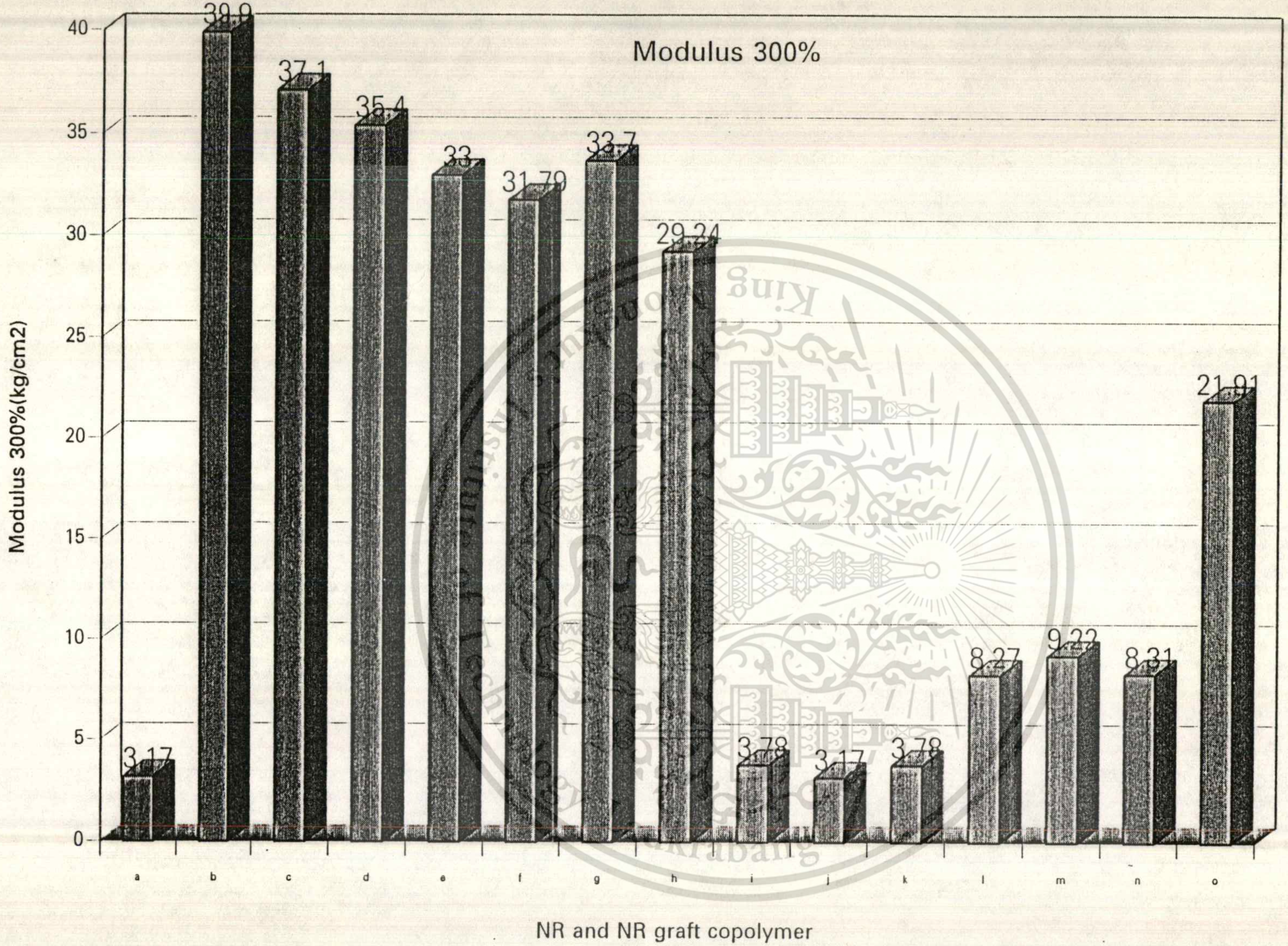

Modulus 300%
Modulus 300%(kg/cm2)
0
5
10
15
20
25
30
35
40
3.17
39.9
37.1
35.4
33
31.79
33.7
29.24
3.78
3.17
3.78
8.27
9.22
8.31
21.91
a
b
c
d
e
f
g
h
i
j
k
l
m
n
o
NR and NR graft copolymer

Fig. A-8

From the Fig. A-8

a = Natural rubber .
b = NR-g-MMA 30%
c = NR-g-MMA 50%
d = NR-g-MMA 70%
e = NR-g-MMA 30% + Acrylic acid 5%
f = NR-g-MMA 30% + Acrylic acid 10%
g = NR-g-MMA 30% + Acrylic acid 20%
h = NR-g-MMA 30% + Acrylic acid 5% (200 L.)
i = NR-g-2-Ethylhexyl acrylate 70%
j = NR-g-Ethyl acrylate 50%
k = NR-g-Ethyl acrylate 70%
l = NR-g-Vinyl acetate 30%
m = NR-g-Acrylic acid 30%
n = NR-g-Acrylamide 30%
o = NR-g-Acrylamide 50%

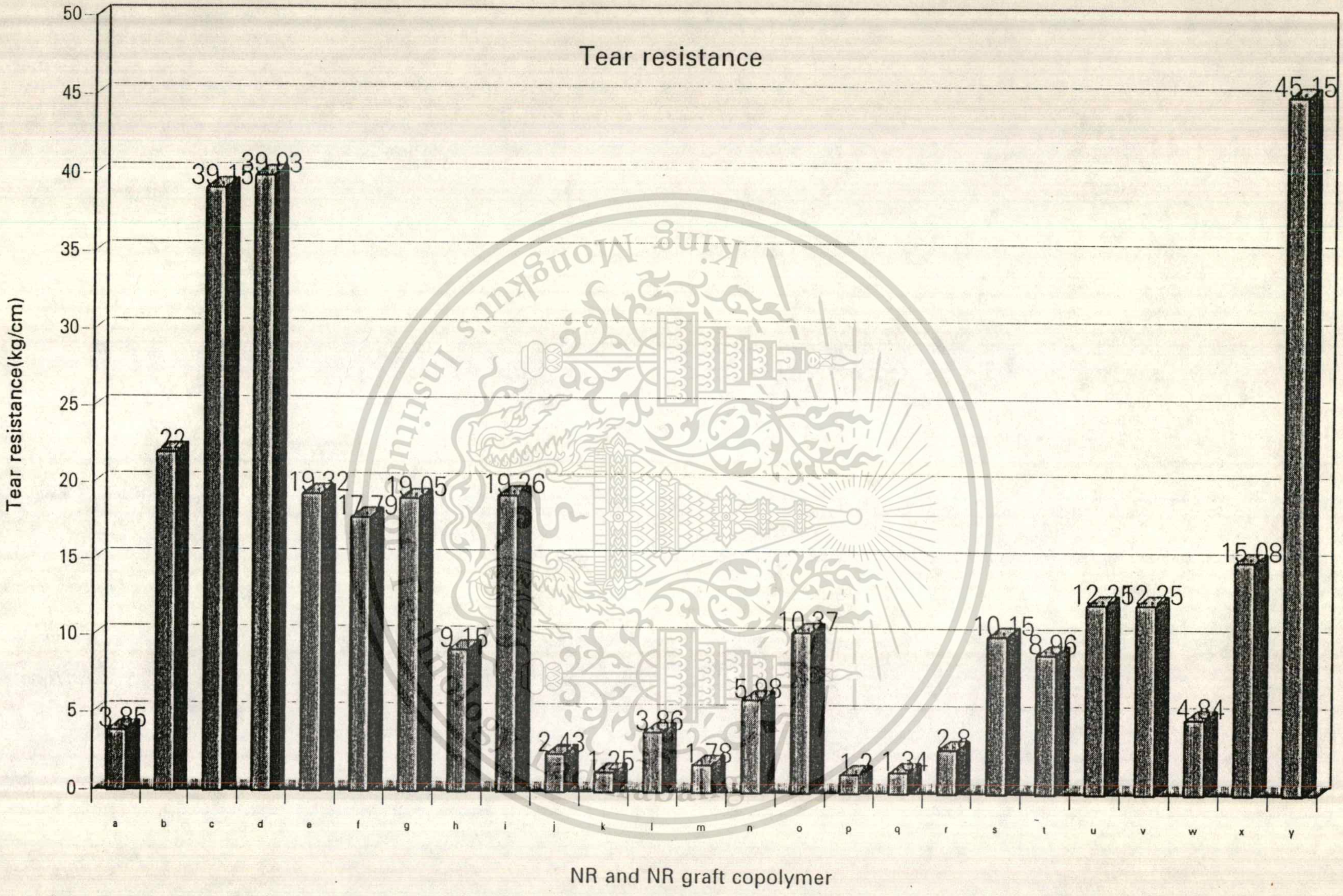

Tear resistance
Tear resistance(kg/cm)
50
45
40
35
30
25
20
15
10
5
0
3.85
22
39.15
39.93
19.32
17.79
19.05
9.15
19.26
2.43
1.25
3.86
1.78
5.98
10.37
1.2
1.34
2.8
10.15
8.86
12.25
12.25
4.84
15.08
45.15
a
b
c
d
e
f
g
h
i
j
k
l
m
n
o
p
q
r
s
t
u
v
w
x
y
NR and NR graft copolymer

Fig. A-9

From the Fig. A-9

a = Natural rubber .
b = NR-g-MMA 30%
c = NR-g-MMA 50%
d = NR-g-MMA 70%
e = NR-g-MMA 30% + Acrylic acid 5%
f = NR-g-MMA 30% + Acrylic acid 10%
g = NR-g-MMA 30% + Acrylic acid 20%
h = NR-g-MMA 30% + Acrylic acid 30%
i = NR-g-MMA 30% + Acrylic acid 5% (200 L.)
j = NR-g-2-Ethylhexyl acrylate 30%
k = NR-g-2-ethylhexyl acrylate 50%
l = NR-g-2-Ethylhexyl acrylate 70%
m = NR-g-Ethyl acrylate 30%
n = NR-g-Ethyl acrylate 50%
o = NR-g-Ethyl acrylate 70%
p = NR-g-Butyl acrylate 30%
q = NR-g-Butyl acrylate 50%
r = NR-g-Butyl acrylate 70%
s = NR-g-Vinyl acetate 30%
t = NR-g-Acrylic acid 30%
u = NR-g-Acrylic acid 50%
v = NR-g-Acrylic acid 70%
w = NR-g-Acrylamide 30%
x = NR-g-Acrylamide 50%
y = NR-g-Acrylamide 70%

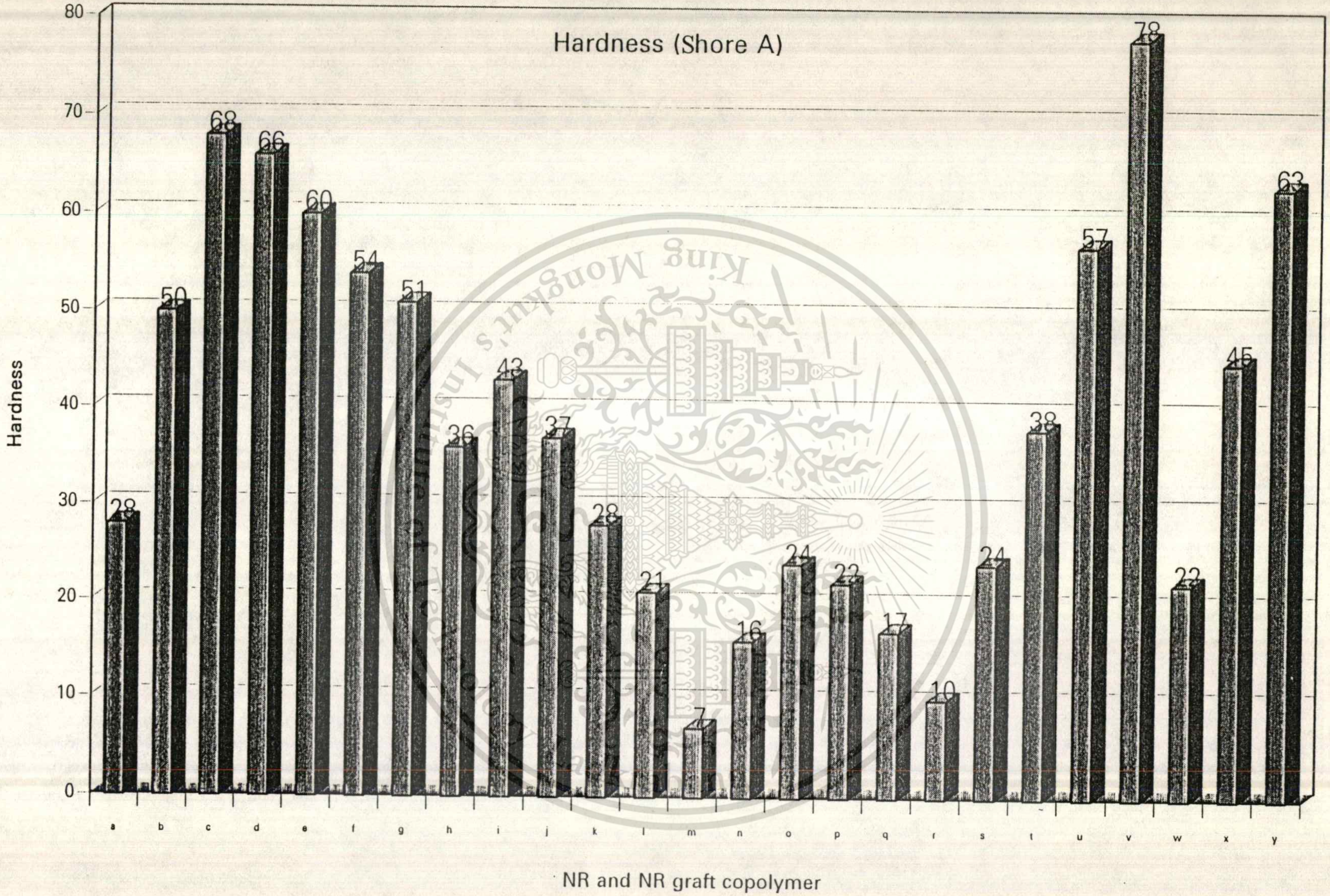

Hardness (Shore A)
Hardness
NR and NR graft copolymer
0
10
20
30
40
50
60
70
80
a
b
c
d
e
f
g
h
i
j
k
l
m
n
o
p
q
r
s
t
u
v
w
x
y
28
50
68
66
60
54
51
36
43
37
28
21
7
16
24
22
17
10
24
38
57
78
22
45
63

Fig. A-10

From the Fig. A-10

a = Natural rubber .
b = NR-g-MMA 30%
c = NR-g-MMA 50%
d = NR-g-MMA 70%
e = NR-g-MMA 30% + Acrylic acid 5%
f = NR-g-MMA 30% + Acrylic acid 10%
g = NR-g-MMA 30% + Acrylic acid 20%
h = NR-g-MMA 30% + Acrylic acid 30%
i = NR-g-MMA 30% + Acrylic acid 5% (200 L.)
j = NR-g-2-Ethylhexyl acrylate 30%
k = NR-g-2-ethylhexyl acrylate 50%
l = NR-g-2-Ethylhexyl acrylate 70%
m = NR-g-Ethyl acrylate 30%
n = NR-g-Ethyl acrylate 50%
o = NR-g-Ethyl acrylate 70%
p = NR-g-Butyl acrylate 30%
q = NR-g-Butyl acrylate 50%
r = NR-g-Butyl acrylate 70%
s = NR-g-Vinyl acetate 30%
t = NR-g-Acrylic acid 30%
u = NR-g-Acrylic acid 50%
v = NR-g-Acrylic acid 70%
w = NR-g-Acrylamide 30%
x = NR-g-Acrylamide 50%
y = NR-g-Acrylamide 70%

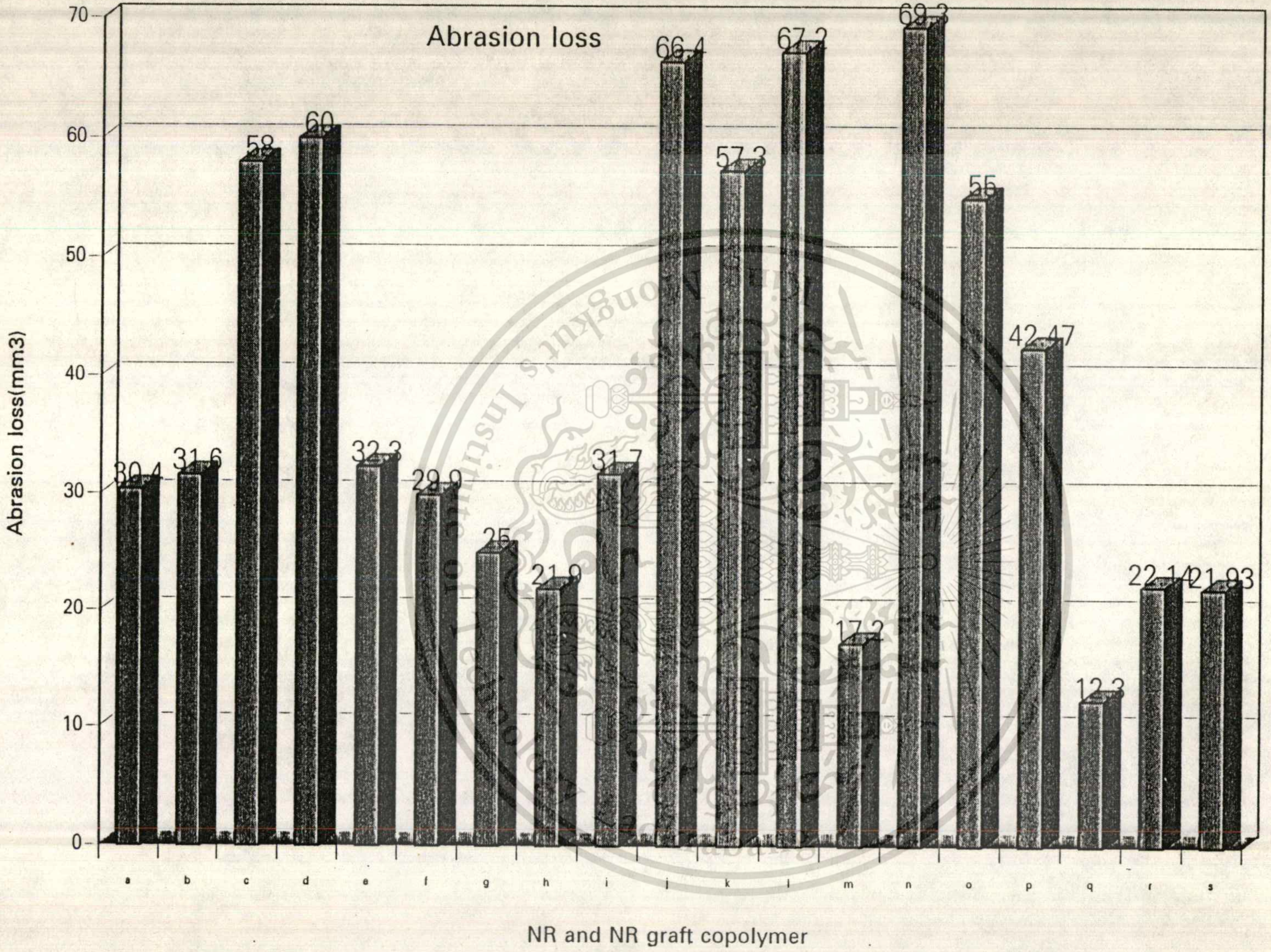

Abrasion loss
Abrasion loss(mm3)
70
60
50
40
30
20
10
0
30.4
31.6
58
60
32.3
29.9
25
21.9
31.7
66.4
57.3
67.2
17.2
69.3
55
42.47
12.3
22.14
21.93
a
b
c
d
e
f
g
h
i
j
k
l
m
n
o
p
q
r
s
NR and NR graft copolymer

Fig. A-11

From the Fig. A-11
a = Natural rubber .
b = NR-g-MMA 30%
c = NR-g-MMA 50%
d = NR-g-MMA 70%
e = NR-g-MMA 30% + Acrylic acid 5%
f = NR-g-MMA 30% + Acrylic acid 10%
g = NR-g-MMA 30% + Acrylic acid 20%
h = NR-g-MMA 30% + Acrylic acid 30%
i = NR-g-MMA 30% + Acrylic acid 5% (200 L.)
j = NR-g-2-Ethylhexyl acrylate 70%
k = NR-g-Ethyl acrylate 50%
l = NR-g-Ethyl acrylate 70%
m = NR-g-Vinyl acetate 30%
n = NR-g-Acrylic acid 30%
o = NR-g-Acrylic acid 50%
p = NR-g-Acrylic acid 70%
q = NR-g-Acrylamide 30%
r = NR-g-Acrylamide 50%
s = NR-g-Acrylamide 70%

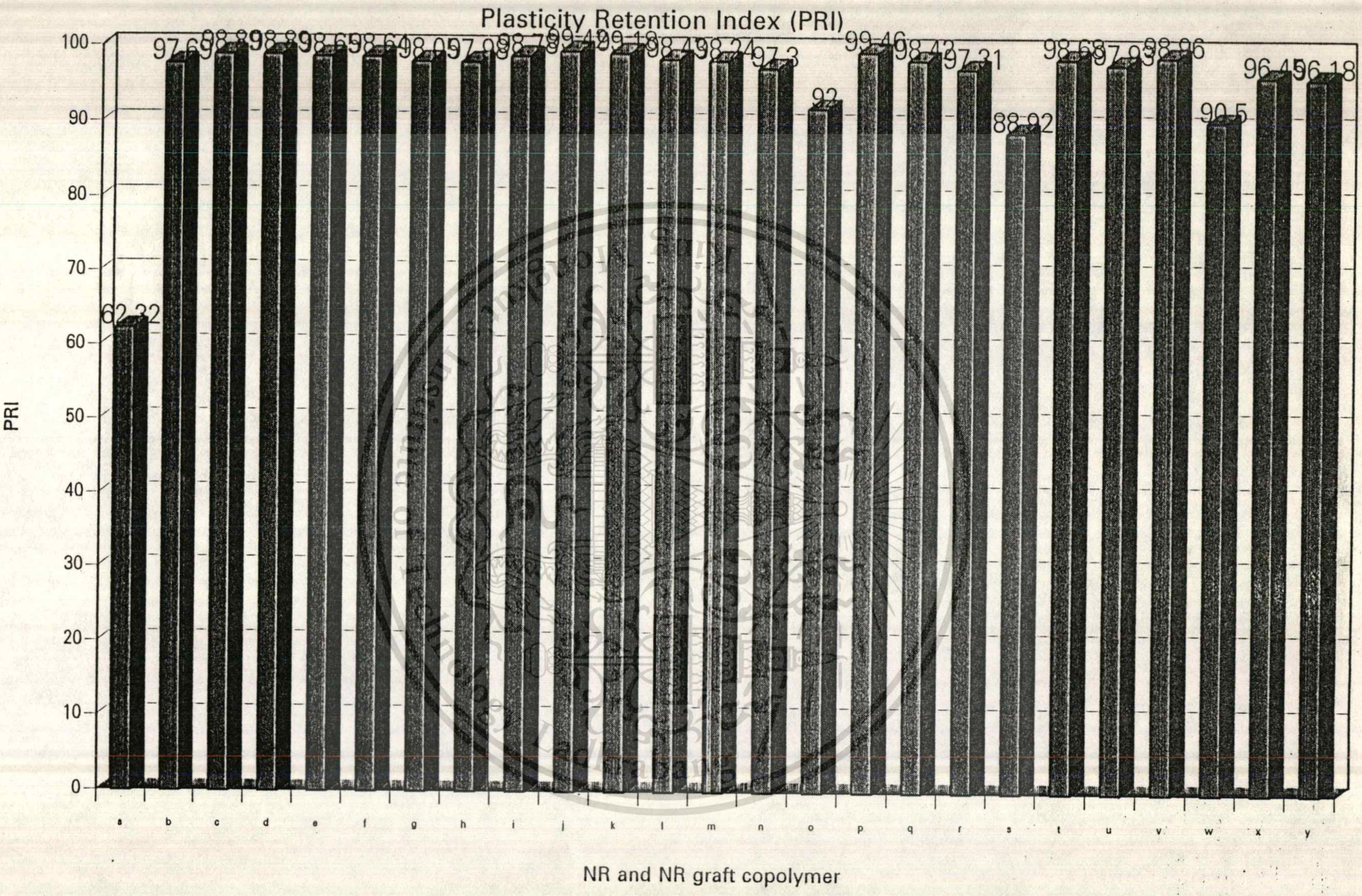

Plasticity Retention Index (PRI)
PRI
100
90
80
70
60
50
40
30
20
10
0
62.32
97.69
98.89
98.89
98.65
98.64
98.05
97.09
98.79
99.42
99.18
98.49
98.24
97.3
92
99.46
98.42
97.31
88.92
98.68
97.93
98.96
90.5
96.45
96.18
a
b
c
d
e
f
g
h
i
j
k
l
m
n
o
p
q
r
s
t
u
v
w
x
y
NR and NR graft copolymer

Fig. A-12

From the Fig. A-12

a = Natural rubber .
b = NR-g-MMA 30%
c = NR-g-MMA 50%
d = NR-g-MMA 70%
e = NR-g-MMA 30% + Acrylic acid 5%
f = NR-g-MMA 30% + Acrylic acid 10%
g = NR-g-MMA 30% + Acrylic acid 20%
h = NR-g-MMA 30% + Acrylic acid 30%
i = NR-g-MMA 30% + Acrylic acid 5% (200 L.)
j = NR-g-2-Ethylhexyl acrylate 30%
k = NR-g-2-ethylhexyl acrylate 50%
l = NR-g-2-Ethylhexyl acrylate 70%
m = NR-g-Ethyl acrylate 30%
n = NR-g-Ethyl acrylate 50%
o = NR-g-Ethyl acrylate 70%
p = NR-g-Butyl acrylate 30%
q = NR-g-Butyl acrylate 50%
r = NR-g-Butyl acrylate 70%
s = NR-g-Vinyl acetate 30%
t = NR-g-Acrylic acid 30%
u = NR-g-Acrylic acid 50%
v = NR-g-Acrylic acid 70%
w = NR-g-Acrylamide 30%
x = NR-g-Acrylamide 50%
y = NR-g-Acrylamide 70%

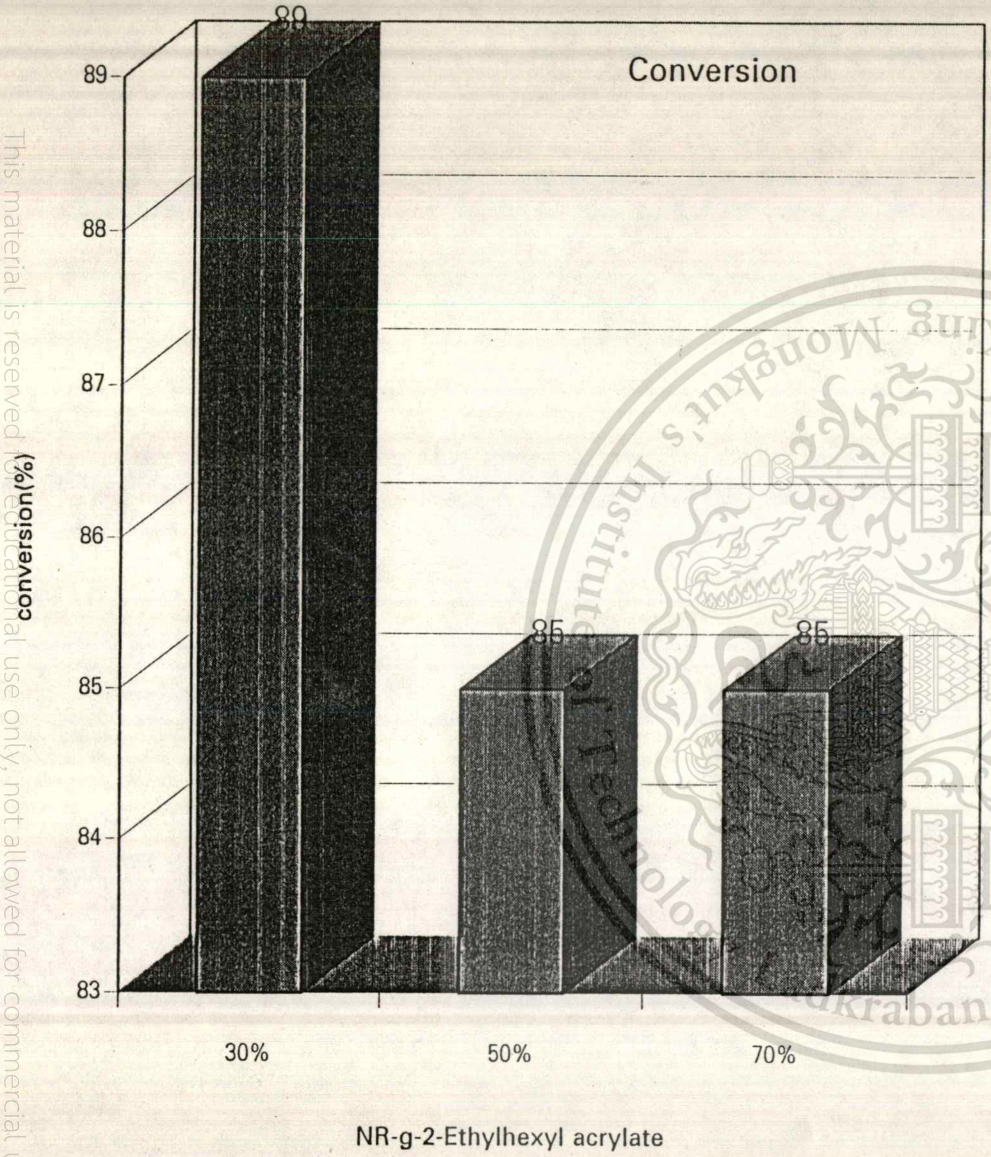

Conversion
conversion(%)
89
88
87
86
85
84
83
89
85
85
30%
50%
70%
NR-g-2-Ethylhexyl acrylate

Fig. A-13

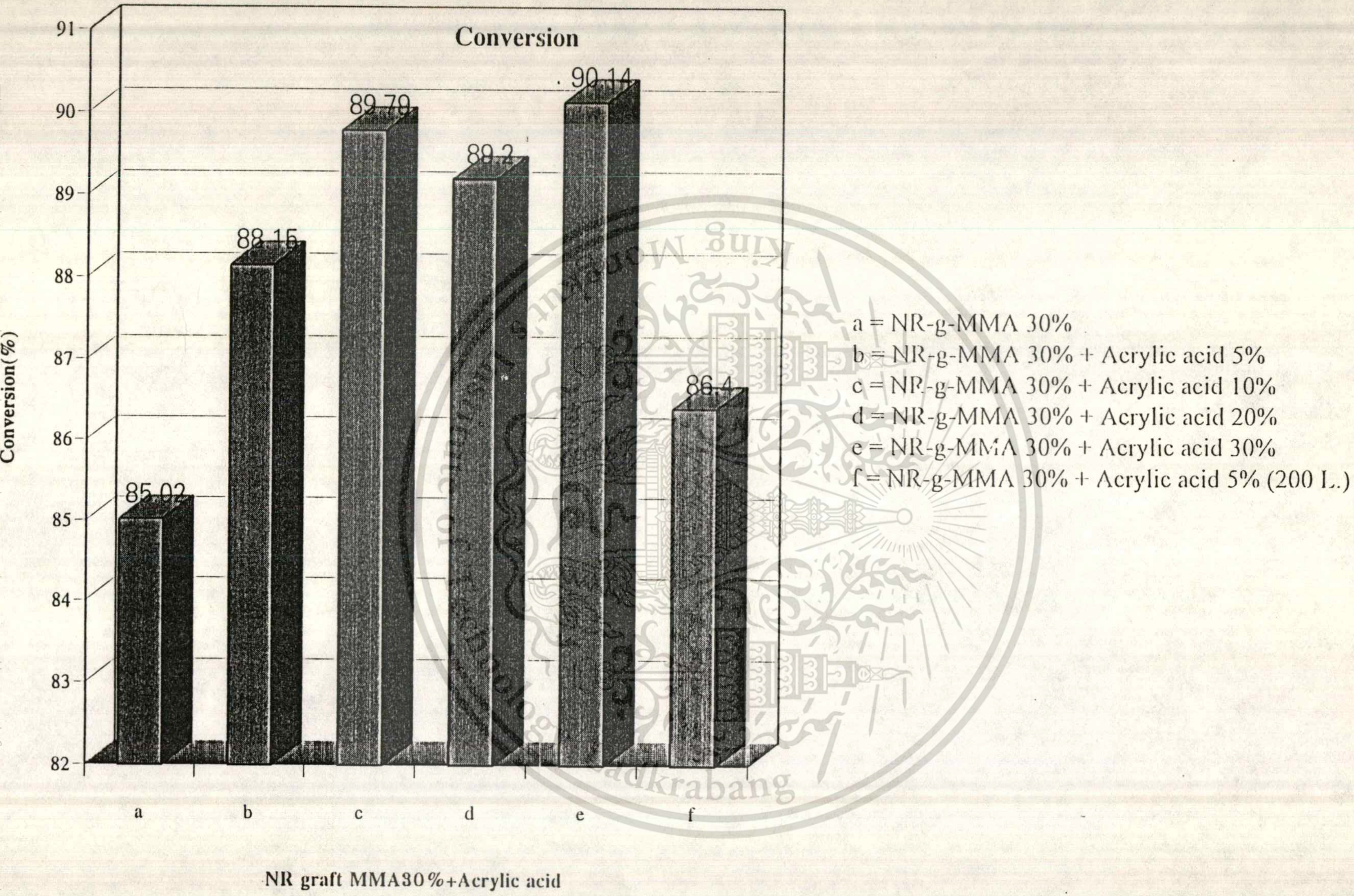

Conversion
Conversion(%)
91
90
89
88
87
86
85
84
83
82
85.02
88.15
89.79
89.2
90.14
86.4
a
b
c
d
e
f
NR graft MMA30%+Acrylic acid
a = NR-g-MMA 30%
b = NR-g-MMA 30% + Acrylic acid 5%
c = NR-g-MMA 30% + Acrylic acid 10%
d = NR-g-MMA 30% + Acrylic acid 20%
e = NR-g-MMA 30% + Acrylic acid 30%
f = NR-g-MMA 30% + Acrylic acid 5% (200 L.)

Fig. A-14

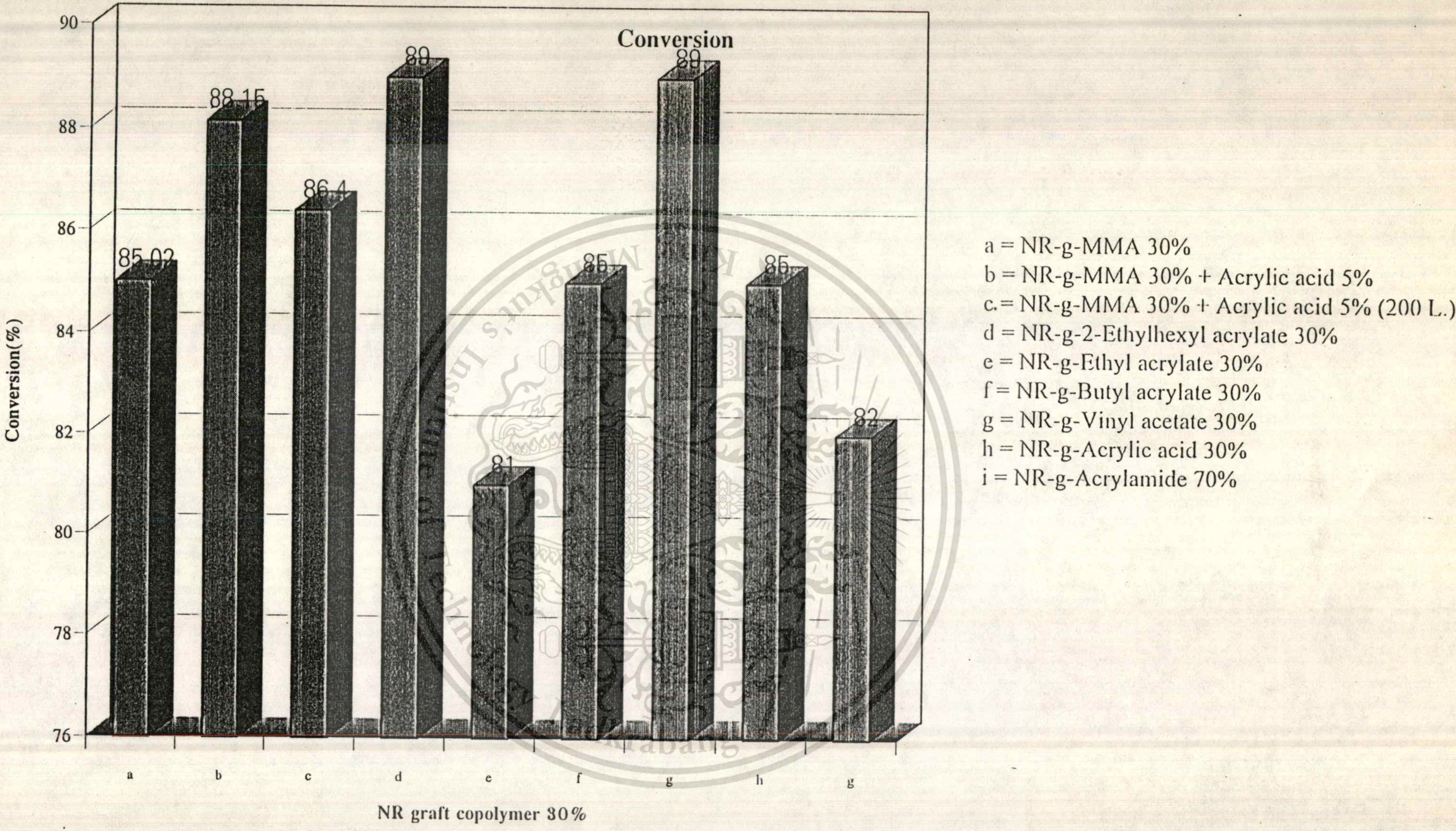

Conversion
Conversion(%)
90
88
86
84
82
80
78
76
85.02
88.15
86.4
89
81
85
89
85
82
a
b
c
d
e
f
g
h
g
NR graft copolymer 30%
a = NR-g-MMA 30%
b = NR-g-MMA 30% + Acrylic acid 5%
c.= NR-g-MMA 30% + Acrylic acid 5% (200 L.)
d = NR-g-2-Ethylhexyl acrylate 30%
e = NR-g-Ethyl acrylate 30%
f = NR-g-Butyl acrylate 30%
g = NR-g-Vinyl acetate 30%
h = NR-g-Acrylic acid 30%
i = NR-g-Acrylamide 70%

Fig. A-15

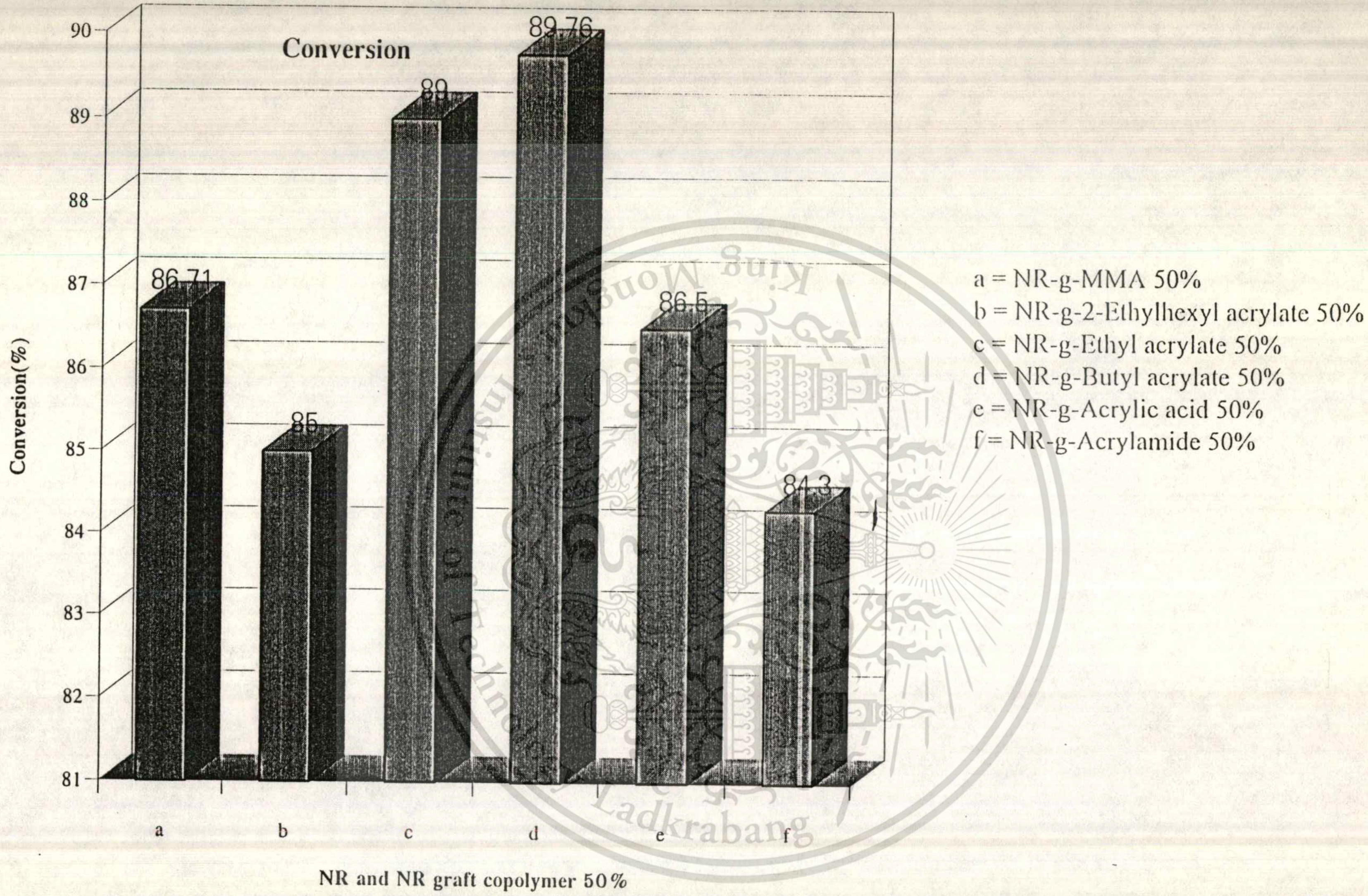

Conversion
Conversion(%)
90
89
88
87
86
85
84
83
82
81
86.71
85
89
89.76
86.5
84.3
a
b
c
d
e
f
NR and NR graft copolymer 50%
a = NR-g-MMA 50%
b = NR-g-2-Ethylhexyl acrylate 50%
c = NR-g-Ethyl acrylate 50%
d = NR-g-Butyl acrylate 50%
e = NR-g-Acrylic acid 50%
f = NR-g-Acrylamide 50%

Fig. A-16

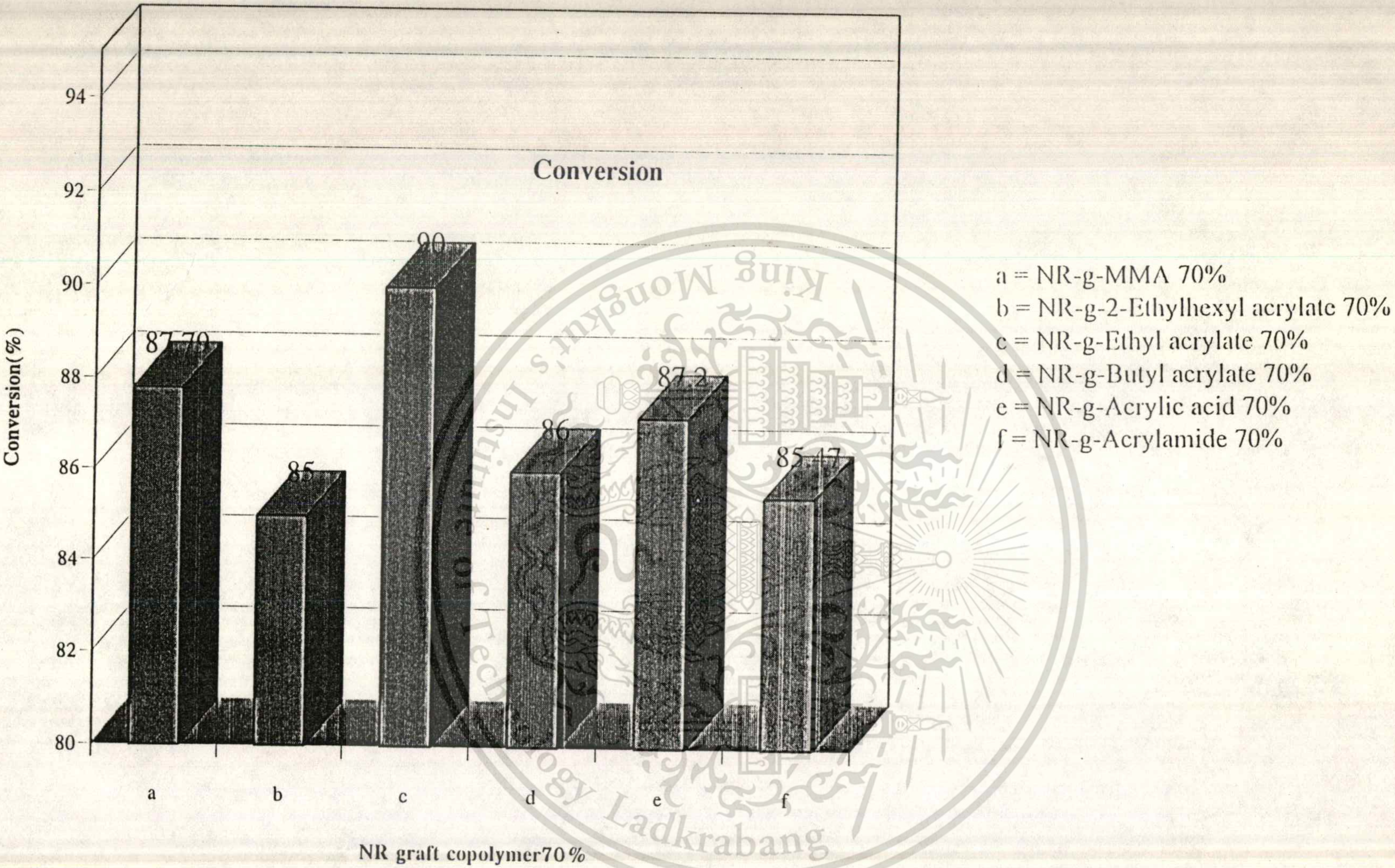
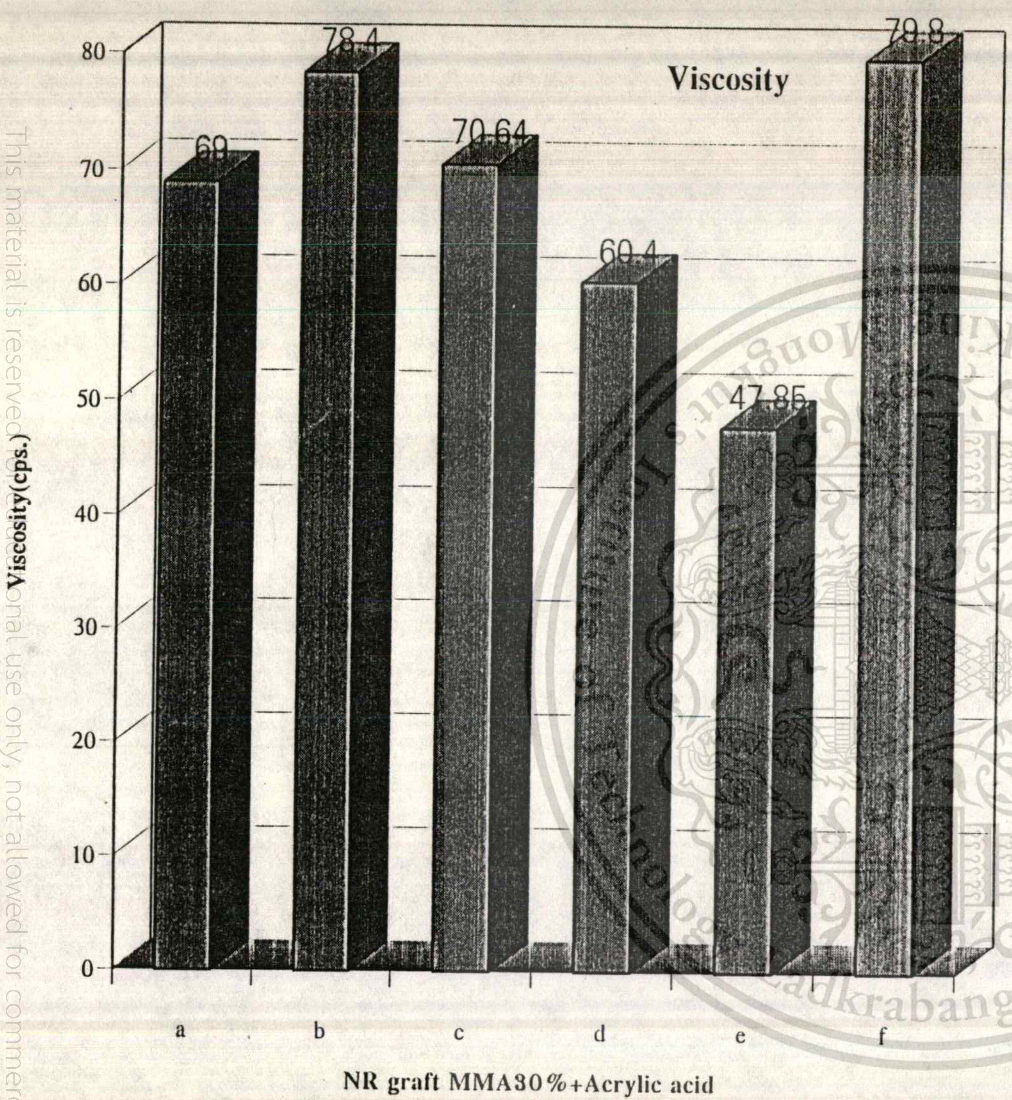

Conversion
Conversion(%)
94
92
90
88
86
84
82
80
87.70
85
90
86
87.2
85.47
a
b
c
d
e
f
NR graft copolymer70%
a = NR-g-MMA 70%
b = NR-g-2-Ethylhexyl acrylate 70%
c = NR-g-Ethyl acrylate 70%
d = NR-g-Butyl acrylate 70%
e = NR-g-Acrylic acid 70%
f = NR-g-Acrylamide 70%

Fig. A-17



a = NR-g-MMA 30%
b = NR-g-MMA 30% + Acrylic acid 5%
c = NR-g-MMA 30% + Acrylic acid 10%
d = NR-g-MMA 30% + Acrylic acid 20%
e = NR-g-MMA 30% + Acrylic acid 30%
f = NR-g-MMA 30% + Acrylic acid 5% (200 L.)

Fig. A-18

Appendix B

1.Calculation of monomer content using in the synthesis.

Example 1. NR-g-MMA 30%

The natural rubber latex has 60 dry rubber content (DRC).

Then The natural ruber 100 g. has DRC 60 g.

The repeating unit of natural ruber has the molecular weight 68

Then The natural rubber 100 g.has DRC $\frac{60}{68}$ mole

MMA 30% (Mw of MMA = 100)

Use to MMA = $\frac{60}{68} \times 100 \times \frac{30}{100}$ g.

2. Calculation of graft copolymer, free rubber and free polymer from natural rubber graft copolymer by extraction technique.

Weight of natural rubber graft copolymer X g
Weight loss of natural rubber by extraction with light petroleum ether Y g.
Weight loss of natural rubber by extraction with acetone Z g.
Final weight from extraction F g.

Free rubber = $\frac{Y}{X} \times 100$ %

Free polymer = $\frac{Z}{X} \times 100$ %

Graft copolymer = $\frac{F}{X} \times 100$ %

3. Calcalation of total solid content (TSC).

Use the natural rubber 100 g. and monomer Y g. (from example 1.)

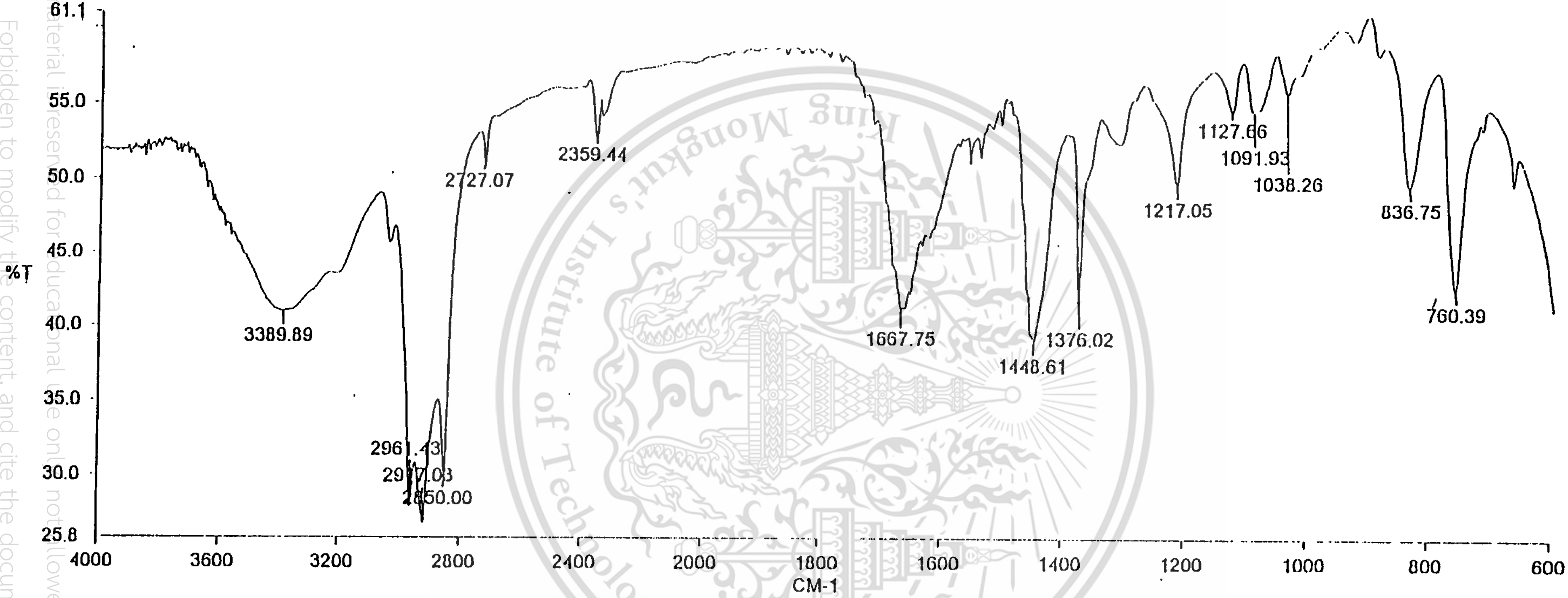
In system 100+Y g. has TSC = 60+Y g.
100 g. = $\frac{(60+Y) \times 100}{(100+Y)}$
TSC = Z %

If the system has TSC 60%
Then , added water = $\frac{[Z \times (100+Y)]}{60} - (100-Y)$
= W g.

Appendix C

Show the Fourier IR spectrum of graft copolymers

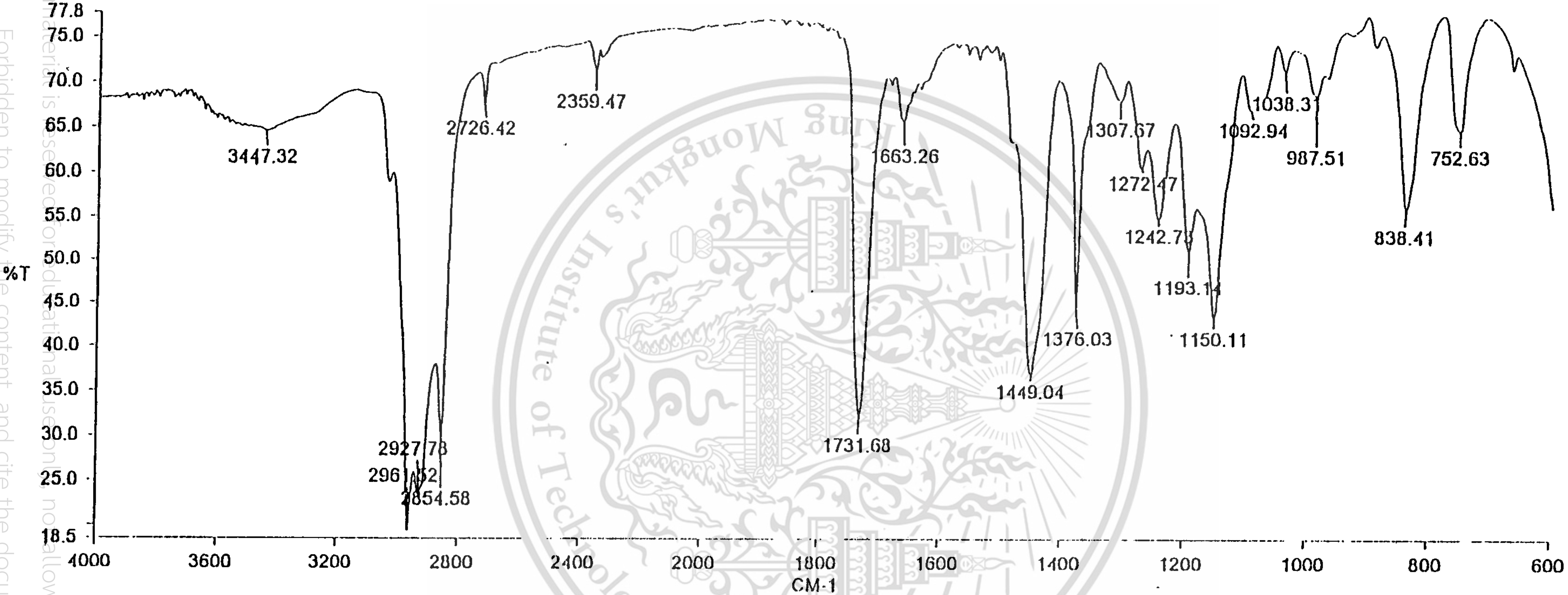
Date: 01/09/1995



Natural rubber

Fig. C-1

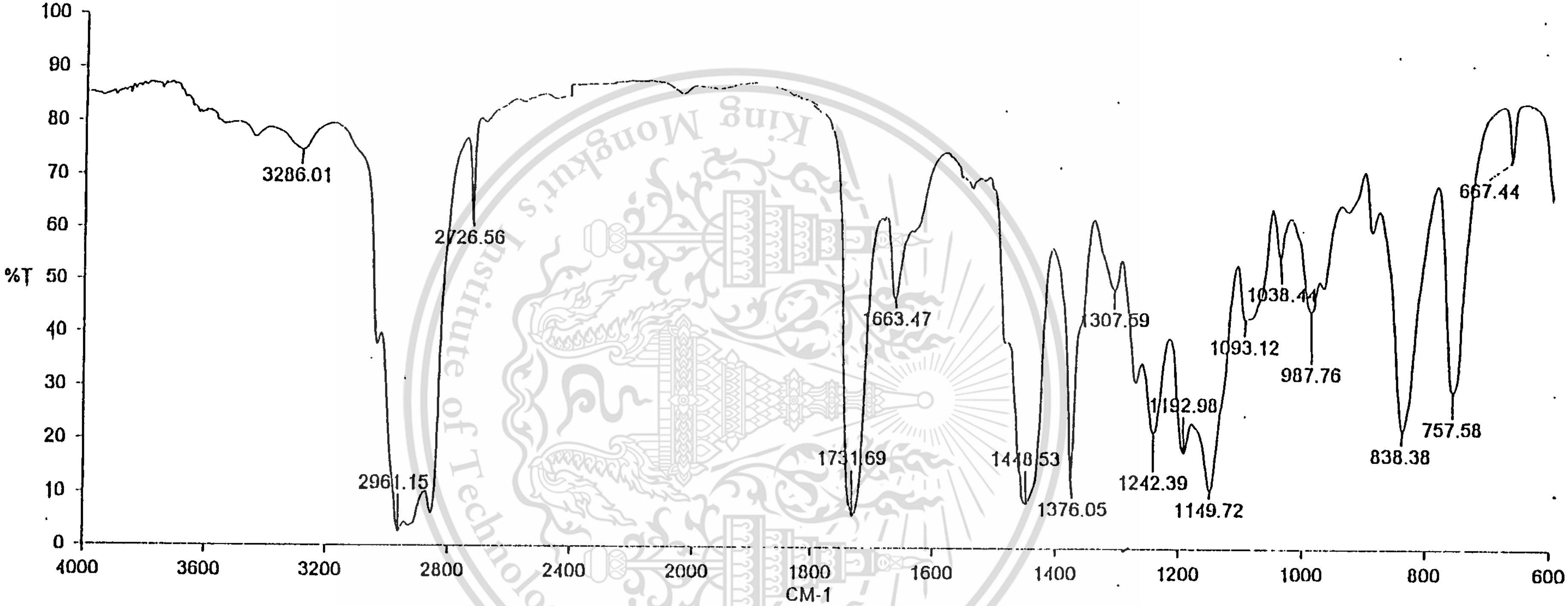
Date: 01/09/1995



NR-g-MMA 30%

Fig. C-2

Date: 12/06/1994

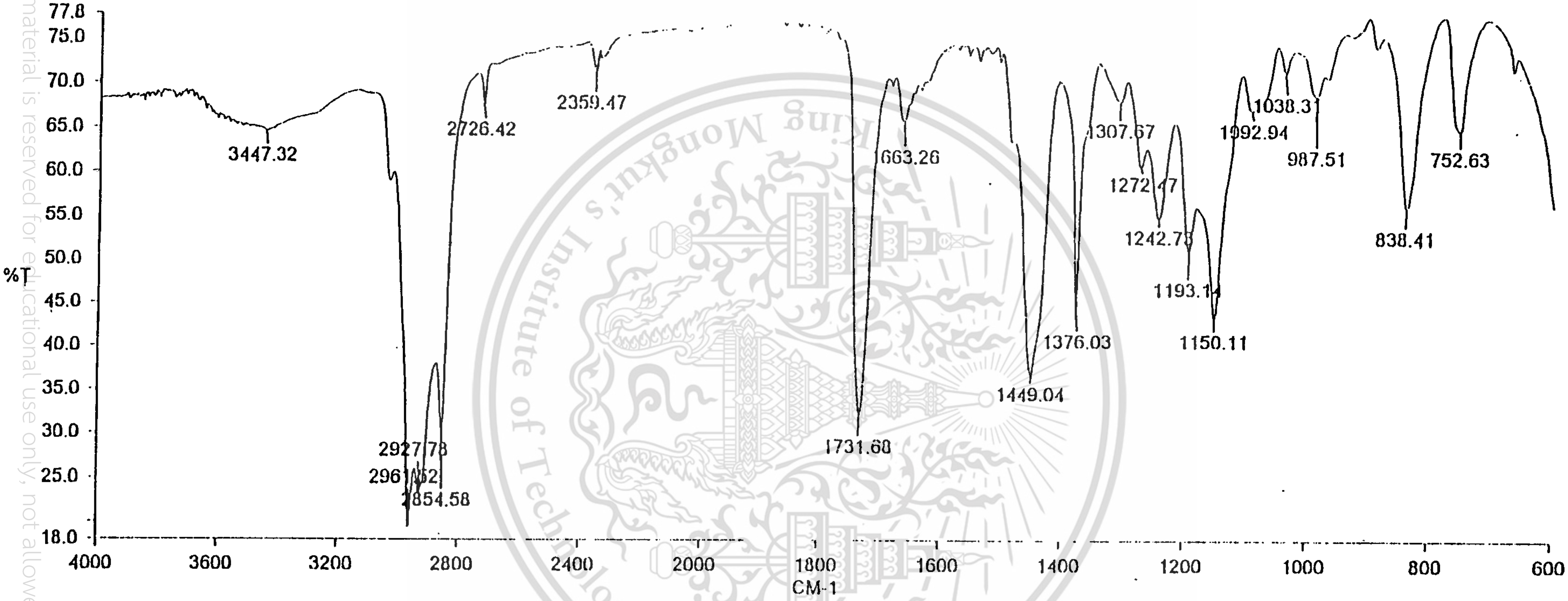


NR-g-MMA 30%+Acrylic acid 5%

Resolution: 4.00 CM-1 Accumulations: 16

Fig. C-3

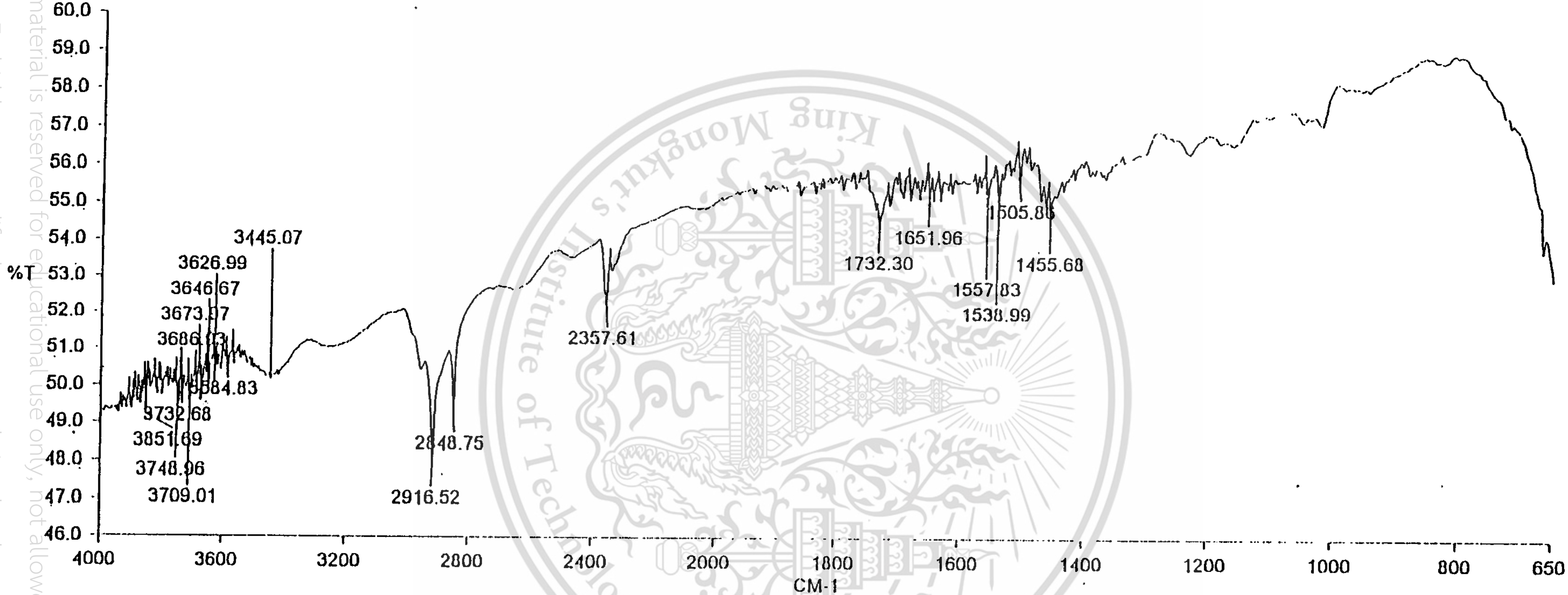
Date: 01/09/1995



NR-g-MMA 30%+Acrylic acid 5% (200 L.)

Fig. C-4

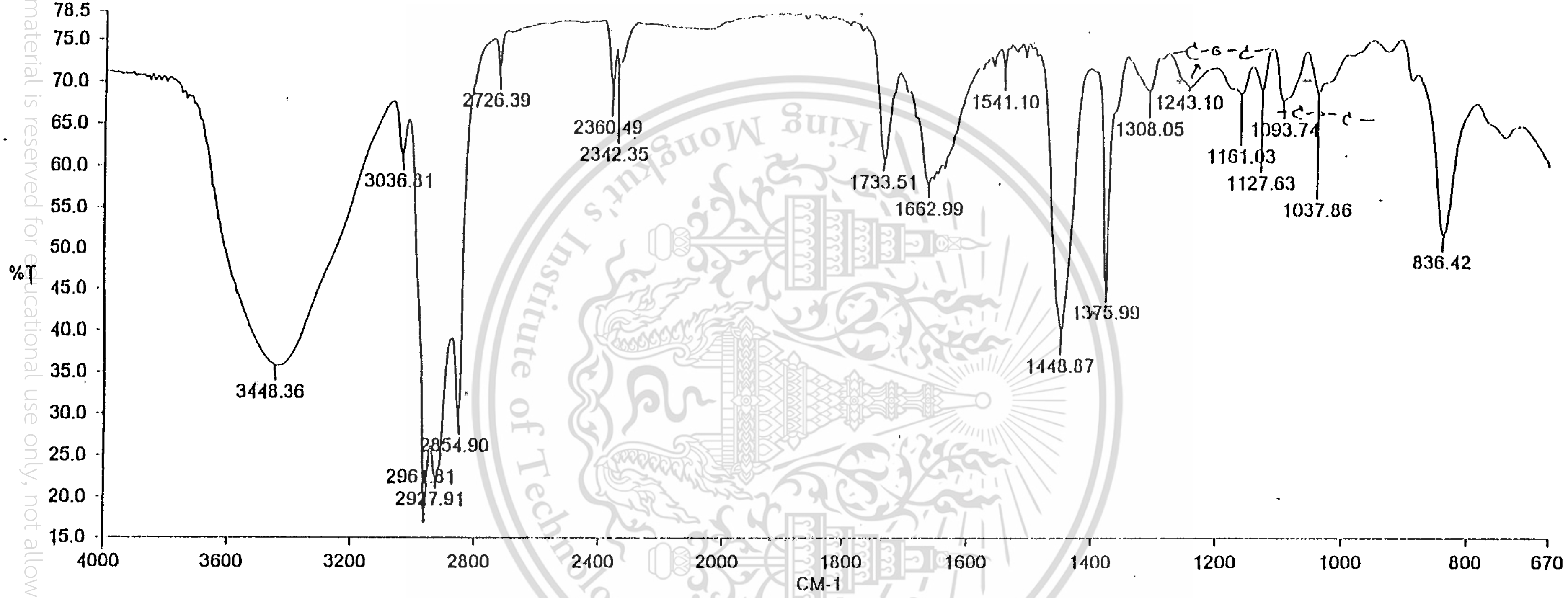
Date: 01/09/1995



NR-g-2EHA 30%

Fig. C-5

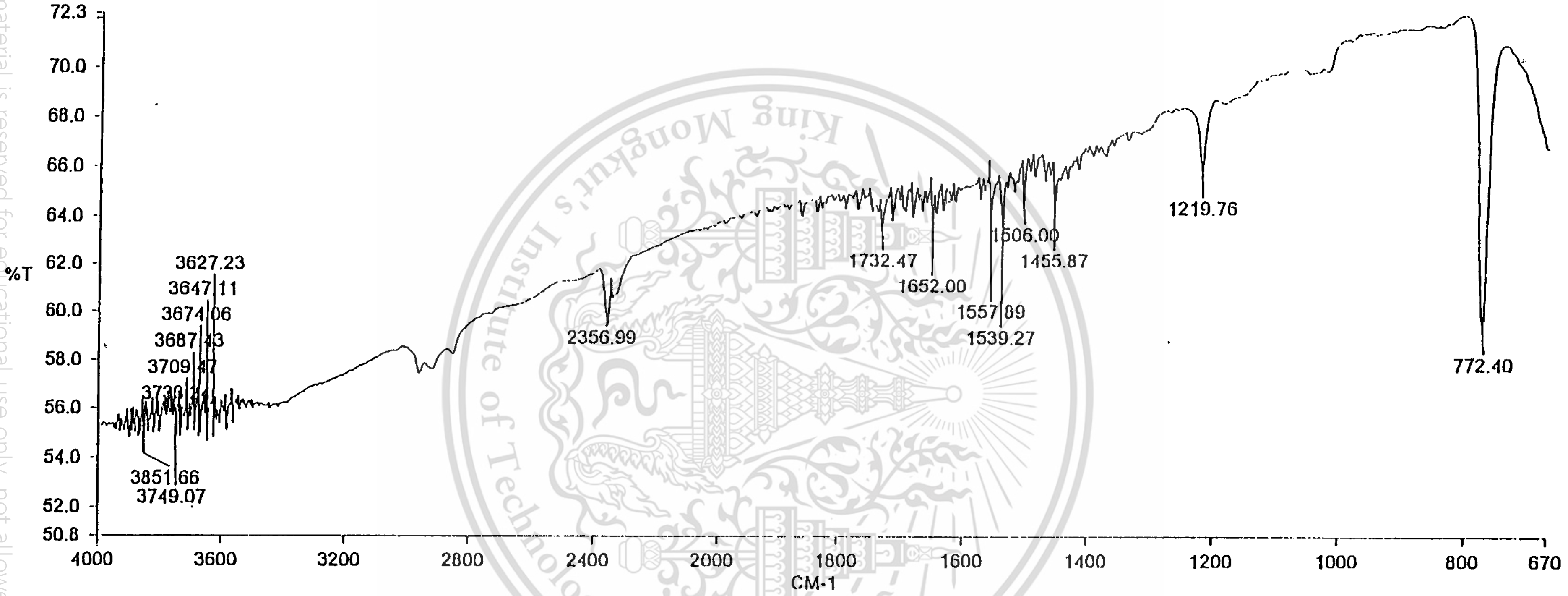
Date: 01/09/1995



NR-g-Ethyl acrylate 30%

Fig. C-6.

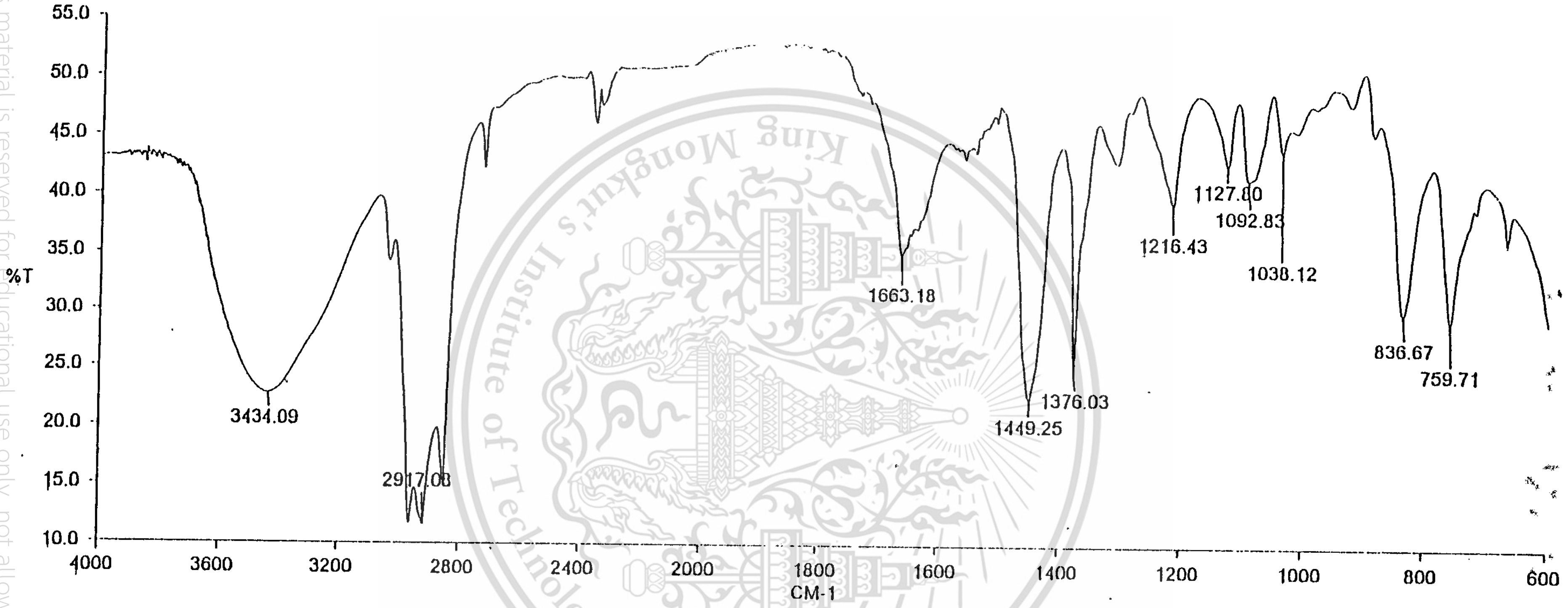
Date: 01/09/1995



NR-g- Butyl acrylate 30%

Fig. C-7

Date: 01/09/1995



NR-g-Acrylic acid 30%

Fig. C-8

Date: 01/09/1995

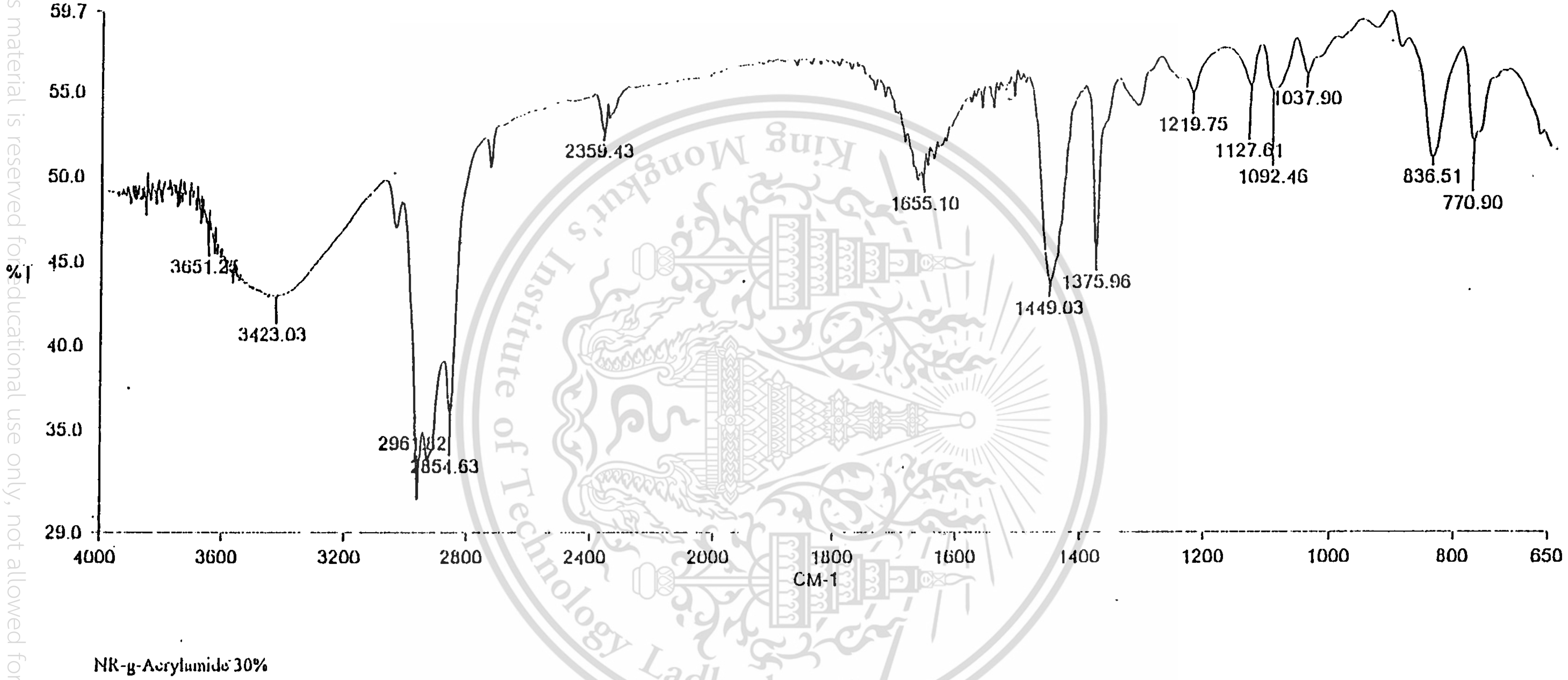
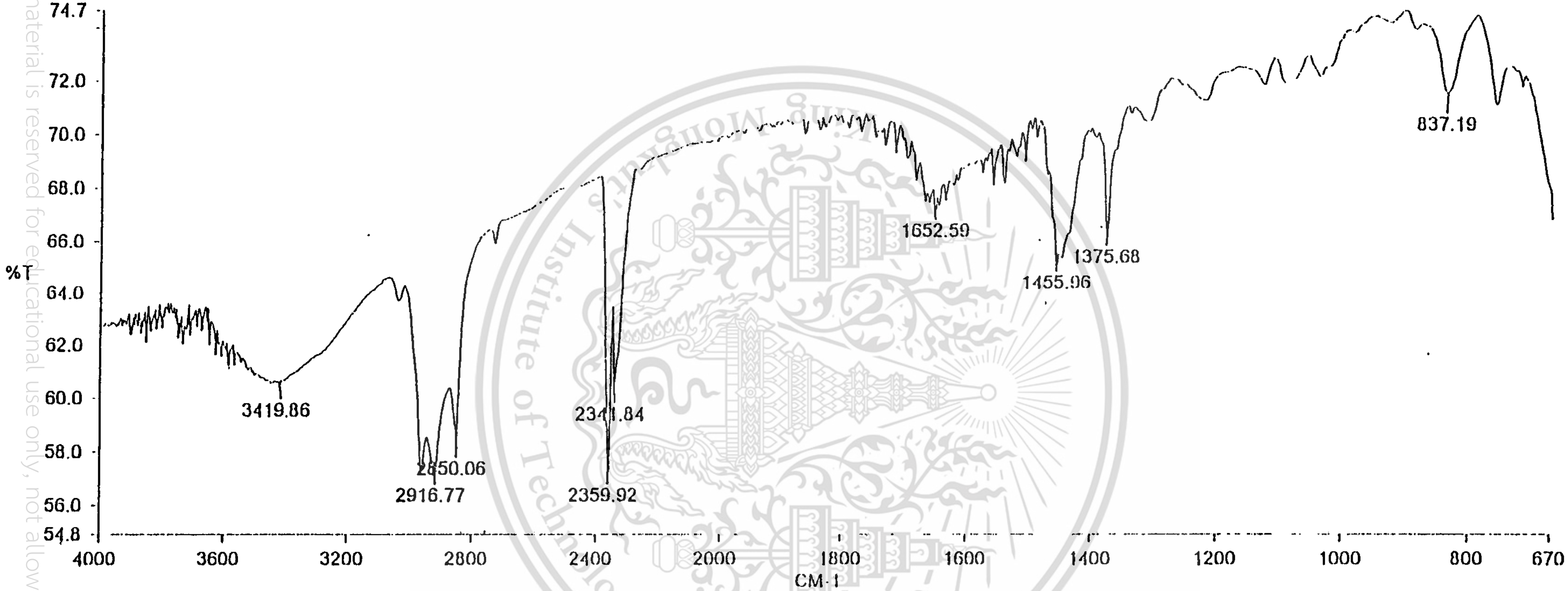


Fig. C-9

Date: 01/09/1995



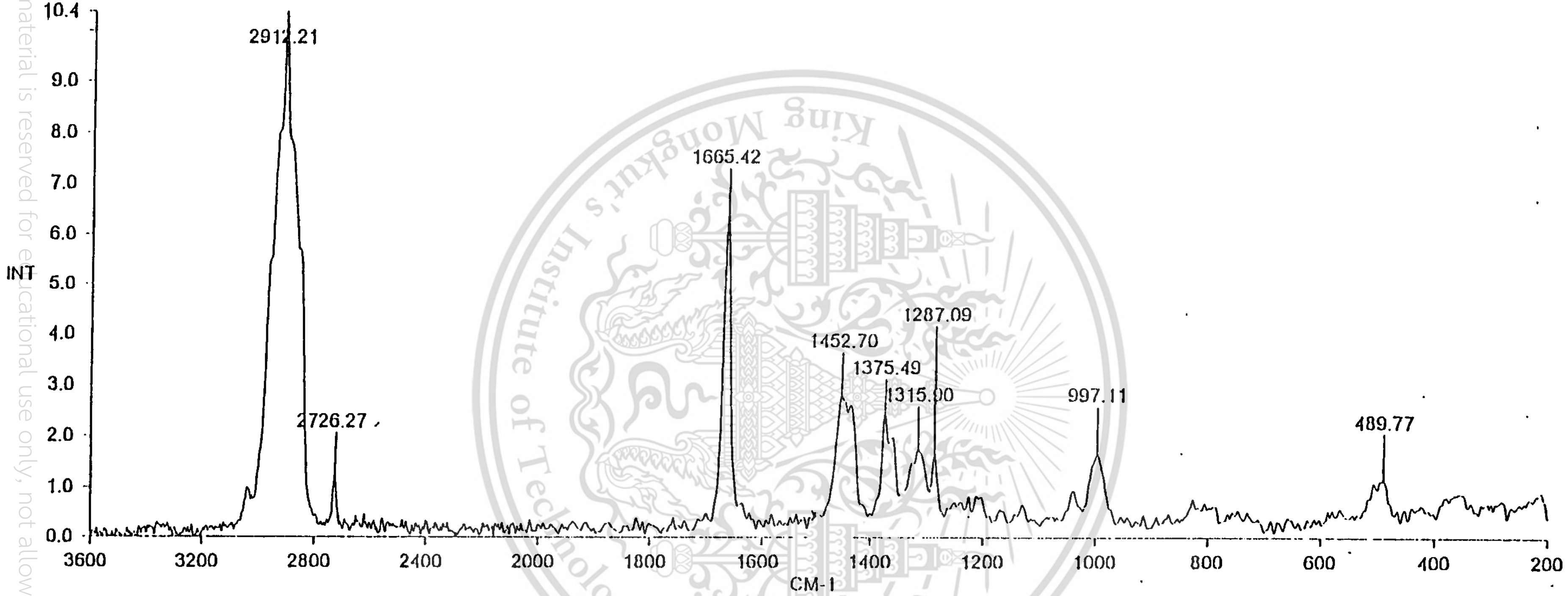
NR-g-Vinyl acetate 30%

Fig. C-10

Appendix D

Show the Raman spectrum of natural rubber and graft copolymers.

Date: 01/09/1995



Natural rubber

Fig. D-1

Date: 01/09/1995

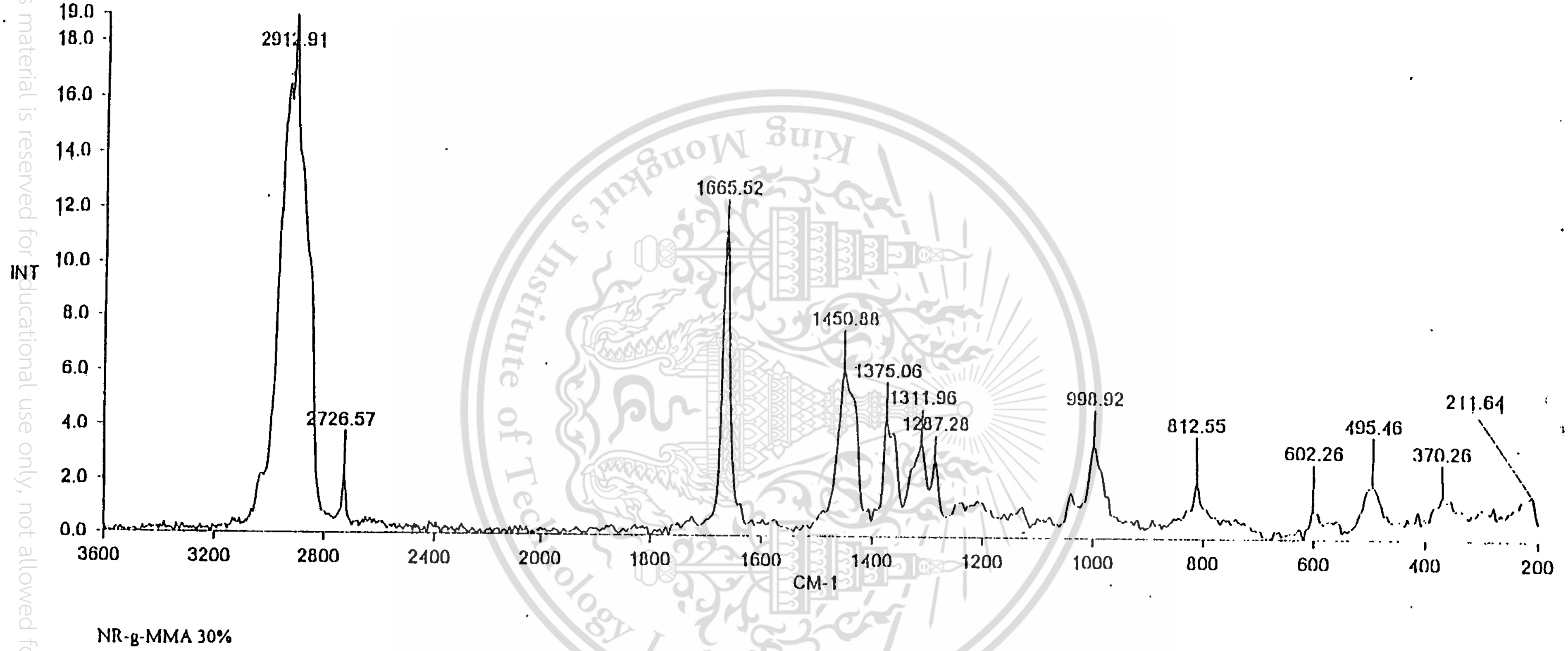
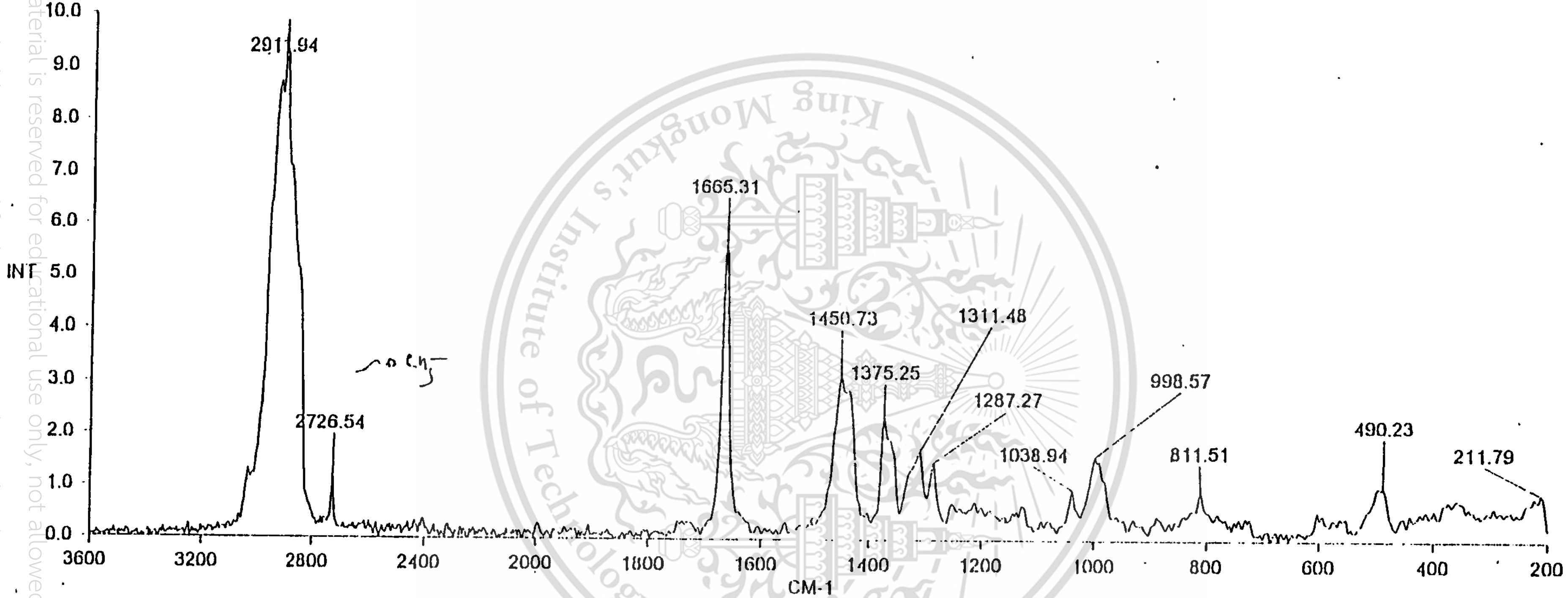


Fig. D-2

Date: 12/01/1994

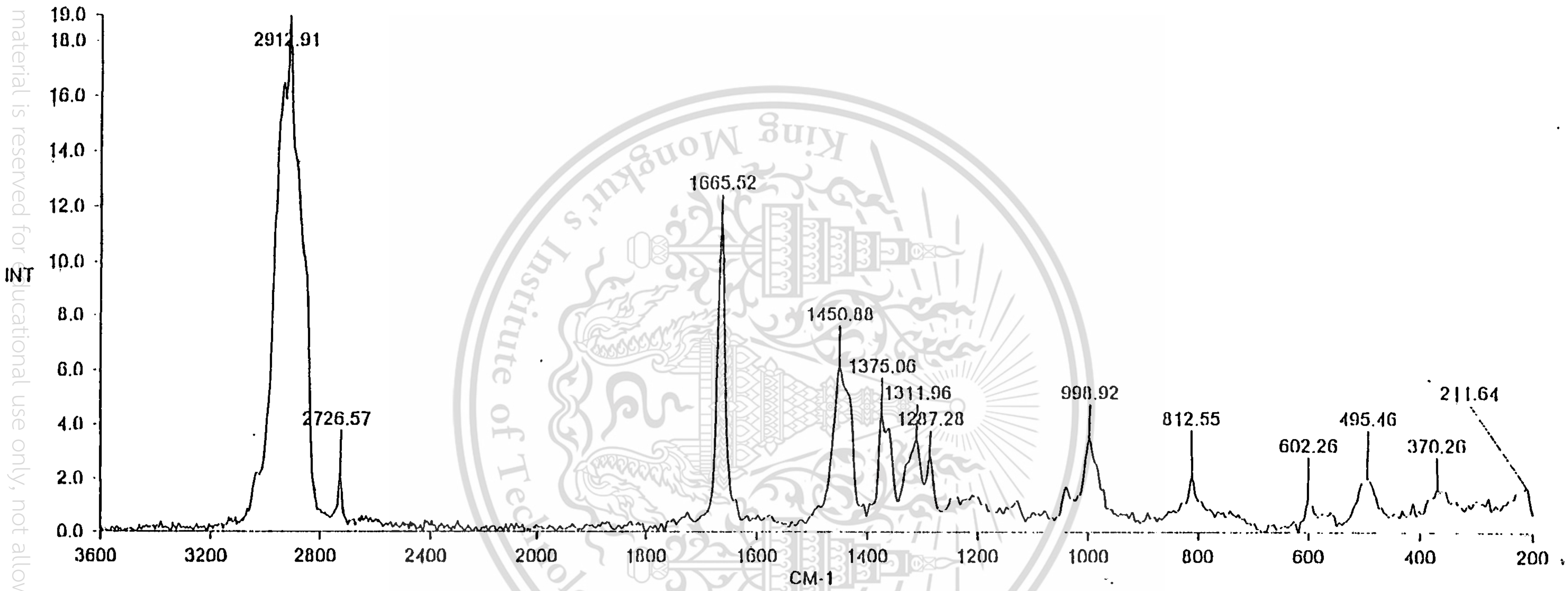


NR-g-MMA 30%+Acrylic acid 5%

Fig. D-3

Resolution: 4.00 CM-1 Accumulations: 40

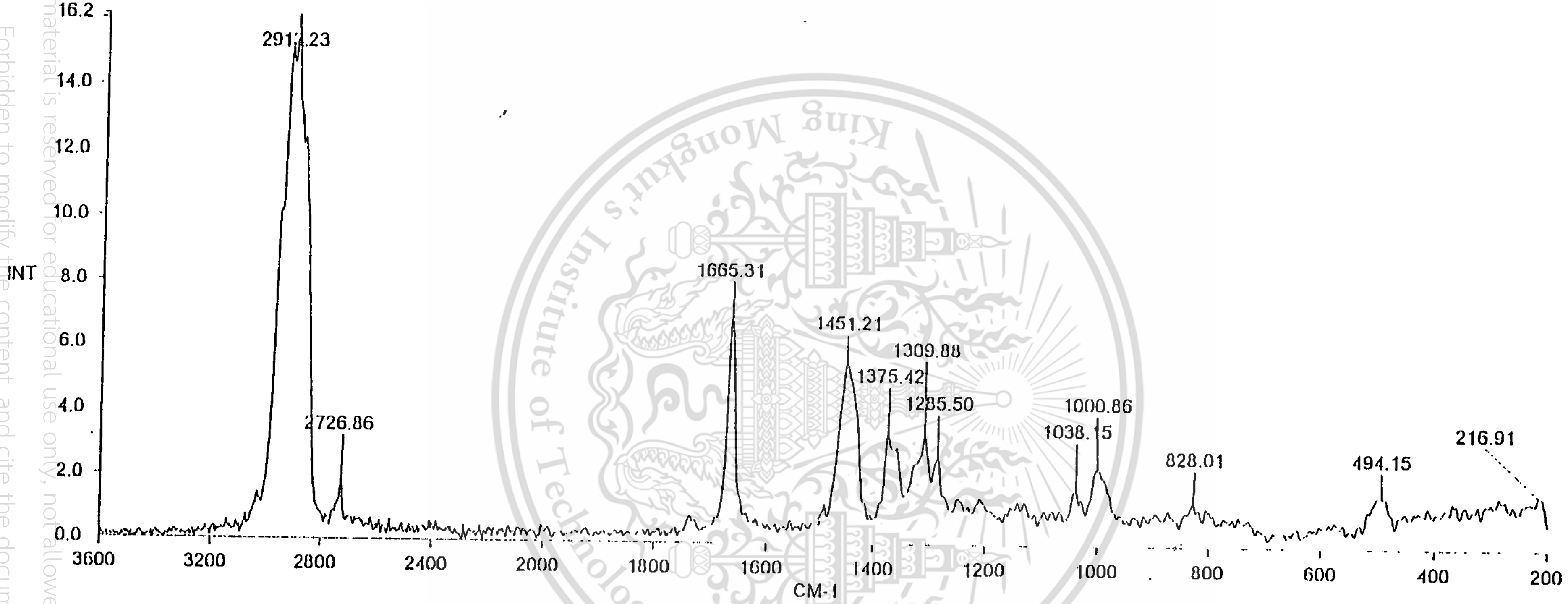
Date: 01/09/1995



NR-g-MMA 30%+Acrylic acid 5% (200 L.)

Fig. D-4

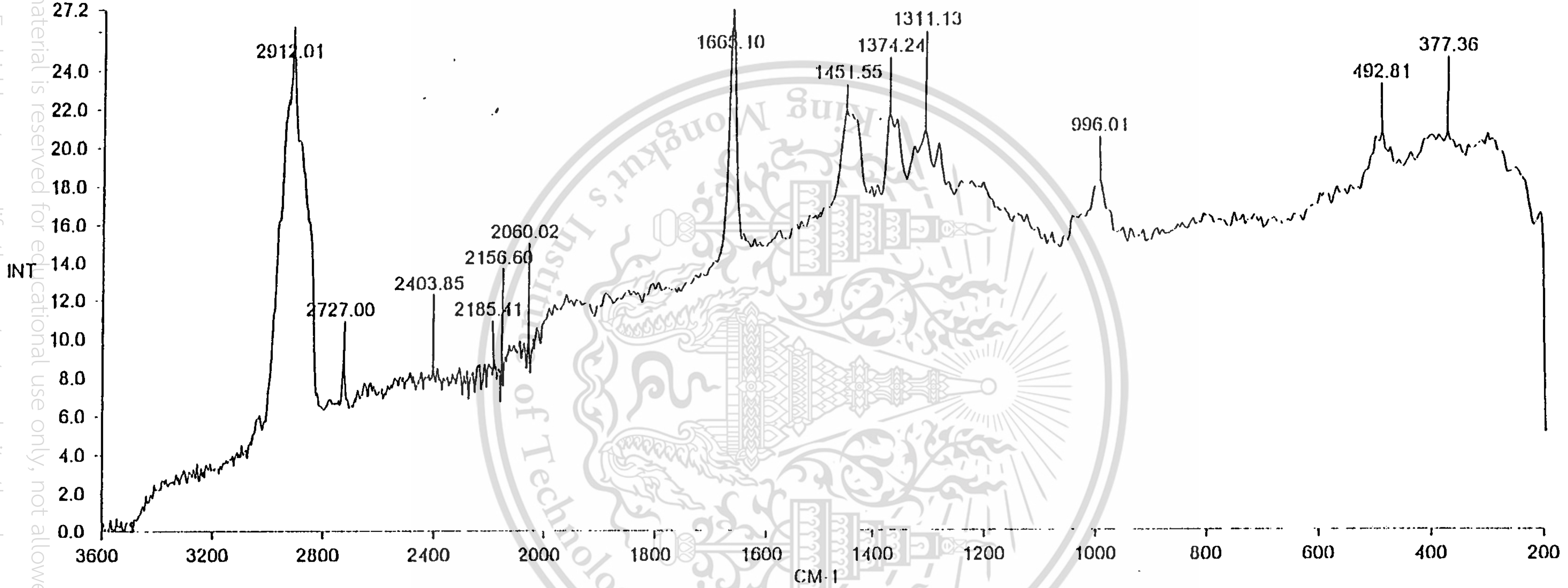
Date: 01/09/1995



NR-g-2EHA 30%

Fig. D-5

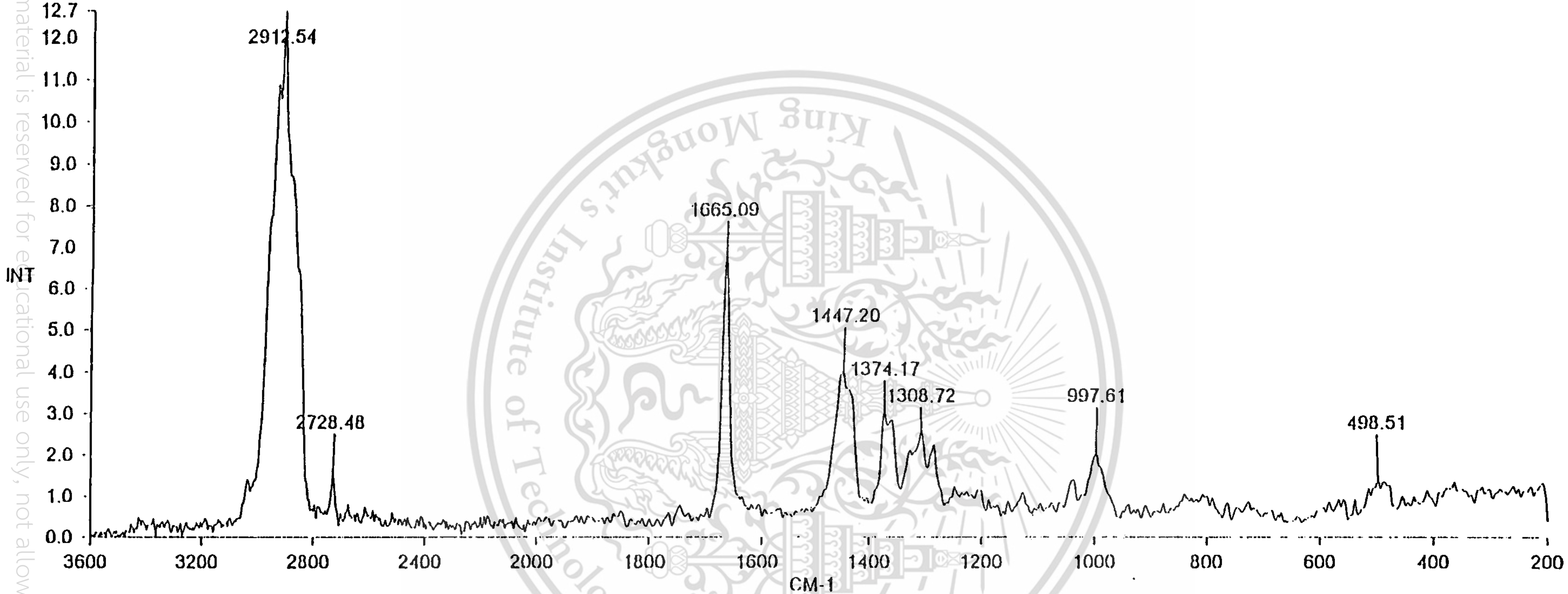
Date: 01/09/1995



NR-g-Ethyl acrylate 30%

Fig. D-6

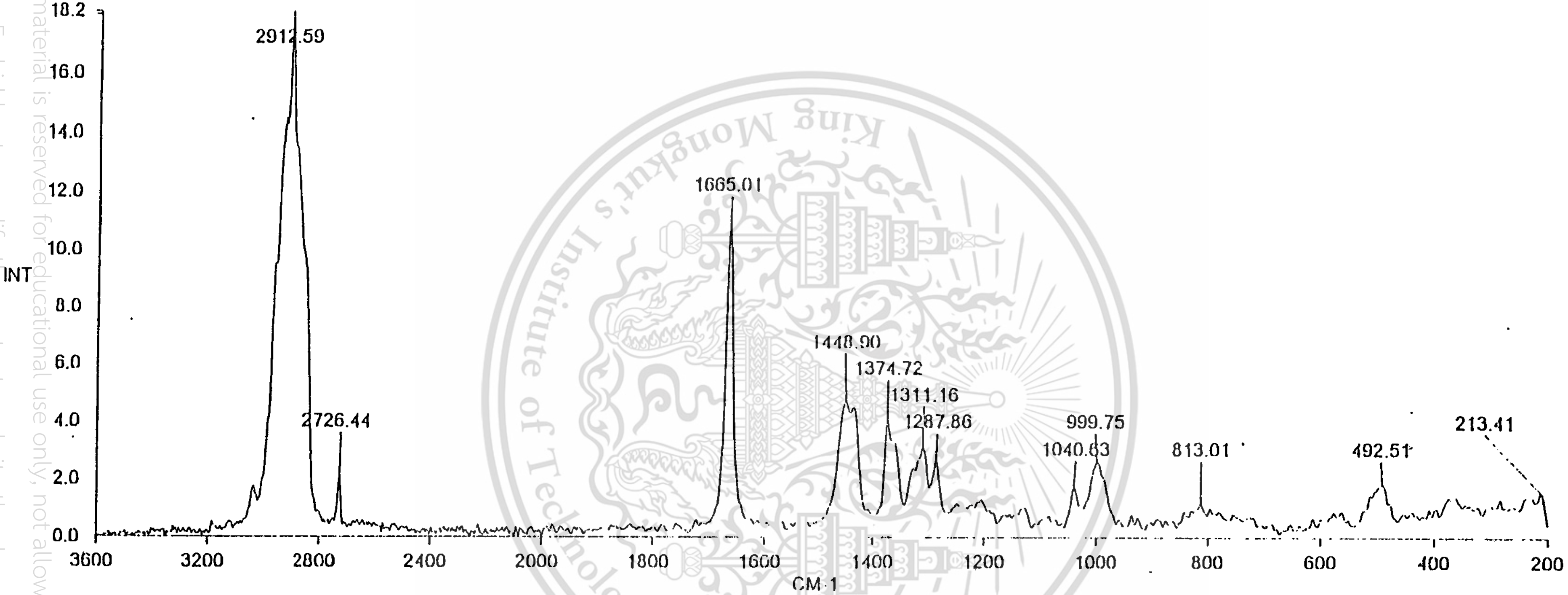
Date: 01/09/1995



NR-g-Butyl acrylate 30%

Fig. D-7

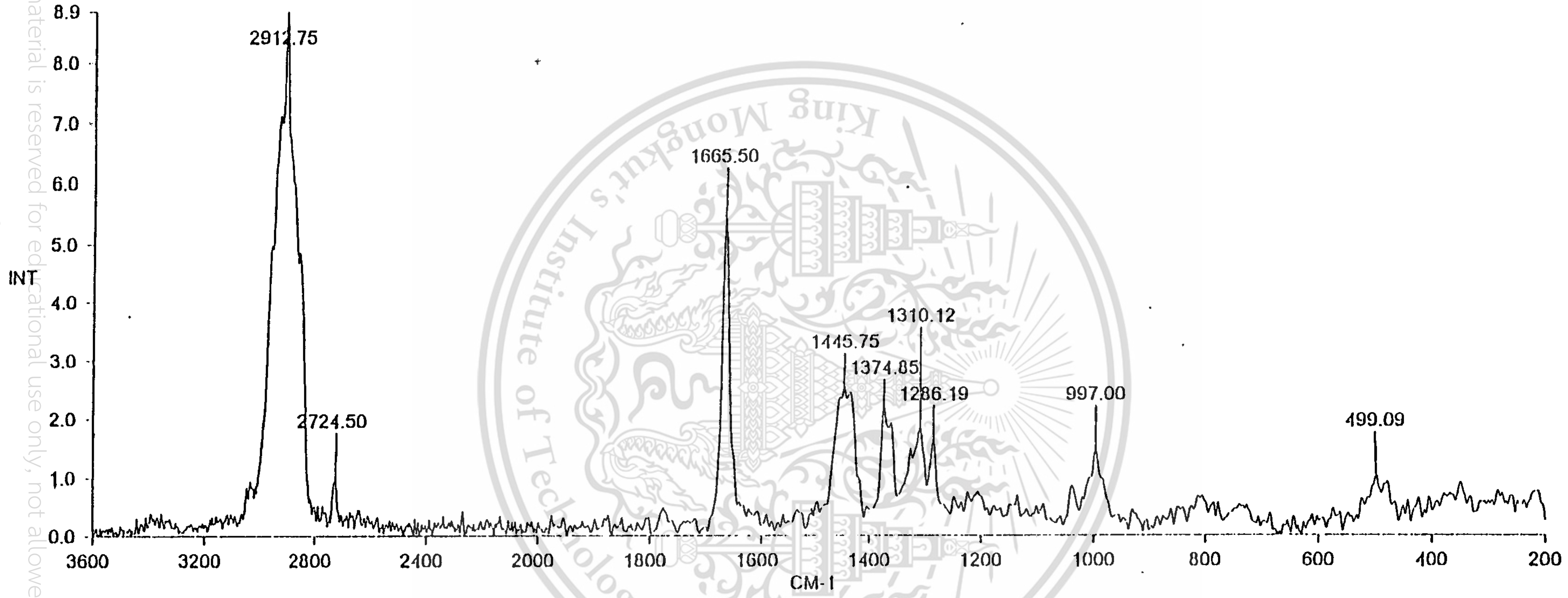
Date: 01/09/1995



NR-g-Acrylic acid 30%

Fig. D-8

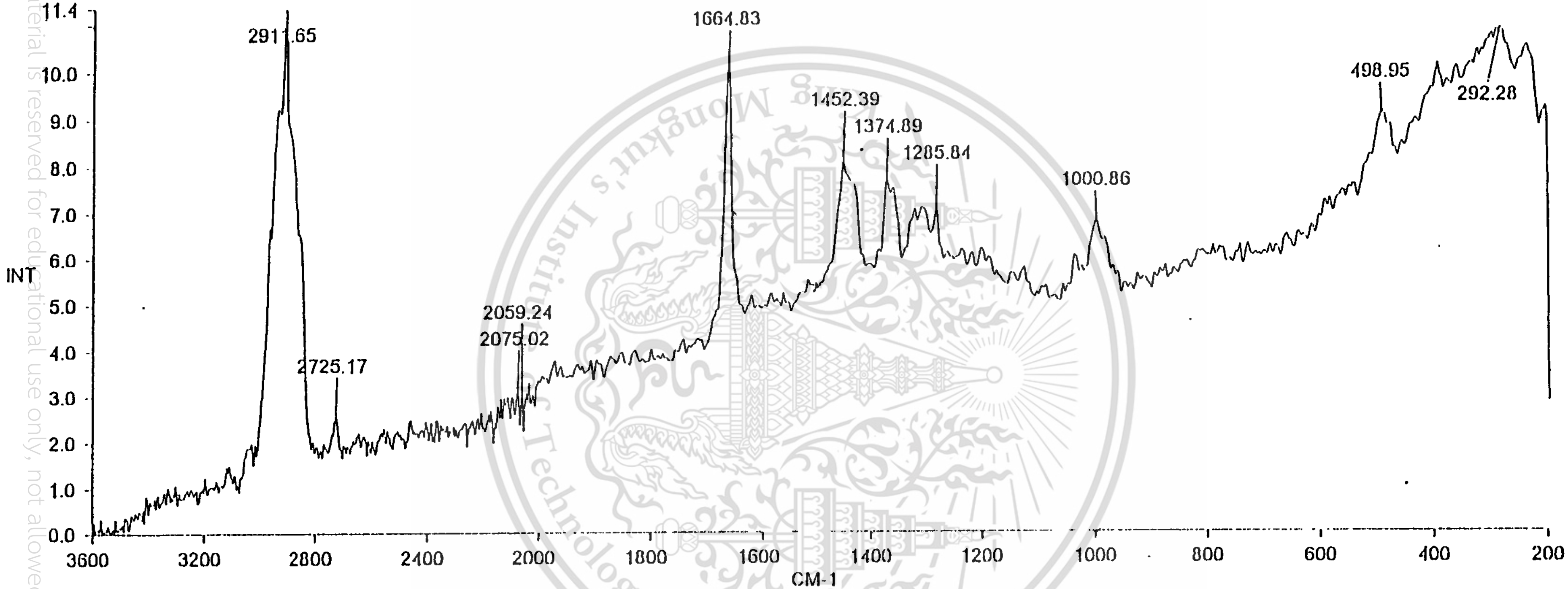
Date: 01/09/1995



NR-g-Acrylamido 30%

Fig. D-9

Date: 01/09/1995

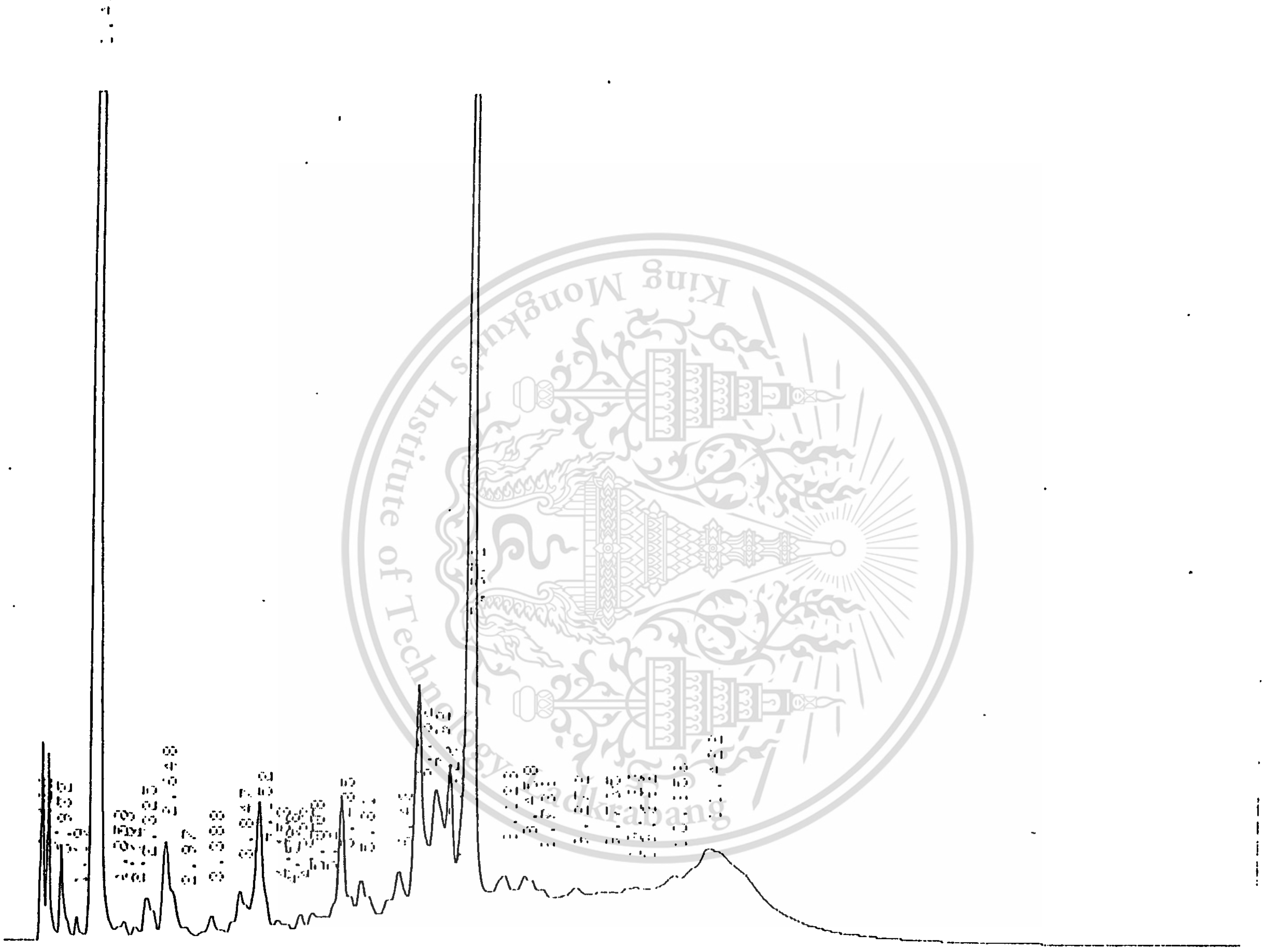


NR-g-Vinyl acetate 30%

Fig. D-10

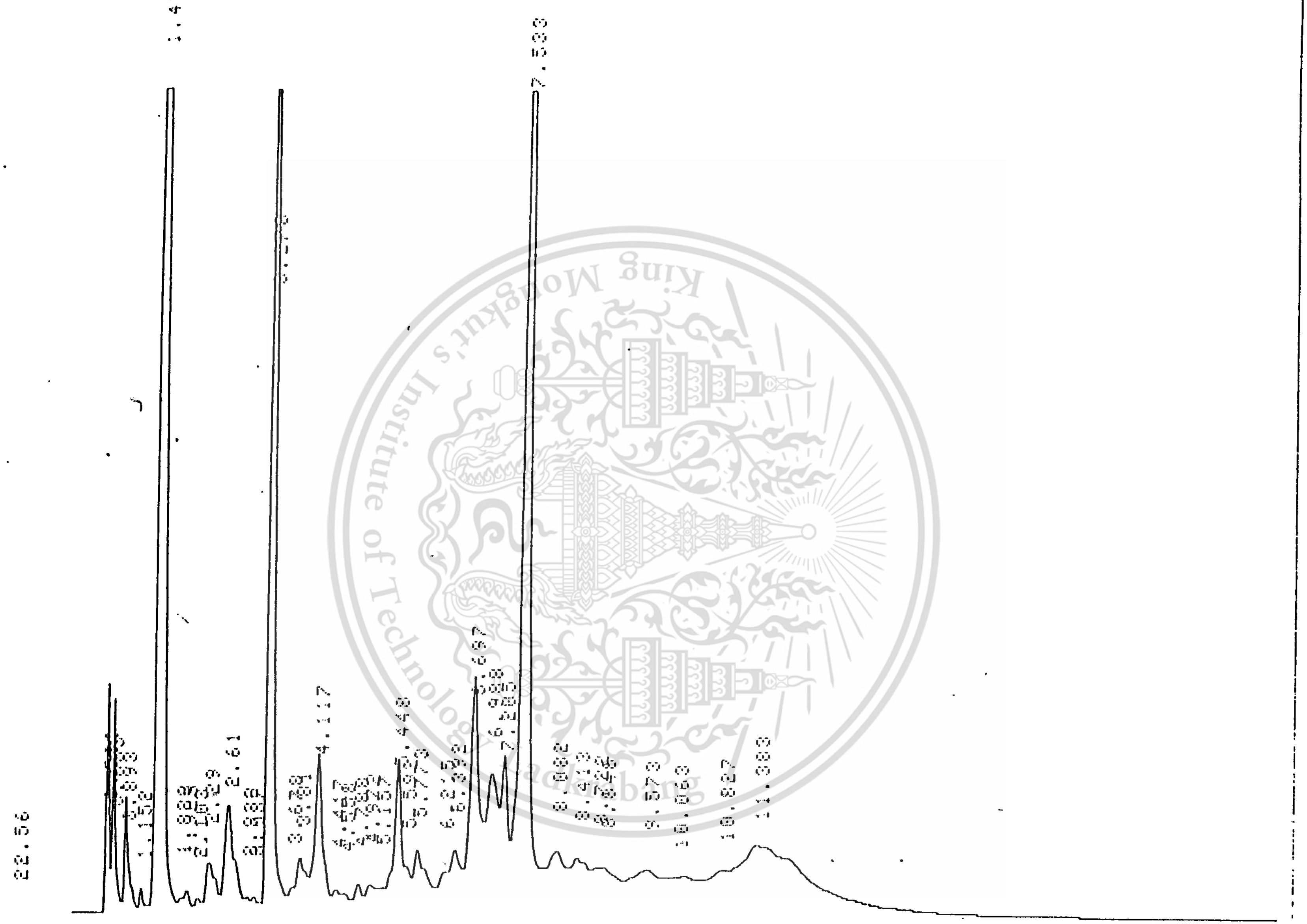
Appendix E.

Show the pyrolysis gas chromatrogram of natural rubber and graft copolymers.



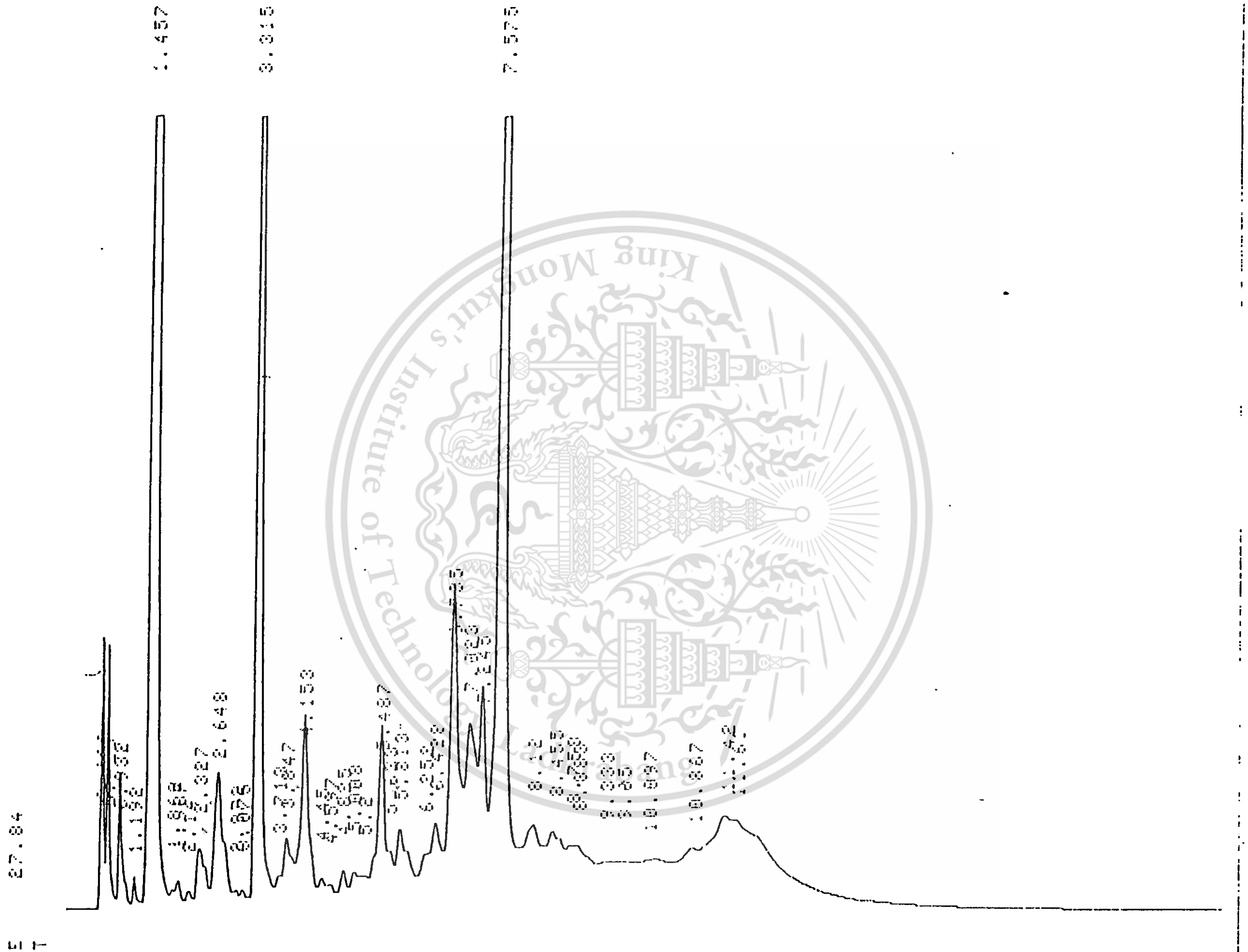
Natural Rubber

Fig. E-1



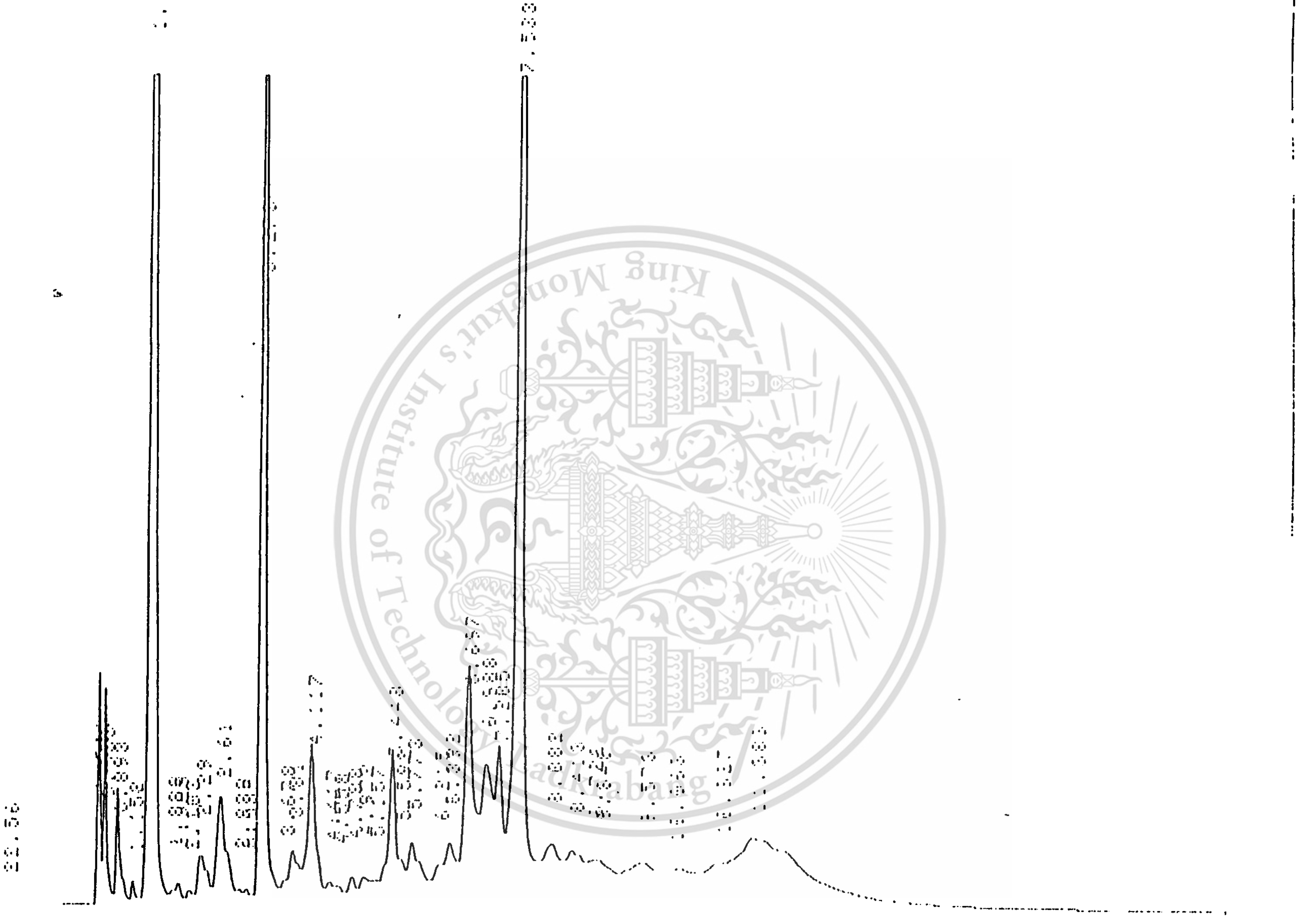
NR-*g*-MMA 30%

Fig. E-2



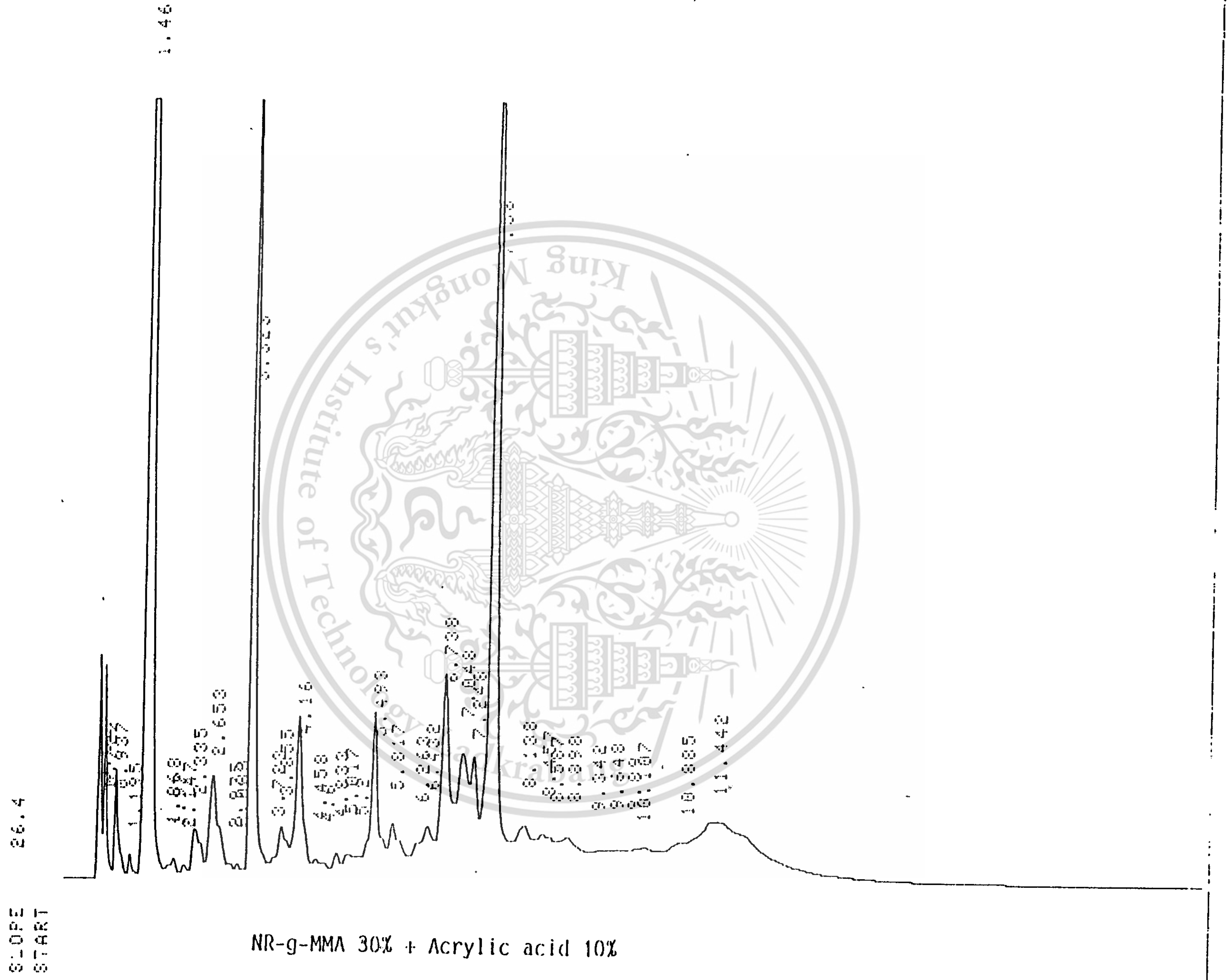
NR-g-MMA 30% + Acrylic acid 5%

Fig. E-3



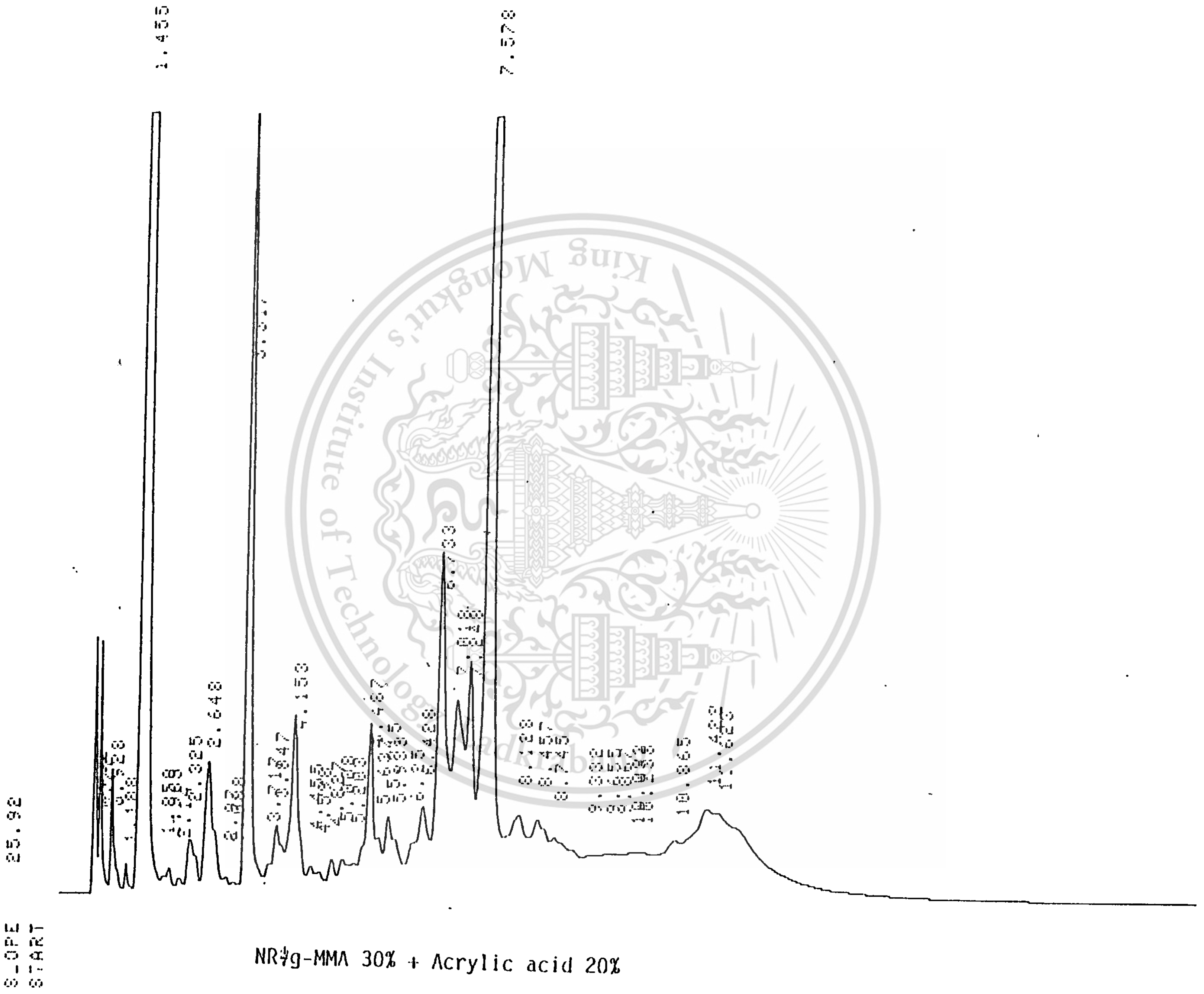
NR-g-MMA30% + Acrylic acid 5% (200 l.)

Fig. E-4



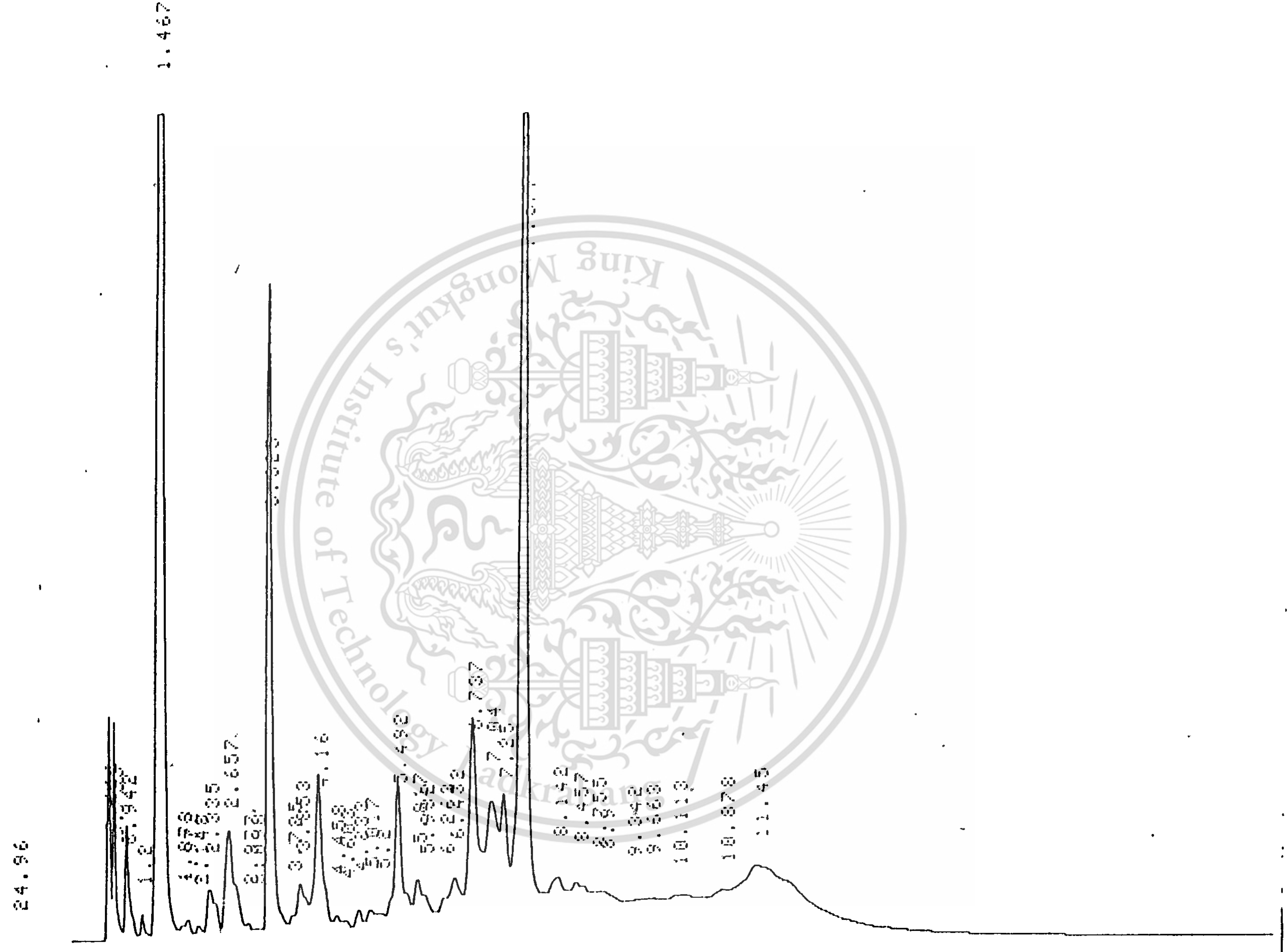
NR-g-MMA 30% + Acrylic acid 10%

Fig.B-5



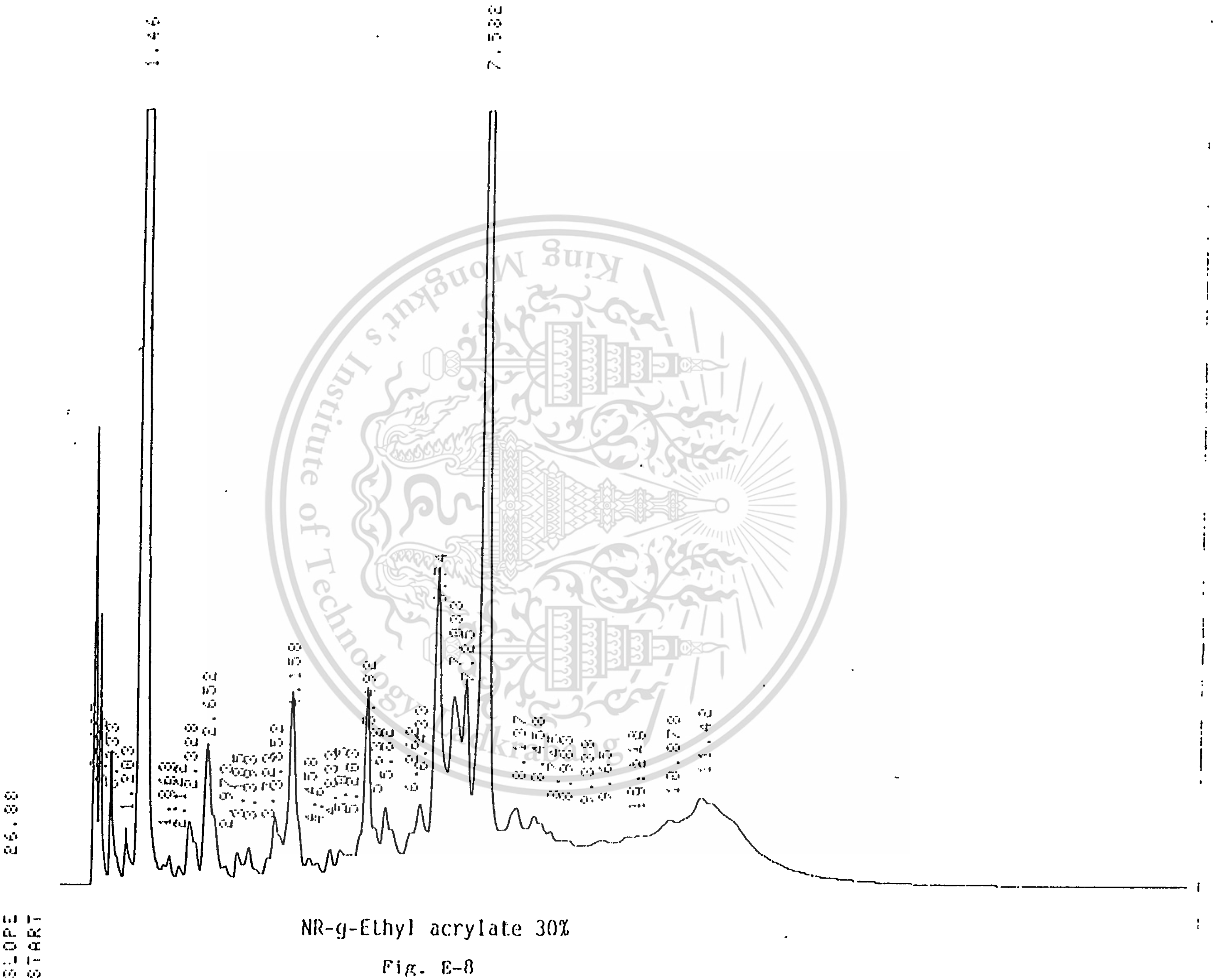
NR-g-MMA 30% + Acrylic acid 20%

Fig. E-6



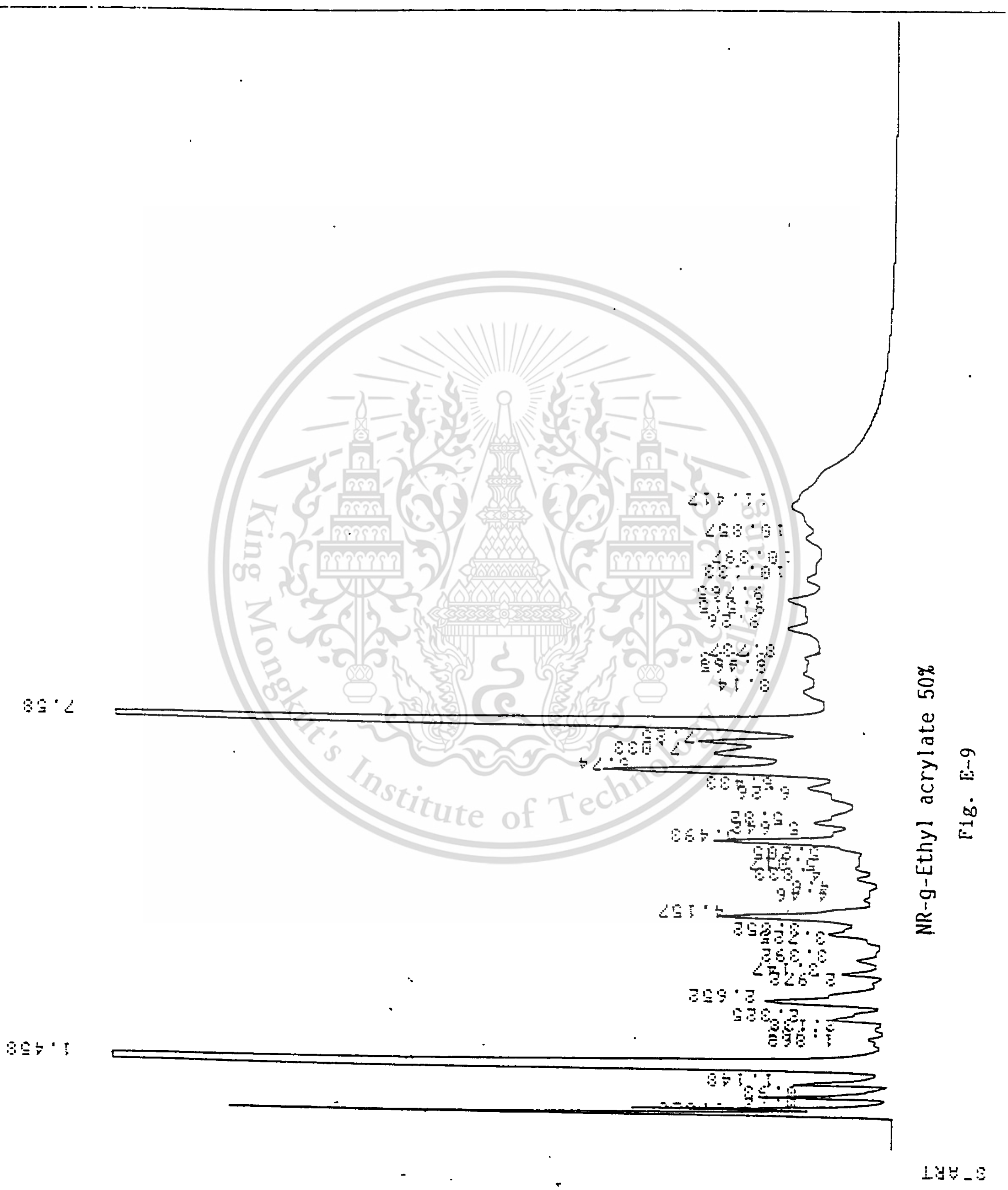
NR-g-MMA30%+Acrylic acid30%

Fig. E-7



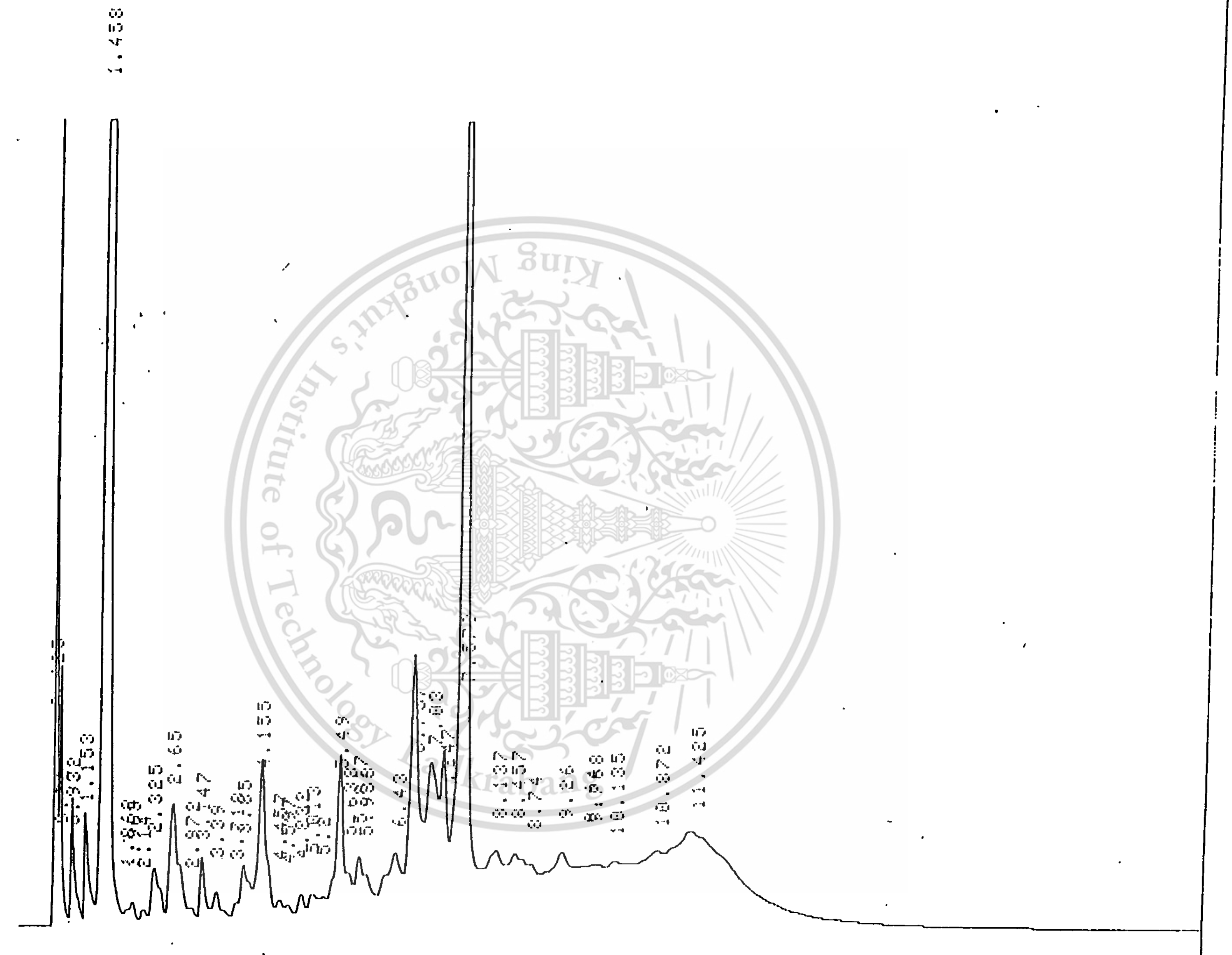
NR-g-Ethyl acrylate 30%

Fig. E-8



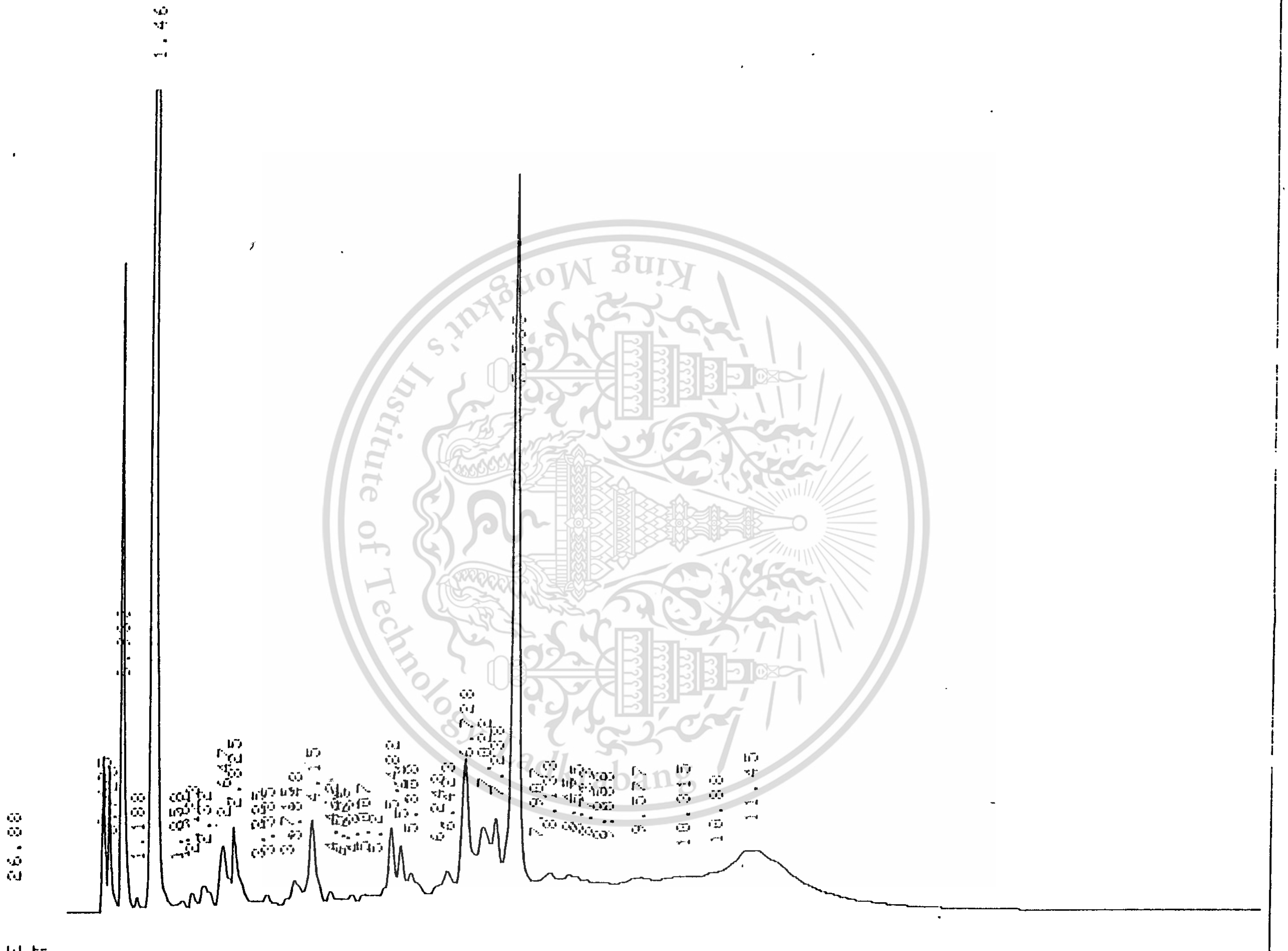
NR-g-Ethyl acrylate 50%

Fig. E-9



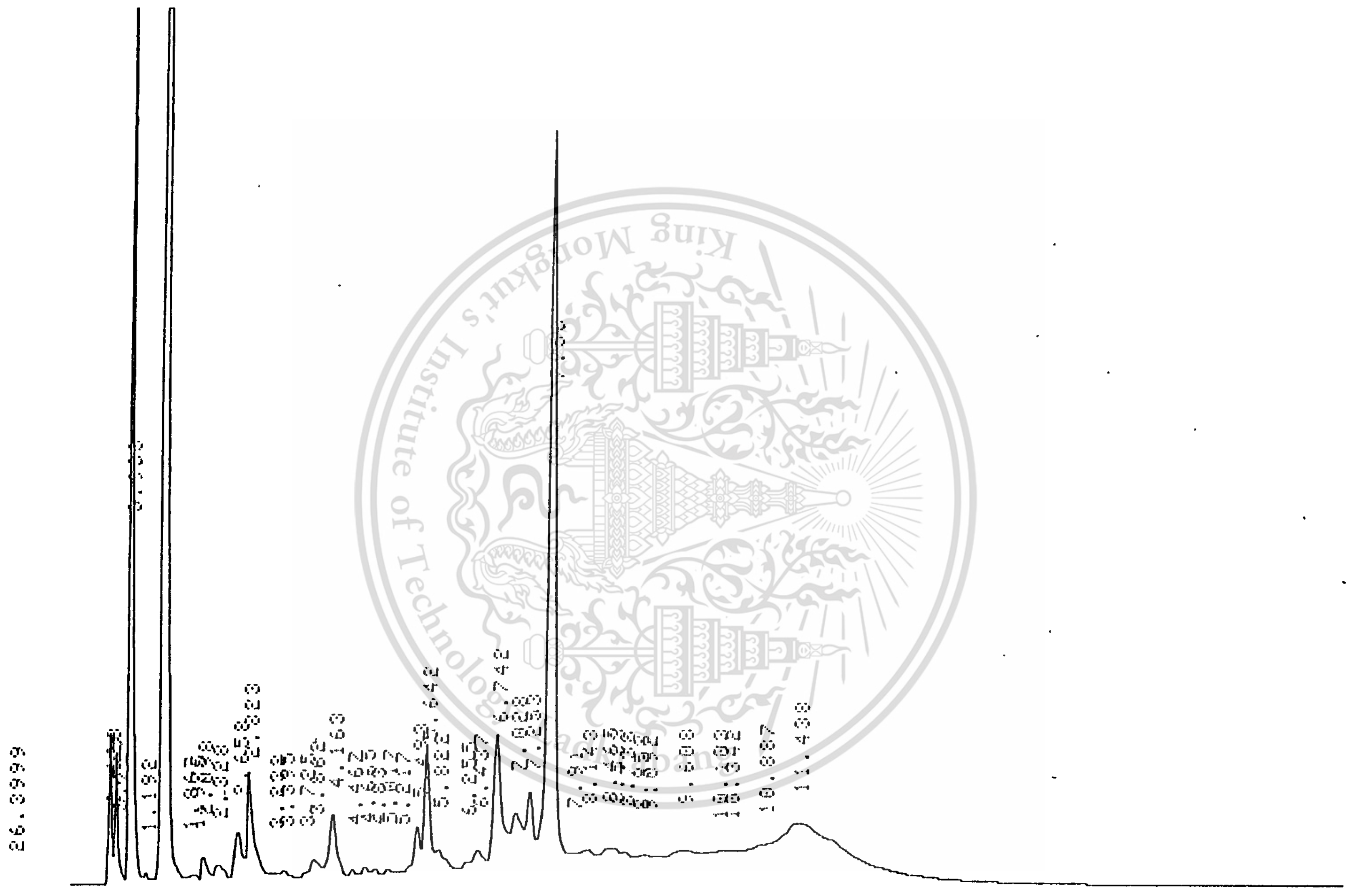
NR-g-Ethyl acrylate 70%

Fig. E-10



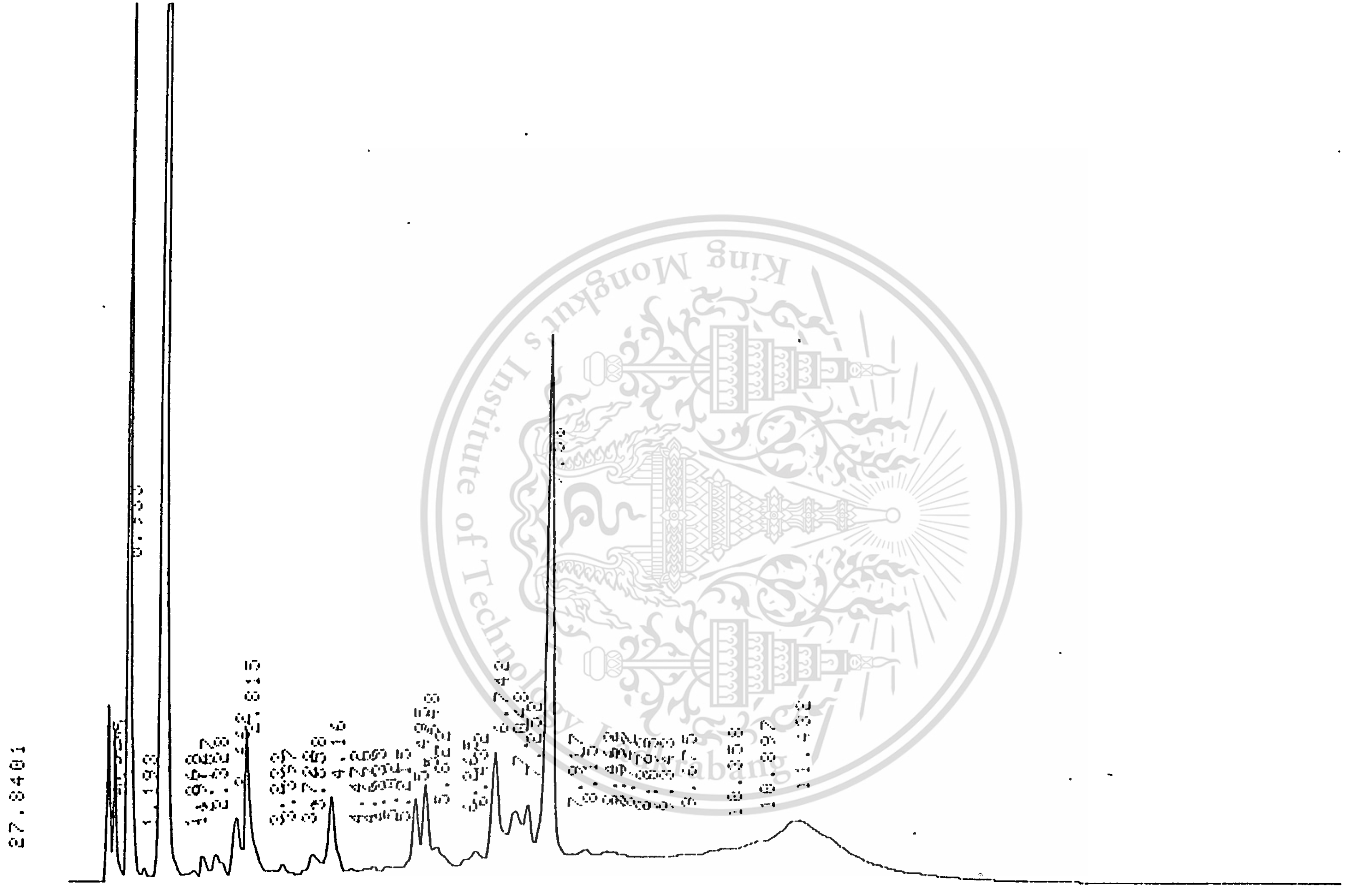
NR-g-Butyl acrylate 30%

Fig. E-11



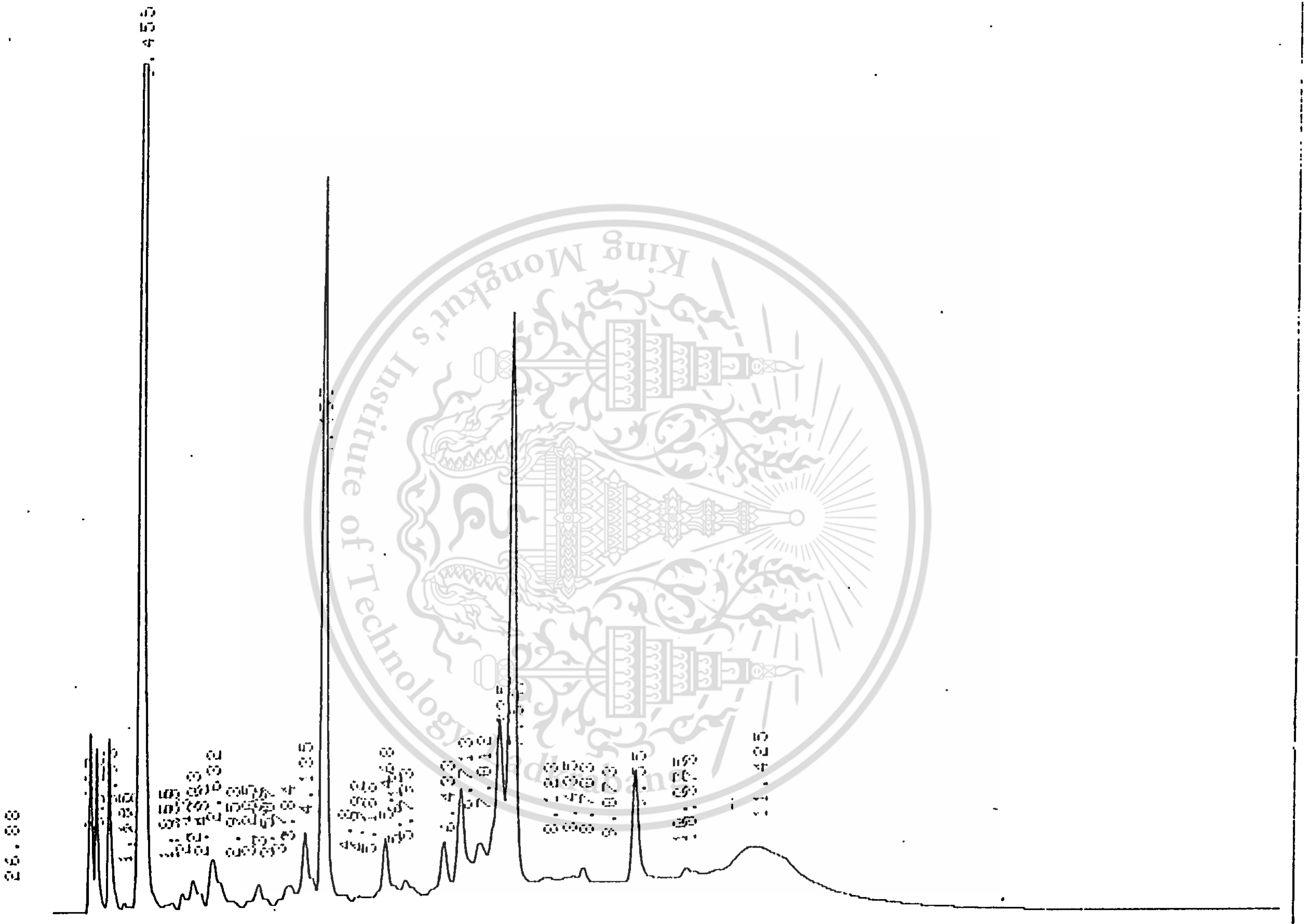
NR-g-Butyl acrylate 50%

Fig. E-12



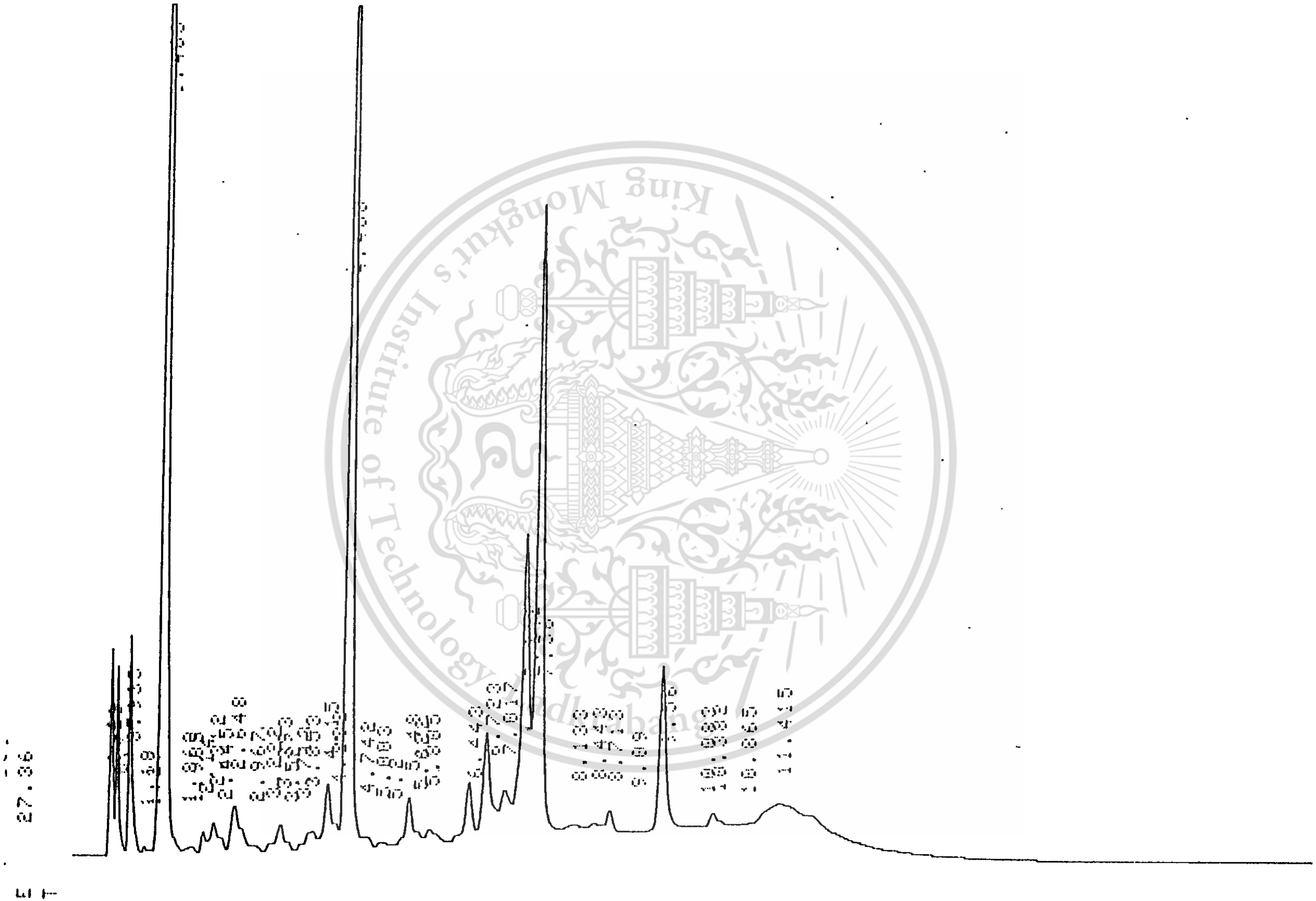
NR-g-Butyl acrylate 70%

Fig. E-13



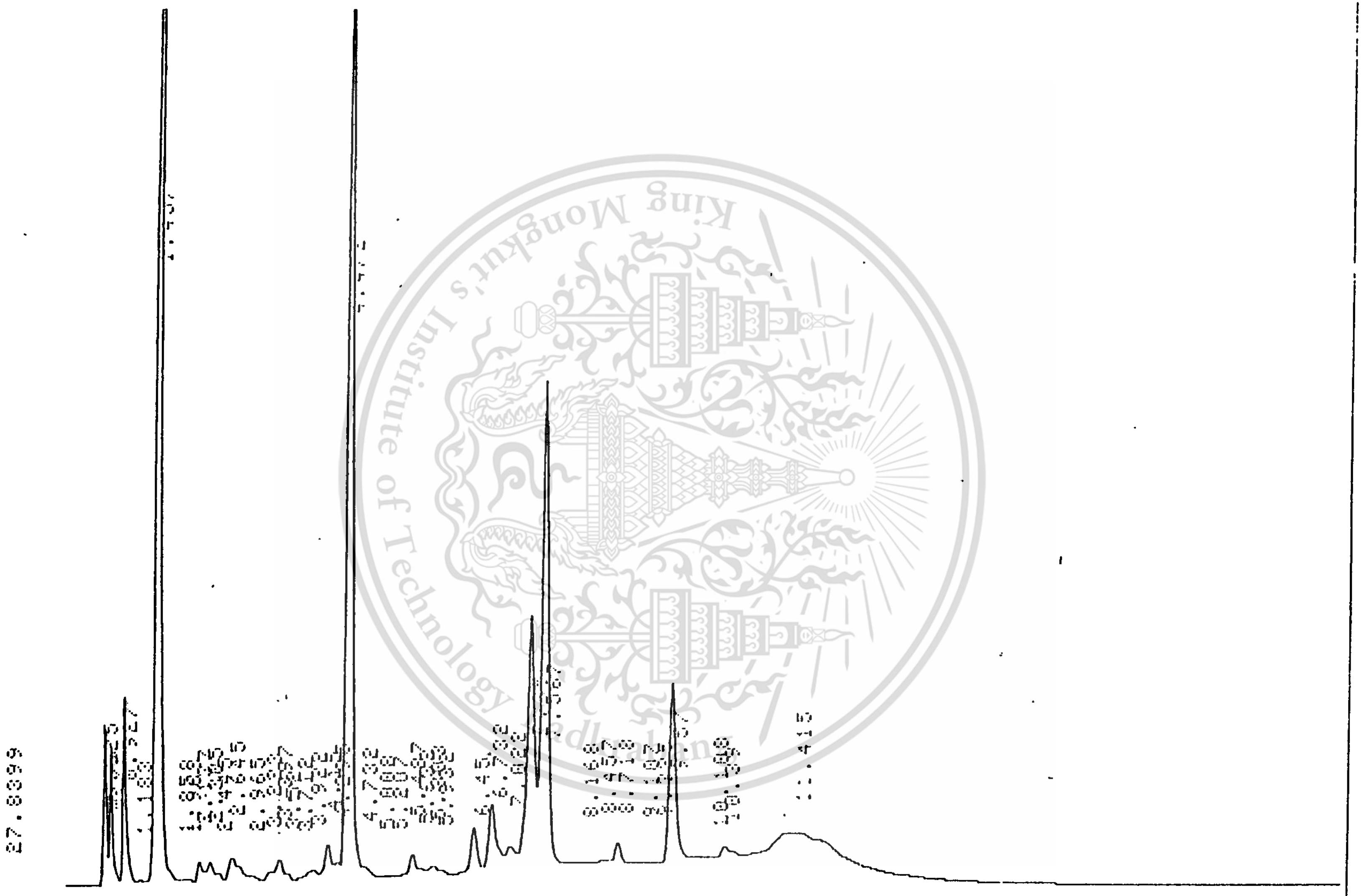
NR-g-2-Ethylhexyl acrylate 30%

Fig. E-14

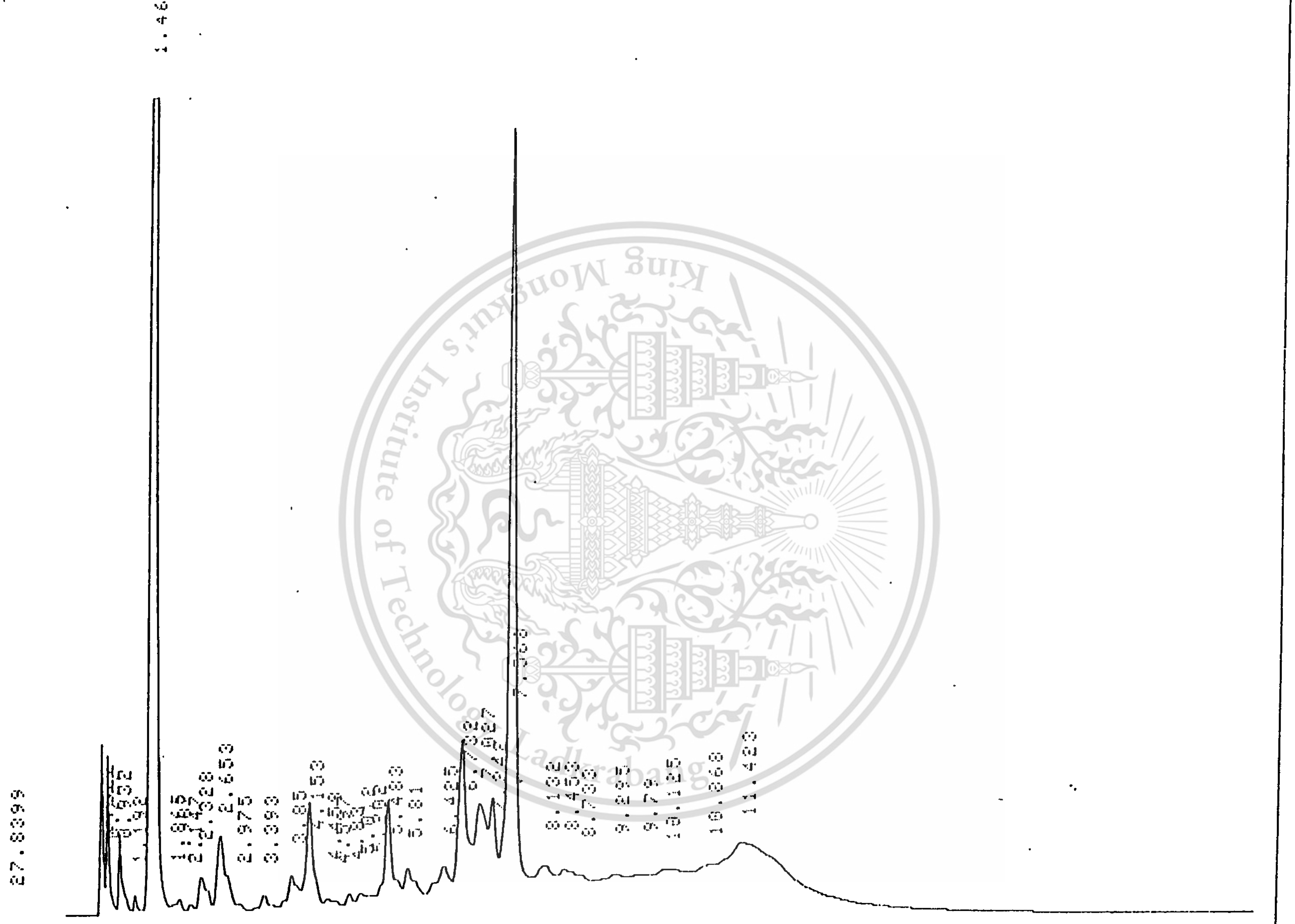


NR-g-2-Ethylhexyl acrylate 50%

Fig. E-15

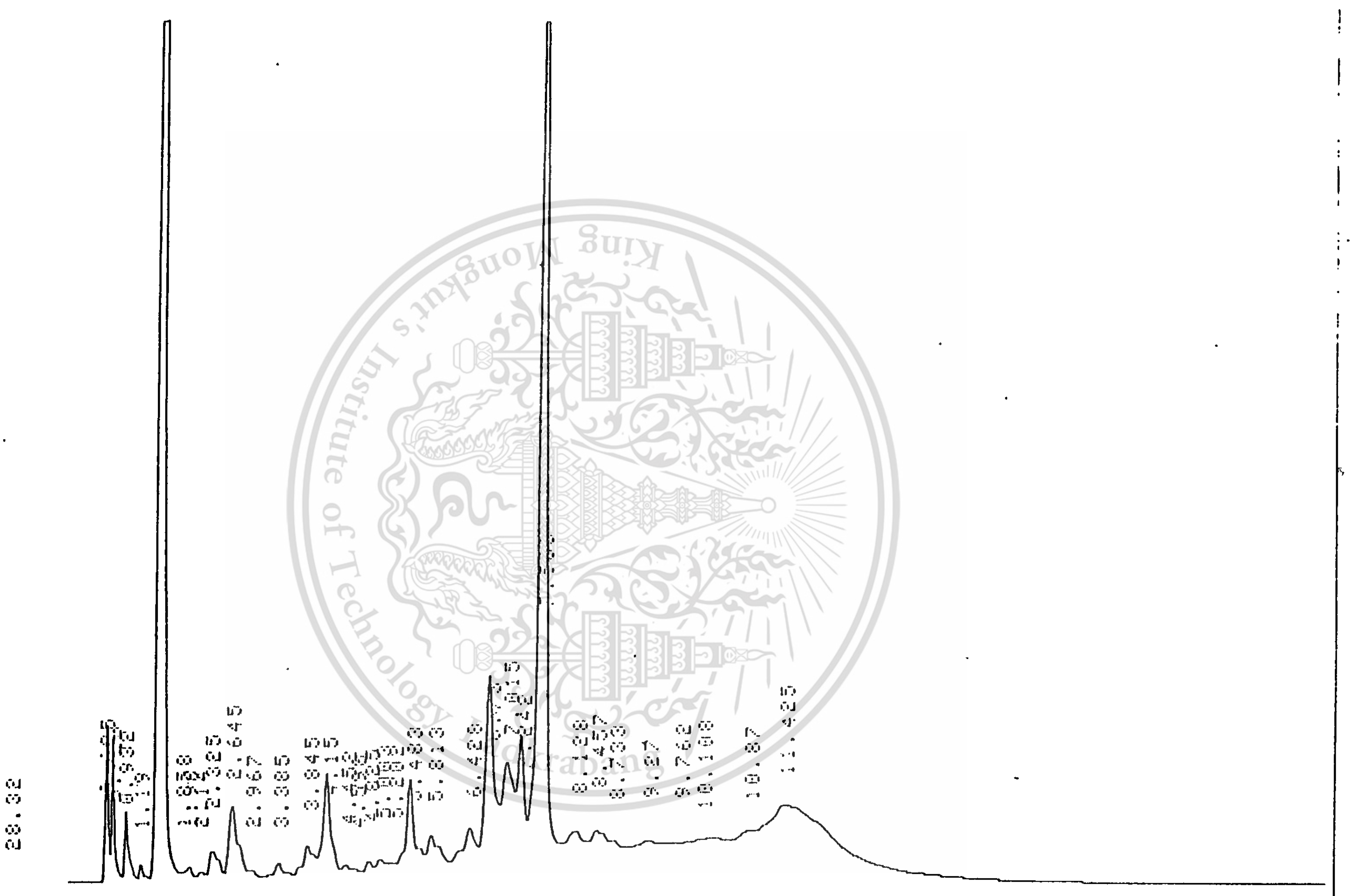


NR-g-2-Ethylhexyl acrylate 70%
Fig. E-16



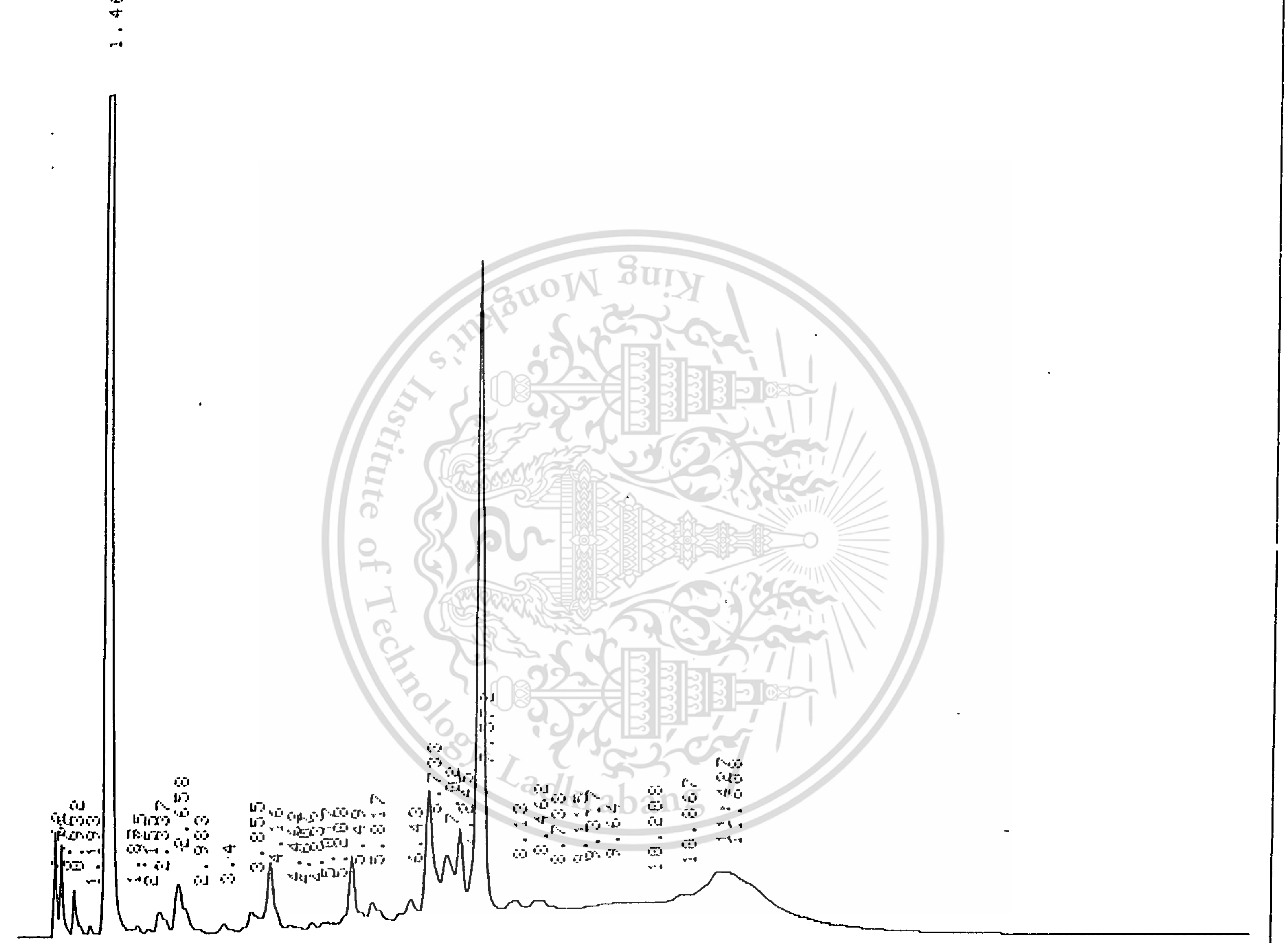
NR-g-Vinyl acetate 30%

Fig. E-17



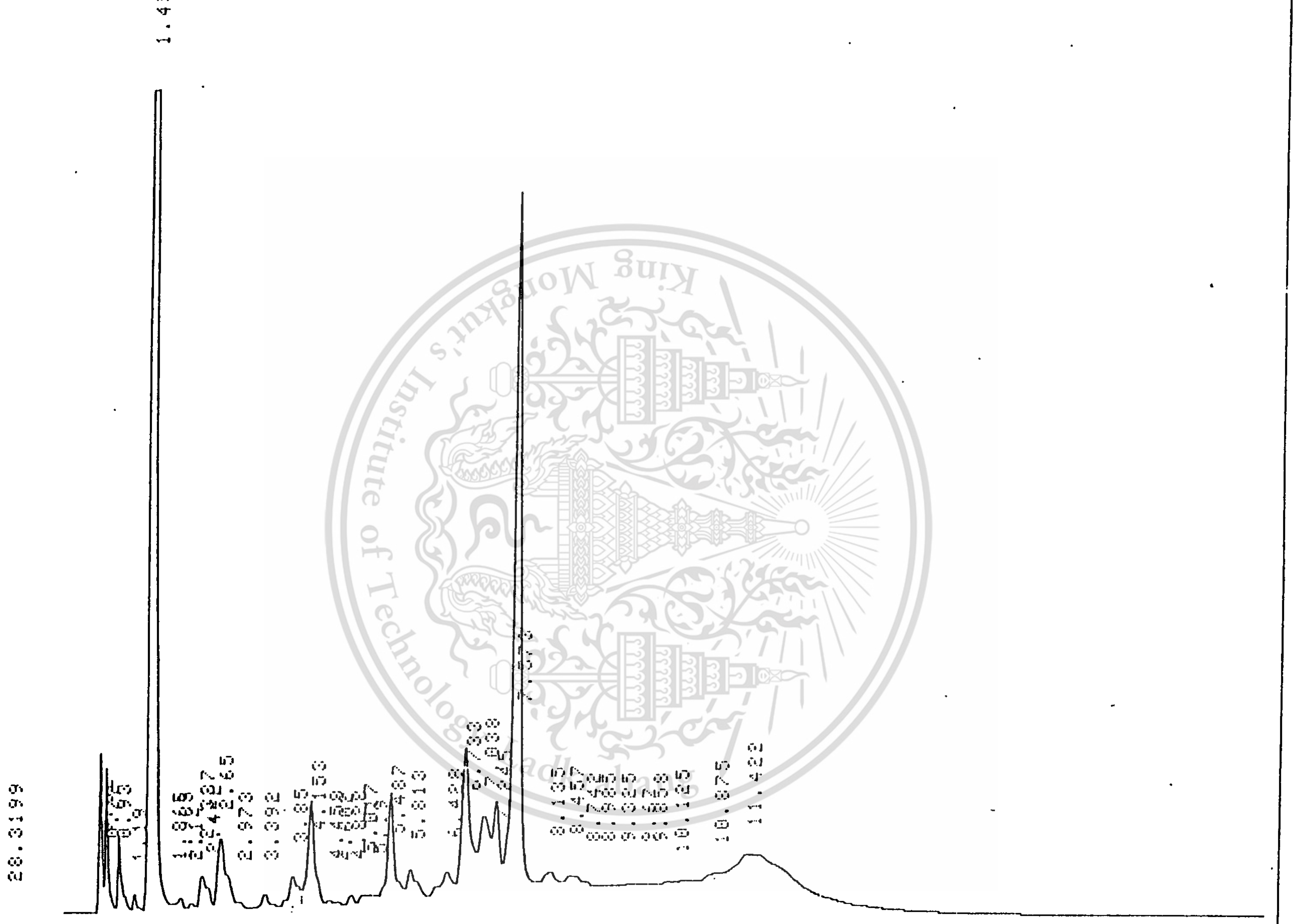
NR-g-Acrylic acid 30%

Fig. E-18



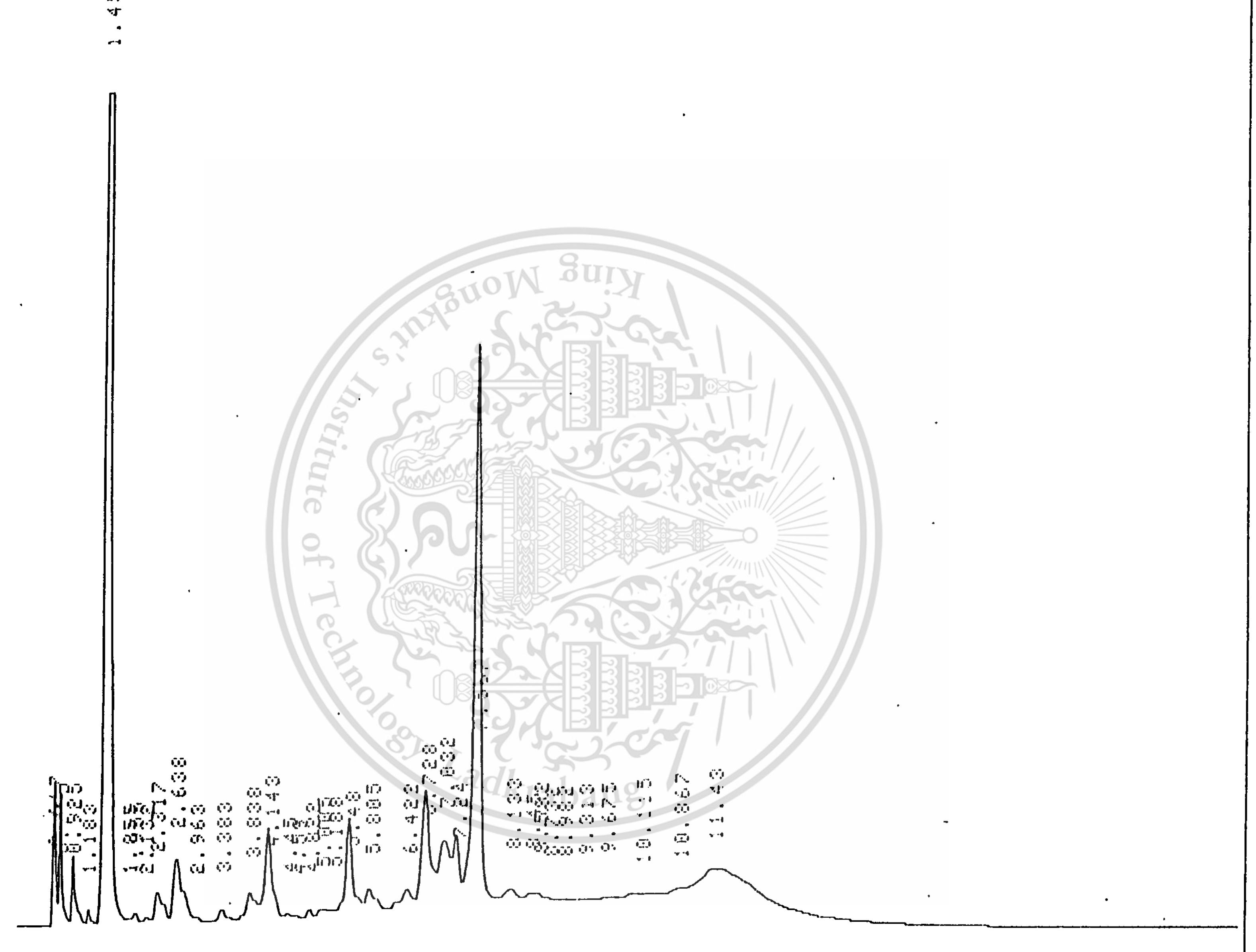
NR-g-Acrylid acid 50%

Fig. E-19



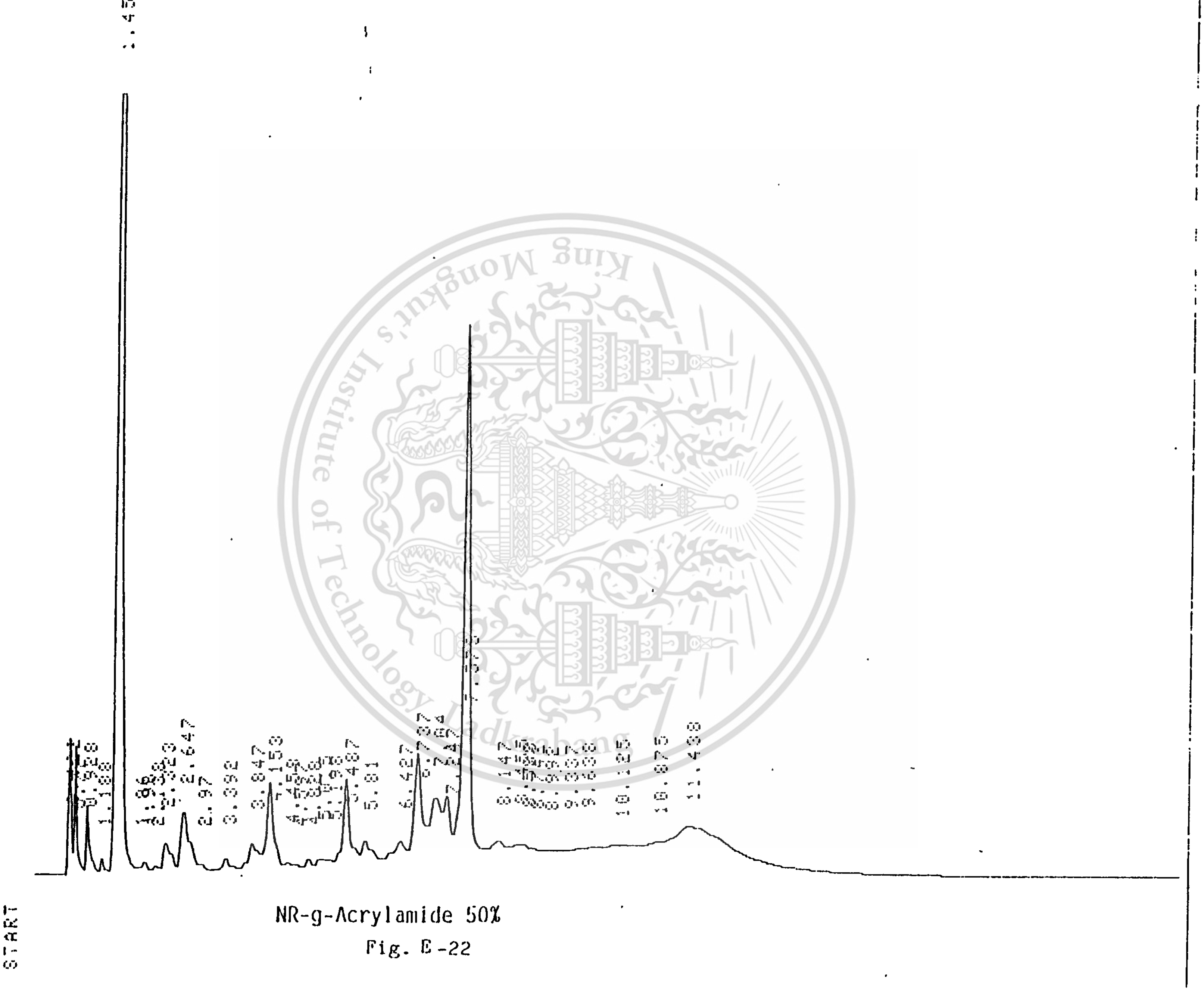
NR-g-Acrylic acid 70%

Fig. E-20



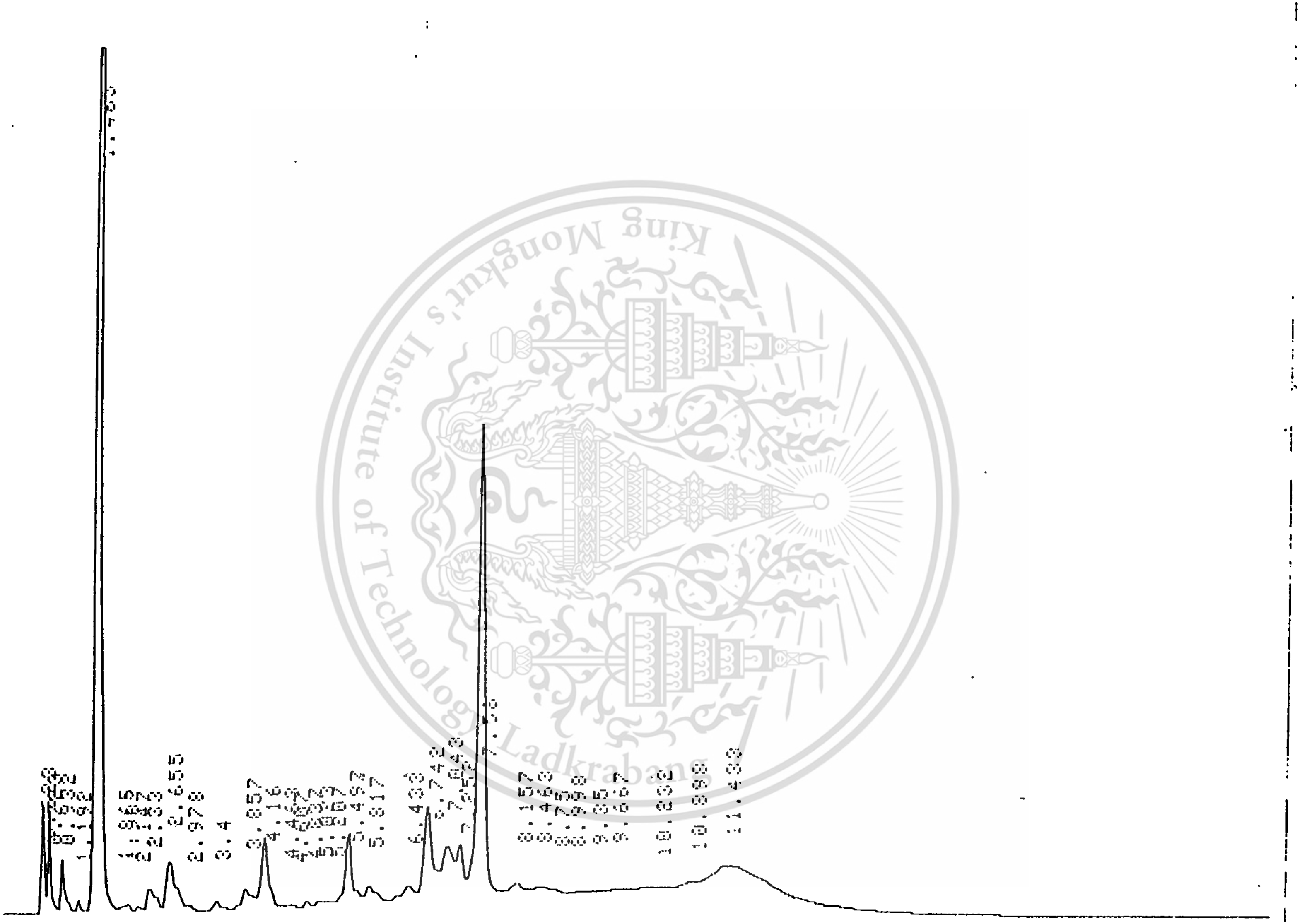
NR-g-Acrylamide 30%

Fig. E-21



NR-g-Acrylamide 50%

Fig. E-22



NR-g-Acrylmide 70%

Fig. E-23

Appendix F

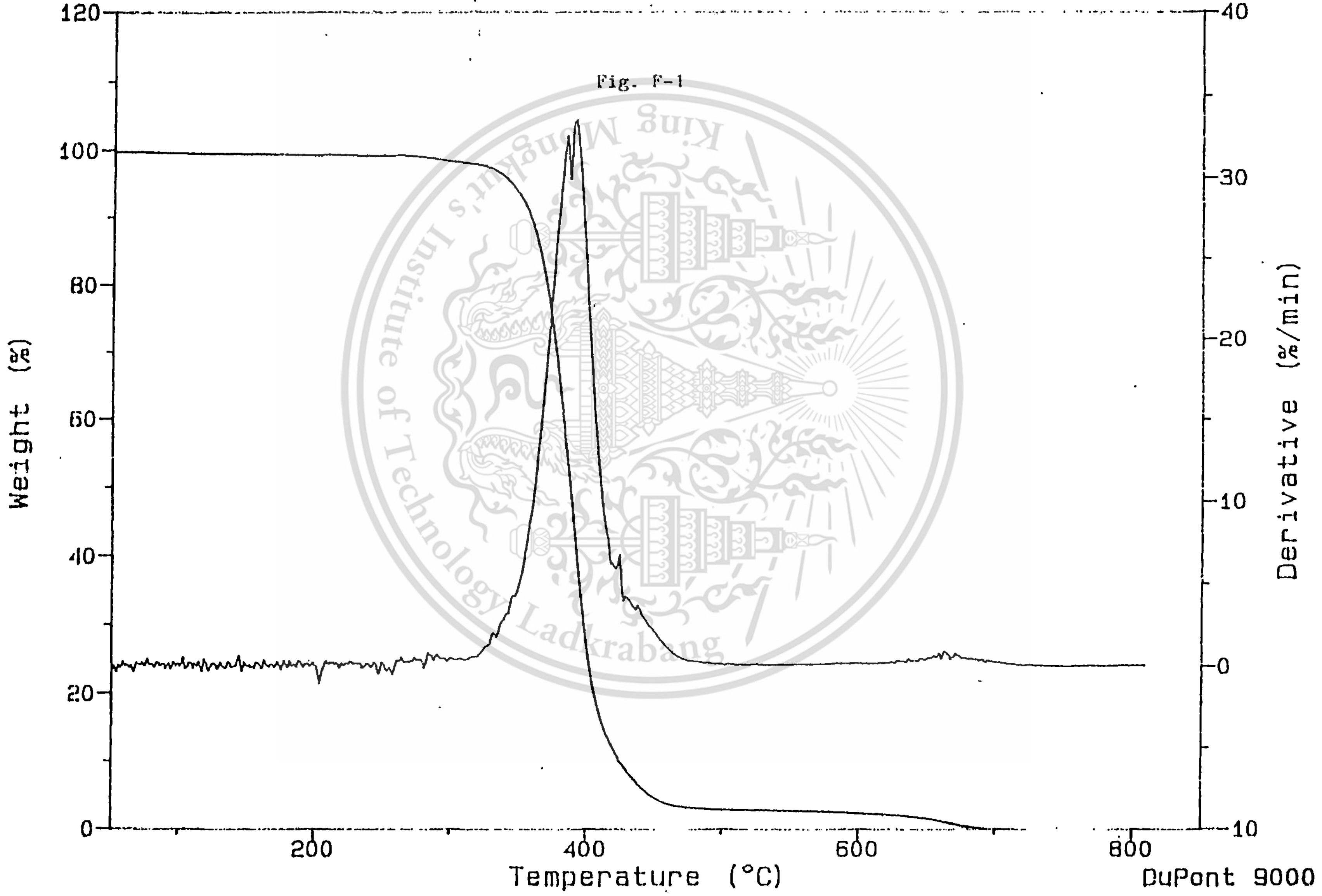
Show the TGA thermogram of natural rubber and graft copolymers.

Sample: NR.
Size: 6.0840 mg Kcell: 1.0000
Method: NR.
Comment: N2

TGA

Run: 17
Operator: PC
CONTROL

Fig. F-1

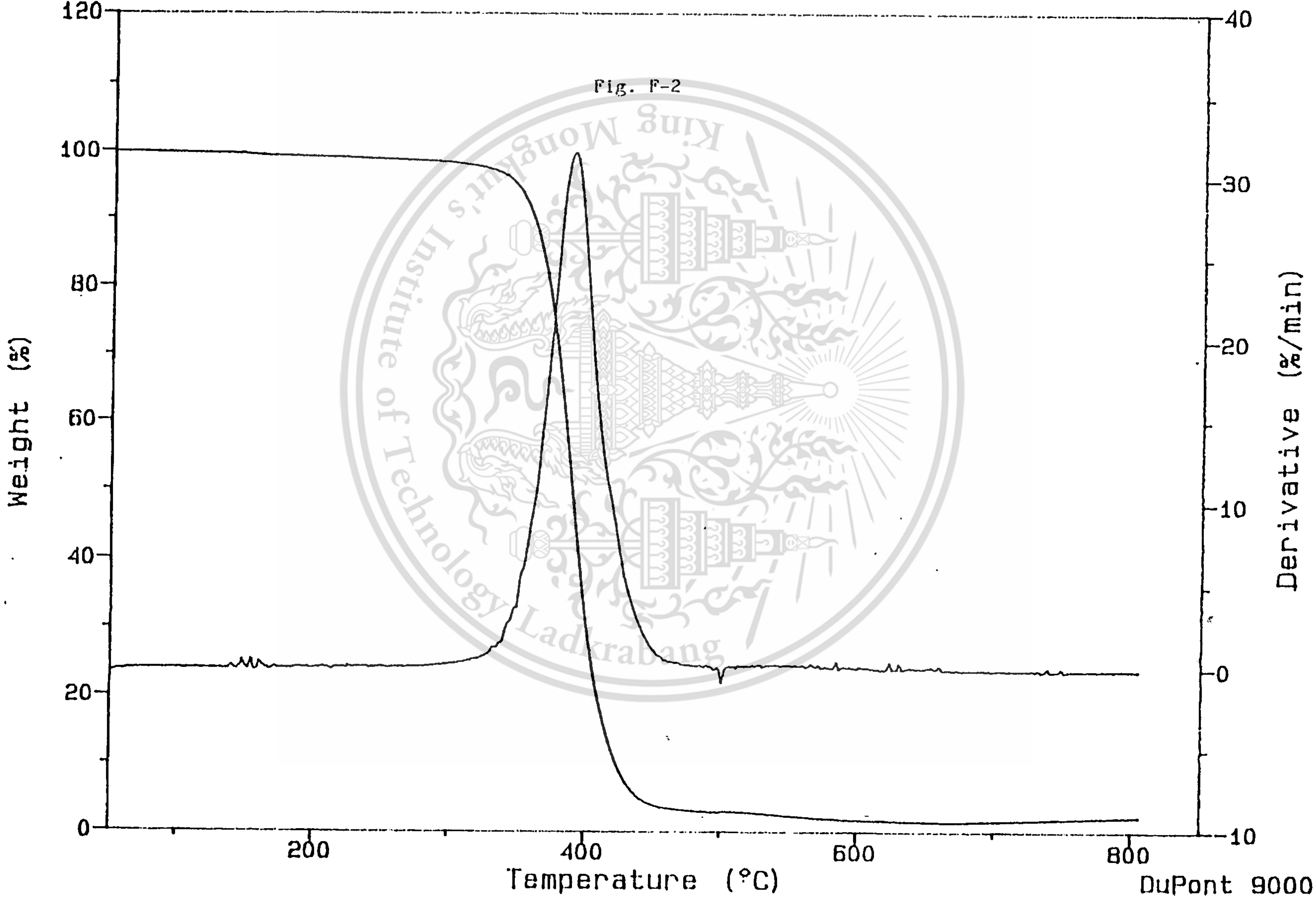


Sample: MMA30%
Size: 6.9920 mg Kcell: 1.0000
Method: MMA30%+ACRYLIC5%
Comment: N2

TGA

Run: 9
Operator: PC
CONTROL

Fig. F-2



Sample: MMA30%+ACRYLIC5%
Size: 6.9920 mg Kcell: 1.0000
Method: MMA30%+ACRYLIC5%
Comment: N2

TGA

Run: 9
Operator: PC
CONTROL

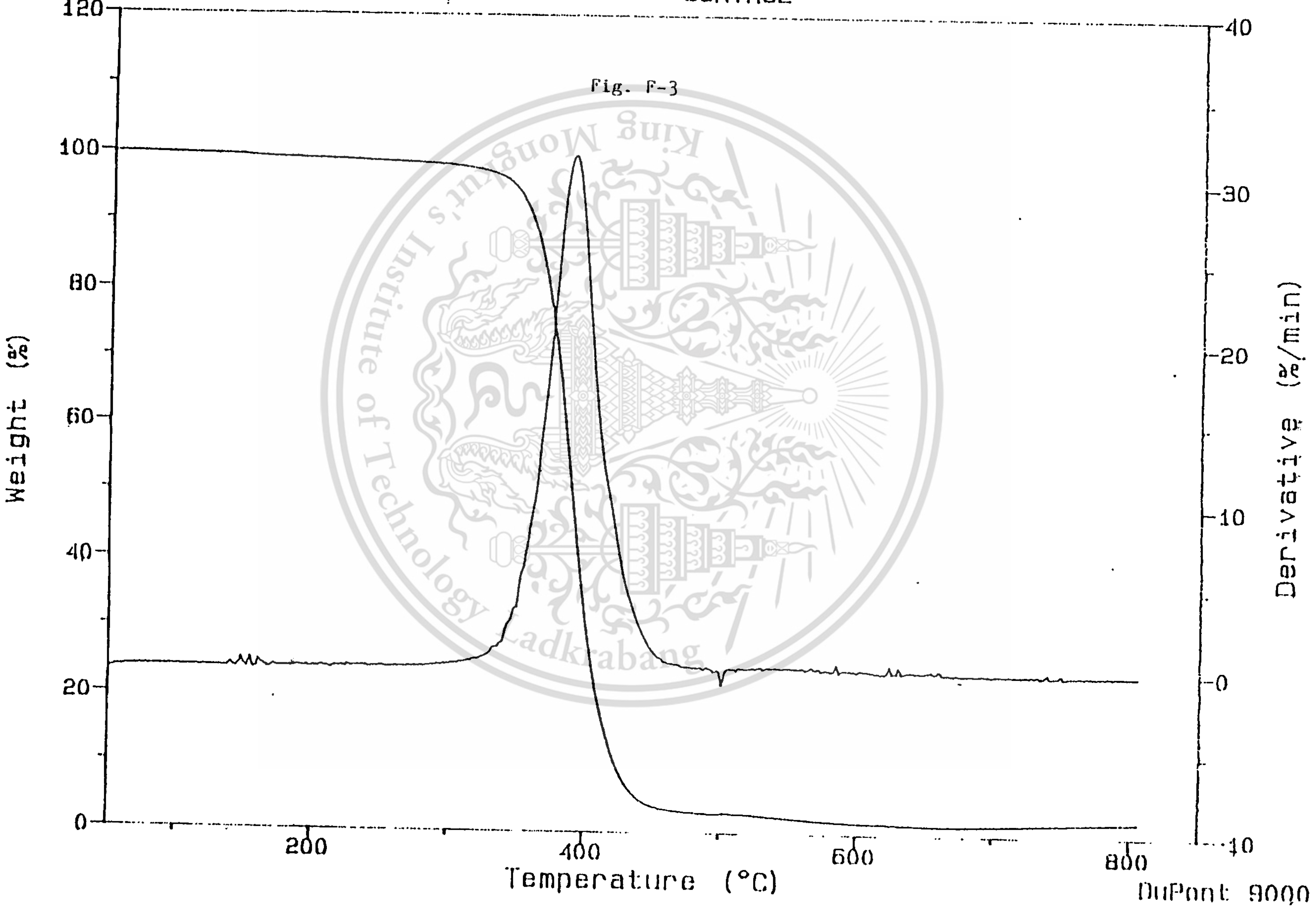


Fig. F-3

Sample: MMA30%+ACRYLIC5% (200 L.)
Size: 6.9920 mg Kcell: 1.0000
Method: MMA30%+ACRYLIC5%
Comment: N2

TGA

Run: 9
Operator: PC

CONTROL

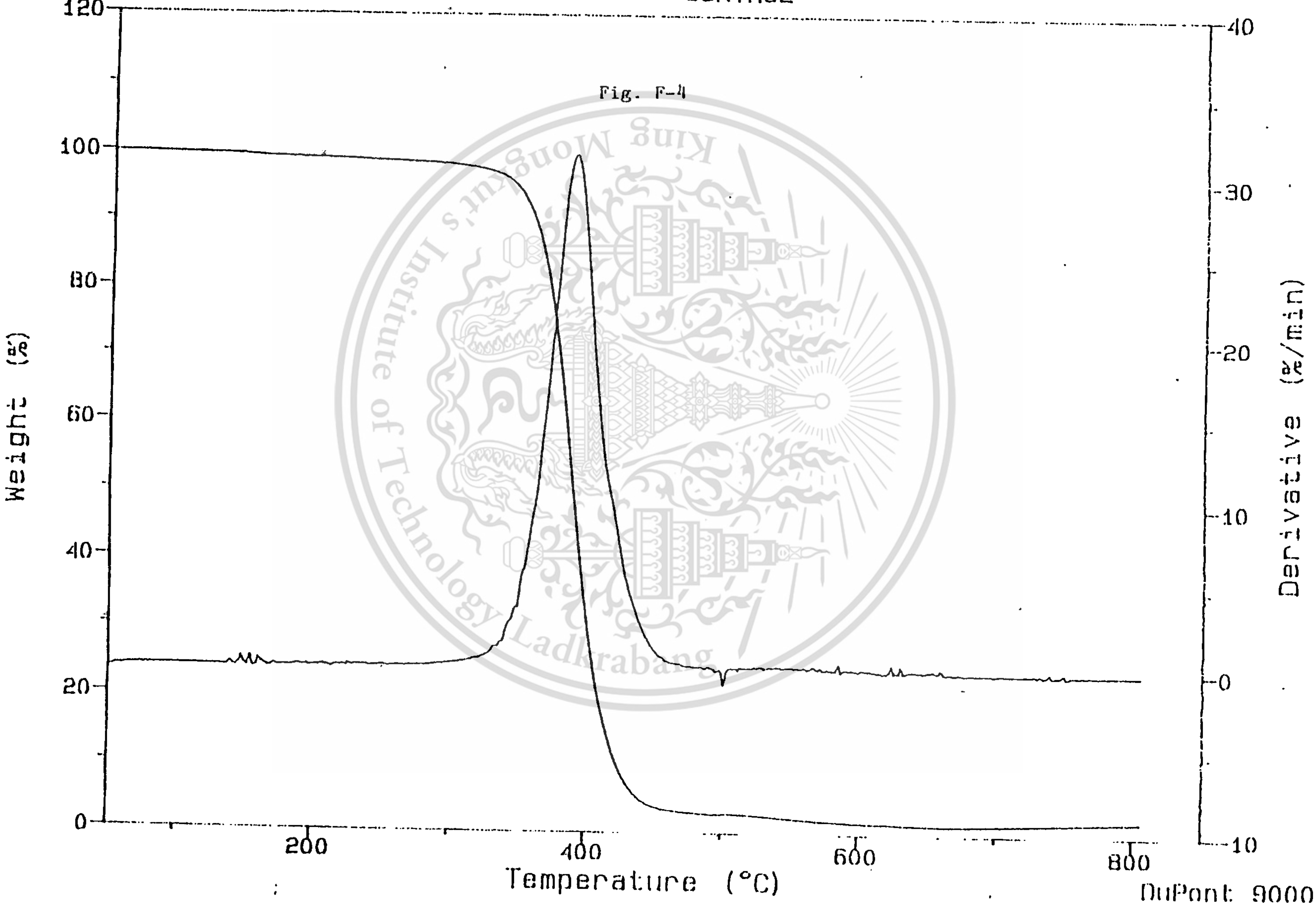


Fig. F-4

Sample: MMA30%+ACRYLIC10%
Size: 7.0430 mg Kcell: 1.0000
Method: MMA30%+ACRYLIC10%
Comment: N2

TGA

Run: 2
Operator: PC
CONTROL

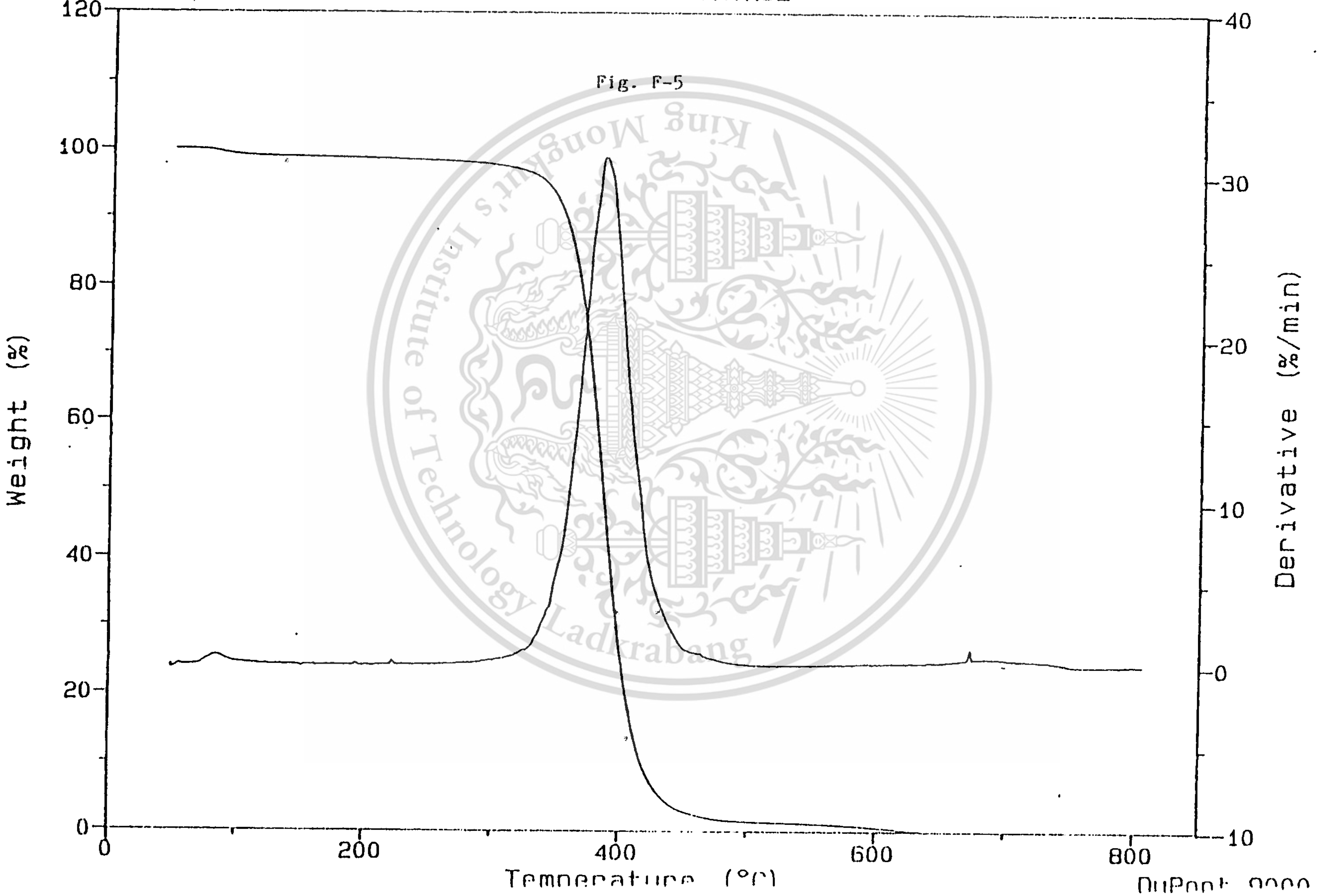


Fig. F-5

Sample: MMA30%+ACRYLIC20%
Size: 13.0170 mg Kcell: 1.0000
Method: MMA30%+ACRYLIC20%
Comment: N2

TGA

Run: 3
Operator: PC
CONTROL

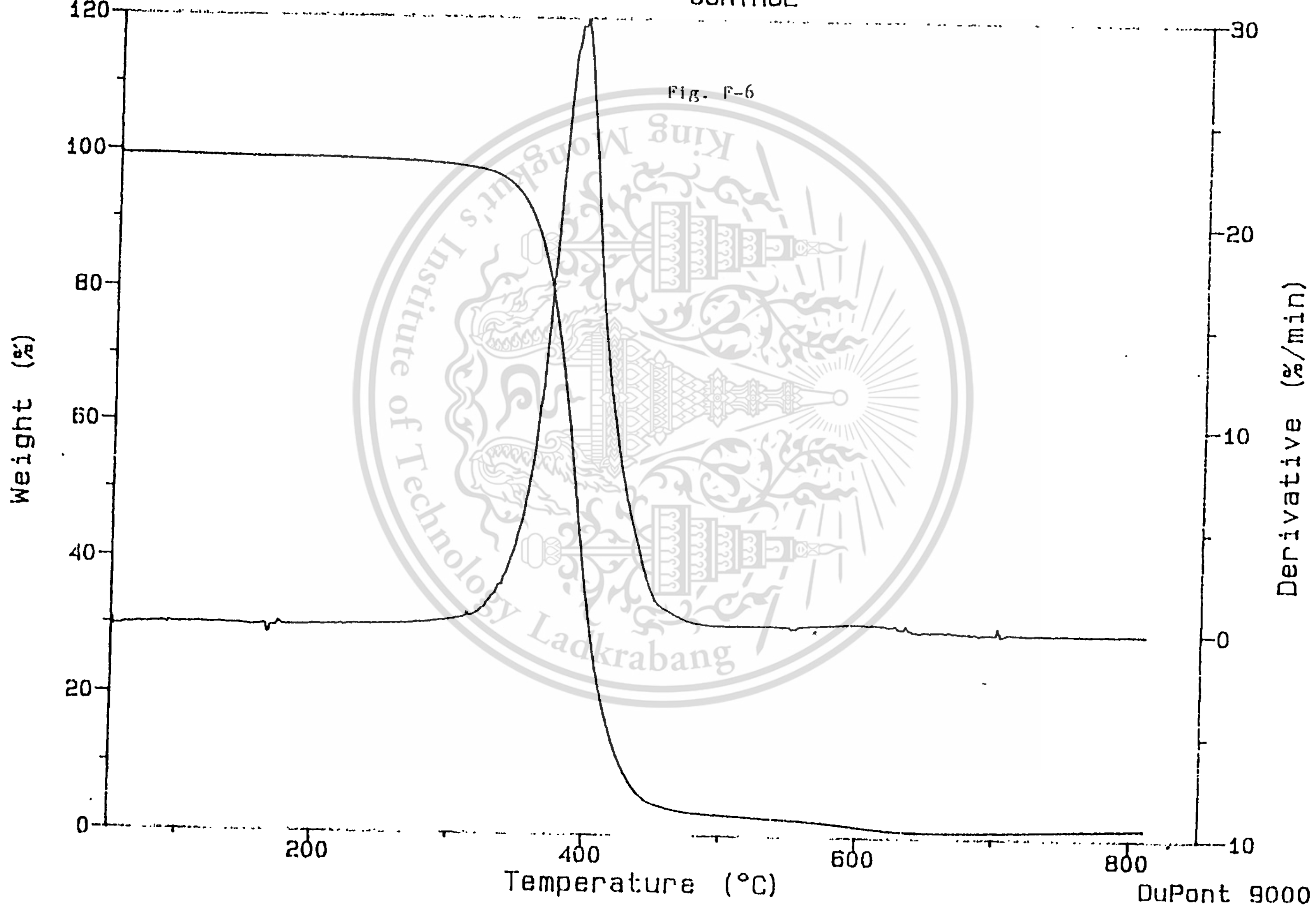


Fig. F-6

Sample: MMA30%+ACRYLIC30%
Size: 9.6770 mg Kcell: 1.0000
Method: MMA30%+ACRYLIC30%
Comment: N2

TGA

Run: 4
Operator: PC
CONTROL

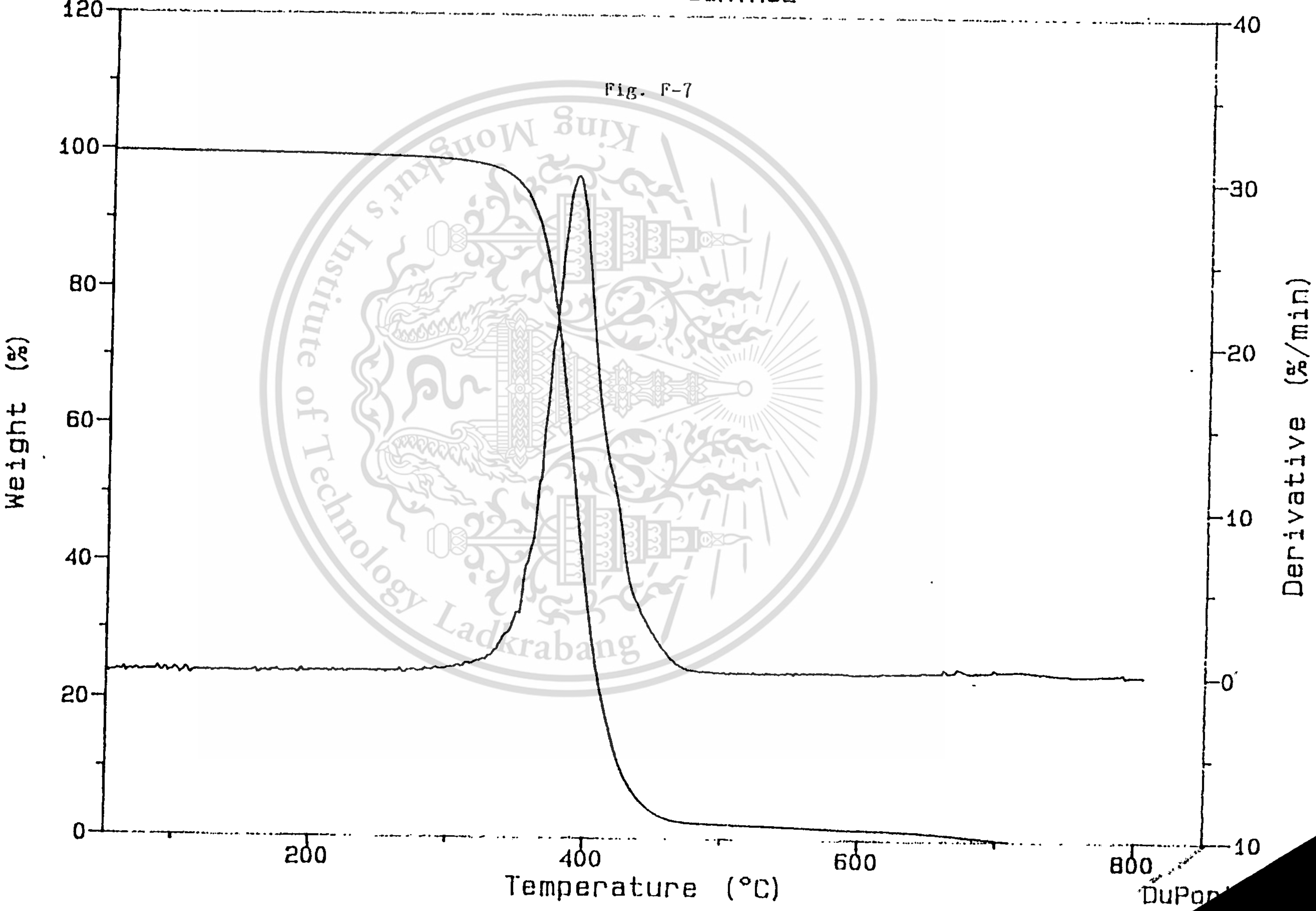


Fig. F-7

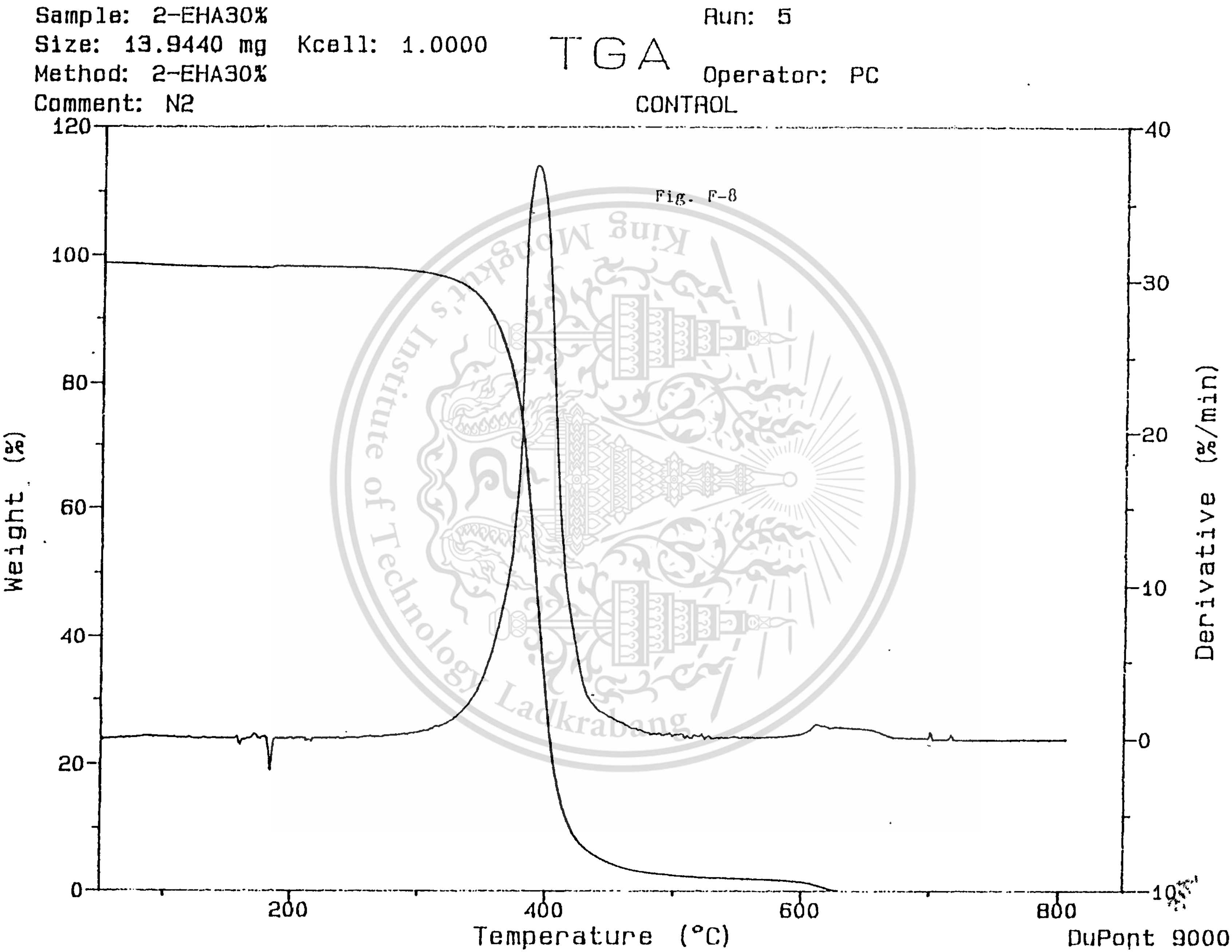

Sample: 2-EHA30%
Size: 13.9440 mg Kcell: 1.0000
Method: 2-EHA30%
Comment: N2
TGA
Run: 5
Operator: PC
CONTROL
Weight (%)
120
100
80
60
40
20
0
Derivative (%/min)
40
30
20
10
0
-10
200
400
600
800
Temperature (°C)
DuPont 9000

Fig. F-8

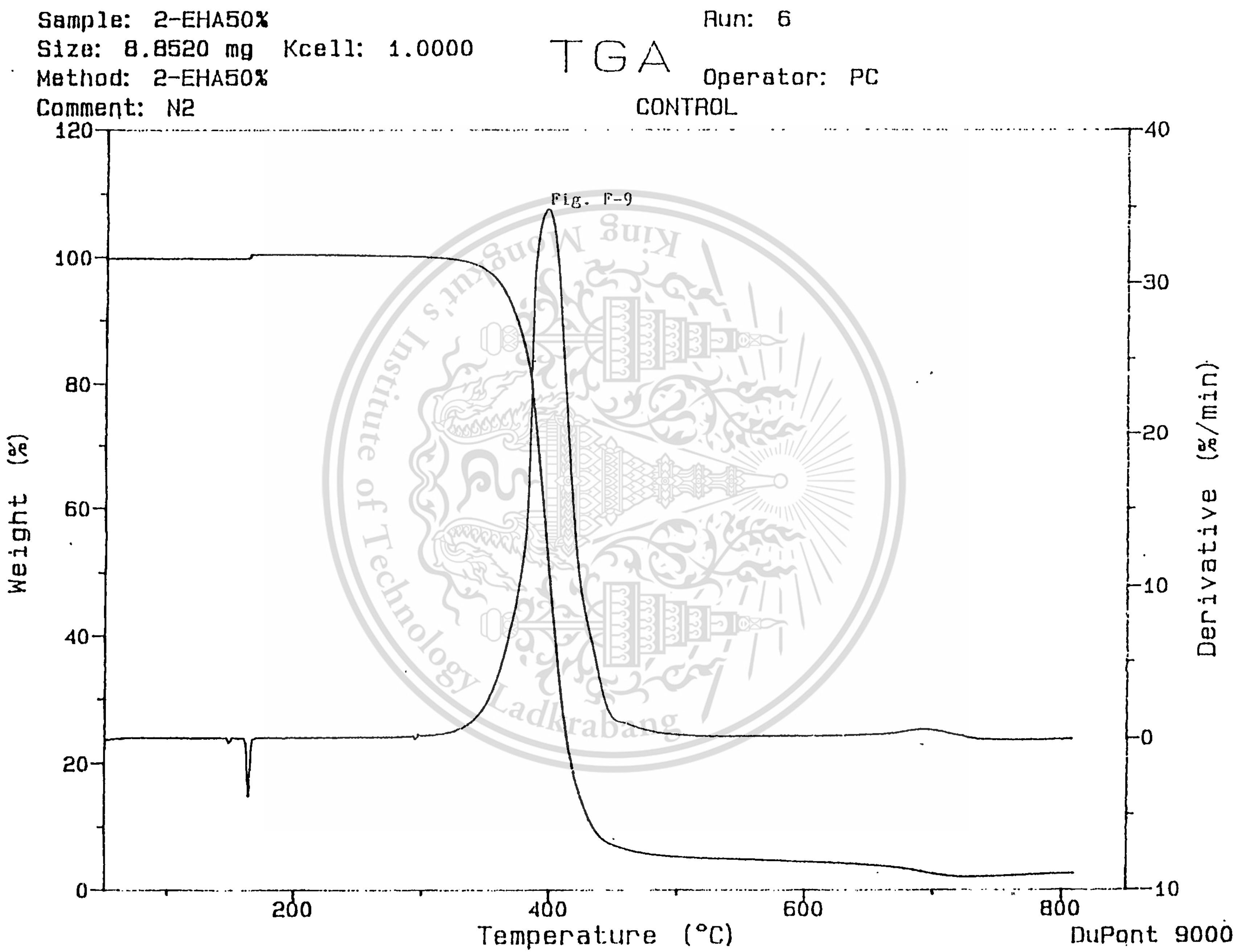

Sample: 2-EHA50%
Size: 8.8520 mg Kcell: 1.0000
Method: 2-EHA50%
Comment: N2
TGA
Run: 6
Operator: PC
CONTROL
Weight (%)
120
100
80
60
40
20
0
Derivative (%/min)
40
30
20
10
0
-10
200
400
600
800
Temperature (°C)
DuPont 9000

Fig. F-9

Sample: 2-EHA70%
Size: 6.7930 mg Kcell: 1.0000
Method: 2-EHA70%
Comment: N2

TGA

Run: 8
Operator: PC
CONTROL

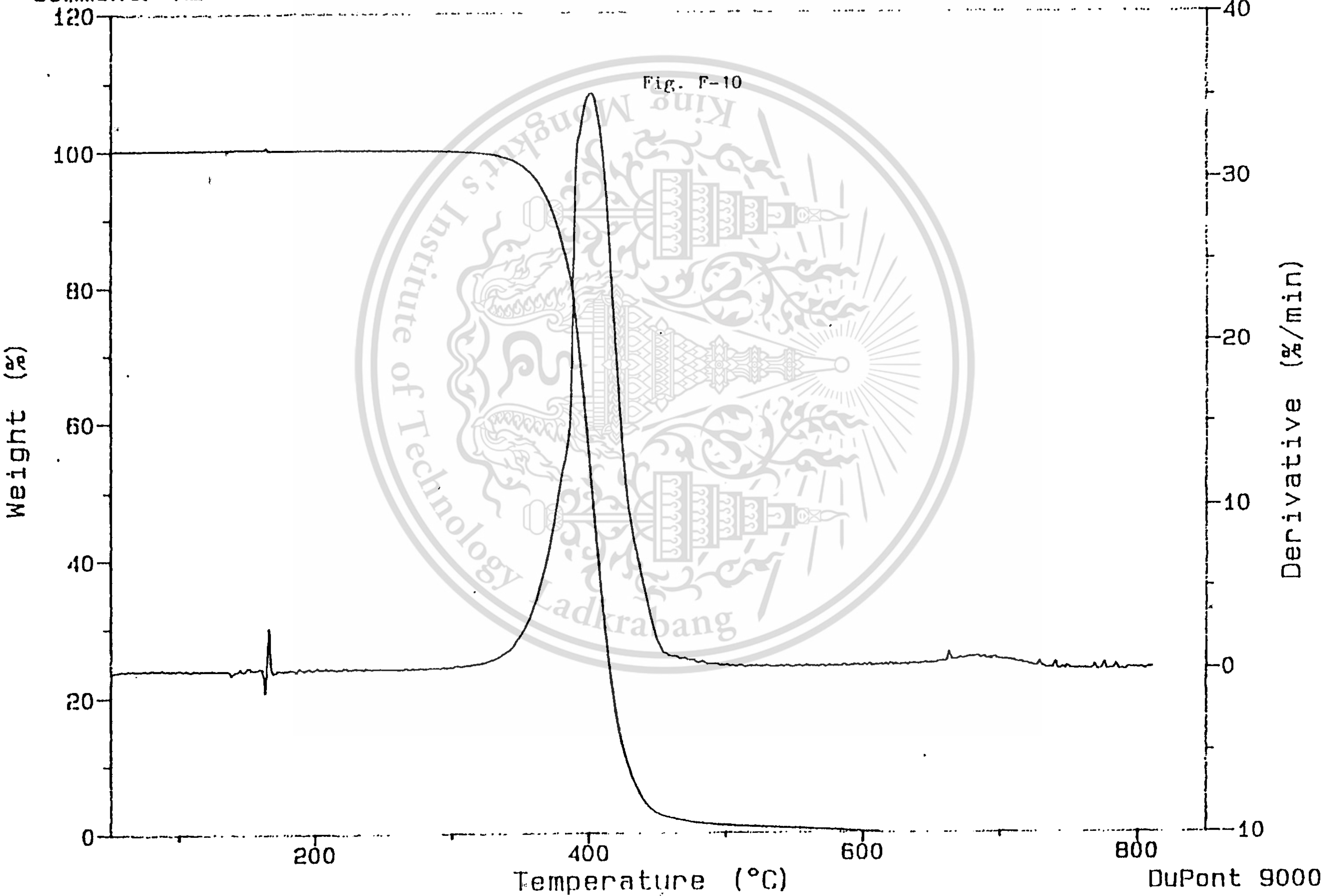
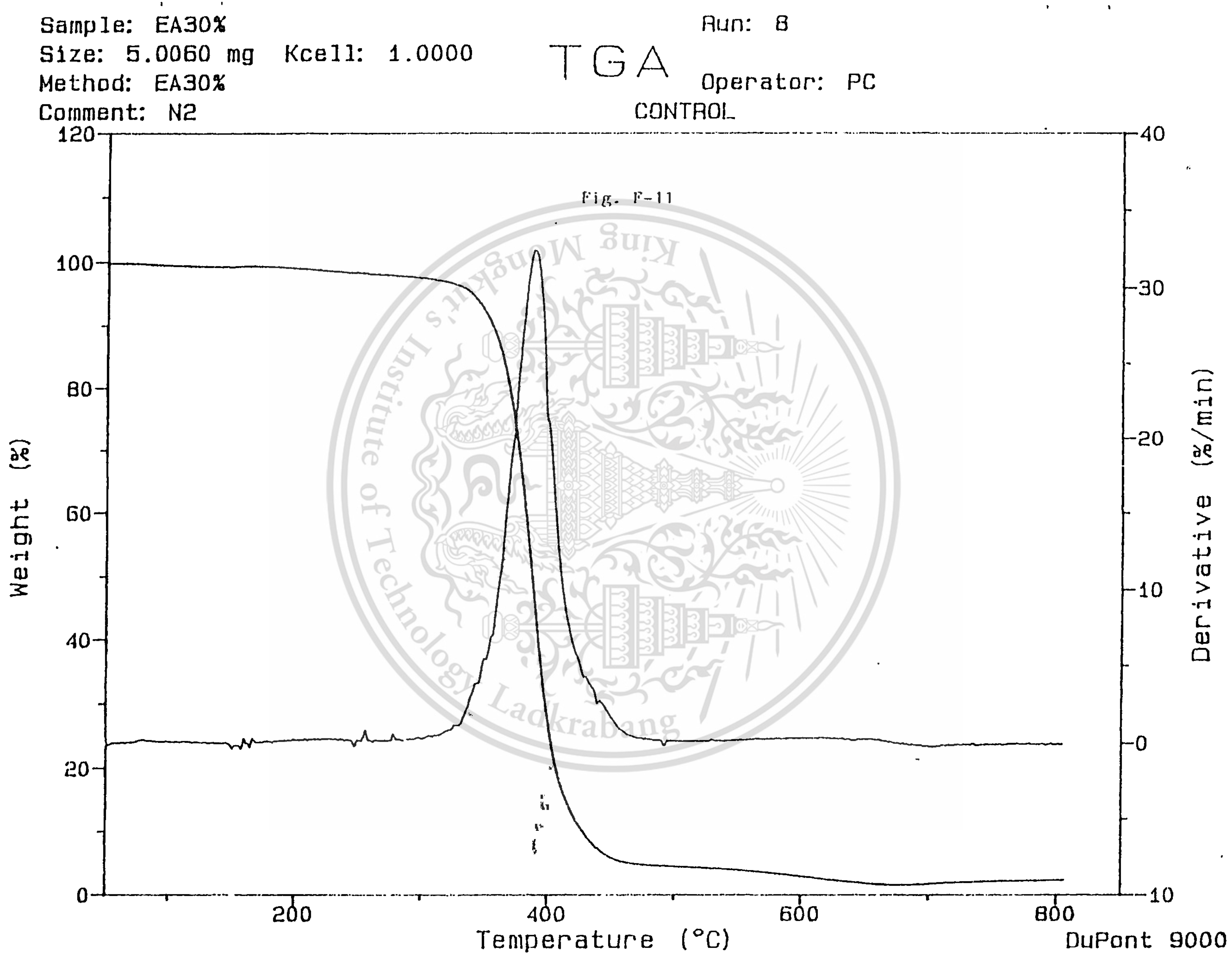


Fig. F-10

Fig. F-11


Sample: EA30%
Size: 5.0060 mg Kcell: 1.0000
Method: EA30%
Comment: N2
TGA
Run: 8
Operator: PC
CONTROL
Weight (%)
120
100
80
60
40
20
0
Derivative (%/min)
40
30
20
10
0
10
200
400
600
800
Temperature (°C)
DuPont 9000

Sample: BA30%
Size: 6.1760 mg Kcell: 1.0000
Method: BA30%
Comment: N2

Run: 11

TGA

Operator: PC

CONTROL

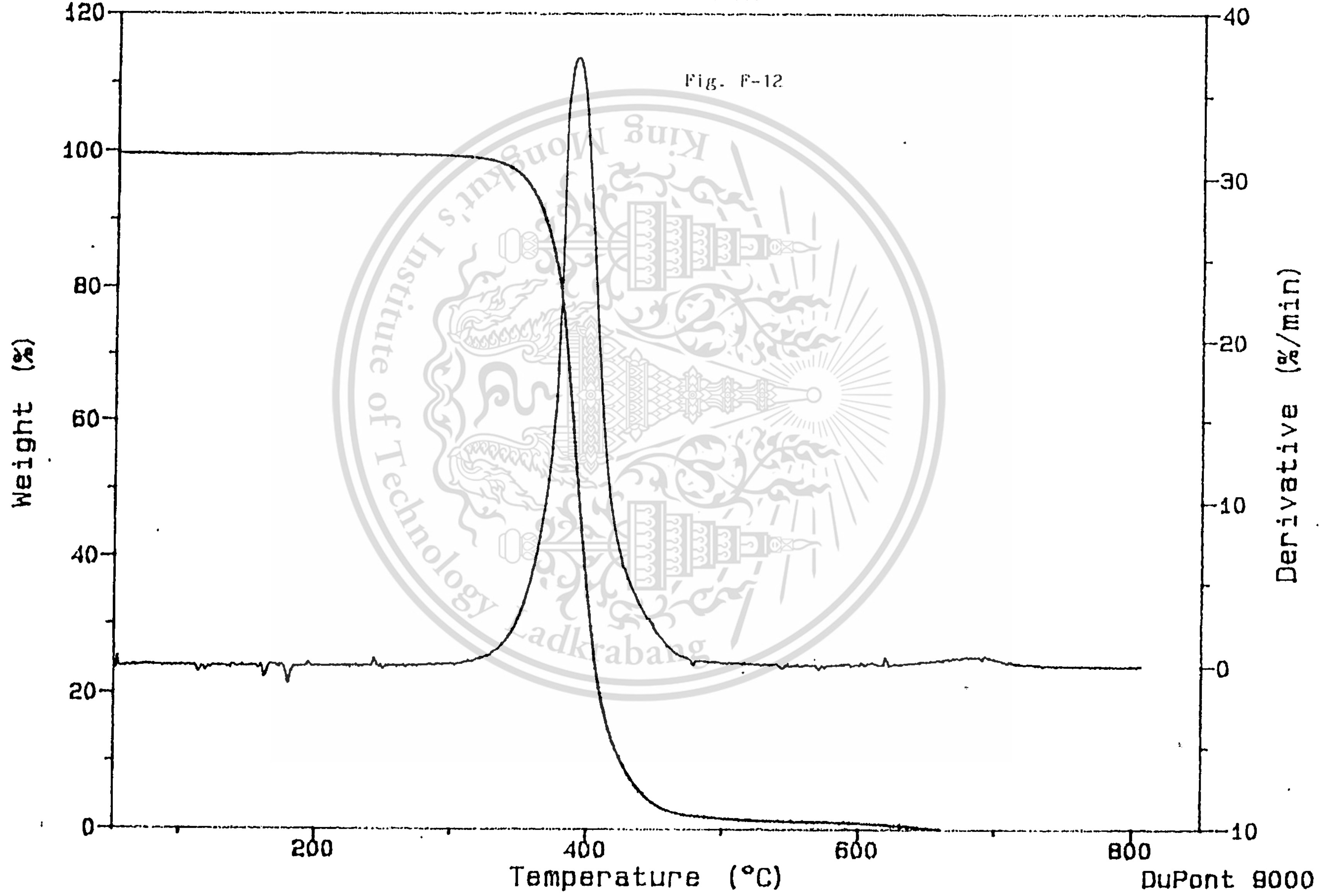


Fig. F-12

Sample: ACRYLIC ACID30%
Size: 6.0010 mg Kcell: 1.0000
Method: ACRYLIC ACID30%
Comment: N2

TGA

Run: 16
Operator: PC
CONTROL

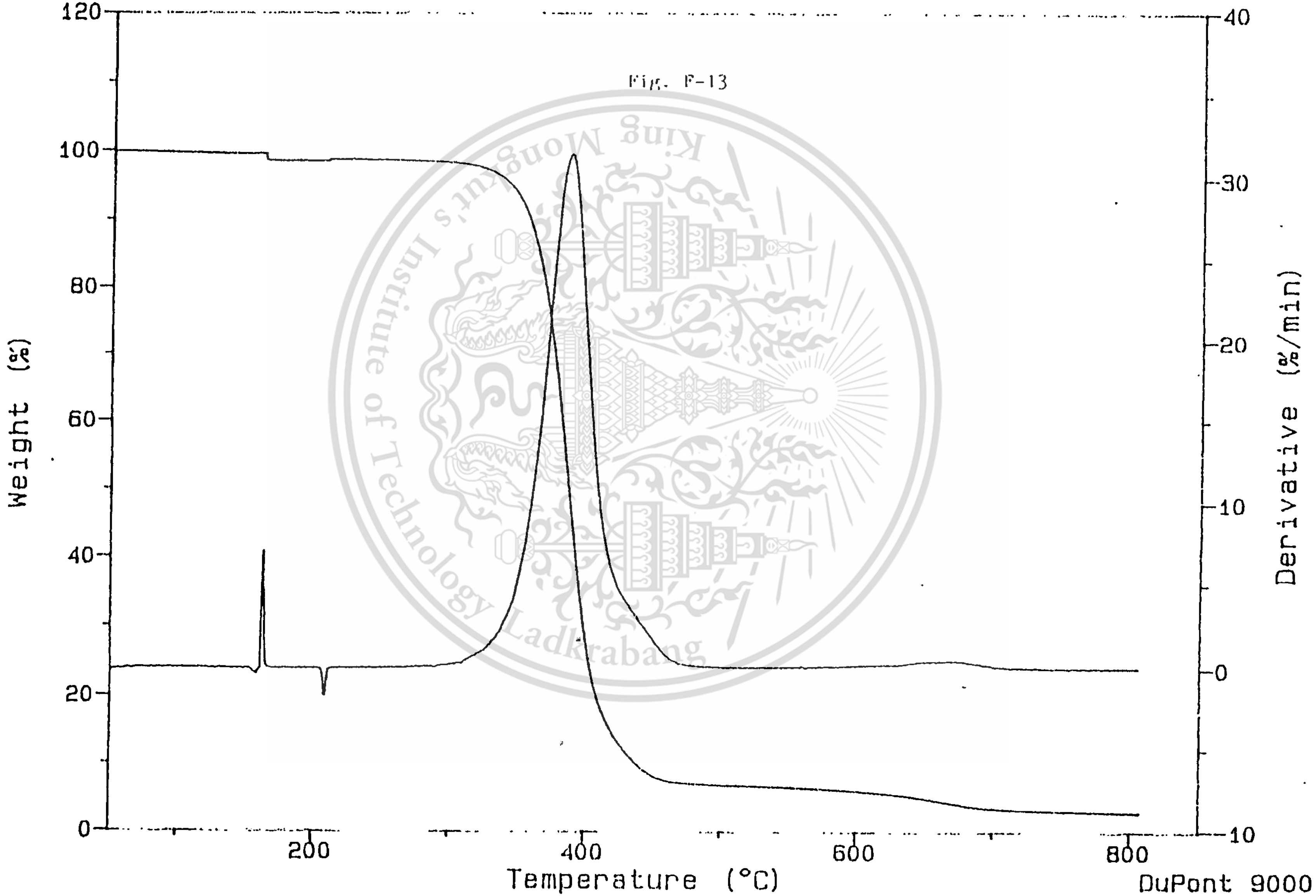


Fig. F-13

Sample: ACRYLAMIDE30%
Size: 8.5460 mg Kcell: 1.0000
Method: ACRYLAMIDE30%
Comment: N2

Run: 15

TGA

Operator: PC

CONTROL

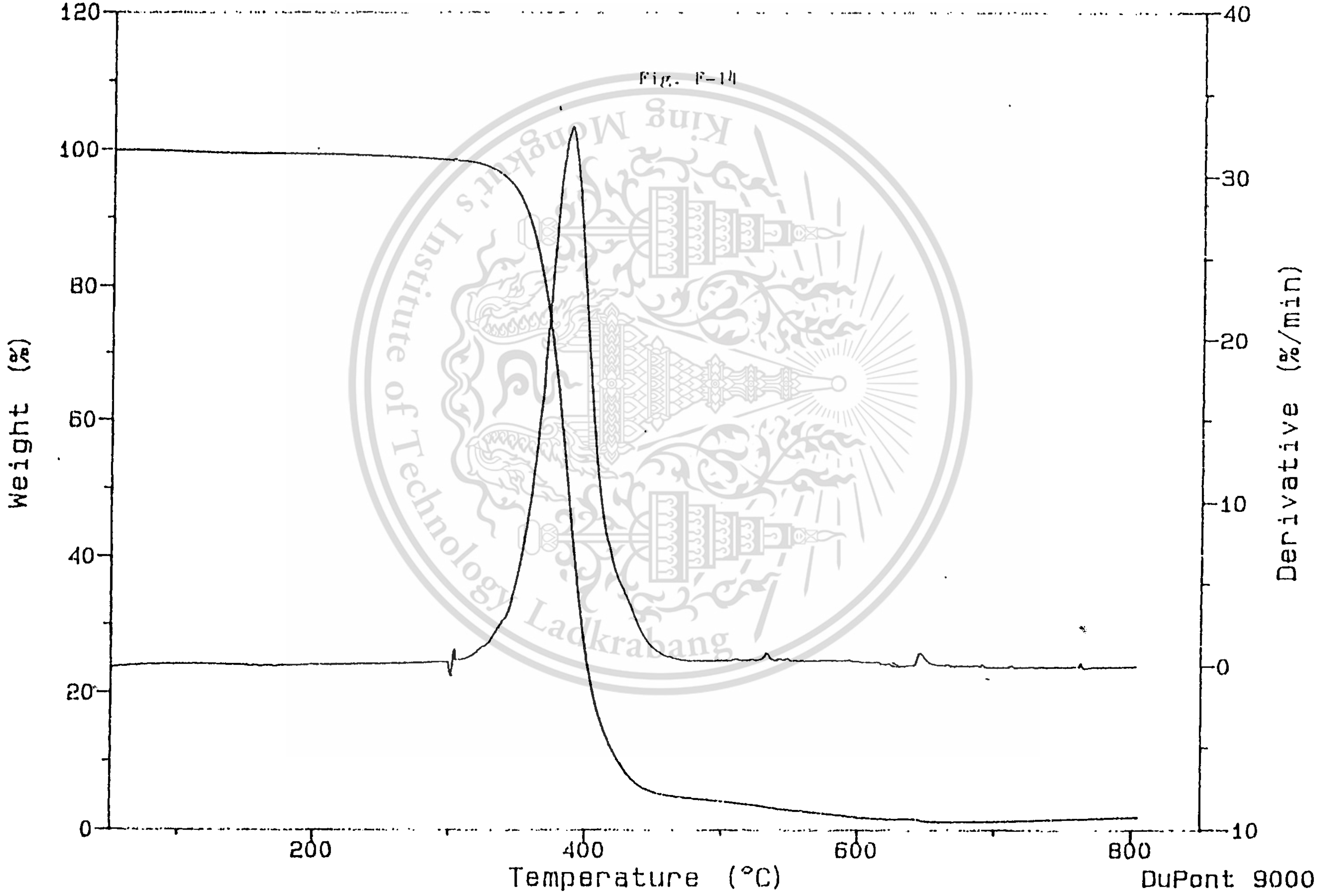


Fig. F-14

Sample: VINYL ACETATE30%
Size: 8.2400 mg Kcell: 1.0000
Method: VINYL ACETATE30%
Comment: N2

Run: 14

TGA

Operator: PC

CONTROL

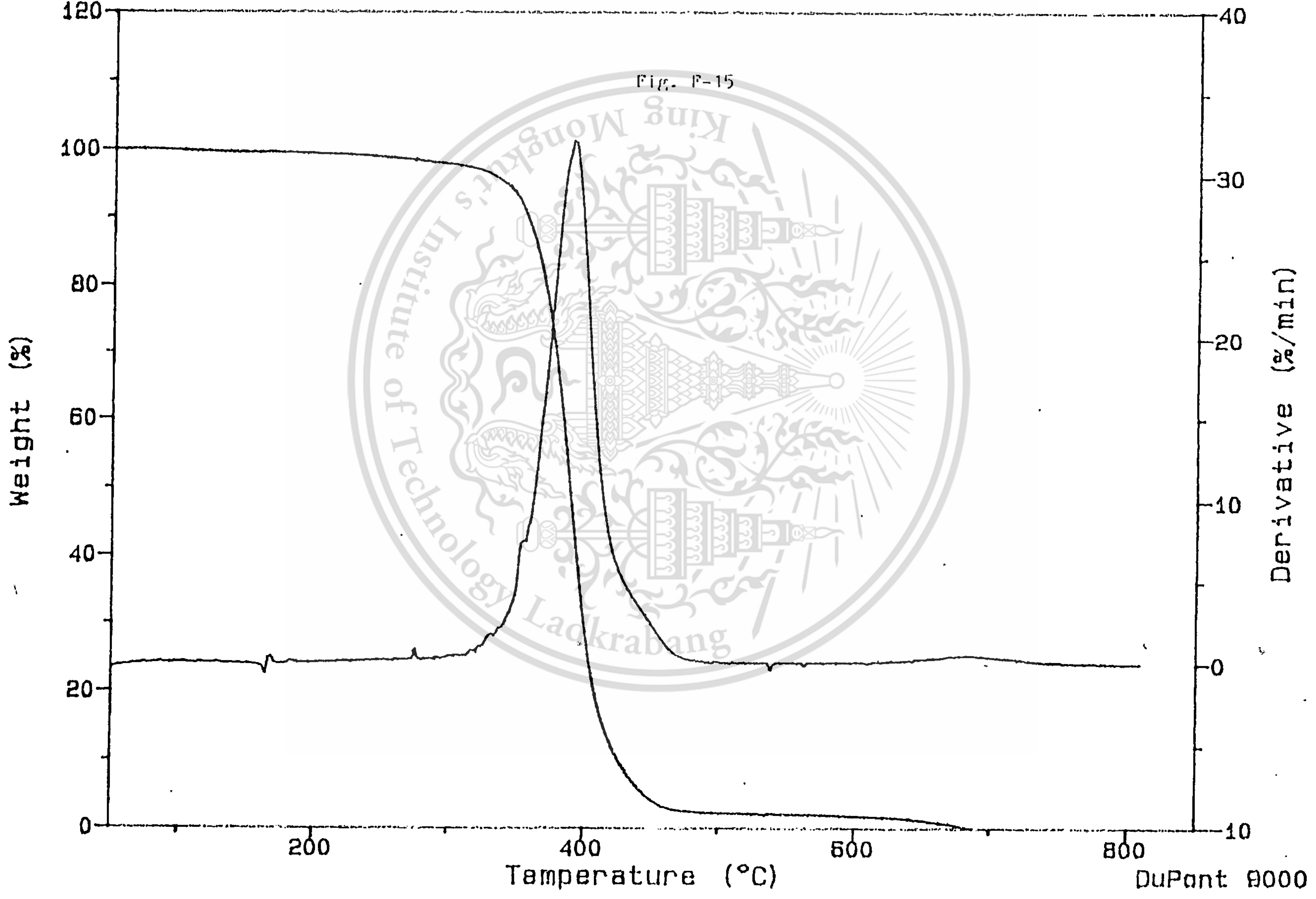


Fig. F-15

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