การสังเคราะห์พอลิ[เอ็น-ไอโซโพรพิลอะคริลาไมด์-โค-[2-(เมทิลไทโอ) เอทิลเมทาคริเลต]] สำหรับการดูดซับไอออนทอง(III)

นางสาวสุวิมล เหมวัสดุกิจ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2551

SYNTHESIS OF POLY[*N*-ISOPROPYLACRYLAMIDE-*co*-[2-(METHYLTHIO)ETHYL METHACRYLATE]] FOR GOLD(III) ION ADSORPTION

Miss Suwimol Hemvasdukij

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
Faculty of Science
Chulalongkorn University
Academic Year 2008

Thesis Title	SYNTHESIS OF POLY[*N*-ISOPROPYLACRYLAMIDE-*co*-[2-(METHYLTHIO)ETHYL METHACRYLATE]] FOR GOLD(III) ION ADSORPTION
By	Miss Suwimol Hemvasdukij
Field of Study	Petrochemistry and Polymer Science
Advisor	Assistant Professor Apichat Imyim, Ph.D.

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สุวิมล เหมวัสดุกิจ : การสังเคราะห์พอลิ[เอ็น-ไอโซโพรพิลอะคริลาไมด์-โค-[2-(เมทิลไทโอ) เอทิลเมทาคริเลต]]สำหรับการดูดซับไอออนทอง(III). (SYNTHESIS OF POLY[*N*-ISOPROPYLACRYLAMIDE-*co*-[2-(METHYLTHIO)ETHYL METHACRYLATE]] FOR GOLD(III) ION ADSORPTION) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ.ดร.อภิชาติ อิ่มยิ้ม, 114 หน้า.

สังเคราะห์โคพอลิเมอร์ชนิดใหม่ระหว่างพอลิ(เอ็น-ไอโซโพรพิลอะคริลาไมด์) และ 2-(เมทิลไทโอ) เอทิลเมทาคริเลต โดยผ่านปฏิกิริยาพอลิเมอไรเซชันแบบฟรีแรดิคัล และเชื่อมขวางด้วยบิส(อะคริลาไมด์) สภาวะที่เหมาะสมในการสังเคราะห์พอลิเมอร์แบบเนื้อเดียวและแบบเนื้อผสมของพอลิ[เอ็น-ไอโซโพรพิลอะคริลาไมด์-โค-[2-(เมทิลไทโอ) เอทิลเมทาคริเลต]] ได้แก่ 10 มิลลิโมลาร์ของ 2-(เมทิลไทโอ) เอทิลเมทาคริเลตใน 5.0 %(v/v) เอทานอล และ 30 มิลลิโมลาร์ของ 2-(เมทิลไทโอ) เอทิลเมทาคริเลตใน 20.0 %(v/v) เอทานอล ตามลำดับ หาลักษณะเฉพาะของพอลิเมอร์ที่สังเคราะห์ได้ด้วยฟูริเออร์ทรานสฟอร์มอินฟราเรดและรามานสเปกโทรสโกปี กล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด การวิเคราะห์เชิงความร้อน และการวิเคราะห์กลาสทรานซิชัน พอลิเมอร์แบบเนื้อเดียวมีอุณหภูมิที่ทำให้พอลิเมอร์ไม่รวมตัวกับน้ำอยู่ที่ประมาณ 32 องศาเซลเซียส ศึกษาภาวะที่เหมาะสมในการดูดซับไอออนทอง(III) ด้วยการสกัดแบบแบทช์ พอลิ[เอ็น-ไอโซโพรพิลอะคริลาไมด์-โค-[2-(เมทิลไทโอ) เอทิลเมทาคริเลต]] มีประสิทธิภาพดูดซับทอง(III) สูงกว่าพอลิเมอร์ที่ไม่มี 2-(เมทิลไทโอ) เอทิลเมทาคริเลต พีเอชที่เหมาะสมในการดูดซับทองของพอลิเมอร์แบบเนื้อเดียวและแบบเนื้อผสมคือ 1-3 และ 1-5 ตามลำดับ โดยการดูดซับทองจะเข้าสู่สมดุลภายในเวลา 3 ชั่วโมงที่อุณหภูมิ 50 องศาเซลเซียส เมื่อใช้พอลิเมอร์รูปทรงกระบอกที่มีเส้นผ่านศูนย์กลาง 0.7 เซนติเมตร ยาว 1 เซนติเมตร พฤติกรรมการดูดซับทองเป็นไปตามแลงเมียร์และฟรุนด์ลิชไอโซเทอร์มสำหรับพอลิเมอร์แบบเนื้อเดียว และเป็นไปตามฟรุนด์ลิชไอโซเทอร์มสำหรับพอลิเมอร์แบบเนื้อผสม โดยไอออนทอง(III) ที่ถูกดูดซับบนพอลิเมอร์สามารถชะออกได้โดยใช้ 0.1 โมลาร์ไทโอยูเรียใน 5% กรดไฮโดรคลอริก ยกเว้นเจลพอลิ(เอ็น-ไอโซโพรพิลอะคริลาไมด์) แบบเนื้อผสมสามารถชะออกด้วยน้ำปราศจากไอออน ภายในเวลา 2-3 ชั่วโมงที่อุณหภูมิ 10 องศาเซลเซียส

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต สุวิมล เหมวัสดุกิจ
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SUWIMOL HEMVASDUKIJ: SYNTHESIS OF POLY[*N*-ISOPROPYLACRYLAMIDE-*co*-[2-(METHYLTHIO)ETHYL METHACRYLATE]] FOR GOLD(III) ION ADSORPTION. ADVISOR: ASST.PROF. APICHAT IMYIM, Ph.D., 114 pp.

A new copolymer poly[*N*-isopropylacrylamide-*co*-[2-(methylthio)ethyl methacrylate]], poly(NIPA-*co*-MTEMA), with bis(acrylamide) as a crosslinking agent was synthesized by free radical polymerization. The optimum condition for the synthesis of homogeneous and heterogeneous poly(NIPA-*co*-MTEMA) could be achieved with 10 mM MTEMA in 5.0 %(v/v) ethanol and 30 mM MTEMA in 20.0 %(v/v) ethanol, respectively. The copolymers were characterized by Fourier transforms infrared and Raman spectroscopy, scanning electron microscope, thermal gravimetric analysis and differential scanning calorimetry. The lower critical solution temperature (LCST) of homogeneous poly(NIPA) and poly(NIPA-*co*-MTEMA) polymers was nearly about 32°C. The adsorption of gold(III) ion was studied in batch method. The optimum pHs for the adsorption of homogeneous and heterogeneous polymers were 1-3 and 1-5, respectively. The suitable adsorption time was 3 hours at 50°C when using a rod shape copolymer (0.7 cm diameter and 1 cm length). The adsorption behavior of homogeneous polymers fitted to the Langmuir and Freundlich isotherms. For heterogeneous polymers fitted to the Freundlich isotherm. The desorption equilibria were reached within 2-3 hours at 10°C by 0.1 M Thiourea in 5% HCl except for heterogeneous poly(NIPA) for which DI water was appropriate.

Field of Study : Petrochemistry and Polymer Science Student's Signature Suwimol Hemvasdukij

Academic Year 2008 Advisor's Signature

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Finally, I am grateful to my family for their love, entirely care, encouragement and support throughout the entire education. The usefulness of this work, I dedicate to my father, my mother and all the teachers who have taught me since my childhood.

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LIST OF SYMBOLS AND ABBREVIATIONS

APS	Ammonium peroxodisulfate
°C	Degree Celsius
cm^{-1}	Percentimeter
DSC	Differential scanning calorimetry
FAAS	Flame atomic absorption spectrometry
FT-IR	Fourier transforms infrared spectroscopy
FT-Raman	Fourier transforms Raman spectroscopy
i.d.	Internal diameter
LCST	Lower critical solution temperature
MBAA	*N,N′*-Methylenebisacrylamide
mg L^{-1}	Milligram per litre
mL	Millilitre
mM	Millimolar
MTEMA	2-(Methylthio)ethyl methacrylate
NIPA	*N*-Isopropylacrylamide
nm	Nanometre
NMR	Nuclear magnetic resonance spectroscopy
SEM	Scanning electron microscopy
TEMED	*N,N,N′,N′*-Tetramethylethylenediamine
TGA	Thermogravimetric analysis
UV-Vis	Ultraviolet-visible spectrophotometry
s	Singlet (^{1}H-NMR spectrum)
t	Triplet (^{1}H-NMR spectrum)
ν	Stretching vibration
δ	Bending vibration

CHAPTER I

INTRODUCTION

1.1 Statement of the Problem

Stimuli-sensitive polymers change their properties in response to the change in their surroundings such as solvent composition [1], temperature [2-4], pH [5] and supply of electronic field etc. Many temperature sensitive polymers [4,6-8] such as poly(*N*-substituted acrylamide), poly(vinyl methyl ether), poly(diethylacrylamide), and poly(*N*-vinylcaprolactam) have been reported so far and they have been utilized in the gel form for diverse technological applications to controlled drug delivery systems [9-10], chemical separation process [11-12], immobilization of enzyme [13], sensors and actuator [14]. Moreover, these polymers can solve environmental problems with adsorption metal ions in water.

Superabsorbent polymers, SAPs have drawn much interest since the early 1970's because SAPs are three-dimensional networks composed of hydrophilic polymers that are capable to absorb and retain water within their network structure without disintegrating [15]. These polymers have so many called names as hydrogel, or water containing gels, or highly water absorbing polymers (HWAPs), etc. Not only are they high fluid absorbing capacity, but also the absorbed fluid is hard to release.

In recent years, considerable attention has been paid to intelligent hydrogels which contain functional groups that are capable to undergo quite strong and abrupt physical or chemical changes in response to small external changes in the environmental conditions such as pH, temperature, ionic strength, electric and magnetic field, pressure, light intensity, and solvent composition [15]. Because of the unique properties such as softness, elasticity, capacity to store a large amount of fluids within the networks, and biocompatibility, these polymeric gels have found attention due to their potential applications in chemical engineering, medicine, pharmacy, and environmental fields. Within the group of intelligent hydrogels, poly(*N*-isopropylacrylamide) or poly(NIPA) was widely studied for a representative of temperature-responsive polymer since it exhibits a sharp phase transition in water. It exhibits remarkable hydration–dehydration changes in aqueous solutions in response to relatively small temperature changes around 32 °C [16], owing to a phase transition that occurs at the lower critical solution temperature (LCST). Below the LCST, favorable polymer–water interactions via hydrogen bonding lead to dissolution of the NIPA polymer. Above the LCST, breaking of hydrogen bonds leads to a coil-globule transition and polymer precipitation. Poly(NIPA) was prepared by free radical copolymerization in aqueous solution.

Copolymerization is used to change polymer properties and to allow the synthesis of an almost unlimited number of different products by variations in the nature and relative amounts of the two monomer units in the copolymer product. The main advantages of copolymerization lie in the modified properties of the polymers obtained e.g. a change in solubility or a crosslinked structure. The required physical form of crosslinked polymers containing the functional groups can be achieved during the polymerization process itself by copolymerizing monomer with divinyl compounds [17]. Copolymerization of acrylamide can occur with many vinyl monomer for example acrylic acid, methacrylic acid, dimethylaminoethylmethacrylate, diallyldimethylammonium chloride.

To improve the selectivity towards gold(III) ion, the temperature-responsive copolymers superabsorbent are very attractive. These copolymers consists of two main parts, the first part is a main monomer, It is well known that poly(*N*-isopropylacrylamide), poly(NIPA) forms swollen hydrogels of crosslinked species due to the presence of both hydrophilic amide groups and hydrophobic isopropyl groups in its sidechains. The poly(NIPA) hydrogel in an aqueous solution exhibits a rapid and reversible hydration-dehydration change in response to small temperature change around its LCST. The second part is a comomer, 2-(methylthio)ethyl methacrylate (MTEMA), containing sulfur atom in the molecule, that can act as an appropriate donor atom for gold(III) ion. We attempt to combine the advantages of poly(NIPA) and MTEMA for using as adsorbent of gold(III) ion.

This research focused on the synthesis and characterization the novel copolymer of poly(*N*-isopropylacrylamide) and 2-(methylthio)ethyl methacrylate (MTEMA) cross-linked with bis(acrylamide) was synthesized by free radical polymerization. This MTEMA comonomer composes of sulfur donor atom in the molecule, that can be used efficiently to adsorb gold(III) ion in aqueous solution.

1.2 Objectives

1.2.1 To synthesize and characterize a new copolymer between *N*-isopropyl acrylamide and 2-(methylthio)ethyl methacrylate (MTEMA).

1.2.2 To study phase change at Lower Critical Solution Temperature (LCST) of homogeneous polymers.

1.2.3 To investigate gold(III) ion adsorption and desorption properties of the synthetic polymers in aqueous solution.

1.3 Scope of the Research

The scope of this research was firstly a synthesis and characterization of the new copolymers. The Fourier Transforms Infrared Spectroscopy (FT-IR), Fourier Transforms Raman Spectroscopy (FT-Raman), Scanning Electron Microscopy (SEM), Thermo Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) were used for the characterization of the synthesized polymers. Moreover, the Lower

Critical Solution Temperature (LCST) of homogeneous polymers was studied by UV-Vis spectrophotometer. Afterward, the synthesized polymers were brought to find suitable conditions for the adsorption of gold(III) ion by batch method and to study the following parameters: i.e. the effect of pH and temperature of gold(III) ion solution, the effect of adsorption time, the effect of adsorbent size and surface area, adsorption isotherm (in adsorption studied), types of desorbing solution, the effect of adsorption time and temperature (in desorption studied). The concentrations of gold(III) ion in the solution was determined by using Flame Atomic Absorption Spectrometry (FAAS).

1.4 The Benefits of This Research

In this research, the new copolymers which have gold(III) ion adsorption property were achieved.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Superabsorbent Polymers

Superabsorbent polymers (SAPs) are three-dimensionally crosslinked hydrophilic polymers capable of swelling and retaining possibly huge volumes of water in swollen state. Since the first superabsorbent polymer was reported by the US Department of Agriculture [18], SAPs have received significant attention, especially in the past 30 years, because of their considerable applications in many fields, such as hygienic products, agriculture, horticulture, gel actuators and drug delivery systems, as well as the purification of waste water and stabilization of mineral sediments. In recent years, it was determined that hydrogels having functional groups could be used as complexing agents for the removal of metal ions from aqueous solutions. Therefore, a great deal of interest has been observed in relation to the applicability of hydrogels as adsorbent for the removal and separation of metal ions from heavy metal contaminated water, and the recovery and pre-concentration of precious metal ions from different media [19].

The classification of SAPs from composition and preparation methods (polymer composition, networks formation, introduction of hydrophilic groups and product form) is indicated in Table 2.1 [20].

Table 2.1 Four classifications of superabsorbent polymers

Classification of SAPs	*Preparation methods*
A) Polymer composition (raw materials)	
a) Starch	Graft polymerization Carboxymethylation
b) Cellulose	Graft polymerization Carboxymethylation
c) Synthetic polymer	Poly(acrylic acid) Poly(vinyl alcohol) Poly(acrylamide) Poly(oxymethelene)
B) Network formation (insolubilization)	
a) Graft polymerization	
b) Crosslinked copolymerization	
c) Network forming reaction of water-soluble polymer	
d) Self-crosslinked polymerization	
e) Radiation crosslinking	
f) Introduction of crystalline structure or hydrophobic groups	
C) Hydrophilic groups	
a) Polymerization of hydrophilic monomers	
b) Carboxymethylation of hydrophilic monomers	
c) Graft polymerization of hydrophobic polymers with hydrophilic monomers	
d) Hydrolysis of nitrile or ester groups	
D) Product form	
a) Power	Globular, Amorphous
b) Film	
c) Fiber	Short fiber, Long fiber, Non-woven fiber

2.1.1 General Properties of Superabsorbent Polymers

SAPs are remarkably well to form hydrogel structures with adsorbed water. These polymers materials can absorb water more than 20 times its own weight and keep this water under pressure. The absorbed water can be released slowly when the SAPs is put in dry air to maintain the moisture of the environment. Most SAPs are in principle crosslink hydrophilic polymers [21].

Hydrogel swells in water for the same reason that the hydrophilic polymer molecules dissolve in water. The polymer chains that make up the network do not dissolve in water because they are connected to each other through either covalent or noncovalent bonds. The hydrogels with covalently bonded polymer chains are known as physical gels. Swelling in water is one of the inherent properties of hydrogels.

There are many methods to prepare SAPs from various staring materials, such as copolymerizing a hydrophilic monomer with a cross-linking agent, grafting monomers with starch, cellulose, synthetic fiber, and polysaccharide, crosslinking linear hydrophilic polymer with polyvalent metal ions or organic multifunctional group materials etc. The product of SAPs can be in the form of small particles, powder, fiber, membrane, micro beads and even liquid.

The SAPs can be classified with different methods. From a morphological point of view, they can be divided into particle, powder, spherical, fiber, membrane and emulsion types etc. The morphology of SAP is designed to respond the different requirements of the applications. For example, the powder product can be put in the multilayer sheet to form sanitary napkin and diapers, the particle and spherical product can be used as deodorant, the fiber product can be used as antistatic electric fiber, the membrane product can be used as sheet while the emulsion product can be used in soaking and painting.

2.1.2 Physical Behavior of Superabsorbent Polymers

Superabsorbent polymers (SAPs) are crosslinked networks of flexible polymer chains. The most efficient water absorbers are polymer networks that carry dissociated, ionic functional groups. SAPs function by means of a diffusive mechanism. Diffusion is a molecular phenomenon wherein molecules move in a random, nonorganized manner as a result of their thermal energy. Increasing the temperature makes the molecules move faster, and the diffusive process occur therefore at a faster rate. The molecules are in constant motion and will move from their average position in space toward regions of lower activity by purely statistical means. The adsorption mechanism before and after swelling in a dilute salt solution of an example of a superabsorptive resin, in the case of a crosslinked polymer with sodium carboxylate group is shown in Figure 2.1. Before absorption, long chains of polymers are interwoven and polymers make a three-dimensional structure by crosslinking between the chains to make a dense phase. These SAPs instantaneously absorb water and swell with dissolution of Na^+, owing to the hydrophilic ionic groups, and becoming a gel [20].

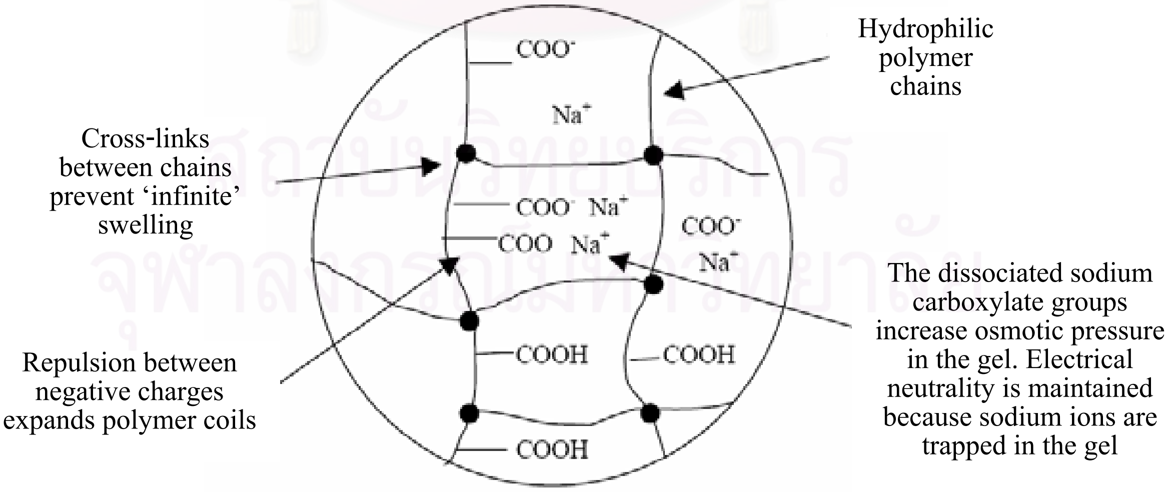


Figure 2.1 Mechanism of swelling of superabsorbent polymers [20].

During absorption, water moves into a particle of superabsorbent polymers because the activity of water is initially lower in the interior of the particle. As water diffuses into the particle, the particle volume increases and the polymer chains that form the superabsorbent polymer network must also move, generally in a direction opposite to that of water molecules, in order to accommodate the volume of the additional molecules of water. After absorption, the change in volume is apparent due to polymer molecules are much larger than water molecules, they diffuse much more slowly. Not only are the polymer molecules larger, but they are also connected one to the other by the crosslinks, so that the polymer dose not eventually dissolve in the water and become as a superabsorbent.

Therefore, the absorbency is mainly dependent upon three factors;

a) the osmotic pressure.

b) the molecular chain expansion resulting from electrical repulsion between the electrolyte anions in the polymer chains.

c) the extent of cross-linkage affecting the degree of swelling of polymer.

The equilibrium swelling results usually from a balance between dispersive (repulsive) and cohesive (attractive) forces acting simultaneously in the fluid. Factors affecting the swelling of polymer are listed in Table 2.2.

Table 2.2 Factors affecting polymer hydrogel swelling [22]

Increase swelling	*Decrease swelling*
Dispersing forces	Cohesive forces
Hydrophilic groups and moieties	Hydrophobic groups and moieties
Low crosslinking density	High crosslinking density
High chain flexibility	Low chain flexibility
High free volume	Low free volume
Osmotic potential	Dipole-dipole interaction
Electrostatic repulsion	Impurities in the fluid

2.1.3 Applications of Superabsorbent Polymers

Superabsorbent polymers process a number of attributes that make then attractive in many different applications. SAPs have supplanted much of the traditional absorbents in infant diapers and have made significant improvements in the performance of feminine hygiene products and adult incontinence products as a result of superior water-absorbing properties. The basic property of water absorption has suggested the use of superabsorbent polymer in many other applications, including paper towels, surgical sponges, meat trays, disposable mats for outside doorways and in bathrooms, and for household pet litter, bandages and wound dressings. The ability of the swollen gels to release the water to the surrounding as vapor has also been used in various ways, for example, as humidity-controlling products or as soil conditions. Superabsorbent polymer may also be used to release water-soluble substances from within the network structure into the surrounding as a solution. For example, pharmaceuticals and fertilizers may be incorporated into superabsorbent polymer to yield controlled release products.

Another characteristic of the swollen polymer is its rubbery nature, which has been use to control the consistency of products as diverse as cosmetics or concrete or to contribute a soft, yet dry, feel to product like a hot or cold pack for sore muscles. The soft, rubbery nature may also be employed to impart sealing properties to products that are in contact with water or aqueous solution, for example, underground wires and cables. In recent their applications are being extended into other industrial areas as shown in Table 2.3 [20].

Table 2.3 Possible applications of superabsorbent polymers

Properties fields	*Water absorption and retention*	*Swelling in volume*	*Gelling ability*	*Increase in viscosity*
Sanitary products	-Sanitary napkins -Diapers -Breast pads			
Agriculture gardening	-Water-retaining -Agents in soil -Seed coatings -Drying preventives for samplings -Artificial moss		-Cultivation plot for mushroom -Seed beds in fluid	
Civil engineering architecture	-Dew preventing agents in walls -Water-retaining agents in concretes	-Water-sealing agents -Substitutes for sandbags	-Sludge solidification agents -Lubricants in drilling works -Slurry explosives	-Mud shielding works
Cosmetics, Toiletries	-Sweat absorbing and kitchen papers		-Gelaromatics -Pocket warmers -Disposable chamber pots	
Medical	-Wound dressings -Sheets for surgical operation	-Control release agents for drug -Disintegrators in tables	-Gelation of blood wastes	-Wet plasters
Food industry	-Agents for preservation of freshness		-Gelling agents -Cold keeping hydrogels	-Viscosity enhancing additive
Others	-Fog preventing film -Dehydrating agents in oil -Moisture sensor -Ink jet for printer	-Toys swelling when soaked in water	-Hydrogel for fire fighting -Artificial snow -Water bed	-Emulsion paints

2.2 Stimuli-responsive Polymers

Stimuli-responsive polymers are polymers that undergo relatively large, physical or chemical property changes in response to small external stimuli such as changes in temperature, pH, solvent composition, supply of electric field or ionic strength. Such polymers are widely found in living systems and can take many forms. Recent interest in intelligent polymer systems has focused on aqueous polymer solutions, aqueous-solid interfaces and crosslinked hydrogels [23].

Stimuli-responsive polymers have been utilized in various forms as follows [6];

1. Cross-linked (permanently) hydrogels
2. Reversible hydrogels
3. Micelles
4. Modified interfaces
5. Conjugated solutions

Hydrogels are crosslinked (whether physically or chemically) polymeric materials that are highly water swollen, typically >90% water by volume. Responsive hydrogels can be synthesized by incorporation of functional monomers into the network structure during polymerization. The most commonly studied structures are thermoresponsive and are usually composed of poly(alkylacrylamides) with poly(*N*-isopropylacrylamide); poly(NIPA) being the most common. Poly(NIPA) linear and network structures posses the ability to respond to changes in temperature by undergoing reversible swelling/deswelling transitions.

If properties of polymers change upon temperature, the term “thermosensitive” is used. The thermosensitive (also called thermoresponsive or temperature-sensitive) hydrogels undergo volume collapse (or shrinkage) upon heating above a certain temperature. Temperature is the most widely used stimulus in environmentally responsive polymer systems. One of the unique properties of temperature-responsive polymers is the presence of a critical solution temperature. Because the volume is reduced, these thermosensitive hydrogels are commonly called thermoshrinking hydrogels. The thermosensitive property comes from the monomers that have the lower critical solution temperature (LCST) phenomenon in the uncrosslinked homopolymer form in aqueous solution. The temperature responsive synthetic polymers are for example poly(dimethylaminoethyl methacrylate), poly(vinyl methyl ether), poly(diethylacrylamide), poly(*N*-vinylcaprolactam) [6]. However, these polymers have been less extensively investigated than the most commonly used LCST monomers that are *N*-substituted acrylamide derivatives, such as *N*-isopropylacrylamide, *N*-*n*-propylacrylamide, and *N*-cyclopropylmethacrylamide because they are easy to obtain or prepare. The main interaction among LCST monomers is hydrophobic in nature and it is enhanced as the temperature increase due to the breaking of hydrogen bonds among water molecular surrounding the hydrophobic moieties. Thus, the hydrogels made of LCST monomers collapse at temperatures higher than the LCST. These hydrogels swell again as the temperature falls again below LCST. The thermoreversibility is attributed to the reassociation of the excluded water with the polymer matrix upon reversal in temperature. These hydrogels showed a typical thermoresponsive, that is swelling at low temperature and deswelling at high temperature.

2.3 Poly(*N*-isopropylacrylamide)

2.3.1 *N*-isopropylacrylamide Monomer

The structure and physical/chemical properties of *N*-isopropylacrylamide as shown in Figure 2.2 and Table 2.4, respectively.

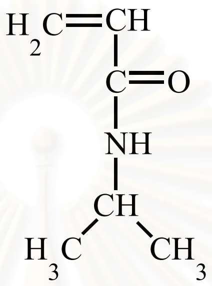


Figure 2.2 The structure of *N*-isopropylacrylamide monomer.

Table 2.4 Physical and chemical properties of *N*-isopropylacrylamide monomer [24]

Properties	*Value*
Appearance	White crystalline solid
Synonym	2-Propenamide
Formula	$C_6H_{11}NO$
Molecular weight (g mol^{-1})	113.16
Melting point	60 - 63°C
Boiling point	89 - 92°C
Water Solubility	Soluble

2.3.2 Properties of Poly(*N*-isopropylacrylamide)

Poly(*N*-isopropylacrylamide), poly(NIPA), is one of the most extensively investigated synthetic water soluble temperature-responsive polymer attracting great interest as a basic building block of smart materials. This temperature dependent deswelling is known as a volume phase transition (VPT) and occurs in the vicinity of 32ºC, which is the lower critical solution temperature (LCST) for poly(NIPA). When temperature is raised above 32ºC, the hydrophobic backbone and isopropyl groups of the polymer tend to associate. This causes intra- and intermolecular aggregation leading to the collapse of the poly(NIPA) chains and phase separation of the polymer. This temperature is also known as the cloud point. This phenomenon is reversible when the stimulus is reversed, although the rate of reversion is often slower as the polymer redissolves. If NIPA monomer is copolymerized with more hydrophilic monomers, the cloud point increases and may even disappear. On the other hand, hydrophobic modification of poly(NIPA) decreases the cloud point and affects significantly the polymer demixing with increasing temperature.

This differential solvation behavior is due to the unique interactions of poly(NIPA) with water molecules in a temperature dependent fashion where the interactions between the water molecules and polymer are weakened, while the polymer-polymer interactions are strengthened at high temperature, as depicted in Figure 2.3. At temperatures below the LCST of poly(NIPA) water is a good solvent for poly(NIPA) but as the temperature of the solution is increased the polymer becomes a better solvent for itself resulting in an entropy driven expulsion of water.

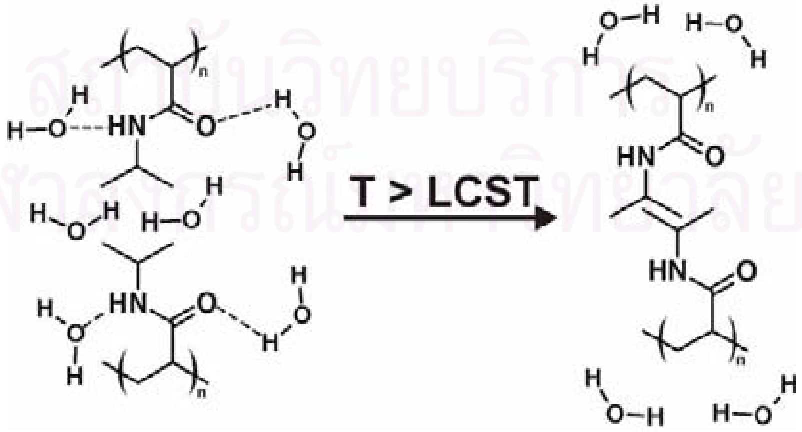


Figure 2.3 Molecular level view of the water dissociation process for poly(NIPA) [25].

Poly(NIPA) is one of water-soluble polymers contain hydrophilic groups, which are able to interact strongly with water molecules. Polar groups in a polymer structure, such as amide groups, are prone to create water solubility. The formation of hydrogen bonds between hydrophilic groups and water molecules is the initial driving force for dissolution. On the other hand, vinyl backbones are hydrocarbons and thus hydrophobic. Water molecules re-orientate and form ordered hydration layers around the non-polar domains. The re-structuring of the water molecules is entropically unfavorable, and thus in order to minimize the entropic loss of the system, hydrophobic regions tend to segregate. This phenomenon is known as the hydrophobic effect and it induces hydrophobic interactions.

The swelling behavior is the most important characteristic of hydrogel polymers. There are many ways to measure water absorption capacity (WAC), however, there is no standard yet. Usually, the WAC is measured using the volumetric method. The volumetric method is to measure the volume changes of polymer (or the water) before and after the absorption, the gravimetric method is to measure the changes in the weight of the polymer and the microwave method is to measure the microwave absorption by energy changes. The WAC of hydrogels depends upon its composition and structure generated from the preparation method, as well as the presence of electrolytes in the water.

2.3.3 Preparation of Poly(*N*-isopropylacrylamide)

The poly(NIPA) hydrogel can be synthesized from aqueous solution of the monomer by using a redox initiator, ammonium peroxodisulfate (APS) and *N,N,N',N'*-tetramethylethylenediamine (TEMED) (Figure 2.4) in the presence of *N,N'*-methylenebis acrylamide (MBAA), as a crosslinker. The polymerization at room temperature proceeds in a homogeneous solution. Poly(NIPA) hydrogels can also be synthesized by starting the polymerization below the LCST, then elevating the temperature above it. In this way macroporous gels with fast temperature response were obtained [26].

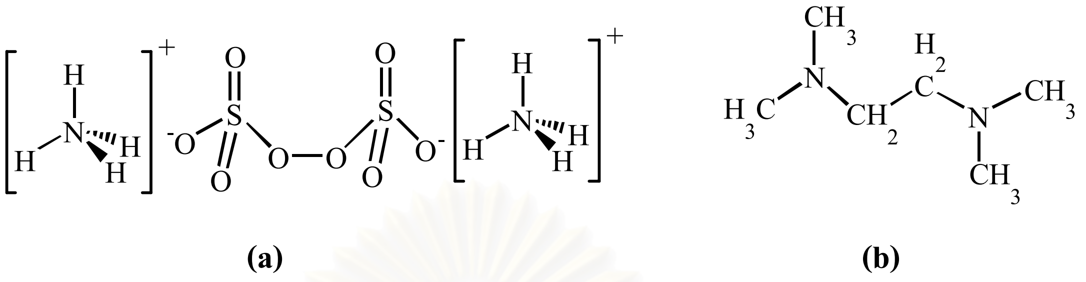


Figure 2.4 The structure of (a) ammonium peroxodisulfate (APS) and (b) *N,N,N',N'*-tetramethylethylenediamine (TEMED).

According to the previous works, the actual reaction temperature T deviates from the value of the gel preparation temperature (T_{prep}) due to the exothermic reaction profiles of the crosslinking copolymerization of NIPA. Depending on the surface-to-volume ratio of the reactor as well as on the composition of the reaction mixture, T attains larger values than T_{prep} during the course of the polymerization. The exothermic nature of NIPA polymerization lead to the appearance of turbidity in the gel formation system well below the LCST of poly(NIPA). The homogeneous polymers called gel prepared at T_{prep} is lower LCST, while the heterogeneous polymers called gel prepared at T_{prep} is higher LCST.

Hietala *et al.* (2008) [27] studied of the isotactic A blocks poly(NIPA). It was only barely soluble in water at room temperature but dissolved completely upon cooling to 5ºC, the forming transparent viscous solutions. Upon heating the aqueous polymer solutions above 32ºC, they become cloudy and at the studied concentration, precipitate. Figure 2.5 displays the photographs of isotactic A blocks poly(NIPA), taken directly from 5ºC, at room temperature, and after heating up to 50ºC. As may be seen in the figure, the solution is clear viscous liquid at low temperatures but further viscosifies upon warming to room temperature and behaves as a hydrogel.

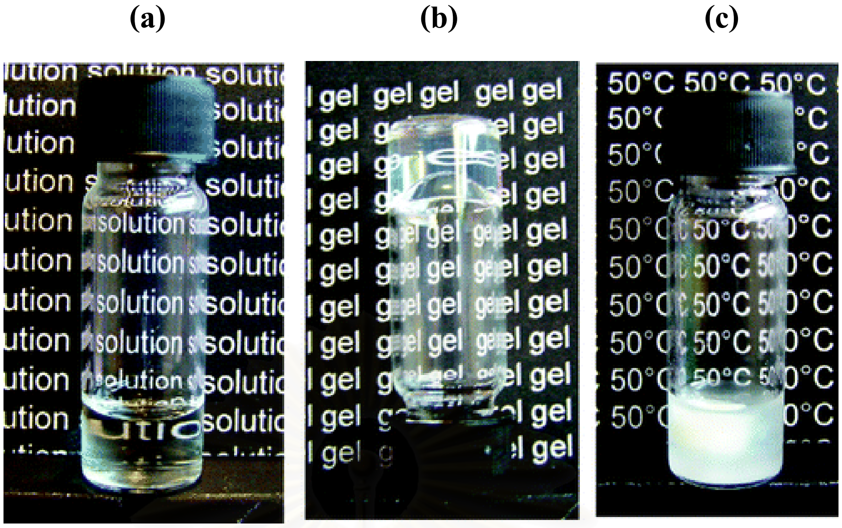


Figure 2.5 Photograph illustrating isotactic A blocks poly(NIPA) solution at (a) 5ºC, (b) room temperature, and (c) 50ºC.

Sayil *et al.* (2001) [28] observed formation of glassy polymers below 22.5°C whereas opaque gels were obtained above this temperature. Further, opacity increased as T_{prep} is increased. Since the opacity is a result of light scattering from the spatial inhomogeneities of the gel refractive index, these results indicate existence of domains in poly(NIPA) gels in the order of the wavelength of visible light. A gel sample prepared at 50°C at various swelling times is shown in Figure 2.6. Swelling was accompanied with the deformation of the gel sample. The extent of deformation increased with increasing T_{prep}, indicating increasing inhomogeneity in the network structure on raising the gel preparation temperature. The inhomogeneities in poly(NIPA) gels depending on T_{prep} have been extensively investigated using light scattering techniques.

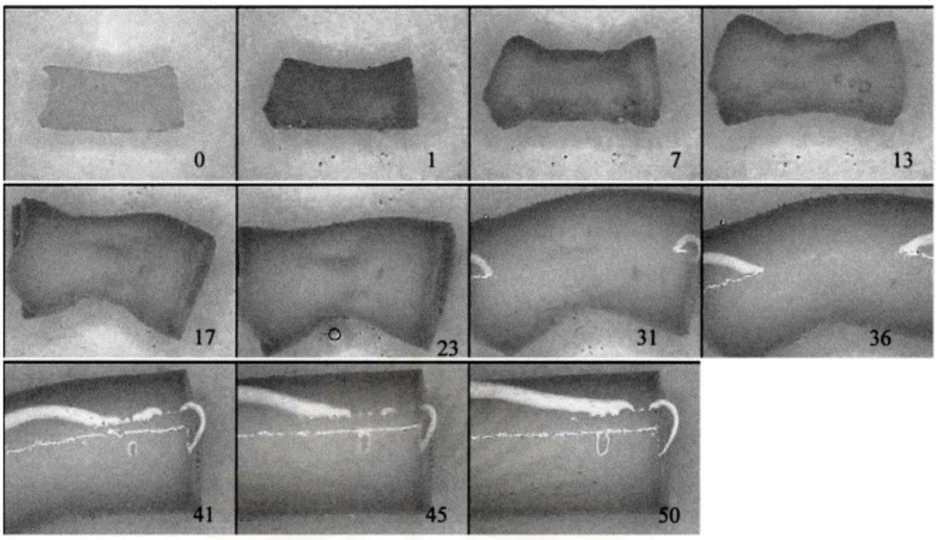


Figure 2.6 A series of photographs taken during the swelling process of a poly(NIPA) network sample prepared at 50°C. Swelling times in minutes are given in the photographs.

2.3.4 Phase Transition of Poly(*N*-isopropylacrylamide)

When two polymers do mutually dissolve, they are generally found to phase-separate at some higher temperature rather than at some lower temperature. This is called a lower critical solution temperature (LCST). The lowest temperature of the phase separation curve on concentration–temperature diagram is shown in Figure 2.7 [29]. This unusual result can be interpreted by considering the unusual features of the mixing process. At the critical point, the heat of mixing must balance the entropy of mixing times and the absolute temperature. The latter is known to be unusually small, so that the free energy of mixing is the difference between two small quantities [30].

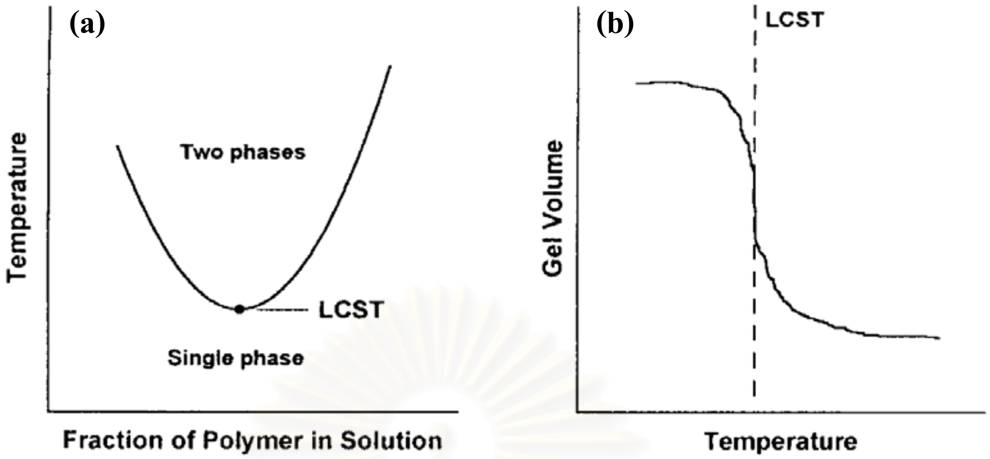


Figure 2.7 (a) The phase diagram and (b) the gel volume change around the lower critical solution temperature (LCST).

Responsive gels typically show volume changes over a similar range of conditions where corresponding uncrosslinked polymers undergo changes in solvent interaction, whether due to solubility or ionization effects. Poly(NIPA) hydrogels that display temperature-sensitive behavior in water are synthesized from polymers that exhibit a LCST. Below the LCST, the polymer is soluble in water due to extensive water-polymer hydrogen bonding but at temperature above the LCST, polymer-polymer hydrophobic interactions dominate, polymer-solvent hydrogen bonds are disrupted, and the polymer precipitates from solution. Otherwise, it is called a higher critical solution temperature (HCST) or upper critical solution temperature (UCST). However, because of the crosslinks, a gel made from the same polymer can only swell. At temperature higher than the LCST, the gel will collapse into a polymer-dense state rather than precipitate.

2.3.5 Poly(*N*-isopropylacrylamide) Copolymer

Poly(NIPA) structures can also be easily rendered multifunctional by the polymerization of two or more functional monomers into the network structure. Performing this copolymerization results in a hydrogel that changes its solvation state in response to multiple stimuli where the energetics involved in responsivity are dictated by the component of the network that has the strongest interaction with water.

Poly(NIPA) has been widely used as stimuli-sensitive polymers, hence the modified properties of these polymer by copolymerization was interesting. In recent years, many papers reported the modified poly(NIPA) via copolymerization with several comonomer in this manner.

Zha *et al.* (2002) [31] studied monodisperse cationic thermosensitive latex microgels prepared by radical-initiated precipitation copolymerization of poly(*N*-isopropylacrylamide-*co*-dimethylaminoethylmethacrylate);poly(NIPA-*co*-DMAEMA). It was found that the hydrodynamic diameter of all the latex particles was found to decrease upon increasing the ionic strength of the dispersion medium and the colloidal stability of the microgel latexes is increased upon raising the DMAEMA concentration owing to the electrostatic interaction.

Kesim *et al.* (2003) [32] synthesized and characterized of thermal and pH sensitive poly(*N*-isopropylacrylamide-*co*-maleic anhydride) with polyethyleneglycol (PEG) and polyethyleneimine (PEI) have been studied as a way to obtain new reactive amphiphilic water soluble polymers potentially useful as carriers for gene delivery.

Caykara *et al.* (2006) [33] prepared poly(*N*-isopropylacrylamide-*co*-acrylamide) by free radical polymerization. It was shown that the swelling behavior of this hydrogel can be controlled by changing the amount of crosslinker. The swelling equilibrium of the poly(NIPA-*co*-AAm) was also investigated as a function of temperature in aqueous solutions of the anionic surfactant sodium dodecyl sulfate

(SDS) and the cationic surfactant dodecyltrimethylammonium bromide (DTAB). It was found that the electric conductivity of the poly(NIPA-*co*-AAm) surfactant systems depended strongly on both the type and concentration of surfactant solutions.

Cao *et al.* (2007) [10] synthesized a novel polymer, poly(NIPA)-chitosan by using 2,2'-azobisisobutylonitrile (AIBN) as initiator in situ gel-forming properties and potential utilization for ocular drug delivery. The thermal sensitivity and LCST were determined by the cloud point method had a LCST of 32°C, which is close to the surface temperature of the eye.

Mohan *et al.* (2007) [15] prepared stimuli-responsive poly(*N*-isopropylacrylamide-*co*-sodium acrylate) hydrogel networks by aqueous free radical polymerization in the presence of different amount of MBAA crosslinker. The high swelling capacities and equilibrium water content values of these hydrogels are expected to find applications in bioengineering fields.

Ma *et al.* (2007) [34] prepared and characterized of sodium carboxymethylcellulose/poly(*N*-isopropylacrylamide)/clay semi-interpenetrating polymer network (IPN) nanocomposite hydrogels. The temperature- and pH-responsive behaviors, the mechanical properties of these hydrogels. The CMC/PNIPA/Clay hydrogels exhibited a volume phase transition temperature around 32°C with no significant deviation from the conventional poly(NIPA) hydrogels. The swelling ratio of the CMC/PNIPA/Clay hydrogels gradually decreased with increasing the contents of clay. The influence of pH value on swelling behaviors showed that there is a maximum swelling ratio at pH 5.9. Moreover, the CMC/PNIPA/Clay hydrogels exhibited excellent mechanical properties with high tensile stress and elongation at break.

Fares *et al.* (2008) [35] synthesized thermosensitive *N*–isopropylacrylamide-*alt*-2–hydroxyethyl methacrylate copolymers. The LCST of various NIPA-*alt*-HEMA molar ratios first increased as result of increasing NIPA content from 35°C [pure poly(HEMA)] to a maximum value of 36.7°C at 50 mol % NIPA, and then it declined to 33°C, the LCST of pure poly(NIPA). This behavior was attributed to the increase in the hydrophobicity as the NIPA content (mol %) increased.

2.4 Free Radical Polymerization

Polymerization is the formation of long chains of covalently bonded monomer units, and it is commonly subdivided into condensation and chain polymerization. Herein the chain polymerization mechanism is considered.

Free radical polymerization is one of the most important type of chain polymerization technique and it is a very useful method for large scale production of a variety of polymers. Most of the vinyl polymers can be produced industrially by free radical polymerization. Compared to other polymerization techniques, free radical polymerization is much less sensitive to impurities, it is not sensitive to water and actually sometimes it is carried out in aqueous media. Free radical polymerization, like other chain or chain growth polymerization mechanism, has mainly three basic reaction types occurring simultaneously during polymerization. These include: initiation reactions that continuously generate radicals, propagation reactions that are responsible for the growth of polymer chain by monomer addition to a radical center and termination reactions between two radical centers that give a net consumption of radicals.

Initiation in free radical polymerization consists of two reactions. First (Equation 2.1a), the initiator (I) decomposes to form two radical species ($R\bullet$).

$$I \xrightarrow{k_d} 2R\bullet \tag{2.1a}$$

where k_d is the rate constant for the initiator dissociation.

In the second step of the initiation, a monomer molecule (M) reacts with the initiator radical (Equation 2.1b), forming a monomer radical.

$$R\bullet + M \xrightarrow{k_i} M_1\bullet \qquad (2.1b)$$

where k_i is the rate constant for the initiation step.

The propagation step is the growth of the active (free radical) chain by sequential addition of monomers. Each addition creates a new radical which has the same identity as the one previously mentioned, except that it is larger by one additional monomer unit. This propagation steps is indicated in Equation 2.2.

$$M_n\bullet + M \xrightarrow{k_p} M_{n+1}\bullet \qquad (2.2)$$

where k_p is the propagation rate constant for propagation.

The propagation reaction will continue until some termination process occurs. One obvious termination mechanism occurs when two propagating radical chains react to form a single dead chain (Equation 2.3). This termination mechanism is called termination by combination or coupling.

$$M_n\bullet + M_m\bullet \xrightarrow{k_{tc}} M_{n+m} \qquad (2.3)$$

where k_{tc} is the rate constant for termination by coupling.

Termination can also occur by a disproportionation reaction to give two dead chains. One of the dead chains will have an unsaturated chain end while the other will have a saturated chain end. Equation 2.4 illustrates the mechanism of termination by disproportionation.

$$M_n\bullet + M_m\bullet \xrightarrow{k_{td}} M_n + M_m \qquad (2.4)$$

where k_{td} is the rate constant for termination by disproportionation.

The termination step produces dead polymer chains: the growth of the polymer chain is terminated and the active centers are irreversibly annihilated. This implies that it is impossible to form block copolymers by adding a new monomer and re-activating the polymerization system.

In addition to termination by combination and disproportionation, another mechanism of termination is chain transfer by hydrogen abstraction from any H-containing reactant present in the system (Equation 2.5).

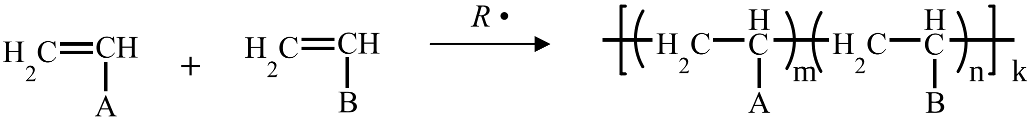
$$M_n\bullet + TH \longrightarrow M_n + T\bullet \qquad (2.5)$$

where *TH* represents monomer, initiator, solvent, polymer or any substance in the reaction media that can have a hydrogen atom abstracted by the polymer radical chain [36].

2.4.1 Copolymerization

There are several ways of changing the properties of a polymeric material. For example, additives can be used to incorporate desirable properties into an existing polymer material for new applications. Another approach is to combine the properties of different polymer structures. The simplest way to achieve this is to blend two polymers to give a material with mechanical and rheological properties that are better than those of the individual polymers. However, because few polymers are miscible, they tend to phase separate in most blends which, consequently, often have poor physical properties due to inadequate interfacial strength between the phases. An alternative way is to copolymerize different monomers into a single polymeric material (Figure 2.8).

Copolymerization is the best way to produce a polymer with properties that are intermediate between the properties of the respective homopolymers. It is an important process from a commercial point of view because it can produce new polymers with completely different properties. An unlimited number of polymeric structures with a wide range of properties and applications can be synthesized via copolymerization of a few different types of comonomers.



$$H_2C{=}CH{-}A + H_2C{=}CH{-}B \xrightarrow{R\bullet} \left[\left(H_2C{-}\overset{H}{\underset{A}{C}} \right)_m \left(H_2C{-}\overset{H}{\underset{B}{C}} \right)_n \right]_k$$

Figure 2.8 General copolymerization reaction.

One way to classify copolymers is based on their architecture. Figure 2.9 shows how copolymers are classified as statistical, alternating, block, and graft. In statistical or random copolymers, the placement of the comonomers in the chain is random. In alternating copolymers, comonomer molecules alternate in the chain. If long sequences of one comonomer are followed by long sequences of the other comonomer, the resultant copolymer is called block copolymer. Block copolymers can be diblock, triblock or multiblock depending on the number of comonomer types used during polymerization. Graft copolymers are branched polymers where the backbone is made of one copolymer type and the branches are made of another copolymer type [37].

—AABBBABBAABBBABABAAABABBBABAABB— statistical copolymer

—ABABABABABABABABABABABABABABABA— alternating copolymer

—AAAAAAAAAAAAAAAABBBBBBBBBBBBBBB— block copolymer

BBBBBBBBBBB
|
—AAAAAAAAAAAAAAAAAAAAAAAAAAAAAA— graft copolymer
|
BBBBBBBBBBB

Figure 2.9 Types of copolymer.

2.4.2 Types of Copolymerization Behavior

Different types of copolymerization behavior are observed depending on the values of the monomer reactivity ratios. The terminal type to describe copolymerization was first suggested by Benoit *et al.* (1936) [38]. The terminal type is based upon the assumption that the chemical reactivity of a propagating polymer chain is independent of the size or composition of the chain and is only influenced by the chemical nature of the active end group [39]. When two monomers are used, M_1 and M_2 have four possible propagation events. The growing chain with a M_1 moiety on the end $RM_1\bullet$ can react with the another molecule M_1 with a rate constant k_{p11} or with a molecule M_2 with a rate constant k_{p12}. Likewise, when M_2 moiety $RM_2\bullet$ is at the end of the growing chain, it can add to M_1 with a rate constant k_{p21} or to M_2 with a rate constant k_{p22} as shown in Equation 2.6.

$$RM_1\bullet + M_1 \xrightarrow{k_{p11}} RM_1M_1\bullet \qquad (2.6a)$$

$$RM_1\bullet + M_2 \xrightarrow{k_{p12}} RM_1M_2\bullet \qquad (2.6b)$$

$$RM_2\bullet + M_1 \xrightarrow{k_{p21}} RM_2M_1\bullet \qquad (2.6c)$$

$$RM_2\bullet + M_2 \xrightarrow{k_{p22}} RM_2M_2\bullet \qquad (2.6d)$$

The monomer reactivity ratios r_1 and r_2 are defined these relative rates of copolymerization reactions by Equation 2.7 and 2.8.

$$r_1 = \frac{k_{p11}}{k_{p12}} \qquad (2.7)$$

$$r_2 = \frac{k_{p22}}{k_{p21}} \qquad (2.8)$$

From the values of the reactivity ratios, different types of copolymerization behaviors can be distinguished. Random copolymerization occurs when $r_1 = r_2 = 1$ due to the equal reactivity of the monomers towards both types of propagating chain ends and the resulting copolymer composition will directly reflect the comonomer feed. When $r_1r_2 = 1$ (ideal polymerization), the two different types of propagating chain ends add preferentially to one of the monomers. Block copolymers are formed when r_1 and r_2 are much greater than one and alternating copolymerization happens when $r_1r_2 = 0$.

2.4.3 Monomer Concentration

The concentration of monomer in the reaction solution affects the properties of the resulting polymer, the kinetics of the reaction and the economics of the process. High monomer concentration results in increasing toughness of the intermediate gel polymer as the polymerization progresses. The toughness of the gel affects the design of equipment, the size of gel particles produced during agitation of the reaction mass and the method of heat removal. In addition, chain transfer to polymer increases with monomer concentration, especially at a high extent of conversion, this results in increasing amounts of branching and self-crosslinking reactions that affect product properties. Chain-transfer agents are useful to conflict these side-reactions. Another factor influencing the choice of monomer concentration is that the efficient use of the crosslinker increases with monomer concentration because the solubility of crosslinkers typically not very water soluble often increases with monomer concentration due to the increasing organic content of the monomer phase [40].

2.4.4 Initiators

The polymerization in an aqueous phase is initiated by free radicals which originate from the decay of initiator molecules. The initiator may arise from thermal degenerator by means of a reduction-oxidation (redox) reaction or by a combination of these. Peroxo compounds like hydrogen peroxide, sodium or ammonium peroxodisulfate and water soluble azo-compounds like 2,2'-azobis-(2-amidinopropane)-dihydrochloride or 2,2'-azobis-(4-cyanopentanoic acid) are the preferred radical sources. Examples for redox systems are peroxodisulfate/hydrogen sulfite, peroxodisulfite/thiosulfate, peroxodisulfate/ascorbic acid or iso-ascorbic acid and hydrogen peroxide/ascorbic acid.

The polymerizations frequently are initiated at room temperature with the aid of redox couple. After the reaction mass is heated up the polymerization proceeds further by the thermal decay of a secondary initiator. Starting at lower temperature minimizes undesirable high peak temperatures. Initiator concentrations are always adapted to the monomer concentration with particular regard to the decay rates of the initiators. Usually there is a practical balance struck between high conversions (low residual monomer), high conversion rates at high initiator concentrations and products having low fractions of soluble polymer but high monomer residues at low initiator concentration [41].

Ammonium peroxodisulfate (APS) is widely used in the polymerization of water soluble vinyl monomers. The polymerization reaction is a vinyl addition catalyzed by free radicals. The reaction is initiated by *N,N,N',N'*-tetramethylethylenediamine (TEMED), which induces and accelerates free radical formation from APS. The free radicals transfer electrons to the acrylamide/bisacrylamide monomers, radicalizing them and causing them to react with each other to form the polyacrylamide chain. When APS-TEMED is used as redox initiator for free radical polymerization, the free radical (I) is one of the initial free radicals responsible for the initiation of vinyl polymerization in addition to sulfate free radical (II). The following mechanism represents the production of initial radicals for the polymerization as shown in Figure 2.10.

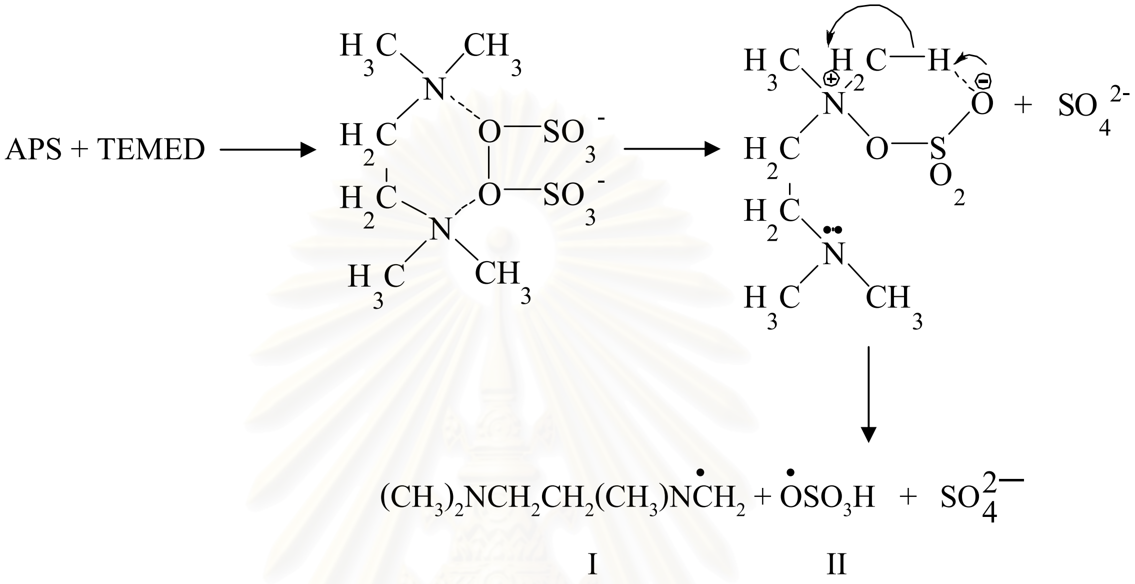


Figure 2.10 Mechanism of initiator for free radical polymerization [42].

2.4.5 Crosslinker

2.4.5.1 Chemical Crosslinking

The mechanism for most severely molecular freedom is chemical crosslinking which links the polymer chains together through covalent or ionic bonds to form a network. Occasionally the term curing is used to denote crosslinking. There are a number of crosslinking ways, but basically they fall into two categories [43]:

1) crosslinking during polymerization by the use of polyfunctional monomer instead of difunctional monomers.
2) crosslinking in a separate processing step after the linear (or branched) polymer is formed.

The crosslinks may contain the same structural features as the main chains, which is usually the case with the former, or they may have an entirely different structure, which is the unique characteristic of the latter. A number of extreme changes accompany crosslinking. If previously soluble, the polymer will no longer dissolve (except in the case of some ionically crosslinked polymers). In the presence of a solvent, a crosslinked polymer swells as solvent molecules penetrate the network. The degree of swelling depends on the affinity of solvent and polymer for one another, as well as on the level of crosslinking. It may be recalled that a solvent-swollen crosslinked polymer is called a gel. Covalently crosslinked polymer also loses their flow properties. They may still undergo deformation, but the deformation will be reversible; that is the polymer will exhibit elastic properties. Ionically crosslinked polymers will flow at elevated temperatures. With network polymers, it is common to speak of the crosslink density, that is the number of crosslinked monomer unites per main chain. The higher the crosslink density, the more rigid the polymer. Very high crosslink densities lead to embrittlement because crosslinking reduces segmental motion, it is frequently employed to increase the glass temperature.

2.4.5.2 Physical Crosslinking

When polymer chemists use the term crosslinking, they invariably mean covalent chemical crosslinking. Once crosslinked, a polymer cannot be dissolved or molded. One approach has been to investigate thermally labile crosslinks, that is chemical crosslinks that break apart on heating and reform on cooling. Ionic crosslinks fall into this category. The other approach has been to introduce strong secondary bonding attraction between polymer chains such that the polymer exhibit properties of the thermosetting material while remaining thermoplastic. Crystalline polymers fit into this category. Because of the very strong secondary forces rising from close chain packing, many mechanical and solution properties of crystalline polymers resemble those of crosslinked amorphous polymers. Certain materials intermolecularly associate through hydrogel bonds also behave like crosslinked polymers [43].

2.4.5.3 Crosslink Density

One of the most important structural parameters characterizing crosslinked polymers is $\overline{M_c}$, the average molecular weight between crosslinks, which is directly related to the crosslink density. The magnitude of $\overline{M_c}$ significantly affects the physical and mechanical properties of crosslinked polymer and its determination has great practical significance. Equilibrium swelling is widely used to determine $\overline{M_c}$. Early research by Flory and Rehner proposed the foundation for the analysis of equilibrium swelling. According to the theory of Flory and Rehner, the $\overline{M_c}$ for a perfect network can be written as in Equation 2.9 [44].

$$\overline{M_c} \quad = \quad -V_l \rho_p \frac{(\phi_p^{1-3} - \phi_p / 2)}{[In(1-\phi_p) + \phi_p + \chi_{12}\phi_p^2]} \tag{2.9}$$

Where $\overline{M_c}$ is the number average molecular weight of the polymer between crosslinks

V_l is the molar volume of the solvent

ρ_p is the polymer density

ϕ_p is the volume fraction of polymer in the swollen gel

χ_{12} is the Flory-Haggins interaction parameter between solvent and polymer.

The swelling ratio, *S*, is equal to $1/\phi_p$. Here, the crosslink density, *q*, is defined as the mole fraction of crosslinked units

$$q = \frac{M}{\overline{M_c}} \tag{2.10}$$

Where M is the molecular weight of polymer repeating unit. q in Equation 2.10 is defined in order to simplify a direct comparison with the mole fraction of divinyl monomers in copolymerization.

2.5 Adsorption

The adsorption is a phenomenon of the sorption that occurs between the liquid or gas phase and solid phase. The species in the liquid or gas phase are moved and can be attracted on the surface of solid phase, which is called mass transfer. The solid phase and the target species in the liquid or gas phase are called adsorbent and adsorbate, respectively. The adsorption can be further split into two types, the physisorption and chemisorption [45].

Physisorption

This physical adsorption is the attraction between adsorbates and adsorbents via van der Waals force, generating from London dispersion force and the electrostatic force. Furthermore, it can occur the multilayer sorption on the adsorbent surface, when the concentration of adsorbates increases. The reaction of this adsorption is called outer-sphere surface reaction or non-specific, that the analytes are independently adsorb on the surface of adsorbents and the adsorption is reversible. The reversibility of reaction depends upon the attraction force of target ions or molecules with adsorbent, their concentration and temperature.

Chemisorption

The interaction between adsorbate and adsorbent in chemisorption is the chemical or covalent bonds, which is stronger than van der Waals force in physisorption. This mechanism may occur when the surface of adsorbents has active sites which is specific for irreversible reaction. The chemical adsorption can be called inner-sphere surface reaction.

2.5.1 Determination of Metal Adsorption

Flame atomic absorption spectroscopy (FAAS) is one of techniques used to determine qualitatively and quantitatively a milligram per litre concentration level of analyte in a liquid sample. The basic principle of FAAS is the absorption of element specific radiation by free atoms in the ground state. The free atoms in the gas phase are generated by flame. Due to the absorption of specific quanta, the amount of atoms in an exciting state increases and hence leads to a depopulation of the atoms in ground state. The value of the absorbed light corresponds to the initial concentration of atoms in the ground state and therefore correlates as well to the concentration of the element. The common instrumental diagram is shown in Figure 2.11.

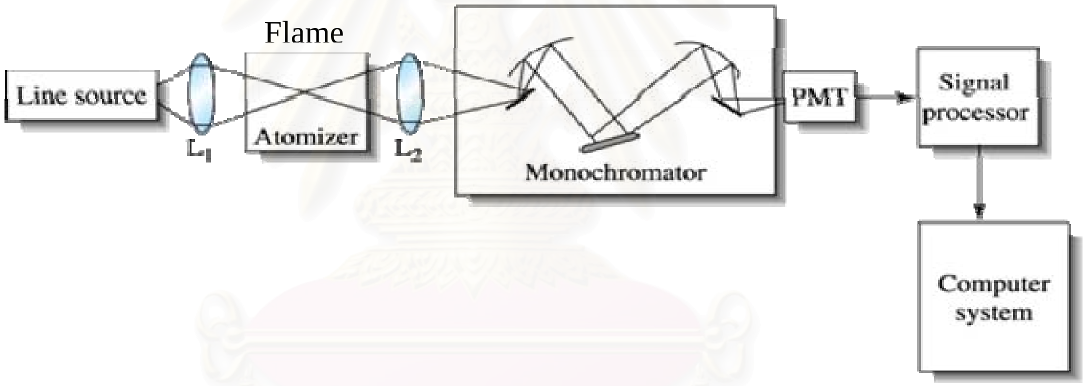


Figure 2.11 Block diagram of general atomic absorption spectrometer [46].

Atomic absorption spectrometry is commonly used for quantitative analysis and only one element can be measured at a time by conventional instrument. Based on the measurement of absorbed radiation, a quantitative determination of the amount of analyte in the sample is possible with the Lambert-Beer's law (Equation 2.11) [47].

$$A_{abs} = -\log T = \log\left(\frac{I_o}{I}\right) \tag{2.11}$$

where A_{abs} = absorbed radiation (absorbance) of the material

T = light transmission (transmittance) of the material

I_0 = incident intensity without absorption

I = transmitted intensity of light which has passed through and emerges from the solution

2.5.2 Adsorption Isotherms

The adsorption process that refers to the partition of analytes at equilibrium of constant temperature is called adsorption isotherm which can be obtained by the relationship between aqueous phase and adsorbent (solid phase). There are the several isotherm equations describing the equilibrium and the most common of them are Langmuir and Freundlich isotherm [48].

2.5.2.1 Langmuir Adsorption Isotherm

The most important model of monolayer adsorption is Langmuir isotherm. The assumptions of the Langmuir isotherm are: (1) adsorption energy is constant over all sites (2) adsorbed atoms or molecules are adsorbed at definite, localized sites (3) each site can accommodate only one molecule or atom (4) there is no interaction between adsorbates. This isotherm is given as

$$N_f = \frac{bN_sC}{1+bC} \tag{2.12}$$

$$\frac{C}{N_f} = \frac{1}{bN_s} + \frac{C}{N_s} \tag{2.13}$$

where C = the metal residual concentration in solution at equilibrium (mol L^{-1})

N_f = the amount of metal ions adsorbed per gram of sorbent (mol g^{-1})

N_s = the maximum sorption capacity of the sorbent (mol g^{-1})

b = Langmuir constant related to energy of adsorption (L mol^{-1})

Data are plotted either as shown in Figure 2.12 or in one of the two alternate linear forms shown in Figure 2.13. The model is described by Equation 2.13. The second linear form gives extra weight to higher values of *C* and is useful because quite often these are more reliable due to poor analytical sensitivity at low concentrations.

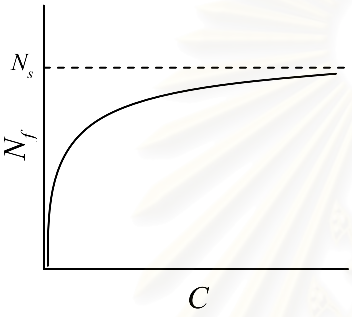


Figure 2.12

Form of Langmuir adsorption isotherm.

Approximation of the linear form is not necessary for the Langmuir isotherm, and the first plot of the data (assuming the data are of satisfactory quality) will demonstrate whether or not the model is applicable and also will allow determination of the coefficients. In many cases, a single model will not be satisfactory for a wide range of concentrations but will serve in narrow regions.

Figure 2.13 (a) Conventional linear form of Langmuir adsorption isotherm (b) Modified form of Langmuir adsorption isotherm emphasizing higher concentration data.

2.5.2.2 Freundlich Adsorption Isotherm

The Freundlich isotherm is used to describe multilayer adsorption isotherm for heterogeneous surface or surface active sites of varied affinities. The common form of the Freundlich is expressed by the following Equation 2.14.

$$N_f = K_f C^{1/n} \tag{2.14}$$

where K_f is the Freundlich adsorption coefficient. A plot of N_f versus C results in a curve of the form shown in Figure 2.14. From Equation 2.14 is generally used in the linear form, represented by:

$$log\, N_f = log\, K_f + \left(\frac{1}{n}\right) log\, C \tag{2.15}$$

As noted earlier, Equation 2.15 is empirical but has been found to fit experimental data quite often. Usually the Freundlich isotherm is plotted on log-log scale (Figure 2.15) to facilitate determination of the model's validity and the values of the coefficients K_f and n.

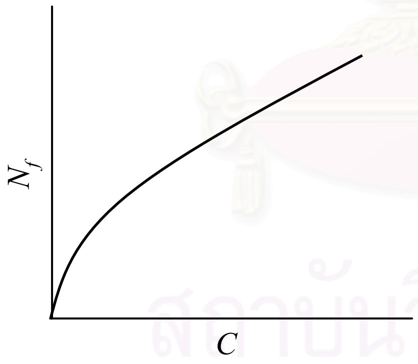


Figure 2.14
Form of Freundlich adsorption isotherm.

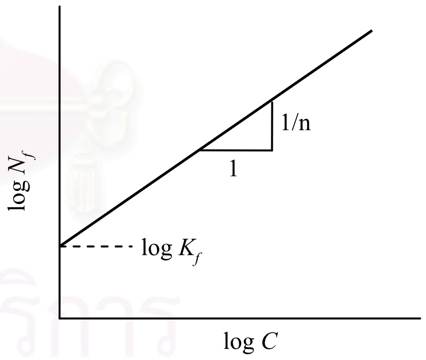


Figure 2.15 Linear form of Freundlich adsorption isotherm.

2.6 Characterization Techniques of Copolymers

The characterization of copolymer is necessary to confirm the achievement of the synthesis polymer. This research used several characterization techniques, i.e., FT-

IR, FT-Raman, SEM, TGA, and DSC before adsorption studies. The principles of these techniques are depicted below.

2.6.1 Fourier Transforms Infrared Spectroscopy (FT-IR)

The FT-IR spectroscopy is a very powerful technique to provide distinct identification and information about the structure of a wide variety of unknown samples as well as to confirm identities of known sample structures. Samples are applied to FT-IR can be either gaseous, liquid, solid, powders or polymers. Most FT-IR spectrometers work in the mid-infrared region (4000 cm^{-1} to 400 cm^{-1}) and offer high sensitivity and accuracy as well as improve speed data collection compared to dispersive instruments, because the whole spectra is measured at the same time and hence multiple scanning of the sample is possible [49].

The basic principle of IR-spectroscopy is the correlation between the wavenumbers at which a molecule or functional group absorbs IR-radiation and its structure. More functional groups are able to absorb infrared radiation regardless of the structure of the rest of the molecule. Hence the presence of different functional groups in a sample can be detected simultaneously resulting in a vibrational spectra that is unique and characteristic of the molecule. FT-IR is a beneficial instrument to detect functional groups in a sample but it can not be used to clarify the complete structure of an unknown molecule. Samples for FT-IR can be prepared in many ways. For liquid samples, the easiest is to place one drop of sample between two plates of sodium chloride (salt), which is transparent to infrared light. Solid samples can be milled with potassium bromide (KBr) to form a very fine powder. This powder is then compressed into a thin pellet which can be analyzed [50]. The water should be removed from sample if possible because it will disturb the analysis.

2.6.2 Fourier Transforms Raman Spectroscopy (FT-Raman)

The results of FT-Raman and FT-IR spectrum for a given species often resemble one another quite closely. However, the difference between the kind of groups that are infrared and Raman active to make the techniques complementary rather than competitive. An important advantage of Raman spectra over infrared lies in the fact that water does not cause interference because there is no spectrum of water.

Raman spectroscopy is about the inelastic scattering of photons and provides information about molecular vibrations that can be used for functionalized polymer identification. The Raman spectra are obtained by irradiating a sample with powerful source of visible monochromatic light (laser) which irradiates onto a sample and excites molecules in the sample, which then scatter the light. During irradiation, the spectrum of the scattered radiation is measured at some angle usually at 90 degree with a suitable visible-region spectrometer. At the very most, the intensities of Raman lines are 0.001% of the source. This inelastically scattered light is called Raman scatter. The energy difference between the monochromatic light and the Raman scattered light is equal to the energy involved in changing the molecule is vibrational state. Several different Raman shifted signals will often be observed; each being associated with different vibrational or rotational motions of molecules in the sample [51].

2.6.3 Scanning Electron Microscopy (SEM)

SEM uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties [52].

In SEM, a fine electron probe scans in a raster across the surface of a specimen that has to be conductive, stable in vacuum as well as not temperature-sensitive. Hence sample preparation is necessary depending on the nature of the sample. The magnification of the specimen depends on the area scanned in the raster pattern relative to the fixed size of the display.

The incident electrons are elastically (high energy) and inelastically (lower energy) scattered by the specimen. Especially the inelastic scattering is of great interest, because it leads to the excitement of the electrons in the specimens atoms that can leave the specimen as secondary electrons (SE) from a thin surface layer (1–10 nm). SE have an energy of less than 50 eV and give evidence of the topography of the surface of the sample. However the full image is formed by measuring the signal of SE but also X-ray quanta, auger electrons and backscattered electrons, which modulate the intensity of the detector in synchronism. SEM offers high resolution analysis and inspection. It gives information about the relief surfaces on a solid, its size, electrical properties and is widely used in flaw detection of microelectronic devises [53].

2.6.4 Thermal Gravimetric Analysis (TGA)

TGA is one of the basic methods in thermal analysis that measures a weight loss (or weight gain) of a material monitored against time or temperature. Normally, the heating is first carried out in an inert atmosphere (N_2 or Ar) to study the mass decrease of the sample due to the loss of volatile sample components and moisture. This technique is usually used to determine the thermal stability and composition of both organic and inorganic materials, especially in polymer [54].

TGA gives qualitative and quantitative information about the sample. The onset temperature is the temperature at which a mass loss occurs and can be used for qualitative information, because it can be compared to values for standards that were measured under identical conditions. Quantitative analysis is done by measuring the weight loss obtained when a known molecular weight component is vaporized from the sample [47]. In determination of polymer, TGA commonly provides the information about degradation temperatures, residual solvent levels, absorbed moisture content, and the amount of inorganic (noncombustible) filler in polymer or composite material compositions.

2.6.5 Differential Scanning Calorimetry (DSC)

DSC is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned. The main application of DSC is in studying phase transitions, such as melting, glass transitions, or exothermic decompositions. These transitions involve energy changes or heat capacity changes that can be detected by DSC with great sensitivity.

The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as phase transitions, more or less heat will need to flow to it than the reference to maintain both at the same temperature. Whether more or less heat must flow to the sample depends on whether the process is exothermic or endothermic. As a solid sample melts to a liquid, it will require more heat flowing to the sample to increase its temperature at the same rate as the reference.

This is due to the absorption of heat by the sample as it undergoes the endothermic phase transition from solid to liquid. Likewise, as the sample undergoes exothermic processes (such as crystallization) less heat is required to raise the sample temperature. By observing the difference in heat flow between the sample and reference, DSC are able to measure the amount of heat absorbed or released during such transitions. DSC may also be used to observe more subtle phase changes, such as glass transitions.

Any transition accompanied by a change in specific heat produces a discontinuity in the power signal, and exothermic or endothermic enthalpy changes give peaks whose areas are proportional to the total enthalpy change as shown in Figure 2.16 [55].

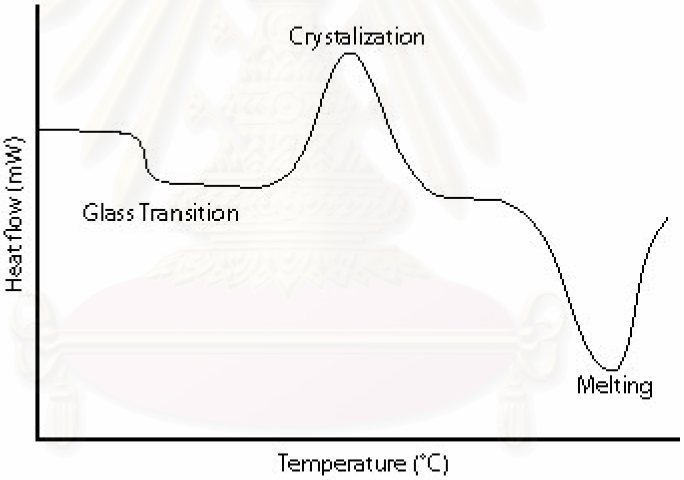


Figure 2.16 DSC curve demonstrating the appearance of several common feature [55].

2.7 Application of Copolymer in Metal Ion Adsorption

2.7.1 Gold(III) Ion Adsorption

Poly(NIPA) has been used for adsorbing gold(III) ion for example: Wang *et al.* (2007) [56] synthesized the block copolymer poly(*N*-isopropylacrylamide)-*b*-poly(4-vinyl pyridine); poly(NIPA-*b*-P4VP) by sequential atom transfer radical polymerization (ATRP). The thermoresponsive micelle-supported gold nanoparticles and their responsive catalysis were studied. In addition, Tokuyama *et al.* (2007) [57] investigated the adsorption of gold(III) ion by poly(NIPA) gel. It was found that gel has a high degree of affinity for gold(III) ion. The amount of gold(III) ion adsorbed is low at 10ºC and high at 50ºC, and the amount adsorbed increases in a stepwise manner with temperature around 32ºC, the lower critical solution temperature (LCST) of poly(NIPA). Gold(III) ion tends to be well adsorbed on shrunken gel, but are adsorbed poorly on swollen gel. The adsorption capacity of 0.637 mmol g^{-1} gel at 50ºC was obtained from a Langmuir isotherm.

2.7.2 Other Metallic Ions

There are many reports on the poly(NIPA) for metal ion adsorption.

Saitoh *et al.* (2003) [58] synthesized thermoresponsive chelating polymers, poly(NIPA)-*co*-vinylimidazole (-Im), poly(NIPA)-*co*-carboxylic acid (-COOH) and poly(NIPA)-*co*-iminodiacetic acid (-IDA). Poly(NIPA)-Im was useful for collecting Cu(II) Ni(II) Co(II) and Pb(II) but was ineffective for Cd(II) recovery. In contrast, poly(NIPA)-COOH collected Cd(II), while insufficiently recovered Co(II) and Ni(II). Poly(NIPA)-IDA was the best choice for collecting all metal ions in neutral pH.

Tokuyama *et al.* (2005) [59] studied the adsorption of Cu(II) with the copolymer of NIPA and 4-(vinylbenzyl)ethylenediamine (VBEDA) as a chelating agent (Figure2.17).

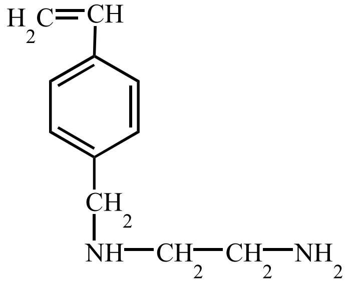


Figure 2.17 The structure of 4-(vinylbenzyl)ethylenediamine (VBEDA).

Equilibria and kinetics for the adsorption/desorption for a temperature swing of 34/10°C were investigated. Adsorption equilibria, expressed as the Langmuir isotherms, indicated that one Cu(II) ion was strongly coordinated to two VBEDA groups at 34°C and weakly coordinated to one VBEDA group at 10°C (Figure 2.18).

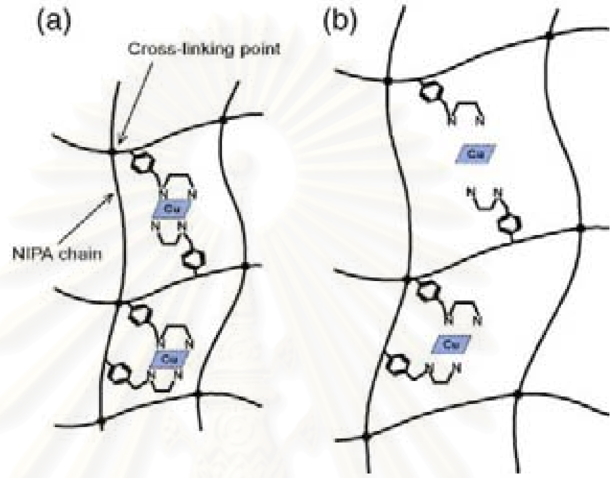
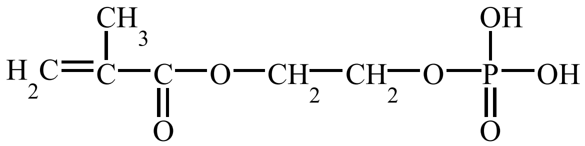


Figure 2.18 Schematic diagram of the reconstruction/destruction of adsorption sites in an imprinted NIPA–VBEDA gel (a) Reconstruction in a shrinking gel at the appropriate temperature and (b) Destruction in a swelling gel at a lower temperature [59].

Moreover, Tokuyama *et al.* (2006) [60] prepared the gel-type and polymer-type adsorbents, composed of NIPA and 2-(methacryloyloxy)ethyl phosphate (MEP) as an interactive component as shown in Figure 2.19.



$$H_2C{=}C(CH_3){-}C({=}O){-}O{-}CH_2{-}CH_2{-}O{-}P({=}O)(OH){-}OH$$

Figure 2.19 The structure of 2-(methacryloyloxy)ethyl phosphate (MEP).

The NIPA-*co*-MEP gel swelled and shrunk reversibly in water in accordance with the temperature swing between 30 and 40°C. The amount of Cu(II) adsorbed and desorbed in temperature 40 and 30°C, respectively. Taking into account the phase transitions and the dissociation of phosphate group, in the shrinking gel at 40°C, two MEP groups became positioned in the vicinity, interacting with one Cu ion, while in the swelling gel at 30°C, Cu(II) was desorbed from an isolated MEP group (Figure 2.20).

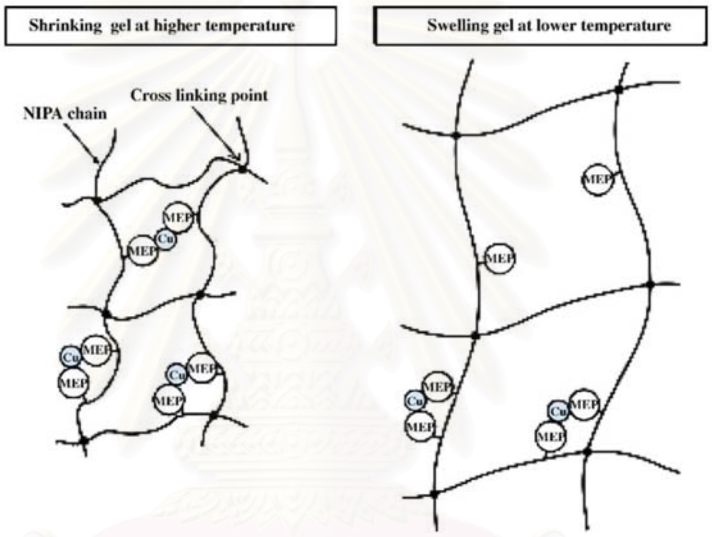


Figure 2.20 Schematic diagram of the temperature swing adsorption of Cu(II) to NIPA-*co*-MEP gels [60].

Yin *et al.* (2006) [61] reported the thermo-sensitive and fluorescent complex of poly(NIPA) and Tb(III). The results from the experiments indicated that there is a strong interaction between poly(NIPA) and Tb(III), leading to a decrease in the electron density of nitrogen and oxygen atoms and an increase in the electron density of Tb(III) in the poly(NIPA) containing Tb(III). The fluorescence intensity is related the weight ratio of Tb(III) and poly(NIPA). The complex may be useful in the fluorescence systems and the biomedical field.

2.7.3 2-(Methylthio)ethyl methacrylate (MTEMA) Comonomer

The structure and physical/chemical properties of 2-(methylthio)ethyl methacrylate as shown in Figure 2.21 and Table 2.5, respectively.

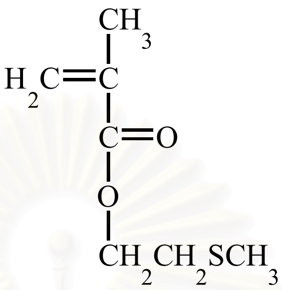


Figure 2.21 The structure of 2-(methylthio)ethyl methacrylate comonomer.

Table 2.5 Physical and chemical properties of 2-(methylthio)ethyl methacrylate comonomer [62]

Properties	*Value*
Appearance	Liquid
Formula	$C_7H_{12}O_2S$
Molecular weight (g mol^{-1})	160.24
Boiling point	38°C
Flash point	88°C
Density	1.04 g/mL at 25°C
Stability	Strong oxidizing agents

The MTEMA comonomer is available and representative of vinyl monomer which has hydrogen bonding for hydrophilic-hydrophobic interactions. In addition, MTEMA can easily coordinate with metal ion because of sulfur donor atom in the molecule. Thus, the modification polymer with MTEMA comonomer was interesting.

In recent years, there were papers reported about application of MTEMA such as Baker *et al.* (2004) [63] prepared random copolymers containing both ferrocene groups and thioether groups synthesized by free radical copolymerization of vinylferrocene and MTEMA, and the random nature of the copolymerization was confirmed by spectroscopic studies. Copolymers with ferrocene-to-thioether ratios of 8 : 1 and 1.2 : 1 were used to modify the surfaces of gold electrodes, and the behaviors of the resulting surface-modified electrodes were investigated by cyclic voltammetry.

Matsuura *et al.* (2004) [64] prepared poly(methylphenylsilane)/2-(methylthio) ethyl methacrylate block copolymer, poly(MPS-*co*-MTEMA), has been synthesized by a photopolymerization of MTEMA with poly(MPS) as a macro-photo-initiator. It was found that poly(MPS-*co*-MTEMA) was held by a chemisorption on a gold substrate through the gold-sulfur interaction. Furthermore, gold colloids were prepared by aging poly(MPS-*co*-MTEMA)/Au at temperatures higher than 150°C, which was confirmed by the plasmon resonance absorption at 550-600 nm in the UV-Vis absorption spectra.

Corain *et al.* (2005) [65] synthesized the functional resin poly[(MTEMA)-(2-(methylthio)ethylmethacrylate)-(*N*,*N*-dimethylacrylamide)] behaving as a macromolecular ligand towards Pd(II) and Au(III) in water and acetonitrile, respectively. M^{n}/resin complexes were easily reduced with $NaBH_4$ in water to M^0/resin composites and exhibited useful catalytic properties in various chemical transformations, under mild conditions in water.

In this research, we are interested in combining properties of poly(NIPA) and MTEMA via free radical polymerization, to improve the adsorption efficiency of gold(III) ion in aqueous solution.

CHAPTER III

EXPERIMENTAL SECTIONS

3.1 Apparatus

3.1.1 Flame Atomic Absorption Spectrometer

A flame atomic absorption spectrometer (FAAS) model AAnalyst 100 (Perkin-Elmer) was used for the determination of metal concentration. The instrumental parameters are listed in Table 3.1.

Table 3.1 FAAS conditions for the determination of gold concentration in solution

Operating conditions	*Au*
Wavelength (nm)	242.8
Slit width (nm)	0.70
Lamp type	HCL (Hallow Cathode Lamp)
Lamp current (mA)	15
C_2H_2 flow-rate (mL min^{-1})	3
Air flow-rate (mL min^{-1})	10

3.1.2 UV-Vis Spectrophotometer

A UV-Vis spectrophotometer model HP 8453 (Hewllet Packard) was used in transmittance measurement mode for determination of phase transition of homogeneous poly(NIPA) and poly(NIPA-*co*-MTEMA).

3.1.3 Fourier Transform Infrared Spectrometer

A Fourier transform infrared spectrometer (FT-IR) model Nicolet FT-IR Impact 410 was used for the characterization of all polymers. Infrared spectra were recorded from 400 to 4000 cm^{-1} in transmittance mode by KBr pellet technique.

3.1.4 Fourier Transform Raman Spectrometer

A Fourier transform Raman spectrometer (FT-Raman) model Spectrum GX (Perkin-Elmer) was used for the characterization of all polymers.

3.1.5 Scanning Electron Microscope

A scanning electron microscope (SEM) model JSM 5410LV (JEOL) was used for surface analysis of all polymers. Samples for SEM were carefully cut into small pieces and exposed to gold vapor deposition to prepare photogenic sample, and put in an electron probe analyzer to give the SEM photographs of polymer surface. The accelerated voltage was 15 kV.

3.1.6 Thermogravimetric Analyzer

Thermogravimetric analysis was performed to measure the weight loss of all polymers as a function of temperature by using Simultaneous Thermal Analyzer

(STA) model 409 (Netzsch) from 24-800 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

3.1.7 Differential Scanning Calorimeter

A differential scanning calorimeter (DSC) model 200 (Netzsch) based on a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of polymer samples and the reference as a function of temperature was used to determine the glass transition temperature of the synthesized polymers.

3.1.8 Nuclear Magnetic Resonance Spectrometer

A nuclear magnetic resonance spectrometer (NMR) model Varian Mercury Plus 400 was used for the study of the interaction between gold(III) ion and the synthesized polymers. NMR spectra were recorded in $CDCl_3$.

3.1.9 pH Meter

The pH meters model pH 211 (Hanna instruments) and Orion 2-Star pH Benchtop Meter (Thermo Fisher Scientific) were used for all pH measurements.

3.1.10 Thermostatic Water Bath and Ultrasonic Bath

A thermostatic water bath model RCS 6-D (Lauda Brinkmann) was used to control temperature of water for the Lower Critical Solution Temperature (LCST) determination of homogeneous polymers by UV-Vis spectrophotometer.

An ultrasonic bath was used to sonicate the solutions before bringing to synthesize the polymers.

3.2 Chemicals and Preparation of Reagents

3.2.1 Chemicals

All chemicals were analytical reagent grade listed in Table 3.2.

Table 3.2 Chemical list

Chemicals	*Suppliers*
Acetone	Fluka
Ammonium peroxodisulfate (APS)	Fluka
Chloroform D1	Merck
N,*N*-Dimethylformamide	Fluka
1,4-Dioxane	Carlo Erba Reagenti
Ethanol	Merck
Gold(III) standard solution (1000 mg L^{-1})	Merck
Hydrochloric acid 37%	Merck
N-Isopropylacrylamide 97% (NIPA)	Sigma-Aldich
Methanol	Merck
N,N′-Methylenebisacrylamide 98% (MBAA)	Sigma-Aldich
2-(Methylthio)ethyl methacrylate 96% (MTEMA)	Sigma-Aldich
Nitrogen gas 99.99%	Praxair
Potassium bromide	Merck
Potassium hydroxide	Merck
N,N,N′,N′-Tetramethylethylenediamine 99% (TEMED)	Sigma-Aldich
Thiourea	Sigma-Aldich

3.2.2 Preparation of Reagents

All solutions were prepared by using deionized (DI) water.

a) Gold(III) standard solutions

Working standard solutions of gold(III) were prepared by dilution of 1000 mg L^{-1} stock standard solution to the required concentrations.

b) Hydrochloric acid solutions

Hydrochloric acid (1% v/v, 5% v/v and 1 M) solutions for pH adjustment were prepared by subsequent dilutions from the concentrated solution.

c) Potassium hydroxide solutions

Potassium hydroxide solutions (1% w/v, 5% w/v and 1 M) for pH adjustment were prepared by dissolving the appropriate amount of KOH in DI water.

d) Thiourea

Thiourea (0.1 M and 1 M) were prepared daily by dissolving the appropriate amount of thioura in DI water.

3.3 Synthesis of Copolymers

The preparation conditions were based on the ones shown in Table 3.3. These conditions were adapted from the literatures [66-67].

Table 3.3 Synthesis conditions of copolymers

Chemical substance	*Function*	*Final concentraction (mM)*	
		Homogeneous	*Heterogeneous*
N-isopropylacrylamide (NIPA)	Monomer	1000	1500
2-(methylthio)ethyl methacrylate (MTEMA)	Comonomer	10-30	15-45
N,N'-methylenebisacrylamide (MBAA)	Cross-linker	50	60
N,N,N',N'-tetramethylethylenediamine (TEMED)	Accelerator	10	10
Ammonium peroxodisulfate (APS)	Initiator	1	1

3.3.1 Homogeneous Polymers

The appropriate amount of *N*-isopropylacrylamide (NIPA), *N,N'*-methylenebisacrylamide (MBAA), *N,N,N',N'*-tetramethylethylenediamine (TEMED) following the conditions in Table 3.3 were dissolved in DI water in a test tube (0.7 cm i.d.). Then 2-(methylthio)ethyl methacrylate (MTEMA) in ethanol (500 µL) adjusted the volume to 9 mL was added. The mixture solution was sonicated at 10°C for 15 minutes and placed in a cold water bath at 10°C under nitrogen purging for 1 hour. After that, the polymerization was performed by adding ammonium peroxodisulfate (APS) in the mixture solution.

The resulting cylinder-shaped copolymer was obtained and taken out form the test tube and afterwards cut into small pieces about 1.0 cm length and washed with DI water in order to remove unreacted monomers. The copolymer was transparent hydrogel as shown in Figure 3.1. Poly(*N*-isopropylacrylamide); poly(NIPA), was also prepared by the same manner without MTEMA comonomer. The synthesis pathway is depicted in Figure 3.3.

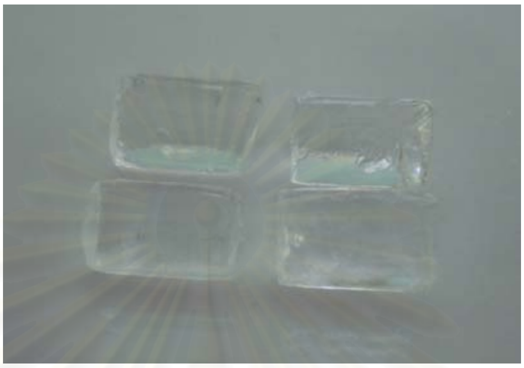


Figure 3.1 Homogeneous polymer.

3.3.2 Heterogeneous Polymers

This reaction was proceeded by the same methodology as 3.3.1 but 2-(methylthio)ethyl methacrylate (MTEMA) in ethanol (2 mL) was used and the mixture was placed on a water bath at 50^{o}C under nitrogen atmosphere for 30 minutes. The copolymer obtained was unclear white hydrogel as shown in Figure 3.2. Poly(NIPA) was also prepared by the same manner without MTEMA comonomer.

Figure 3.2 Heterogeneous polymer.

The synthesis pathway of copolymers was displayed in Figure 3.3.

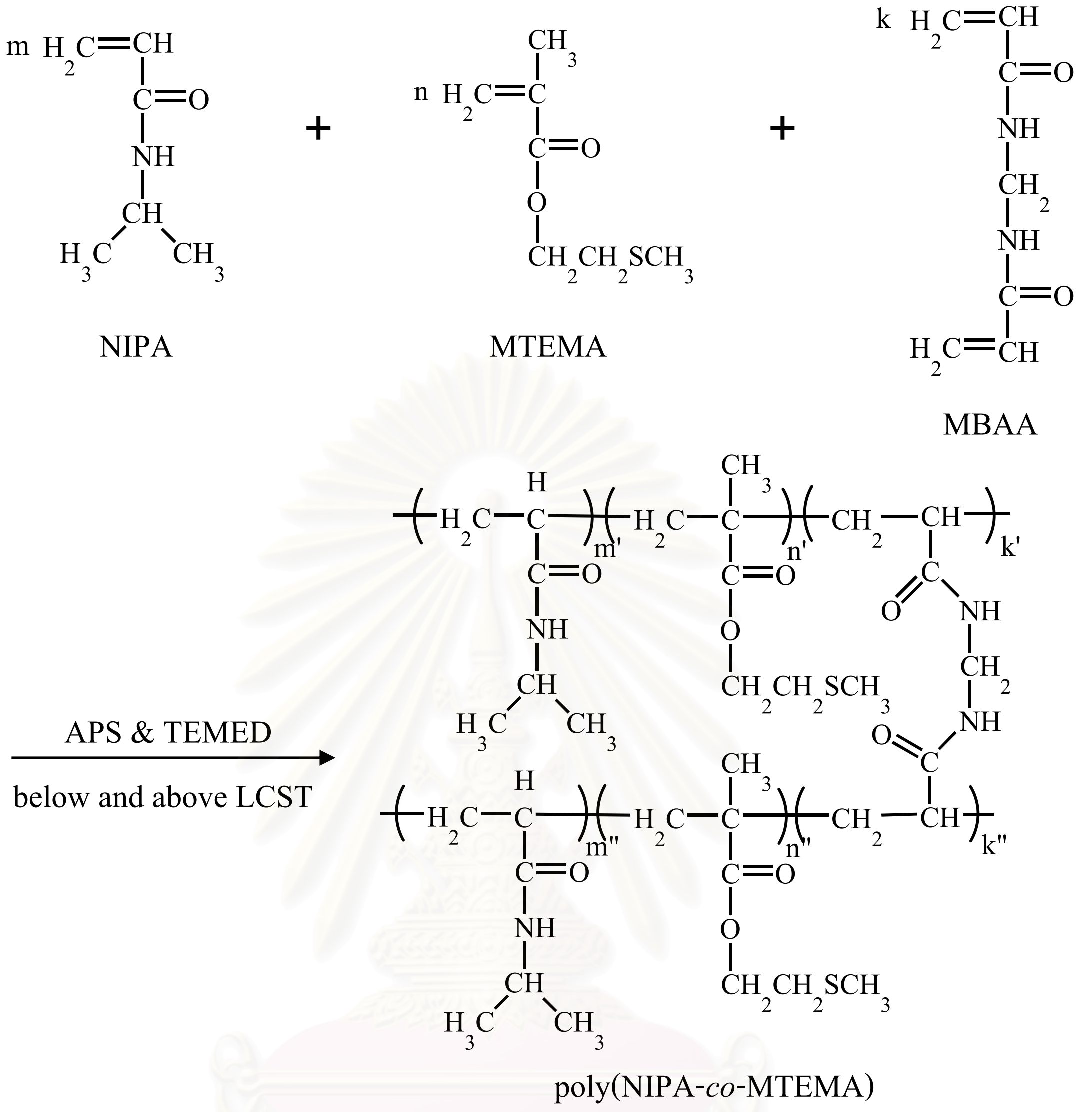


Figure 3.3 The synthesis pathway of copolymers.

3.4 Characterization

The synthesized copolymers were characterized by Fourier Transforms Infrared Spectrometer (FT-IR), Raman Spectrometer (FT-Raman), Scanning Electron Microscope (SEM), Thermal Gravimetric Analyzer (TGA), and Differential Scanning Calorimeter (DSC).

3.5 Swelling Behavior

The synthesized polymers in cylindrical shape of the adsorbents with 0.7 cm width and 1.0 cm length were immersed in water until saturation and brought to weigh. Later on, they were dried in an oven at 110^{o}C until the weight of dry polymer was constant.

3.6 Phase Transitions of Homogeneous Polymer

Homogeneous polymers were synthesized in a plastic cuvette for phase transition behavior study. The preparation conditions were similar to Table 3.3. These polymers were studied by determining the optical transmittance of the system conducted by using UV-Vis spectrophotometer in transmittance mode at the wavelength of 600 nm over the temperature range of 24–40°C. The polymers were placed with water from a thermostatic water bath for temperature control at least 10 minutes in order to reach equilibrium prior to optically measurement. From the point of inflection of the turbidity curve, the lower critical solution temperature (LCST) of homogeneous polymers can be determined.

3.7 Gold(III) Ion Adsorption Studies

Various parameters influencing the adsorption of gold(III) were studied as follows. Gold(III) solution was in chloroaurate form; $[AuCl_4]^-$. All adsorption experiments were performed in triplicate.

3.7.1 Effect of pH

The effect of pH of gold solution was investigated in the range of pH 1.0-7.0. The basic pH was not studied because gold would be partially converted to insoluble $Au(OH)_3$. pH adjustments were made with HCl (1 and 5 %v/v) and KOH (1 and 5

%w/v). A rod of gel adsorbent (0.7 cm diameter and 1.0 cm length) and an aqueous solution of $HAuCl_4$ 3 mL were mixed in a test tube (size 14 mL, 1.5 cm i.d.), and the initial concentration of gold(III) in the solution was 10 mg L^{-1}. The test tube was placed in a water bath at 50^oC for 1 hour. Thereafter, the initial and residual concentrations of gold(III) in the solution were determined by FAAS.

3.7.2 Effect of Adsorption Time

The effect of adsorption time was investigated by varying the adsorption time in the range of 0.5-8 hours for homogeneous polymers and 0.5-5 hours for heterogeneous polymers. Adsorbent samples with the size of 0.7 cm diameter and 1.0 cm length were immersed in 3 mL of 10 mg L^{-1}gold(III) ion solution in a test tube. The remaining gold(III) concentration in the solutions was determined by FAAS.

3.7.3 Effect of Adsorbent Size and Surface Area

Different size of adsorbents using a cylindrical shape of the polymers with 0.7 cm diameter and different lengths varying from 0.25-1.0 cm were put into gold(III) ion solution containing 10 mg L^{-1} (3 mL). The surface of the adsorbent was increased by dividing the 0.25 cm length gel into 4 and 8 pieces. The adsorbent were immersed in the gold(III) solution for 3 hours. The remaining gold(III) concentration in the solutions was determined by FAAS.

3.7.4 Effect of Temperature

The effect of temperature was investigated by varying the temperature in the range of 10-50 °C. The initial concentration of gold(III) ion in the solution was 20 mg L^{-1} at optimum pH and adsorption time of each polymer. The size of adsorbents was 0.7 cm diameter and 1.0 cm length.

3.7.5 Adsorption Isotherm

The adsorption isotherm was studied by using various concentrations of gold(III) ion solution in the range of 10-500 mg L^{-1}. The temperature of the solutions was thermostatically controlled at 50±1°C for 3 hours. Afterward, the residual concentration of gold(III) in the solutions was determined by FAAS. The results were treated with Langmuir and Freundlich adsorption isotherm to describe the adsorption mechanism at the solid-liquid interface and to estimate the maximum sorption capacity of the polymers. Homogeneous polymers was investigated by using the size of 0.7 cm diameter and 1.0 cm length while heterogeneous polymers was reduced by half (0.5 cm length gel was used).

3.8 Gold(III) Ion Desorption Studies

Various parameters such as types of desorbing solution, desorption time, and temperature were studied using the following experimental procedures. All desorption experiments were performed in triplicate and using a cylindrical shape of the adsorbents with 0.7 cm diameter and 1.0 cm length.

3.8.1 Types of Desorbing Solution

Polymer containing adsorbed gold(III) ion under optimum pH and adsorption time was contacted with 3 mL of various types and concentrations of stripping solutions i.e. DI, HCl, Thiourea for 2 hours. Gold(III) ion concentration in desorbing solutions was determined by FAAS.

3.8.2 Effect of Desorption Time

The optimum desorption time was studied under suitable desorbing solution at different time in the range of 0.5-4 hours. Gold(III) ion concentration in desorbing solutions was determined by FAAS.

3.8.3 Effect of Temperature

The effect of temperature was investigated by varying the temperature in the range of 10-50°C for 2 hours. Gold(III) ion concentration in desorbing solutions was determined by FAAS.

CHAPTER IV

RESULTS AND DISCUSSION

This chapter consists of seven parts including (1) synthesis and (2) characterization of the polymers, (3) study of swelling behavior of the synthesized polymers, (4) study of phase transitions of the homogeneous polymers, (5) investigation of the interaction of the polymers towards gold(III) ion, (6) gold(III) ion adsorption and (7) desorption studies.

4.1 Synthesis of Copolymers

In this research, the hydrogel copolymers consisting of *N*-isopropylacrylamide (NIPA) and 2-(methylthio)ethyl methacrylate (MTEMA); poly(NIPA-*co*-MTEMA), with *N,N'*-methylenebisacrylamide as a crosslinking agent were synthesized by free radical copolymerization, initiated by adding a redox initiator [68]. The synthesis procedure was adapted from the literature [69].

In 2007, Tokuyama and his collaborators used different organic solvents in the polymerization of poly(*N*-isopropylacrylamide) hydrogels or poly(NIPA) [69]. They found that swelling and elastic properties of hydrogels were similar to the hydrogels synthesized in water. In addition, Shibayama and collaborators reported that the hydrogels synthesized in water showed a good reactivity and hydrophilic/hydrophobic transition [70]. From this information, water seems to be a good solvent for the synthesis of hydrogels. Therefore, the synthesis of the hydrogel copolymers in aqueous system was investigated.

Since MTEMA comonomer used is slightly soluble in water, thus organic solvents should be added in order to dissolve the comonomer. Some commonly used organic solvents such as ethanol, methanol, acetone, 1,4-dioxane and *N*,*N*-dimethylformamide (DMF) were firstly investigated. When an appropriate solvent was selected, synthesis conditions were optimized by varying the ratio of the comonomers and the amount of organic solvent added.

As mentioned in Chapter III, two kinds of copolymer, called homogeneous and heterogeneous polymers were synthesized. The homogeneous polymer was prepared at 10°C, while the heterogeneous polymer was prepared at 50°C.

4.1.1 Effect of Types of Solvent

In order to study the effect of solvent for facilitating the dissolution of MTEMA comonomer, the adsorption efficiency towards gold(III) ion was considered. The copolymer was synthesized by the same condition for both homogeneous and heterogeneous copolymers, previously described in section 3.3, in different solvents i.e. ethanol, 1,4-dioxane, acetone and *N*,*N*-dimethylformamide (DMF). A piece of obtained copolymer was immersed in 3 mL of 10 mg L^{-1} $HAuCl_4$ solution (pH 2-3) for 1 hour. The experiment was performed in triplicate. The remaining gold(III) ion in the solution was then determined by FAAS. The adsorption efficiency was reported in term of adsorption percentage or % adsorption. The result is shown in Figure 4.1.

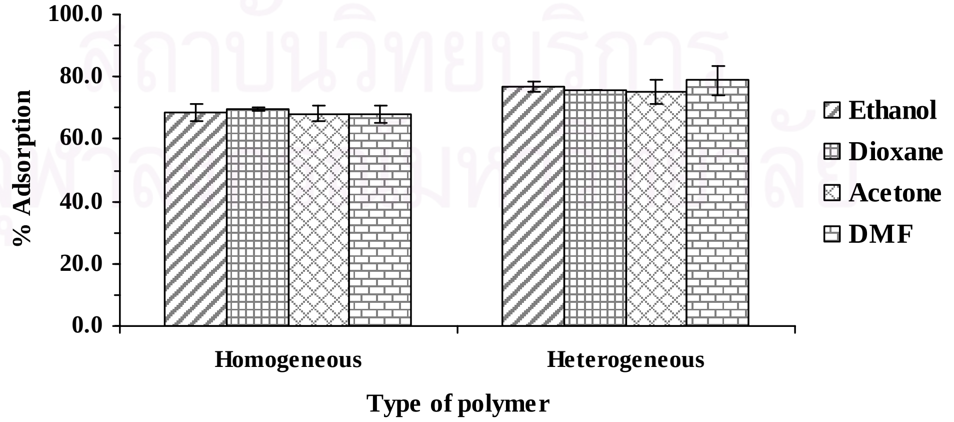


Figure 4.1 Adsorption percentage of gold(III) ion at 50°C on copolymers prepared in different solvents.

It was found that all solvents used in the copolymer synthesis showed comparable % adsorption of gold(III) ion. Consequently, ethanol was selected to dissolve MTEMA due to its miscibility with water and low toxicity.

4.1.2 Effect of Mole Fraction of Comonomers and Ethanol Used in the Synthesis of Copolymers

Homogeneous polymer

The MTEMA solutions were firstly prepared by dissolving an appropriate amount of the comonomer in 50, 75, 100, and 150 μL of ethanol to obtain the final concentrations of 10, 15, 20, and 30 mM, respectively. The polymerization was performed at 10°C. Five different homogeneous poly(NIPA-*co*-MTEMA) transparent rods (0.7 cm i.d., 9 cm length) were obtained and afterward cut into 1 cm length pieces. After that, a piece of copolymers were immersed in 3 mL of 10 mg L^{-1} $HAuCl_4$ solution (pH 2-3) for 1 hour at 10°C, ambient temperature (25°C), and 50 °C. The experiment was performed in triplicate. The remaining gold(III) ion in the solution was then determined by FAAS. The adsorption efficiency of the copolymers was reported in term of adsorption percentage or % adsorption. The adsorption efficiency of poly(NIPA) was investigated with the same manner. The results are displayed in Figure 4.2 (the notations of 10, 15, 20, and 30 correspond to the final concentration of MTEMA).

The results showed that the adsorption efficiencies of poly(NIPA) towards gold(III) ion increased with increasing of temperature, agreed with the results published by Tokuyama *et al.* [57,71]. Poly(NIPA-*co*-MTEMA) showed similar adsorption behavior. Further adsorption experiments were then performed at 50 °C due to the highest % adsorption.

Considering the effect of the amount of MTEMA on % adsorption at 50°C in Figure 4.2, when the amount of MTEMA added in the solution increased, the % adsorption slightly increased. There was no significant difference. Thus the minimum final concentration of MTEMA (10 mM) was chosen for next experiments.

Comparing overall % adsorption of poly(NIPA) and poly(NIPA-*co*-MTEMA), it was obviously found that the % adsorption of poly(NIPA-*co*-MTEMA) was higher than that of poly(NIPA). This observation revealed that the comonomer MTEMA could be incorporated in the final product. The copolymerization was successful.

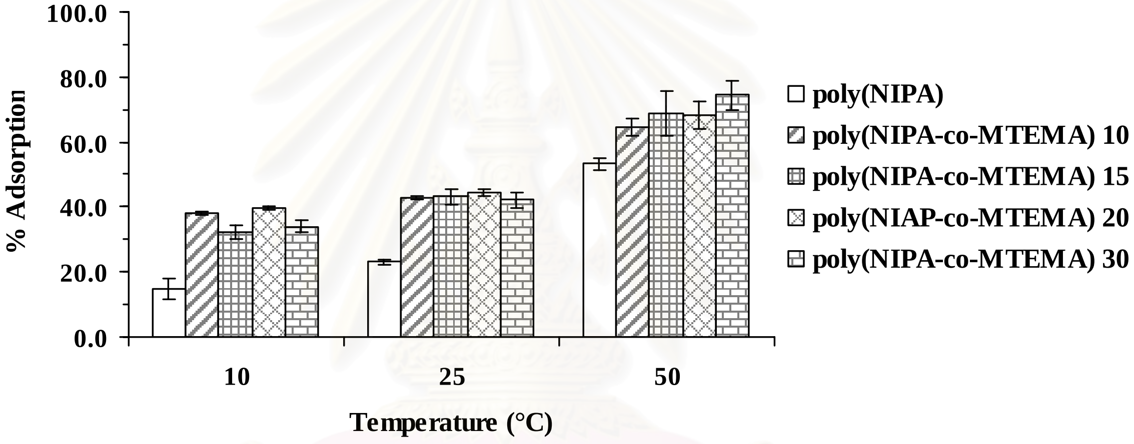


Figure 4.2 Adsorption percentage of gold(III) ion on homogeneous polymers at different temperatures and concentrations of MTEMA comonomer.

From the results, the wide error bars indicated that the % adsorptions of gold(III) ion swung, probably due to uncontrolled ionic strength of the solution. So, the preparation of the gold(III) ion solution containing 0.001 M NaCl for controlling the ionic strength of the solution was studied but the precision of the adsorption was not better. This swung % adsorption may attribute to experimental random errors caused by an unequal surface area of the gel or a fluctuation of AAS signal. Thus in further experiments, the ionic strength of gold(III) solution would not be controlled.

The effect of the amount of ethanol added on gold adsorption was also investigated. The results are shown in Figure 4.3. The poly(NIPA-*co*-MTEMA) gel (filled bars) has higher adsorbability towards gold(III) than poly(NIPA) gel (blank bar). By fixing the final concentration of MTEMA at 10 mM and the total volume of solution for polymerization at 10.0 mL, the adsorbability of the copolymer gels increased when increasing the amount of ethanol added. These results indicate that ethanol can facilitate the dissolution of MTEMA and consequently MTEMA can more incorporate in copolymer network. The adsorbability reached the maximum around 74 % when 10.0 % (v/v) ethanol was used, however the poly(NIPA-*co*-MTEMA) gel turned undesirably opaque. Therefore, the optimum condition for the synthesis of homogeneous poly(NIPA-*co*-MTEMA) could be achieved with 10 mM MTEMA in 5.0 %(v/v) ethanol.

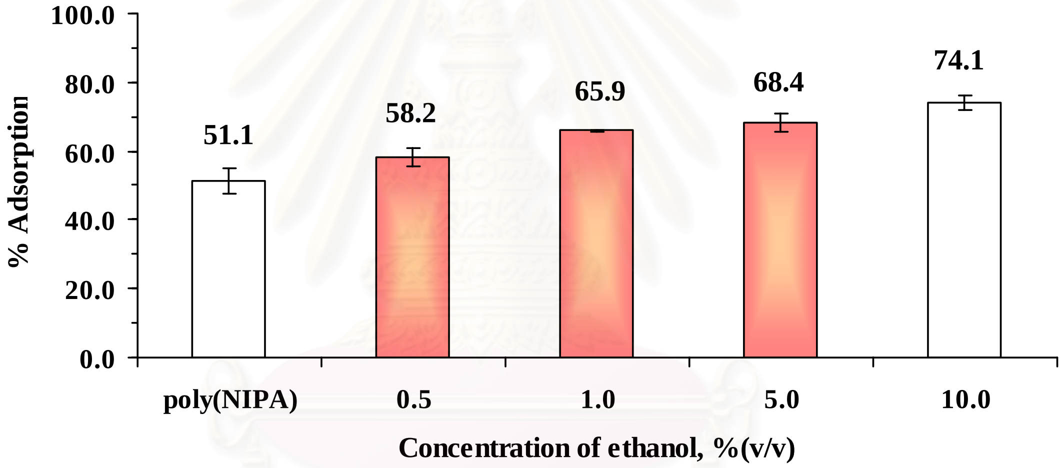


Figure 4.3 Adsorption percentage of gold(III) ion at 50°C on homogeneous polymers prepared in various concentrations of ethanol.

Heterogeneous polymer

Heterogeneous poly(NIPA-*co*-MTEMA) was prepared with the same manner as homogeneous copolymer except that the final concentrations of MTEMA were 15, 30, 45 mM, prepared by dissolving an appropriate amount of monomer in 75, 150, 225 μL of ethanol, respectively. The polymerization was performed at 50°C. Heterogeneous poly(NIPA-*co*-MTEMA) opaque rods were obtained. Their adsorption ability towards gold(III) ion was tested with the same procedure used for homogeneous copolymers at 50°C. The results of gold(III) ion adsorption are shown in Figure 4.4.

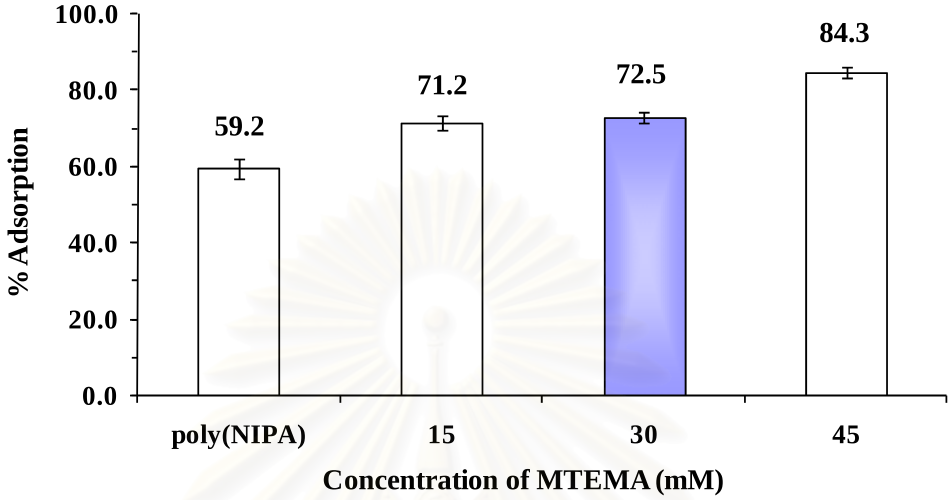


Figure 4.4 Adsorption percentage of gold(III) ion at 50°C on heterogeneous poly(NIPA) and poly(NIPA-*co*-MTEMA) prepared in various concentrations of MTEMA comonomer.

The adsorbability of the copolymer gels slightly increased when increasing the amount of MTEMA comonomer. During the polymerization using 45 mM MTEMA, two immiscible phases were visually observed as follows; yellow upper organic phase and clear lower aqueous phase. The polymerized gel was obtained only from the lower phase. This observation indicated that using 45 mM MTEMA was too high, resulting in non homogeneous solution, which was inappropriate for the polymerization. Therefore, 30 mM MTEMA was chosen for next experiments.

The effect of the amount of ethanol added on gold adsorption was also investigated. The total volume of solution was fixed at 10.0 mL and the concentrations of ethanol were varied from 1.5 to 50 %(v/v). The gold(III) adsorption percentages of the gels, displayed in Figure 4.5, increased when increasing the concentration of ethanol. The adsorbability reached the maximum around 85 % when the concentration of ethanol was above 20 %(v/v). Similarly to homogeneous copolymers, the poly(NIPA-*co*-MTEMA) gels (filled bars) had higher adsorbability towards gold(III) than poly(NIPA) gel (blank bar). This observation revealed that the comonomer MTEMA could be incorporated in the heterogeneous final product.

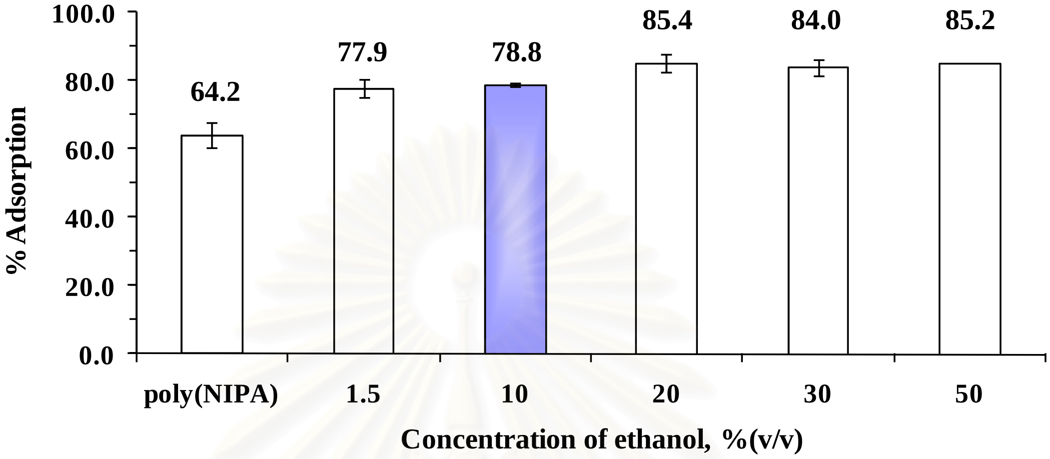


Figure 4.5 Adsorption percentage of gold(III) ion at 50°C on heterogeneous polymers prepared in various concentrations of ethanol.

In conclusion, the optimum condition of the synthesis of heterogeneous poly(NIPA-*co*-MTEMA) can be achieved with the concentration of MTEMA at 30 mM in 20 %(v/v) ethanol.

4.2 Characterization of Copolymers

The synthesized poly(NIPA-co-MTEMA) copolymers were characterized by Fourier Transforms Infrared Spectroscopy (FT-IR), Fourier Transforms Raman Spectroscopy (FT-Raman), Scanning Electron Microscopy (SEM), Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). The results were illustrated and discussed in the following.

4.2.1 Fourier Transforms Infrared Spectroscopy

The FT-IR spectra of the synthetic polymers were recorded using potassium bromide technique. The FT-IR spectra of poly(NIPA) (Homo), poly(NIPA) (Hetero), poly(NIPA-*co*-MTEMA) (Homo) and poly(NIPA-*co*-MTEMA) (Hetero) are displayed in Figure 4.6 (a-d). The signs (Homo) and (Hetero) correspond to homogeneous and heterogeneous, respectively. All FT-IR spectra exhibit the adsorption bands at 2970 and 2870 cm^{-1} which are assigned to the asymmetric and symmetric ν(C–H) of the methyl groups of *N*-isopropyl groups, respectively. The band at 2923 cm^{-1} is ascribed to the asymmetric ν(C–H) of the methylene groups of the polymer backbone. Since the monosubstituted amide chains are included in the poly(NIPA) structure, the signals of CO-NHR stretching at 1100-1230 and 1648 cm^{-1} are ascribed to amide I (mainly the carbonyl stretching ν(C=O)) and the band at 1540 cm^{-1} is ascribed to amide II (mainly the N–H bending δ(N-H)). In addition, the appearance of a broad band in the range of 3200-3500 cm^{-1} may be assigned to amide stretching ν(N-H). Further, two typical peaks were noticed at 1360-1380 cm^{-1}, corresponding to the ν(C–H) vibration of $–CH(CH_3)_2$ in the poly(NIPA) repeat units. No significant difference absorption peak was observed between homogeneous and heterogeneous gels.

The FT-IR spectrum of MTEMA comonomer is shown in Figure 4.6 (e). The structure of MTEMA resembles NIPA but the position of COOR is different. The characteristic peaks of MTEMA are concerned to ν(C–H) of $-CH_2-$ and -C-O-C-, which appeared in the range of 2800-3000 cm^{-1} and 1150-1280 cm^{-1}, respectively. The spectra of poly(NIPA) and poly(NIPA-*co*-MTEMA) show only small difference which is a peak of -C-O-C- in poly(NIPA-*co*-MTEMA) at 1170 cm^{-1} appeared at little higher frequency than poly(NIPA).

In the conclusion, FT-IR characterization is not entirely clear for confirming the copolymerization of MTEMA comonomer onto the NIPA polymer because the MTEMA spectrum peak appeared to overlay on NIPA polymer. Moreover, few amount of MTEMA added in copolymers does not make their spectra different form poly(NIPA). Next, the polymers were characterized with FT-Raman spectroscopy.

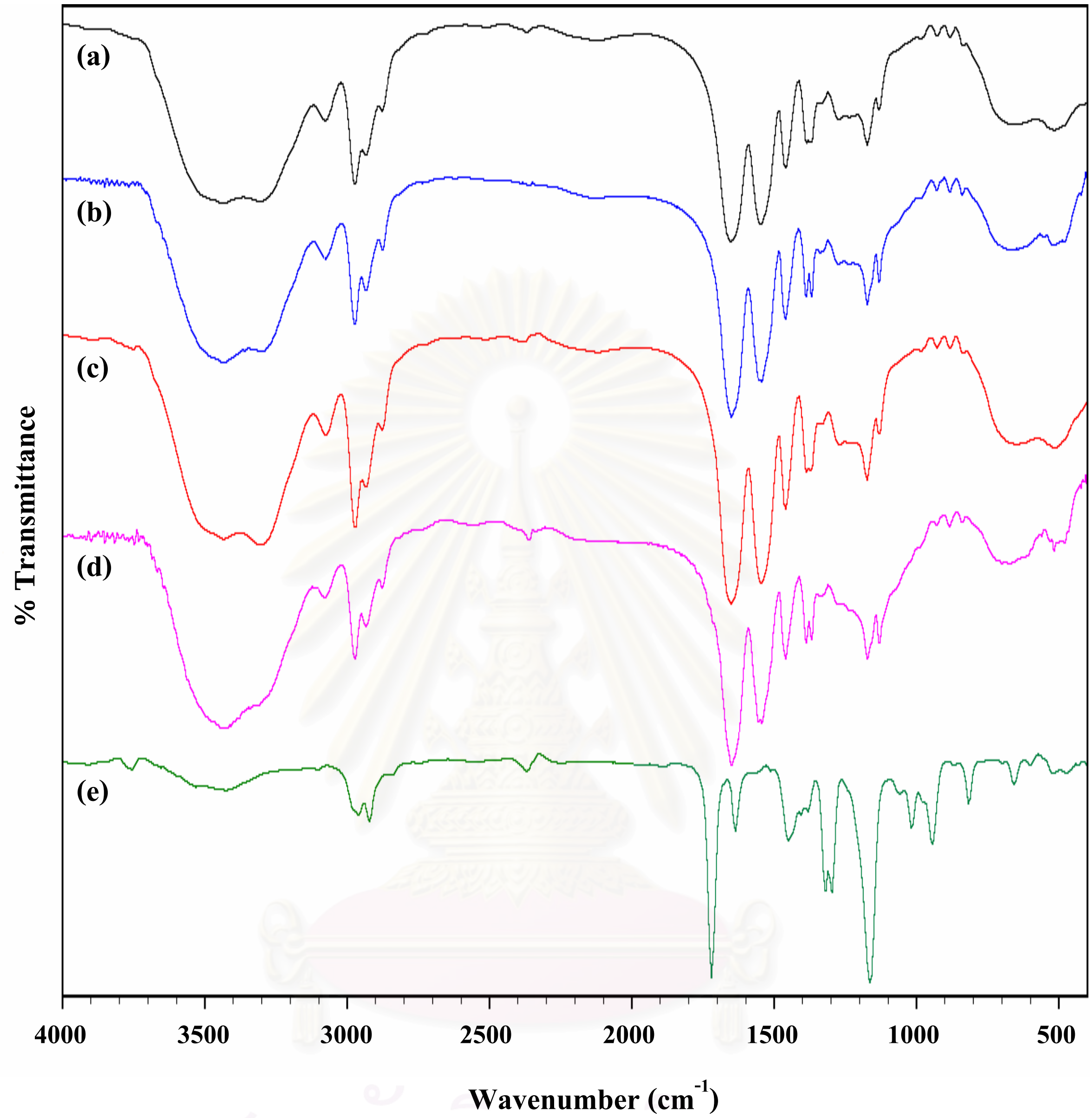


Figure 4.6 FT-IR spectra of (a) poly(NIPA) (Homo), (b) poly(NIPA) (Hetero), (c) poly(NIPA-*co*-MTEMA) (Homo), (d) poly(NIPA-*co*-MTEMA) (Hetero) and (e) MTEMA comonomer.

4.2.2 Fourier Transforms Raman Spectroscopy

The Raman spectra were illustrated in Figure 4.7. Since infrared spectra cannot confirm the attachment of MTEMA comonomer onto the NIPA polymer chain.

Another way to identify the functional groups on the polymer chain was a Raman spectroscopic technique. Therefore, this research used Raman spectroscopy in order to get more information about the polymer structure and we expected to see differences of the spectra aside from seeing in infrared spectra because Raman spectra are usually much simpler than infrared spectra, especially in overtone region where C-S stretching signals appear.

The Raman spectra gave many sharper peaks for all polymers than FT-IR spectra. The obvious band around 2800-3000 cm^{-1} are assigned to the ν(C–H) stretching vibrations of the methyl groups of *N*-isopropyl groups. Meanwhile, for the spectra of ν(N-H) amide stretching vibration occurs at approximately 3300-3550 cm^{-1}. NIPA monomer and MTEMA comonomer have different spectra of CO-NHR and CO-OR'. Nevertheless, the spectra of ν(C–N) stretching vibration about 1070-1380 cm^{-1} in poly(NIPA) overlapped with the spectra of ν(C–O–C) stretching vibration about 1025-1140 cm^{-1} in MTEMA comonomer. However, in heterogeneous polymer (Figure 4.7-d), the appearance of a small peak is ascribed to ν(C–S) stretching vibration of poly(NIPA-*co*-MTEMA) in the range of 570-790 cm^{-1} while poly(NIPA) does not have any peak at these frequencies.

The Raman spectra of the polymers were compared with the IR spectra. The spectra are mostly similar because of the detection limits for Raman spectrometry are often inferior to those obtained with IR spectrometry.

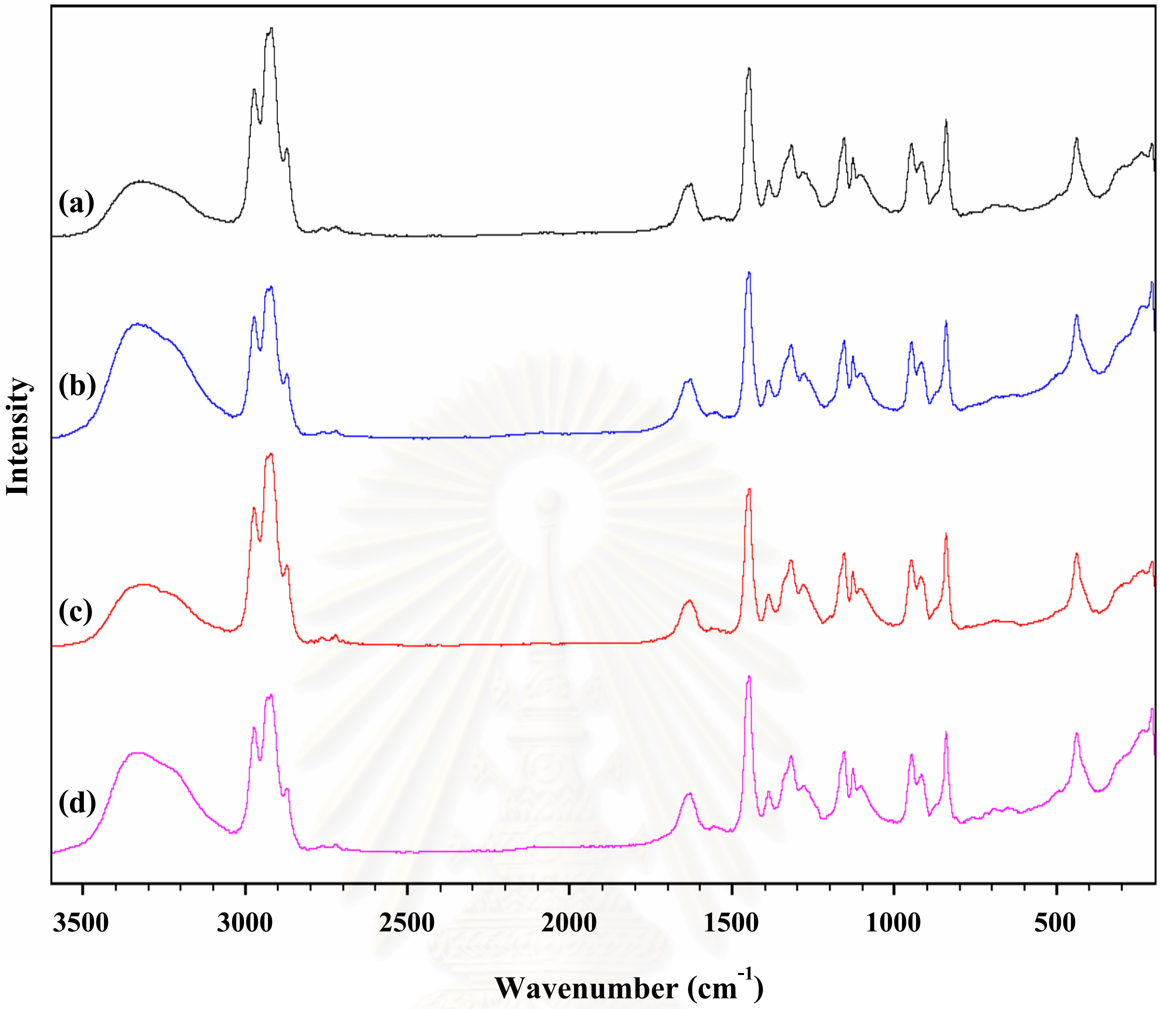


Figure 4.7 Raman spectra of (a) poly(NIPA) (Homo), (b) poly(NIPA) (Hetero), (c) poly(NIPA-*co*-MTEMA) (Homo) and (d) poly(NIPA-*co*-MTEMA) (Hetero).

4.2.3 Scanning Electron Microscopy

The SEM micrographs, as shown in Figure 4.8, exhibit the difference between poly(NIPA) and poly(NIPA-*co*-MTEMA) surface image. The result indicates the difference in shape and particle size between poly(NIPA) and poly(NIPA-*co*-MTEMA). For homogeneous polymers, poly(NIPA) surface is rougher than poly(NIPA-*co*-MTEMA) surface. While for heterogeneous polymers, the difference of particle size between poly(NIPA) and poly(NIPA-*co*-MTEMA) was observed.

Therefore, from the SEM micrographs it can be implied that the comonomer was attached in polymer chains.

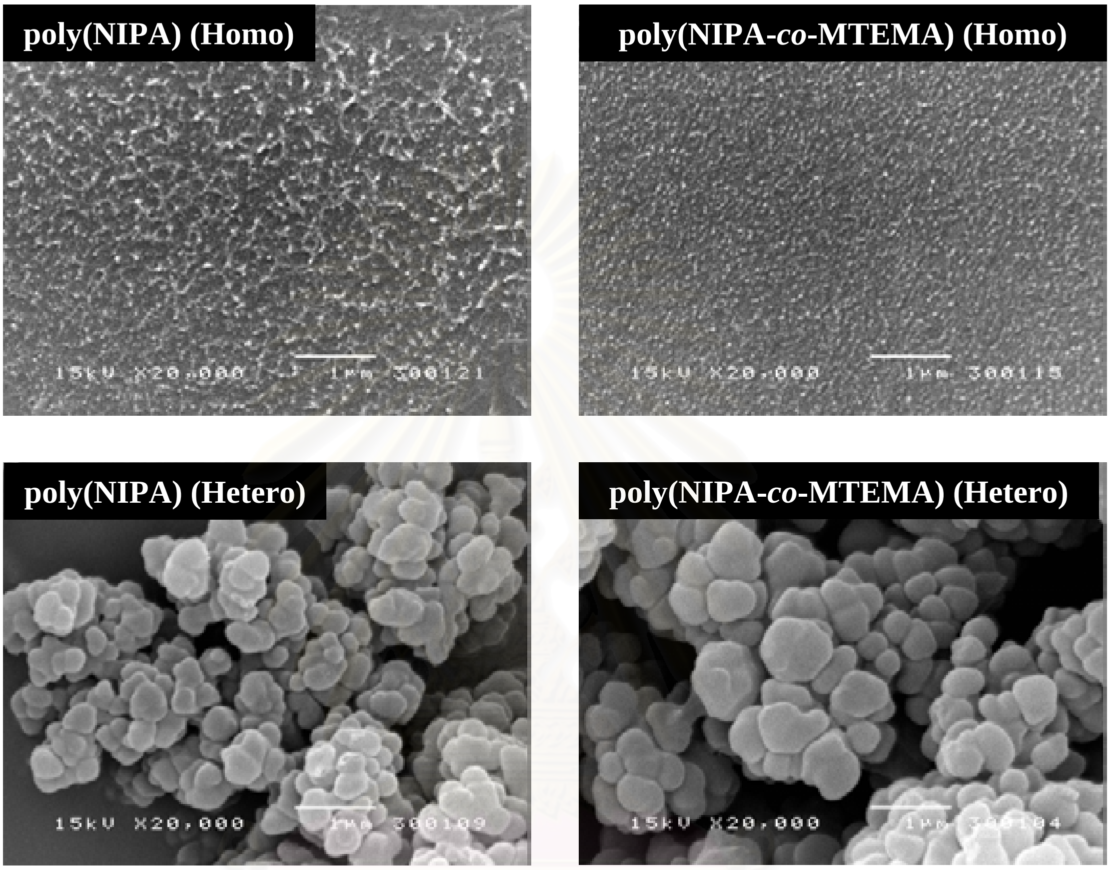


Figure 4.8 SEM photographs of poly(NIPA) and poly(NIPA-*co*-MTEMA) surface.

4.2.4 Thermogravimetric Analysis

The thermal stability of the synthetic copolymers was investigated using thermogravimetric analysis (TGA). TGA curves of poly(NIPA) (Homo), poly(NIPA) (Hetero), poly(NIPA-*co*-MTEMA) (Homo) and poly(NIPA-*co*-MTEMA) (Hetero) were displayed in Figure 4.9.

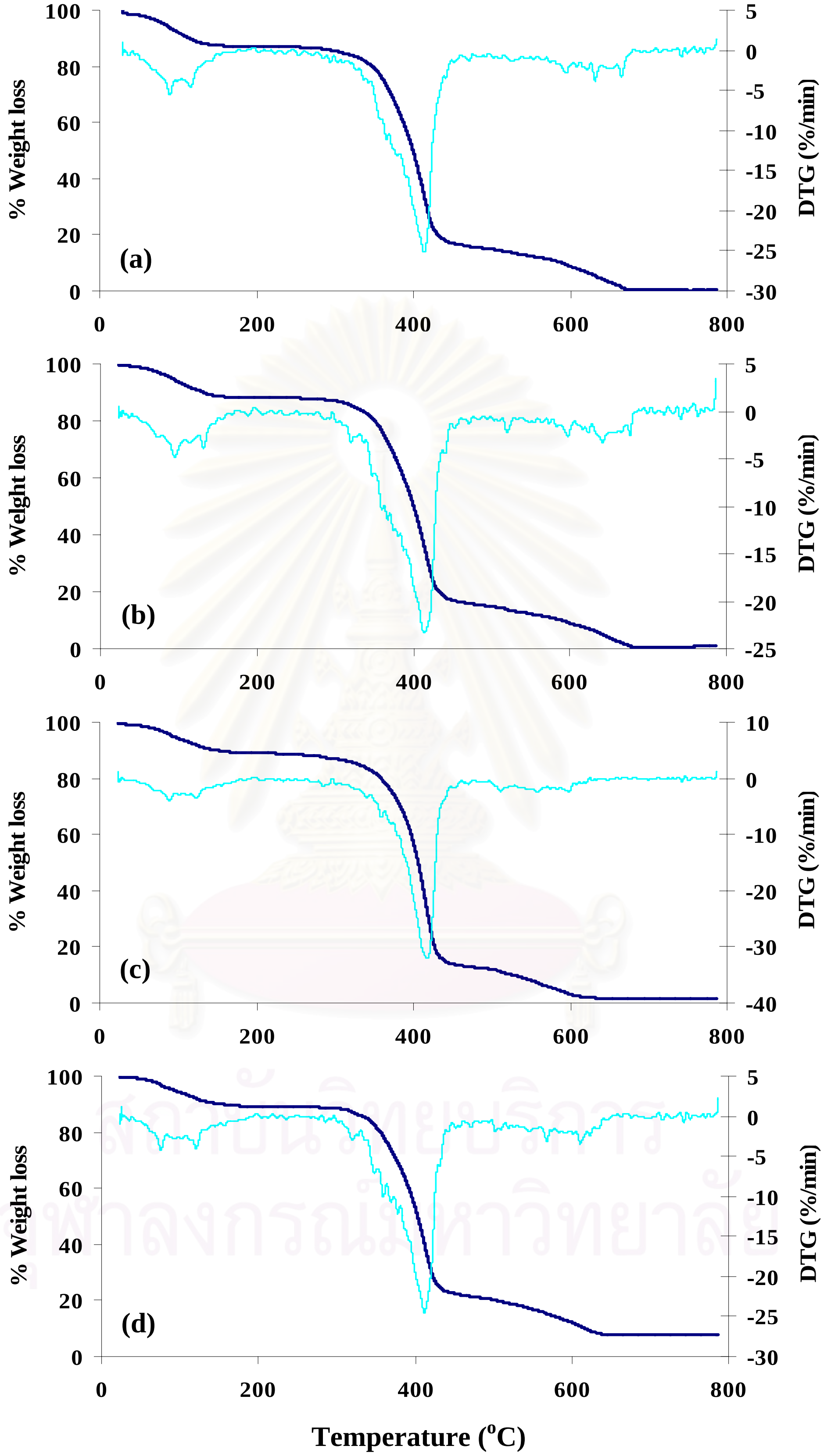


Figure 4.9 TGA-DTG curves of (a) poly(NIPA) (Homo), (b) poly(NIPA) (Hetero), (c) poly(NIPA-*co*-MTEMA) (Homo) and (d) poly(NIPA-*co*-MTEMA) (Hetero).

The thermograms consisting of weight loss (%) and differential weight loss (DTG, %/min) show three distinctly different weight losses. The first stage was observed at 10.8-12.8 % weight loss in the range of 50-200^{o}C due to the loss of water physically adsorbed on the polymers and decomposition of low molecular weight compounds. The second stage showed maximum weight loss around 66.6-75.7 % in the wide range of 200-460^{o}C, which is ascribed to a complex process including dehydration and decomposition of aliphatic moieties on polymers. And the third stage showed weight loss at 11.7-16.0 % between 460-700^{o}C. This change was probably due to the decomposition of organic moieties. Unfortunately, TGA could not provide sufficient evidence of the incorporation of MTEMA comonomer into the polymer chain.

4.2.5 Differential Scanning Calorimetry

The glass transition temperature (T_g) of all polymers were measured to get an estimation of the compatibility of the chemically different block copolymer by using differential scanning calorimetry (DSC) as displayed in Figure 4.10.

The value of glass transition temperature of poly(NIPA) without cross-linking was found from the literature [72] to be in the range of 135-140^{o}C. The T_g of poly(NIPA) block copolymer slightly increased to 158^{o}C [23]. The results obtained from DSC curves were illustrated in Table 4.1. The T_g values of homogeneous and heterogeneous poly(NIPA) polymers were 159.7 and 157.5^{o}C, respectively. These values were agreed with the the literature [23]. The T_g values of homogeneous and heterogeneous poly(NIPA-*co*-MTEMA) copolymers were slightly lower than that of poly(NIPA). The difference in T_g reveals that poly(NIPA) and poly(NIPA-*co*-MTEMA) are different.

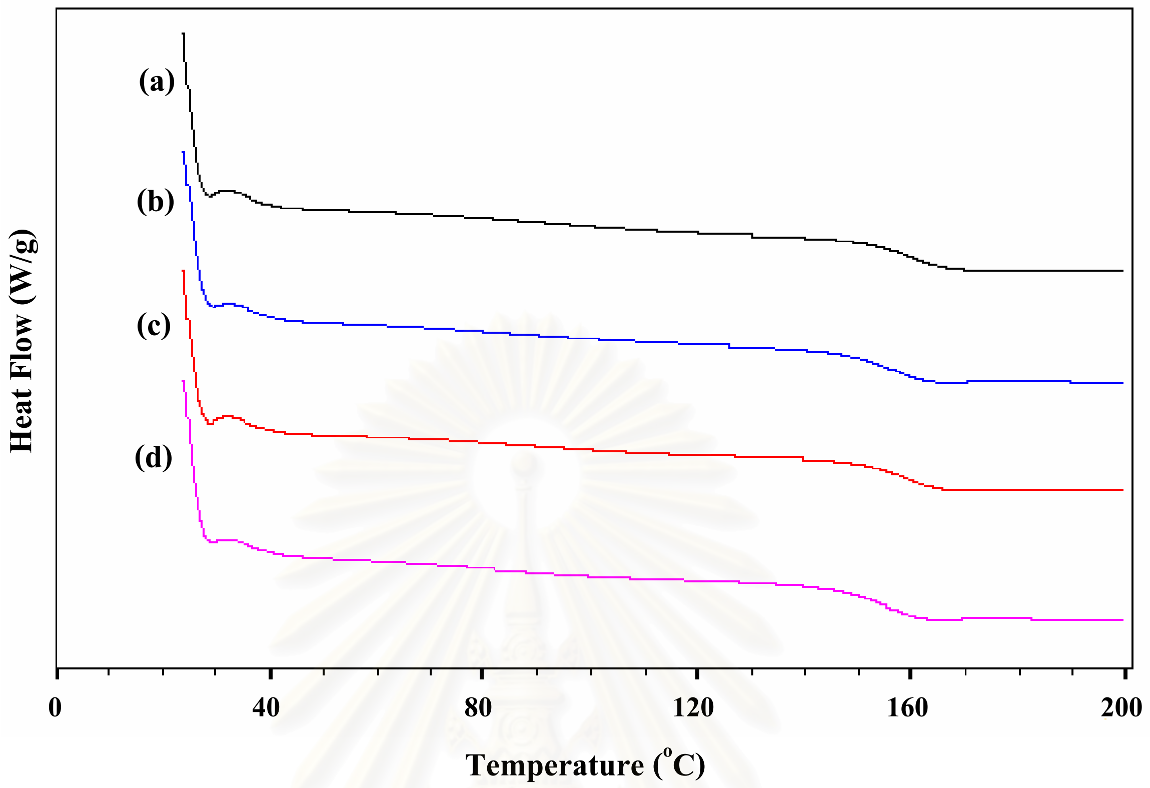


Figure 4.10 DSC thermograms of (a) poly(NIPA) (Homo), (b) poly(NIPA) (Hetero), (c) poly(NIPA-*co*-MTEMA) (Homo) and (d) poly(NIPA-*co*-MTEMA) (Hetero).

Table 4.1 Glass transition temperature (T_g) of polymers

Types of polymer	*Glass transition temperature (T_g), °C*	
	Homogeneous	*Heterogeneous*
poly(NIPA)	159.7	157.5
poly(NIPA-*co*-MTEMA)	157.5	155.0

In conclusion, the results of characterization by FT-IR, FT-Raman, SEM, TGA, and DSC cannot evidently confirm the successful copolymerization of the NIPA monomer with the comonomer MTEMA through free radical copolymerization. Even though, we believed that copolymerization of NIPA and MTEMA was achieved due to the fact that the previous results of gold(III) ion adsorption showed significantly the different adsorbabilities between poly(NIPA) and poly(NIPA-*co*-MTEMA).

The properties of synthesized copolymers and the adsorption and desorption of gold(III) ion in aqueous solution were thus further investigated.

4.3 Swelling Behavior

The degree of swelling was determined gravimetrically by using the procedure previously used in the literature [73, 74]. Dried synthesized polymer gels were immersed in deionized water at room temperature. The swollen gels were periodically weighed after the excess water at the surface was removed by filter paper. The experiment was repeated until the wet weight of the gel was constant. The results were displayed in Table 4.2. The degree of swelling was determined according to the following Equation 4.1.

$$\text{Swelling ratio (\%)} = \frac{(W_t - W_d)}{W_d} \times 100 \qquad (4.1)$$

where W_t = the weight of the swollen gel at time t (g)

W_d = the weight of dried gel (g)

The synthesized polymers were swollen in water on the account of the hydrophilic pendant (amide and methacrylate groups) in their structure. Both homogeneous poly(NIPA) and poly(NIPA-*co*-MTEMA) had quite similar swelling ratio because these two gels possess fairly organized structure. While heterogeneous poly(NIPA) and poly(NIPA-*co*-MTEMA) showed significantly different swelling ratios, indicating that copolymers were successfully synthesized.

Table 4.2 Degree of swelling for copolymers

Types of polymer	*Swelling ratio, %* [a]	
	Homogeneous	*Heterogeneous*
poly(NIPA)	588 ± 26	731 ± 63
poly(NIPA-*co*-MTEMA)	540 ± 28	551 ± 37

[a] Mean value ± SD, n = 3.

4.4 Phase Transitions of Homogeneous Polymer

The lower critical solution temperature (LCST) of both homogeneous poly(NIPA) and poly(NIPA-*co*-MTEMA) polymers was determined by light transmittance measurements using UV-Vis spectrophotometer at 600 nm [75]. A plastic cuvette packed with the synthesized polymers was placed in water circulated from a thermostated water bath where the temperature was raised from 24 to 40°C. By increasing the temperature, polymers underwent phase transition, resulting in turbid gels. Figure 4.11 showed that the polymer was transparent at low temperature and became opaque above a critical temperature.

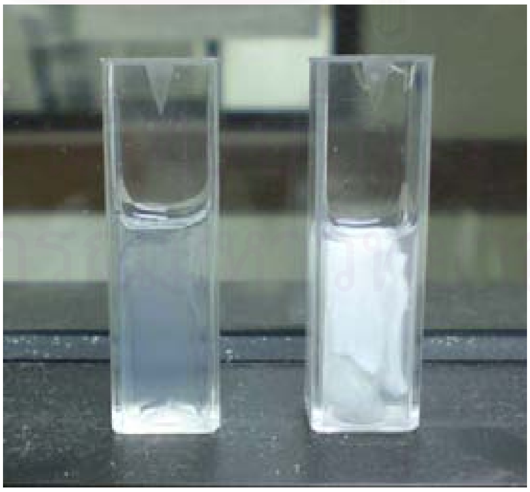


Figure 4.11 The synthesized homogeneous polymer in plastic cuvette at below LCST (left) and above LCST (right).

In Figure 4.12, the transmittance of the gels decreases steeply with increasing temperature especially when the temperature was close to the LCST. This experiment was performed in four replicates and the values were brought to an average value. The LCST was the temperature at half transmittance in the graph [35].

The LCST of poly(NIPA) was 32.2°C in comparison with poly(NIPA-*co*-MTEMA) which existed few lower at 32.0°C. The lower LCST of poly(NIPA-*co*-MTEMA) attributed to the incorporation of the comonomer, agreed with the results published by Ni *et al.* [76]. They reported that the LCST of poly(*N*-isopropylacrylamide-*co*-*N*-diacetone acrylamide) or poly(NIPA-*co*-DAA) decreased as the increasing of DAA in copolymers, owing to hydrophobicity of the comonomer.

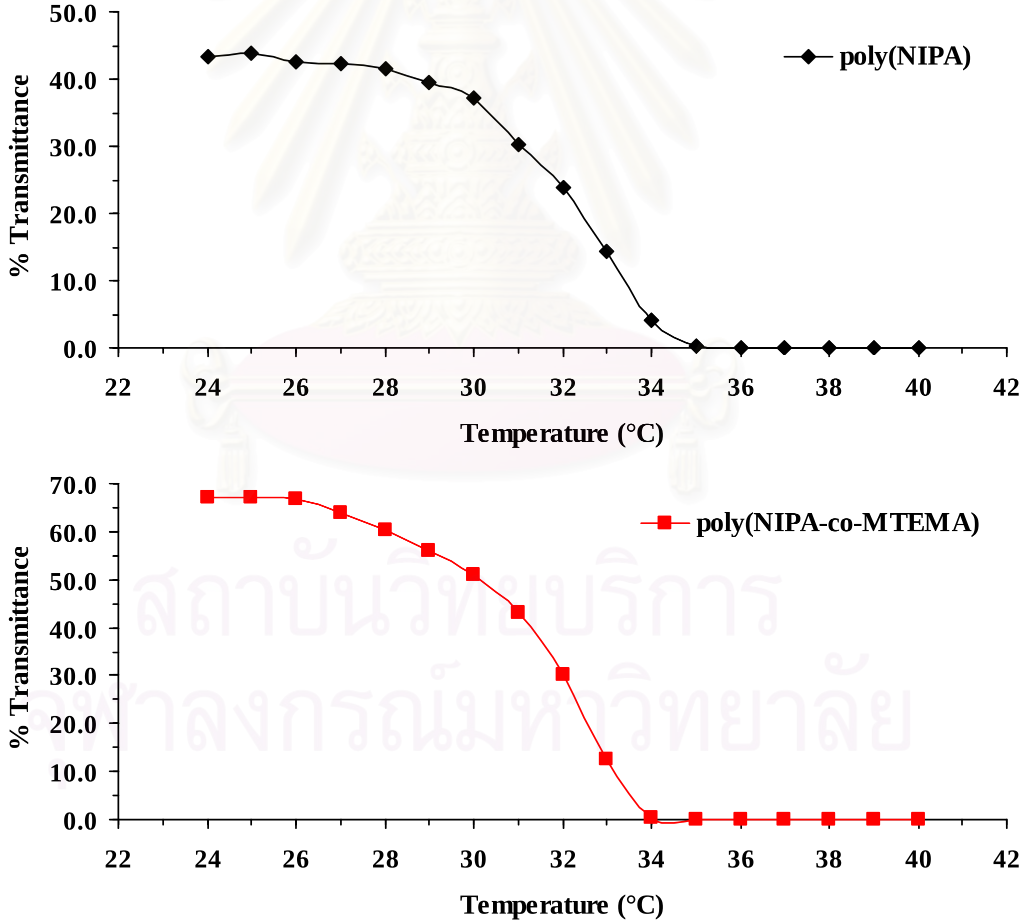


Figure 4.12 Temperature dependence of light transmittance of the homogeneous polymer.

4.5 Study of Interaction between Comonomer and Gold(III) Ion

The interaction between MTEMA comonomer and gold(III) ion was investigated by nuclear magnetic resonance spectroscopy (NMR). The hypothesis was that any interaction between sulfur donor atom and gold(III) ion could result in change of proton signal. The ^{1}H-NMR spectrum of MTEMA comonomer was recorded in $CDCl_3$ (Figure 4.13(a)). Aliphatic proton signals could be found as follow: δ(ppm) 6.15 and 5.58 (*s*, $C\underline{H}_2CCO$), 4.32 (*t*, $OC\underline{H}_2CH_2$), 2.72 (*t*, $CH_2C\underline{H}_2SCH_3$), 2.18 (*s*, $SC\underline{H}_3$), 1.93 (*s*, $C\underline{H}_3CCH_2$). A liquid-liquid extraction technique was used to produce a gold(III)-MTEMA complex as follows; MTEMA comonomer in $CDCl_3$ (2 mL) was contacted with 10 mg L^{-1} gold(III) solution (2 mL, pH 2-3) in a test tube, the mixture was manually and violently shaken for several minutes. The remaining gold(III) ions in the aqueous solution were determined by FAAS. The result showed that gold(III) ions could transfer from aqueous phase to organic phase. The $CDCl_3$ was then separated and subject to ^{1}H-NMR measurement (Figure 4.13(b)). Unfortunately, the proton signals were similar in position to that of MTEMA. The interaction between MTEMA comonomer and gold(III) ion could not be confirmed by ^{1}H-NMR techniques.

In fact, the interaction between the sulfur donor atom on MTEMA comonomer towards gold (III) ion can be occurred and basically explained by the hard soft acid base principle (HSAB) that was defined as follows: “Hard (lewis) acids prefer to bind to hard (lewis) bases and soft (lewis) acids prefer to bind to soft (lewis) bases” [77]. Therefore, gold(III) ion which is a soft acid shall form coordination complex with the sulfur atom on MTEMA which is a soft base.

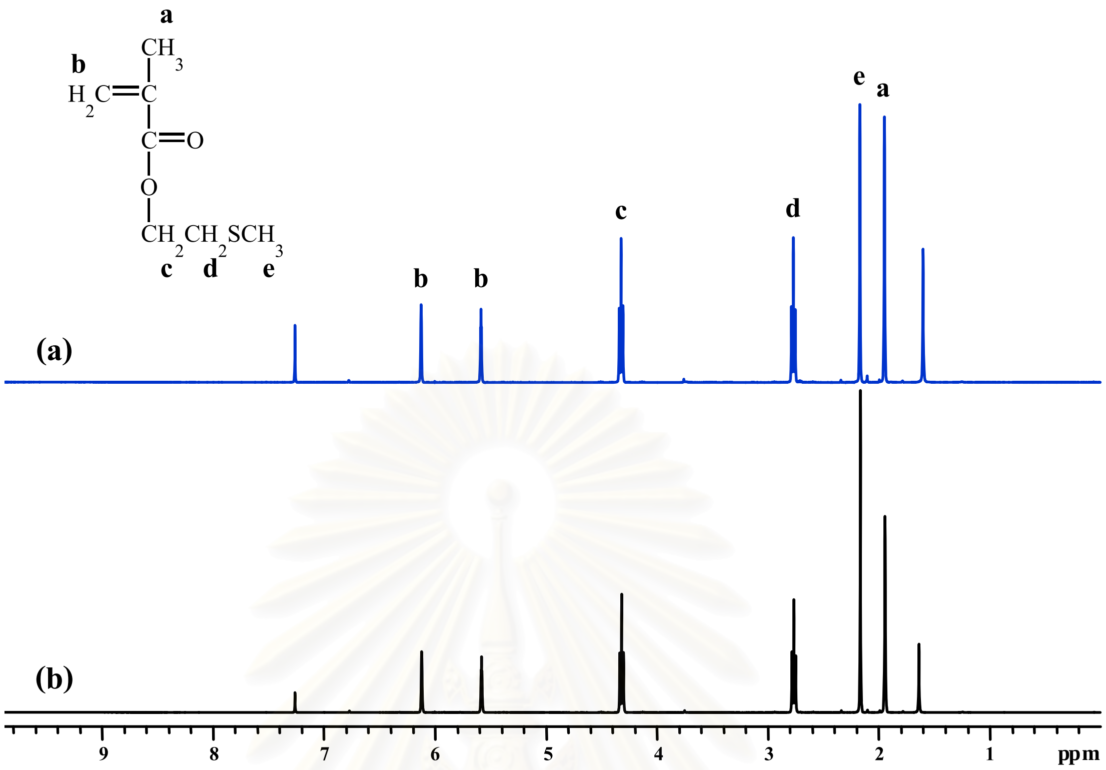


Figure 4.13 ^{1}H-NMR spectra of (a) MTEMA comonomer and (b) MTEMA comonomer possessing gold(III) ion.

4.6 Gold(III) Ion Adsorption Studies

The synthesized copolymers were used in adsorption study for gold(III) ion in aqueous solution using batch method. The effect of various parameters such as pH and temperature of gold(III) ion solution, adsorption time, adsorbent size and surface area were investigated. The adsorption isotherms were also studied.

The gold(III) adsorption efficiency is represented in term of percentage adsorption, calculated according to Equation 4.2.

$$\%\ \text{adsorption} = \frac{(C_i - C_e)}{C_i} \times 100 \qquad (4.2)$$

where C_i = initial concentration of gold(III) ion in the solution (mg L^{-1})

C_e = equilibrium concentration of gold(III) ion in the solution (mg L^{-1})

4.6.1 Effect of pH

The pH of solution is very important parameter to be studied, because of its great influence on the species distribution of gold(III) in aqueous solution [78]. Therefore, the effect of pH on gold(III) adsorption should be preliminary studied.

The effect of gold solution with the pH range of 1-7 was investigated, and the adsorption time was fixed at 1 hour. The result of gold(III) adsorption on the adsorbent was displayed as a function of pH in Figure 4.14. The adsorption efficiency of poly(NIPA-*co*-MTEMA) was clearly greater than that of poly(NIPA). For homogeneous polymers, it was found that the adsorption behavior of both poly(NIPA) and poly(NIPA-*co*-MTEMA) was similar in the wide pH range between 1-5 due to the fact that the amide group (-CONH-) was possibly protonated and became a positive charge moiety while gold(III) ion is present in chloroaurate form ($AuCl_4^-$) and the adsorption mechanism occurs probably via ion-exchange. In case of heterogeneous polymers, both polymers had great adsorption ability in a wide acidic range (pH 1-5). However, the adsorption percentage of poly(NIPA-*co*-MTEMA) was noticeably higher than that of poly(NIPA). This observation could confirm the success of the copolymerization and the copolymers could better adsorb gold(III) ion via complexation mechanism. The higher adsorption capacity of the copolymers strongly showed an evidence that the comonomer MTEMA played an important role for gold(III) adsorption and the copolymers were successfully synthezised.

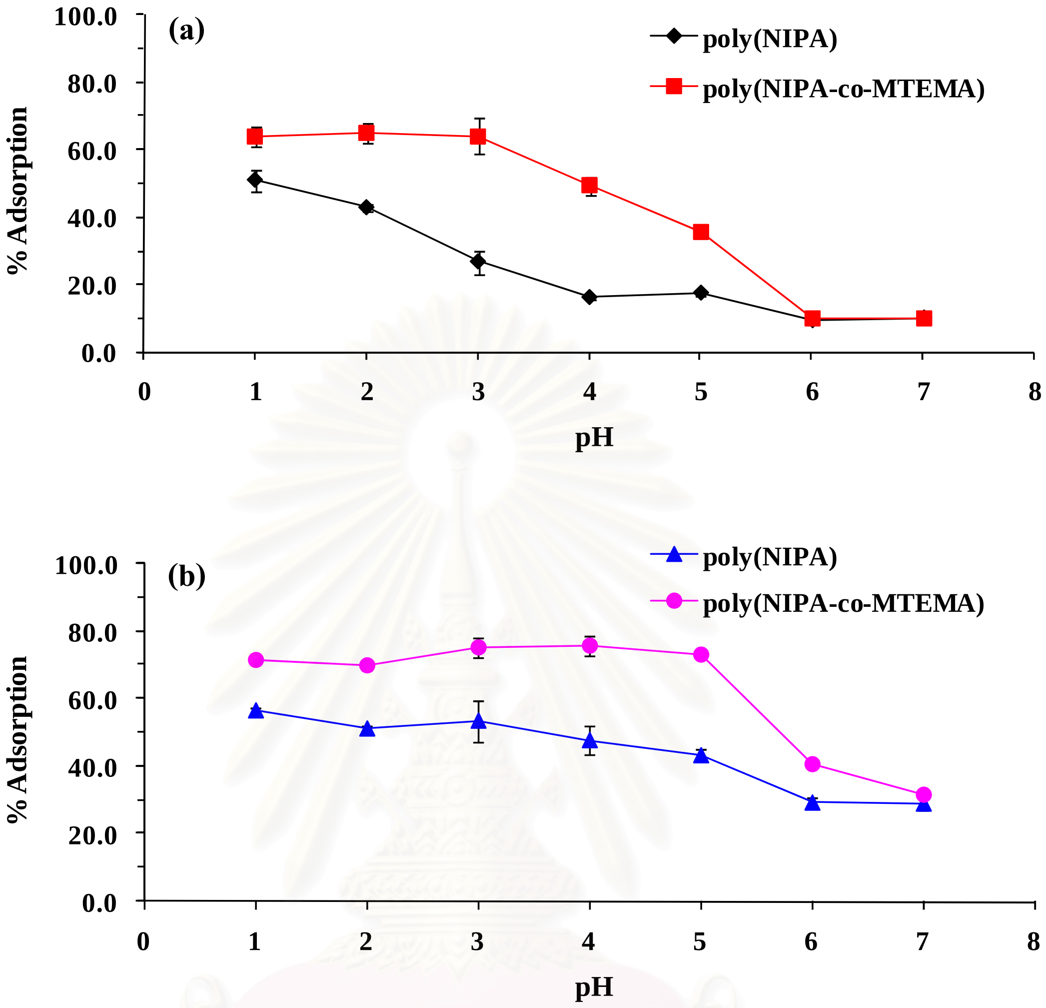


Figure 4.14 Effect of pH on gold(III) ion adsorption onto (a) Homogeneous and (b) Heterogeneous polymers.

As mentioned above, the Au(III) species distribution varies with the pH. The coexistence of hydroxide, chloride, and hydroxide-chloride complexes of gold makes its speciation very complex [78]. Figure 4.15 displays the effect of the addition of chloride ion to the Au-H_2O system. In the top left-hand quarter of the diagram there has been imposed a region in which the most stable and predominant species is $AuCl_4^-$. The extent of this domain varies directly with the concentration of gold in solution. It is important to note that a part of the domain of stability of $AuCl_4^-$ (shown shaded) falls within the region of stability of water. Therefore, in the presence of chloride ion, gold can exist in an oxidized form in contact with water under acid conditions. If a stronger ligand than chloride was present, the domain of stability of the oxidized species would be correspondingly increased [79].

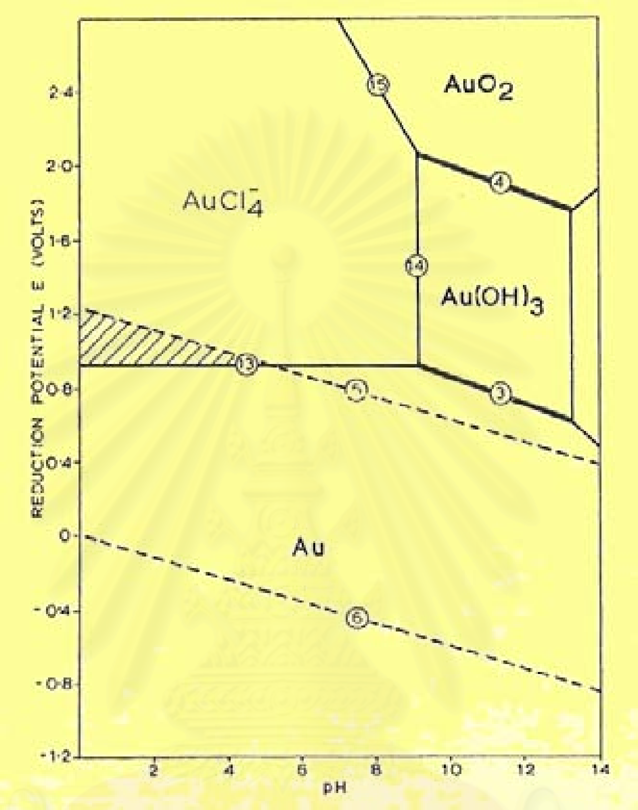


Figure 4.15 Pourbaix diagram for the system Au-H$_2$O-Cl$^-$ at 25 °C, [Au(III)] = 10^{-2} M, [C1$^-$] = 2 M.

Moreover, under the experimental conditions corresponding to about 0.05 M Cl$^-$ the predominant species at acidic pH is $AuCl_4^-$. Near the neutral pH-region the existence of $AuOHCl_3^-$ (pH 3.5 – 6.5) and $Au(OH)_2Cl_2^-$ (pH 4.5 – 8.0) are favorable. But also species like $Au(OH)_3Cl^-$ and $Au(OH)_3$ are likely to exist in a higher pH values [78, 80]. In acidic pH, the following equilibrium is presumed:

$$HAuCl_{4(aq)} \rightleftharpoons AuCl^-_{4\ (aq)} + H^+ \qquad (4.3)$$

This equilibrium is driven to the left side under strong acidic conditions and hence $AuCl_4^-$ is less dissociated and the predominant species in solution is chloroauric acid [81]. The higher affinity of MTEMA towards the undissociated neutral species at pH 1.0 to 4.0 can be explained by the theory of hard-soft-acids-bases (HSAB) after Pearson [82] as mentioned in the introduction. Neutral molecules offer a softer character than metal ions. Therefore, the undissociated chloroauric acid, a softer acid than the corresponding ion, can form coordination bond well with the sulfur donor atom (soft base) of MTEMA. As the main sorption mechanism is considered to be coordination, the adsorption efficiency decreased with increasing pH.

In summary, the optimum pH range for gold(III) ion adsorption was observed at pH 1-3 for homogeneous polymer while the adsorption of heterogeneous polymer was independent of the pH value. The suitable pH was in the range of 1-5. Hence, the solution would be used in further studies without adjusting pH.

4.6.2 Effect of Adsorption Time

The adsorption of liquid (solute) on solid (adsorbent) can be described by boundary layer models. The overall mechanism are achieved according to the following steps: (i) solute transport from the bulk solution to the boundary film, (ii) solute transfer from the boundary film to the surface of the adsorbent, (iii) transfer from the surface to the intraparticle active sites, and (iv) uptake on the active sites, via complexation, sorption or precipitation. However the adsorption and complexation occur rapidly, so the fourth step is also unimportant in the overall of sorption kinetics [83]. Thus adsorption phenomena are mainly controlled by the external diffusion and interparticle diffusion which their kinetics of mass transport are depended on the time. In this experiment, the effect of adsorption time was investigated to obtain the equilibrium time of the adsorption process.

The effect of adsorption time on gold(III) ion onto polymers at optimum pH with various times was studied. The estimation can be performed by increasing time until the adsorbent provides the constant value of adsorption. The result, as shown in Figure 4.16, indicates that the adsorption capacity increased with the increasing of adsorption time and reached the equilibrium after 180 minutes for heterogeneous polymers, while the adsorption efficiency of homogeneous polymers slightly increased by increasing the adsorption time up to 180 minutes. Moreover, the polymer gel crack was observed when the adsorption time took longer. Therefore, the adsorption time of 180 minutes was chosen for adsorption in further experiments of both polymers to assure the adsorption equilibrium.

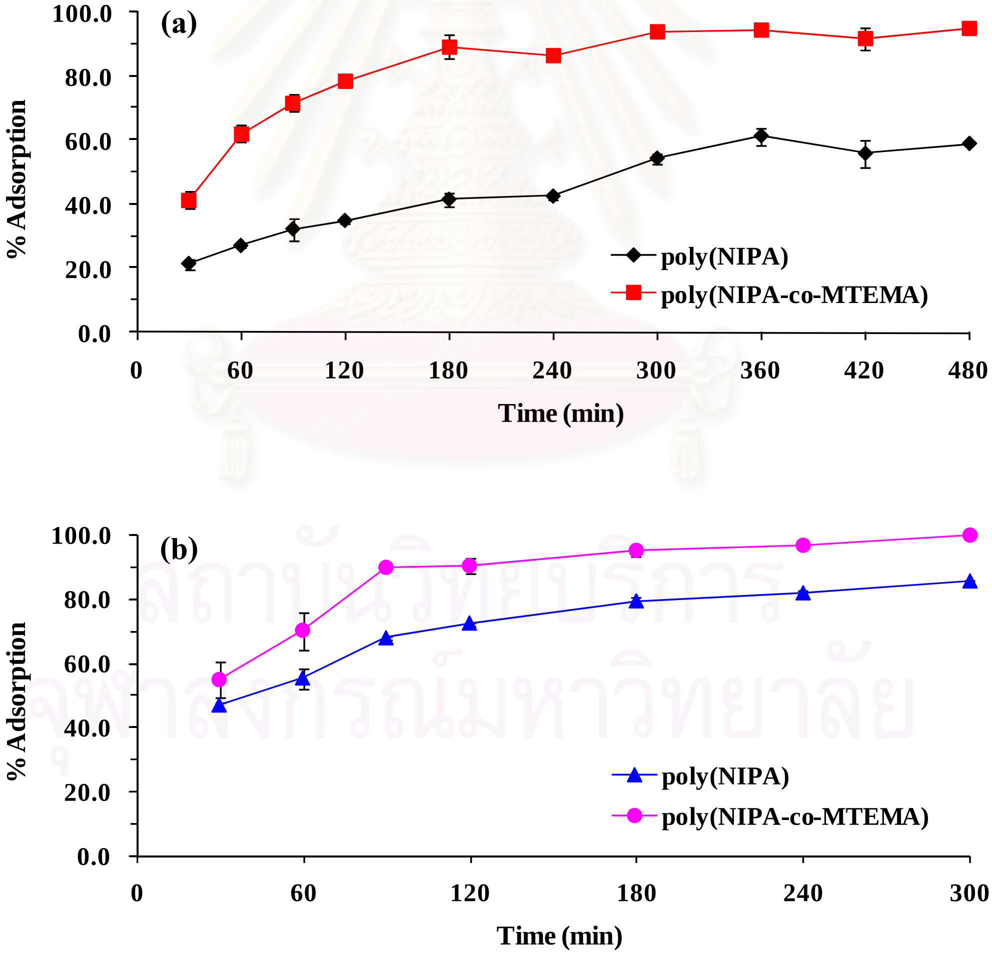


Figure 4.16 Effect of adsorption time on gold(III) ion adsorption onto (a) Homogeneous and (b) Heterogeneous polymers.

4.6.3 Effect of Adsorbent Size and Surface Area

The effect of adsorbent size and surface area were studied. Adsorption behavior of the polymers was investigated by varying the size of 0.7 cm diameter adsorbent including 0.25, 0.50, 0.75 and 1.0 cm length. In addition, surface area of adsorbent was increased by splitting the 0.25 cm length gel into 4 and 8 pieces before immersing in 3 mL of 10 mg L^{-1} gold(III) ion solution.

A decrease of the adsorption efficiency was observed when decreasing the length of adsorbent, shown in Figure 4.17. It could be explained that the adsorption ability depended on the amount and surface of adsorbent. Poly(NIPA-*co*-MTEMA) (Hetero) showed the highest % adsorption, and both copolymer gels had higher adsorption ability than the poly(NIPA) gels.

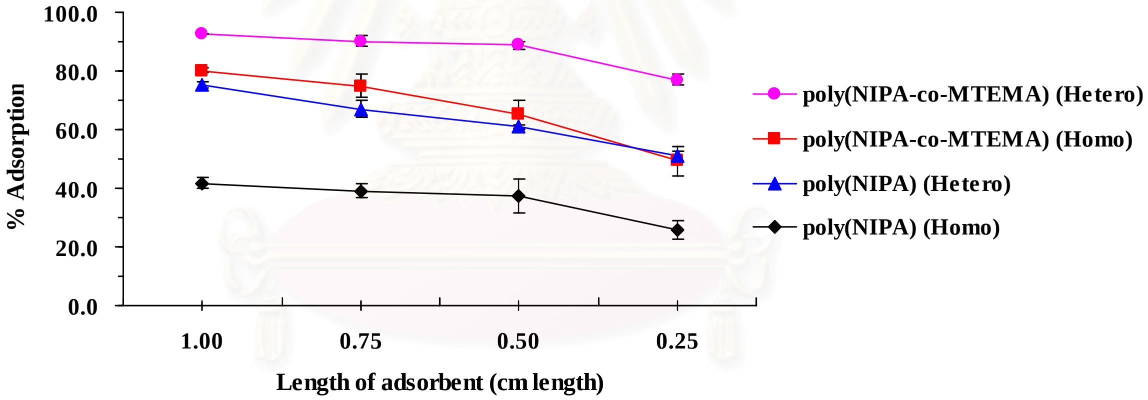


Figure 4.17 Effect of adsorbent size on gold(III) ion adsorption onto 0.7 cm diameter gels.

The results of gold(III) ion adsorption on different surface area of the gels were illustrated in Figure 4.18. The trend of % adsorption of all polymers were fairly similar, except for poly(NIPA) (Homo). So, these experimental data showed that surface area affected the adsorption of gold(III) ion. The adsorption isotherm study would confirm this phenomenon.

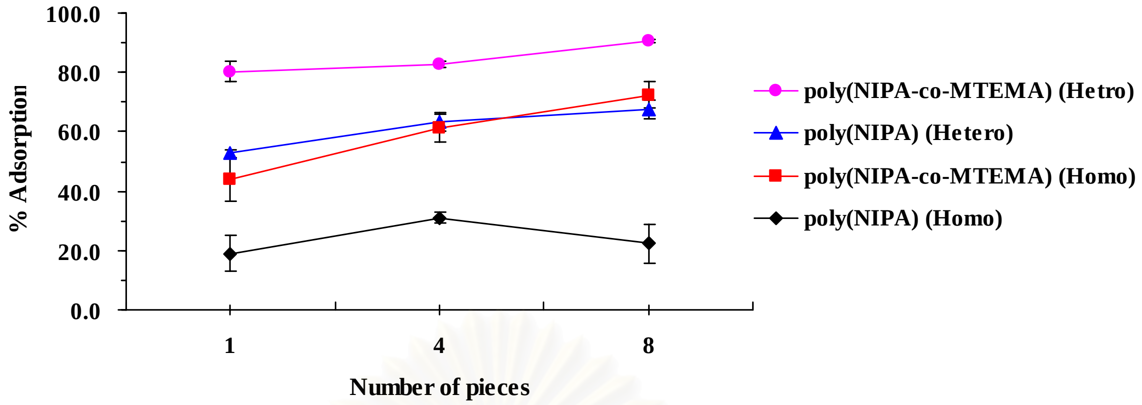


Figure 4.18 Effect of adsorbent surface area on gold(III) ion adsorption onto 0.7 cm diameter x 0.25 cm length gel.

4.6.4 Effect of Temperature

The adsorption capacity of all polymers towards gold(III) ion were investigated as a function of temperature at optimum pH and appropriate contact time. From the literature it has been known that poly(NIPA) hydrogel is a representative of temperature-responsive polymer since it exhibits a sharp phase transition in water. It has a lower critical solution temperature (LCST) in the vicinity of 32°C. It means that below this temperature [10 and 23 °C (ambient temperature) in the experiment] the hydrogel is swollen, hydrated and hydrophilic, have poor adsorbability towards gold(III) ion whereas above the LCST (35 and 50°C), the hydrogel shrinks and forms a collapsed, dehydrated and hydrophobic state. The polymers have a good adsorption efficiency of gold(III) in aqueous solution [57].

Figure 4.19 demonstrated the % adsorption of each polymer towards gold(III) ion at different temperature. It was seen that the adsorption ability increased with raising temperature due to the fact that the gel could shrink and trap gold(III) ion into the polymer chain. The difference in % adsorption of poly(NIPA) gels at low and high temperature was more obvious than that observed for poly(NIPA-*co*-MTEMA) gels, which was nearly 10 % difference. Poly(NIPA-*co*-MTEMA) (Hetero) had the highest

% adsorption. Unless the incorporation of MTEMA comonomer in polymer chain reduced the thermosensitive adsorption property comparing with poly(NIPA) gels, the synthesized copolymers exhibited a thermosensitive adsorption property for gold(III) ion.

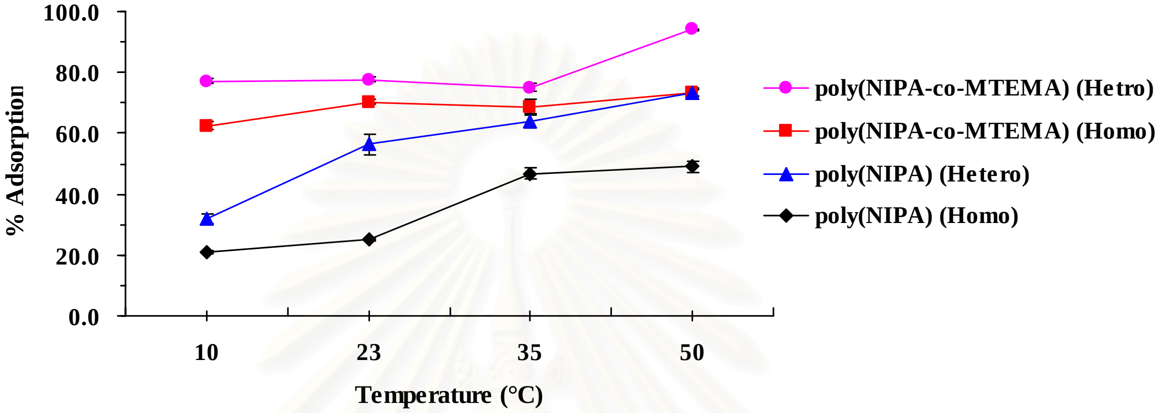


Figure 4.19 Effect of temperature on gold(III) ion adsorption.

4.6.5 Adsorption Isotherm

The adsorption equilibrium between gold(III) ion in aqueous solution and the adsorbent through liquid/solid interface can be described by several adsorption isotherms. Langmuir and Freundlich isotherms are the two models commonly used in the study of the adsorption behavior [84]. Both isotherm Equations can be transformed to a linear form and so their two adjustable parameters are easily estimated either by graphical means or by linear regression. Langmuir isotherm is based on the assumptions that metal ions are chemically adsorbed at a fixed number of well defined sites. Each site can hold only one ion (monolayer adsorption), all sites are energetically equivalent (homogenous surface) and there is no interaction between the ions [85, 86]. Whereas, Freundlich isotherm is based on the assumption that the uptake of metal ions occurs on a heterogeneous surface by monolayer adsorption [87] or a multi-layer adsorption if the adsorption isotherm lacks a plateau [86].

The experimental data were treated by both adsorption isotherms. The linearized Langmuir isotherm allows the calculation of adsorption capacities and the Langmuir constant. The model is described by Equation 4.4 [88].

$$\frac{C}{N_f} = \frac{1}{bN_s} + \frac{C}{N_s} \tag{4.4}$$

where C = the metal residual concentration in solution at equilibrium (mol L^{-1})
N_f = the amount of metal ions adsorbed per gram of sorbent (mol g^{-1})
N_s = the maximum sorption capacity of the sorbent (mol g^{-1})
b = Langmuir constant related to energy of adsorption (L mol^{-1})

And the linearized form of Freundlich isotherm is shown in Equation 4.5.

$$log\, N_f = log\, K_f + \left(\frac{1}{n}\right) log\, C \tag{4.5}$$

where K_f = Freundlich constant related to adsorption capacity (mol g^{-1})
n = the numerical value of Freundlich constant

The experiment was carried out by using a fixed amount of polymer gel in various initial concentrations of gold(III) ion solution at 50±1°C which is the best temperature for adsorption. The equilibrium had to be attained, the remaining concentration of the metal ion in solution was determined using FAAS. The results in Figure 4.20 and 4.23 showed the saturation of binding sites on the polymer gels after increasing the gold(III) ion concentration. The gold(III) ion adsorption increased rapidly at low initial concentration. The trested experimental data were plotted to illustrate the linear regression line in order to confirm the applicability of Langmuir and Freundlich adsorption isotherm (Figure 4.21-4.22 and 4.24-4.25). The obtained linear equations gained by fitting curve were listed in Table 4.3 and 4.4. The Langmuir and Freundlich parameters were also calculated.

<u>Homogeneous polymers</u>

The result was shown in Table 4.3 and 4.4 with the correlation coefficient (r^2) indicates that the adsorption isotherm of gold(III) onto homogeneous polymers were obeyed both the Langmuir and Freundlich model. The maximum sorption capacity (N_s) determined from the Langmuir plot were 58.24, 62.77 mmol g^{-1} for poly(NIPA) and poly(NIAP-*co*-MTEMA), respectively. It can be assumed that the surface is homogeneous and all binding site are equivalent. The solute uptake occurs by a monolayer sorption at definite and localized sites due to a well-organized structure of homogeneous polymers.

As a smaller Langmuir constant (*b)* corresponds to weaker binding affinity, it can conclude that poly(NIPA) had weaker binding affinity to gold(III) ion than poly(NIPA-*co*-MTEMA). However, the Langmuir constants (*b)* obtained are low for adsorption of gold(III) ion onto the adsorbent. It indicates that the adsorption mechanism is physisorption rather than chemisorption onto sulfur donor sites of the MTEMA comonomer.

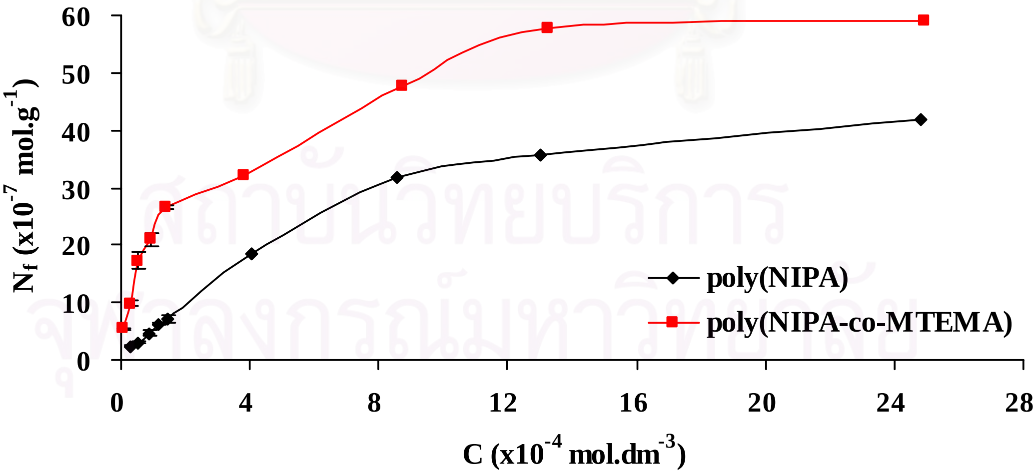


Figure 4.20 Saturation adsorption isotherms of gold(III) ion at pH 3 and 50±1°C.

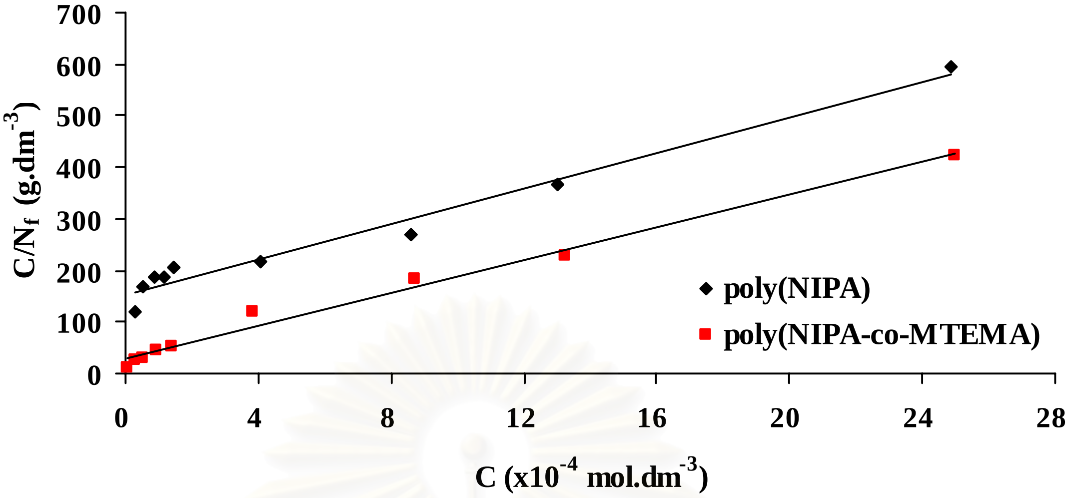


Figure 4.21 Langmuir adsorption isotherm plots of gold(III) ion onto homogeneous polymers at pH 3 and 50±1°C.

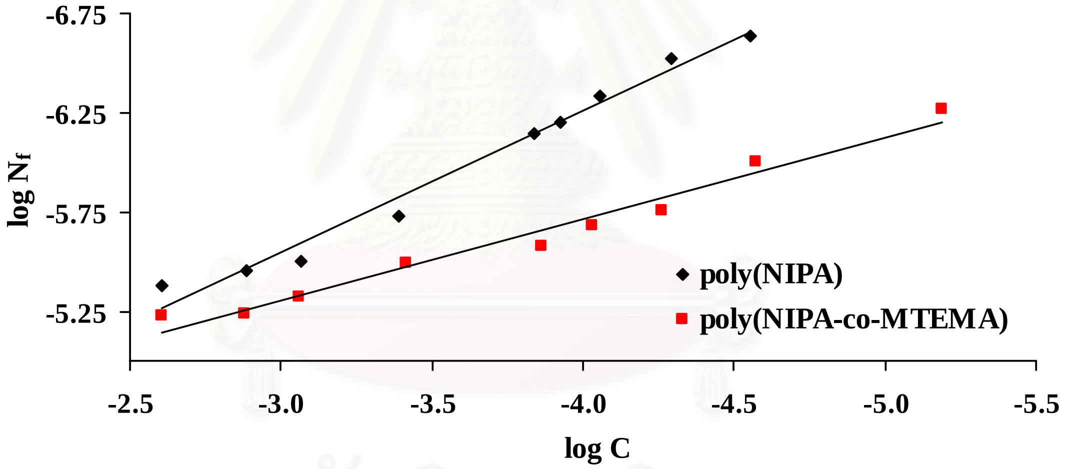


Figure 4.22 Freundlich adsorption isotherm plots of gold(III) ion onto homogeneous polymers at pH 3 and 50±1°C.

Heterogeneous polymer

The adsorption behavior of heterogeneous gels was preceded similarly to homogeneous polymers but the size of adsorbents was reduce by half (0.5 cm length gel was used) owing to high adsorption capacity. The experimental results of adsorption gold(III) onto heterogeneous polymers could better fit to Freundlich model with higher correlation coefficient (r^2) than the Langmuir one, as shown in Table 4.3 and 4.4. It indicated that the adsorption occurred on heterogeneous surface or supporting sites of various affinities.

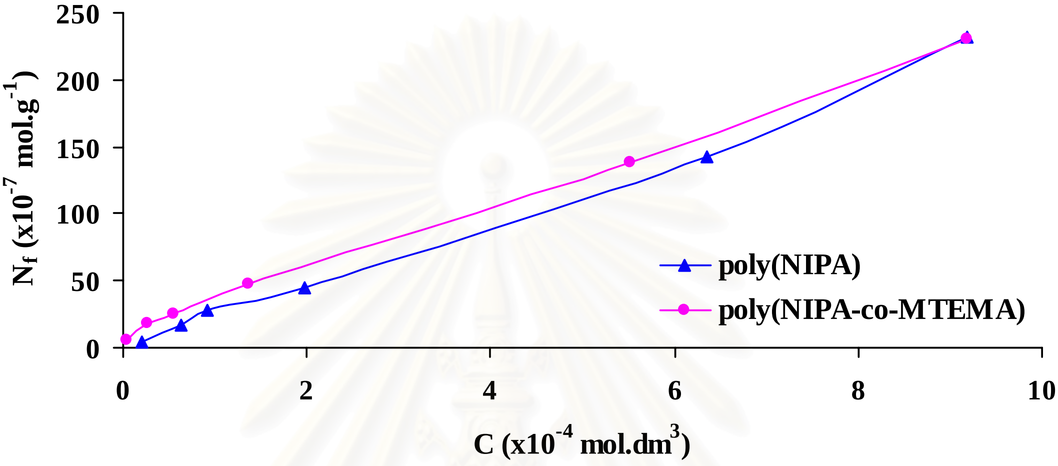


Figure 4.23 Saturation adsorption isotherms of gold(III) ion at 50±1°C.

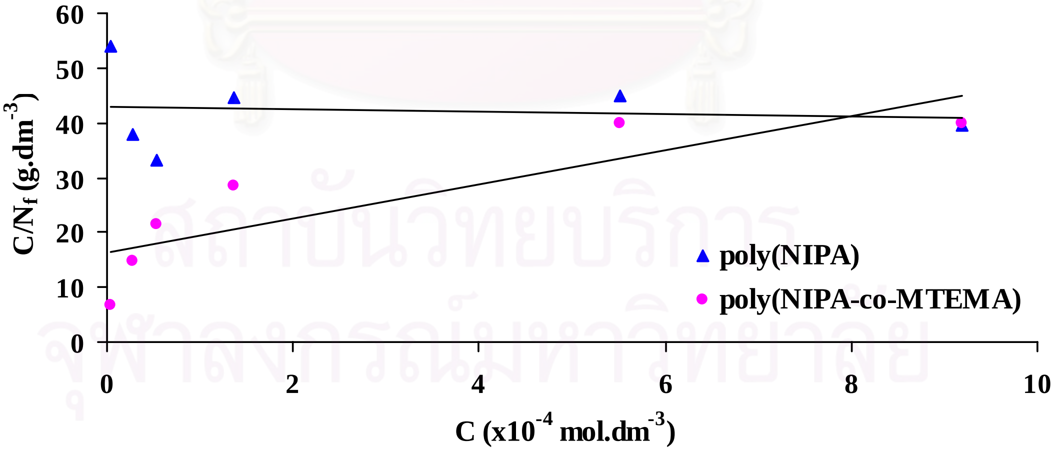


Figure 4.24 Langmuir adsorption isotherm plots of gold(III) ion onto heterogeneous polymers at 50±1°C.

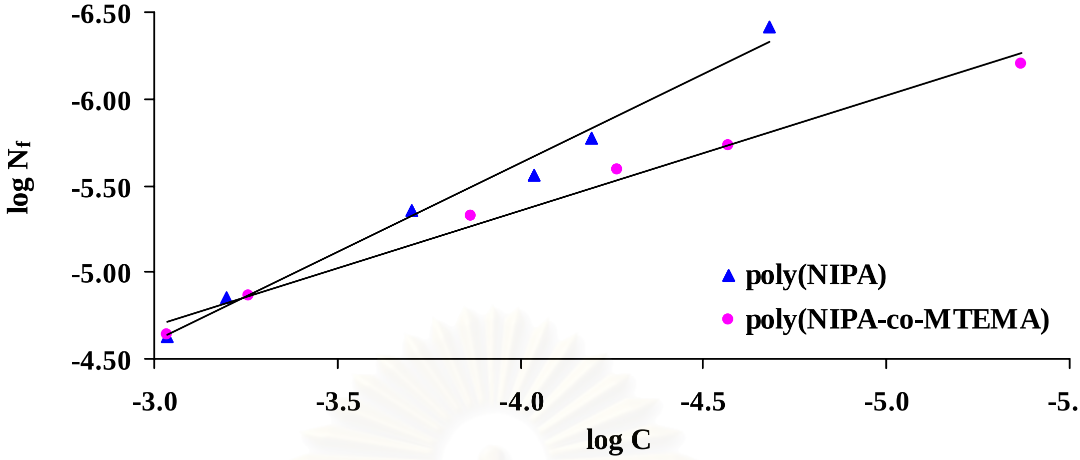


Figure 4.25 Freundlich adsorption isotherm plots of gold(III) ion onto heterogeneous polymers at 50±1°C.

Table 4.3 Langmuir parameters for the adsorption of gold(III) ion at 50±1°C

Type of polymer	*Code*	*Equation*	*r^2*	*b (L mol^{-1})*	*N_s(mmol g^{-1})*
Homo	poly(NIPA)	y = 17.1698x + 153.1949	0.9762	0.11	58.24
	poly(NIPA-*co*-MTEMA)	y = 15.9323x + 28.9783	0.9890	0.55	62.77
Hetero	poly(NIPA)	y = -0.2079x + 42.9003	0.0118	NA	NA
	poly(NIPA-*co*-MTEMA)	y = 3.1023x + 16.4339	0.7342	0.19	322.34

NA = Not available

Table 4.4 Freundlich parameters for the adsorption of gold(III) ion at 50±1°C

Type of polymer	*Code*	*Equation*	*r^2*	*K_f (mmol g^{-1})*	*1/n*
Homo	poly(NIPA)	y = 0.7132x - 3.4036	0.9809	0.39	0.71
	poly(NIPA-*co*-MTEMA)	y = 0.4095x - 4.0772	0.9714	0.08	0.41
Hetero	poly(NIPA)	y = 1.0275x - 1.5168	0.9882	30.42	1.03
	poly(NIPA-*co*-MTEMA)	y = 0.6654x - 2.6894	0.9900	2.04	0.67

4.7 Gold(III) Ion Desorption Studies

The desorption of gold(III) ion from synthesized polymers was studied using batch method. Gold(III)-adsorbed gels were put in a desorbing solution (3 mL). The effect of various parameters such as types of desorbing solution, desorption time and temperature were investigated.

The gold(III) ion desorption efficiency is expressed in term of percentage desorption or elution, calculated according to Equation 4.6.

$$\%\ \text{elution} = \frac{m_d}{m_a} \times 100 \qquad (4.6)$$

where m_d = amount of gold(III) ion eluted from adsorbent (mg)

m_a = amount of gold(III) ion adsorbed onto gel (mg)

4.7.1 Types of Desorbing Solution

The desorption of gold(III) ion was studied using different types and concentrations of eluent. Suitable eluent has to be compatible with the determination technique if an analytical application is desired. The selection of eluent depends on the adsorption mechanism and the possibility to perturb interaction between gold(III) ion and functional group of polymer.

As previously mentioned that the equilibrium of chloroaurate anion was driven to neutral chloroauric acid in strong acedic medium, an acidic solution was thus attractive as eluting solution. In addition, for the determination of gold(III) ion using FAAS, hydrochloric acid (HCl) solution was appropriate and firstly selected as an eluent. 5% (v/v) HCl solution was preliminarily tested to elute gold(III) ion but the elution percentage was low, especially in the cases of copolymers. This unsatisfactory result attributed to high affinity of gold(III) towards sulfur active sites [89] that might also lead to irreversible binding [90]. In addition, Iglesias *et al.* [91] also noted that due to the soft character of sulfur and gold(III) ions, the desorption was quite difficult.

The alternative way for desorption is an elution by an eluent containing a ligand that should form stronger complex with gold(III) ion than MTEMA. Thiourea (TU), which is a well known complexing agent and has a high formation constant with many metal ions, was chosen. There are many reports that thiourea can form stable complexes with several metal ions such as Ag(I), Au(III), Cu(II), and Hg(II) [92-94]. According to the Hard and Soft Acid and Bases (HSAB) theory [95], the sulfur and the nitrogen atoms in thiourea have an easily polarizable lone pairs of electrons and is considered as a soft base, which would have a tendency to create complex with gold(III) ion as a soft acid. HSAB theory confirms that, the selective polymers containing sulfur or nitrogen donor atoms interact strongly with soft acid like gold(III) ion even in the presence of high concentration of protons. The released proton (H^+) can be attributed to the deprotonation of thiol form of thiourea moiety at the end of reaction as shown in Figure 4.26 [96].

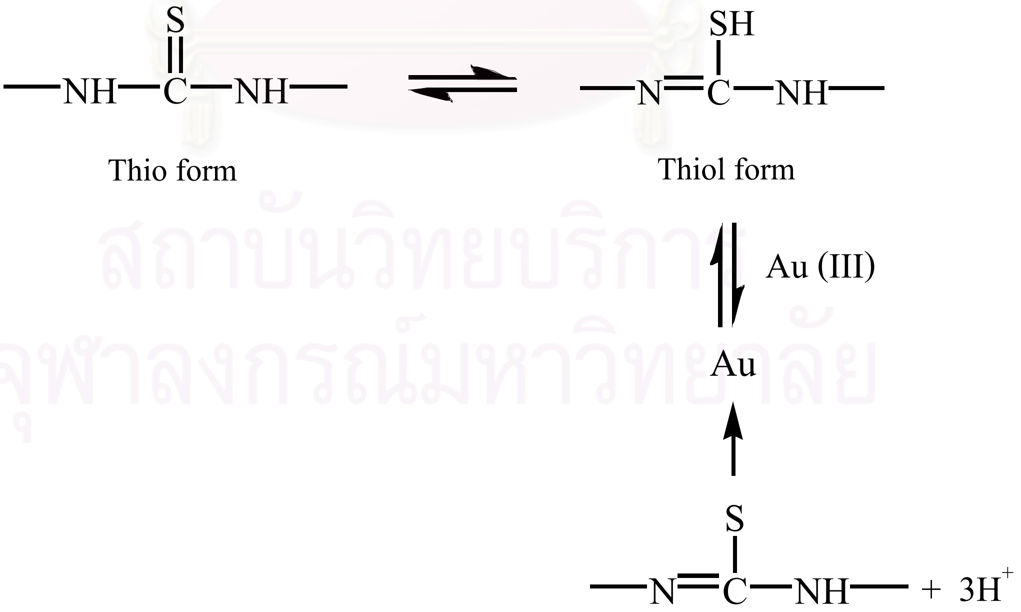
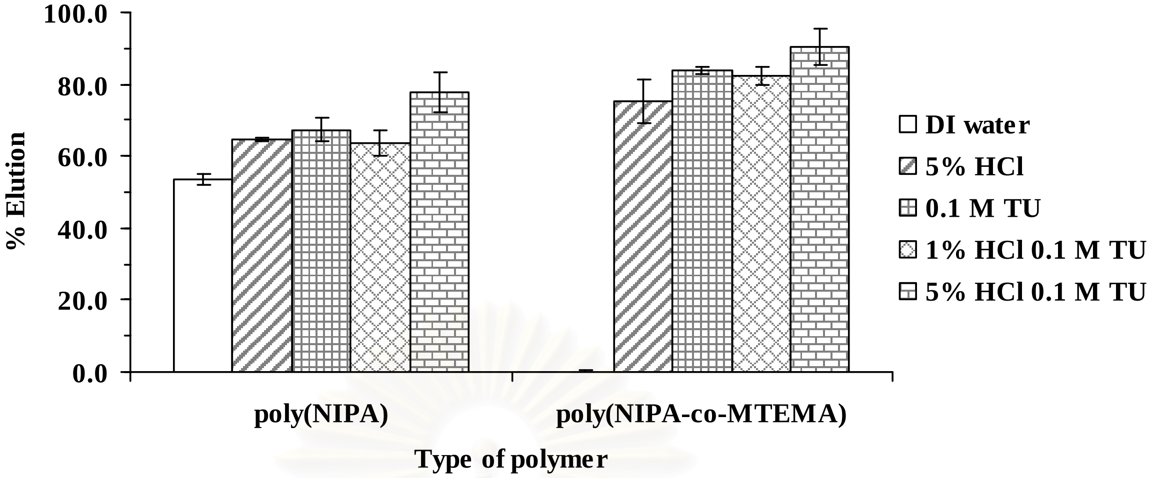


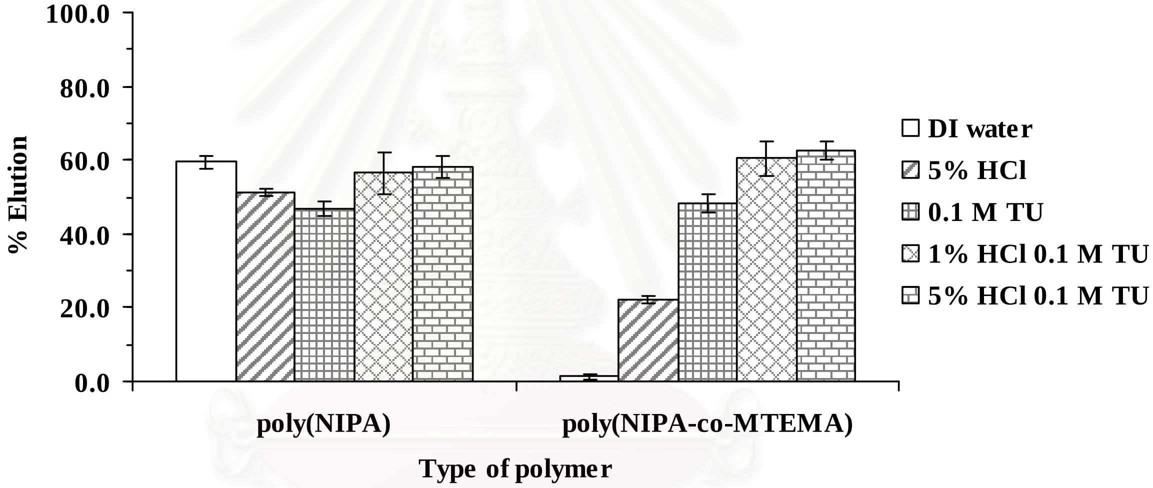
Figure 4.26 The deprotonation of thiol form of thiourea moiety at the end of reaction.

The desorption of gold(III) ion from the polymer was examined. Some different types and concentrations of desorption agent were tested for this purpose, for example DI water, HCl and TU, and TU in HCl solutions. Most eluents could desorb gold(III) ion from all polymers. Using of TU or TU in HCl could raise the elution percentage. There was no significant difference in % elution using 0.1 and 1 M TU. Next elution experiment would set up in triplicate using 5 different elutents, i.e. DI water, 5 % (v/v) HCl, 0.1 M TU, 0.1 M TU in 1 % (v/v) HCl, and 0.1 M TU in 5 % (v/v) HCl. The results were shown in Figure 4.27. The highest elution percentages were achieved with 0.1 M TU in 5 % (v/v) HCl for poly(NIPA) (Homo), poly(NIPA-*co*-MTEMA) (Homo), and poly(NIPA-*co*-MTEMA) (Hetero) with 77, 90, and 58 % elution, respectively. There was no significant difference in % elution (about 60 %) using DI water and 0.1 M TU in 5 % (v/v) HCl for poly(NIPA) (Hetero). Gold(III) ion was the most easily desorbed from poly(NIPA-*co*-MTEMA) (Homo).

In conclusion, the most suitable eluent was 0.1 M TU in 5 % (v/v) HCl for all polymer except for poly(NIPA) (Hetero) for which DI water was suitable. These eluents would be used in the next experiment.



(a)



(b)

Figure 4.27 Desorption percentage of gold(III) ion in different types of desorbing solution (a) homogeneous polymers and (b) heterogeneous polymers.

4.7.2 Effect of Desorption Time

The rate of desorption was investigated at 10 °C. The results in Figure 4.28 showed the desorption of gold(III) ion by 0.1 M TU in 5 % (v/v) HCl and DI water as a function of time. Gold(III) ion adsorbed in homogeneous polymers could be more eluted than that adsorbed in heterogeneous polymers. The elution percentages increased gradually until 2 hours after that the equilibrium was attained. The highest elution percentages occurred after 2-3 hours. The homogeneous polymers exhibited higher elution percentages (about 80-90%) than the heterogeneous polymers (about 50-60%).

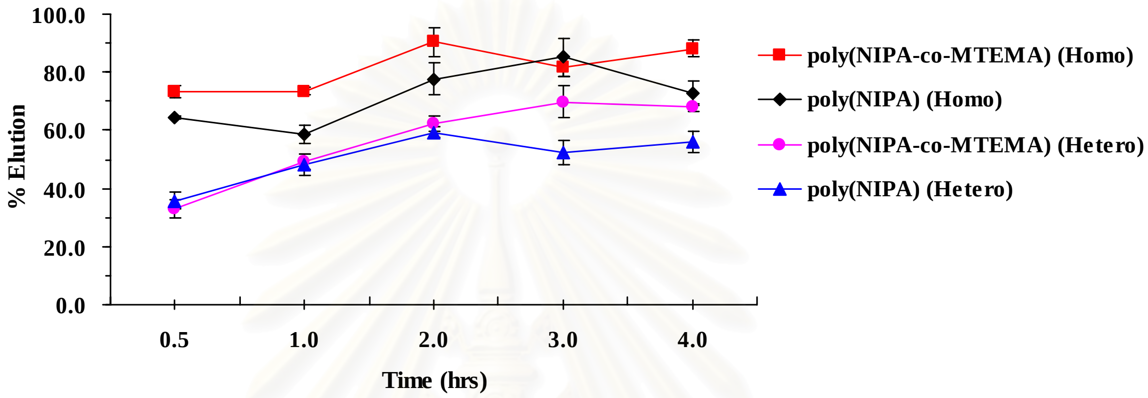


Figure 4.28 Effect of time on gold(III) ion desorption at 10°C.

4.7.3 Effect of Temperature

The desorption of gold(III) ion from each kind of polymer was examined in term of temperature using its appropriate eluent and 2 hours desorption time. The results are presented in Figure 4.29, the desorption of gold(III) ion gradually decreased with increasing the temperature. This result agreed with the properties of poly(NIPA) hydrogel as previously mentioned (see 4.6.4) that below the LCST (10°C) good desorption occurred. The highest % elution was around 60-90%. Furthermore, the temperature had a greater effect on the elution efficiency from poly(NIPA) gels more than that from poly(NIPA-*co*-MTEMA) gels. The elution from poly(NIPA-*co*-MTEMA) (Hetero) was not affected by temperature.

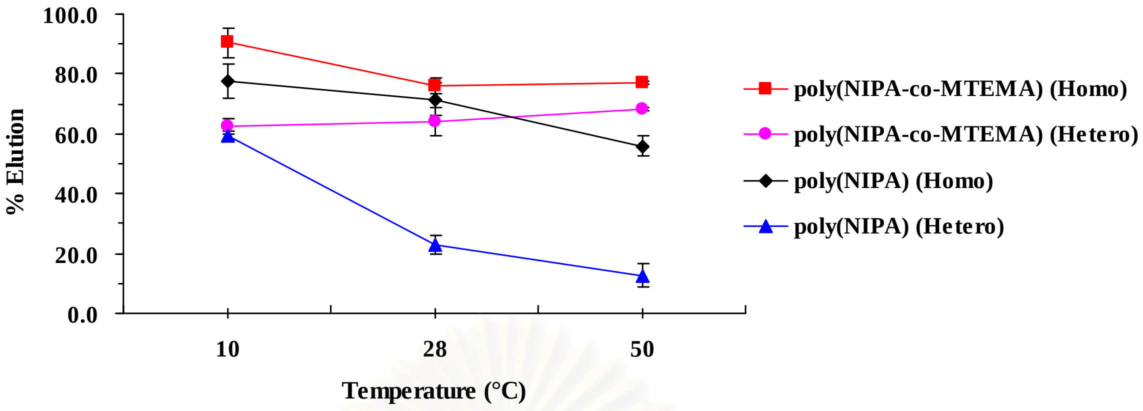


Figure 4.29 Effect of temperature on gold(III) ion desorption onto polymer.

In conclusion, the temperature was significant only for the desorption of gold(III) ion from poly(NIPA) gels. It reveals that poly(NIPA-*co*-MTEMA) gels exhibit less thermosensitive property than poly(NIPA) gels. And finally this result could confirm that the gold(III) ion adsorbed onto the copolymer gels via complexation mechanism.

CHAPTER V

CONCLUSION

A new random copolymer poly(NIPA-*co*-MTEMA) consisting of two monomers which are *N*-isopropylacrylamide (NIPA) and 2-(methylthio)ethyl methacrylate (MTEMA) crosslinked with bis(acrylamide) was successfully synthesized through free radical copolymerization in an aqueous system using $(NH_4)_2S_2O_8$ as initiator. Two kinds of poly(NIPA-*co*-MTEMA) called homogeneous and heterogeneous copolymer were prepared at $10^{o}C$ and $50^{o}C$, respectively. The homogeneous poly(NIPA-*co*-MTEMA) behaved temperature-responsive or hydrogel property and had a lower critical solution temperature (LCST) in water in the vicinity of $32^{o}C$. The synthesized copolymers were exposed to gold(III) ion adsorption comparing with poly(*N*-isopropylacrylamide) or poly(NIPA). Various parameters influencing the adsorption and physical property of the copolymers were studied. The optimum condition for the synthesis of homogeneous and heterogeneous poly(NIPA-*co*-MTEMA) could be achieved with 10 mM MTEMA in 5.0 %(v/v) ethanol and 30 mM MTEMA in 20.0 %(v/v) ethanol, when starting with 1.0 and 1.5 M NIPA as main monomer, and 50 and 60 mM *N,N'*-methylenebisacrylamide (MBAA) as cross-linker, respectively.

The synthetic copolymers were characterized by Fourier Transforms Infrared (FT-IR) and Raman (FT-Raman) Spectroscopy, Scanning Electron Microscopy (SEM) Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). The results from all characterization techniques cannot evidently confirm the successful copolymerization probably due to a few amount of MTEMA.

The swelling behavior of the synthetic polymer was also investigated. It was found that both homogeneous poly(NIPA) and poly(NIPA-*co*-MTEMA) had quite similar swelling ratio while heterogeneous poly(NIPA) and poly(NIPA-*co*-MTEMA) showed significantly different swelling ratios, indicating that copolymers were successfully synthesized.

The synthesized polymers were used for the adsorption of gold(III) ion in aqueous solutions using batch method. The effect of pH and temperature of gold(III) ion solution, adsorption time, adsorbent size and surface area was investigated. The adsorption isotherms were also studied. Moreover, in the desorption study, the effect of types of desorbing solution, desorption time and temperature was investigated. The adsorption and desorption optimum conditions towards gold(III) ion are summarized in Table 5.1. Heterogeneous poly(NIPA-*co*-MTEMA) showed the highest adsorption efficiency but less thermosensitive polymers.

Table 5.1 Optimum conditions for the adsorption and desorption of gold(III) ion

Experimental parameters	*Homogeneous copolymer*	*Heterogeneous copolymer*
Adsorption		
Solution pH	1-3	1-5
Adsorption time (hours)	3	3
Temperature (^{o}C)	50	50
Adsorption isotherm	Langmuir & Freundlich	Freundlich
Desorption		
Type of desorbing solution	0.1 M TU in 5 % HCl	0.1 M TU in 5 % HCl
Desorption time (hours)	2-3	2-3
Temperature (^{o}C)	10	10

Suggestions for Future Work

- The synthesized copolymers shall be applied for real sample such as jewelry industry wastewater for gold and other precious metal recovery.
- Only rod form of the synthesized hydrogels was proposed in this study. There was limitation in the application. Other preparation method shall be examined to obtain other forms such as thin film, small particle or fiber in order to increase the specific or exchange surface area.
- These copolymers may be applied to prepare composite incorporating absorbents by filling inorganic constituent such as silica, hydroxyapatite for developing their properties.

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