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นางกุสุมภ์จิณณ์ ศรีรัตนัย

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

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ENCAPSULATION OF LEWIS ACID CATALYSTS

Mrs. Kusoomjin Srirattnai

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

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By	Mrs.Kusoomjin Srirattnai
Field of Study	Chemical Technology
Thesis Advisor	Professor Somsak Damronglerd, Dr. Ing.
Thesis Co-advisor	Professor Shinzo Omi, Ph.D.
Thesis Co-advisor	Associate Professor Sophon Roengsumran, Ph.D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Doctor's Degree

……..Deputy Dean for Administrative Affairs Acting Dean, Faculty of Science
(Associate Professor Pipat Karntiang, Ph.D.)

THESIS COMMITTEE

…….. Chairman
(Associate Professor **Pornpote Piumsomboon,** Ph.D.)

…….…. Thesis Advisor
(Professor Somsak Damronglerd, Dr. Ing.)

…….. Thesis Co-advisor
(Professor Shinzo Omi, Ph.D.)

…….. Thesis Co-advisor
(Associate Professor Sophon Roengsumran, Ph.D.)

…….. Member
(Professor Pramote Chaivej, Ph.D.)

…….. Member
(Associate Professor Amorn Petsom, Ph.D.)

…….. Member
(**Assistant Professor Somkiat Ngamprasertsith**, Dr.de l'INPT)

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จุดประสงค์ของงานวิจัยนี้คือการใช้เทคนิคเอนแคปซูเลชันเพื่อเพิ่มเสถียรภาพของตัวเร่งปฏิกิริยากรดลิวอิสที่ใช้เป็นตัวเร่งปฏิกิริยาเคมีอย่างกว้างขวางในอุตสาหกรรมต่างๆ งานวิจัยนี้แบ่งออกเป็น 6 ส่วนแยกตามเทคนิคหรือชนิดของพอลิเมอร์ที่ใช้เป็นผนังแคปซูล ส่วนแรกใช้พอลิสไตรีนเป็นผนังแคปซูลในระบบ o/w, ส่วนที่ 2 ใช้ พอลิเอไมด์เป็นผนังแคปซูลโดยเทคนิค อินเตอร์เฟเชียลพอลิคอนเดนเซชัน, ส่วนที่ 3 ใช้โคพอลิเมอร์ระหว่างสไตรีนและไดไวนิลเบนซีนเป็นผนังแคปซูล, ส่วนที่ 4 ใช้พาราฟินแวกซ์และขี้ผึ้งเป็นผนังแคปซูล, ส่วนที่ 5 ใช้ พอลิสไตรีนเป็นผนังแคปซูลในระบบ o/o, ส่วนที่ 6 ใช้พอลิบิวตะไดอีน และโคพอลิเมอร์ระหว่างสไตรีนและไดเมทิลอะมีโนเอทิลเมทาคริเลตเป็นผนังแคปซูล ส่วนสารที่ถูกเคลือบไว้ภายในใช้ กรดลิวอิสสแคนเดียมไตรฟลูออโรมีเทนซัลโฟเนตและอะลูมิเนียมไตรคลอไรด์ ผลการทดลองพบว่าแคปซูลที่เตรียมโดยใช้ไฮโดรจีเนตพอลิบิวตะไดอีน และโคพอลิเมอร์ระหว่างสไตรีน และไดเมทิลอะมีโนเอทิลเมทาคริเลตเป็นผนังแคปซูล, อะลูมิเนียมไตรคลอไรด์เป็นสารที่ถูกเคลือบไว้ภายในโดยเทคนิคระเหยตัวทำละลายมีเสถียรภาพมากที่สุดที่ภาวะดังนี้ 10%โดยมวลของไฮโดรจีเนตพอลิบิวตะไดอีน และ 10%โดยมวลของโคพอลิเมอร์ระหว่างสไตรีนและไดเมทิลอะมีโนเอทิลเมทาคริเลต, ปริมาณตัวทำให้เสถียรพอลิบิวตะไดอีนเหลว 2% โดยมวล แคปซูลที่ได้เป็นตัวเร่งปฏิกิริยาที่มีประสิทธิภาพในปฏิกิริยาอัลคิลเลชันของเบนซีนและ 1-โดเดคซีน โดยผลจากการวิเคราะห์ด้วยเครื่องแก๊สโครมาโทกราฟีได้สารประกอบอัลคิลเบนซีนต่างๆ เป็นผลิตภัณฑ์ คือ 2-phenyl dodecane, 3-phenyl dodecane, 4-phenyl dodecane, 5-phenyl dodecane และ 6-phenyl dodecane นอกจากนี้แคปซูลที่เตรียมได้ยังสามารถรักษาประสิทธิภาพในการเร่งปฏิกิริยาได้ในระยะยาว

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ภาควิชา เคมีเทคนิค	ลายมือชื่อนิสิต .....
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KUSOOMJIN SRIRATTNAI : THESIS TITLE ENCAPSULATION OF LEWIS ACID CATALYSTS THESIS ADVISOR : PROF. SOMSAK DAMRONGLERD, Dr. Ing., THESIS COADVISOR : PROF. SHINZO OMI, Ph.D., ASSOC. PROF. SOPHON ROENGSUMRAN, Ph.D., 119 pp. ISBN 974-031-089-3.

The emphasis in this study was on the establishment of an encapsulation procedure to preserve highly reactive Lewis acids which are widely used in organic reaction and industries but easily lose activity in the air or a highly moist atmosphere by using encapsulation techniques. The capsules were prepared by six different polymer walls and several techniques: polystyrene as wall material in an oil/water system, polyamide as wall material with interfacial polycondensation, poly(styrene-DVB) as wall material, paraffin and beeswax as wall materials, polystyrene as wall material in oil/oil system, and poly(styrene-*co*-dimethylaminoethyl methacrylate), P(St-*co*-DMAEMA) and hydrogenated telechelic polybutadiene (Sat. PB) as wall materials. For the core material, scandiumtrifluorometanesulfonate (ScTf) and aluminium trichloride ($AlCl_3$) were used. The capsules prepared by using 10 wt% P(St-*co*-DMAEMA), 10 wt% Sat. PB, 2 wt% of stabilizer liquid polybutadiene (PBD), and $AlCl_3$ as the core material by solvent evaporation technique gave a high stability and catalytic activity in the reaction of benzene and 1-dodecene, and also keep capsules for the long-term use. Using gas chromatography-mass spectrometry, the positional isomers of phenyl dodecane (2-, 3-, 4-, 5- and 6-) were obtained.

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

Department Chemical Technology Student's signature .....
Field of Study Chemical Technology Advisor's signature .....
Academic Year 2001 Co-advisor's signature .....
Co-advisor's signature .....

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CHAPTER 1

INTRODUCTION

INTRODUCTION

Friedel-Crafts reactions are amongst the most important reactions in organic synthesis. In the course of more than 100 years of Friedel-Crafts chemistry, only two catalysts, $AlCl_3$ and BF_3, have gained wide recognition [1]. Especially, anhydrous $AlCl_3$ has maintained its use ever since it was introduced by Friedel and Crafts [2], despite some unfavorable properties such as decomposition or deactivation in water, safety and lack of recoverability. Lewis acid catalyzed reactions are still of great interest because of unique reactivities and selectivities that can be achieved as well as the mild conditions used [3].

The alkylbenzenes are widely used as raw materials for detergents. Two kinds of alkylated products have gained industrial importance as intermediates for the production of anionic surfactants by subsequent processing to alkylarylsulfonates: The branched-chain type refered to “hard detergent alkylate” which had a rapid growth for ten years until 1965. Its use as a raw material for domestic detergents was discontinued because of foaming in rivers and at sewage-treatment plants, caused by the low rate of biodegradation. The “linear detergent alkylates“ or soft detergent alkylates have replaced ABS (alkylbenzene sulfonate) wherever high consumption and regulations require a more rapid and complete degradation. Replacement of ABS has taken place in almost all countries. The propylene tetramer type is still manufactured for use in countries that have not reached a high consumption and where accumulation in the environment has not yet been legislated. It is also used for specialized purposes such as agricultural emulsifiers. “Linear alkylbenzenes” are known as LAB, and after conversion by sulfonation to “linear alkylbenzenesulfonates”, they are called LAS. Production of LAB, together with the detergent alcohol, has experienced continued growth as a result of increased per-capita consumption of detergents, a change in detergent formulation and the proven biodegradability of these materials. LAB is derived exclusively from benzene and petroleum or natural gas-based feedstocks, in general paraffins derived from kerosene. Olefins derived from ethylene are sometimes used in place of paraffins. The market of LAB is expected to increase faster in developing countries as a result of the increased

per-capita surfactant use and the replacement of laundry bar soap and nonbiodegradable alkylbenzene [4].

LAB production by alkylation of benzene is normally carried out by using Lewis acid as a catalyst. There are two major catalysts for the industrial production of LAB: $AlCl_3$ and HF. However, most Lewis acids decompose or deactivate in water. Water often interferes with an organic reactions. Although Lewis acids or organometallic reagents have played an important role in modern organic synthesis, even a small amount of water stops reactions using these reagents because the reagents immediately react with water rather than the substrates [5]. Therefore, polymer catalysts are alternative choices.

The utilization of polymer-supported catalysts offers several advantages in preparative procedures. The simplification of the workup and separation of products and catalysts are useful for industrial processes. There are a few examples of polymer-supported Lewis acids [6-11]. They comprise a polymer carrier attached by weak chemical or physical interactions to Lewis acid. The Lewis acid can be partially washed out of the polymer support during reaction [12]. For the polymer-supported scandium based Lewis acids using Nafion [13] and a polyacryronitrile derivative [14], reactivities were lower than that of the monomeric Lewis acid. For polymer-supported aluminium chloride [7], $AlCl_3$ was immobilized onto polymer or inorganic support materials, but successful applications have been limited [3].

The research for novel techniques used for the modifying of catalyst properties is necessary. Microencapsulation, which is one of those techniques, has been widely investigated for several years, and it is still of great interest and useful today. Microencapsulation is a process of applying relatively thin coatings to particles of solids or droplets of liquids. There are several advantages of this useful technique; one of these is the stabilization of substances sensitive to environmental conditions. Microcapsules may be prepared by a number of methods. This research is expected that encapsulated Lewis acid catalysts could have higher activities than the monomeric Lewis acid and precedent polymer-supported Lewis acid. In this research, scandium trifluoromethanesulfonate (scandium triflate, $Sc(OTf)_3$) and Aluminium trichloride ($AlCl_3$) were selected as Lewis acid catalysts to be encapsulated using various coating materials to preserve highly reactive Lewis acid which easily loses its

activity in the air or a highly moist atmosphere. In addition, the properties and catalytic activity for organic reaction were investigated.

The objectives of this study are :

1. To study the optimum processing conditions for preparation of encapsulated Lewis acid catalysts using different wall materials.
2. To determine and compare the physicochemical characteristics of encapsulated Lewis Acid catalysts preparing from different wall materials.
3. To evaluate the effectiveness of encapsulated Lewis Acid catalysts in the Friedel-Crafts alkylation of benzene with dodecene.
4. To investigate the stability of encapsulated Lewis Acid catalysts for long-term use in the Friedel-Crafts alkylation of benzene with dodecene.

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CHAPTER 2

LITERATURE REVIEW

Theory

Microencapsulation can be described as a process in which very thin coatings of polymeric material(s) are deposited around particles of solids or droplets of liquids, and the products from this process are called microcapsules or microspheres [15-16]. The microcapsules consist of core material enclosed in a coating as shown in Figure 1. The core may also be referred to as the nucleus or fill; the coating, the wall or shell. Depending on the manufacturing process, various types of microcapsule structure can be obtained as illustrated in Figure 1. The most common type is the mononuclear spherical. The particle size of microcapsules is defined in various ranges but can be varied from approximately 1 μm to 5,000 μm [17-22]. The microencapsulation processes have been used in many industries such as pharmaceutical industry, food, food additives, cosmetics, adhesives, household products, agricultural materials, aerospace industry, and many others.

2.1 Core and Coating Materials

A core material, which is defined as the specific material to be coated, plays a significant role in microencapsulation [17-18]. It dictates the process as well as the polymer used as a coating material. It should be insoluble and nonreactive with the coating material and the manufacturing vehicle. Water soluble and insoluble solids, water immiscible liquids, solution, and dispersion of solids in liquids can be microencapsulated. The solid core can be a mixture of active constituents, stabilizers, diluents, excipients, and release rate retardants or accelerators.

Characteristics of the Core

The first consideration in choosing an encapsulation system would be the physical and chemical properties of the core material itself. This is important since solids cannot always be encapsulated by the same systems which are suitable for the encapsulation of liquids. Assuming an aqueous and/or water-soluble core is to be

encapsulated, there would be difficulties using either the simple or complex coacervation methods. On the other hand, encapsulation of the core may be accomplished by several other techniques including interfacial polymerization, polymer deposition, and several mechanical methods [23].

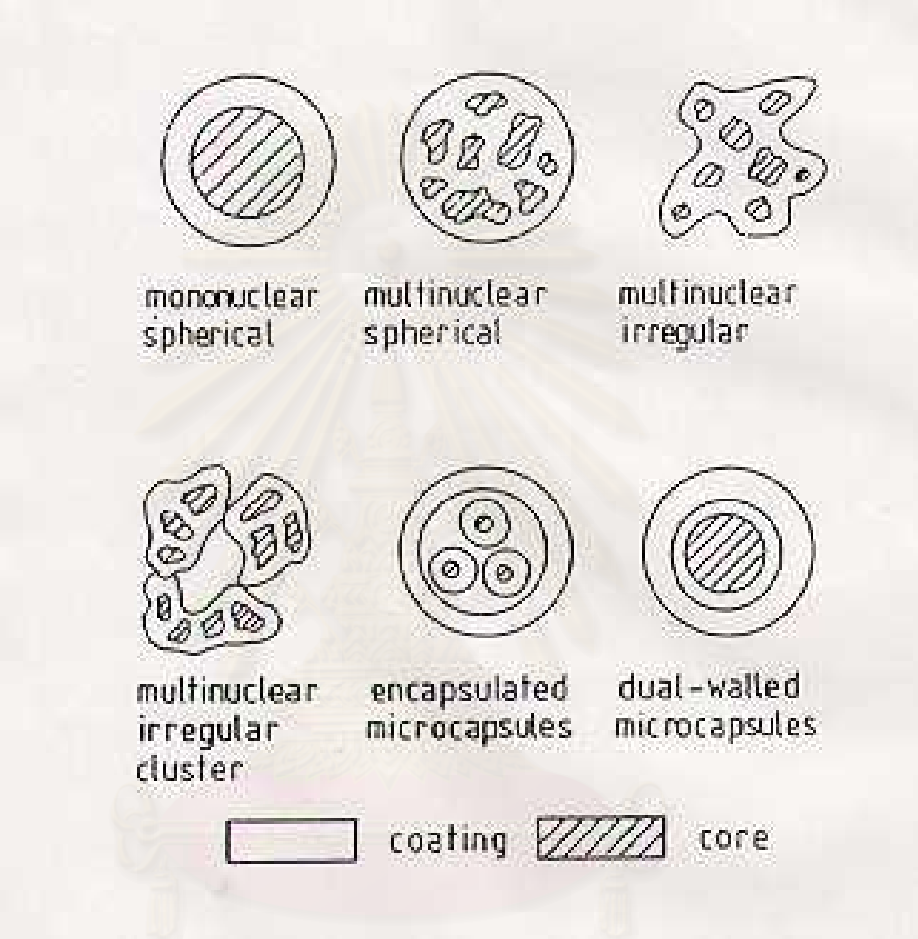

Figure 1. Some typical structure of microcapsules

The microcapsule coating can be chosen from a wide variety of natural and synthetic polymers [17-18]. The selection of the appropriate coating material dictates, to a major degree, the resultant physical and chemical properties of the microcapsules, and consequently, the selection must be given by consideration. The coating material should be capable of forming a film that is adhesive with the core material It should be chemically compatible and nonreactive with the core material, and provides the desired coating properties such as strength, flexibility, permeability, optical properties and stability.

The acidity or alkalinity of the core materials may also preclude the use of certain wall materials. For example, it may not be possible to encapsulate an aqueous core containing a water-soluble acidic material by using a nylon shell deposited by interfacial polymerization. This is due to the potential interaction of the acid and amine in the aqueous phase. The system could, however, be reversed so that the amine were in a continuous aqueous phase and the acid core material placed in the nonaqueous and now dispersion phase with the acid halide. Even in the reversed system, the partitioning characteristic of the acid core and, consequently, its likelihood of entering into the polymerization reaction must be considered [23].

2.2 Microencapsulation Procedures

There are difficulties to classify microencapsulation procedures simply under any one heading because the techniques employed in these methods exhibit a large degree of overlaps. The classification previously proposed by Kondo is reproduced in Table 1 together with supplements. However, this classification is not all inclusive, since some processes extend over two classes or stand at a boundary between two classes [24]. The coacervation or phase separation and solvent evaporation techniques will be presented in more details in the next topic.

Table 1 Classification of Microencapsulation

Chemical processes
1. Interfacial polymerization
2. In situ polymerization
3. Rapid insolubilization of polymer (orifice method)
Physicochemical processes
1. Phase separation from aqueous solution (coacervation)
2. Phase separation in organic solution (coacervation)
3. Desolvent in liquid vehicle (complex emulsion)
4. Meltable dispersion and solidifying
5. Powder bed
Mechanical processes
1. Air suspension coating (Wurster)

2. Spray drying
3. Vacuum coating
4. Electrostatic aerosol
5. Centrifugal multiorifice

2.2.1 Coacervation/Phase Separation Procedures

Coacervation is one of the oldest and most common microencapsulation techniques in current use. The term “coacervation” is used to describe the phenomenon of salting out or phase separation of lyophilic colloids into liquid droplets rather than into solid aggregates [15,16,19]. Microencapsulation by coacervation-phase separation can use non-aqueous or aqueous vehicles which are safe and less toxic. It was first developed commercially by the National Cash Register Co. (NCR), in 1954. The coacervation has been classified into two categories: simple and complex coacervations. Simple coacervation concerns with only one colloid. The process involves the addition of a strongly hydrophilic substance to reduce the solubility of the macromolecule and cause two phases to be formed. Microencapsulation by complex coacervation involves the use of more than one colloid and concerns with the charges. The wall is formed by electrostatic interaction between the positive charge of the polymer chain and the negative charge on the counter polyanion backbone [25-27]

2.2.2 Coacervation-Phase Separation Procedures Using Aqueous Vehicles

For microencapsulation of water-soluble core materials, the wall-forming polymer is dissolved in water. This process is termed ‘aqueous phase separation’ [15,17,28]. Microencapsulation by coacervation-phase separation using aqueous manufacturing vehicles was first developed commercially by the National Cash Register Co. (NCR), Dayton, Ohio, in 1954. In a series of patents [29-31] ascribed to Green and Schleicher, gelatin and gelatin-acacia (gum arabic) coating systems were described for the encapsulation of dye material used in the manufacture of carbonless carbon paper which eliminated the need of the carbon paper in multipart business

forms. Because of the lack of toxicity of the coating materials employed and the comparative simplicity of the procedures, the technique was quickly developed.

Generally, these microencapsulation processes consist of three steps (Figure 2) as follows:[15,17,19]

1. Formation of three immiscible phases, the liquid-vehicle phase, the core material, and the liquid polymer coating;
2. Deposition of the coating material;
3. Solidification of the coating material.

The coating material was formed by utilizing one of the methods, phase separation or coacervation by simple or complex coacervation. Simple coacervation was induced by a change in conditions which resulted in molecular dehydration of the macromolecules. This may be achieved by the addition of poor solvent, the addition of electrolyte such as sodium or ammonium sulfate (salting out effect), or a temperature change, all of which promoted polymer-polymer interactions over polymer-solvent interactions. Complex coacervation was driven by electrostatic interactive forces between two or more macromolecules. The deposition of the coating material was promoted by a reduction of the total free interfacial energy of the system, brought about by a decrement of the coating material surface area during coalescence of the liquid polymer droplets. The coating could be hardened in a variety of ways by thermal, crosslinking, or desolvation methods, to form a rigid microcapsule.

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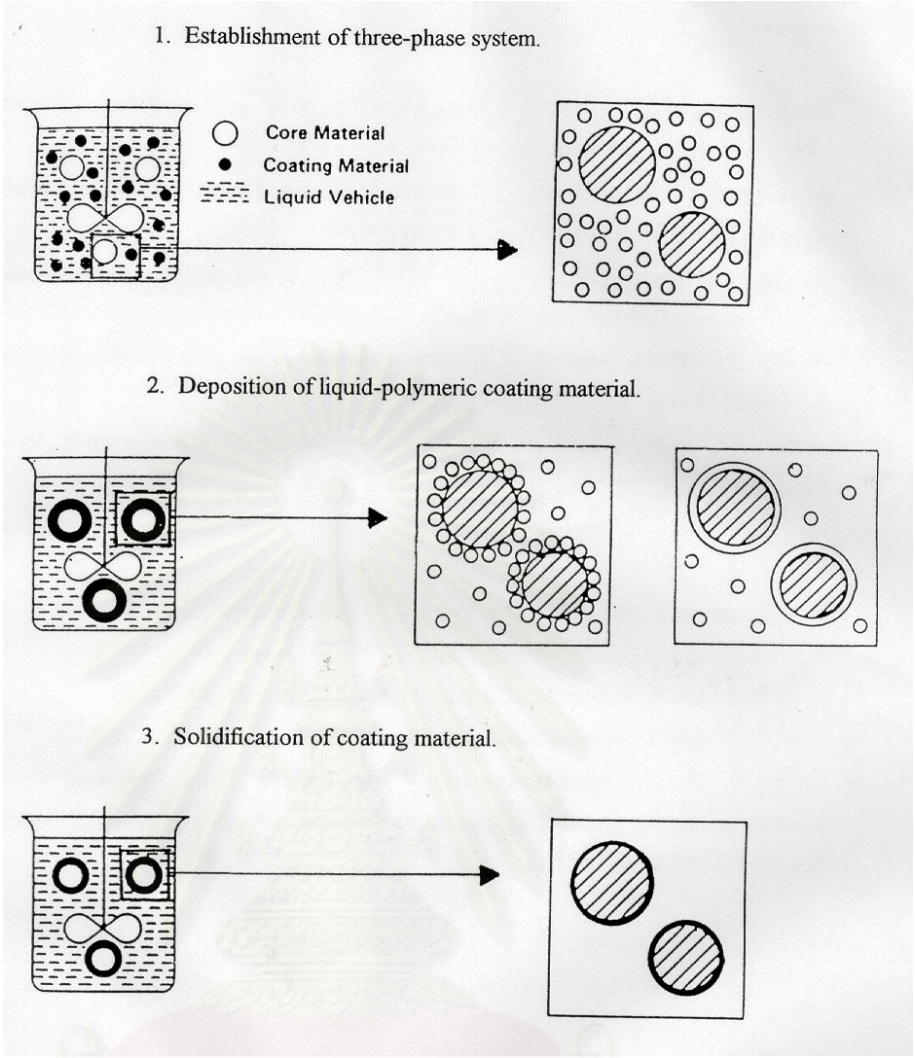

(core, coacervate droplets, coating, hardened coating)

Figurer 2. General process description of coacervation technique [19]

2.2.3 Coacervation/Phase Separation Procedures Using Non-aqueous Vehicles

When the substance to be encapsulated is water-soluble and the wall-forming polymer is dissolved in an organic hydrophobic solvent, the microencapsulation process is called ‘nonaqueous phase separation [15,17-18,21].

Many core materials are moderate to very good water-soluble and would be unsuitable for encapsulation by procedures using aqueous vehicles, especially for core materials sensitive to moisture. Accordingly, various techniques have been developed for coating such a core materials. The techniques employ organic liquids in which the core materials is insoluble but the coating polymer is soluble under certain conditions. Phase separation of the polymer may be induced by different methods such as temperature change, addition of incompatible polymer, or non-solvent addition [15,17-18]. The coacervated polymer enclosed the core material to form the microcapsule wall. Usually, low polymer concentrations are required for encapsulation by the coacervation technique involving separation into polymer-rich and polymer-poor regions. The phase separation must be gradual; this enables the concentrated polymer solution to deposit and flow uniformly over the surface of the core material to form a satisfactory coating. Higher polymer concentrations tend to give a rapid demixing effect upon phase separation which is unsuitable for microencapsulation [19,32].

Many different coacervation-phase separation procedures involving nonaqueous manufacturing vehicles have been developed, In 1970 Fanger et al. [33], in a patent assigned to NCR, outlined a very simple process for the encapsulation of heat-stable drugs with ethylcellulose. The process involves dissolving ethylcellulose in the cyclohexane at 80 to 81^{o}C and gradually cooling the solution so that the polymer separates as a liquid coacervate and encloses particles of core material that are dispersed by vigorous agitation in the system. The deposited wall material may be hardened by continuing to lower the temperature. Scheu et al. [34] used a nonaqueous coacervation procedure to apply crosslinked polyethyleneimine to water-soluble core particles of gold sodium trisulfate, amaranth, or sodium chloride.

2.2.4 Coacervation Induced by Temperature Change

Microencapsulation by temperature change involves a polymer soluble in a solvent at elevated temperature but insoluble in the same solvent at room temperature. When certain polymers are dispersed in a cold solvent with a core material present, heating the mixture with agitation to a selected temperature and slowly cooling the dispersion back to room temperature can result in the microencapsulation.

Figure 3 illustrates a general temperature-composition phase diagram for a binary system comprised of a polymer and a solvent. A system having an overall composition represented as point X on the abscissa exists as a single-phase, homogeneous solution at all points above the phase-boundary or binodal curve, FEG. As the temperature of the system is decreased from point A along the arrowed line AEB; the phase boundary is crossed at point E and the two-phase region is entered. The phase -boundary curve indicates that with decreasing temperature, one phase becomes lean in polymer (the microencapsulation vehicle phase) and the second phase becomes polymer-rich (the coating material phase). At point B, for instance, the segmented tie-line suggests that vehicle phase is essentially pure solvent, point C, whereas the coexisting phase, point D, is a concentrated polymer-solvent mixture.

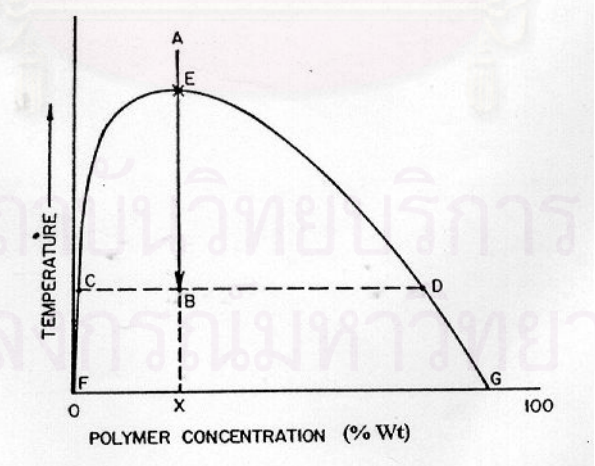

Figure 3. General phase diagram of thermally induced coacervation [18]

2.2.5 Coacervation Induced by Addition of Incompatible Polymers

Microencapsulation by polymer-polymer incompatibility is probably the most classical method to produce microcapsule using the Dobry effect to induce liquid polymer phase separation. The Dobry effect primarily uses organic liquids as the solvent for the polymers. The Dobry effect involves the cohesive energy density and/or solubility parameters of polymers (Table 2-3). As the numerical values of the solubility parameters of polymers and solvents move away from each other, incompatibility occurs.

When dissimilar polymer pairs are dissolved in a common solvent, incompatibility is the rule; compatibility, the exception. In many cases, when two solutions of different kinds of polymers dissolved in the same kind of solvent are mixed, liquid-liquid phase separation occurs. If this is done with agitation in the presence of a core material, microcapsules form. The polymer that is most tenaciously sorbed at the core material-solvent interface becomes the coating film, and the microcapsule thus formed are dispersed in a solution of the other polymer. The noncoating material can be removed from the microcapsule by washing them with a solvent for this polymer in which the coating material is insoluble. Typical coating polymers are ethylcellulose, polymethyl methacrylate, and polystyrene. Polymer that can be used to induce phase separation include polyethylene, polybutadiene, and polymethylsiloxane. Common solvents such as cyclohexane, toluene, ethanol, acetone, and methyl ethyl ketone are used in many processes. Consequently, this process is best used for microencapsulation of solvent-insoluble or, more specifically, water-soluble solids.

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Table 2. Solubility parameters of selected polymers.

Polymer	δ ($cal^{1/2}$ $cm^{-3/2}$)
Silicone, polydimethyl	7.3
Polyethylene	7.9
Polyisobutylene	8.1
Natural rubber	8.3
Polybutadiene	8.6
Polystyrene	9.1
Neoprene GN rubber	9.2
Polyvinyl acetate	9.4
Polymethyl methacrylate	9.5
Polyvinyl chloride	9.7
Polymethyl chloroacrylate	10.1
Ethylcellulose	10.3
Cellulose dinitrate	10.6
Polymethacrylonitrile	10.7
Cellulose diacetate	10.9
Cellulose nitrate, 1/2s	11.5
Polyvinylidone chloride	12.2
Nylon type 8	12.7
Nylon 66	13.6
Polyacrylonitrile	15.4

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Table 3. Solubility parameters of selected solvents arranged by chemical types.

Solvent	δ ($cal^{1/2}$ $cm^{-3/2}$)
Isobutylene	6.7
Petroleum ether	7.1
Hexane	7.3
Diethyl ether	7.4
Octane	7.6
Diisobutyl ketone	7.8
Methyl amylacetate	8.0
Butyl butyrate	8.1
Cyclohexane	8.2
Isobutyl acetate	8.3
Isopropyl acetate	8.4
Butyl acetate	8.5
Carbon tetrachloride	8.6
Xylene	8.8
Toluene	8.9
Ethyl acetate	9.1
Diacetone alcohol	9.2
Methyl ethyl ketone	9.3
Tetrachloroethylene	9.4
2-Ethylhexanol	9.5
Methyl acetate	9.6
Methylene chloride	9.7
Ethylene dichloride	9.8
Acetone	10.0
n-Octanol	10.3
2-Ethylbutanol	10.5
n-Hexanol	10.7
sec. Butanol	10.8
n-Butanol	11.4
Isopropanol	11.5
Ethanol	12.7
Ethylene glycol	14.2
Methanol	14.5

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2.2.6 Coacervation Induced by Nonsolvent addition

Microencapsulation by nonsolvent addition is a classical example of using the Dobry effect. Phase separation is induced by adding an organic solvent that must be miscible with the first organic solvent but must be a nonsolvent for the polymer dissolved in the first. The ability of the nonsolvent to cause the polymer separation is measured by the solubility parameter (Table 2-3). Depending on the difference of solubility parameters of the nonsolvent vehicle and the polymer, liquid phase separation occurs. Thus, due to the decreased solubility of the polymeric wall materials in the new solvent system, the wall material is phased out and forms a film around the hydrophilic nucleus particles. This process is designed to produce microcapsules of solids which are insoluble in the solvent-nonsolvent pairs. Many polymers can be used as coating material including cellulosics, acrylics, styrene, rubbers, vinyl acetates, and others.

2.2.7 Solvent Evaporation Procedures

Microencapsulation by solvent evaporation is conceptually a simple procedure [18,35]. It involves, first, the emulsification of a polymer solution containing core materials (either dissolved or dispersed) into the other immiscible liquid phase containing an emulsifier to form a dispersion core-polymer-solvent droplets. In the second step, the solvent is removed from the dispersed droplets by application of heat, vacuum or by allowing evaporation at room temperature to leave a suspension of core containing polymer microcapsules or microsphere that can then be separated by filtration or centrifugation; the microcapsule or microsphere can then be washed and dried (Figure 4). In the case in which the core material is dispersed in the polymer solution, polymer shrinks around the core. In the case in which the core material is dissolved in the coating polymer solution, a matrix-type microsphere is formed. This technique can be tailored to produce microspheres over a wide size range, from less than 200 nm to several hundred microns.

A range of different microspheres have been prepared by dissolving or dispersing during in a solution of a polymer in a single or mixed organic solvent

having a low boiling point. The phase is then emulsified into a continuous aqueous phase containing a low concentration of hydrophilic colloid or surfactant to stabilize the oil-in-water (o/w) emulsion formed. Reduced pressure and/or heat is then often applied to the emulsion while stirring to evaporate the organic solvent, and the microspheres formed are collected by filtration or centrifugation [19]. The process is the subject of a patent by Morishita et al. [36]. Mortada [37] dispersed sulfathiazole in a solution of ethylcellulose in trichloromethane. This was then emulsified into 0.04% sodium lauryl sulfate solution and the organic solvent evaporated by stirring at room temperature for 5 hr to form an ethylcellulose microspheres. A similar approach was also used by Wakiyama et al. [38-40] to encapsulate butamben, tetracaine or dibucaine. The organic solvent was evaporated and the microspheres formed by phase separation were recovered.

In an interesting series of patents [41-42], aqueous solutions or dispersion core materials were emulsified into hydrophobic polymer material dissolved in a water-immiscible solvent having a boiling point below 100^0C, e.g., polystyrene in methylene chloride. An initial w/o emulsion was formed and this emulsion was in turn emulsified into an aqueous solution of a hydrophilic colloid to form a w/o/w emulsion. By raising the temperature the organic solvent evaporated, causing phase separation of the polymer coating around the inner aqueous droplets. Alternatively, the organic solvent could be removed by adding a liquid that is miscible with both the solvent and water but a nonsolvent for the polymer and core material. Various other polymers, such as acrylates, cellulose derivatives, and polyamides, could be used in association with suitable organic solvents. Loss of water-soluble core substances tended to occur during encapsulation by their migration from the inner water droplets across the organic solvent layer into the outer continuous water phase before the polymer coating was properly deposited. To prevent this problem occurring, a saturated concentration of the intended core material could be dissolved in the outer aqueous phase, provided that it does not precipitate the dissolved hydrophilic colloid present.

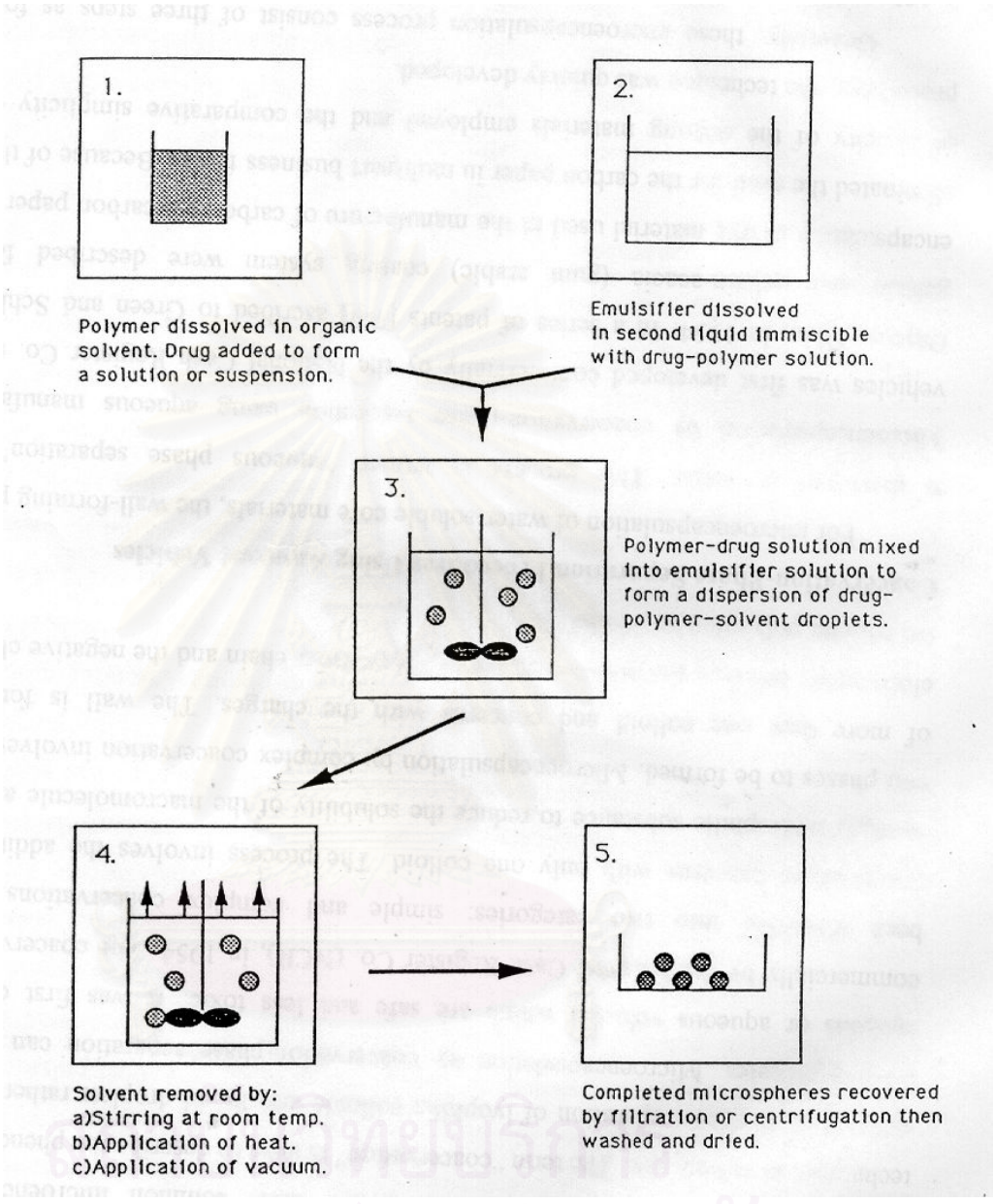


Figure 4. Schematic diagram of microsphere formation by solvent evaporation procedure [35].

For core materials with high water solubility and moisture sensitivity, the emulsification into an aqueous phase is unexpected, generally unsuccessful in

producing entrapment core materials since the core materials will rapidly partition from the more hydrophobic polymer-solution phase into the aqueous surroundings. This problem can be solved by the use of oil-in-oil (o/o) type emulsion system or nonaqueous solvent evaporation technique [33,43-44]. The polymer and core material, which are contained in a polar solvent, are emulsified into an immiscible lipophilic phase. Mineral oil is commonly used. The wall material used is hydrophobic and practically water insoluble [45-46].

2.3 Emulsifier

The role of emulsifier in microsphere production by solvent evaporation is the short-term stabilization of the suspended polymer droplets. Stabilization to prevent aggregation and coalescence is only a short-term requirement. Once adequate solvent evaporation has taken place to induce some hardening of the polymer droplets, coalescence and aggregation should not occur.

Most published oil-in-water techniques utilize polymeric stabilizers such as gelatin, polyvinyl alcohol (PVA), and methylcellulose. These polymers increase solution viscosity that may affect microsphere properties [47-48]. Other o/w stabilizers used include polysorbate 80 and sodium dodecyl sulfate (SDS) [49-50].

The emulsifiers used in microencapsulation by o/o type solvent evaporation technique include sorbitan trioleate, Span 80, and Tween 80 [44-45,51-52].

2.4 Polymerization Procedures

Polymerization-related techniques are normally carried out in the liquid phase by bulk, suspension, emulsion, or micelle process. The nonreactive, biologically active material may be incorporated into the polymer during polymerization if it is adequately stable or may be subsequently incorporated into the preformed polymer. The monomers normally chosen are those whose polymers have already gained wide medical acceptance, often for prostheses other than encapsulation, such as polymethacrylates for absorbable suture material. Other nontoxic polymers can also be used, provided that they are free from harmful unreacted monomer, catalyst/initiator, and other materials used in their preparation [19].

2.4.1 Bulk Polymerization

In bulk polymerization only a monomer or mixture of monomers and possibly the biologically active material are usually heated, often in the presence of a catalyst/initiator to increase the reaction rate. As the polymer forms through the reaction of functional groups in a stepwise manner, there is a progressive increase in the amount and molecular weight of polymer formed. This is accompanied by a progressive rise in apparent viscosity of the system, which may be maintained in the fluid state by keeping the temperature high. The process has the advantage of forming a relatively pure polymer, which solidifies as a block on cooling. However, the process has a number of disadvantages. It is difficult to dissipate the high exothermic heat of reaction which, if not removed, may have an adverse effect on a material. The polymer block formed may need to be mechanically fragmented to produce fine particles having irregular size, shape, and release properties.

2.4.2 Suspension Polymerization

Suspension Polymerization is often referred to bead polymerization or pearl polymerization. Typically it involves heating a water-insoluble liquid monomer or monomers and possibly a biologically active material as a dispersion of droplets (usually 100 to 5000 μm in diameter) in a continuous aqueous phase. The droplets may also contain an initiator and are formed by suitable mechanical agitation. The aqueous phase may contain stabilizers such as thickening agents to increase the viscosity of the continuous phase, electrolytes to increase the interfacial tension between the phases, and finely divided insoluble filler to interfere agglomeration mechanically. Minor amounts of emulsifiers and buffers may also be needed. Adhesion between droplets often becomes a particularly troublesome problem when polymerization proceeded to a critical point where the surface of polymer beads became tacky. The kinetics of polymerization are the same as those of bulk polymerization, again resulting in the formation of a relatively pure polymer. On completion of polymerization, the product is washed to remove stabilizers and is dried as beads or pearls. The major advantage of the process is that the continuous phase

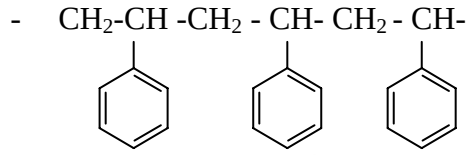
absorbs the heat of the polymerization reaction and., as a coolant, prevents excessive temperature rise. Also, the product is in the form of spherical beads of relatively uniform size and release characteristics. The major disadvantages associated with the process are difficulty in removing the product of unwanted stabilizers and other additives, and coalescence problems with soft polymer beads.

The most frequently employed polymeric network used is a copolymer of styrene and divinylbenzene that may be produced by a suspension polymerization process in a spherical bead form. The free radical polymerization may be initiated by heat or irradiation. However, it is more commonly achieved by adding an initiator such as benzoyl peroxide or azobisisobutyronitrile that decomposes into free radicals on heating [19,23]. Yoshida et al. dissolved polymethyl methacrylate or polystyrene in a large excess of various acrylic monomers in which the drug potassium chloride was dispersed [53].

During recent years considerable interest has been shown in the entrapment of drug molecules of lower molecular weight in various acrylic polymers and copolymers. In 1970 Khanna et al. [54] reported the first application of suspension polymerization for the production of sustained-release dosage forms whereby a drug was embedded during the polymerization or copolymerization. Other polymerization techniques were also tried. Emulsion and solution polymerization were considered undesirable because of the high concentration of unreacted monomer left in the product, as was the bulk polymerization technique because the poorly dissipated exothermic heat of reaction liberated might cause degradation with thermolabile core materials. Methacrylic acid, methyl methacrylate, and crotonic acid were used as monomers, benzoyl peroxide or azobisisobutyronitrile as initiator, and carboxyvinyl polymer (Carbopol) or polyvinylpyrrolidone was used as stabilizer to increase the viscosity of the continuous water phase. A high concentration of sodium sulfate was used to decrease the solubility of the monomers in the water phase by a salting-out effect which, however, must not flocculate the stabilizers. Sulfuric acid was added to prevent the ready hydrolysis of monomer under basic conditions.

Styrene is a colorless liquid, sparingly soluble in water, which may be polymerized by bulk, suspension, or emulsion technique. Spherical particles of polystyrene can be prepared by heating a dispersion of the monomer in water to about 90^0C in the presence of a free radical initiator such as benzoyl peroxide and suitable

stabilizers [55]. Alternatively, ionizing radiation may be used to initiate the polymerization by its formation of free radicals. The typical head-to-tail structure of polystyrene produced is shown below.



In the preparation of expandable polystyrene spheres, the styrene is usually polymerized in the presence of a low-boiling-point hydrocarbon, which becomes entrapped in the polystyrene spheres formed. When these are then heated with steam, the resultant combination of polymer softening, volatilization of hydrocarbon, and diffusion of steam into the spheres causes them to expand to about 40 times their original size [32].

Reyes [56], in a patent assigned to International Business Machines Corp., described a process whereby a suitable hydrophobic monomer or polymer such as polystyrene in a suitable organic solvent is graph-polymerized as a coating onto a gelled hydrophilic polymer core such as agar or an alginic acid derivative in water using ionizing radiation.

2.4.3 Emulsion Polymerization

Emulsion polymerization differs from the superficially similar suspension polymerization procedure in three important respects. The initiator is initially located in the aqueous phase. More vigorous agitation is employed, as a result of which the droplet size is usually below 100 μm and is often less than 1 μm, i.e., in the nanometer range. The surfactant concentration employed is much higher, being usually well in excess of its critical micelle concentration (CMC). This results in an altered mechanism of polymerization, which may be summarized as follows. Excess surfactant molecules form micelles whose hydrophobic interior take up part of the available monomer, causing them to swell. Initiator radicals generated in the aqueous medium, often by heating or irradiation, diffuse into these swollen micelles to start polymerization. As the monomer is consumed, it is replaced by progressive diffusion of the remaining monomer from its location as emulsified droplets into the micelles,

which continue to enlarge as polymerization proceeds. The associated enlarging surfaces compete for available surfactant, thus influencing the number of available micelles that can form polymer as a result of their fortuitous gain of initiator radicals. Polymerization can also occur in systems containing surfactant below its CMC by homogeneous nucleation onto polymer-radical complexes. This mechanism may also be partially responsible for particle formation in systems containing surfactant above its CMC. Nonaqueous –based emulsion polymerization procedures, whereby an aqueous solution of hydrophilic monomer such as acrylic acid or acrylamide is emulsified in a continuous oil phase using a water-in-oil (w/o) emulsifier/surfactant and an oil-soluble initiator, have been reported.

The main advantages of emulsion polymerization are that higher-molecular-weight polymer is usually formed at a faster rate and a lower temperature. The heat of reaction is readily dissipated. The process is particularly suitable for the formation of minute spherical particles for injectable and other use. However, a major disadvantage of the process is usually high associated concentration of unreacted monomer, many of which are quite toxic and difficulties to free the product of. There are also increased difficulties in recovering the particles from the dispersion because of their minute size.

2.5 Interfacial Polycondensation

Interfacial Polycondensation involves reaction of various monomers at the interface between two immiscible liquid phases to form a film of polymer that encapsulates the disperse phase. Usually two reactive monomers are employed, one dissolved in the aqueous disperse phase containing a solution or dispersion of the core material, and the other dissolved in the nonaqueous continuous phase after the emulsification step. The water-in-oil (w/o) emulsion formed requires the addition of a suitable emulsifier as stabilizer. Figure 5 shows a schematic representation of the process, which is often referred to as interfacial polymerization. The monomers diffuse together and rapidly polymerize at the interface between the phases to form a thin coating, and the by-product of the reaction normally acid is neutralized by added material such as an alkaline buffer. The degree of polymerization can be controlled by the reactivity of the monomers chosen, their concentration, the composition of either phase vehicle, and by the temperature of the system. Variation in droplet size of the

disperse phase controls the capsule size of the product. The reaction between the monomers is quenched by depletion of monomer, which is frequently accomplished by adding excess amount of the continuous-phase vehicle to the emulsion [19].

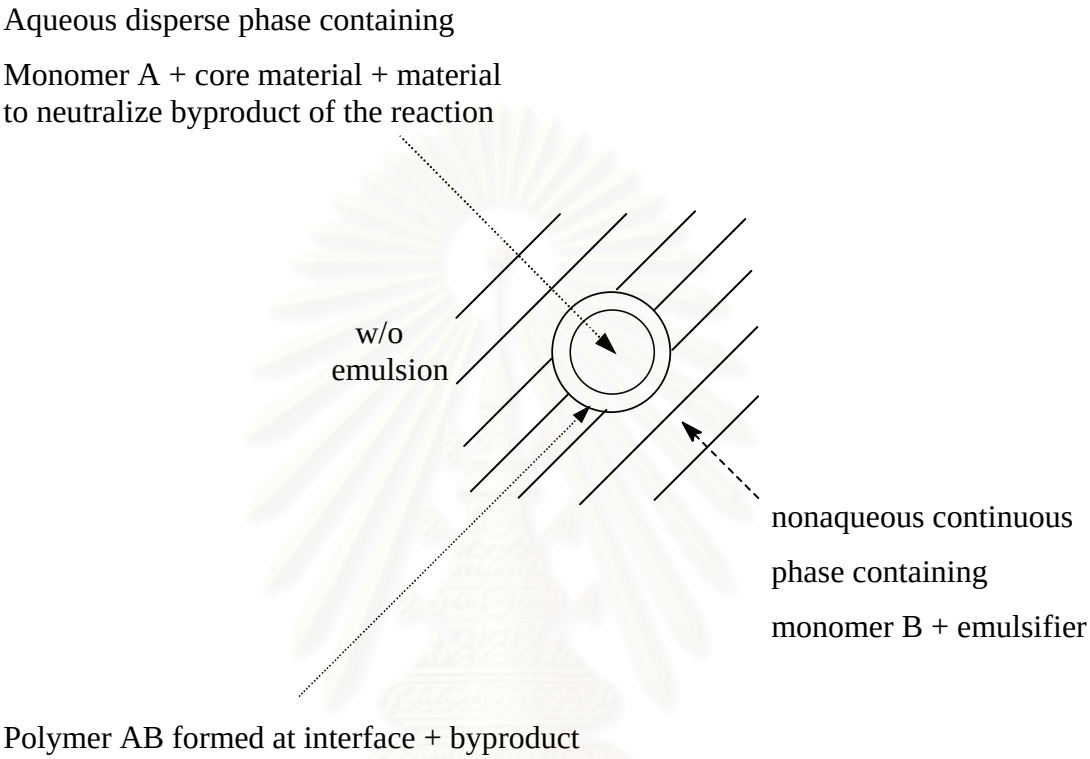


Figure 5. Schematic representation of microencapsulation of a droplet by interfacial polycondensation [19].

Interest to the technology has grown enormously since 1959, when Du Pont, at a national American Chemical Society meeting, demonstrated how polyamide fiber could be prepared by interfacial polymerization. In the last 40 years many different monomer combinations have been investigated for the microencapsulation of pharmaceuticals. Table 4 lists polymers formed from various monomer combinations.

However, despite the considerable interest in medical applications of the process, very few have been commercially exploited. This frequently arises because of (1) toxicity problems associated with unreacted monomer, the polymer, or other constituents of the system; (2) excessive drug degradation caused by reaction with monomer; (3) high permeability of the coating formed against low-molecular-weight species; (4) the fragility of the microcapsules formed; and (5) the lack of

biodegradability products. Polyamide encapsulation is the most extensively investigated of the procedures involving interfacial polymerization for the coating of high-molecular-weight material.

Table 4 Principal Monomer Combinations Investigated for the Microencapsulation by Interfacial Polycondensation.

Aqueous phase monomer A	Nonaqueous phase monomer B	Polymer AB wall material formed
1. Polyamine	Polybasic acid halide	Polyamide
e.g., 1,6- Hexamethylene-diamine	sebacoyl chloride	nylon 6-10
piperazine	terephthaloyl chloride	polyterephthal-amide
L-lysine	terephthaloyl Chloride	poly(terephtha-loyl L-lysine)
2. Polyphenol	Polybasic acid halide	Polyester
e.g., 2,2-bis-(4-hydroxy-phenyl)propane	sebacoyl chloride	polyphenyl ester
3. Polyamine	Bischloroformate	Polyurethane
e.g., 1,6- Hexamethylene-diamine	2,2-dichlorodiethyl ether	polyurethane

Polyamide

Nylon 6,10 Microcapsules

The first published details of an interfacial polycondensation process involving a Schotten-Baumann type of the reaction between an acid dichloride and a compound containing reactive hydrogen atom (-NH, -OH, -SH). As an example of this type of nucleophilic reaction, a poly(hexamethylene sebacamide) polymer was formed at the interface between a solution of 1,6-hexamethylene diamine in water and sebacoyl chloride in a water-immiscible solvent as follows:

$$nH_2N(CH_2)_6NH_2 + nClC(CH_2)_8CCl \longrightarrow [HN(CH_2)_6NHC(CH_2)_8C]_n + nHCl$$

An inorganic base such as sodium carbonate or sodium hydroxide in the aqueous phase was used to neutralize the hydrogen chloride formed in the condensation. The polyamide polymer formed is called nylon 6-10, the first and second numbers representing the number of carbon atoms in the diamine and acid dihalide, respectively.

Surfactant

The addition of surfactants in microencapsualtion procedures is important for the formation of emulsion. Surfactant also plays an important role in the transfer of the diamine to the organic phase. Kondo and coworkers have investigated the effect of Span 85 (Sorbitan trioleate) on the partition coefficients of various diamines and bisphenols [57-61]. In general, increasing the concentration of surfactant results in an increase in the amount of diamine which is transferred to the organic phase. For preparation of poly(lysine terephthalamide) microcapsules, a surfactant concentration (sorbitan trioleate) of 20% v/v was successful.

The choice of surfactant used in studies where aqueous solution is encapsulated in semipermeable membranes has been limited mainly to sorbitan trioleate, which has a particularly low HLB (hydrophile-lyophile-balance) value. The main requirement of any surfactant is that it does not react with the diacid chlorides, and it does not have impurities which would interfere the polymerization reaction.

Solvent

Chloroform-cyclohexane mixture in the ratio 1:4 or 1:3 has been widely used. Morgan [62] discussed the polymer-solvent interactions of nylon 6,10 and has shown that thick films are expected from chloroform system, where as cyclohexane produces thin films. Good solvents tend to produce high molecular weight polymer when compared with nonsolvents.

The density of the organic solvent used in the w/o emulsion in microencapsulation procedures will affect the stability of the emulsion and will

determine whether the microcapsules sediment or float in the organic phase. This will affect the isolation technique used to obtain the newly formed microcapsules. In generally, organic solvents have been chosen from solvents with low toxicity and toxic solvents have been avoided.

Transfer rates of salts

An important consideration is the elimination of HCl formed in the polycondensation reaction. This product is removed by the formation of the hydrochloride salt of the amine which, being poorly soluble in the organic phase, diffuses to the aqueous phase where the HCl is neutralized by buffer included for this purpose. Hydrochloride salt of diamines are not able to react with diacid chloride and, therefore, if buffer is not included in the aqueous phase, the diamine itself will function as an acid acceptor. In most case, the transfer of hydrochloride salts will be faster than the fransfer, in the opposite direction, of diamine to the reaction site.

2.6 Hydrophobic congealable system-Waxes, Fats and Oils

Congealable Disperse-Phase Encapsulation Procedure is a simple type of encapsulation procedure involves dispersing fine particles of core material at high temperature in a hydrophilic or hydrophobic liquid vehicle that will solidify when cooled to normal ambient temperature. Alternatively, the core material may be dissolved in the liquid vehicle. Suitable hydrophilic vehicles include gelatin, agar, and starch. Suitable hydrophobic vehicles include various waxes such as Japanese, Glycowax, and beeswax, and hardened oils and fats such as hydrogenated castor oil and hydrogenated beef tallow.

The cooling melted dispersion process utilizes the thermal behavior of wax or similar materials. In this process a dispersion of core material in a melted wax such as paraffin wax or hydrogenated fat is poured into solution of a temperature lower than the melting point of the wax material, which is thus solidified and forms the capsule wall. The cooling speed and the agitation condition are the key factors in determining the shape of microcapsules [23,32].

A large number of encapsulation procedures involving a meltable dispersion followed by a cooling process were listed by Kondo [63]. Suitable wall material included paraffin wax, glyceryl tristearate, and Japanese wax.Yazawa et al. [64], in a patent assigned to Fuji Photo Film Co., Ltd., described how amino acids or polypeptides could be dispersed in a molten mixture of a fat and/or oil and hardened as microcapsules by being extruded as droplets into cold water. The oil was used to reduce the mechanical strength of the microcapsules. Kowarski et al. [65] dispersed fine particles of sulfamethazine in molten Japanese synthetic wax at elevated temperature.

In a patent assigned to NCR, Powell [66] described how to treat performed ethylcellulose microcapsules containing drugs such as paracetamol with solutions of waxy materials in cyclohexane.

2.7 Literature Review

In 1972, D. C. Neckers reported the first use of a tightly bound complex of styrene-divinylbenzene copolymer and anhydrous aluminum chloride, as a mild Lewis acid catalyst for certain organic preparations. The complex of the polymer and $AlCl_3$ provides a shelf-stable acidic material, the active ingredient of which can be called out by an appropriate polymer swelling solvent at the time it is desired [6].

In 1985, Iso et al. studied coacervation induced from polystyrene (PS)-cyclohexane solution by the addition of nonsolvent, n-hexane, for microencapsulation of glass beads as a model core material and anhydrous sodium sulfate (ASS) employed for the measurement of controlled release. Percentage of PS utilized as wall remarkably increased as compared with the result, where coacervation was induced by temperature lowering of PS-cyclohexane solution. They found that the addition of talcum powder was yet unavoidable to prevent microcapsules from adhering each other. Controlling of PS wall thickness was quite successfully performed by adjusting PS concentration in cyclohexane solution, encapsulated temperature and amount of n-hexane [67]. After that Iso et al. studied coacervation in polystyrene (PS)-cyclohexane solution induced by the lowering of temperature. It was utilized to investigate the fundamental problems involved in the microencapsulation procedure. Polydispersity of PS played a vital role in determining variables at the critical state of phase separation, such as the composition of coacervate (dense) and lean phase. They found

that this also depended on temperature. Observation revealed that microcapsules of glass beads consist of a wall with a thin film of PS covered with a thick shell of talc. Poor utilization of PS may limit practical applications of this system unless effective measures are taken for the recovery of unutilized PS. Moreover, they successfully investigated controlled release behaviour from microcapsules by using encapsulated anhydrous sodium sulphate (ASS) particles, and applying the Higuchi model to the estimation of the effective diffusion coefficient of ASS through the composition wall [68].

Scandium trifluoromethanesulfonate (scandium triflate), a Lewis acid developed in 1993 by Kobayashi 's group. $Sc(OTf)_3$ was first tested as a Lewis acid catalyst in the Diels-Alder reaction. It is quite effective and the use of even 1 mol% of $Sc(OTf)_3$ is enough to complete the reaction. While most Lewis acids are decomposed or deactivated under the influence of water, $Sc(OTf)_3$ is stable and can efficiently behave as a Lewis acid even in aqueous solution. Another characteristic feature of $Sc(OTf)_3$ as a Lewis acid catalyst is that it can be easily recovered and reused. $Sc(OTf)_3$ is almost quantitatively recovered and the recovered catalyst is also effective in the Diels-Alder reaction. It should be noted that the yields of 2^{nd} and 3^{rd} runs were comparable to that of 1^{st} run [69].

In 1993, Ruicheng and co-worker reported the synthesis of a polystyrene-bonded Ti(IV) chloride catalyst by the reaction of a polystyryl lithium (PS-$TiCl_2$) or a polystyryl magnesium (PS-$TiCl_3$) combined with titanium tetrachloride. The catalyst produced is a polymeric organometallic compound containing various amount of Ti and Cl, depending on the method of synthesis. Both catalysts showed very good stability and good catalytic activity in repeated usage without losing its catalytic activity [70].

In 1994, Omi and co-worker studied uniform polymeric microspheres, the coefficients of variation being close to 10% by the BPO-initiated suspension polymerization of styrene monomers. Unlike the conventional stirred-tank system, a particular microporous glass membrane (SPG) provided uniform monomer droplets continuously when monomer was allowed to permeate through the micropore. The monomer droplets were suspended in an aqueous solution containing the stabilizing agents, transferred to a stirred vessel, and polymerized. Up to 10 μm spheres, of a fairly narrow size distribution than those obtained by conventional microsuspension polymerization spheres, were retained with the successful suppression of secondary

particle nucleation by the addition of hydroquinone in the aqueous phase [71]. In addition, they investigated 100 μm porous poly(styrene-co-divinylbenzene) (PS-DVB) microspheres by employing a particular membrane emulsification technique, and subsequent swelling of the seed droplets. DVB dissolving a water-insoluble substrance, hexadecane (HD), and an initiator was permeated through a SPG (Shirasu porous glass) membrane. The uniform (seed) droplets were released to a stabilizer solution acting as the continuous phase. The average droplet size was around 30 μm, and this emulsion was mixed with a secondary emulsion of much smaller size consisting of more hydrophilic components, a mixture of styrene, middle chain alcohol, dichorobenzene, and isoamyl acetate [72].

In 1996, Kobayashi and Nagayama studied a new method for preparation of a quinoline library using a polymer-supported scandium catalyst, (polyallyl) scandium trifylamide ditriflate (PA-Sc-TAD) which is partially soluble in an appropriate solvent and is precipitated after completion of the reaction and recovered quantitatively by filtration. One of the drawbacks of polymer-supported catalysts is their low reactivity, which may be ascribed to the insolubility of the catalysts. Moreover, in this year, they described a polymer-supported scandium catalyst by using Nafion (NR-50) as the supporting framework then tested this Nafion-Sc catalyst in several synthetic reaction. The polymer-supported Sc catalyst has all the advantages of $Sc(OTf)_3$ catalyst as far as they tested and has its own advantages originating from its polymer base; the simplification of product workup, separation, and isolation as well as reuse of the catalyst including reaction using flow reactors may provide an economical automation system [13]. In this year, they reported a new methodology for combinatorial synthesis: “ Preparation of Diverse Quinoline Derivatives Using a Novel Polymer-Supported Scandium Catalyst ”. They studied a new method for preparation of a quinoline library using a new polymer-supported scandium catalyst. It has been shown that a quinoline library of high quality and quantity can be readily prepared [14].

In 1998, Kobayashi and Nagayama prepared the microencapsulated catalyst by simply stirring powdered scandium triflate in a solution of polystyrene in cyclohexane at $40^{o}C$ for one hour. The prepared catalyst works very well, showing better activity than the unencapsulated version and maintaining activity even after seven recycles in

imino aldol reaction. However, the amount of microencapsulated scandium triflate used in reactions are much higher than ordinarily catalytic amounts [3].

Huirong and Yingde used salicylic acid resin as a support of $FeCl_3$ Lewis acid catalyst in organic reaction in 1998. They investigated catalytic effects on the esterification of alcohol and carboxylic acid and on acetalization (ketal formation) of aldehyde (ketone) and alcohol. Experimental results has shown that this catalyst can shorten the esterification reaction time, increase the product yield. It has improved resistance to hydrolysis. And it is also separated from reactants and be used repeatedly [11].

Microparticles of novel branched copolymers of lactic acid and amino acids were prepared and characterized by Caponetti et al. in 1999. The microparticles produced from a new class of functionalized, biodegradable, comblike graft copolymers is presented. The copolymers are polyester-polyamino acid hybrids, composed of a poly(L-lactic acid-co-L-lysine) (PLAL) backbone, and poly(L-lysine), poly(D,L-alanine) or poly(L-aspartic acid) side chains extending from the lysine residues of PLAL. The results indicated that the polyamino acid side chains tend to localize at the surface of the particles, the particles carrying poly(lysine) chains have an unusual porous structure, most probably due to the combined effects of the amphiphilic, polyelectrolyte, and chemical nature of the composing copolymer, as well as of the particular preparation technique employed. The capabilities of the microparticles to serve as carriers in controlled drug release and delivery devices were demonstrated by encapsulation and release of rhodamine B, a low molecular weight drug model [73].

A phenoxyethoxymethyl-polystyrene (PEM)-based polymer-supported osmium catalyst has been developed by Kobayashi et al. in 2001. The catalyst was readily prepared from PEM polymer based on a microencapsulation technique, and asymmetric dehydroxylation of olefins has been successfully performed using (DHOD)(2)PHAL as a chiral ligand and $K_3Fe(CN)_6$ as a cooxidant in H_2O/acetone. The catalyst was recovered quantitatively by simple filtration and reused several times without loss of activity [74].

CHAPTER 3

EXPERIMENTAL

3.1 MATERIALS AND APPARATUS

Water-soluble stabilizers polyethylene glycol molecular weight 20,000 (PEG 20000), Poly(oxyethylene nonylphenylether) with 23 units of ethylene oxide (PEO-23) were purchased from Kao Chemical Co., Japan. The following chemicals were supplied by Kishida Chemical Industries Co. Ltd. Electrolyte sodium sulfate ($NaSO_4$), diethylenetriamine (DETA), 1,6-hexamethylenediamine (HMDA), sorbitan trioleate (Span 85), sodium carbonate (Na_2CO_3), sebacoyl chloride (SCB), oil-soluble initiator benzoyl peroxide (BPO) and oil-soluble crosslinker divinyl benzene (DVB). Initiator 2,2'-azobis-2,4-dimethylvaleronitrile (ADVN), V-65 is reagent grade from Wako Pure Chemical Co., Ltd. (Osaka). Polymer dispersant polybutadiene (PBD, M_n = 2794, M_w = 7103, M_w/M_n = 2.54) from Nippon Zeon Co. Ltd., white Beeswax and Paraffin (from Japan). Dimethyl aminoethyl methacrylate (DMAEMA, Tokyo Chemical Co., Tokyo) is reagent grade, and was used as received. Sat. PB (Trade name: PG CI-1000 hydrogenated, M_n = 3459, M_w = 5340, M_w/M_n = 1.54) is hydrogenated telechelic polybutadiene with carbonyl groups at both ends obtained from Nippon Soda Co., Japan. Lewis acid catalysts-scandiumtrifluoromethane sulfonate (ScTf), aluminium trichloride ($AlCl_3$), were supplied by Wako Chemical Co., Japan. Polystyrene was prepared for different molecular weights.

Cyclohexane (CH), chloroform ($CHCl_3$), hexane (HX), benzene and 1-dodecene were supplied by Wako Pure Chemical Co. Ltd. , Japan. These reagents were used without further purification.

Styrene, DVB, kerosene and n-dodecane, are commercial grade. These reagents were distilled under reduced pressure. The initiator BPO, V-65 and PBD used without further purification.

An optical microscope (Olimpus DP-10, Tokyo), scanning electron microscopy (SEM) (JEOL JSM-5310, Japan and JEOL JSM-6400), Fourier transforming infrared spectrometer (FT-IR) (Nicolet 360, Avatar) gas chromatograph-mass spectrometer (VG TRIO 2000, FISONS), transmission electron microscope

(TEM) (H-700H, Hitachi, Japan) and gas chromatograph (GC 163, Hitachi, Japan and GC 14B, Shimatsu) were used. The FT-IR spectrum was measured using a tablet of potassium bromide (KBr) mixed with powder of dry capsule.

3.2 PREPARATION OF CAPSULES

3.2.1 Part 1: Encapsulation by using polystyrene wall in o/w system

Polystyrene wall

The capsules of $Sc(OTf)_3$ were prepared by a solvent evaporation technique. A polymerization reactor used has 500 ml capacity fitted with a flanged 4 port cover. A stirrer was mounted through the center port and connected to the chuck of a variable speed motor. The remaining ports were used to provide the reactor with a condenser. The lower part of the reactor was heated by immersion in a water bath (Figure 6).

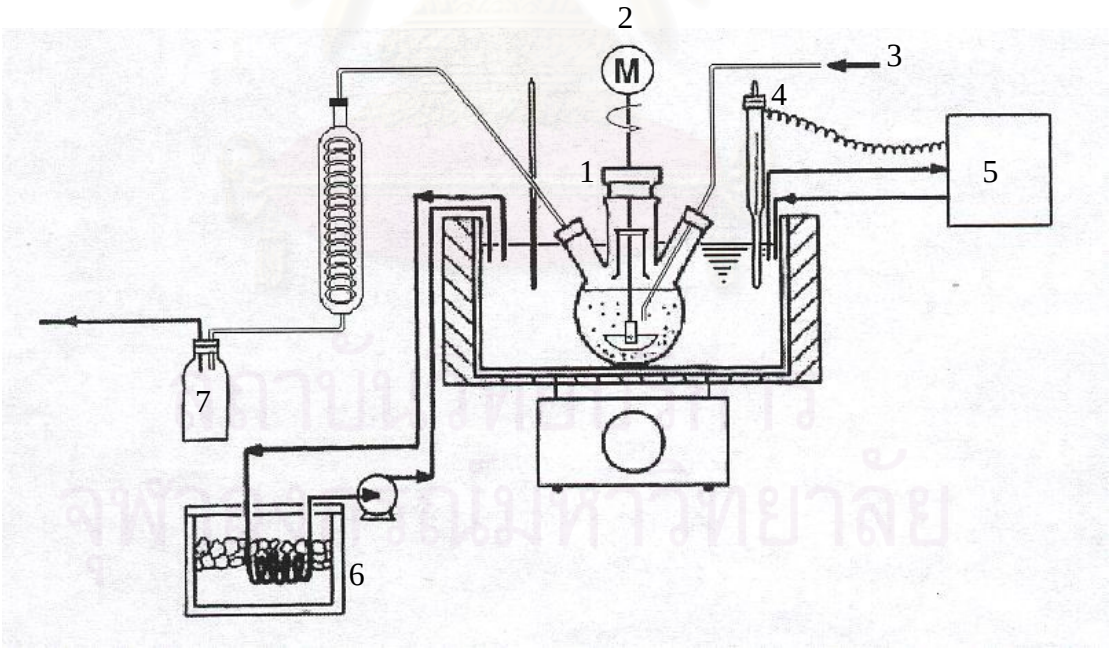


Figure 6. Apparatus of capsule preparation. (1) 500 ml glass flask, (2) speed motor, (3) nitrogen line, (4) thermoregulater, (5) temperature circuit, (6) ice bath, (7) ice trap.

Polystyrene was dissolved in cyclohexane at 40 ^{o}C. ScTf 0.8 g was added into the polymer solution. The mixture was then stirred until it dispersed well. After that, 5 ml of hexane was gradually added in the previous mixture and this suspension was then poured in a solution of stabilizer containing PEG 20000 and/or PEO-23 in water into the reactor with a constant stirring for 1 hour. After evaporation of the solvent at 35-40 ^{o}C under vacuum, the supernatant was separated by filtration. The capsules were dried in vacuum. The flow diagram for the preparation of capsules is illustrated in Figure 7.

The following capsules were prepared using the above procedure for investigating the effects of stabilizers, polymer wall concentration on properties of capsules.

Run No.	1	2	3	4	5	6
PS (g)	2	3	3	3	3	3
CH (ml)	15	15	15	15	15	15
$Sc(OTf)_3$ (g)	-	-	0.8	0.8	0.8	0.8
Hexane (ml)	10	10	10	10	10	10
Na_2SO_4 (g)	1	1	1	-	2	2
PEG 20,000	2	2	2	2	2	2
PEO-23 (g)	8	8	8	8	8	-
H_2O (ml)	200	200	200	200	200	200

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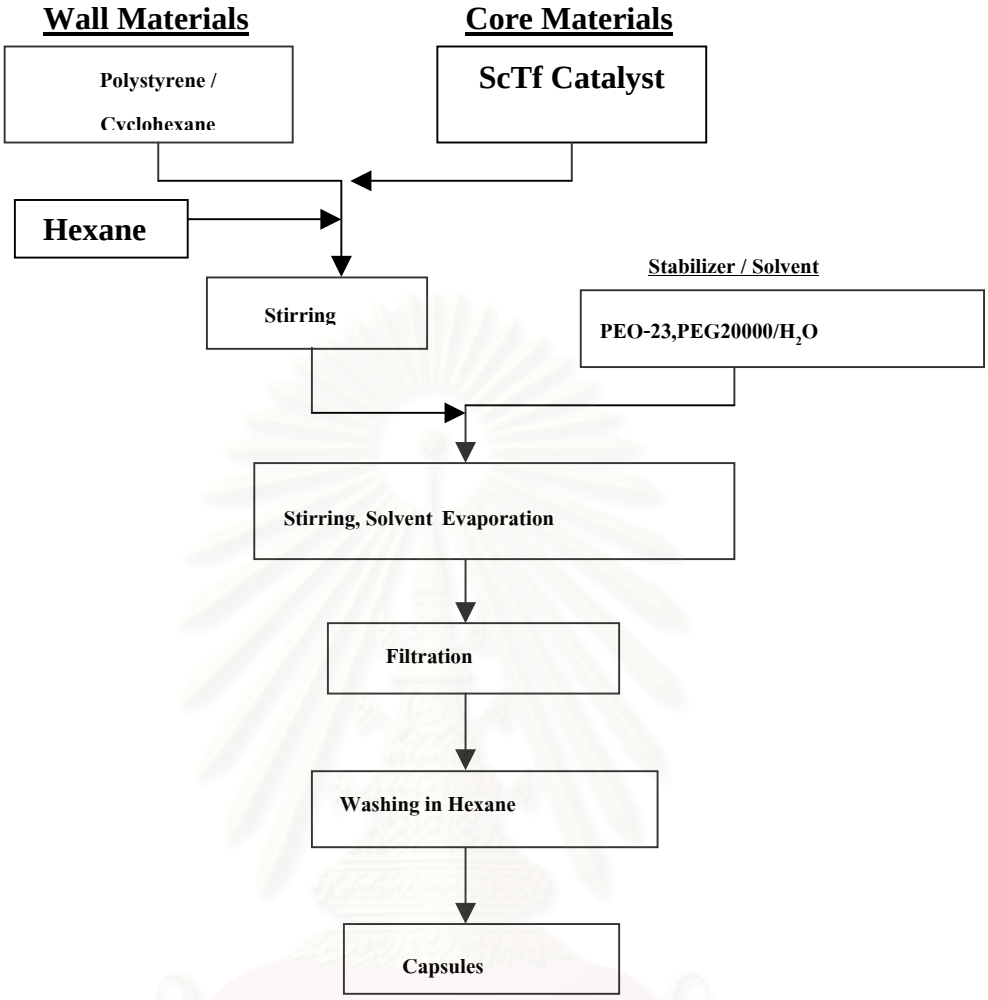


Figure 7. Flow sheet of capsule preparation.

3.2.2 Part 2: Encapsulation by using polyamide wall

Polyamide wall

The capsules of $Sc(OTf)_3$ were prepared by an interfacial condensation polymerization technique. The capsules were prepared by reaction between a water-soluble monomer, 1,6-Hexamethylenediamine or diethylene triamine (DETA) and a monomer soluble in immiscible organic solvents, sebacoyl chloride. An aqueous solution of the water-soluble monomer containing sodium carbonate to neutralize the liberated hydrogen chloride was emulsified in organic solvents to form a W/O emulsion using span 85 as a nonionic emulsifier. Sebacoyl chloride in organic solvent

was then added to the continuous phase. The container was immersed in ice to absorb liberated heat during a polymerization reaction. The capsules were separated by centrifugation and then dried in vacuum.

The following capsules were prepared using the above procedure for investigating the effects of monomer and solvent on properties of capsules.

Run No.	1	2	3	4	5
HMDA (g)	0.343	-	-	-	-
DETA (g)	-	0.206	0.206	0.206	0.206
Na_2CO_3 (g)	0.354	0.354	0.354	-	0.354
H_2O (ml)	15	15	15	15	15
Catalyst (1g)	-	-	-	-	ScTf
Span 85 (ml)	3.8	3.8	3.8	3.8	3.8
$CHCl_3$ (ml)	15	15	-	-	-
CH (ml)	60	60	75	75	75
SBC (g)	0.717	0.717	0.717	0.717	0.717
$CHCl_3$ (ml)	15	15	-	-	-
CH (ml)	60	60	75	75	75

3.2.3 Part 3: Encapsulation by using P(St-DVB) wall

Copolymer P(Styrene-DVB) wall

The capsules were prepared by a crosslink copolymerization technique. A mixture containing 9.4 g of styrene monomer, 0.6 g of DVB and 0.6 g of ADVN was added into a mixture of ScTf or $AlCl_3$ 1 g in a solution of stabilizer (polybutadiene 15.2 g in 190 ml of dodecane) in a reactor with a stirrer. After the mixture was bubbled with nitrogen gas for an hour at room temperature, the nozzle was lifted up above the surface of the mixture and the temperature was elevated to 70 ^{o}C gradually for the polymerization. The polymerization was carried out for 20 h under a nitrogen atmosphere. The polymer was precipitated by methyl alcohol, separated by

centrifugation and dried. The flow diagram for the preparation of capsules is shown in Figure 8.

The following capsules were prepared using the above procedure for investigating the effects of formulation variables on properties of capsules.

Run No.	1	2	3	4	5
PBD (g)	15.2	15.2	15.2	15.2	15.2
Dodecane (ml)	190	190	190	190	190
Catalyst (1g)	-	TiO_2	ScTf	$AlCl_3$	ScTf
Styrene (g)	9.4	9.4	9.4	9.4	9.4
DVB (g)	0.6	0.6	0.6	0.6	0.6
Initiator (0.6g)	V-65	V-65	V-65	V-65	BPO

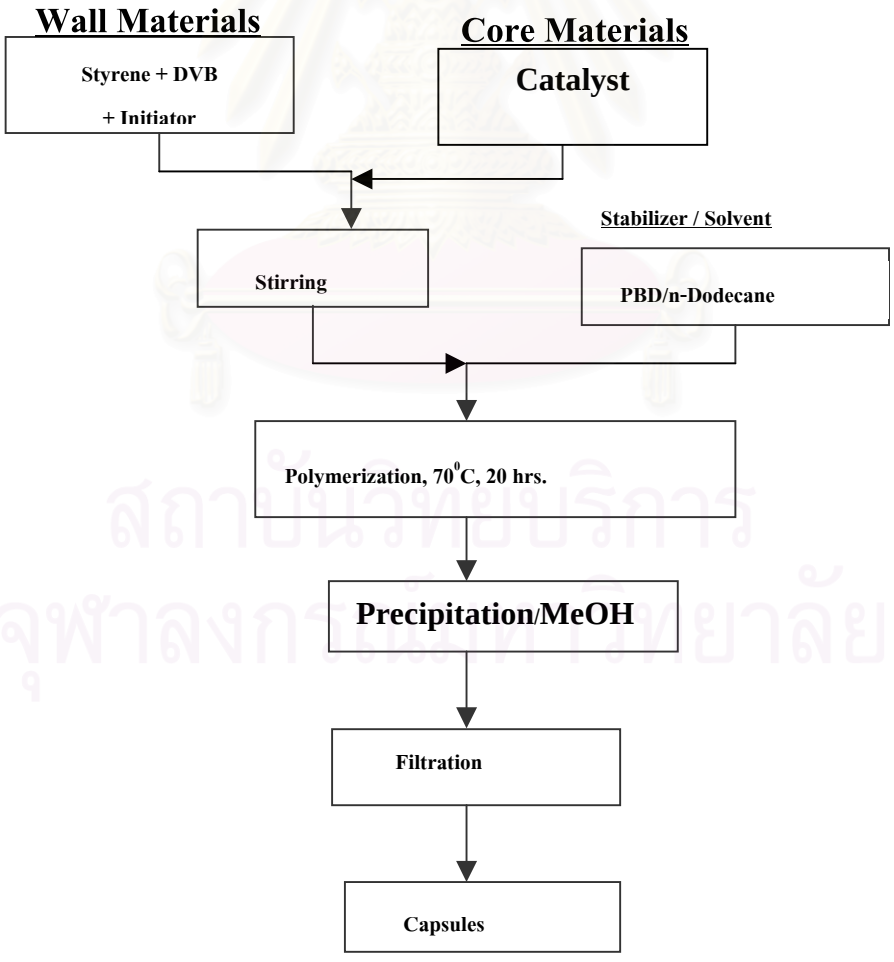


Figure 8 Flow sheet of capsule preparation.

3.2.4 Part 4: Encapsulation by using Beeswax and paraffin wall

Beeswax and paraffin Wall

The capsules of $Sc(OTf)_3$ and $AlCl_3$ were prepared by a solvent coacervation technique. Beeswax 1.2 g and paraffin 0.8 g were dissolved in hot hexane. ScTf or $AlCl_3$ was added into a polymer solution. The mixture was stirred and cooled down gradually in an ice bath. After that, the mixture was added dropwise in a solution of stabilizer; polybutadiene in dodecane with constant stirring at 5 ^{o}C for 1 hr. The supernatant was separated by simple filtration. The capsules were washed with cool hexane, and then dried in a vacuum. The flow diagram for the preparation of capsules is illustrated in Figure 9.

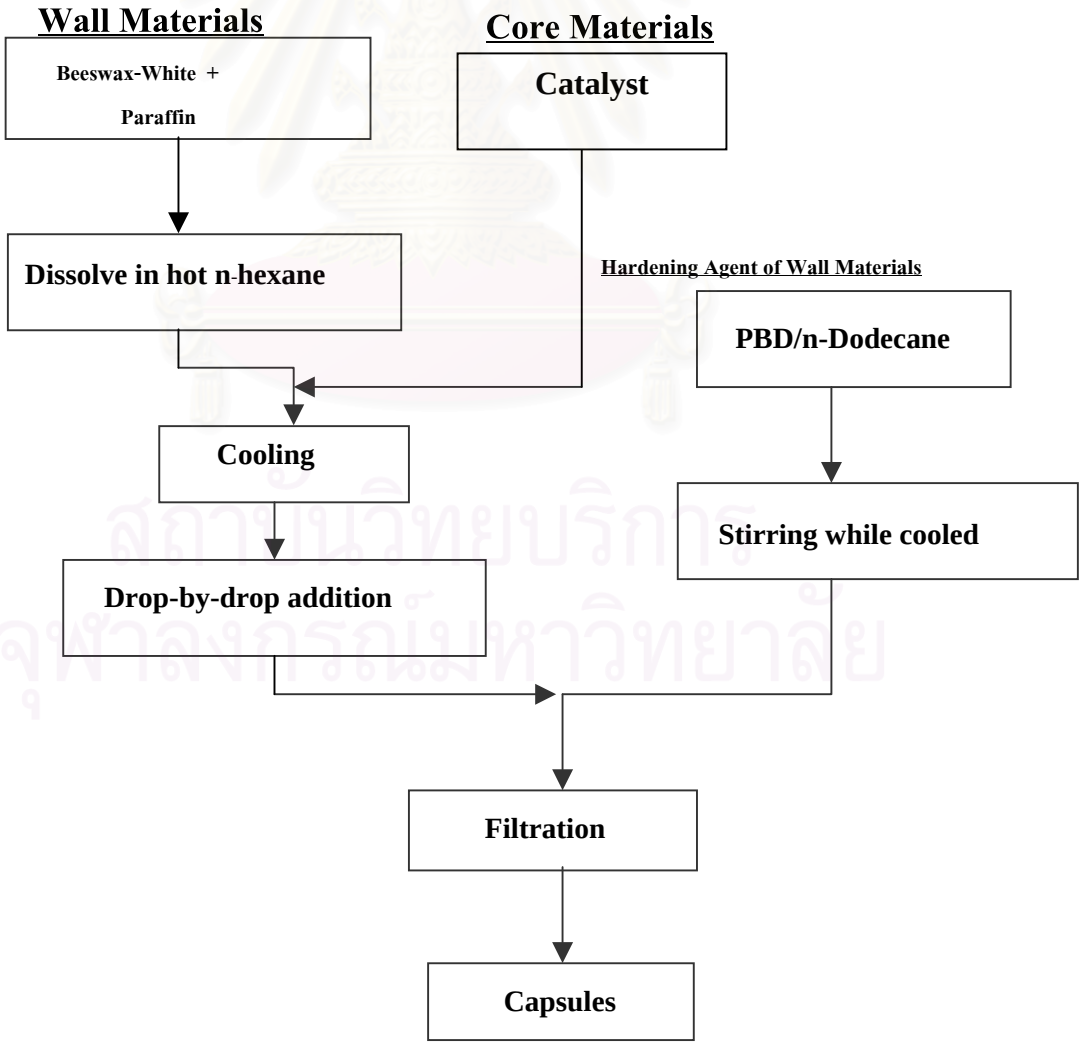


Figure 9 Flow sheet of capsule preparation.

The following capsules were prepared using the above procedure for observing the effects of formulation variables on properties of capsules.

Run No.	1	2	3	4	5
Beeswax (g)	1.2	1.2	1.2	1	1.2
Paraffin (g)	0.8	0.8	0.8	1	0.8
HX (ml)	20	20	20	20	20+PBD(4g)
Catalyst (1g)	ScTf	$AlCl_3$	$AlCl_3$	$AlCl_3$	$AlCl_3$
PBD (g)	4	4	4	4	4
Solvent (100ml)	Kerosene	Kerosene	Dodecane	Dodecane	Dodecane

3.2.5 Part 5: Encapsulation by using polystyrene wall in o/o system

Polystyrene wall

3.2.5.1 Encapsulated ScTf

The capsules were prepared by a solvent evaporation technique. The polymerization reactor used in this reaction was previously mentioned in section 3.2.1.

Polystyrene was dissolved in cyclohexane at 40 ^{o}C. Catalyst 0.8 g was added into the polymer solution. The mixture was then stirred until it dispersed well. After that, the mixture was added to a solution of stabilizer (PBD in dodecane) in the reactor with a constant stirring for 30 min. After evaporation of the solvent at 35-40 ^{o}C under vacuum, the supernatant was separated by centrifugation. The capsules were washed with hexane, and dried under nitrogen atmosphere. The schematic diagram of a method for preparation of capsules is illustrated in Figure 10.

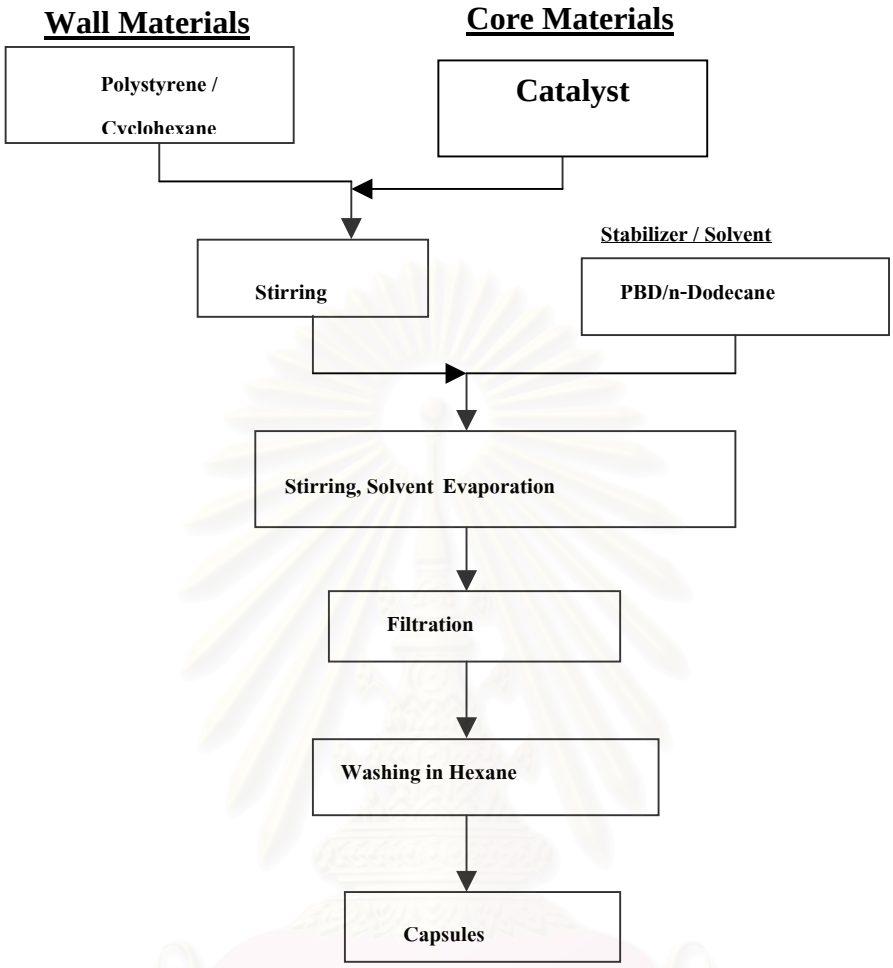


Figure 10 Flow sheet of capsule preparation.

Effect of molecular weight of polystyrene used as polymer wall

The following capsules were prepared using the above procedure for investigating the effects of molecular weight of polystyrene on properties of capsules.

Run No.	1	2	3	4	5
ScTf (g)	0.8	0.8	0.8	0.8	0.8
PS sample No.(3g)	1	2	3	4	5
CH (ml)	20	20	15	15	20
PBD (g)	4	4	4	4	12
Dodecane (ml)	160	160	160	160	160

The capsules were prepared with polystyrene with various molecular weight while other factors were controlled. The average molecular weight (M_w) and number-average molecular weight (M_n) of polystyrene were determined using gel permeation chromatography (GPC). The measurement was carried out by employing tetrahydrofuran (THF) as an elution solvent. The molecular weight of polystyrene is summarized in Table 5. The polystyrene providing the highest stability of capsules was selected for investigating the effect of the amount of stabilizer (PBD).

Table 5. Molecular weights of polystyrene samples employed as wall material

Sample number	**Molecular weight**		**Dispersion index** (M_w/M_n)
	Number average (M_n)	**Weight average** (M_w)	
1	23400	50900	2.17
2	20810	89050	4.28
3	18860	65100	3.45
4	4203	40110	9.54
5	2723	31180	11.45

Effect of stabilizer concentration

The capsules were prepared using polybutadiene (PBD) as stabilizer. 0, 0.25 and 0.05 %w/w stabilizer were added into dodecane to produce capsules.

The following capsules were prepared using the above procedure for investigating the effects of the amount of stabilizer on properties of capsules.

Run No.	1	2	3
ScTf (g)	0.8	0.8	0.8
PS (g)	3	3	3
CH (ml)	20	20	20
PBD (g)	-	4	8
Dodecane (ml)	160	160	160

3.2.5.2 Encapsulated $AlCl_3$

The capsules were prepared using the same procedure as an encapsulation of ScTf in the various amount of polybutadiene (PBD) stabilizer. The stabilizer solution was prepared by dissolving PBD in distilled dodecane with an amount of 0.25, 0.05 or 0.075 %w/w of dodecane

The following capsules were prepared using the above procedure for observing the effects of stabilizer on properties of capsules.

Run No.	1	2	3
$AlCl_3$ (g)	1	1	0.8
PS (g)	3	3	3
CH (ml)	20	20	20
PBD (g)	4	8	12
Dodecane (ml)	160	160	160

3.2.6 Part 6: Encapsulation by using insoluble salt polymer wall

3.2.6.1 Preparation of material wall

Copolymerization of P(St-co-DMAEMA)

A typical procedure was as follows: A mixture containing 90 g of St, 13 g of DMAEMA, and 1 g of ADVN in 20 ml of toluene was added into a reactor while the mixture was stirred. After nitrogen gas was bubbled into the mixture for 1 hr at room temperature, the nozzle was lifted up above the surface of the mixture and the temperature was gradually elevated to 50 ^{o}C for polymerization. The polymerization was carried out for 24 hr under nitrogen atmosphere. The polymer was precipitated by methyl alcohol, separated by centrifugation and dried in a vacuum at room temperature.

3.2.6.2 Preparation of $AlCl_3$ capsule

Insoluble salt polymer Wall

$AlCl_3$ capsules were prepared by a solvent evaporation technique. The polymerization reactor used had 500 cm^3 capacity fitted with a flanged 4 port cover. A stirrer was mounted through the center port and connected to the chuck of a variable speed motor. The remaining ports were used to provide the reactor with a condenser and a nitrogen inlet. The lower part of the reactor was heated by immersion in a water bath.

The hydrogenated telechelic polybutadiene (Sat. PB) with two carbonyl end groups was dissolved in cyclohexane, $AlCl_3$ 0.8 g was added into the polymer solution and stirred in the reactor at 40 ^oC. Then the solution of P(St-co-DMAEMA) in cyclohexane was added dropwise at 40 ^oC with constant stirring for 30 min, resulting in formation of crosslinking polymer around the surface of $AlCl_3$ capsules. The solution of stabilizer (PBD/dodecane) was added into the previous mixture while stirring. After evaporation of the solvent at 35-40 ^oC under a vacuum, the supernatant was separated by centrifugation. The capsules were washed with hexane, and dried under nitrogen atmosphere. The schematic of a method for preparation of capsules is illustrated in Figure 11.

The following capsules were prepared using the above procedure for investigating the effects of formulation variables on properties of capsules.

Run No.	Sat.PB (wt.%)	PS-DMAEMA (wt.%)	PBD (wt.%)	Agitation rate(rpm)
1	10	10	1	250
2	10	10	2	250
3	10	10	5	250
4	5	10	2	250
5	2.5	10	2	250
6	10	15	2	250
7	10	5	2	250

8	10	10	2	375
9	10	10	2	120

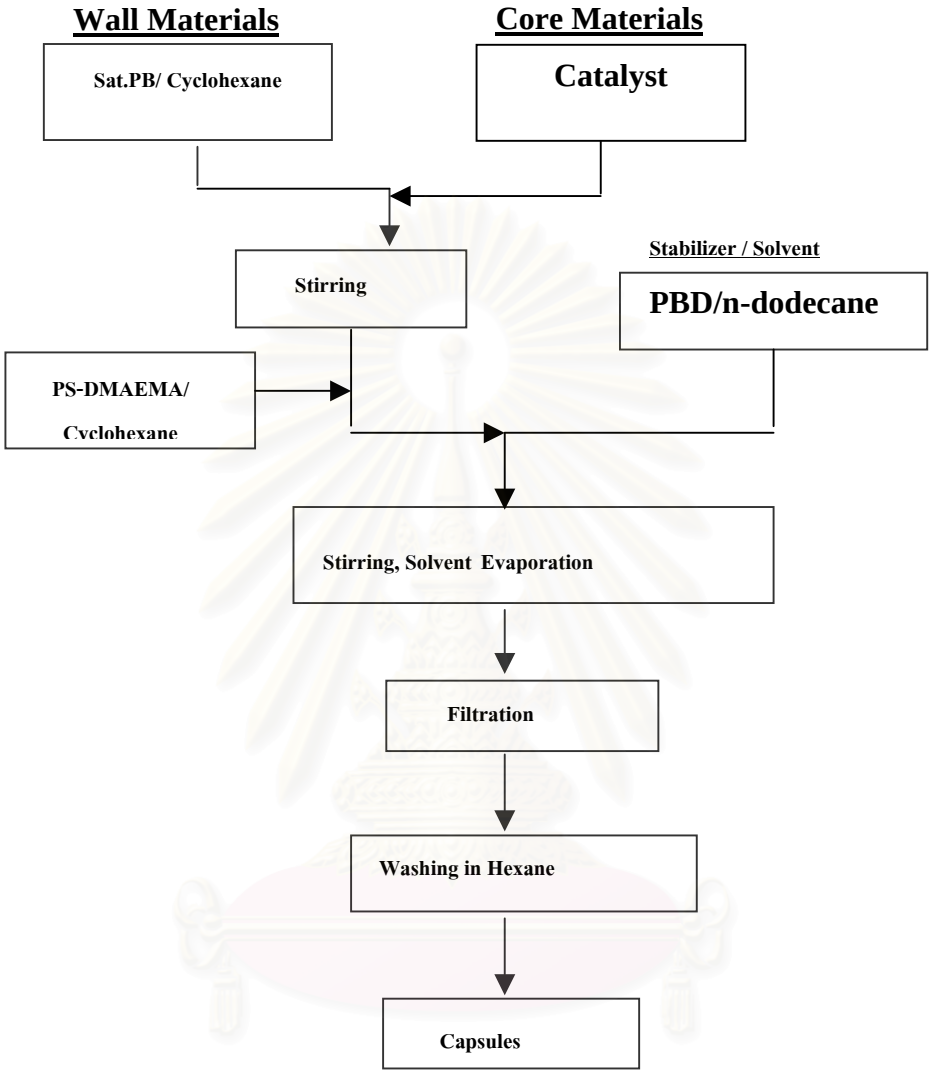


Figure 11 Flow sheet of capsule preparation.

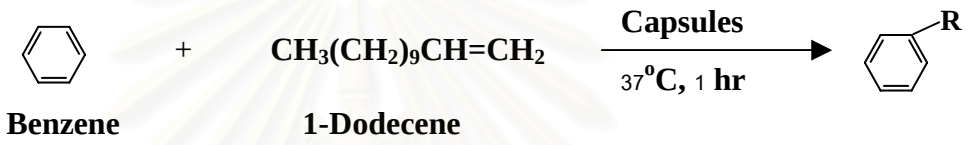
3.3 CHARACTERIZATION

An optical microscope and scanning electron microscopy were used to observe the surface morphology and pore structures of various capsules. The SEM samples were prepared by placing the dried capsules on a stage covered with double-faced conducting carbon tape, some samples covered with silver paste and coated with a

thin gold film, some samples coated with thin carbon film to prevent charging up during observation.

3.4 CATALYTIC ACTIVITY OF PREPARED CAPSULES

The reaction was carried out as the following: 1-dodecene (0.015g. 0.089 mmol) was gradually added to a mixture of encapsulated $AlCl_3$ (30 mg) and benzene (0.885g. 11.3 mmol) at 36 ^oC for 1 hr. The capsules were separated by simple filtration. Benzene was evaporated, and the product was analyzed by gas chromatography and gas chromatography-mass spectrometry.



Benzene **1-Dodecene**

R = $CH_3(CH_2)_{10}$ -CH_2-

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CHAPTER 4

RESULTS AND DISCUSSION

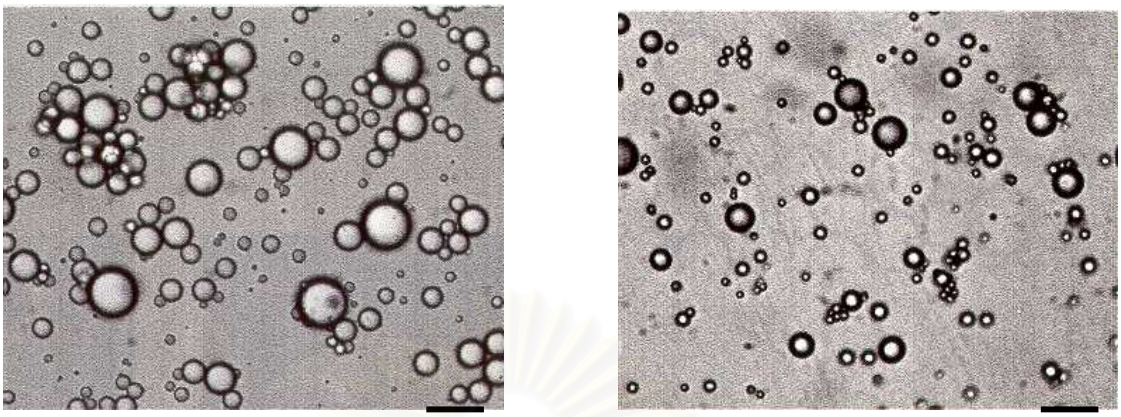
4.1 Part 1: Encapsulation by using polystyrene wall in o/w system

The surface morphology, structures and size of various capsules were observed by optical microscope and scanning electron microscope. The location of catalyst that was inside or adsorbed outside the capsules was also observed.

In this study, polystyrene was used as a coating wall, and scandiumtriflate as a core material. The color of the capsules was white. Their shape could be investigated by visual observation since most of capsules have a form in large particles.

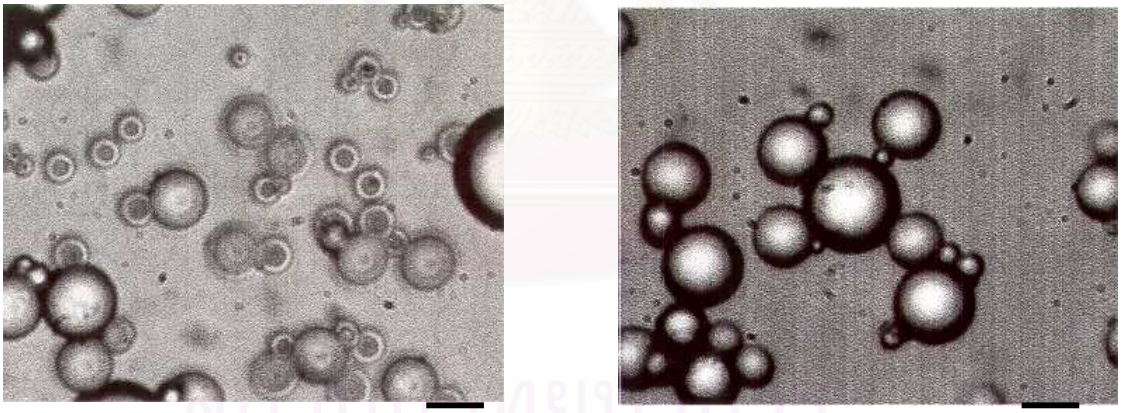
Figures 12-15 show the shape of prepared capsules from different conditions. The wall of the prepared capsules having higher polystyrene concentration caused thicker wall than those having lower concentration (Figures 12, Run 1 and Run 2).

From the Figures 12 and 13, it was indicated that the wall of capsules was transparent. This means that ScTf catalyst was not inside capsules. The shapes of capsules, Figure 13; with Na_2SO_4 (Run 3), without Na_2SO_4 (Run 4) and Figure 14, with PEO-23 (Run 5), without PEO-23 (Run 6) were compared. It was demonstrated that the capsules with Na_2SO_4 and PEO-23 have less aggregation. From these results, it was indicated that the roles of emulsifier in microencapsulation by solvent evaporation technique were both facilitated the emulsification process and stabilized the suspended polymer droplets to prevent aggregation and coalescence of the capsules. This result was found to be in agreement with the previous research [35]. However, the smaller amount of Na_2SO_4 and PEO-23 was not enough for acting as the emulsifying agent. When the amount of Na_2SO_4 and PEO-23 increased, the capsules were found to have less aggregation, observed by SEM micrographs. From scanning electron micrographs of the capsules in Figure 15, most of capsule particles were found to be spherical in shape. The distribution of the size of all the capsules was not in a wide range because the capsules have a tendency to agglomerate.



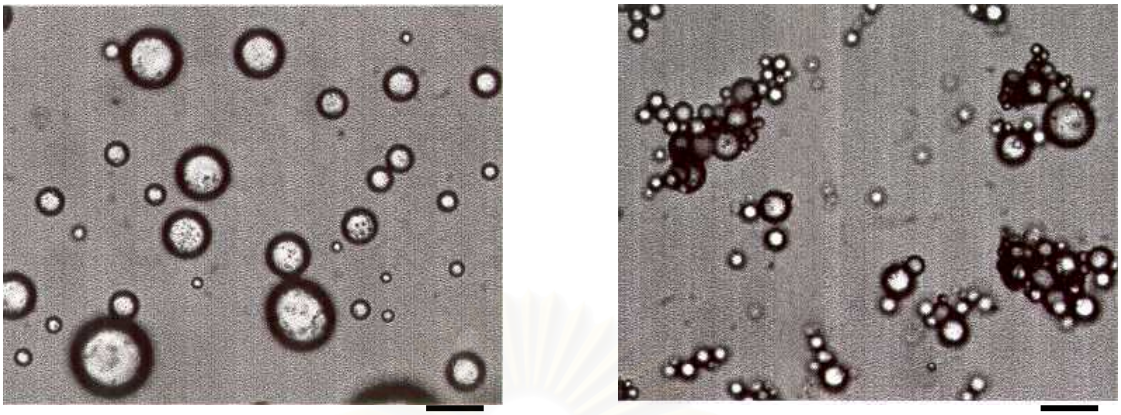
(a) Run 1. 13.3 % PS/Cyclohexane (b) Run 2. 20 % PS/Cyclohexane

Figure 12 Optical micrographs of the capsules using polystyrene as wall material in o/w system at different polymer wall concentration.



(a) Run 3. with Na_2SO_4 salt (1g) (b) Run 4. without Na_2SO_4 salt

Figure 13 Optical micrographs of the capsules using polystyrene as wall material in o/w system at affected by Na_2SO_4 salt



(a) Run 5.with PEO-23 stabilizer (b) Run 6.without PEO-23 stabilizer

Figure 14 Optical micrographs of the capsules using polystyrene as wall material in o/w system at affected by PEO-23 stabilizer.

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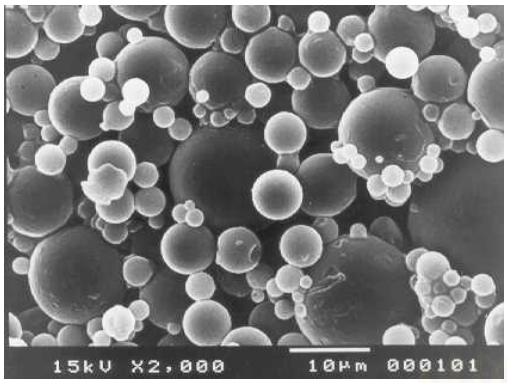
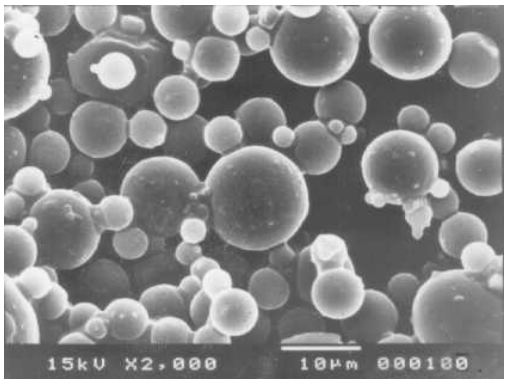
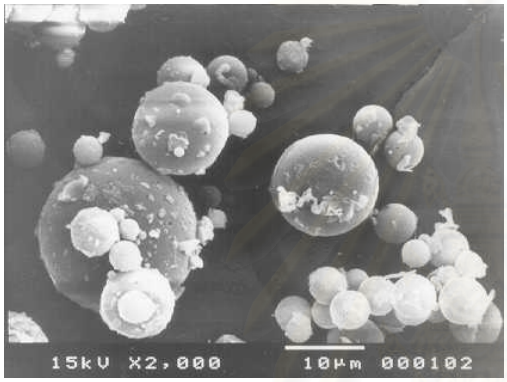


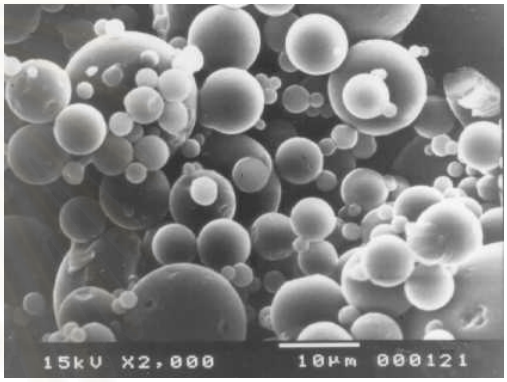
(a) Run 1



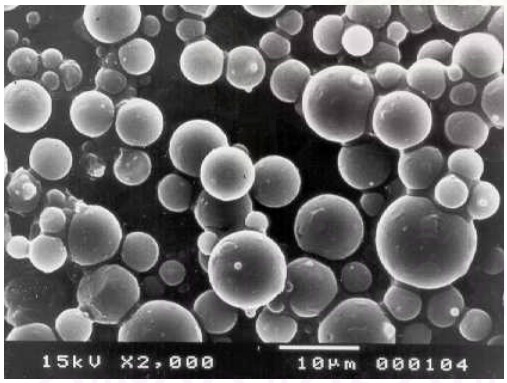
(b) Run 2.



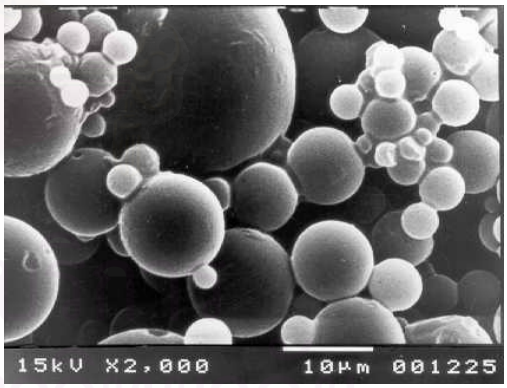
(c) Run 3



(d) Run 4.



(e) Run 5



(f) Run 6.

Figure 15 Scanning electron micrographs of the capsules at various formulation variables.

4.2 Part 2: Encapsulation by using polyamide wall

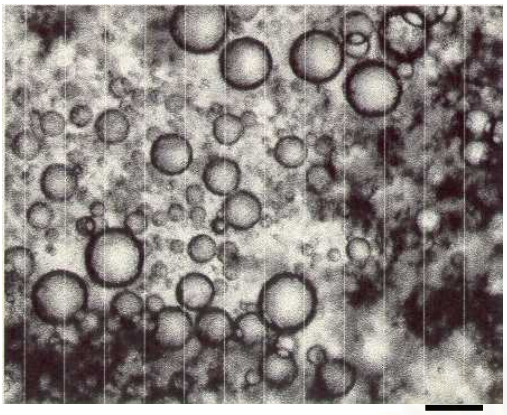
In this study, polyamide was formed by the reaction between 1,6-Hexamethylenediamine (HMDA) or diethylene triamine (DETA) and sebacoyl chloride (SBC), using sorbitan trioleate (Span 85) as a stabilizer.

The color of each formulated capsule was white, and almost all of them had a spherical shape which can be observed by optical micrographs. The morphology and capsule size were not much different when a different monomer was used (see Figure 16; Run 1 and 2). The capsules of Run 1 and Run 2 were prepared by the reaction of SBC with HMDA and DETA, respectively. For the formation of capsule wall, an amino group of HMDA or DETA is capable to interact with a carbonyl group of SBC to form polyamide. It was found that morphology of the capsules at different monomers (Run 1 and 2) was not much different when the capsules were prepared in different solvents (Run 2 and 3). This was because the capsule wall was formed from the same reaction, the amine group provided from HMDA in Run 1 or DETA in Run 2, reacted with carbonyl group in SBC to form polyamide. However, the thickness and stability of capsules were affected by the solvents.

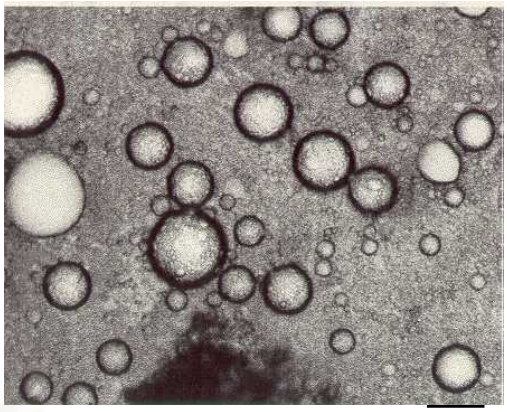
The capsules without Na_2CO_3 (Run 4) have small particles adhering to the surface. It may have occurred from the side reaction with the HCl in the reaction. Therefore, Na_2CO_3 should be used to neutralize generated HCl in the polycondensation reaction.

The optical micrograph of prepared capsules with adding core material, ScTf (Run 5), showed that some of the ScTf catalyst were encapsulated inside the capsules.

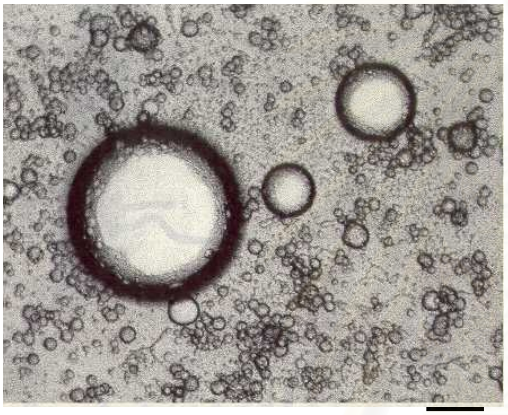
The effectiveness and the catalytic activity of encapsulated ScTf capsules were studied by using alkylation reaction of benzene and 1-dodecene as a reaction model. It was found that the capsules have no catalytic activity in this reaction because the small amount of ScTf catalyst inside the prepared capsules and ScTf may be deactivated due to the water system during encapsulation process.



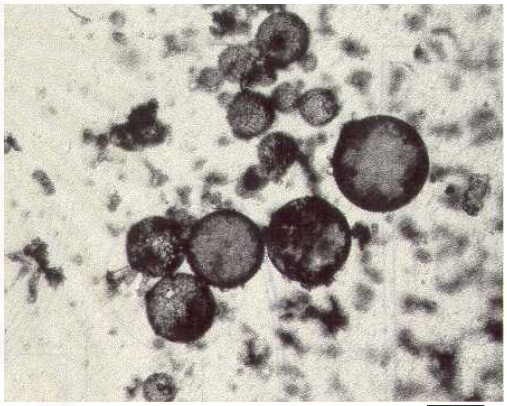
(a) Run 1



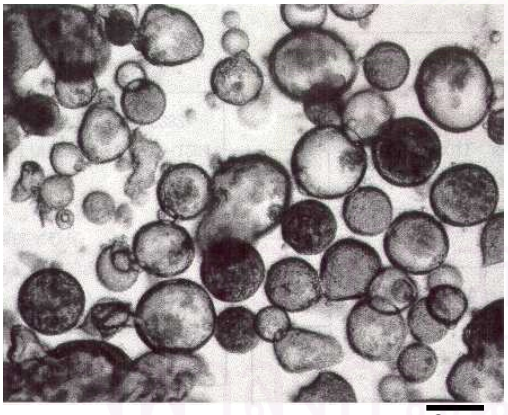
(b) Run 2.



(c) Run 3



(d) Run 4.



(e) Run 5

Figure 16 Optical micrographs of the capsules at various formulation variables.

4.3 Part 3: Encapsulation by using P(St-DVB) wall

In this section, styrene and divinylbenzene (DVB) were utilized as wall material for capsules by using 6% of DVB.

First, TiO_2 was used as the core material for investigating the possibility for encapsulation of the Lewis acid catalysts, ScTf and $AlCl_3$, because TiO_2 is an inert substance and has small spherical powder in shape. The encapsulated TiO_2 was observed by transmission electron microscopy (TEM) and optical microscopy as shown in Figure 17 and 18 (a), respectively. From TEM micrograph of encapsulated TiO_2, it was considered that the dark particles inside capsules indicated the particles of TiO_2.

When the morphology of the capsules contained three different core materials (TiO_2, ScTf and $AlCl_3$), using 2,2'-Azobis-2,4-dimethylvaleronitrile (ADVN, V-65) as an initiator, were compared, it was demonstrated that the capsules prepared using TiO_2 as a core material had a smaller particle in size and more spherical in shape than the capsules using ScTf and $AlCl_3$ as core materials (Figure 18, Run 1, Run 2 and Run 3, Figure 19). It was also found that the TiO_2 does not react with any substances during the polymerization process. On the other hand, encapsulation of ScTf or $AlCl_3$ cannot be performed. The polymerization reaction of styrene and DVB monomer gave a low yield due to some reactions occurred during polymerization which was observed by generated HCl acid in the reactor. In addition, in the presence of BPO-initiator (Figure 18, Run 4.), the result was shown that the polymerization reaction was not occurred, so that the reaction product could not precipitate in methyl alcohol. This may be caused by the side reaction between ScTf catalyst and the styrene or DVB monomers and/or BPO initiator, whereas in the presence of V-65, the polymerization reaction resulted in a low yield, as determined by gravimetric method. It was found that the monomer conversion was less than 10%. Therefore, it was very difficult to observe the dried capsules by SEM.

Catalytic property of prepared capsules

Alkylation reaction of benzene with 1-dodecene was chosen as a model reaction to study the catalytic activity of the capsules. From Table 6, it was suggested that the alkylation of benzene with 1-dodecene gave the phenyldodecanes (2-p, 3-p, 4-

p, 5-p and 6-phenyldodecane) as products. It was shown that the prepared capsules had a very low catalytic activity for the Friedel-Crafts alkylation reaction of benzene with 1-dodecene (Run 4-5). However, the prepared capsules can be easily recovered by simple filtration. When the reaction was performed in the presence of unencapsulated ScTf and $AlCl_3$ (free ScTf and free $AlCl_3$) under the same conditions, a higher product yield was obtained. This is because some amount of catalyst can react with the monomers or initiator during the polymerization process, resulting in a small amount of active catalyst encapsulated inside the capsules. However, the catalytic activity of $AlCl_3$ is higher than that of ScTf in all experiments.

Table 6. Catalytic activity for Friedel-Crafts alkylation reaction of benzene with dodecene

Catalyst	Conversion (%)
Free ScTf	17
Free $AlCl_3$	97
Encapsulated ScTf (Run. 3)	2
Encapsulated $AlCl_3$ (Run. 4)	18.8

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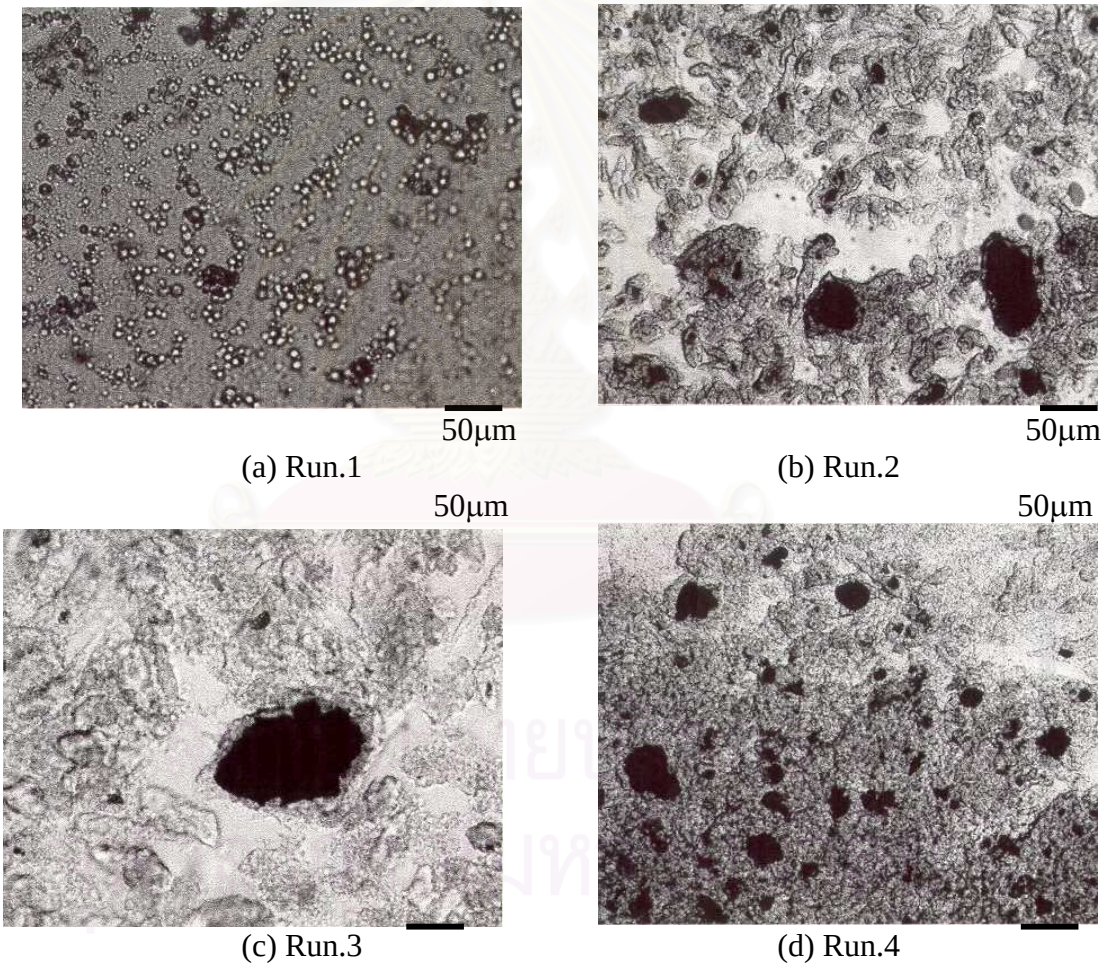
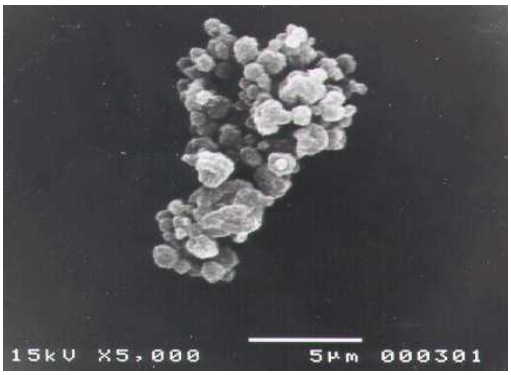
Figure 17 Transmission electron micrograph of capsule repared by using TiO_2 as core material.

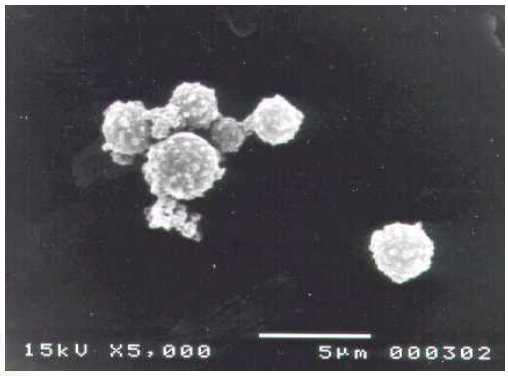


(a) Run.1 (b) Run.2

(c) Run.3 (d) Run.4

Figure 18 Optical micrographs of the capsules prepared by using P(St-DVB) as capsule wall at different core materials and initiators.
For V-65 initiator: (a) TiO_2 core material, (b) ScTf core material, (c) $AlCl_3$ core material, For BPO initiator: (d) ScTf core material





(a) Run. 1 (b) Run.2

Figure 19 Scanning electron micrographs of the capsules prepared by using P(St-DVB) as capsule wall at different core materials.
(a) without core material,(b) TiO_2 as core material

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4.4 Part 4: Encapsulation by using beeswax and paraffin wall

In this process, a dispersion of core material in a melted paraffin and beeswax solution was solidified when it was cooled in a solution of hardening, and formed the capsule wall.

The morphology of the prepared capsules at different formulation systems was observed by optical microscopy and scanning electron microscopy as shown in Figures 20 and 21, respectively. The capsules prepared using ScTf as a core material gave a smaller size when compared with those using $AlCl_3$ as a core material because

$AlCl_3$ capsules have a tendency to agglomerate and the size of $AlCl_3$ particles is usually larger than ScTf particles.

Figure 20 shows a comparison of the wall structure of prepared capsules performed by using solvent as kerosene (Figure 20a and 20b) and dodecane (Figure 20c, 20d and 20e). It was found that the dispersion and wall thickness of the capsules were affected by the solvent of hardening solution. The capsules can be dispersed in dodecane better than kerosene. It was indicated that thin film of capsules prepared using dodecane could cover the surface of core material, and also has the thicker wall than the capsules prepared using kerosene. In comparison with the capsules prepared from 1:1 and 1.2:0.8 of beeswax: paraffin, latter capsules were found to encapsulate greater amount of catalyst. However, the prepared capsules using 1.2:0.8 of beeswax: paraffin and additional amount of 20 %w/v of PBD in hexane (Run.5) gave more complete encapsulation than the other formulation systems.

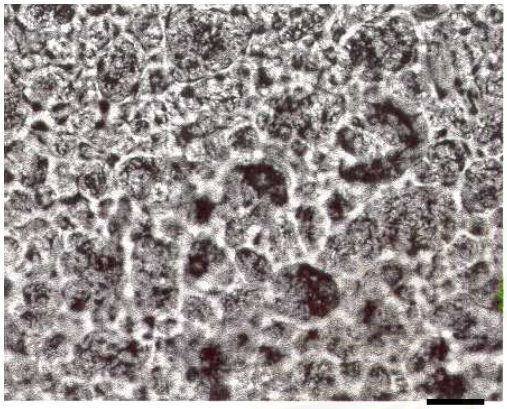
Table 7. Catalytic activity for Friedel-Crafts alkylation reaction of benzene with dodecene

Catalyst	% Conversion
Encapsulated ScTf (Run. 1)	3
Encapsulated $AlCl_3$ (Run. 2)	12
Encapsulated $AlCl_3$ (Run. 3)	25
Encapsulated $AlCl_3$ (Run. 4)	24
Encapsulated $AlCl_3$ (Run. 5)	38.5

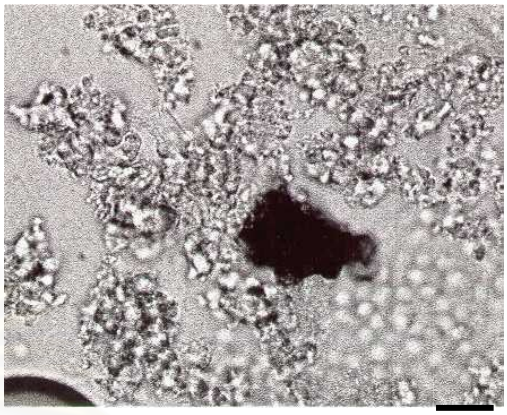
Catalytic property of prepared capsules

Alkylation reaction of benzene with 1-dodecene was performed, and used as a model reaction for investigating the catalytic activity of the capsules as similar to the previous sections. Table 7. shows the 1-dodecene conversion. From GC and GC-MS analysis, the alkylation reaction of benzene with 1-dodecene gave five positional isomers of phenyldodecanes (2-, 3-, 4-, 5- and 6-phenyldodecanes) as products. The prepared capsules had a very low catalytic activity for the Friedel-Crafts alkylation reaction of benzene with 1-dodecene. Moreover, the capsules were hardly recovered

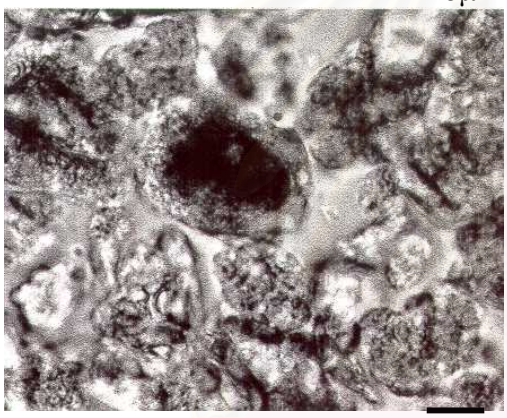
due to the wall materials because beeswax and paraffin can be easily melted or dissolved in benzene during the reaction.



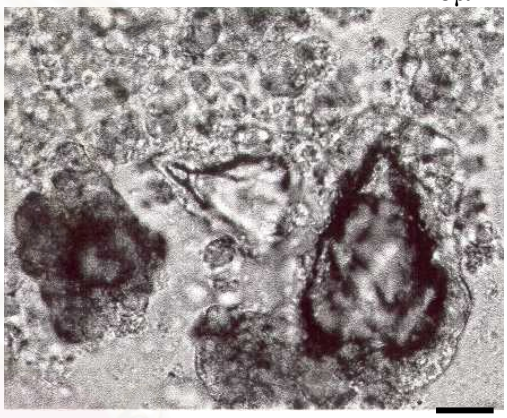
(a) Run.1



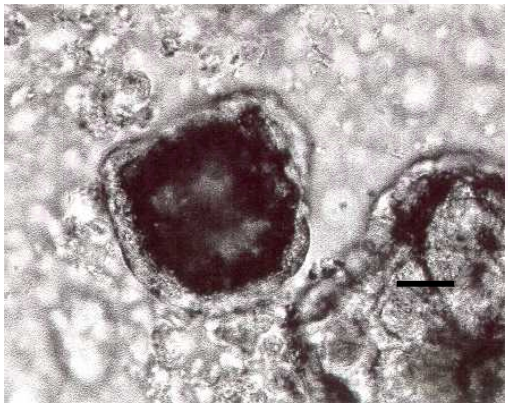
(b) Run.2



(c) Run.3

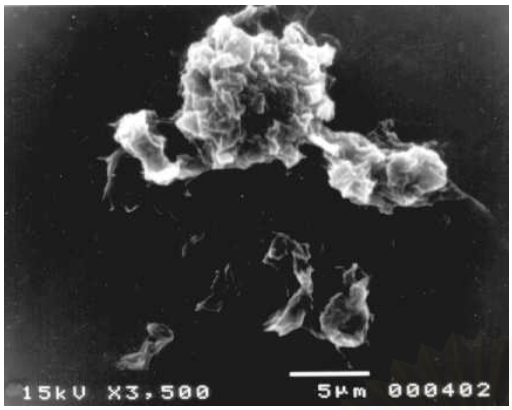


(d) Run.4

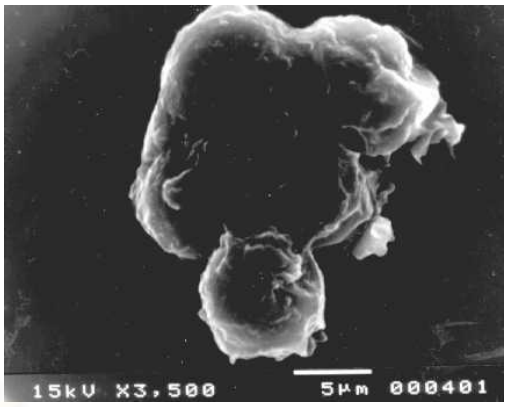


(e) Run.5

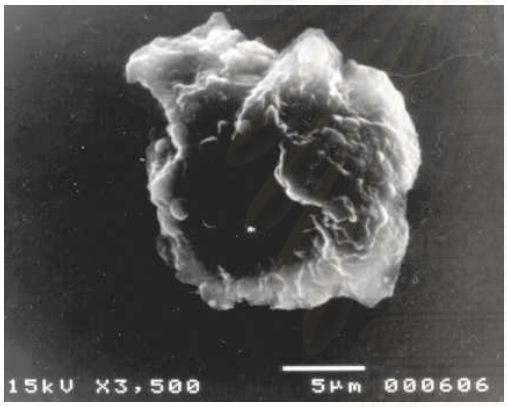
Figure 20 Optical micrographs of the capsules prepared by using beeswax and paraffin wax as capsule wall at different conditions.



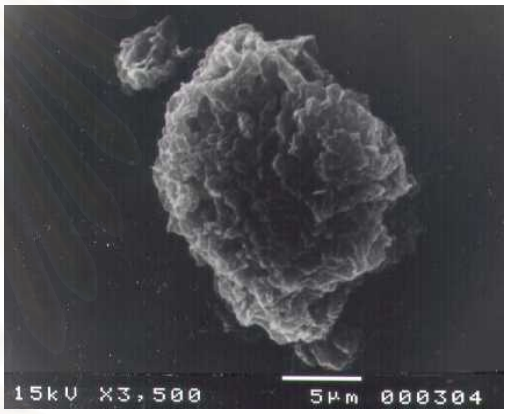
(a) Run.1



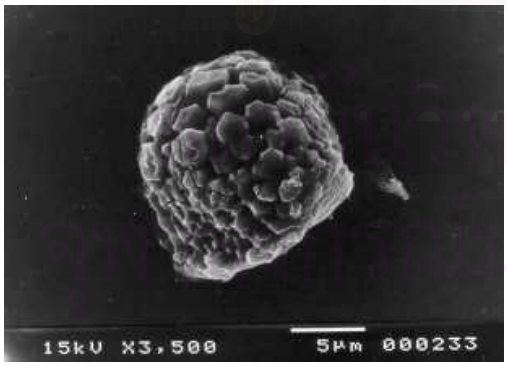
(b) Run.2



(c) Run.3



(d) Run.4



(e) Run.5

Figure 21 Scanning electron micrographs of the capsules prepared by using beeswax and paraffin wax as capsule wall at different conditions.

4.5 Part 5: Encapsulation by using polystyrene wall in an o/o system

In this system, the capsules were prepared by using polystyrene as wall material and ScTf catalyst as core material in an o/o system. The morphology of the capsules at various molecular weight of polystyrene can be observed by optical microscopy and scanning electron microscopy as shown in Figures 22 and 23, respectively. It was indicated that the particle size of the capsules increases with an increasing in the molecular weight of the polystyrene, but the agglomerated particles still occurred in all runs. This may be due to the dispersion phase of polystyrene in cyclohexane having a tendency to agglomerate in continuous phase contained dodecane to result in the coagulation and irregular shape. In case of preparing capsules at various amounts of PBD stabilizer, the particle size and shape of capsules were not quite different. This indicated that 0.25 wt% of PBD was enough to stabilize the capsules during the reaction (Figures 24 -25).

Encapsulated $AlCl_3$

The morphology of the capsules with the different amount of stabilizer, PBD in dodecane, is shown by optical microscopy (Figure 26) and scanning electron microscopy (Figure 27). The capsules prepared using $AlCl_3$ as a core material was found to have a larger size than the prepared capsules using ScTf as a core material. This may be explained that $AlCl_3$ capsules have a tendency to agglomerate and the particle size of $AlCl_3$ is also larger than that of ScTf. ScTf may be dispersed in polymer solution better than $AlCl_3$. From optical micrographs, the dark core represents $AlCl_3$ catalyst inside capsules. When compared with encapsulated ScTf, the encapsulated $AlCl_3$ can be entrapped inside capsules, and the capsules had thicker wall and more complete encapsulation.

Catalytic property of prepared capsules

Alkylation reaction of benzene with 1-dodecene was performed as a reaction model for investigating the catalytic activity of the capsules as similar to the previous

parts. Table 8. shows the 1-dodecene conversion. The alkylation reaction of benzene with 1-dodecene give yields five positional isomers of phenyldodecanes (2-, 3-, 4-, 5- and 6-phenyldodecanes) as products as previously mentioned. When compared with encapsulated ScTf, the encapsulated $AlCl_3$ is more active catalyst for the Friedel-Crafts alkylation reaction of benzene with 1-dodecene. This is because the ScTf is a weaker or milder catalytic activity catalyst. This result was found to be in agreement with the previous sections, because the reaction performed in the presence of unencapsulated ScTf and $AlCl_3$ (free ScTf and free $AlCl_3$) under the same conditions gave a higher yield in the presence of $AlCl_3$. However, the capsules were hardly recovered because the wall materials, polystyrene, can be dissolved in benzene during the reaction.

Table 8. Catalytic activity for Friedel-Crafts alkylation reaction of benzene with dodecene

Catalyst	% Conversion
Encapsulated ScTf (Run. 1)	3
Encapsulated ScTf (Run. 2)	2
Encapsulated ScTf (Run. 3)	2.5
Encapsulated ScTf (Run. 4)	1.8
Encapsulated ScTf (Run. 5)	2.3
Encapsulated $AlCl_3$ (Run. 1)	96
Encapsulated $AlCl_3$ (Run. 2)	97
Encapsulated $AlCl_3$ (Run. 3)	95

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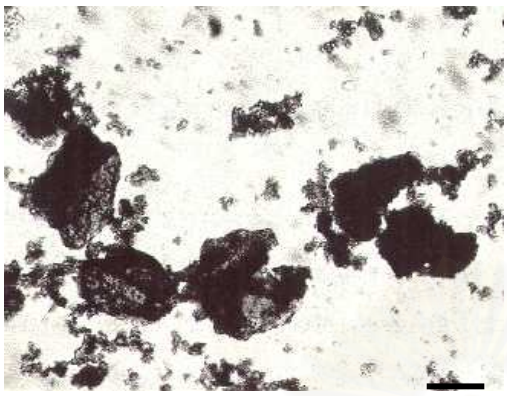
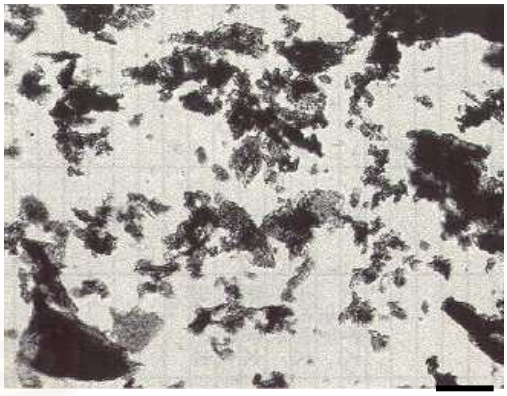
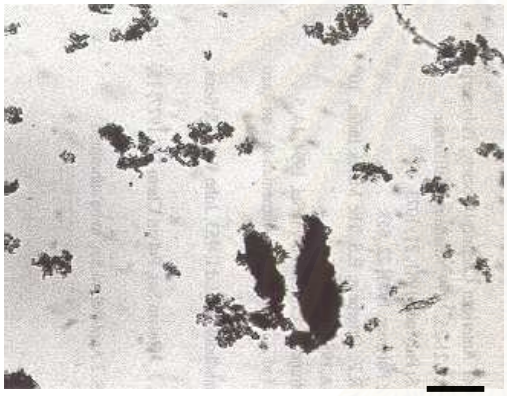


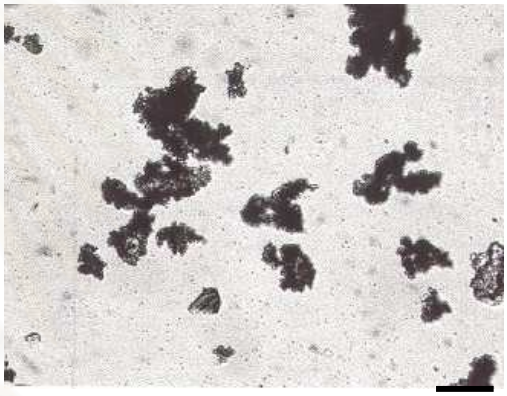
(a) Run.1



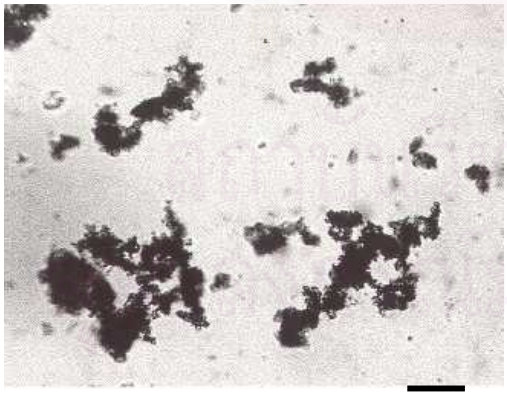
(b) Run.2



(c) Run.3



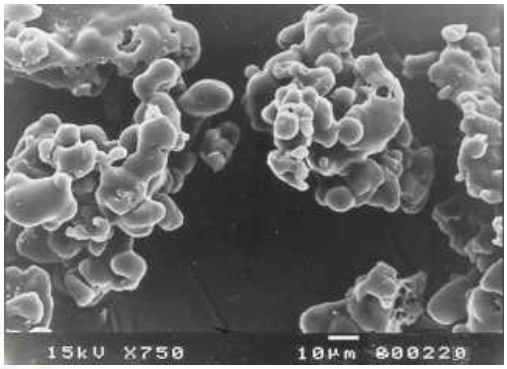
(d) Run.4



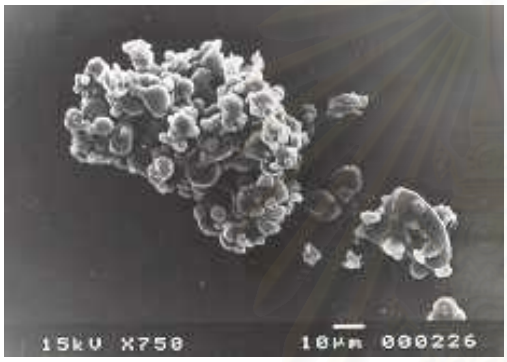
(e) Run.5

Figure 22 Optical micrographs of the capsules prepared by using PS as capsule wall in o/o system, ScTf as core material at different molecular weight of polymer wall.

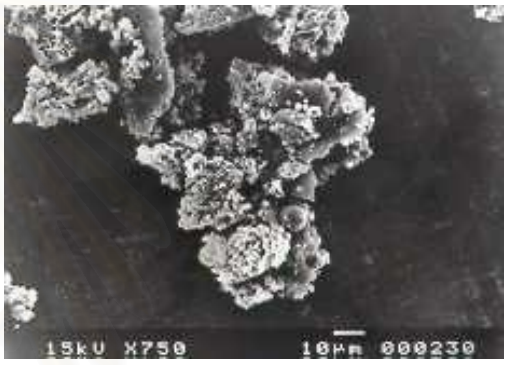
(a) Run.1



(b) Run.2



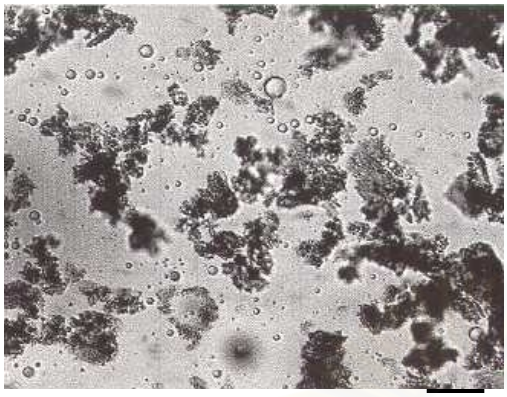
(c) Run.3



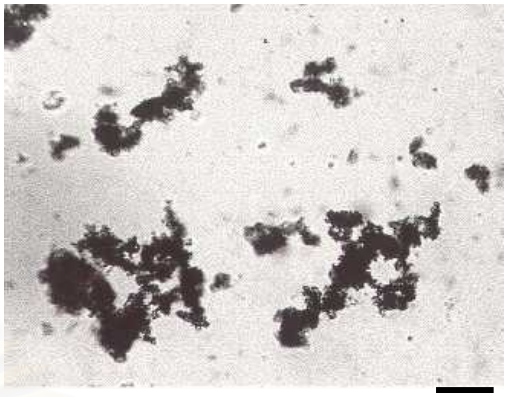
(d) Run.4

(e) Run.5

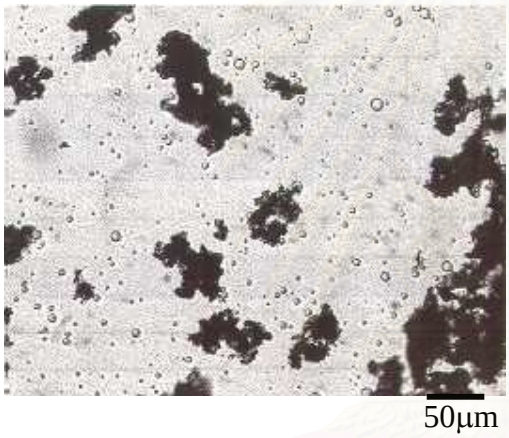
Figure 23 Scanning electron micrographs of the capsules prepared by using PS as capsule wall in o/o system, ScTf as core material at different molecular weight of polymer wall.



(a) Run.1



(b) Run.2



(c) Run.3

Figure 24 Optical micrographs of the capsules prepared by using PS as capsule wall in o/o system, ScTf as core material at different amount of stabilizer. (a) 0% PBD, (b) 0.25%PBD, (c) 0.5%PBD.

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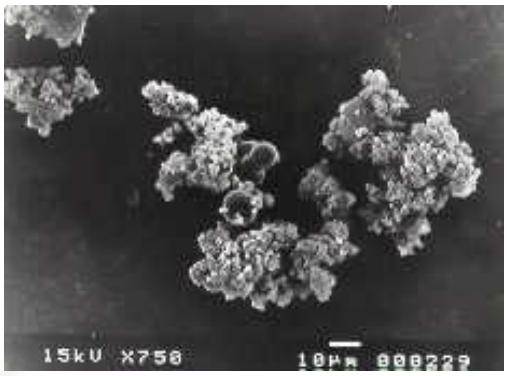
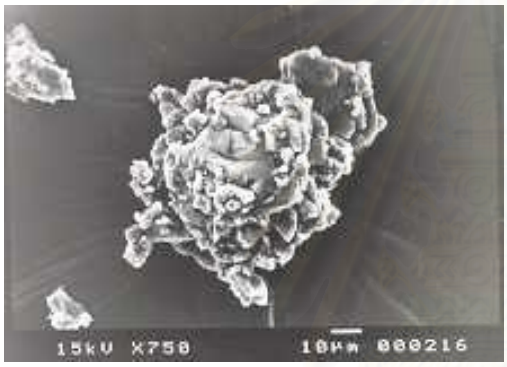
(a) Run.1



(b) Run.2



(c) Run.3

Figure 25 Scanning electron micrographs of the capsules prepared by using PS as capsule wall in o/o system, ScTf as core material at different amount of stabilizer. (a) 0% PBD, (b) 0.25%PBD, (c) 0.5%PBD

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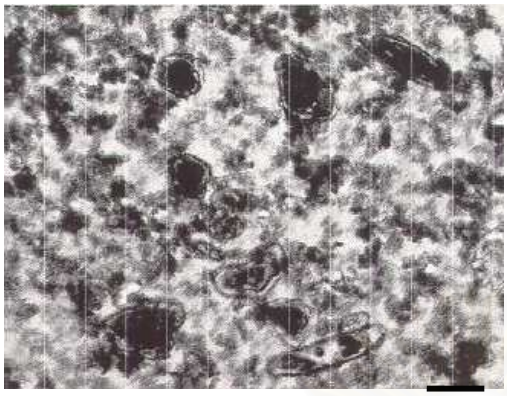
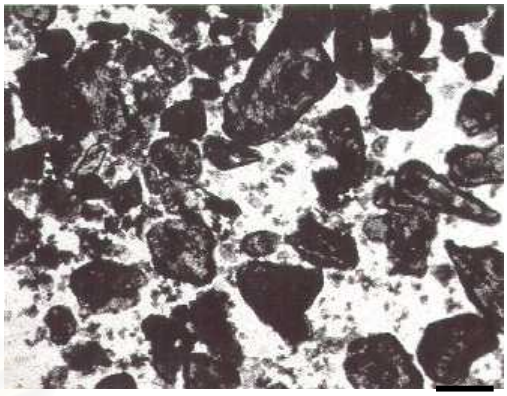
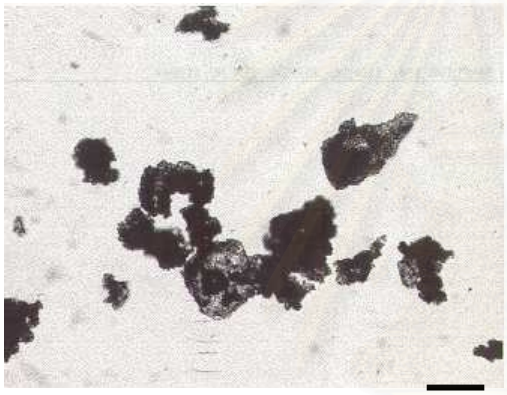


(a) Run.1



(b) Run.2



(c) Run.3

Figure 26 Optical micrographs of the capsules prepared by using PS as capsule wall in o/o system, $AlCl_3$ as core material at different amount of stabilizer. (a) 0.25% PBD, (b) 0.5%PBD, (c) 0.75%PBD

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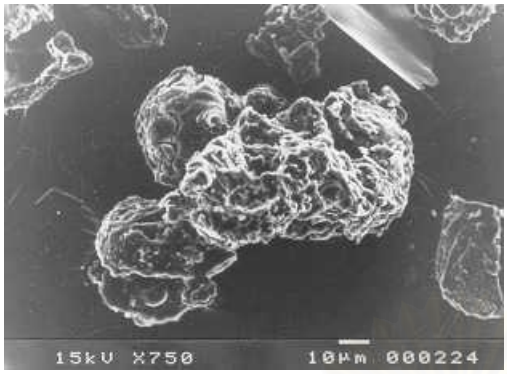
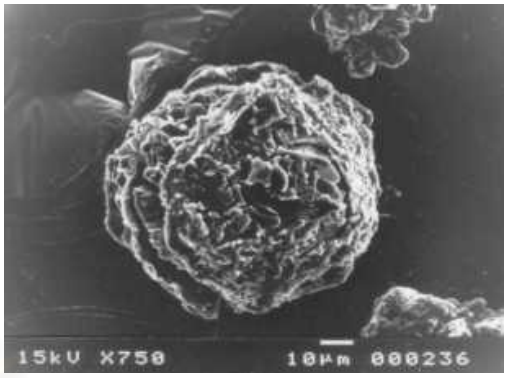
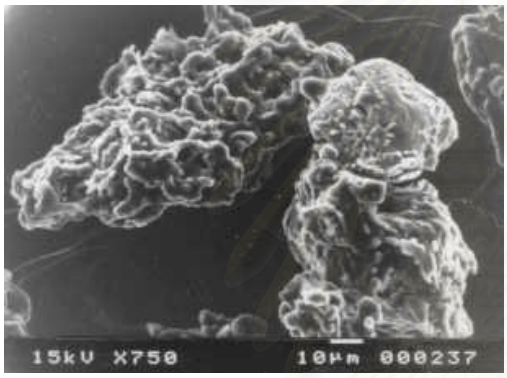


(a) Run.1



(b) Run.2



(c) Run.3

Figure 27 Scanning electron micrographs of the capsules prepared by using PS as capsule wall in o/o system, $AlCl_3$ as core material at different amount of stabilizer. (a) 0.25% PBD, (b) 0.5%PBD, (c) 0.75%PBD

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4.6 Part 6: Encapsulation by using insoluble salt polymer wall

The emphasis in this study was on the establishment of an encapsulation procedure to preserve highly reactive $AlCl_3$ which easily loses activity in the air or a highly moist atmosphere by using polymer wall which have high stability to keep catalytic activity for long-term using. Moreover, it should be resisted or stable in organic solvents.

The polymer wall was formed by the reaction of the dimethylamino groups of poly(styrene-*co*-dimethylaminoethyl methacrylate), P(St-*co*-DMAEMA) and –COOH groups of hydrogenated telechelic polybutadiene (Sat. PB) to form the insoluble salt of the polymer (Figure 28) by using liquid polybutadiene (PBD) as a stabilizer. Figures 29 and 30 illustrates optical micrographs and scanning electron micrographs of the capsule particles with the different amounts of co-wall materials, amounts of stabilizer and the rate of agitation.

The XRD (X-ray diffraction) data analysis indicates that the catalyst was still in the form of $AlCl_3$.

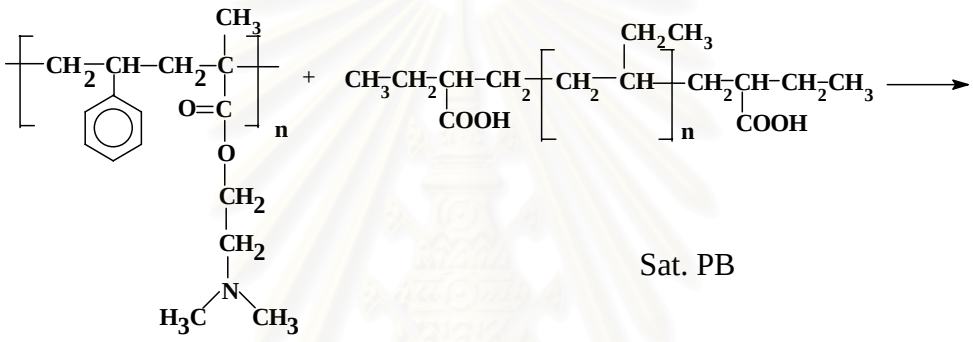
In this study, the size distribution of all the capsules was not in a wide range because the $AlCl_3$ capsules have a tendency to agglomerate as shown by optical microscopy (Figure 29) and scanning electron microscopy (Figure 30). At 10 wt% of Sat. PB, 10 wt% of P(St-*co*-DMAEMA) and 2 wt% of PBD, the capsules had a smoother surface and achieved more complete encapsulation than the prepared capsules with the other ratios.

Effect of polymer wall concentration

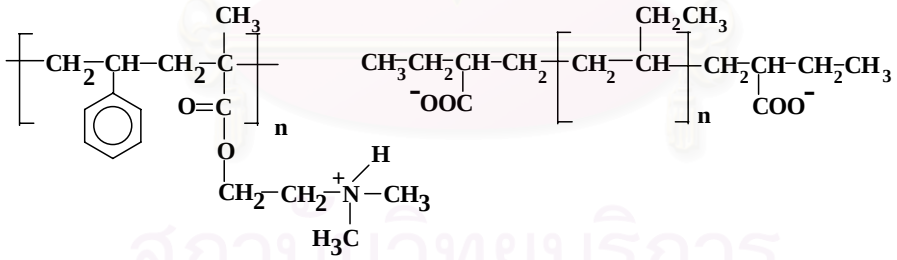
The wall thickness of the capsules increased with an increasing of the amount of hydrogenated telechelic polybutadiene (Sat. PB). In the same token when the amount of P(St-*co*-DMAEMA) increased from 10 wt% to 15 wt% or decreased from 10 wt% to 5 wt%, the capsules achieved less complete encapsulation than at 10 wt% of P(St-*co*-DMAEMA) because the Sat. PB was not completely reacted with P(St-*co*-DMAEMA).

Effect of agitation

Nixon and Hasson showed that the faster stirring speeds produced small coacervate droplets and smaller range in size distribution of gelatin-acacia complex coacervated microcapsules of thiabendazole [75]. However, the average particle diameters and size distributions of alumina-acacia coacervates prepared by Burgess and Singh at different stirring rate were not significant [76]. In this study, the size distribution of capsules at various agitation was not quite different. It was due to the tendency of $AlCl_3$ to form agglomerates.



P(St-*co*-DMAEMA)



insoluble salt polymer

Figure 28. The insoluble salt formation of the polymer wall from the P(St-*co*-DMAEMA) and Sat.PB

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The effect of stabilizer amount

The encapsulated $AlCl_3$ was affected by the amounts of stabilizer. It was found that at 2 wt% of PBD stabilizer, the capsules had more polymer wall thickness than with other amount of stabilizer.

Table 9. Catalytic activity of capsules in the alkylation reaction of benzene with 1-dodecene

Run No.	Sat.PB (wt.%)	PS-DMAEMA (wt.%)	PBD (wt.%)	Agitation (rpm)	% Conversion[c]
1	10	10	1	250	74
2	10	10	2	250	97
3	10	10	5	250	97
4	5	10	2	250	97
5	2.5	10	2	250	94
6	10	15	2	250	76
7	10	5	2	250	13
8	10	10	2	375	97
9	10	10	2	120	95
10[a]	-	-	-	-	97

[a] Unencapsulated $AlCl_3$ (free $AlCl_3$)

Catalytic property of prepared capsules

Table 9. illustrates catalytic activity of prepared capsules at various polymer wall concentrations, stabilizer and agitation rate. The alkylation reaction of benzene with 1-dodecene yielded the five positional isomers phenyldodecanes (2-, 3-, 4-, 5- and 6- phenyldodecanes) except the 1-phenyl isomer. The effectiveness of capsules at different amount of Sat. PB was not quite different when compared with prepared capsules at different amount of P(St-*co*-DMAEMA). It was found that at 10wt% of Sat. PB and 10wt% of P(St-*co*-DMAEMA), the prepared capsules had highest conversion and complete encapsulation.

It also has been shown that the encapsulated catalysts prepared under various agitation rate during encapsulation process resulted in the same compositions of

products. On the other hand; the catalytic activity of encapsulated $AlCl_3$ was affected by the amounts of stabilizer. It indicated that 2 wt% of PBD was enough to stabilize the capsules. Most conventional Friedel-Crafts catalysts generally give complex reaction mixtures which could be worked up and separated with difficulty [77] and with the loss of generally catalysts, producing environmentally unfriendly, toxic waste [4]. The reaction in the presence of unencapsulated $AlCl_3$ (free $AlCl_3$) under the same conditions gave a similar yield to those of encapsulated $AlCl_3$. In this case, the capsules could be dispersed well in benzene and remained in the solid state, thus could be conveniently separated quantitatively at the end of the reaction by simple filtration. The capsules showed very good stability to organic solvents and to a high temperature system. They also exhibited good catalytic activity. Therefore, the encapsulated $AlCl_3$ produced $AlCl_3$ safer and more convenient to handle.

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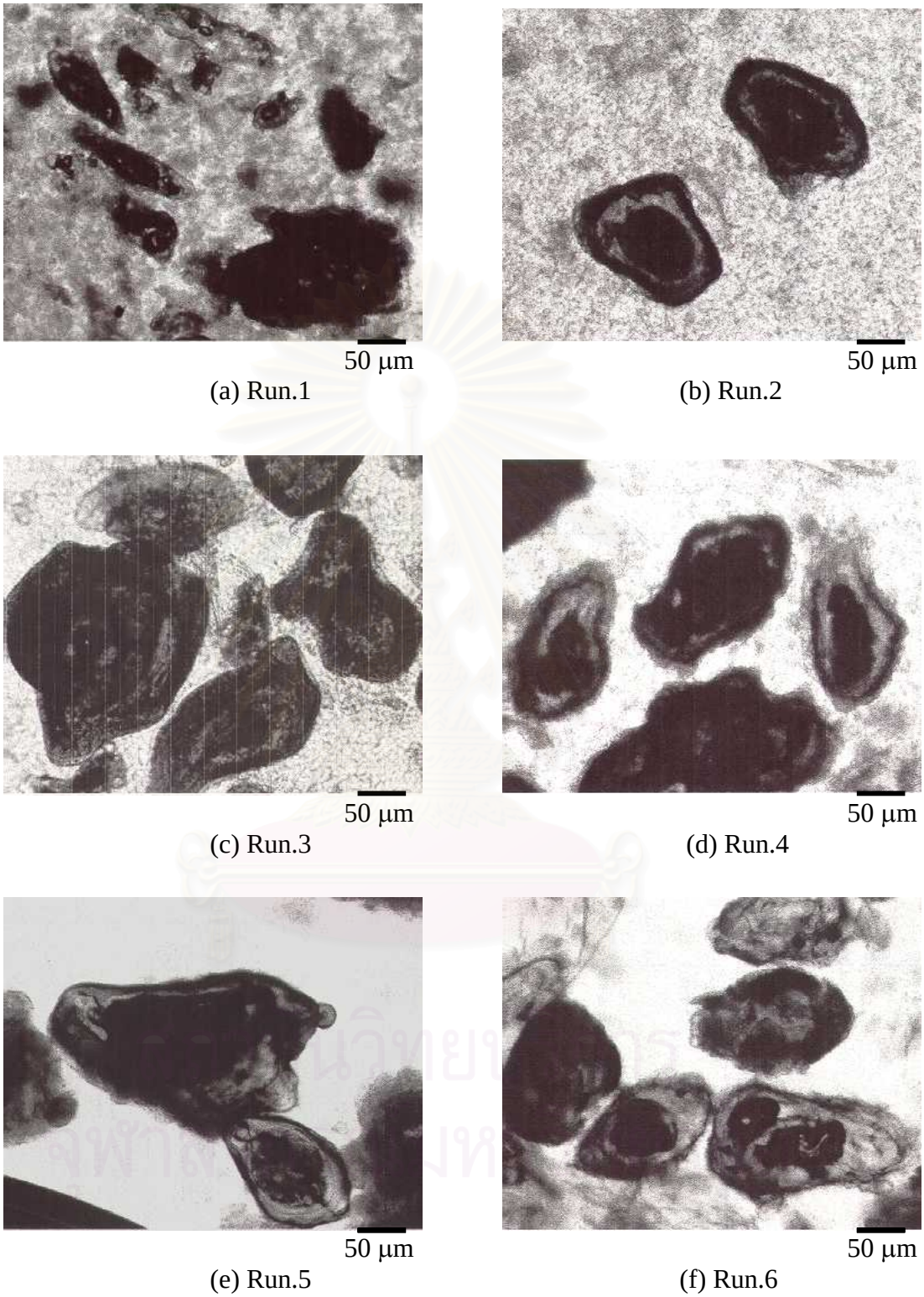
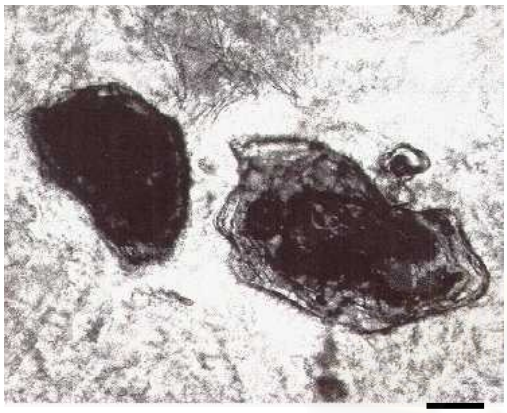
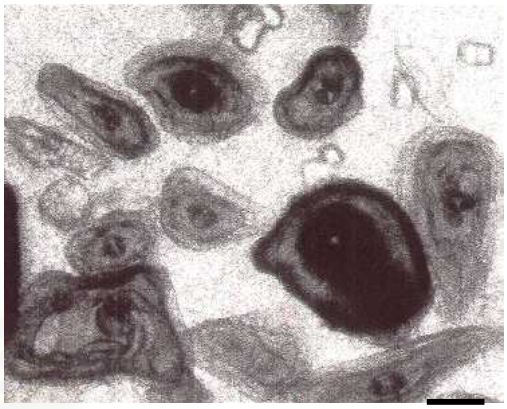


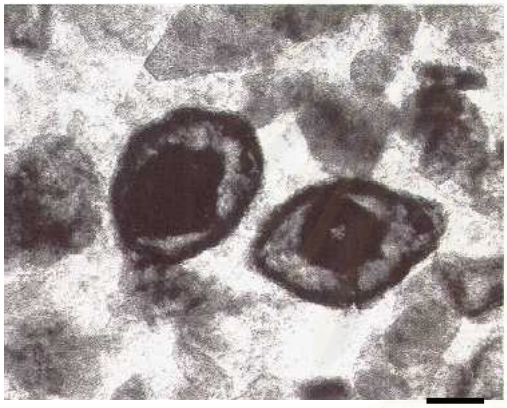
Figure 29 Optical micrographs of the encapsulated $AlCl_3$ by using P(St-*co*-DMAEMA) and Sat. PB as wall materials at various conditions.



(g) Run.7



(h) Run.8



(i) Run.9

Figure 29(cont.) Optical micrographs of the encapsulated $AlCl_3$ by using P(St-*co*-DMAEMA) and Sat. PB as wall materials at various conditions.

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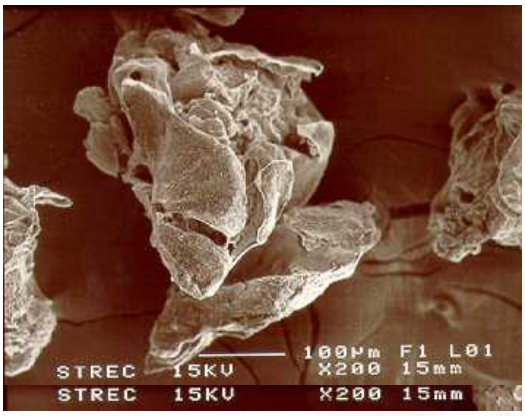
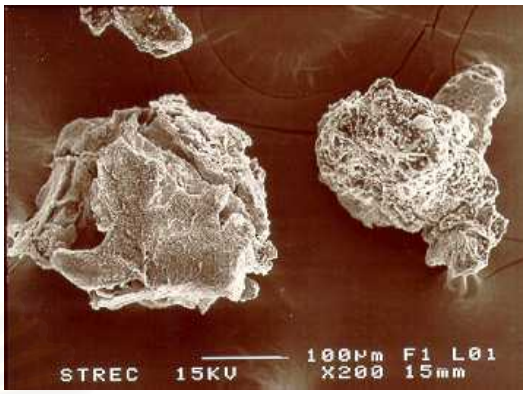
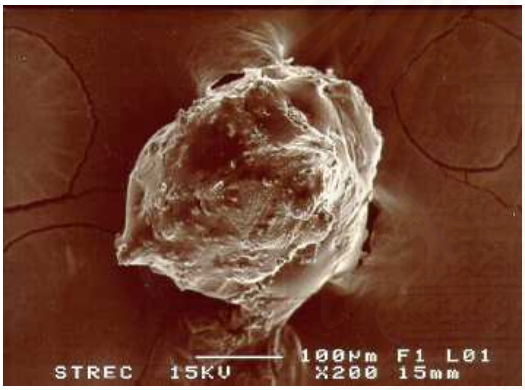


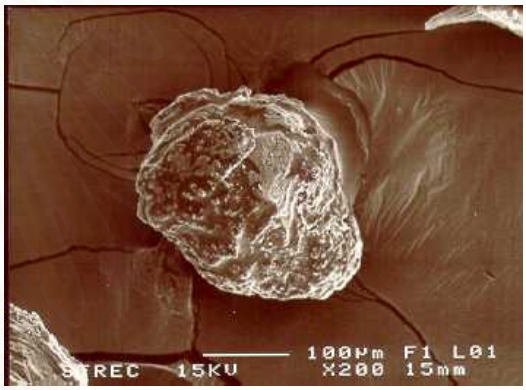
(a) Run.1



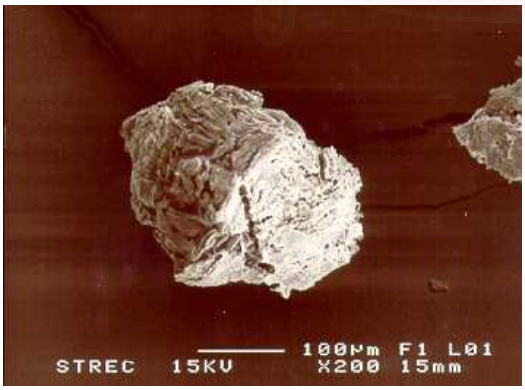
(b) Run.2



(c) Run.3



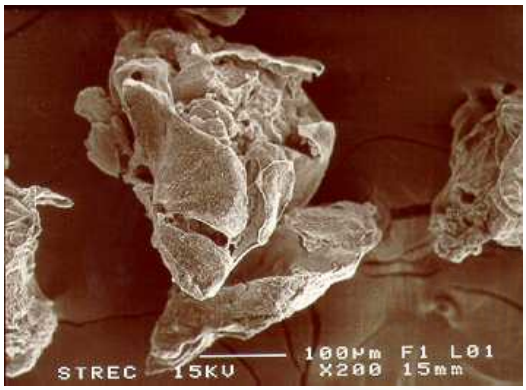
(d) Run.4



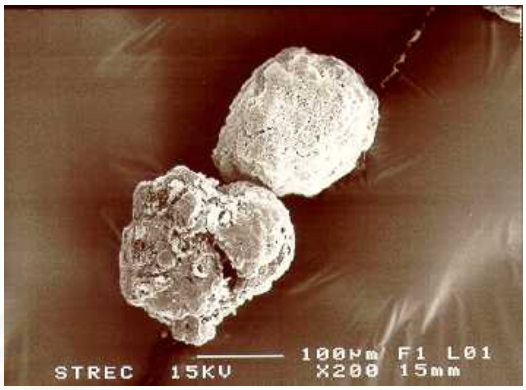
(e) Run.5

(f) Run.6

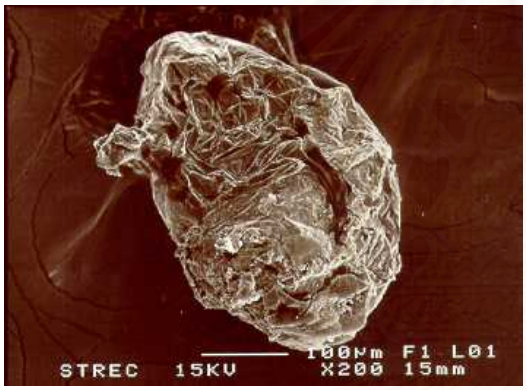
Figure 30 Scanning electron micrographs of the encapsulated $AlCl_3$ by using P(St-*co*-DMAEMA) and Sat. PB as wall materials at various conditions.



(g) Run.7



(h) Run.8



(i) Run.9

Figure 30 (cont.) Scanning electron micrographs of the encapsulated $AlCl_3$ by using P(St-*co*-DMAEMA) and Sat. PB as wall materials at various conditions.

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CHAPTER 5

CONCLUSIONS

Part 1. Encapsulation by using polystyrene wall in o/w system

In this study, it was found that the morphology of capsules prepared by solvent evaporation technique using polystyrene as a wall material was affected by the addition of soluble salt Na_2SO_4 and stabilizer PEG 20000. The particle size of capsules was also affected by change of polystyrene-cyclohexane solution concentration. The core material ScTf becomes soluble in water during the operation, resulting in the capsules without core material inside. Thus the capsules have no effectiveness because the ScTf catalyst is easy to dissolve and deactivated in water during encapsulation process.

It could be concluded that this method is not suitable for encapsulation core materials which are sensitive to moisture or easily deactivate in water.

Part 2. Encapsulation by using polyamide wall

The morphology of capsules prepared by an interfacial polycondensation technique using polyamide as a wall material and span 85 as a stabilizer were affected by the addition of Na_2CO_3 and solvent. Some amount of ScTf catalyst can be encapsulated despite the presence of the water in process because of fast formation of polyamide wall. However, the capsules have no effectiveness because most of the ScTf can be dissolved and deactivated in water during encapsulation process and the amount of ScTf catalyst in capsules was not enough to act as the effective catalyst in the alkylation reaction.

It could be concluded that this method is not suitable for encapsulation core materials which are sensitive to moisture or easily deactivate in water.

Part 3. Encapsulation by using P(St-DVB) wall

It was found that the morphology of capsules prepared by copolymerization of styrene and DVB were affected by the addition of different core materials. In the presence of ScTf and $AlCl_3$, the irregular shape was

obtained, whereas in the presence of TiO_2, spherical particles were formed. Moreover, the reaction was interfered by ScTf and $AlCl_3$, resulting in the lower yield in polymerization reaction. A BPO initiator is not suitable to initiate the polymerization reaction in the presence of reactive substance such as Lewis acid catalyst. However, the encapsulated $AlCl_3$ and encapsulated ScTf prepared by using V-65 as an initiator are still have some effectiveness in the reaction of benzene and 1-dodecene, but gave a low conversion.

It was concluded that it is difficult to encapsulate the reactive substances by copolymerization of styrene and DVB.

Part 4. Encapsulation by using beeswax and paraffin wall

It was found that the morphology of capsules prepared by cooling melted dispersion process were affected by the addition of different core materials, solvent of stabilizer, and wall concentration. The capsules obtained by using 1.2 g of beeswax, 0.8 g of paraffin and 20 %w/v of PBD in hexane (Run. 5) had achieved more complete encapsulation than with other conditions and also had highest effectiveness in the reaction of benzene and 1-dodecene.

However, the capsules are unstable because the capsule wall can melt or dissolve in benzene which is a starting material in the alkylation reaction. This result was found to be in agreement with J. R. Nixon, because of the solubility of waxes in most organic solvents. It would be difficult that waxes and long-chain fatty acid/esters could be used as encapsulation agents for organic liquids.

It can be concluded that this process is suitable for water-soluble materials, but not for thermally unstable materials, and the candidate core materials for this process must be adequately heat-stable under the conditions of preparation.

Part 5. Encapsulation by using polystyrene wall in O/O System

It can be concluded that the capsules prepared using polystyrene as a wall material in o/o system were affected by the addition of different core materials, molecular weight of polystyrene and the amount of stabilizer. All of the capsules have agglomerate and are irregular in shape. The encapsulated $AlCl_3$ had higher

effectiveness than encapsulated ScTf in the reaction of benzene and 1-dodecene, and 0.25 wt% of PBD was enough to stabilize the capsules.

This method is suitable to encapsulate moisture-sensitive or water-deactivating substances when compared with in o/w system. However, the capsules are not stable in the reaction containing benzene because polystyrene can be dissolved in benzene, so it is difficult to recover or separate after the reaction.

Part 6. Encapsulation by using insoluble salt polymer wall

The size distribution of all the capsules was not in wide range because the $AlCl_3$ capsules have a tendency to agglomerate. At 10 wt% of Sat. PB, 10 wt% of P(St-*co*-DMAEMA) and 2 wt% of PBD, the capsules had a smoother surface and achieved more complete encapsulation than with other ratios.

It has been shown that the capsules can be an effective catalyst for the Friedel-Crafts alkylation of benzene with 1-dodecene, and the capsules can be easily recovered by a simple filtration. The catalytic activity of the encapsulated $AlCl_3$ was affected by the amounts of stabilizer. This indicated that 2 wt% of PBD was enough to stabilize the capsules. The effectiveness of the capsules at different amounts of Sat. PB was not so different when compared with the capsules with different amounts of P(St-*co*-DMAEMA). It shows that at 10 wt% of Sat. PB and 10 wt% of P(St-*co*-DMAEMA), the capsules had high conversion and complete encapsulation.

For catalytic activity of capsules, it indicated that the yield of reaction was dependent on polymer wall concentration and the amount of stabilizer and also demonstrated that capsules contain $AlCl_3$.

In conclusion, we have found a new method for the encapsulation of $AlCl_3$ using an insoluble polymer wall. The capsules have effectiveness and stability in Friedel-Crafts alkylation reactions. Moreover, they are strong enough for long-term use.

Suggestions for future work

Encapsulation by using insoluble salt polymer wall should be further studied as follows:

1. Catalytic activity of these capsules for other applications should be investigated for example; Friedel-Crafts acylation reactions
2. This techniques should be investigated for other catalysts or substances.

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APPENDICES

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APPENDIX I

Example of retention time of alkylbenzene compounds achieved by gas chromatography analysis

Table I1. Retention Time of alkylbenzene compounds achieved by gas chromatography analysis at various catalysts

Compounds	Catalysts			
	$AlCl_3$	ScTf	Part 4 Run 5	Part 6 Run 2
Benzene	2.01	1.99	2.02	2.0
Dodecene	-	2.26	-	-
2-phenyl dodecane	9.87	9.91	9.86	9.918
3-phenyl dodecane	10.07	10.12	10.08	10.13
4-phenyl dodecane	10.56	10.62	10.57	10.62
5-phenyl dodecane	11.40	11.46	11.40	11.47
6-phenyl dodecane	13.28	13.39	13.29	13.40

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Example of %Yield of alkylbenzene compounds achieved by gas chromatography

Table I2 Wt. of products by synthesis process of alkylbenzene compounds by using $AlCl_3$ and ScTf as a ctalyst.

Catalyst	%Wt. of alkylbenzene compounds				
	2-phenyl dodecane	3-phenyl dodecane	4-phenyl dodecane	5-phenyl dodecane	6-phenyl dodecane
$AlCl_3$	11.56	14.45	12.18	17.89	40.98
ScTf	1.23	1.96	1.65	3.74	8.42
Part 3 Run.4	1.35	1.58	1.46	4.14	10.27
Part 4 Run.5	3.52	4.26	4.32	9.53	16.87
Part 5 Run.3 (encapsulated $AlCl_3$)	10.86	13.57	12.86	19.58	39.13
Part 6 Run.2	11.42	14.18	12.57	18.44	40.39

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APPENDIX II

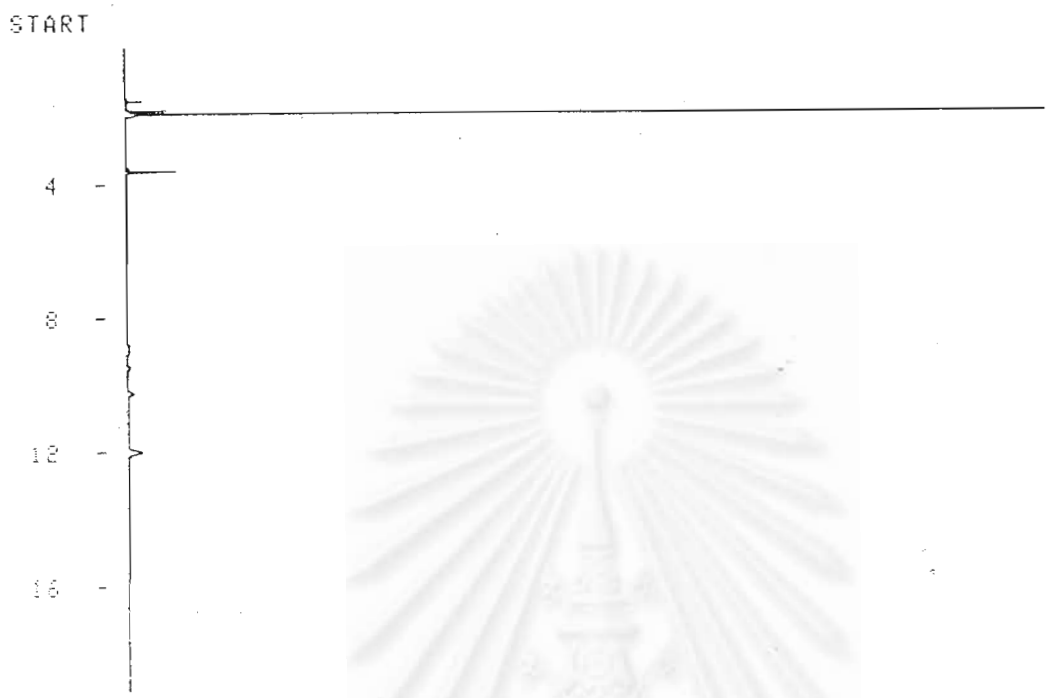

Figure II1. Gas chromatograms of alkylbenzenes using capsules from part 3 Run 3.

Figure II2. Gas chromatograms of alkylbenzenes using capsules from part 3 Run 4.

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Figure II3. Gas chromatograms of alkylbenzenes using capsules from part 3 Run 5.

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APPENDIX III

Figure III1. Gas chromatograms of alkylbenzenes using capsules from part 4 Run 1.

Figure III2. Gas chromatograms of alkylbenzenes using capsules from part 4 Run 2.

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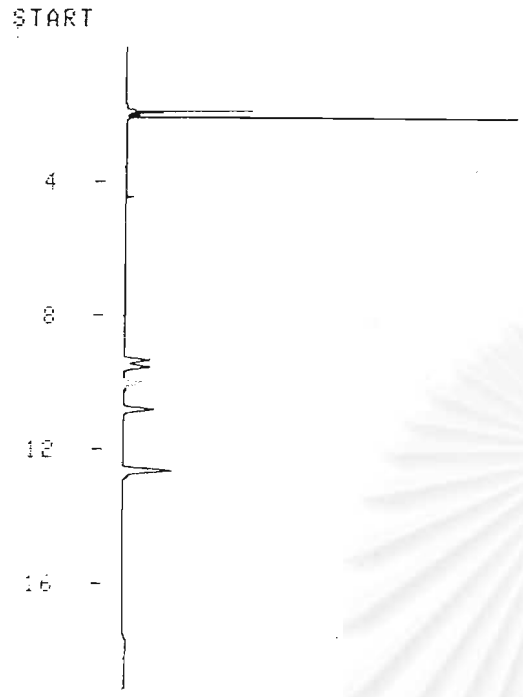

Figure III3. Gas chromatograms of alkylbenzenes using capsules from part 4 Run 3.

Figure III4. Gas chromatograms of alkylbenzenes using capsules from part 4 Run 4.

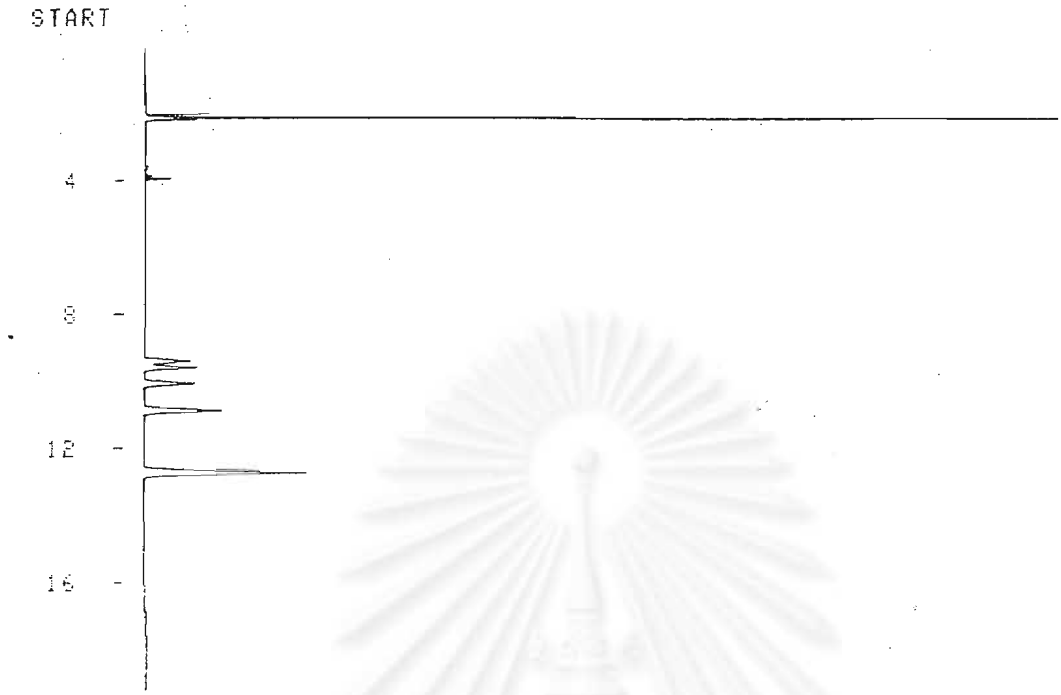

Figure III5. Gas chromatograms of alkylbenzenes using capsules from part 4 Run 5.

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APPENDIX IV

Figure IV1. Gas chromatograms of alkylbenzenes using encapsulated ScTf from Part 5 Run 1.

Figure IV2. Gas chromatograms of alkylbenzenes using encapsulated ScTf from Part 5 Run 2.

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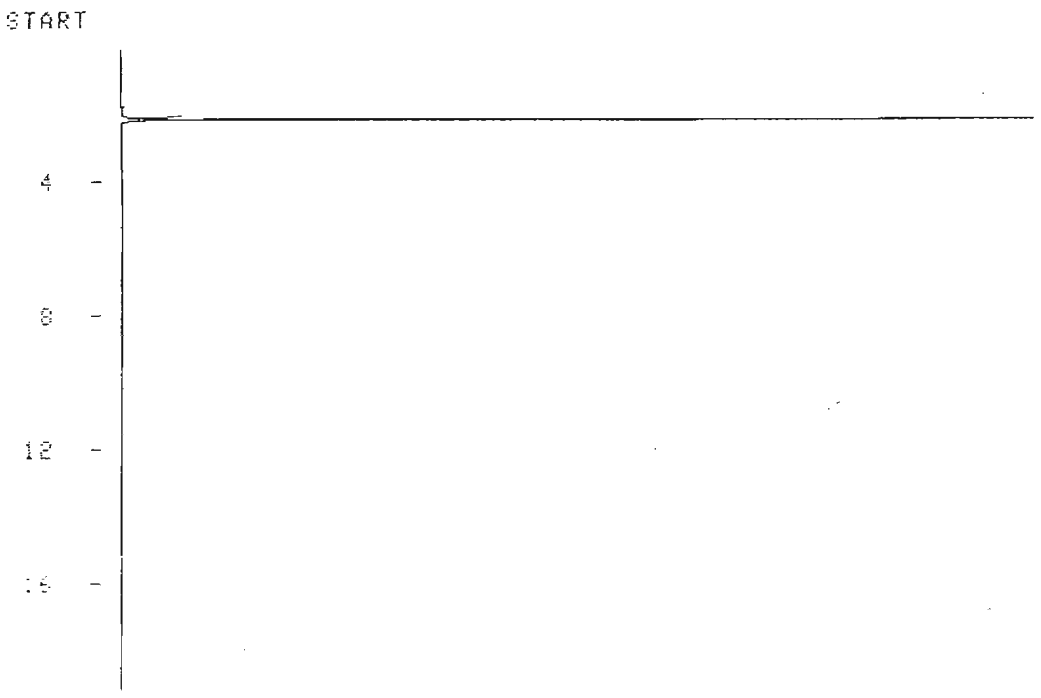

Figure IV3. Gas chromatograms of alkylbenzenes using encapsulated ScTf from Part 5 Run 3.

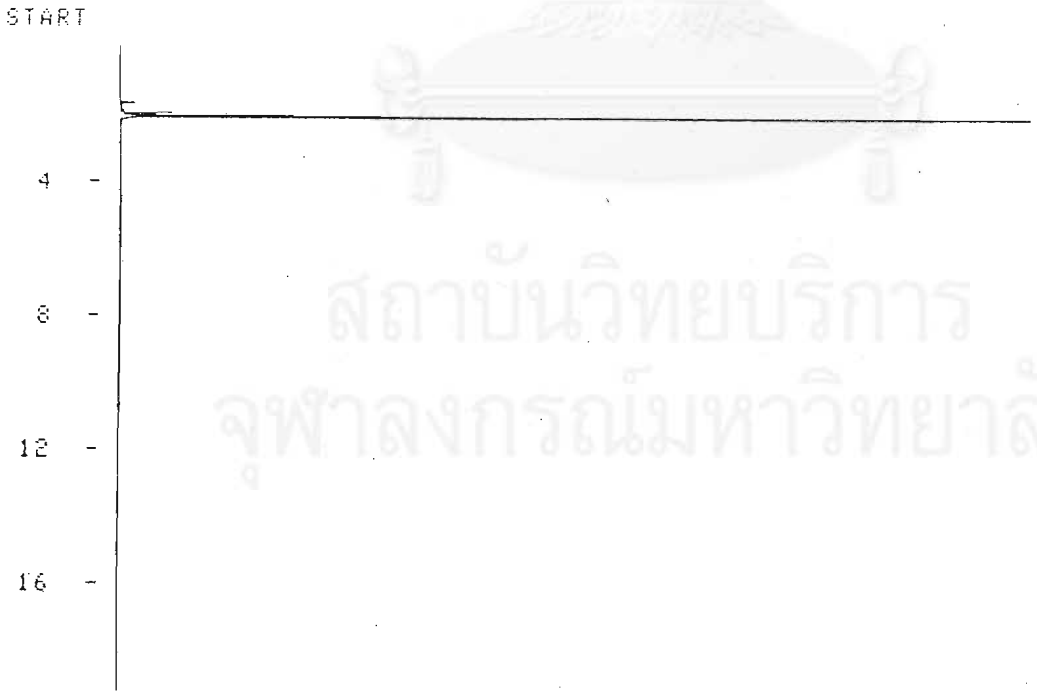

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Figure IV4. Gas chromatograms of alkylbenzenes using encapsulated ScTf from Part 5 Run 4.

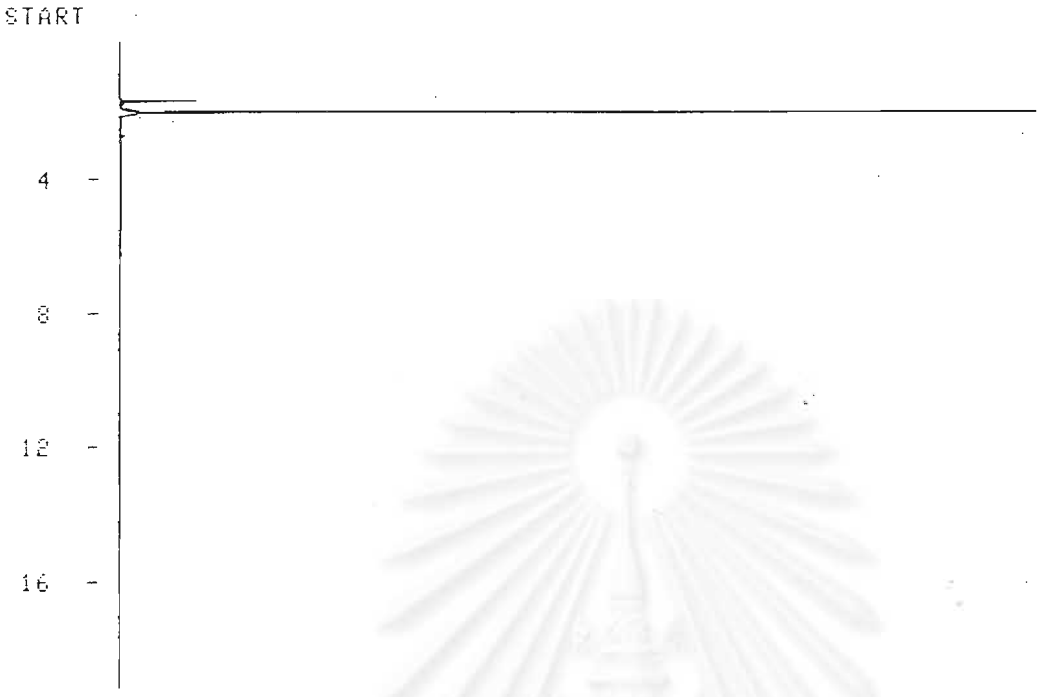

Figure IV5. Gas chromatograms of alkylbenzenes using encapsulated ScTf from Part 5 Run 5.

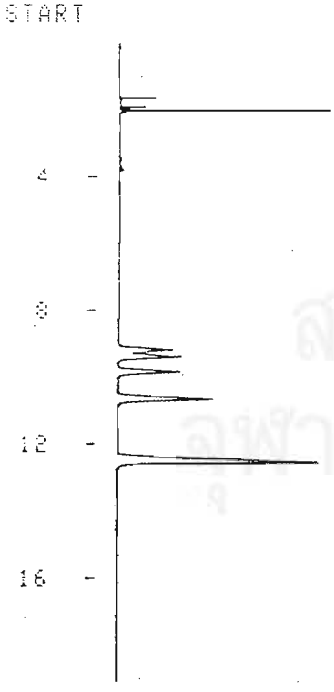

Figure IV6. Gas chromatograms of alkylbenzenes using encapsulated $AlCl_3$ from Part 5 Run 1.

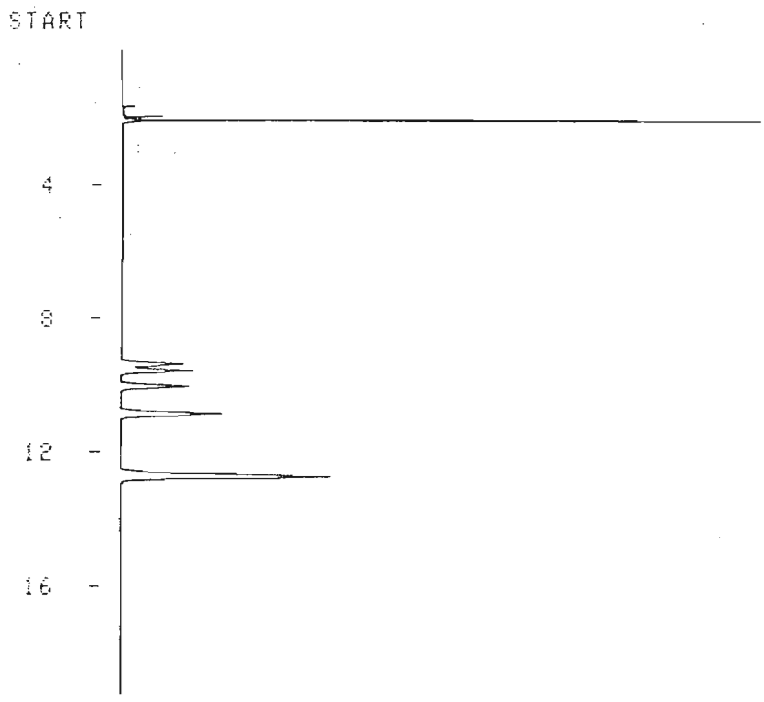

Figure IV7. Gas chromatograms of alkylbenzenes using encapsulated $AlCl_3$ from Part 5 Run 2.

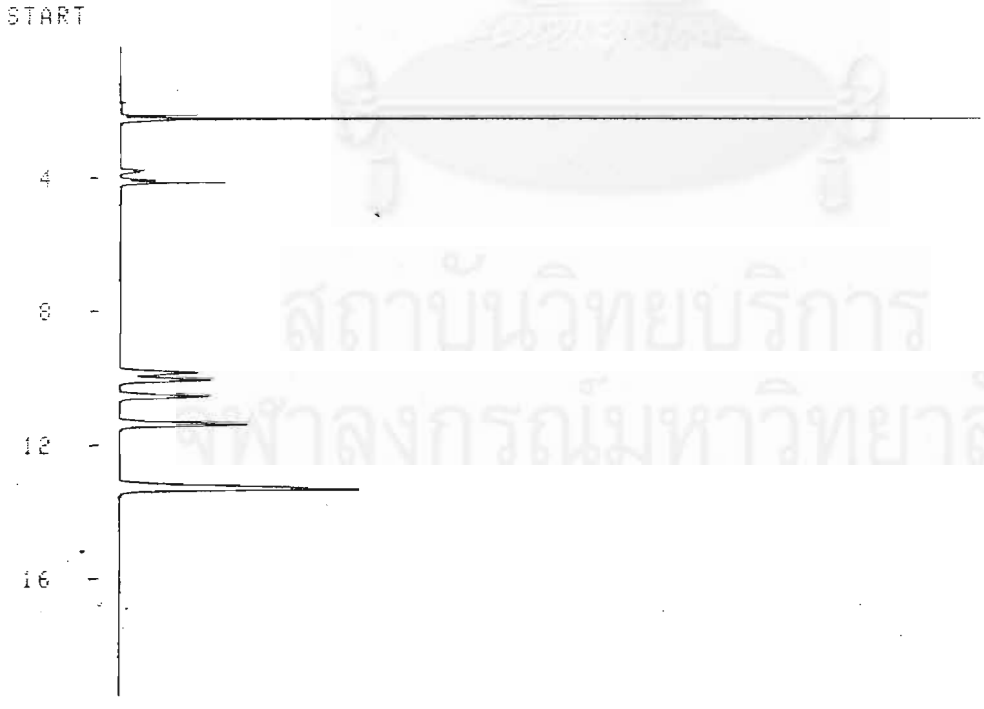

Figure IV8. Gas chromatograms of alkylbenzenes using encapsulated $AlCl_3$ from Part 5 Run 3.

APPENDIX V

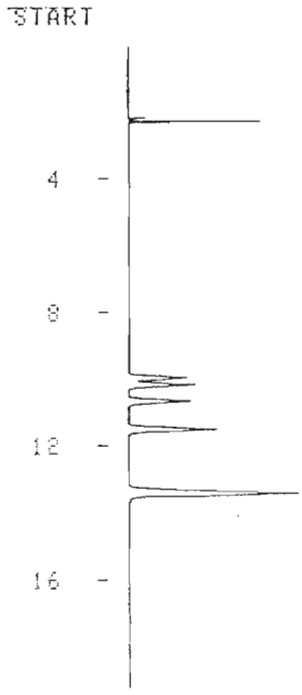

Figure V1. Gas chromatograms of alkylbenzenes using encapsulated $AlCl_3$ from Part 6 Run 1.

Figure V2. Gas chromatograms of alkylbenzenes using encapsulated $AlCl_3$ from Part 6 Run 2.

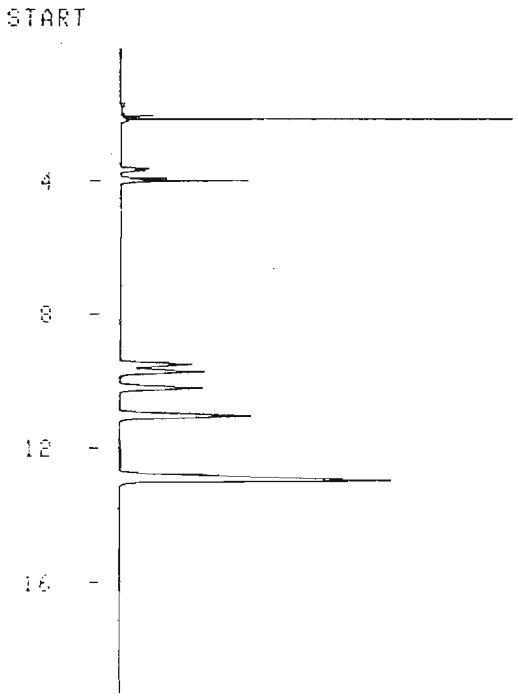

Figure V3. Gas chromatograms of alkylbenzenes using encapsulated $AlCl_3$ from Part 6 Run 3.

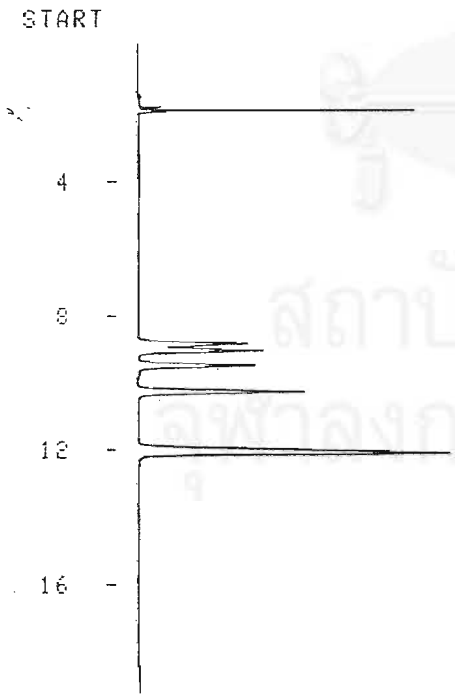

Figure V4. Gas chromatograms of alkylbenzenes using encapsulated $AlCl_3$ from Part 6 Run 4.

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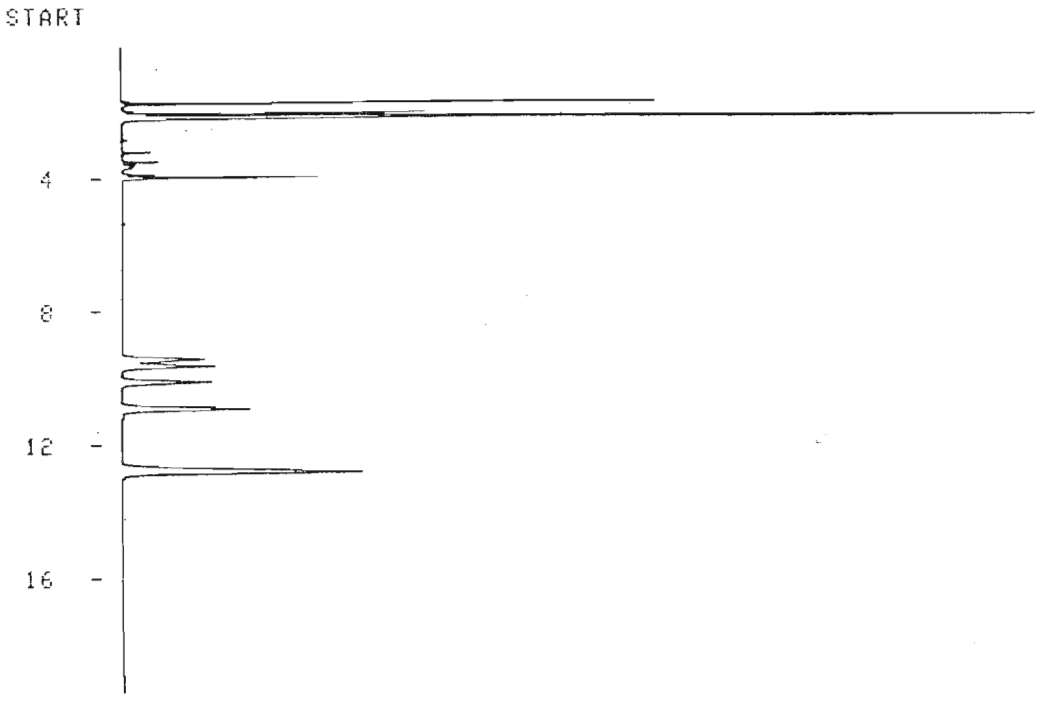

Figure V5. Gas chromatograms of alkylbenzenes using encapsulated $AlCl_3$ from Part 6 Run 5.

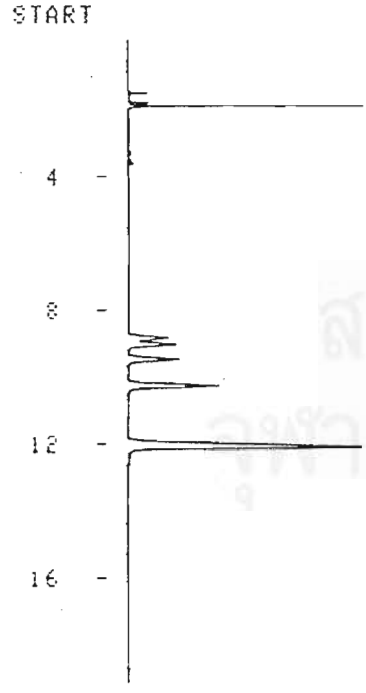

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Figure V6. Gas chromatograms of alkylbenzenes using encapsulated $AlCl_3$ from Part 6 Run 6.

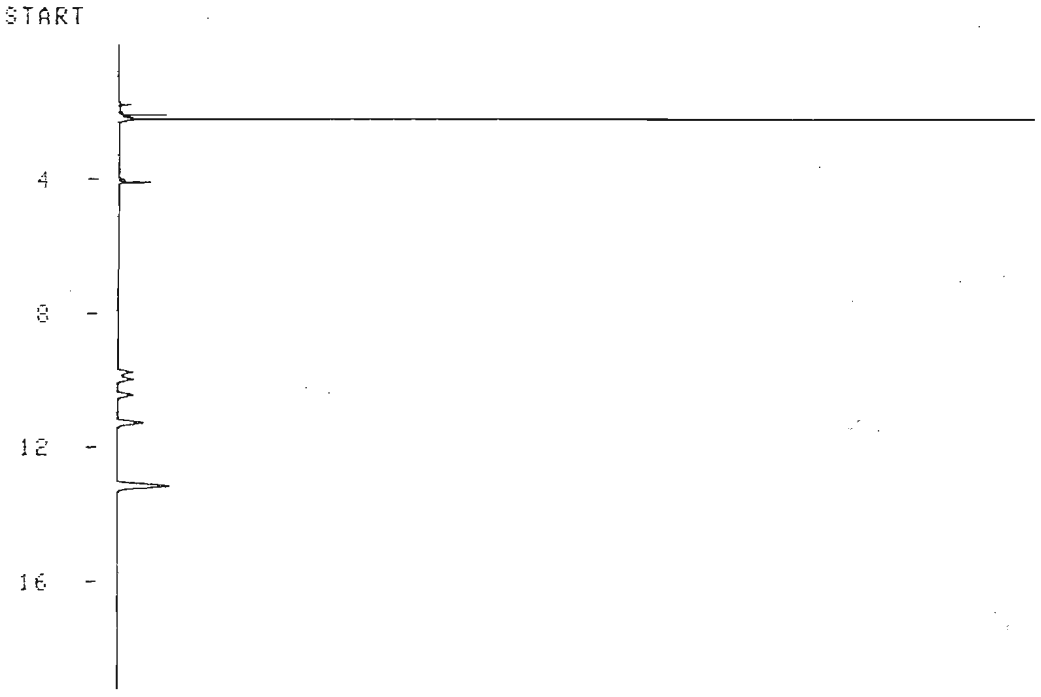

Figure V7. Gas chromatograms of alkylbenzenes using encapsulated $AlCl_3$ from Part 6 Run 7.

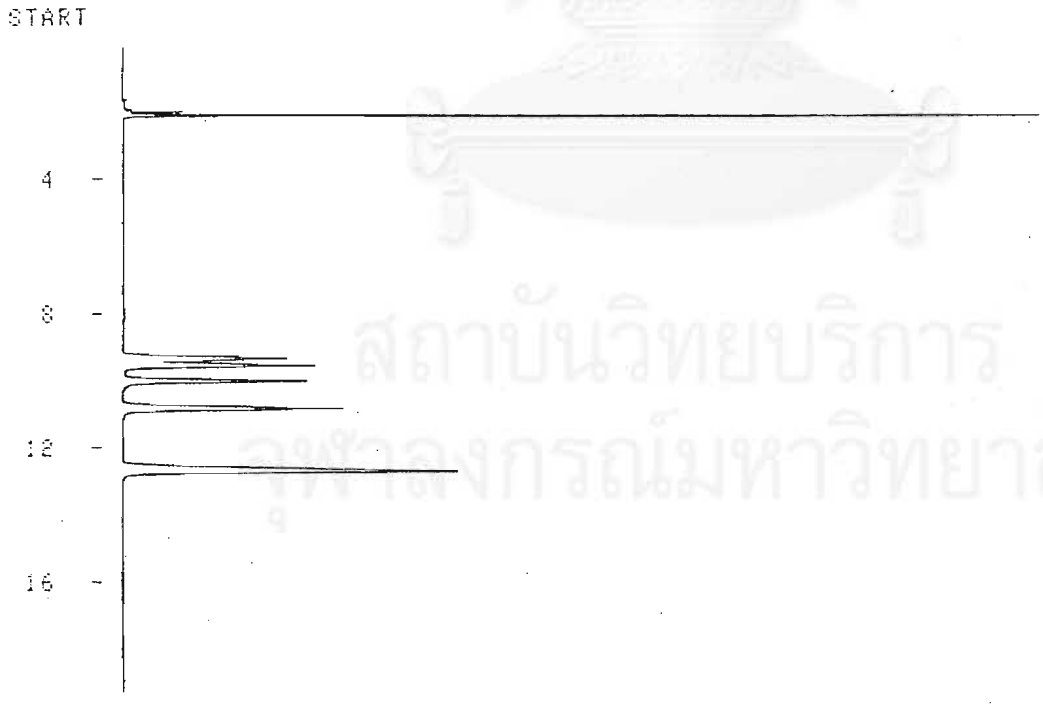

Figure V8. Gas chromatograms of alkylbenzenes using encapsulated $AlCl_3$ from Part 6 Run 8.

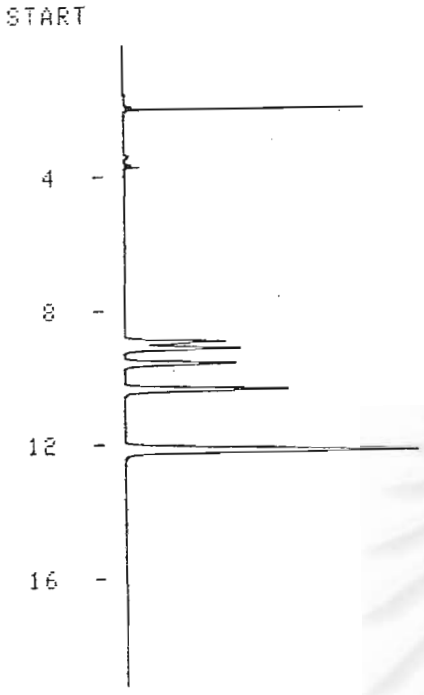

Figure V9. Gas chromatograms of alkylbenzenes using encapsulated $AlCl_3$ from Part 6 Run 9.

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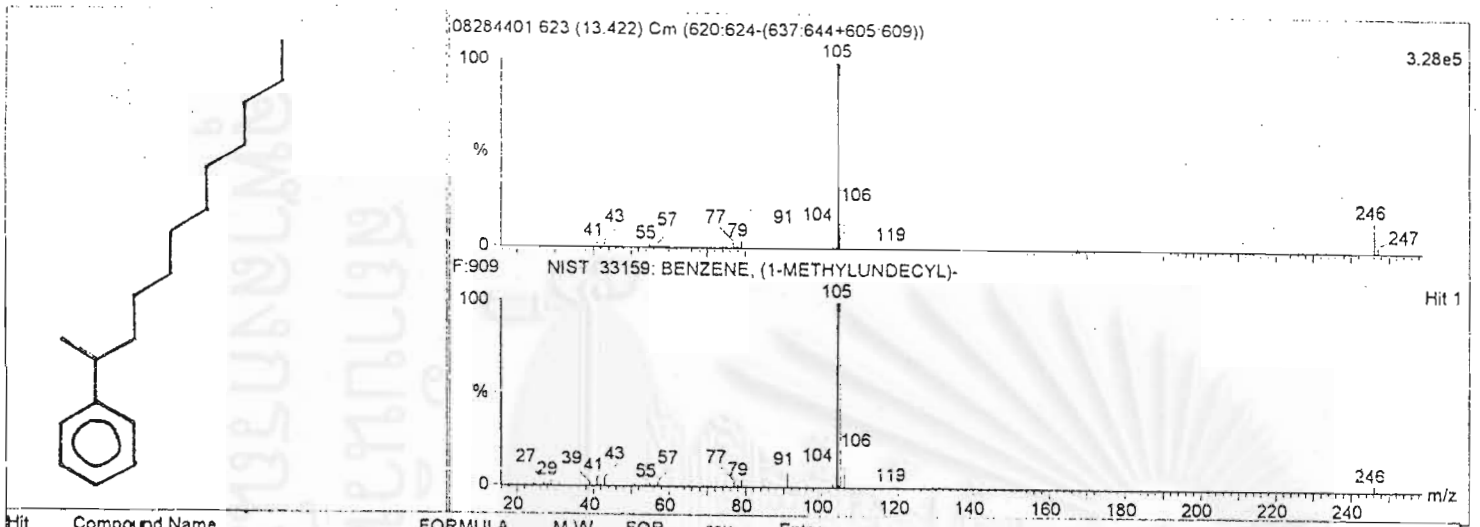
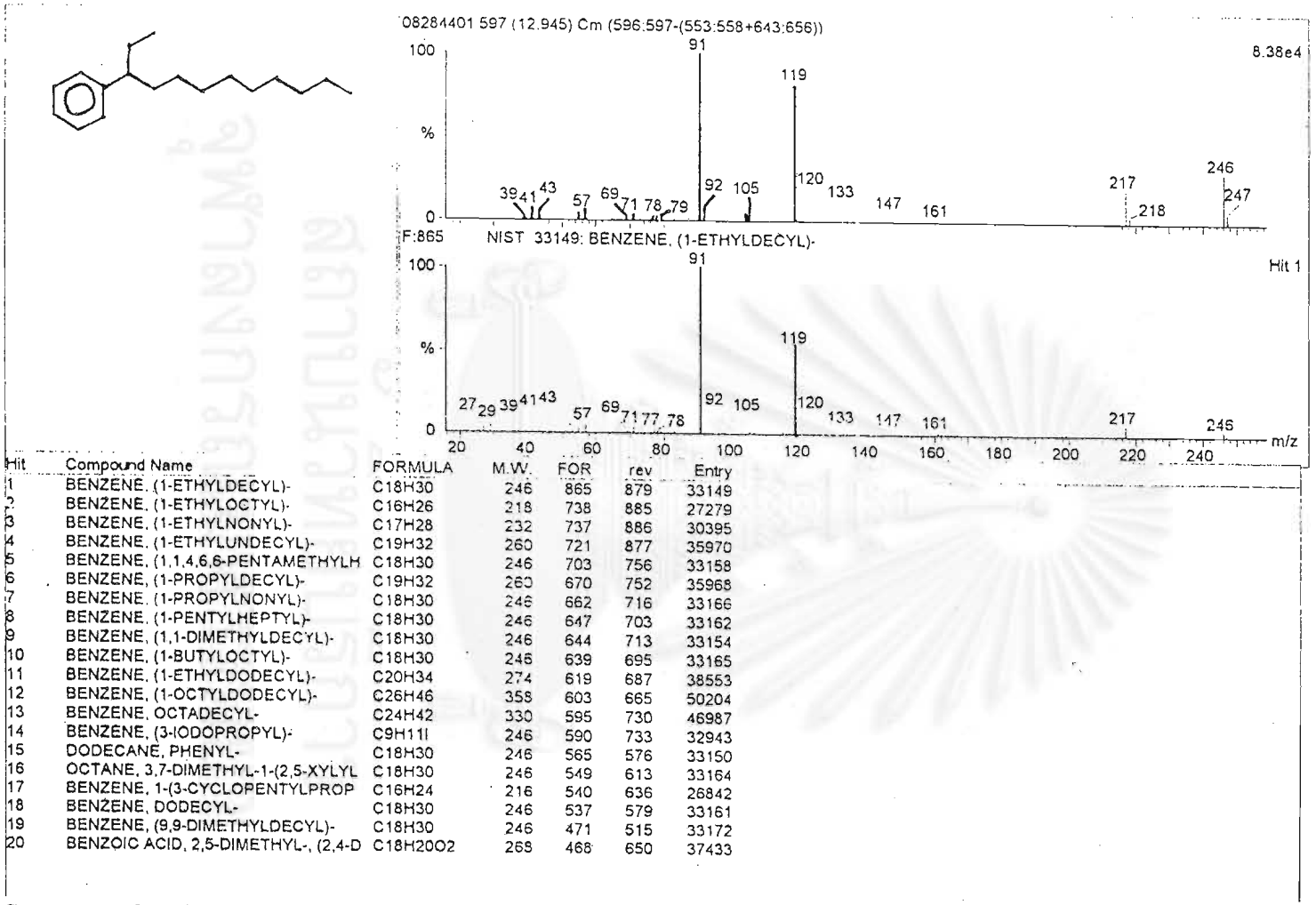


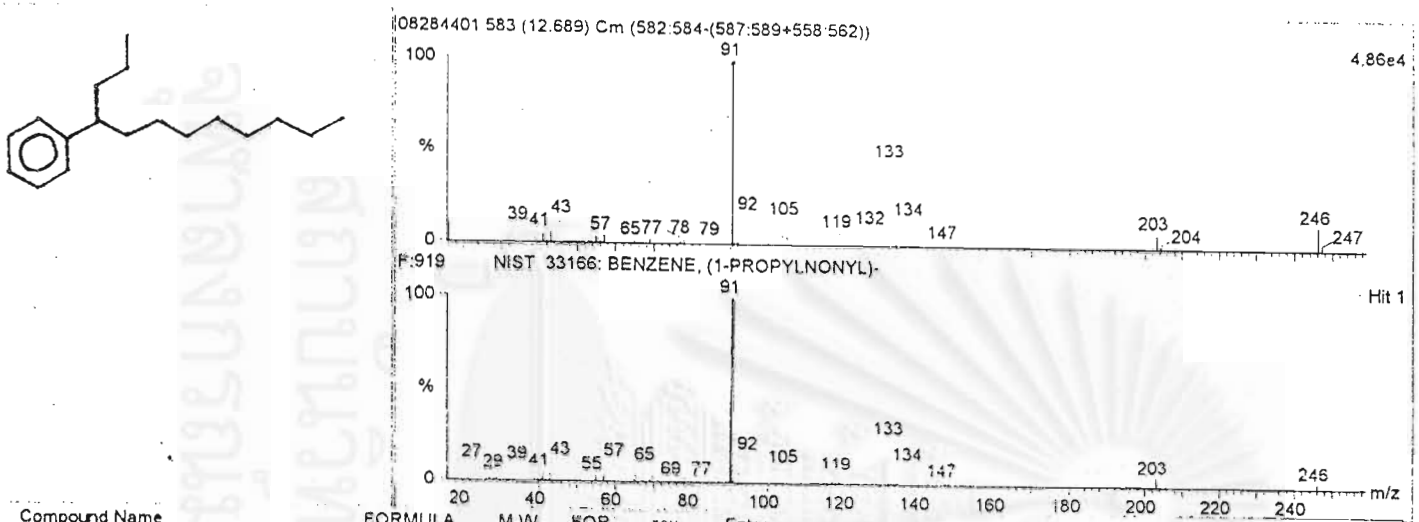
Hit	Compound Name	FORMULA	M.W.	FOR	rev	Entry
1	BENZENE, (1-METHYLUNDECYL)-	C18H30	246	909	916	33159
2	BENZENE, (1-METHYLDECYL)-	C17H28	232	820	925	30396
3	BENZENE, (1-METHYLDODECYL)-	C19H32	260	818	925	35958
4	PENTADECANE, 2-PHENYL-	C21H36	288	791	855	40942
5	BENZENE, (1-METHYLNONYL)-	C16H26	218	786	895	27278
6	BENZENE, (1-METHYLPENTADECYL)-	C22H38	302	783	884	43219
7	BENZENE, (1-METHYLHEPTADECYL)-	C24H42	330	778	883	46986
8	BENZENE, (1-METHYLNONADECYL)-	C26H46	358	771	876	50205
9	BENZENE, (1-METHYLHEPTYL)-	C14H22	190	769	876	20368
10	BENZENE, (1,3-DIMETHYLBUTYL)-	C12H18	162	761	869	13048
11	BENZENE, (1,3-DIMETHYL-3-BUTENY	C12H16	160	689	820	12544
12	BENZENE, 1,1'-(1,4-DIMETHYL-1,4-BU	C18H22	238	681	802	31671
13	BENZENE, (1,2-DIMETHYLPROPYL)-	C11H16	148	676	788	9366
14	BENZENE, 1,1'-(1,2-DIMETHYL-1,2-ET	C16H18	210	675	867	25503
15	BENZENE, 1,1'-(1-METHYL-1,2-ETHAN	C15H16	196	669	806	21991
16	BENZENE, 1,1'-(1,2-DIMETHYL-1,2-ET	C16H18	210	668	813	25499
17	BENZENE, (1,2,2-TRIMETHYL-3-BUTE	C13H18	174	668	783	16371
18	1-METHYL-2-N-HEXYLBENZENE	C13H20	176	664	801	16811
19	BENZENE, 1,1'-(1,2-DIMETHYL-1,2-ET	C16H18	210	663	851	25495
20	BENZENE, (2-ETHENYL-1,4,4-TRIMET	C16H24	216	662	772	26841

Figure VI2. Structure of 2-phenyl dodecane which analyzed by gas chromatography/mass spectrometry chromatogram



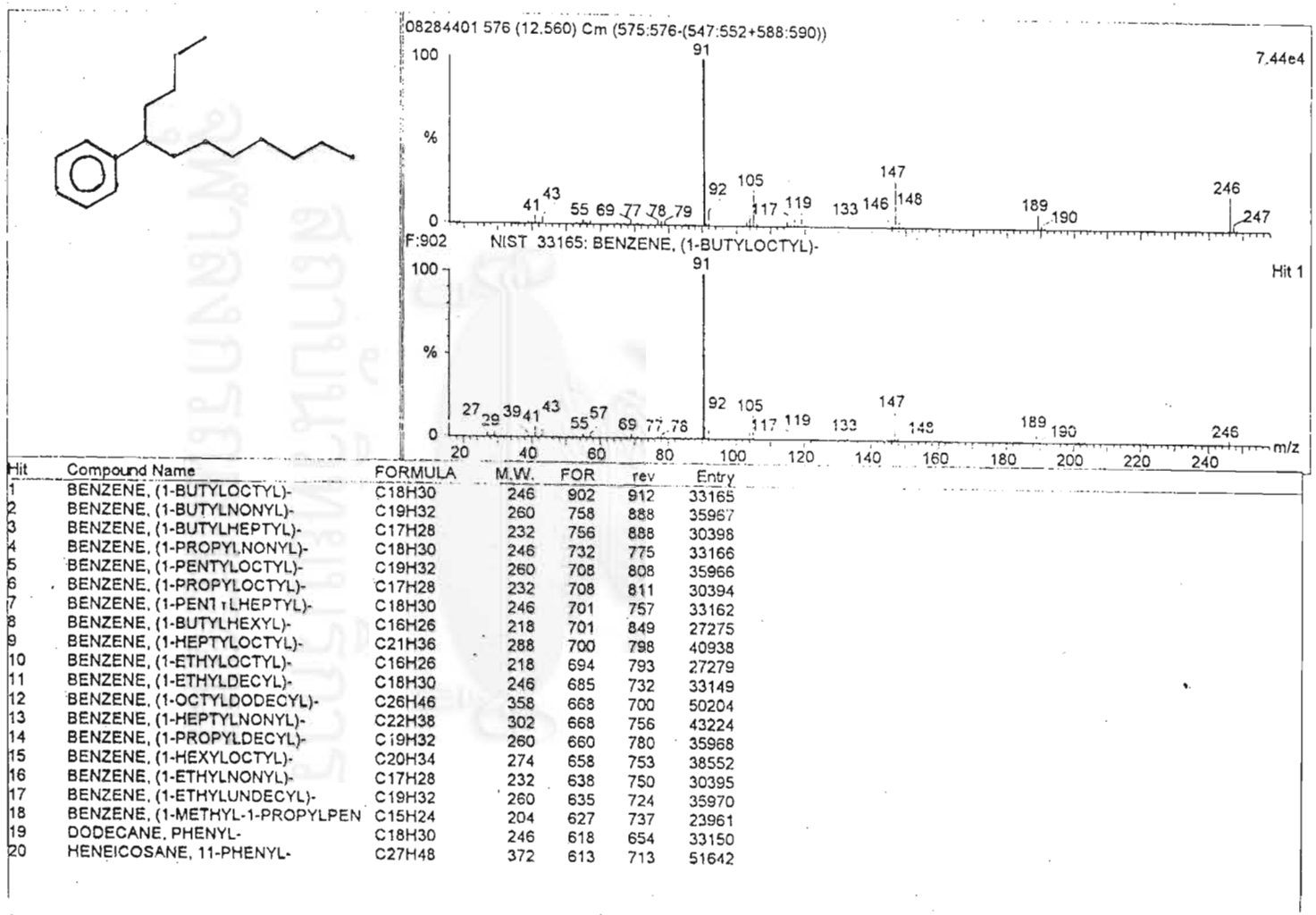
Hit	Compound Name	FORMULA	M.W.	FOR	rev	Entry
1	BENZENE, (1-ETHYLDECYL)-	C18H30	246	865	879	33149
2	BENZENE, (1-ETHYLOCTYL)-	C16H26	218	738	885	27279
3	BENZENE, (1-ETHYLNONYL)-	C17H28	232	737	886	30395
4	BENZENE, (1-ETHYLUNDECYL)-	C19H32	260	721	877	35970
5	BENZENE, (1,1,4,6,6-PENTAMETHYLH	C18H30	246	703	756	33158
6	BENZENE, (1-PROPYLDECYL)-	C19H32	260	670	752	35968
7	BENZENE, (1-PROPYLNONYL)-	C18H30	246	662	716	33166
8	BENZENE, (1-PENTYLHEPTYL)-	C18H30	246	647	703	33162
9	BENZENE, (1,1-DIMETHYLDECYL)-	C18H30	246	644	713	33154
10	BENZENE, (1-BUTYLOCTYL)-	C18H30	246	639	695	33165
11	BENZENE, (1-ETHYLDODECYL)-	C20H34	274	619	687	38553
12	BENZENE, (1-OCTYLDODECYL)-	C26H46	358	603	665	50204
13	BENZENE, OCTADECYL-	C24H42	330	595	730	46987
14	BENZENE, (3-IODOPROPYL)-	C9H11I	246	590	733	32943
15	DODECANE, PHENYL-	C18H30	246	565	576	33150
16	OCTANE, 3,7-DIMETHYL-1-(2,5-XYLYL	C18H30	246	549	613	33164
17	BENZENE, 1-(3-CYCLOPENTYLPROP	C16H24	216	540	636	26842
18	BENZENE, DODECYL-	C18H30	246	537	579	33161
19	BENZENE, (9,9-DIMETHYLDECYL)-	C18H30	246	471	515	33172
20	BENZOIC ACID, 2,5-DIMETHYL-, (2,4-D	C18H20O2	268	468	650	37433

Figure VI3. Structure of 3-phenyl dodecane which analyzed by gas chromatography/mass spectrometry chromatogram



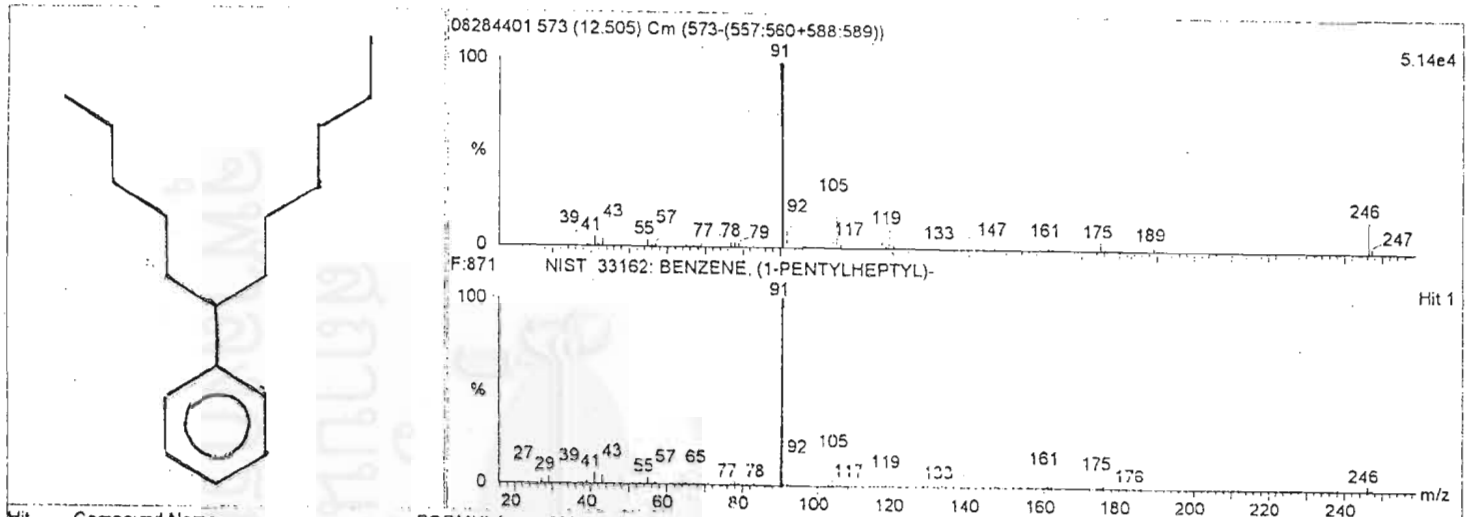
Hit	Compound Name	FORMULA	M.W.	#OR	rev	Entry
1	BENZENE, (1-PROPYLNONYL)-	C18H30	246	919	932	33166
2	BENZENE, (1-PROPYLDECYL)-	C19H32	260	799	869	35968
3	PENTADECANE, 4-PHENYL-	C21H36	288	780	830	40940
4	BENZENE, (1-PROPYLOCTYL)-	C17H28	232	780	878	30394
5	BENZENE, (1-OCTYLDODECYL)-	C26H46	358	732	769	50204
6	BENZENE, (1-PROPYLHEPTYL)-	C16H26	218	729	844	27276
7	BENZENE, (1-BUTYLNONYL)-	C19H32	260	719	781	35967
8	BENZENE, (1-ETHYLNONYL)-	C17H28	232	705	757	30395
9	BENZENE, (1-BUTYLOCTYL)-	C18H30	246	703	749	33165
10	BENZENE, (1-PENTYLHEPTYL)-	C18H30	246	689	733	33162
11	BENZENE, (1-ETHYLDECYL)-	C18H30	246	678	727	33149
12	4-PHENYLNONANE	C15H24	204	658	903	23886
13	BENZENE, DODECYL-	C18H30	246	655	671	33161
14	BENZENE, TRIDECYL-	C19H32	260	610	680	35962
15	10,13-OCTADECADIYNOIC ACID, MET	C19H30O2	290	493	564	41254
16	CYCLOPROPANE, 1-(2-METHYLENE-3	C12H18	162	465	537	13071
17	1-BENZYLCYCLOBUTANOL-1	C11H14O	162	445	581	12983
18	CYCLOHEPTANE, 1,3,5-TRIS(METHYL	C10H14	134	440	530	6209
19	DISPIRO 2.1.2.4 UNDECANE, 8-METH	C12H18	162	431	513	13074
20	DISPIRO 2.0.2.5 UNDECANE, 8-METH	C12H18	162	428	509	13075

Figure VI4. Structure of 4-phenyl dodecane which analyzed by gas chromatography/mass spectrometry chromatogram



Hit	Compound Name	FORMULA	M.W.	FOR	rev	Entry
1	BENZENE, (1-BUTYLOCTYL)-	C18H30	246	902	912	33165
2	BENZENE, (1-BUTYLNONYL)-	C19H32	260	758	888	35967
3	BENZENE, (1-BUTYLHEPTYL)-	C17H28	232	756	888	30398
4	BENZENE, (1-PROPYLNONYL)-	C18H30	246	732	775	33166
5	BENZENE, (1-PENTYLOCTYL)-	C19H32	260	708	808	35966
6	BENZENE, (1-PROPYLOCTYL)-	C17H28	232	708	811	30394
7	BENZENE, (1-PENTYLHEPTYL)-	C18H30	246	701	757	33162
8	BENZENE, (1-BUTYLHEXYL)-	C16H26	218	701	849	27275
9	BENZENE, (1-HEPTYLOCTYL)-	C21H36	288	700	798	40938
10	BENZENE, (1-ETHYLOCTYL)-	C16H26	218	694	793	27279
11	BENZENE, (1-ETHYLDECYL)-	C18H30	246	685	732	33149
12	BENZENE, (1-OCTYLDODECYL)-	C26H46	358	668	700	50204
13	BENZENE, (1-HEPTYLNONYL)-	C22H38	302	668	756	43224
14	BENZENE, (1-PROPYLDECYL)-	C19H32	260	660	780	35968
15	BENZENE, (1-HEXYLOCTYL)-	C20H34	274	658	753	38552
16	BENZENE, (1-ETHYLNONYL)-	C17H28	232	638	750	30395
17	BENZENE, (1-ETHYLUNDECYL)-	C19H32	260	635	724	35970
18	BENZENE, (1-METHYL-1-PROPYLPEN	C15H24	204	627	737	23961
19	DODECANE, PHENYL-	C18H30	246	618	654	33150
20	HENEICOSANE, 11-PHENYL-	C27H48	372	613	713	51642

Figure VI5. Structure of 5-phenyl dodecane which analyzed by gas chromatography/mass spectrometry chromatogram



Hit	Compound Name	FORMULA	M.W.	FOR	rev	Entry
1	BENZENE, (1-PENTYLHEPTYL)-	C18H30	246	871	900	33162
2	BENZENE, (1-BUTYLOCTYL)-	C18H30	246	831	869	33165
3	BENZENE, (1-PENTYLOCTYL)-	C19H32	260	790	900	35966
4	BENZENE, (1-HEXYLHEPTYL)-	C19H32	260	786	880	35959
5	BENZENE, (1-BUTYLHEPTYL)-	C17H28	232	785	888	30398
6	BENZENE, (1-ETHYLDECYL)-	C18H30	246	753	786	33149
7	BENZENE, (1-PROPYLNONYL)-	C18H30	246	751	795	33166
8	BENZENE, (1-HEXYLOCTYL)-	C20H34	274	740	843	38552
9	BENZENE, (1-PENTYLHEXYL)-	C17H28	232	738	834	30397
10	BENZENE, (1-BUTYLHEXYL)-	C16H26	218	734	863	27275
11	BENZENE, (1-OCTYLDODECYL)-	C26H46	358	715	746	50204
12	BENZENE, (1-METHYL-1-PROPYLPEN	C15H24	204	707	795	23961
13	BENZENE, (1-PROPYLHEPTYL)-	C16H26	218	704	841	27276
14	BENZENE, (1-ETHYLNONYL)-	C17H28	232	701	812	30395
15	PENTADECANE, 6-PHENYL-	C21H36	288	686	782	40939
16	BENZENE, (1-ETHYLHEXYL)-	C14H22	190	675	807	20387
17	HENEICOSANE, 11-PHENYL-	C27H48	372	670	762	51642
18	BENZENE, (1-HEXYLTETRADECYL)-	C26H46	358	667	754	50203
19	4-PHENYLNONANE	C15H24	204	581	858	23886
20	MEGASTIGMA-7(E),9,13-TRIENE	C13H20	176	492	578	16786

Figure VI6. Structure of 6-phenyl dodecane which analyzed by gas chromatography/mass spectrometry chromatogram

APPENDIX VI

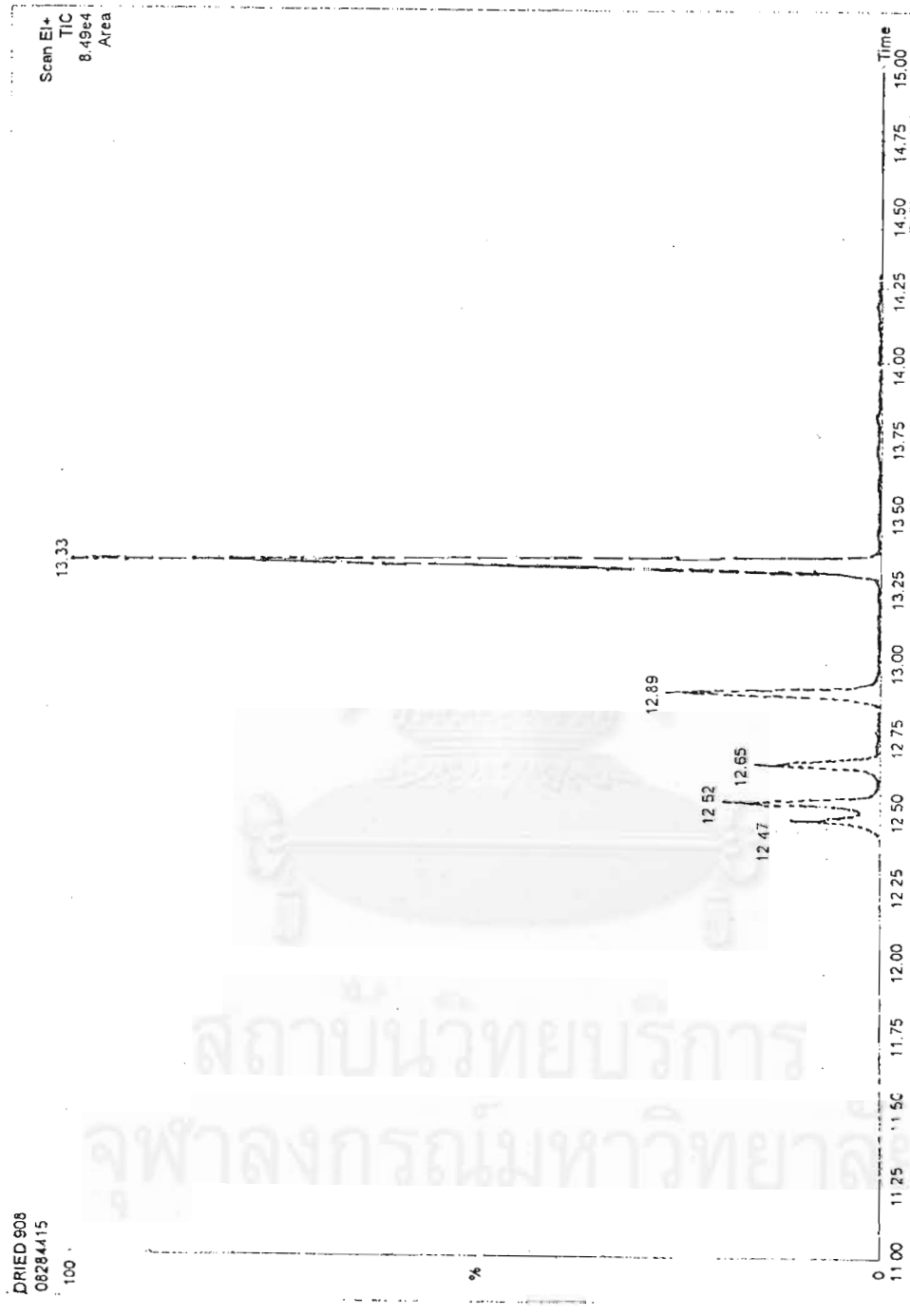


Figure VI1. Gas chromatography/mass spectrometry chromatogram of alkylbenzene compounds

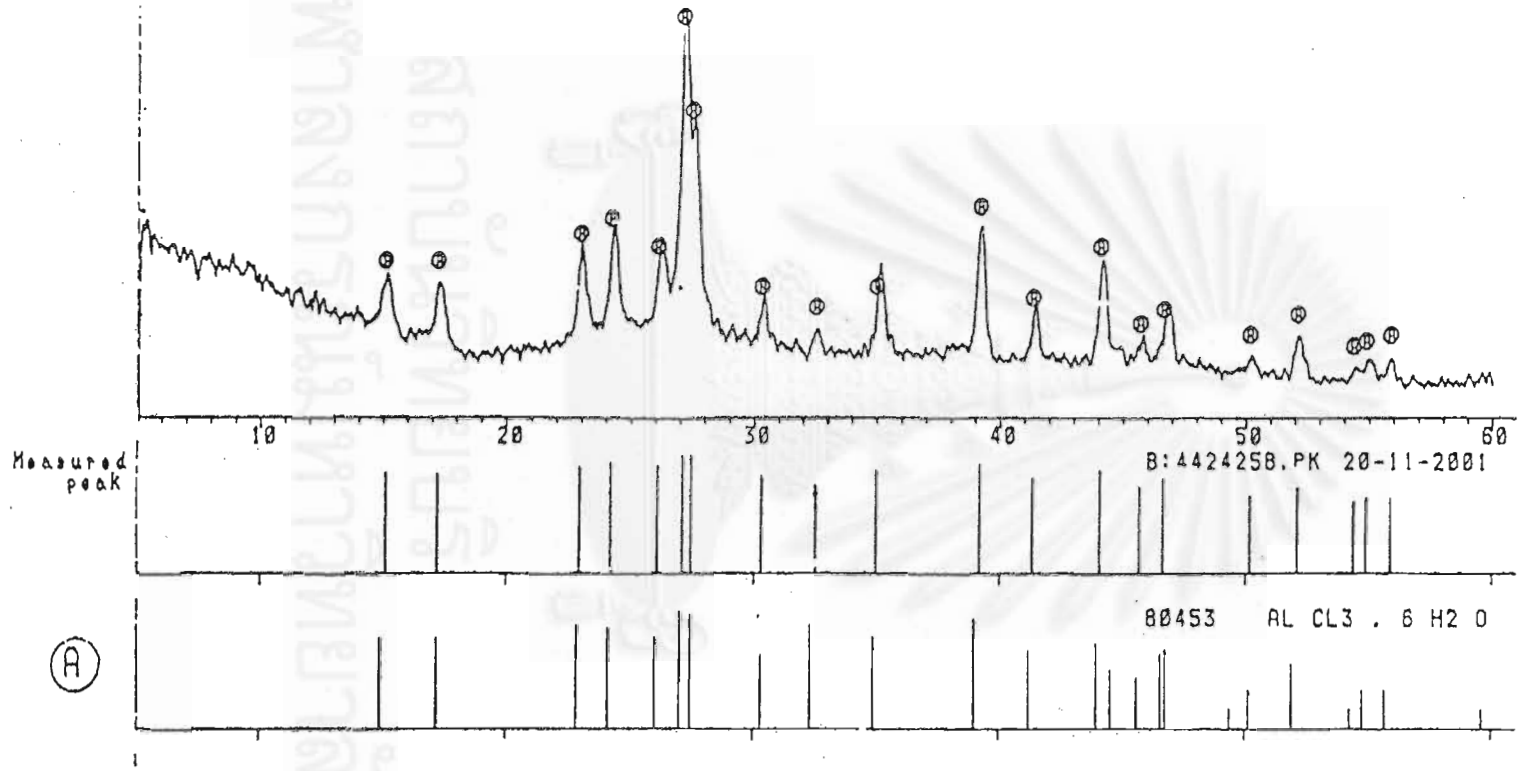


Figure VII1. X-Ray diffraction chromatogram of encapsulated $AlCl_3$

BIOGRAPHY

Mrs. Kusoomjin Srirattnai was born on October 13, 1972 in Samutsongkram, Thailand. She received a Bachelor ’s degree of Science in Chemistry in 1994 and Master ‘s degree of Science in Petrochemical and Polymer Science in 1997, both from the faculty of Science, Chulalongkorn University. Since 1998, she has studied for Doctoral degree in Chemical Technology at the faculty of Science, Chulalongkorn University.

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