สมบัติหยุ่นหนืดและการบวมตัวของไฮโครเจลอะคริลาไมด์โคพอลิเมอร์

นางสาวจิราพร วงแสวง

VISCOELASTIC AND SWELLING PROPERTIES OF ACRYLAMIDE
COPOLYMERIC HYDROGELS

Miss Jiraporn Wongsawaeng

A Thesis Submitted in Partial Fulfillment of the Requirements
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Thesis Title   VISCOELASTIC AND SWELLING PROPERTIES OF ACRYLAMIDE COPOLYMERIC HYDROGELS

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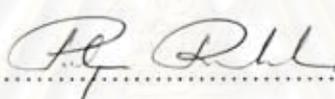
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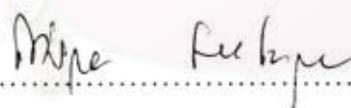
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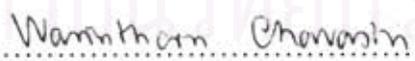
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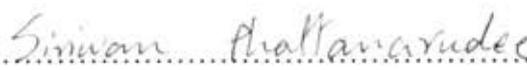
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สมบัติหยุ่นหนืดและการบวมตัวของไฮโครเจลระหว่างอะคริลาไมด์และมอนอเมอร์ร่วมที่
มีส่วนประกอบเป็นหมู่คาร์บอกซิลิก ได้แก่ กรดอะคริลิก กรดโครโทนิก ซึ่งสามารถแตกตัวครั้งได้
เดียว และ กรดมาเลอิก กรดอิทาโคนิก ซึ่งเป็นกรดที่สามารถแตกตัวได้สองครั้ง สังเคราะห์โดย
ปฏิกิริยาพอลิเมอไรเซชันแบบอนุมูลอิสระ ซึ่งริเริ่มปฏิกิริยาโดยคู่รีดอกซ์แอมโมเนียมเพอร์ซัลเฟต
และเอ็น, เอ็น', เอ็น', เอ็น' - เททระเมทิลเอทิลีนไดแอมีน สารเชื่อมขวางคือ เอ็น, เอ็น'- เมทิลีน
บิสอะคริลาไมด์ ภาวะที่เกิดปฏิกิริยาพอลิเมอไรเซชันคือ ความเร็วรอบในการกวน 250 รอบต่อนาที
อุณหภูมิ 45 องศาเซลเซียส ภายใต้บรรยากาศแก๊สไนโตรเจนภายในระยะเวลา 30 นาที ตัวแปรที่
ศึกษาในงานวิจัยนี้ ได้แก่ การกำหนดอัตราส่วนในการเติมทั้งหมด เช่น อัตราส่วนโดยโมลระหว่าง
อะคริลาไมด์ต่อมอนอเมอร์ร่วม ปริมาณสารริเริ่มปฏิกิริยา ปริมาณสารริเริ่มปฏิกิริยาร่วม ปริมาณ
สารเชื่อมขวาง ศึกษาลักษณะเฉพาะของพอลิเมอร์ที่สังเคราะห์ได้โดย RAMAN Spectroscopy และ
Scanning Electron Microscopy ทดสอบความแข็งแรงของไฮโครเจลด้วยเทคนิครีโอโลยี พบว่า ค่า
มอดุลัสสะสม (G') มีค่าสูงเมื่อค่าการดูดซึมน้ำต่ำ การคำนวณหาน้ำหนักโมเลกุลระหว่างการเชื่อม
ขวาง ($\overline{M}_c$) และ χ จากการทดลอง 2 วิธีคือการทำรีโอโลยี และ การทดลองบวมตัวของไฮโครเจล
ที่มีมอนอเมอร์ร่วมเป็นหมู่ของกรดที่มีการแตกตัวได้ครั้งเดียวให้ใช้สมการที่อ้างอิงจากทฤษฎีของ
Flory-Rehner และวิธีการของ Brannon-Peppas และ Peppas ส่วนมอนอเมอร์ร่วมที่มีหมู่เป็นกรดที่
แตกตัวได้สองครั้ง ให้ใช้สมการที่ดัดแปลงจากสมการของ Şen และ Güven พบว่าจากการทดลอง
ทั้ง 2 วิธี ได้ค่า $\overline{M}_c$ ที่แตกต่างกันมาก เนื่องจากในโครงสร้างของไฮโครเจลมีความไม่เป็นเนื้อ
เดียวกัน

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต...
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4872244523: MAJOR PETROCHEMISTRY AND POLYMER SCIENCE

KEY WORD : HYDROGEL / MOLECULAR WEIGHT BETWEEN CROSSLINKS / VISCOELASTIC / SWELLING

JIRAPORN WONGSAWAENG: VISCOELASTIC AND SWELLING PROPERTIES OF ACRYLAMIDE COPOLYMERIC HYDROGELS. THESIS ADVISOR: PROF. SUDA KIATKAMJORNWONG, Ph.D., THESIS CO-ADVISOR: NISPA SEETAPAN, Ph.D., 96 pp.

The viscoelastic and swelling properties of polyacrylamide-based hydrogels containing ionic moiety were investigated as a function of anionic comonomer structure. The hydrogels were synthesized from free-radical crosslinking copolymerization of acrylamide and ionic comonomer; i.e. monoprotic acid: acrylic acid, crotonic acid and diprotic acid: maleic acid, itaconic acid. Initiation by a redox initiator of ammonium persulfate (APS) and $N,N,N',N'-$ tetramethylethylenediamine (TEMED). The N,N'-methylenebisacrylamide (MBA) crosslinking agent was used in the copolymerization. The copolymerization was carried out at 250 rpm, 45 $^\circ$C under nitrogen atmosphere for 30 minutes. Feeding composition of all components, i.e. monomer, comonomer, initiator, co-initiator, and crosslinker was fixed to the same value for all copolymeric systems. The synthesized polymers were characterized by RAMAN Spectroscopy and Scanning Electron Microscopy. The mechanical strength of the swollen hydrogels was measured by a rheological method. The copolymers have a higher storage modulus (G′) which agrees with the lower water absorption. The average molecular weight between crosslinks ($\overline{M}_c$) and polymer-solvent interaction parameter (χ) was determined from swelling data using equations based on Flory-Rehner swelling theory, and the approaches of Brannon-Peppas and Peppas on monoprotic acid-containing hydrogels. The equation modified by Şen and Güven was used for determining $\overline{M}_c$ and χ for diprotic acid-containing hydrogels. Equilibrium elastic modulus was used to determine $\overline{M}_c$ based on the polymer network theory. Large difference between $\overline{M}_c$ from both measurements was observed. This difference on the basis of different theories indicates an existence of an intrinsic heterogeneous structure within the hydrogels.

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

Academic Year: 2007   Advisor's Signature..............................

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CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SCHEME

LIST OF ABBREVIATIONS

SAPs	superabsorbent polymers
AM	acrylamide monomer
AA	acrylic acid monomer
CA	crotonic acid monomer
MA	maleic acid monomer
IA	itaconic acid monomer
N-MBA	*N, N'*-methylenebisacrylamide
APS	ammonium persulfate
TEMED	*N, N, N', N'*,-tetramethylethylenediamine
^{o}C	degrees Celsius
min	minute
rpm	revolutions per minute
% wt	percent by weight
r	reactivity ratio
MW	molecular weight
$\overline{M}_c$	average molecular weight between crosslinks
I	ionic strength of the swelling
v_{2m}	polymer volume fraction in the equilibrium-swollen system
ρ_2	polymer density

v_{2r}	polymer volume fraction in the relaxed state
K_a	dissociation constant of monoprotic acid
K_{a1}	first dissociation constants of diprotic acid
K_{a2}	second dissociation constants of diprotic acid
g	gram
SEM	Scanning Electron Microscopy
TGA	Thermal Gravimetric Analysis
h	hour
Q	the equilibrium water absorbency or equilibrium degree of swelling
q_v	equilibrium swelling by volume
g g^{-1}	gram per gram
psi	pound per square inch
χ	interaction parameter of polymer with solvent
V_1	molar volume of solvent
f_i	mol fraction of the ionic unit
ϕ	number of branches originating from a crosslinking site
c_o	initial concentration of monomers (mol cm^{-3})

M_r	molecular weight of the repeating unit
M_n	molecular weight of a neutral unit
$M_{c\ (stoi.)}$	stoichiometric molecular weight between crosslinks
X	crosslinking ratio
G'	storage modulus
G''	loss modulus
G_e	equilibrium elastic modulus
G^*	complex elastic modulus
η^*	complex viscosity
ω	angular frequency
M	molar
LVE	linear viscoelastic
Hz	hertz
R	gas constant
T	temperature

CHAPTER I

INTRODUCTION

1.1 Scientific Rationale

Superabsorbent polymers (SAPs) are materials that have the ability to absorb and retain large volumes of water and aqueous solutions. It consists of polymers of long chain molecules, crosslinked to create a network and immersed in a liquid medium. Their ability to absorb water is due to the presence of hydrophilic groups such as -OH, -CONH-, $-CONH_2$, -COOH, and $-SO_3H$. The most important application of superabsorbent is their use in personal hygiene products such as incontinence products like disposable diaper for infants and adults or feminine hygiene product, medicine for the drug delivery system, wastewater treatment, gel actuator, etc. Other applications include conservation of water in agriculture and horticulture, insulation of underwater cables and application concerning recreational activities like artificial snow in indoor skiing arenas [1-3].

In recent years, polyacrylamide-based hydrogels have received considerable attention because of their use in many applications: specific sorbents, support carrier in biomedical engineering, aggregating agent, soil improvement agent, polymer processing or improving textiles, paper strengthening agent, adhesive, paints, oil salvaging agents, etc. Desired features of superabsorbents are high swelling capacity, high swelling rate and high strength of the swollen gel. More studies on polyacrylamide gels have focused in the gelation conditions, swelling properties, phase transitions in swollen gels and their application. However, there are few studies

that deal with the determination of the structure of polyacrylamide gels and its derivation from viscoelastic measurements [4-5].

As matter of fact, the viscoelastic and the swelling properties of poly[acrylamide-*co*-(acrylic acid)], poly[acrylamide-*co*-(crotonic acid)], poly[acryl-amide-*co*-(maleic acid)] and poly[acrylamide-*co*-(itaconic acid)] can indicate some insight properties of the superabsorbent polymers. Therefore, the principle objective is to study correlations between gel strength and water absorbency. It was performed by two methods: (i) swelling experiment and, (ii) viscoelastic measurement. The swelling experiment of polymer gels provides a good approach to determination of the average molecular weight of the network chains in the gel. Likewise, the viscoelastic experiment permits us to determine the shear modulus, G, which can be related to the molecular weight of the network chains by the theory of rubber elasticity.

1.2 Objectives of the Research Work

The objectives of this research are as follows:

1.2.1 To synthesis the superabsorbents of poly[acrylamide-*co*-(acrylic acid)], poly[acrylamide-*co*-(crotonic acid)], poly[acrylamide-*co*-(maleic acid)] and poly[acrylamide-*co*-(itaconic acid)] by solution polymerization. Effects of the reaction parameters such as function group of carboxylic acid in vinyl monomer, equilibrium degree of swelling are manipulated to have maximum or minimum water absorption.

1.2.2 To study the swelling properties of the resultant superabsorbent polymers.

1.2.3 To study viscoelastic properties of the swollen gel of the superabsorbent polymer.

1.2.4 To characterize some physical properties of the synthesized superabsorbent polymers.

1.2.5 To study the effect of monoprotic and diprotic acids on water absorption and gel strength.

1.3 Expected Benefits Obtainable from the Development of This Research

1.3.1 Obtained a relation between viscoelastic properties and equilibrium swelling degree of poly[acrylamide-*co*-(acrylic acid)], poly[acryl-amide-*co*-(crotonic acid)], poly[acrylamide-*co*-(maleic acid)] and poly[acrylamide-*co*-(itaconic acid)]

1.4 Scope and Workplan of Research Work

The Acrylamide copolymeric superabsorbent polymers were prepared by free radical polymerization in aqueous solution of acrylamide (AAm) with acrylic acid (AA), crotonic acid (CA), maleic acid (MA) and itaconic acid (IA) as comonomer with ammonium persulphate (APS) and *N, N, N', N'*-tetramethylethylenediamine (TEMED) as an initiator and co-intiator, respectively, and *N, N'*-methylene bisacrylamide (N-MBA) as a crosslinking agent, at the temperature of 45 °C for 30 min. The influences of the reaction parameters on properties of the synthesized

copolymer were investigated. The reaction procedures to obtain the result were as follows:

1.4.1   Literature survey and in-depth study of this research work.

1.4.2   Synthesis of poly[acrylamide-*co*-(acrylic acid)], poly[acrylamide-*co*-(crotonic acid)], poly[acrylamide-*co*-(maleic acid)] and poly[acryl-amide-*co*-(itaconic acid)] at the mole percent of monomer ratio 96/4, 1%wt of APS, 1%wt of N-MBA and 2%wt of TEMED via solution polymerization at 45 $^\circ$C.

1.4.3   Synthesis of poly[acrylamide-*co*-(acrylic acid)], poly[acrylamide-*co*-(crotonic acid)], poly[acrylamide-*co*-(maleic acid)] and poly[acryl-amide-*co*-(itaconic acid)] via solution polymerization by setting the following reaction conditions.

a) The mole percent of monomer ratios (acrylamide/acrylic acid) at 90/10 and 98/2 with 1%wt of APS, 1%wt of N-MBA and 2%wt of TEMED [6].

b) The mole percent of monomer ratios (acrylamide/crotonic acid) at 90/10 and 98/2 with 1%wt of APS, 0.5%wt of N-MBA and 2%wt of TEMED [7].

c) The mole percent of monomer ratios (acrylamide/maleic acid) at 92/8 and 99/1 with 1%wt of APS, 1%wt of N-MBA and 10%wt of TEMED [8].

d) The mole percent of monomer ratios (acrylamide/itaconic acid) at 96/4 and 99/1 with 1%wt of APS, 0.5%wt of N-MBA and 2%wt of TEMED [9].

1.4.4   Characterization of the synthesized polymer by means of:

a) Identification of functional group of copolymer by Raman spectroscopy.

b) Surface morphology of the copolymer by scanning electron microscopy.

c) Thermal properties of the copolymer by thermogravimetric analysis.

d) The water absorbency of the synthesized polymer in distilled water, and in phosphate buffer solution.

1.4.5   Viscoelastic properties of the swollen copolymer gel.

1.4.6   Summarizing the results and preparing a thesis.
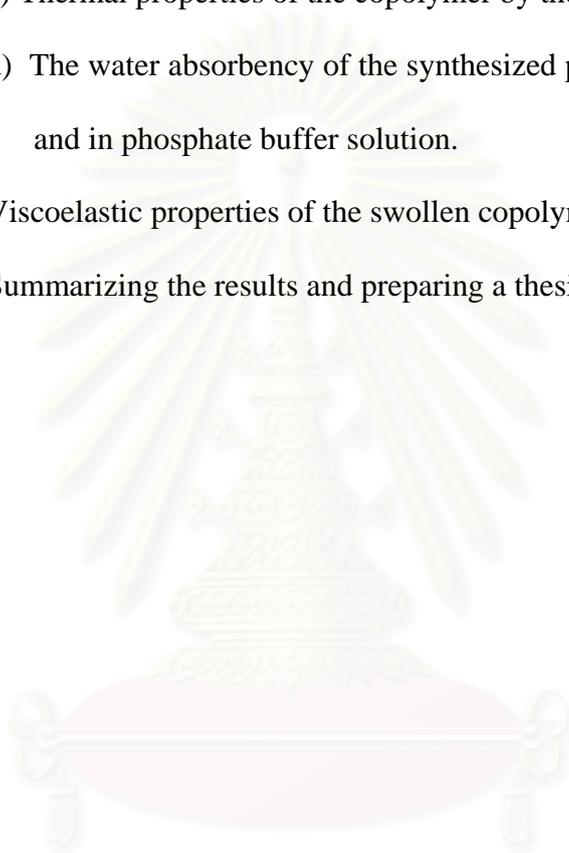
CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Superabsorbent Polymers (SAPs)

2.1.1 General properties of superabsorbent polymers

Superabsorbent polymers are polymeric materials characterized by both hydrophilicity and insolubility in water. They are capable of absorbing very large amounts of aqueous fluids. Their hydrophilicity arises from the presence of water-solubilizing groups such as -OH, -COOH, $-CONH_2$, -CONH-, $-SO_3H$, and so on. The insolubility arises from the presence of a three-dimensional network. The crosslink may be covalent, electrostatic, hydrophobic, or dipole-dipole in character. The water absorption may exceed a factor of 100 based on dry gel weight [10]. These polymers have found extensive commercial applications as sorbents in personal care products such as infant diapers, feminine hygiene products, and incontinence products, and have received considerable attention for a variety of more specialized applications including matrices for enzyme immobilization, biosorbents in preparative chromatography, materials for agricultural mulches and matrices for controlled release devices [11].

They are interesting materials exhibiting both liquid-like and solid-like properties. The liquid-like properties result from the fact that the major constituent of gels is usually a liquid. On the other hand, a gel can retain its shape since it has a shear modulus which becomes apparent when the gel is deformed. The modulus is due to the crosslinking of the polymers in the form of a network. They have an ability to absorb and hold large amounts of water. Superabsorbent polymers can be neutral or

ionic in nature. Superabsorbent polymers take up liquid by a diffusion mechanism whereas traditional absorbents, like cotton, show a convective mechanism. Diffusion is a molecular phenomenon wherein water molecules move at random as a result of their thermal energy. Increasing the temperature makes the molecules move faster, and the diffusion processes occur at a faster rate.

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 the direction opposite to that of the water molecules in order to accommodate the volume of the additional molecules of water. Because polymer molecules are much larger than water molecules, they diffuse much more slowly. Not only are polymer molecules larger, but they are also connected one to the other by the crosslinks, so that polymers do not dissolve in the water and can be used as a superabsorbent [12].

2.1.2 Mechanism of swelling of superabsorbent polymers

In contact with water, the hydrophilic polymer backbone containing hydrophilic functional groups interacts with the solvent accompanied by energy decrease and entropy increase. Hydration and the formation of hydrogen bonds are two sources for such polymer/solvent interactions. The polymer chains also tend to disperse in the given volume of solvent. This leads to a higher number of allowed configurations for the system, which is equivalent to a higher degree of entropy.
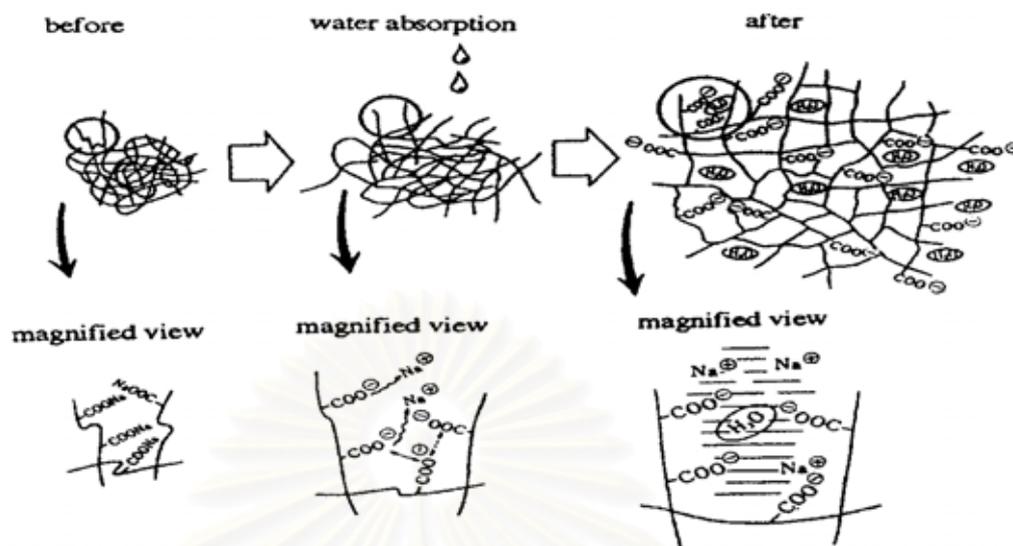
Figure 2.1 Water absorption in ionic polymer network.

For ionic polymers, the solvent/polymer interactions include more simple mixing term. Figure 2.1 shows the absorption mechanism of an example of superabsorptive resin. The negative charges of the carboxyl groups repel one another and are compensated by the positive charges of the sodium ions, in order to maintain electrical neutrality. When the polymer comes into contact with water, the solvent diffuses into the polymer network and solvates the sodium ions. Water with high dielectric constant lowers the attractive forces between the sodium ions and the negative charge of carboxylate groups. As in solutions of simple salts, the sodium ion are released and become freely moveable within the gel. Hence, they contribute to the osmotic pressure. But for them, it is impossible to leave the gel region due to the attraction forces of the negative charges, which are fixed along the polymer backbones. The sodium ions, therefore, behave as if they are trapped by an invisible, semi-permeable membrane. The driving force for swelling is then the difference

between the osmotic pressure inside and outside of the gel. Increasing the salinity and by this the osmotic pressure of any external aqueous solution lowers the absorption capacity of the gel for that fluid [13].

More detailed configuration of the ionic superabsorbent polymers and swelling mechanism are presented in Figure 2.2 are restricted in swelling by elastic retraction forces of the network. The more the chains separate from each other, the more stiffened the originally coiled polymer chains become. This decreases the entropy of the chains. Finally, there is a balance between the trend toward infinite dilution of the chains and the retractive forces. Higher crosslink densities give network with stronger retractive forces and superabsorbent polymers with lower degree of swelling at equilibrium
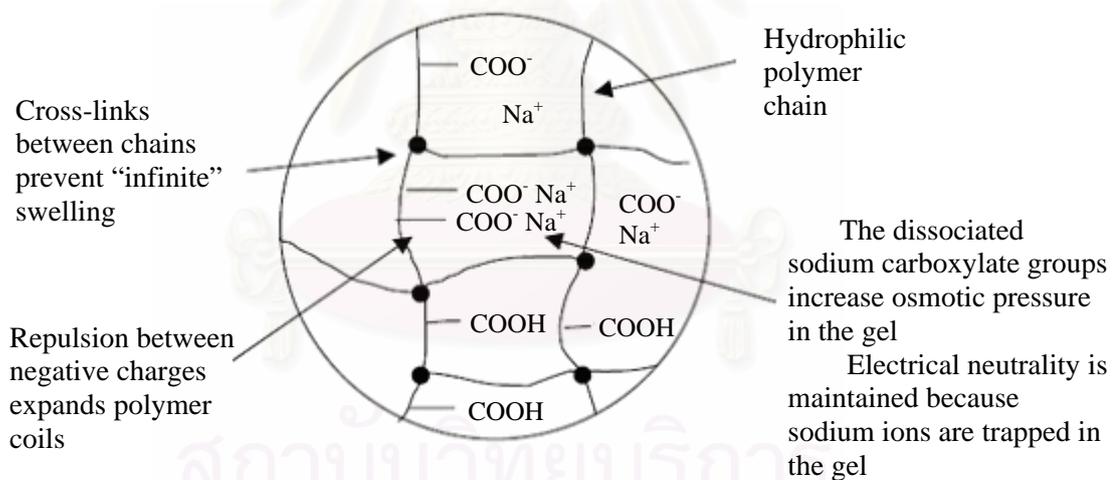
Figure 2.2 Mechanism of swelling of superabsorbent polymers

2.2 Characteristics of the Polymerization

2.2.1 Monomer concentration

The monomer concentration in the polymerization mixture is one of the key parameters affecting both the properties of polymer and the economics of the process.

Polymerization at high temperature favors the termination step of the propagating radical chains, which leads to the low molecular weight. On the other hand, grafting reactions which formally lead to higher crosslink-link densities in the gel can occur preferably at higher polymer concentrations and at high reaction temperatures. When the monomer concentration is raised, higher polymer concentration is achieved at lower conversion and the reaction temperature may increase more rapidly due to the lower heat capacity of polymer compared to water. For these reasons, high monomer concentrations provide unfavorable ratios between the centrifuge capacity and the percentage of soluble polymer [13].

2.2.2 Neutralization

Neutralization can be done either before or after the polymerization. From a technical point of view, preneutralization is preferred due to the relative ease of neutralizing the liquid monomer solution.

The post neutralization step requires an even distribution of the neutralization agent into the gel mass. Preferably this is done during a chopping step. Either a weak base neutralizing agent or a hydrolytically stable cross-linker has to be used in order to avoid extended cleavage of the ester-containing cross-links [13].

2.2.3 Free-radical Initiator

The polymerization in the aqueous phase is initiated by free radicals which originate from the decay of initiator molecules. The initiator may arise from thermal decay or by means of a reduction-oxidation (redox) reaction, or by a combination of these.

Frequently, the polymerizations are initiated at room temperature with the aid of a redox couple. After the reaction mass is heated up, the polymerization proceeds further by the thermal decay of a second initiator. Starting at low temperature minimizes undesirable high peak temperature. Initiator concentrations are always adjusted 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 concentrations [13].

2.2.4 Crosslinkers

The crosslinking agents typically used in the preparation of superabsorbent polymers are di-, tri-acrylate esters such as diethylene glycol acrylate and 1,1,1,-trimethylolpropanetriacrylate, as shown in Figure 2.3 [1].
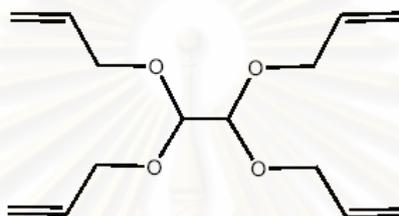
(a) Tetraallylethoxy ethane
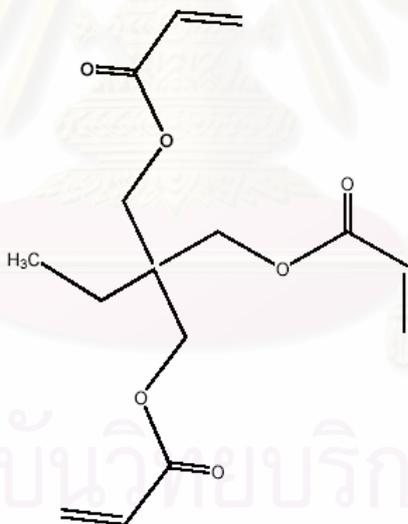
(b) 1,1,1-Trimethylolpropanetricrylate (TMPTA)

Figure 2.3 Some common types of crosslinker.

Crosslinking is the formation of chemical links between molecular chains to form a three-dimensional network. The small amounts of crosslinking agents play the major role in modifying the properties of superabsorbent polymers. The degree of soluble polymer is important in determining the optimum crosslinker level and performance of the product. Small amount of a crosslinker concentration yields superabsorbent polymer with a high swelling capacity and low strength against pressure. The crosslinking agent affects the amount of soluble polymer formed during the polymerization. The tendency of a crosslinking agent to be depleted earlier in the polymerization is reflected in its reactivity ratio with the monomer. The degree of crosslinking and the details of the molecular structure quantified in terms of the crosslink density which have a profound impact on the swelling characteristics of the crosslinked system [13].

2.2.4.1 Chemical crosslinking

Crosslinking is the joining of molecules – generally joining two or more macromolecules with a smaller molecule. The most important type in the case of superabsorbents, and the most common, is the covalent cross-link. In SAP manufacture, the most common types of crosslinker are organic molecules that contain two or more polymerizable double bonds. These molecules are incorporated into the backbone of the polymer chains as they grow during the polymerization reaction shown in Figure 2.4. Several factors determine the incorporation of the crosslinkers into the polymer and their distribution along the polymer backbone. The molecules of monomer and polymerization double bonds are incorporated into the backbone of the polymer chains as they grow during the polymerization reaction.
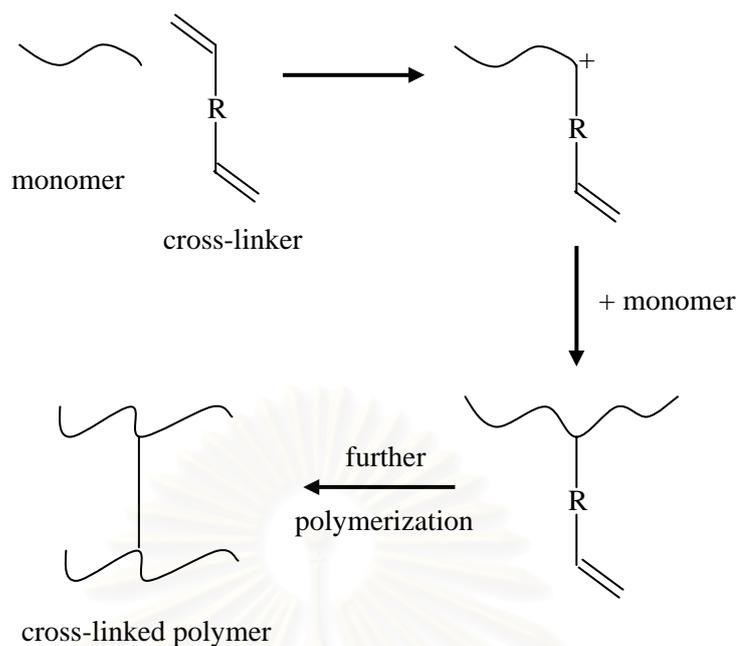
Figure 2.4 Schematic illustration of core crosslinking reaction [1]

2.2.4.2 Surface crosslinking

Surface crosslinking is a newer process step used to improve the absorption pressure profile. Historically, the unavoidable increase in the amount of soluble polymer with decreasing crosslink density was the practical limiting factor in increasing the centrifuge capacity. However, increasing the free swelling capacity of a SAP is accompanied by lower uptake of the liquid when pressure is applied during the swelling period. At a first glance, this may appear contradictory, but it follows from the theories of network behavior. The swollen gel can be considered as a swollen rubber. In agreement with the network theories of rubber elasticity, elastic modulus drops when the crosslinking density in the gel is lowered. The lower the gel modulus, the more likely the gel deforms under an external pressure, and the more thermodynamically compressible it becomes. Deforming of the gel particles closes the voids between the particles which are necessary in order to supply the SAP granules with liquid by capillary forces. Increasing the free swell capacity by conventional

means without changing the particle structure therefore leads to a strong drop in the overall swelling capacity under pressure.

Post cross-linking of the SAP particles significantly improves the property profile in terms of swelling capacity under pressure. The post crosslinking is done at the particle surface after the particles have been brought to their final size. The technology provides a crosslinking density gradient from the center of the particle towards the surface with a higher crosslinking density at the surface, as shown in Figure 2.5 [13].

Lower crosslink density at the centre of the particle

High crosslink density on the particle surface
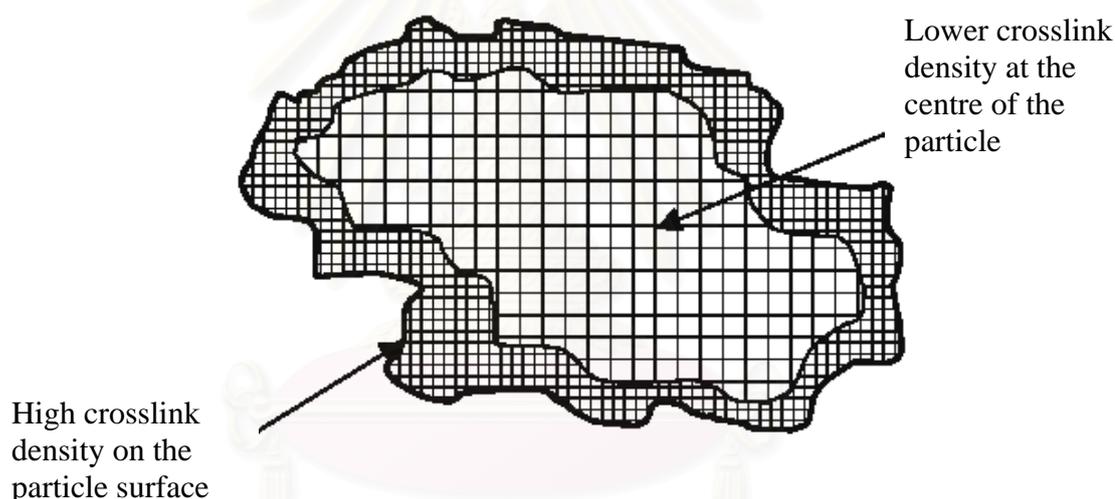
Figure 2.5 A surface-crosslinked superabsorbent particle

In another approach, additional crosslinking agent is brought onto the surface together with some aqueous monomer solution and polymerized. In yet another approach, the polymer granules are heated at high temperature in the presence of an oxidizing agent. Under these conditions, the oxidizing agent cleaves the polymer chains in the particle center, which has an effect equivalent to a reduction in the crosslink density [13].

2.3 Preparation of Superabsorbent Polymers

Monomers used in the synthesis of ionic polymer networks contain either an ionizable group, a group that can be hydrolyzed, or a group that can undergo a substitution reaction after the polymerization is completed. The hydrogels can contain weakly acidic and basic groups such as carboxylic acids, primary or secondary substituted amines, or strongly acidic and basic groups such as sulfonic acids and quaternary ammonium salts. The most commonly used crosslinking agents are ethylene glycol dimethacrylate, *N, N´*-methylene bisacrylamide, and divinyl benzene [3].

2.3.1 Bulk polymerization

Bulk polymerization is the simplest technique which involves only monomer and monomer-soluble initiators. High rate of polymerization and degree of polymerization occur because of the high concentration of monomer. However, the viscosity of reaction increases with the conversion which generates heat during polymerization. These problems can be avoided by controlling the reaction at low conversions.

The advantage of bulk polymerization is that it produces high molecular weight polymer with high purity.

2.3.2 Solution polymerization/crosslinking

In solution co-polymerization/crosslinking reactions, the ionic or neutral monomers are mixed with an appropriate multifunctional crosslinking agent. If the monomers and the crosslinking agent are not miscible, then a common solvent is introduced. The polymerization reaction is initiated thermally, by UV-irradiation, or by a redox initiator system. This mode of polymerization gives a random polymer and

the polymerization is allowed to go to completion. The major advantage of solution over bulk polymerization is that the solvent serves as a heat sink and thus minimizes temperature control problems. The solvent choice can add greater flexibility in processing and in altering the gel properties. The synthesized network needs to be washed to remove unreacted monomers, oligomers and other impurities and can be swollen to equilibrium to give a gel.

If the amount of water present during solution polymerization is greater than the water content corresponding to the equilibrium degree of swelling, a phase separation occurs during co-polymerization/crosslinking and a heterogeneous polymer network (hydrogel) is formed, consisting of domains of highly crosslinked microgels which are connected by loosely crosslinked chains. This phenomenon is known as microsyneresis. If the amount of water present during polymerization is smaller than the water content corresponding to the equilibrium degree of swelling, the ensuing gel is non-porous. [3].

2.3.3 Suspension polymerization

Suspension or emulsion polymerization is a preferred method to synthesize spherical hydrogel microparticles with size ranging from about 1 μm to 1 mm in diameter. In suspension polymerization, the monomer solution is mechanically dispersed into a non-solvent forming droplets and the suspension is stabilized by the addition of a stabilizer. The polymerization is initiated by thermal decomposition of a free radical initiator. The suspending non-solvent phase acts as a heat sink, thereby assuring good temperature control. The formed spherical hydrogel particles can be easily recovered from the suspension and extracted with a good solvent to remove any residual monomers. The particle size, shape, and size distribution depend upon the suspending agent, stirring speed and impeller design [3].

2.3.4 Other crosslinked structure

Hydrogels can be prepared by other method. For example, physical crosslinks including entanglement, charged complexes, junctions due to hydrophobic or specific interactions, or crystallites can lead to the formation of hydrogel. These crystallites can act as physical crosslinks and prevent the gel from dissolving. Linear polymers can form complexes due to hydrogen bonding or ionic interactions.

Various polymerization reactions can be used to control properties of polyelectrolyte networks. The hydrophilic/hydrophobic balance can be manipulated by choosing a proper combination of two monomers. The degree of crosslinking as well as the morphology of the polymer network can be altered or fixed by an appropriate reaction method. Other important characteristics can be controlled such as tacticity, i.e. the arrangement of the ionizable and pendent groups as these are strong functions of the solvent, concentration, and temperature [3].

2.4 Application of Superabsorbent Polymers

The capacity to absorb large amounts of aqueous solution makes superabsorbent polymers attractive in many different applications. Superabsorbent polymers have replaced many 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 polymers 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 surroundings as vapor has also been used in various ways, for example, as humidity-controlling products or as soil conditioners. Superabsorbent polymers may also be used to release water-soluble substances from within the network structure into the surroundings as a solution. For example, pharmaceuticals or fertilizers may be incorporated into superabsorbent polymers to yield controlled release products. Another characteristic of the swollen polymer is its rubbery nature, which has been used to control the consistency of products as diverse as cosmetics or concrete or to contribute a soft, yet dry, feel to a product like a hot or cold pack for sore muscles. The soft, rubbery nature may also be employed to impact sealing properties to products that are in contact with water or aqueous solutions, for example, underground wires and cables [12]. The summarized applications of SAP are shown in Table 2.1.
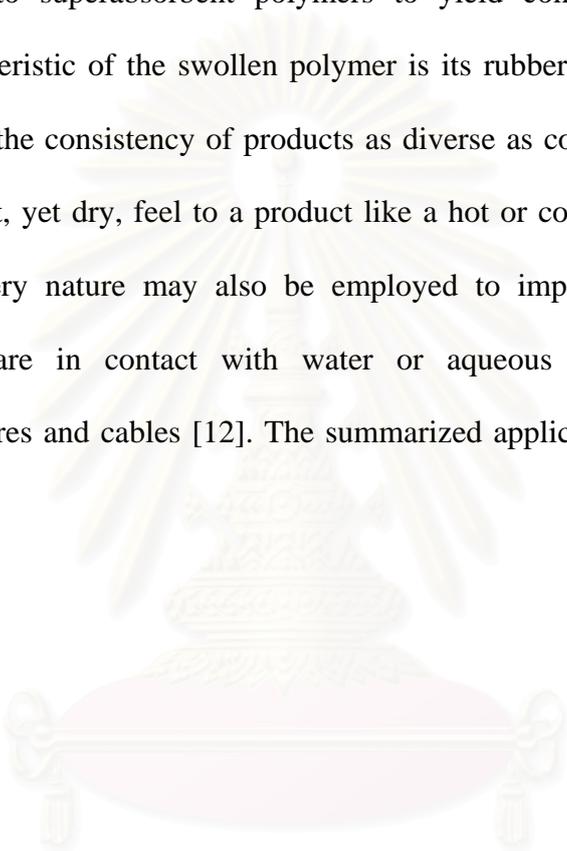
Table 2.1 Possible Applications of Superabsorptive Polymers [14]

Application Fields	Products
Sanitary products	Sanitary napkins, Diapers, Breast pads
Agriculture gardening	Water-retaining agent in soil, Dry preventives for samplings, Cultivation plot for mushroom, Seed beds in fluid
Civil engineering, Architecture	Artificial moss, Dew preventing agents in walls, Water sealing agents, Substitutes for sandbags, Sludge solidification agents
Cosmetics, Toiletries	Water-retaining agents in concretes, Sweat, Gel aromatics, Pocket warmers, Disposal chamber pots, Mud shielding work
Medical	Wound dressings, Sheets for surgical operation, Control release agents for drug, Disintegrators in tablets, Gelation of blood waste, Wet plaster
Food industry	Agent for preservation of freshness, Gelling agents, Cold keeping hydrogels, Viscosity enhancing additives
Others	For preventing film, Dehydration agents in oil, Moisture sensor, Control release agents for drug, Disintegrators in tablets, Hydrogel for fire fighting, Artificial snow, Water bed

2.5 Molecular Weight between Crosslinks

The average molecular weight between crosslinks ($\overline{M}_c$) is a term generally used to explain the network structure of hydrogels. It describes the average molecular weight of polymer chains between two consecutive junctions [15]. Several theories have been developed to determine $\overline{M}_c$ in polymeric networks. Flory and Rehner [16, 17] proposed the equilibrium swelling theory for polymer networks, where polymer chains are reacted in the solid state, and exhibit a Gaussian distribution. This theory deals with neutral polymer chains and tetrafunctional crosslinking within the network. A similar model by Peppas and Merrill [18] was developed for a polymer network system, where crosslinks are introduced in the swollen state as in the case of solution polymerization. Into an expression of Flory and Rehner, the term representing the polymer volume fraction in the relaxed state; i.e. after crosslinking but before swelling, was included.

Later on, the molecular treatment of rubber-like elasticity has been improved by Flory and Erman [19, 20] including detailed swelling-structure relationships [21-24]. These relationships, theories and the results were reviewed for the characterization of model and randomly crosslinked networks [25-27]. In the highly swollen state, the constrained junction theory [19] predicts a real network exhibiting properties closer to those of the phantom network model. The average molecular weight between crosslinks for nonionic networks is expressed as [27]

$$\overline{M}_c = -\frac{\left(1 - \dfrac{2}{\phi}\right)V_1 \rho_2 v_{2r}^{2/3} v_{2m}^{1/3}}{\left[\ln(1 - v_{2m}) + v_{2m} + \chi v_{2m}^{2}\right]}$$

(2.1)

where $\overline{M}_c$ is the average molecular weight between crosslinks, ρ_2 is the polymer density, V_1 is the molar volume of the swelling agent, v_{2m} is the polymer volume fraction in the equilibrium-swollen system, v_{2r} is the polymer volume fraction in the relaxed state, the front factor $(1-2/\phi)$ is for phantom network, ϕ is the number of branches originating from a crosslinking site and χ is the Flory polymer-solvent interaction parameter.

For nonionic network, the swelling behavior is thermodynamically dominated by contributions of the chemical potential of mixing and the chemical potential of elasticity. Upon swelling in aqueous solvent, diffusion of water into the network is driven by forces generated from the difference between the chemical potential of water inside and outside network until the equilibrium swelling is reached. Elastic contribution prevents the network from becoming completely dissolved. If networks contain ionizable groups within polymer chains, an additional force from ionic contribution influences on swelling. An increase in swelling is expected due to charge localization within the ionic hydrogel [28, 29].

Brannon-Peppas and Peppas [30] derived an equation to describe this ionic contribution term on equilibrium swelling behavior of monoprotic acid containing hydrogels. The equation is, however, based on an affine network model and can be used for networks prepared from a crosslinking reaction of homopolymers with a previously known number-average molecular weight. χ had to be determined previously for the application of the equation to calculate the value of $\overline{M}_c$. By combining the prediction of Brannon-Peppas and Peppas [30] to the phantom network model of James and Guth [31], $\overline{M}_c$ and χ of monoprotic acid-containing hydrogels

synthesized by simultaneous polymerization and crosslinking reaction of the monomers were expressed as shown in eq. (2.2) [32]

$$\left[\frac{K_a}{10^{-pH}+K_a}\right]^2 \frac{V_1 f_i^2}{4I\overline{V}_r^2} - v_{2m}^{-2}\ln\left(1-v_{2m}\right) - v_{2m}^{-1} = \chi + \frac{\left(1-\dfrac{2}{\phi}\right)V_1\rho_2 v_{2r}^{2/3} v_{2m}^{-5/3}}{\overline{M}_c} \qquad (2.2)$$

where K_a is the dissociation constant of monoprotic acid, I is the ionic strength of the swelling medium, and f_i is the weight fraction of ionizable polymer in the gel system.

Şen and Güven [33] predicted swelling behavior of hydrogels containing diprotic acid moieties using the approach of phantom network model. The complete expression accounting for the mixing, elastic, and ionic contributions to the chemical potential of diprotic copolymeric networks was given in eq. (2.3).

$$\left[\frac{2K_{a1}K_{a2}}{2\left[\left(10^{-pH}\right)^2+10^{-pH}K_{a1}+K_{a1}K_{a2}\right]}\right]^2 \frac{V_1 f_i^2}{4I\overline{V}_r^2} - v_{2m}^{-2}\ln\left(1-v_{2m}\right) - v_{2m}^{-1} =$$

$$\chi + \frac{\left(1-\dfrac{2}{\phi}\right)V_1\rho_2 v_{2r}^{2/3} v_{2m}^{-5/3}}{\overline{M}_c} \qquad (2.3)$$

where K_{a1} and K_{a2} are the first and second dissociation constants of diprotic acid and f_i is the weight fraction of ionizable polymer in the gel system.

2.6 Rheology

Rheology can be defined as the science of the flow and deformation of matter. For low molecular weight fluids, the study of rheology involves the measurement of viscosity. For such fluids, the viscosity depends primarily upon the temperature and hydrostatic pressure. However, the rheology of high molecular weight liquids, whether neat or filled, is much more complex because polymeric fluids show nonideal behavior. In addition to having complex shear viscosity behavior, polymeric liquids show elastic properties, such as unequal normal stresses in shear and a prominent tensile viscosity in extension. All these rheological properties depend upon the rate of deformation, molecular weight and structure of the polymer, and the concentration of various additives and fillers, as well as temperature. In addition, even at a constant rate of deformation, stresses are found to depend on time.

The subject of rheology is very important for both polymers and polymeric composites, because of two reasons. Firstly, flow is involved in the processing and fabrication of such materials in order to make useful objects. Thus, fluid rheology is relevant to polymer processing and determines stress levels in operations such as extrusion, calendering, fiber spinning, and film blowing. Similarly, rheology influences residual stresses, cycle times, and void content in composite processing operation such as bag molding, compression molding, and injection molding. Clearly, a quantitative description of polymer and composite rheology is essential for developing models of the various polymer processing operations; these models can be employed for process optimization and for predicting the onset of flow instabilities. Generally, mechanical behavior is an important property to determine the application of polymer. However, this behavior is influenced by rheological behavior, and this is

the second important reason for studying polymer rheology. For example, molecular orientation has dramatic effects on the mechanical properties of molded objects, fibers, and films. For short fiber composites, fiber orientation plays the role of molecular orientation in unfilled systems. The kind and degree of molecular or fiber orientation are largely determined by the rheological behavior of the polymer and the nature of the flow in the fabrication process [34].

2.6.1 Rotational viscometry

High-precision, continuously-variable-shear instruments in which the test fluid is sheared between rotating cylinders, cones, or plates, under controlled-stress or controlled-rate conditions, are termed rotational rheometer. Instruments producing oscillatory strains are available, and a few commercial systems permit measurement of the normal stress. The basic rotational system consists of four parts: (i) a measurement tool with a well-defined geometry, (ii) a device to apply a constant torque or rotation speed to the tool over a wide range of shear stress or shear rate values, (iii) a device to determine the stress or shear rate response, and (iv) some means of temperature control for the test fluid and tool. Depending on the design specifications, rheometers may also include built-in corrections or compensations for inertia, drift, and temperature fluctuations during measurement.

Most rheometers depend on the relative rotation about a common axis of one of the tool geometries: concentric cylinder, cone and plate, or parallel plates as shown in Figure 2.6 [35].
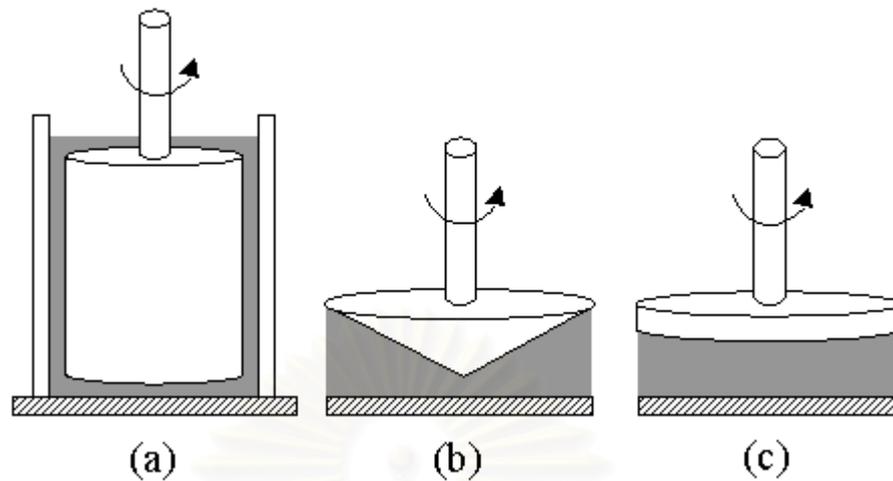
Figure 2.6 Schematic diagram of basic tool geometries for the rotational rheometer: (a) concentric cylinder, (b) cone and plate, (c) parallel plate.

In the concentric cylinder (also called couette or coaxial geometry) either the inner, outer, or both cylinders may rotate, depending on instrument design. The test fluid is maintained in the annulus between the cylinder surfaces.

The cone and plate geometry consists of an inverted cone in near contact with a lower plate. The cone is usually designed with an angle of less than 4°. Either the upper or lower surface may rotate depending on instrument design. The parallel plate geometry can be considered a simplified version of the cone and plate, having an angle of 0°. The test fluid is constrained in the narrow gap between the two surfaces. Cone and plate and parallel plate measurement tools are most often used for highly viscous pastes, gels, and concentrated suspensions [35]. In this study, we chose parallel plate geometry.

2.6.2 Linear viscoelasticity

Viscoelasticity of polymers is often characterized by forced oscillation measurements. The term linear limits data to small strains or stresses so that any elastic response is Hookean and any viscous response is Newtonian. A sinusoidal strain or stress is applied to the system and the instrument measures the peak stress, or peak strain and the phase shift,δ between the input and output wave forms. The stress per unit strain gives the complex elastic modulus, G*. This is made up of the storage modulus G$'$ (related to the elastic storage of energy) and the loss modulus G$''$ which are calculated for the complex modulus [36] by Equations (2.4) and (2.5):

$$G' = G^* \cos \delta \tag{2.4}$$

$$G'' = G^* \sin \delta \tag{2.5}$$

2.6.3 Dynamic viscosity

Periodic or oscillatory viscosity experiments provide a powerful rheological analogue to dynamic mechanical experiments. The theoretical relations are, in fact, closely interlocked. The complex viscosity, η^*, is defined as shown in Equation (2.6) [37].

$$|\eta^*| = (\eta'^2 + \eta''^2)^{1/2} \tag{2.6}$$

The complex viscosity can be determined from dynamic mechanical data shown in Equation (2.7),

$$\eta^* = \frac{\left[(G')^2 + (G'')^2\right]^{1/2}}{\omega} \tag{2.7}$$

where ω is an angular frequency. The individual components (Equations (2.8) to (2.9)) are given by

$$\eta' = \frac{G''}{\omega} \qquad (2.8)$$

and

$$\eta'' = \frac{(G')}{\omega} \qquad (2.9)$$

Thus, the phase relations are the opposite of those for G*. The in-phase, or real component, η' for a viscoelastic liquid approaches the steady-state flow viscosity as the frequency approaches zero.

2.8 Literature Survey

Recent researches on the synthesis of superabsorbent polymers and the development of their physical properties are listed as below:

Ramazani-Harandi et al. [5] investigated the swollen gel strength of superabsorbent polymers (SAPs). Firstly, they determined absorbency under load (AUL) of a typical SAP sample and then the mechanical strength of the swollen sample was measured by a rheological method. The characterization was conducted by a controlled strain rheometer at 25 °C. Dependency of the rheological properties of the sample on strain and frequency was investigated. To determine the linear viscoelastic (LVE) zone, dynamic storage modulus (G′) and loss modulus (G″) measurements were carried out at a constant frequency and in a range of strains on the SAP sample. Furthermore, G′ was obtained at the constant strain over a range of frequencies. The storage modulus of the swollen SAP gel (already absorbed saline under 0.3–0.9 psi) was measured to be above 1,000 Pa at 25 °C.

Fernández et al. [4] investigated viscoelastic and swelling properties of glucose oxidase (GOx) loaded polyacrylamide hydrogels carried out by aqueous

crosslinking copolymerization. The effects of the entrapment of the enzyme on the properties of polyacrylamide gels can be summarized as follows: (i) in the initial state, the introduction of GOx does not affect the gel modulus, (ii) gels loaded with GOx swell to a greater degree than the control gel (without GOx), due to osmotic effects introduced by the presence of the enzyme and therefore (iii) in the equilibrium of swelling, gels loaded with GOx possess a smaller modulus value than the control gel (without GOx). The experimental value of $\overline{M}_c$ determined by viscoelastic differ from the one determined by swelling measurements.

Thorgeirsdóttir et al. [38] investigated the rheological and structural properties of a pharmaceutical multicomponent hydrogel formulation. This formulation consists of a hydrogel-forming poly(acrylic acid) or Carbopol® 974P, microbiocide (monocaprin), nonionic surfactant (Tween® 20 or Tween® 40) and preservatives. The effects of surfactant addition, monocaprin concentration, and pH on the formation were investigated with the aid of various rheological methods. A change of pH from 4 (reduced electrostatic interactions) to higher pH values (prominent electrostatic forces) resulted in a marked impact on both the structural and rheological characteristics, with higher values of the dynamic moduli. At pH 4, the rheological features were strongly influenced by the addition of surfactant and monocaprin concentration, whereas at high values of pH the effect of additives was modest. At all conditions, the rheological results suggest a viscoelastic solid behavior, which is typical for many gels.

Gao et al. [39] prepared radiation-crosslinked polyacrylamide containing bentonite clay particles acting as polymer-absorbing mechanical crosslink sites in the range 50-95% water. Dynamic storage and loss moduli were obtained at several strain amplitudes over a wide range of frequency (ω) from 10^{-2} to 10^{2} rad/s. Rubbery-like

rheology was exhibited in general, and G′ found to depend exponentially on solid content, with parameters only weakly dependent on ω. A practical measure of gel strength, defined in terms of the size of a water-containing cube that is mechanically stable was used to demonstrate that these gels had considerable strength.

Iseki et al. [40] studied viscoelastic properties of xantham gum aqueous solutions and hydrogels. The change of viscoelasticity during annealing the solution and cooling to gelation temperature was examined as functions of annealing time, temperature and frequencies. In the annealing process, G′ increases with increasing annealing time. In the subsequent cooling process, G′ of the annealed solution increased, whereas G′ of non-annealed solution remained almost constant. G′ of hydrogels increased with the increase of annealing temperature and concentration. Based on the experimental results obtained, the structural change of the solution in the annealing process and the structure of gels were investigated.

Chen et al. [41] studied rheological properties and relaxation behavior of the blends of LDPE and PDAP to check miscibility and molecular relaxations in the crystalline and amorphous phases. In the shear rate range studied, all PDAP/LDPE blends exhibited a shear thinning behavior and led to a reduction of the enhanced blend viscosity and the elasticity of the blends.

Yiamsawas et al. [7] synthesized the superabsorbent polymers of acrylamide (AAm)/crotonic acid (CA) by foamed polymerization in an aqueous solution. The influences of the relative contents of CA, crosslinking agent, and initiator, on the swelling properties of the superabsorbent polymer systems were examined. The superabsorbent polymer synthesized with an AAm/CA ratio of 98:2 by mole, 0.5 wt% of N, N′-methylenebisacrylamide and 1 wt% of ammonium persulfate at 250 rpm and 50°C for 30 min of polymerization time produced the highest water absorption of

211±9 times its dried weight and could absorb water up to 162±4 g g^{-1} of the dry copolymer within 10 min.

Hernández et al. [42] prepared poly(vinyl alcohol) (PVA) hydrogels obtained through freezing-thawing cycles. The viscoelastic properties of these gels were evaluated as a function of temperature, time, degree of swelling, concentration and the number of freezing-thawing cycles. The storage modulus was analyzed on the basis of a theoretical model based on the scaling approach. These results provide additional evidence for a non-crystalline nature of the structure of PVA cryogels. The variation of the storage modulus with ferrofluid concentration could not be fitted using classical theories which had been attributed to the small dimensions of the particles in the ferrogels and to the magnetic interactions between particles.

Şen et al. [43] determined average molecular weight between cross-links ($\overline{M}_c$) of itaconic acid-containing poly(vinyl pyrrolidone) and maleic acid containing polyacrylamide hydrogels sensitive to pH changes of the swelling medium investigated. Hydrogels were prepared in water and swollen to equilibrium in phosphate buffer solutions at a pH interval of 2-9. The equation modified by the authors recently for the determination of $\overline{M}_c$ was observed to describe very well the swelling behavior of charged polymeric networks. The experimentally determined equilibrium swelling behaviors of hydrogels were observed to obey very closely the model prediction. Beside the determination of $\overline{M}_c$ values from a linearized form of swelling equation, it was also possible to calculate the polymer-solvent interaction parameter from the same analysis.

Martínez-Ruvalcaba et al. [44] prepared hydrogel by complexation of chitosan and xanthan. The viscoelastic properties of this polysaccharide system were

characterized by oscillatory shear measurements under small-deformation conditions. The complex moduli were frequency dependent, increasing slightly with frequency. Since chitosan-xanthan hydrogels are elastic materials, Then G′ was found to increase with chitosan-xanthan hydrogel concentration. The results showed that chitosan/xanthan hydrogels behaved like a weak gel.

Jiang et al. [45] investigated a phase transition behavior of water within the chitosan/polyacrylate hydrogels by means of oscillatory shear rheology. The crystallization and melting behavior of ice in these hydrogels was greatly affected by the internal structure of the network. Changes in this structure were probed by comparing differences in the rheological measurements at temperatures above and below freezing. Trends among the measured storage and loss moduli, and loss tangent (tan δ) were related to the mobility of water within the gel.

Sahiner et al. [46] studied rheological behavior across the gelation threshold for an affine network of a completely charged cationic monomer (3-acrylamidopropyl)-trimethylammonim chloride (APTMACl) crosslinked with a neutral crosslinker (*N,N'*-methylenebisacrylamide). The elastic modulus near the gel point (during the crosslinking process) showed a power law dependence of the form $G'(t) = \varepsilon^z$, where $\varepsilon = ((t\text{-}t_c)/t_c)$ is the distance from the gel point (t_c). From the equilibrium (after the crosslinking process) rheological measurements of a series of samples, it was inferred that there was a critical crosslinker mole percent (X_c) with respect to the monomer concentration, required to form a well-defined three-dimensional network with a solid-like behavior.

Tang et al. [47] prepared thermosensitive hydrogel through the mixture of chitosan (CS), poly(vinyl alcohol) (PVA) and sodium bicarbonate. The mixture behave like a solution at low temperature (about 4℃), but a gel under physiological

conditions. The effects of hydrogel composition and temperature on both the gel process and the gel strength were investigated from which possible hydrogel formation mechanisms were inferred. The viscoelastic properties, as investigated rheologically, indicated that the gel had good mechanical strength.

Mitsumata et al. [48] synthesized poly(vinyl alcohol) (PVA) gel from mixed aqueous solutions of PVA and sodium silicate using freeze/thaw techniques. Dynamic viscoelastic measurements showed that the storage modulus of the composite gel was one order of magnitude higher than that of pure PVA gel. The storage modulus of the composite gel increased with an increase of the concentration of sodium silicate.
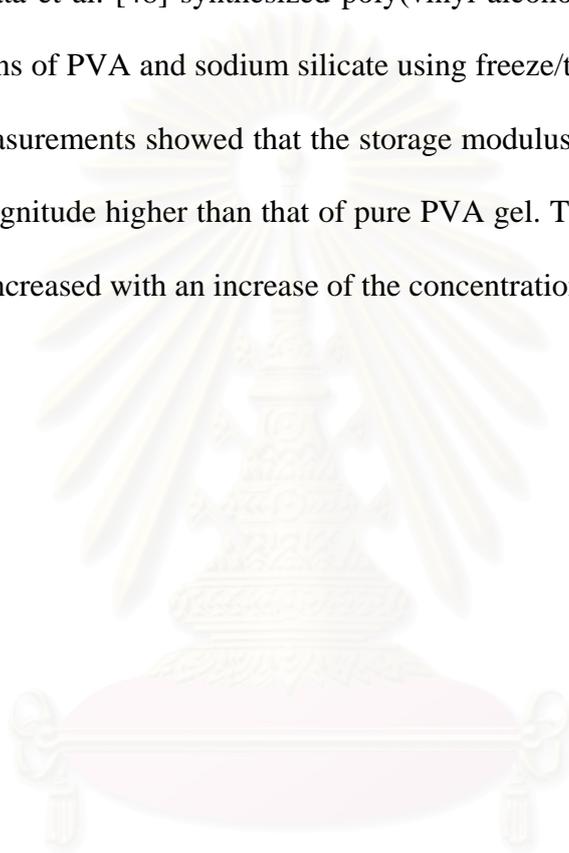
CHAPTER III

EXPERIMENTAL

3.1 Chemicals

3.1.1   Acrylamide (AM) from Siam Chemical & Industry Co., Ltd.

C_3H_5NO, solid

MW = 71.08 g mol^{-1}

3.1.2   Acrylic acid (AA) from Fluka (Buchs, Switzerland)

$C_3H_4O_2$, liquid

MW = 72.06 g mol^{-1}

3.1.3   Crotonic acid (CA) analytical grade from Fluka (Buchs, Switzerland)

$C_4H_6O_2$, solid

MW = 86.09 g mol^{-1}

3.1.4   Maleic acid (MA) analytical grade from Merck (Hohenburnn, Germany)

$C_4H_4O_4$, solid

MW = 116.10 g mol^{-1}

3.1.5   Itaconic acid (IA) analytical grade from Merck (Hohenburnn, Germany)

$C_5H_6O_4$, solid, MW = 130.10 g mol^{-1}

3.1.6 *N, N'*-Methylenebisacrylamide (N-MBA) analytical grade from Fluka

(Buchs, Switzerland)

$C_7H_{10}N_2O_2$, solid

MW = 154.17 g mol^{-1}

3.1.7 Ammonium Persulphate (APS) analytical grade from Merck

(Hohenburnn, Germany)

$(NH_4)_2S_2O_8$, solid

MW = 228.20 g mol^{-1}

3.1.8 *N, N, N', N'*- Tetramethylethylenediamine (TEMED) analytical grade

from Fluka (Buchs, Switzerland)

$C_6H_{16}N_2$, liquid

MW = 116.21 g mol^{-1}

3.1.9 Methyl alcohol (Poole, England)

CH_3OH, liquid

MW = 32.04 g mol^{-1}

3.1.10 Orthophosphoric acid, analytical grade from Ajax (Seven Hills,

Australia)

H_3PO_4, liquid

MW = 98.00 g mol^{-1}

3.1.11   Boric acid, analytical grade from Merck (Hohenburnn, Germany)

H_3BO_3, solid

$MW = 61.83$ g mol^{-1}

3.1.12   Acetic acid, analytical grade from BDH (Poole, England)

CH_3COOH, liquid

$MW = 60.05$ g mol^{-1}

3.1.13   Sodium hydroxide, analytical grade from from Ajax (Seven Hills, Australia)

NaOH, solid

$MW = 20.01$ g mol^{-1}

For a clear understanding between the monoprotic acid- and diprotic acid-containing vinyl monomers, the structures of acrylic acid, crotonic acid, maleic acid and itaconic acid are presented in Figure 3.1.

Acrylic acid   **Crotonic acid**

Maleic acid   **Itaconic acid**
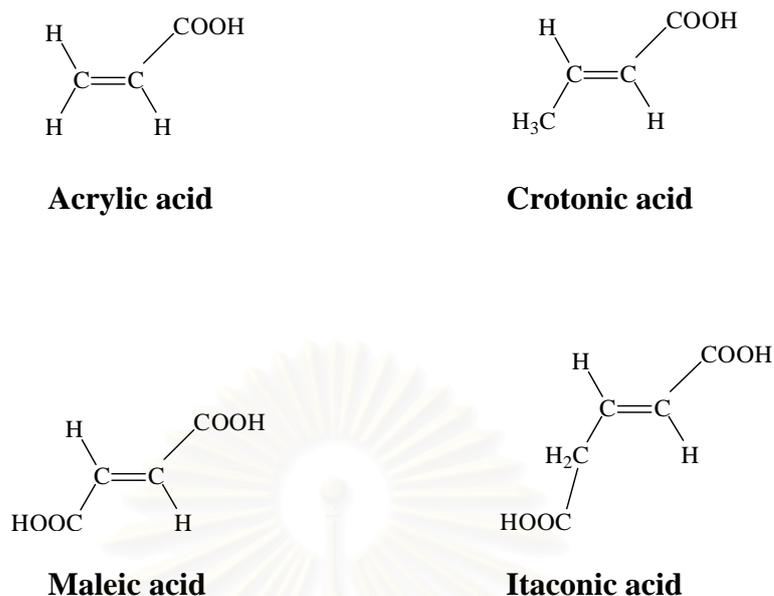
Figure 3.1 Chemical structures of monoprotic acid- and diprotic acid-containing vinyl

monomers employed in the polymerization

3.2 Glassware

3.2.1 Four-necked round bottomed flask, 500-cm^3

3.2.2 Condenser: Bulb or reflux

3.2.3 Thermometer: Mercury

3.2.4 Volumetric flask

3.2.5 Other general laboratory glassware

3.3 Equipment

3.3.1   Flow meter: Cole Parmer, Illinois, USA

3.3.2   Stirring type: Semicircular Teflon Paddle

3.3.3   Mechanical stirrer: IKA Euro-ST B, Germany

3.3.4   Oil Bath**:** Mammert, Swabach, Germany

3.3.5   Oven: D 7200, Tuttlingen, Germany

3.3.6   Magnetic stirrer : Mag-mixer model MD200, Tokyo, Japan

3.3.7   Scanning Electron Microscope (SEM): Jeol model JSM-T 220A, Tokyo, Japan

3.3.8   Fourier Transform Raman Spectrometer: Perkin Elmer, Spectrum GX, Massachusetts, USA

3.3.9   pH meter: Scoth CG 842, Mainz, Germany

3.3.10 Gemini HR Nano Rheometer: Malvern-Bohlin Instruments, Southborough, USA

3.3.11 Ultrapycnometer: Quantachrome, Florida, USA

3.4 Procedure

3.4.1 Synthesis of copolymers

Copolymerization: A mixture of 100 cm^3 aqueous solution containing acrylamide (AM) monomer, monoprotic acid: acrylic acid (AA), crotonic acid (CA) and diprotic acid: maleic acid (MA), itaconic acid (IA) comonomer, *N, N'*-methylenebisacrylamide (N-MBA) crosslinker, ammonium persulfate (APS) initiator was placed in a 500-cm^3 four-necked round bottomed flask. This reaction flask equipped with a mechanical stirrer set at 250 rpm, a condenser, and an inlet tube for nitrogen gas, was immersed in a controlled temperature water bath (45°C).   The ingredients were stirred gently by a small-bladed propeller for 5 min. Then, the *N, N,*

N', N'-tetramethylethylenediamine (TEMED) co-initiator was added and stirred for 30 min. The resulting polymer was dewatered with methanol, cut into small pieces, dried at 50°C for 24 h in a vacuum oven to a constant weight and then milled. All polymerization conditions are shown in Table 3.1.

Table 3.1: Polymerization conditions of copolymers

Material	Concentration of experiment		
	Set 1	Set 2	Set 3
monomer pair 1			
AM:AA %mol	96:4	90:10	98:2
N-MBA*	1.0	1.0	1.0
APS*	1.0	1.0	1.0
TEMED*	2.0	2.0	2.0
monomer pair 2			
AM:CA %mol	96:4	98:2	90:10
N-MBA*	1.0	0.5	0.5
APS*	1.0	1.0	1.0
TEMED*	2.0	2.0	2.0
monomer pair 3			
AM:MA %mol	96:4	92:8	99:1
N-MBA*	1.0	1.0	1.0
APS*	1.0	1.0	1.0
TEMED*	2.0	10.0	10.0
monomer pair 4			
AM:IA %mol	96:4	96:4	99:1
N-MBA*	1.0	0.5	0.5
APS*	1.0	1.0	1.0
TEMED*	2.0	2.0	2.0

* %weight based on the concentration in the monomer

3.4.2 Effect of the number of carboxylic acid functionality

The experiment procedures as described in Section 3.4.1 and Table 3.1 were carried out with monoprotic and diprotic acid vinyl monomer such as acrylic acid (f=1), crotonic acid (f=1) , maleic acid (f=2) and itaconic acid (f=2).

3.4.3 Effect of the equilibrium degree of swelling

The experiment procedures as described in Section 3.4.1 and Table 3.1 were carried out with various mole percent of monomer ratios, %wt of initiator, %wt of crosslinker and %wt of co-initiator.

3.5 Characterization of the Copolymer

3.5.1 Identification of the functional groups of the copolymers

The functional groups of poly[AM-*co*-(AA)], poly[AM-*co*-(CA)], poly[AM-*co*-(MA)] and poly[AM-*co*-(IA)] were examined by RAMAN Spectroscopy (Fourier Transform Raman Spectrometer, Perkin Elmer, Spectrum GX, USA)

3.5.2 Morphology of the copolymers

The surface morphology of poly[AM-*co*-(AA)], poly[AM-*co*-(CA)], poly[AM-*co*-(MA)] and poly[AM-*co*-(IA)] were investigated using scanning electron microscopy (SEM), model JSM-T 220A, Japan JEOL without cross-section. The thickness of gold coated on the copolymer was 25 nm, and SEM was operated with an accelerating voltage 15 kV.

3.5.3 Thermal properties of the synthesized poly(AM-*co*-IA)

The superabsorbent poly[AM-*co*-(IA)] was investigated with a thermogravimetric analysis for their thermal property. The measurements were carried out over a temperature range of 25 to 800°C with a heating rate of 10°C min^{-1}, under the nitrogen flow rate of 60 cm^3 min^{-1}, the weight of superabsorbent polymer used was 2-4 mg.

3.5.4 Determination of swelling properties of the copolymers

3.5.4.1 Equilibrium water absorbency

Equilibrium water absorbencies of the copolymers were carried out with distilled water at room temperature in a closed system to minimize water evaporation. Distilled water (200 ml) was added to 0.1 g of the dry copolymers and it was allowed to equilibrium swelling for 24 h. Then, the swollen gel was filtered through a 100-mesh sieve aluminium screen for 2 h. The equilibrium water absorbency was calculated as shown in Equation (3.1):

$$Equilibrium\ Water\ absorbency(Q) = \frac{(W_e - W_i)}{W_i} \qquad (3.1)$$

W_i = the weight of dry copolymers (g)
W_e = the weight of swollen gel (g)

3.5.4.2 In buffer solutions

The Britton-Robinson buffer [49] solutions were prepared by mixing 1:1:1 of 0.04 M boric acid (2.47 g), phosphoric acid (2.33 mL) and acetic acid (2.29 mL) were dissolved in deionized water and dilute to 1 L in a volumetric flask. This makes a 0.04 M boric acid, 0.04 M phosphoric acid and 0.04 M acetic acid solution.

That is brought at the right pH with 0.2 M sodium hydroxide (8.00 g). Buffer used for the range pH 2 to pH 12.

0.1 g of the dry copolymers was left to swell in a solution of desired pH (2-9), ionic strength $I = 0.1$ M, for 24 h. Then, the swollen gel was filtered through a 100-mesh sieve aluminium screen for 2 h. The equilibrium water absorbency was calculated by the Equation (3.1).

The weight obtained from Equation (3.1) was used to calculate the volume fraction v_{2m} and equilibrium swelling by volume (q_v) of polymer in a given gel sample swollen to equilibrium in water.

$$q_v = \left[1 + \rho/\rho_w\left(w^{-1} - 1\right)\right] \tag{3.2}$$

where ρ and ρ_w are the densities of swollen gel and water; w is the weight fraction of polymer in swollen gel. For the determination of v_{2r} weight fraction of the polymer in a freshly synthesized sample was used for w in Equation (3.2). The equilibrium swelling by volume was defined as [41].

$$q_v = 1/v_{2m} \tag{3.3}$$

3.5.5 Determination of density of the copolymers

The densities of poly[AM-*co*-(AA)], poly[AM-*co*-(CA)], poly[AM-*co*-(MA)] and poly[AM-*co*-(IA)] were examined by the Ultrapycnometer 1000 (Quantachrome, USA), involving Archimedes' principle of fluid displacement and Boyle's law to determine the sample volume. The displaced fluid is a helium gas, which can

penetrate pores within samples. The experiment was performed by purging helium gas into samples at 23°C.

3.5.6 Determination of average molecular weight between crosslinks ($\overline{M}_c$)

The average molecular weights between crosslinks ($\overline{M}_c$) of non-ionic networks and ionic comonomer; i.e. monoprotic acid: acrylic acid, crotonic acid and diprotic acid: maleic acid, itaconic acid were calculated from Equations (2.1-2.3).

3.5.7 Viscoelastic properties

The viscoelastic properties of poly[AM-*co*-(AA)], poly[AM-*co*-(CA)], poly[AM-*co*-(MA)] and poly[AM-*co*-(IA)] were examined by Gemini HR Nano Rheometer as shown in Figure 3.2. The rheological measurements were performed at 25 °C with parallel plate geometry.
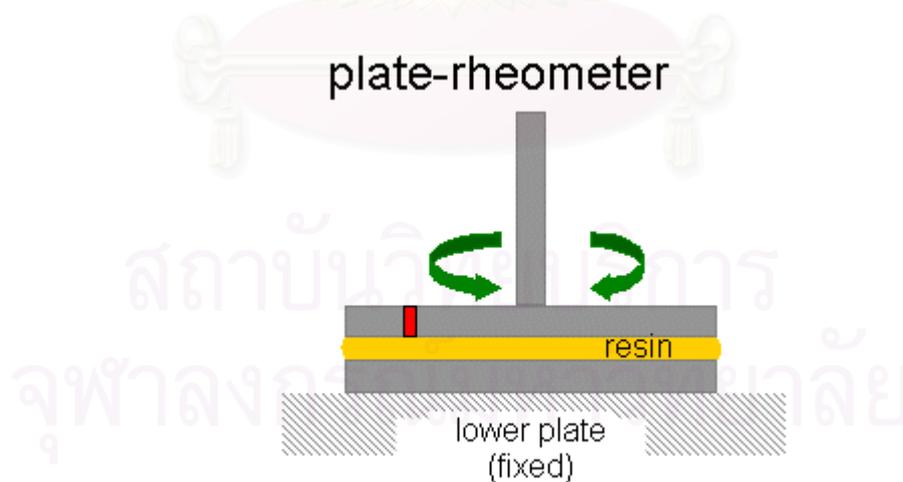
Figure 3.2 Rheometer measurement

3.5.7.1 Stress sweep

The control stress was chosen to be in a linear viscoelastic (LVE) range where G′ (storage modulus) and G″ (loss modulus) are independent of the stress amplitude. For the LVE determination, approximately 100-110 mg of the dried samples with an average particle size of <150 μm was dispersed in 200 ml of distilled water for 24 h swelling. The swollen sample was filtered through a 100-mesh aluminum screen for 2 h at room temperature. A vendor supplied solvent trap was used in order to mitigate solvent (water) loss during the experiments.

3.5.7.2 Frequency sweep

After a stress sweep test, the test condition for the frequency sweeps was selected to ensure that the test is really carried out in the LVE range. The frequency sweep experimental was varied from 0.1 to 10 rad s^{-1}. The swollen gel particles were then placed on the parallel plate of the rheometer, and viscoelastic properties were measured.

CHAPTER IV

RESULTS AND DISSCUSION

In this research, poly[AM-*co*-(AA)], poly[AM-*co*-(CA)], poly[AM-*co*-(MA)] and poly[AM-*co*-(IA)] were prepared by free radical polymerization in aqueous solutions of acrylamide and monomers such as acrylic acid, crotonic acid, maleic acid and itaconic acid using the *N, N'-* methylenebisacrylamide (N-MBA), ammonium persulphate (APS) and *N, N, N', N'*-tetramethylethylenediamine (TEMED) as crosslinking agent, initiator and co-initiator, respectively.

In the polymerization process, the first step is a reaction between APS and TEMED in which the TEMED molecules are left with an unpaired valence electron as shown in Scheme 1 [50]. The activated TEMED molecules can combine with an AM and anionic comonomer such as AA, CA, MA and IA, and N-MBA crosslinker molecules. In the process, the unpaired electron is transferred to the monomeric units, so that they in turn become reactive. Another monomer or comonomer can therefore be attached and activated in the same way. The polymer (AM) or copolymers can continue growing indefinitely, with the active center being continually shifted to free ends of the chain. Crosslinker molecules can incorporate into chains simultaneously and forming a permanent link between them.

Polymerization and crosslinking reaction were taken place for half an hour to achieve formation of a polymeric gel. The crosslinked copolymer is colorless and some of them are semi-transparent. They are soft and elastic with a slippery touch on a delicate surface.
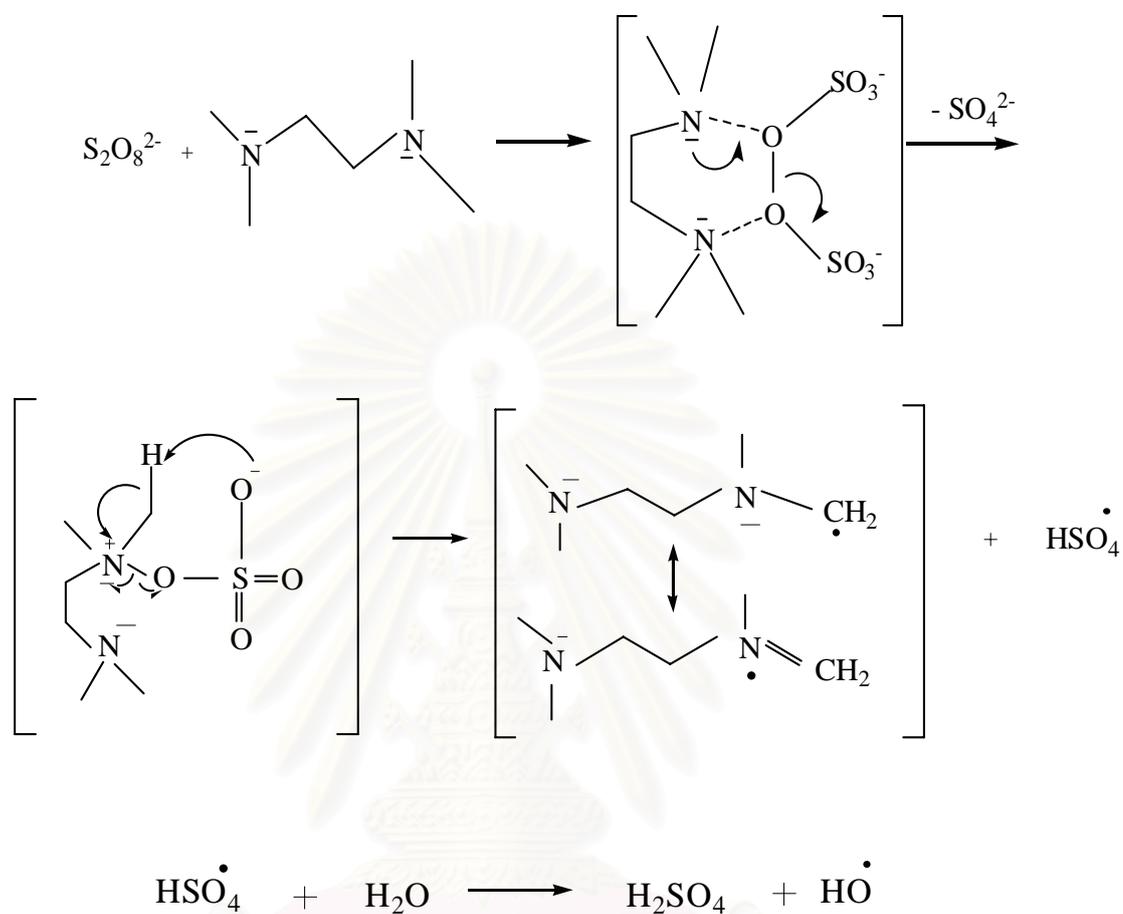
Scheme 1 Formation of radicals from peroxodisulfate and TEMED [50]

4.1 Polyacrylamide Absorbency

4.1.1 Equilibrium water absorbency

The equilibrium water absorbency of polyacrylamide is shown in Table 4.1.

Table 4.1 Equilibrium water absorbency of polyacrylamide

Synthesis condition	Equilibrium water absorbency (Q)(g g^{-1}) at particle size of	
	<150µm	150-300µm
PAM1	33±2	38±2
PAM2	ND	ND

* PAM1: Polymerization reactions were carried out at a mol ratio of 100/0, 1%wt of N-MBA, 1% wt of APS, 2% wt of TEMED, 45°C, and 30 min.

PAM2: Polymerization reactions were carried out for 30 min first, then N-MBA was added into the reaction another 30 min, ND = Not detected.

After the polymerization reaction, the appearance of PAM1 and PAM2 are different. The crosslinked PAM1 appeared as a soft gel and slippery to the touch; however, PAM2 is a viscous liquid. Since polyacrylamide is hydrophilic, its hydrogel has a capability to absorb some amount of aqueous solution. The value of equilibrium water absorbency of PAM1 is 33±2 times its dry weight but equilibrium water absorbency of PAM2 is not detected because N-MBA was added at the later stage during which the crosslinking reaction between PAM and N-MBA could not take place.

4.1.2 FT-IR spectra of polyacrylamide and P(N-MBA)

The functional groups of PAM1, PAM2 and P(N-MBA) were characterized by Fourier Transform Infrared Spectroscopy. The spectra are shown in Figure 4.1 and the assignments are given in Table 4.2. From all the characteristic wavenumbers listed in Table 4.2, one can conclude that the PAM1, PAM2 and P(N-MBA) contain carboxamide group.
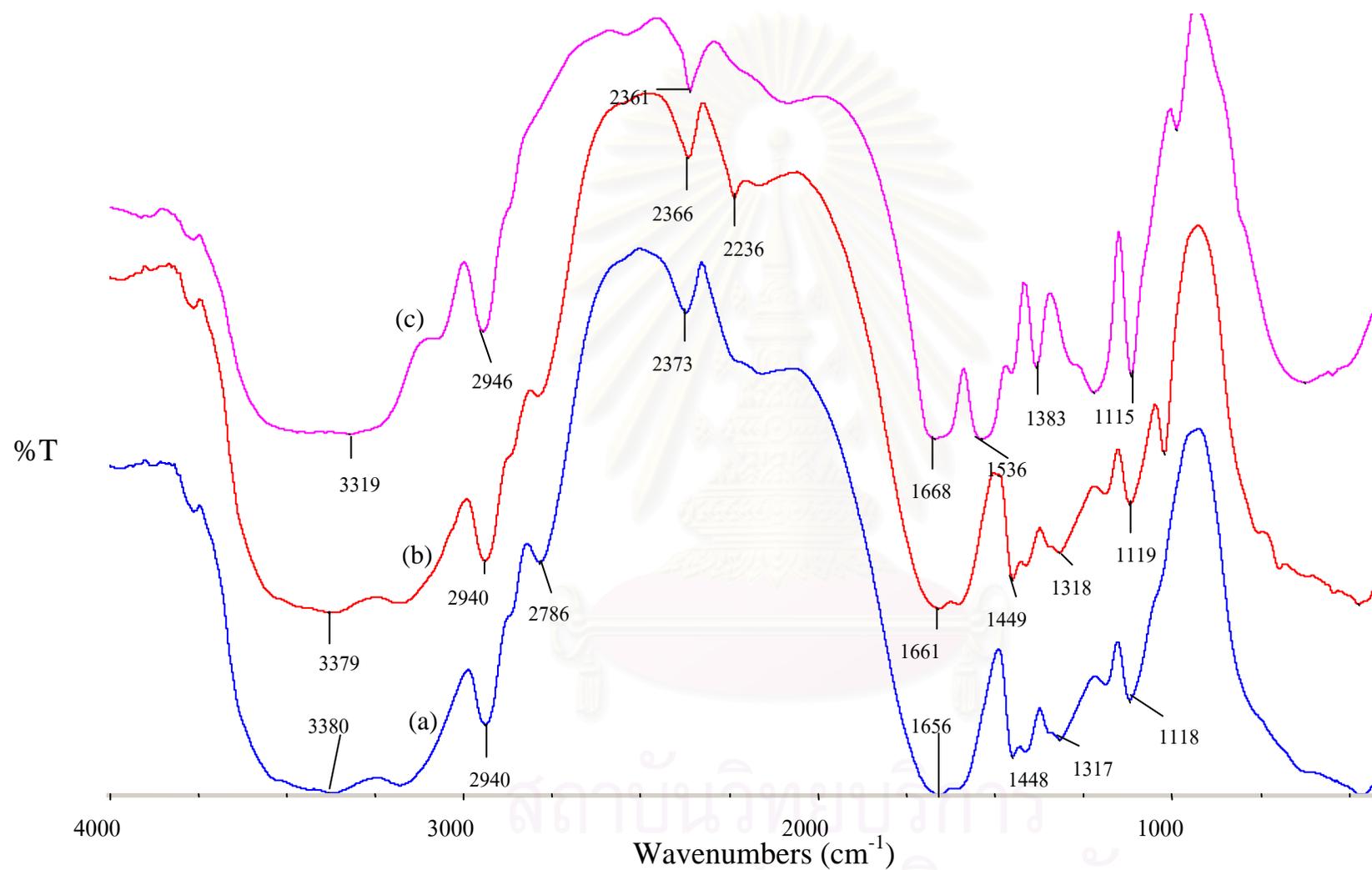
Figure 4.1 FTIR spectrum of polyacrylamide: (a) PAM1, (b) PAM2 and (c) P(N-MBA)

Table 4.2 Assignments for FTIR spectrum of polyacrylamide and P(N-MBA)

Assignments	Wave number (cm^{-1})		
	PAM1	PAM2	P(N-MBA)
N-H stretching of amide	3380	3379	3319
C-H stretching of CH, CH_2	2940, 2786	2940	2946
C=O stretching of $-CONH_2$	1656	1661	1668
C-H bending	1449	1449	1536
C-N stretching of amide	1317	1318	1383

4.1.3 Surface morphology analysis

The synthesized polyacrylamide was investigated by SEM technique to observe the surface appearance. The SEM micrograph of PAM1 shown in Figure 4.3(a) shows many chunk networks and smooth surface with a few pores. It has been reported that the SEM of polyacrylamide all the same [7]. The SEM micrographs of PAM2 in Figure 4.3(b, c) show surface area similar to that of PAM1.
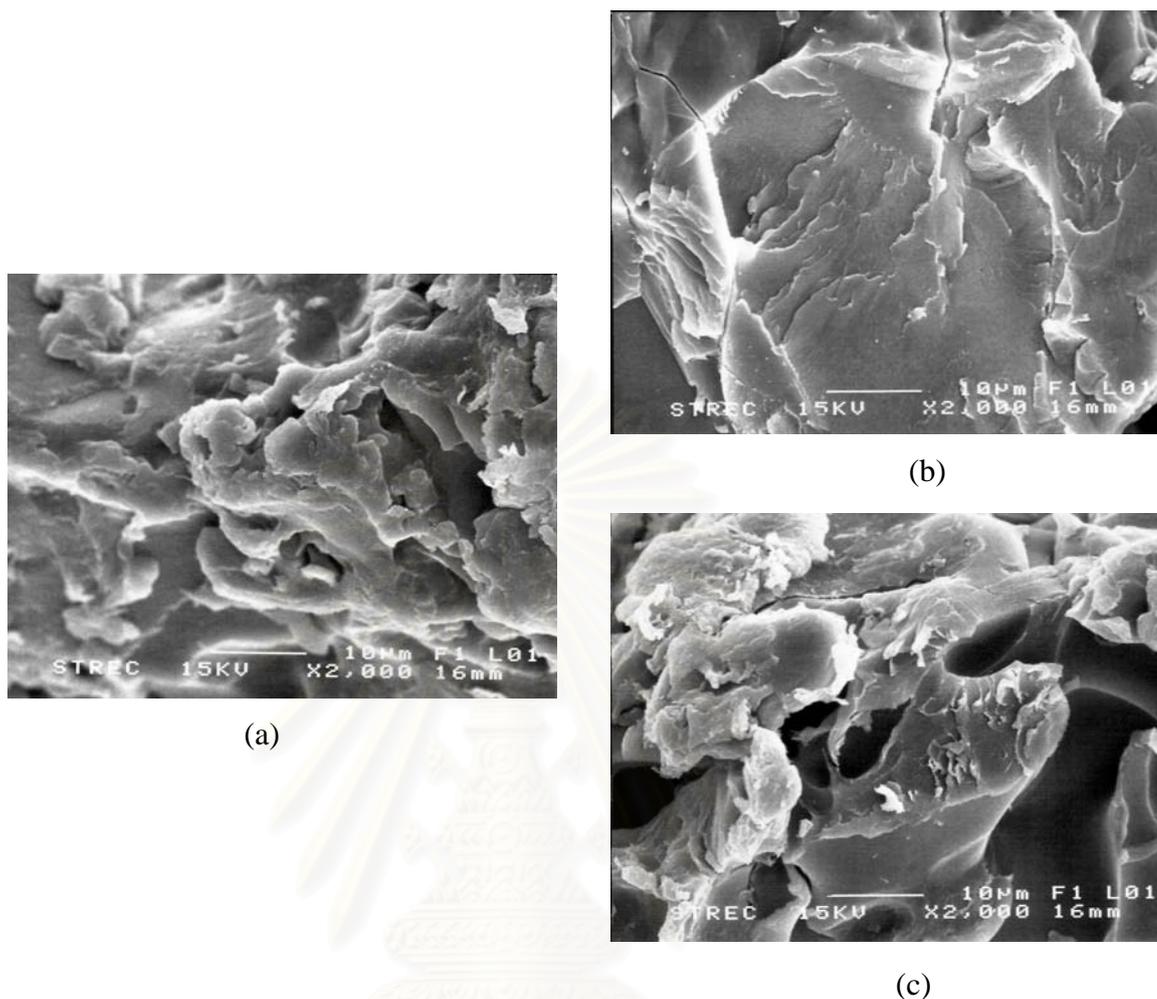
Figure 4.2 SEM micrographs of (a) PAM1 and (b-c) PAM2

In the next section, the mentioned PAM was polyacrylamide synthesized by the same method as PAM1.

4.1.4 Effect of buffer pH solution in water absorption of polyacrylamide

Figure 4.3 represents pH dependence of the water absorbency at equilibrium of PAM hydrogel in Britton-Robinson buffer from pH 2 to 9 at a fixed ionic strength of 0.1M. Equilibrium water absorbency of the PAM was not influenced by pH and ionic strength of the swelling medium as a result of nonionic hydrophilic

nature of the hydrogel. The nonionic hydrogel differs from ionic hydrogel in that the molecules are uncharged when immersed in the swelling medium.
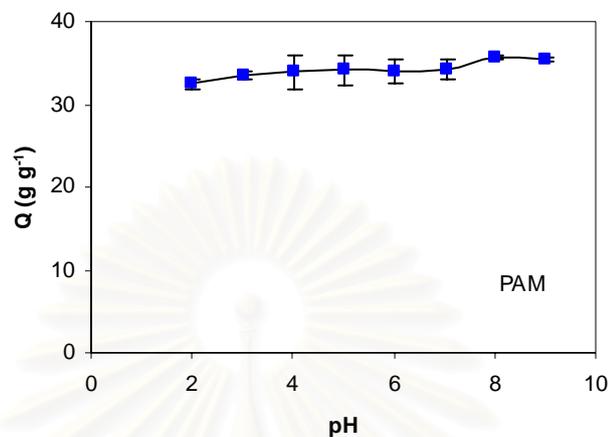
Figure 4.3 Effect of pH on equilibrium water absorbency *(Q)* of polyacrylamide

4.1.5 Viscoelastic properties of polyacrylamide

The stress sweep and frequency sweep of PAM were monitored using a stress-controlled rheometer (Gemini 200HR Nano, Malvern Instruments, UK) at 25 ℃ with an acrylic parallel plate having geometry of 50 mm diameter and 1 mm gap. The results are shown in Figure 4.4.

The stress sweeps were monitored in the range of 0.1-10 Pa at a constant frequency (1 Hz) for determining the linear viscoelastic (LVE) range, where the storage modulus (G′) and loss modulus (G″) are independent of the stress amplitude. Figure 4.4(a) shows that linear viscoelastic range expands all over the stress studied.
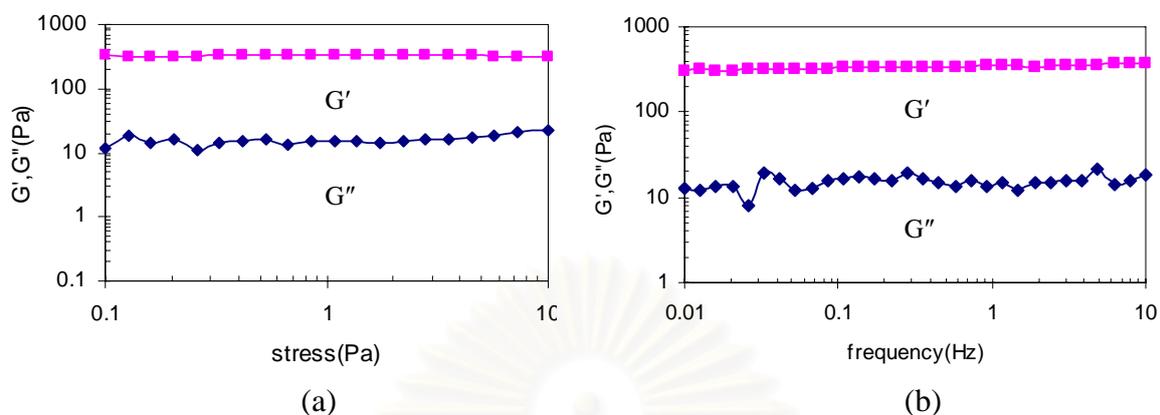
Figure 4.4 (a) Stress sweep and (b) frequency sweep of PAM prepared by 1%wt of N-MBA, 1%wt of APS, 2%wt of TEMED, 45°C, and 30 min.

As expected, G′ values are higher than the G″ values. This indicates that the elastic response of the gel was stronger than the viscous response [47]. The stress in the LVE range was selected to study the effect of frequency on the viscoelasticity of the hydrogel.

As seen in Figure 4.4(b), G′ and G″ are rather frequency independent. It can be seen from this figure that increasing the frequency, G′ and G″ gradually increase. The elastic behavior of the PAM gel predominates over its viscous behavior and the swollen PAM gel exhibits mechanical rigidity [5].

In this study, we attempted to see whether the employed crosslinker (*N,N′*-methylenebisacrylamide) can be used as a polymerizing monomer. Polymerization reaction of N-MBA was carried out by using 1%wt of APS and 2%wt of TEMED at 45°C for 30 min. After the precipitation in methanol, the obtained product can absorb water about 10±1 times its dry weight. Surface morphology of P(N-MBA)

characterized by scanning electron microscopy (SEM) is shown in Figure 4.5. The micrographs indicate various pore radii in the microporous structure.

<div align="center">(a)   (b)</div>
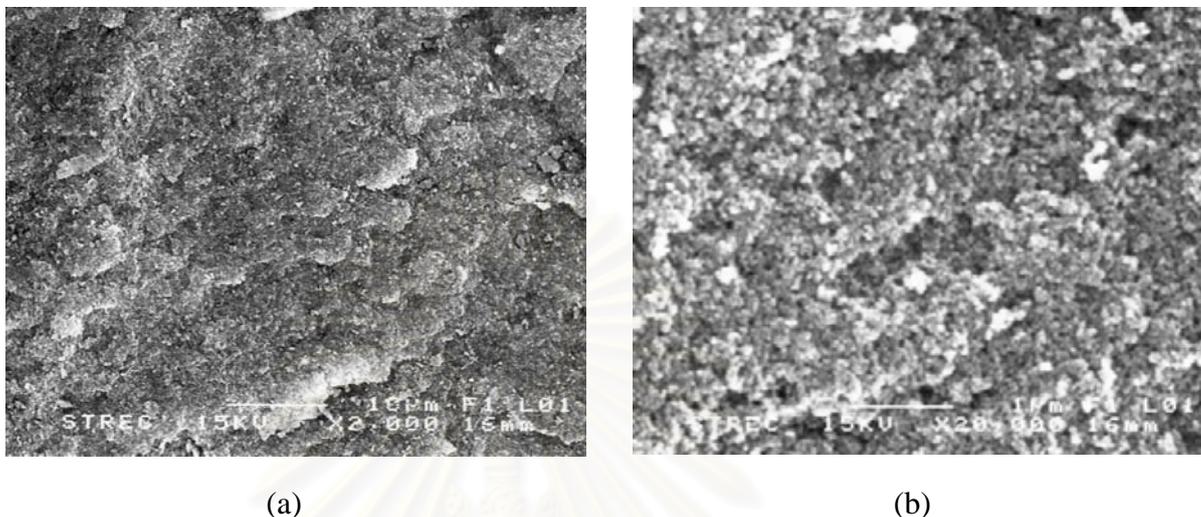
Figure 4.5 SEM micrographs of poly(N,N'-methylenebisacrylamide) at two magnifications (a) x 2,000 and (b) x 20,000.

In the next section, results from the experiments designed in Table 3.1 (as Set 1-Set 3) will be discussed.

4.2 Effect of the Number of Carboxylic Acid Functionality

Equilibrium swelling and viscoelastic properties of the copolymeric hydrogels synthesized from the set 1 polymerization condition, when the feeding composition of nonionic and ionic monomers was fixed at 96:4 (mol/mol), were studied and interpreted as a function of the number of carboxylic acid functionality.

4.2.1 Equilibrium swelling

4.2.1.1 In deionized water

As shown in Table 4.3, the equilibrium water absorbency (Q) of the crosslinked ionic copolymers in deionized water was larger than that of crosslinked

polyacrylamide (PAM) as a result of the ionic pendants (carboxylic groups) in the copolymer structure. The copolymers containing diprotic acid moieties, P(AM/MA) and P(AM/IA), can absorb more water than the monoprotic acid-containing copolymers, P(AM/AA) and P(AM/CA). The reason is that the presence of more ionic groups in the copolymer network can lead to an increase in electrostatic repulsive force between charge sites on carboxylate anions upon their complete dissociation and enhance a more extended configuration [51].

Table 4.3 Equilibrium water absorbency (Q) of hydrogels swollen in deionized water

hydrogels	Equilibrium Water absorbency (Q) (g g^{-1})	
	<150μm	150-300μm
P(AM/AA)	132 ± 6	146 ± 4
P(AM/CA)	44 ± 2	48 ± 2
P(AM/MA)	160 ± 4	127 ± 10
P(AM/IA)	305 ± 12	225 ± 11

*Polymerization reactions were carried out at mol ratio 96/4, 1%wt of N-MBA, 1% wt of APS, 2% wt of TEMED, 45°C, and 30min (indicated as Set 1).

4.2.1.2 In Britton-Robinson buffer solution

Figure 4.6 represents pH dependence of the water absorbency at equilibrium of P(AM/AA), P(AM/MA), and P(AM/IA) in Britton-Robinson buffer from pH 2 to 9 at a fixed ionic strength of 0.1M. The result shows that swelling behavior of P(AM/AA), P(AM/MA), and P(AM/IA) hydrogels increases with increasing pH of the swelling medium due to the polyelectrolyte nature of the

copolymers. However, swelling behavior of P(AM/CA) hydrogel prepared at 96/4 molar ratio of AM/CA fairly responses to the variation of pH of medium. pH-sensitive swelling of P(AM/CA) (96/4 molar ratio) might be attributed to the reactivity ratio and the hydrophobicity of CA.

Swelling of ionic hydrogel is expected to be significantly increased with high content of ionic moiety within the hydrogel. Anionic copolymer hydrogels are ionizable because of the presence of charged carboxylic acid groups. Monoprotic acid has one dissociation constant for example, pK_a of AA = 4.25 and pK_a of CA = 4.69. Diprotic acid possesses two dissociation constants: pK_{a1} = 1.83, pK_{a2} = 6.07 for MA, and pK_{a1} = 3.85, pK_{a2} = 5.45 for IA [49]. Theoretically, one expects to observe a sudden increase as one-step swelling near pK_a of monoprotic acid versus pH, and two-step swelling versus pH for diprotic acid containing hydrogel corresponding to its pK_{a1} and pK_{a2}. Experimentally, if two dissociation constants of diprotic acid are relatively close, swelling of the hydrogel at around these pH values might overlap and only single-step swelling versus pH curve was observed as found in poly(N-vinyl-2-pyrrolidone-itaconic acid) hydrogel [43].
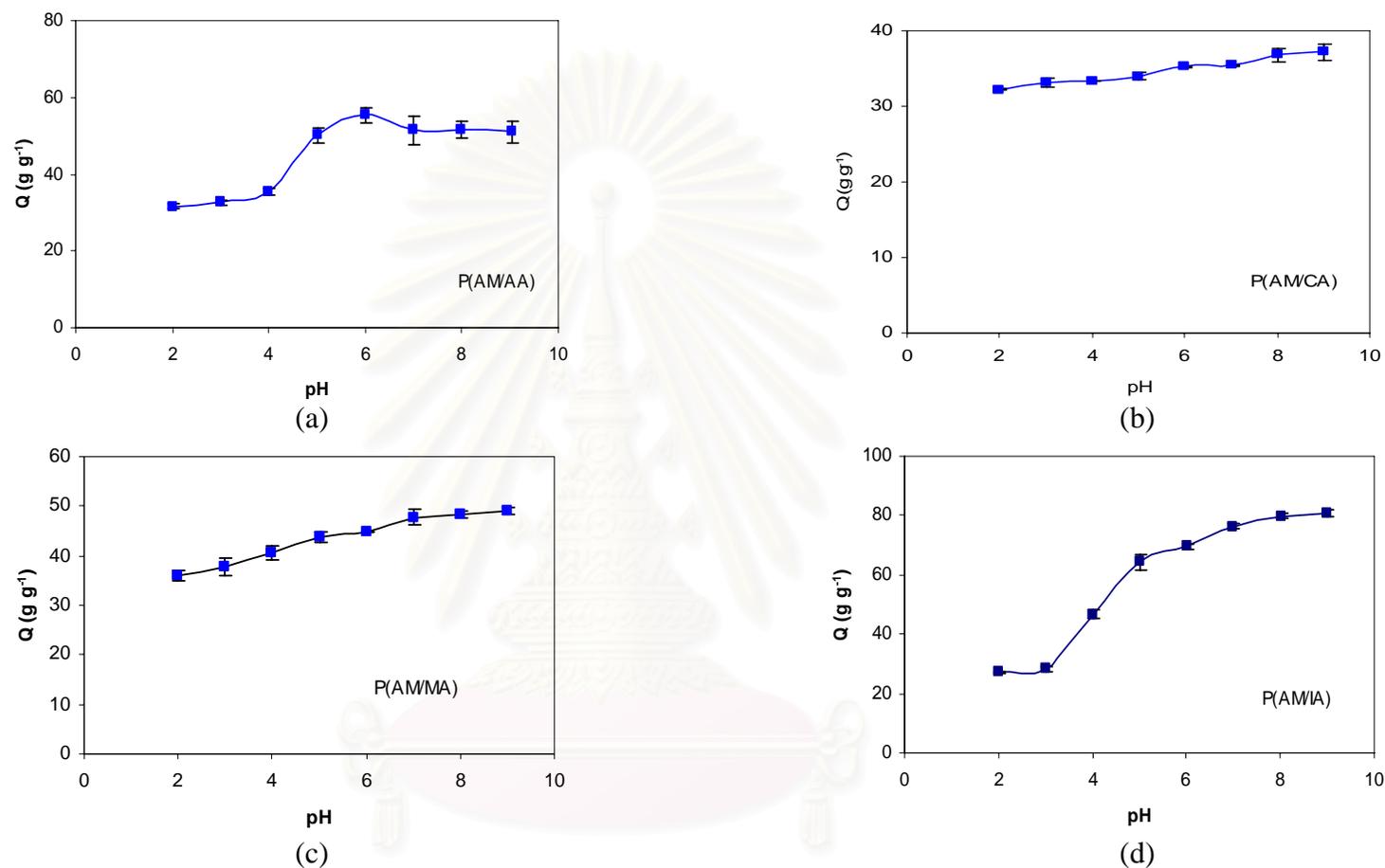
Figure 4.6 Effect of pH on equilibrium water absorbency (Q) of copolymeric hydrogels: (a) P(AM/AA), (b) P(AM/CA), (c) P(AM/MA) and (d)

P(AM/IA). The polymerization reactions were carried out at a mol ratio of 96/4, 1%wt of N-MBA, 1% wt of APS, 2% wt of TEMED, 45°C, and

30min.

The results in Figure 4.6 show that an increase in pH resulted in an increase in equilibrium water absorbency. At a low pH, ionization of the ionic groups in the hydrogels is suppressed by H^+ ions in the swelling medium, and thus, flexibility of the chain is rather low. As pH is increased, the ionic units dissociate and attract cations into the hydrogels to replace H^+ ions. The concentration of mobile ions inside the hydrogels is, therefore, enhanced, which causes an increase in ion swelling pressure. As a consequence, equilibrium water absorbency increases. As illustrated in Figure 4.6, the maximum equilibrium water absorbency of all hydrogels was obtained until pH 7 was reached due to the completion of the ionization of all carboxylic acid groups [52].

4.2.2 Raman spectra of copolymers

Acrylamide-based copolymers; namely P(AM/AA), P(AM/CA), P(AM/MA), and P(AM/IA), were synthesized by free-radical crosslinking copolymerization in the aqueous solution. Raman spectra and peak assignment of the copolymeric hydrogels are given in Figure 4.7 and Table 4.4, respectively.   The strong peak of the carboxylate group at 1648-1651 cm^{-1} for all hydrogels was attributed to the C=O stretching corresponding to a conformation change during the reaction. The results indicate that all samples were copolymers.
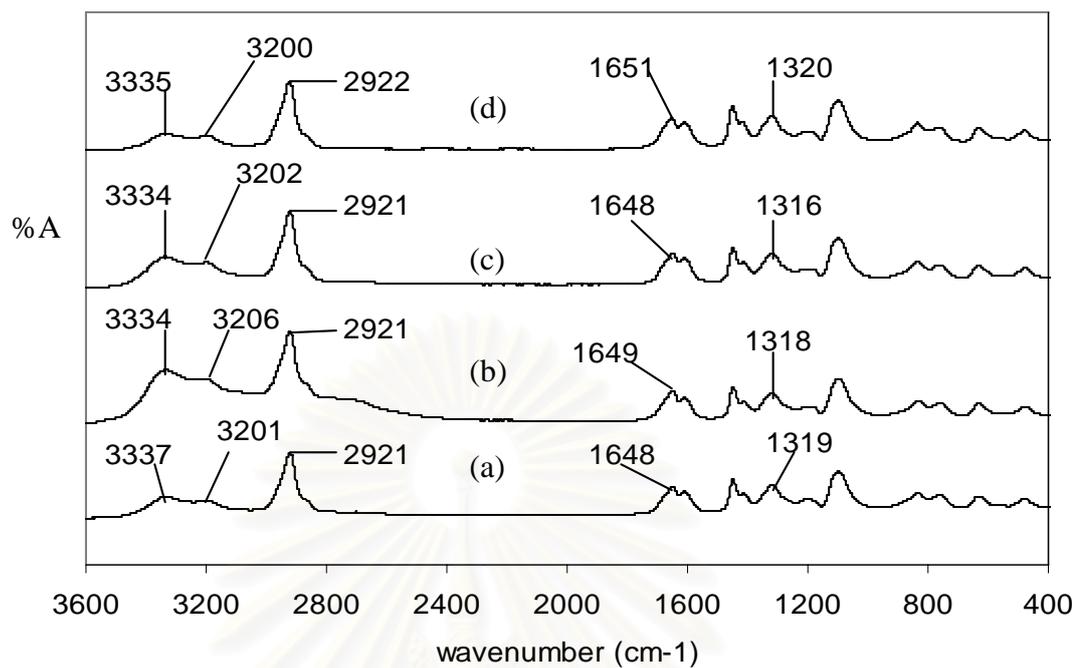
Figure 4.7 Raman spectra of copolymers: (a) P(AM/AA), (b) P(AM/CA), (c) P(AM/MA) and (d) P(AM/IA)

Table 4.4 Assignments for the RAMAN spectra of P(AM/AA), P(AM/CA), P(AM/MA) and P(AM/IA)

P(AM/AA)		P(AM/CA)		P(AM/MA)		P(AM/IA)	
Wave number (cm^{-1})	Assignment	Wave number (cm^{-1})	Assignment	Wave number (cm^{-1})	Assignment	Wave number (cm^{-1})	Assignment
3337, weak	N-H stretching	3334, weak	N-H stretching	3334, weak	N-H stretching	3335, weak	N-H stretching
3201, weak	O-H stretching	3206, weak	O-H stretching	3202, weak	O-H stretching	3200, weak	O-H stretching
2921, sharp and strong	C-H stretching	2921, sharp and strong	C-H stretching	2921, sharp and strong	C-H stretching	2922, sharp and strong	C-H stretching
1648, strong	C=O stretching of COO-	1649, strong	C=O stretching of COO-	1648, strong	C=O stretching of COO-	1651, strong	C=O stretching of COO-
1319, strong	C-N stretching	1318, strong	C-N stretching	1316, strong	C-N stretching	1320, strong	C-N stretching

4.2.3 Surface morphology analysis

4.2.3.1 Monoprotic acid containing copolymer hydrogel

The monoprotic acid containing copolymer hydrogels of P(AM/AA) and P(AM/CA) characterized by scanning electron microscopy (SEM) show the surface morphology in Figure 4.8. The result shows that the copolymers have a lot of microporous structure which assists the storage and transportation of water within the hydrogels.

(a)　　　　　　　　　　　　　　　　(b)

(c)　　　　　　　　　　　　　　　　(d)
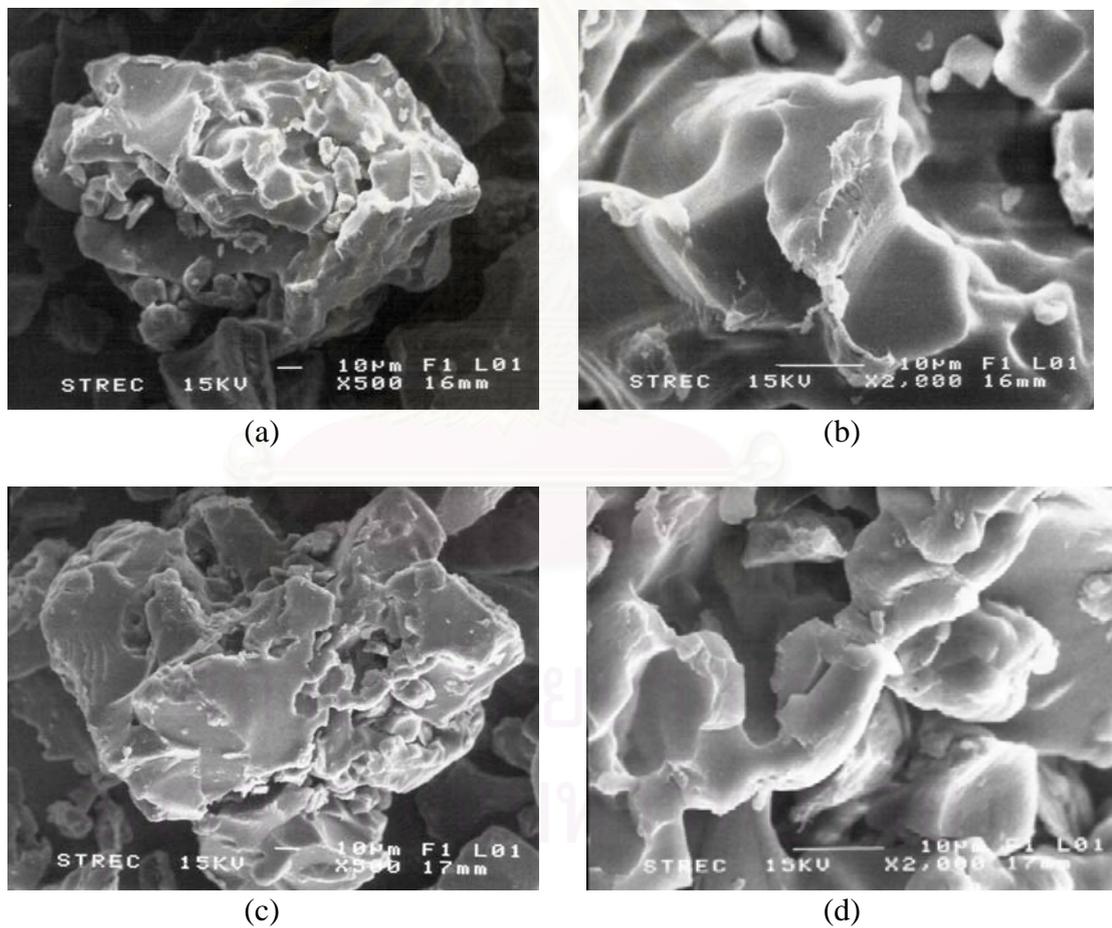
Figure 4.8 SEM micrographs of (a-b) for P(AM/AA) and (c-d) for P(AM/CA)

4.2.3.2 Diprotic acid containing copolymer hydrogel

The diprotic acid containing copolymeric hydrogels of P(AM/MA) and P(AM/IA) characterized by scanning electron microscopy (SEM) have the surface morphology as shown in Figures 4.9. These micrographs verify that copolymers have a porous structure with many smaller pore sizes as compared to the SEM micrographs of monoprotic acid containing hydrogels (Figure 4.8). The presence of smaller pore sizes related to the larger total surface area of pores. Thus, this might be one of the reasons for the higher equilibrium water absorbency of the P(AM/MA) and P(AM/IA) over P(AM/AA) and P(AM/CA) hydrogels.

According to the morphology of the hydrogels illustrated in Figure 4.8 to 4.9, one can expect that these pores are the regions of water permeation and interaction sites of external stimuli with the hydrophilic groups of the copolymers [53].

(a)

(b)

(c)

(d)
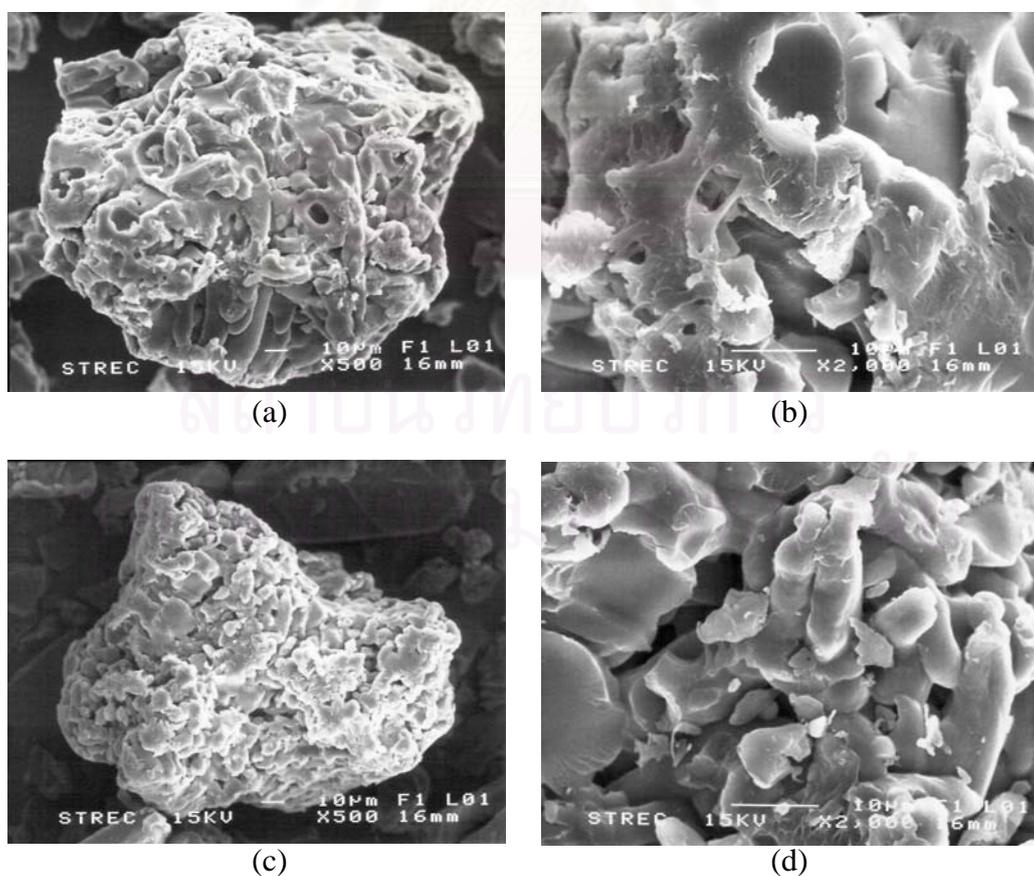
Figure 4.9 SEM micrographs of (a-b) for P(AM/MA) and (c-d) for P(AM/IA)

4.2.4 Density of copolymers

The densities of P(AM/AA), P(AM/CA), P(AM/MA) and P(AM/IA) were investigated. The results are shown in Table 4.5. The density value measured by the Ultrapycnometer 1000 was reported as an average value of five measurements with the standard deviation less than 0.002 g cm^3.

Table 4.5 The densities of P(AM/AA), P(AM/CA), P(AM/MA) and P(AM/IA)

Superabsorbent Polymer	Density (g cm^{-3})
P(AM/AA)	1.317±0.001
P(AM/CA)	1.337±0.002
P(AM/MA)	1.312±0.001
P(AM/IA)	1.332±0.002

Polymerizations were carried out at the monomer ratio of 96/4, 2%wt mole of N-MBA, 1% wt of APS, 2% wt of TEMED, 45°C, and 30 min.

4.2.5 Thermal properties of poly(AM-*co*-IA)

Thermogravimetric analysis (TGA) was employed to characterize the thermal properties of the synthesized P(AM/IA) copolymer as shown in Figure 4.10 and Table 4.6.
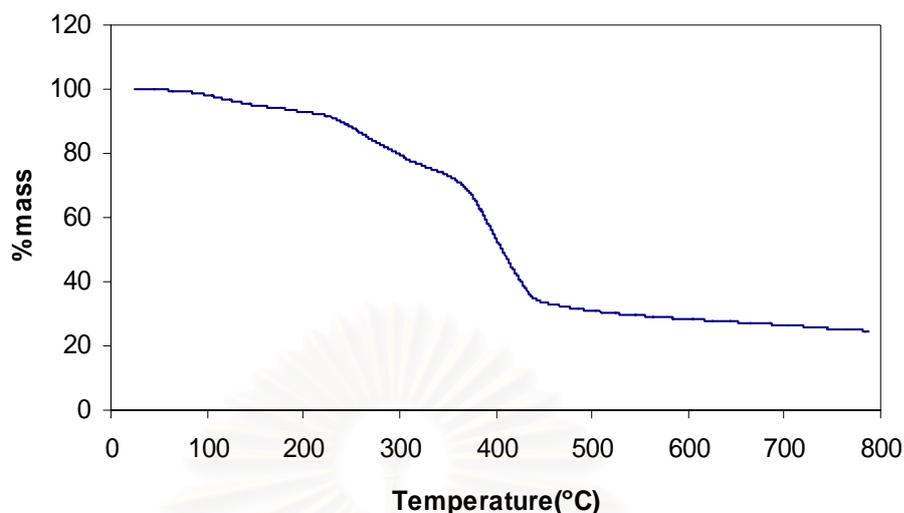
Figure 4.10 TGA thermograms of P(AM/IA) copolymer ratio 96/4, 1%wt of N-MBA,

1% wt of APS, 2% wt of TEMED, 45°C, and 30min.

Table 4.6 Thermogravimetric data of the synthesized P(AM/IA) copolymer

Number of decomposition stage	Temperature range (°C)	Weight loss (%)	Residue at 800°C
1	25-215	7.04	
2	215-325	17.39	24.63
3	325-800	50.94	

DTG = differential thermal gravimetry

The TGA results are shown in Figure 4.10 and Table 4.6. It is observed that there

are three main degradation stages in all formulations. The first stage at 110˚C found

7.04 % weight loss which is due to evaporation of the free water. The second stage at

265 ˚C found 17.39% weight loss according to the decarboxylation of IA coupled

with the chain scission. While at about 400˚C for the final stage of decomposition, a

large amount of weight loss (50.94 %) can be assigned to the degradation of

acrylamide portion. Finally, at a temperature higher than 400 ˚C in which a rapid

decomposition to carbon dioxide and volatile hydrocarbons was anticipated [53]. The remained residue (25%) may be caused by imidization or complexation of Al pan and acrylamide/Itaconic acid.

4.2.6 Viscoelastic properties of copolymers

Figure 4.11 shows storage (G′) and loss (G″) moduli as a function of frequency for the copolymeric hydrogels. The experiments were performed within the linear viscoelastic region as determined from stress sweep experiments shown in Figure 4.11. All hydrogels behave as an elastic solid where G′ is a decade larger than G″ at all frequencies studied. Insignificant frequency-dependent storage modulus was observed for hydrogels of P(AM/AA), P(AM/CA), and P(AM/MA). The P(AM/IA) hydrogel showed somewhat frequency-dependent storage modulus which implied that the structure of this gel is rather sensitive to frequency. The higher water absorbency of P(AM/IA) hydrogel may response to this behavior. Since the storage modulus of all systems was not distinct frequency-dependent, the equilibrium modulus (G_e) was determined from the storage modulus at 0.01 Hz.
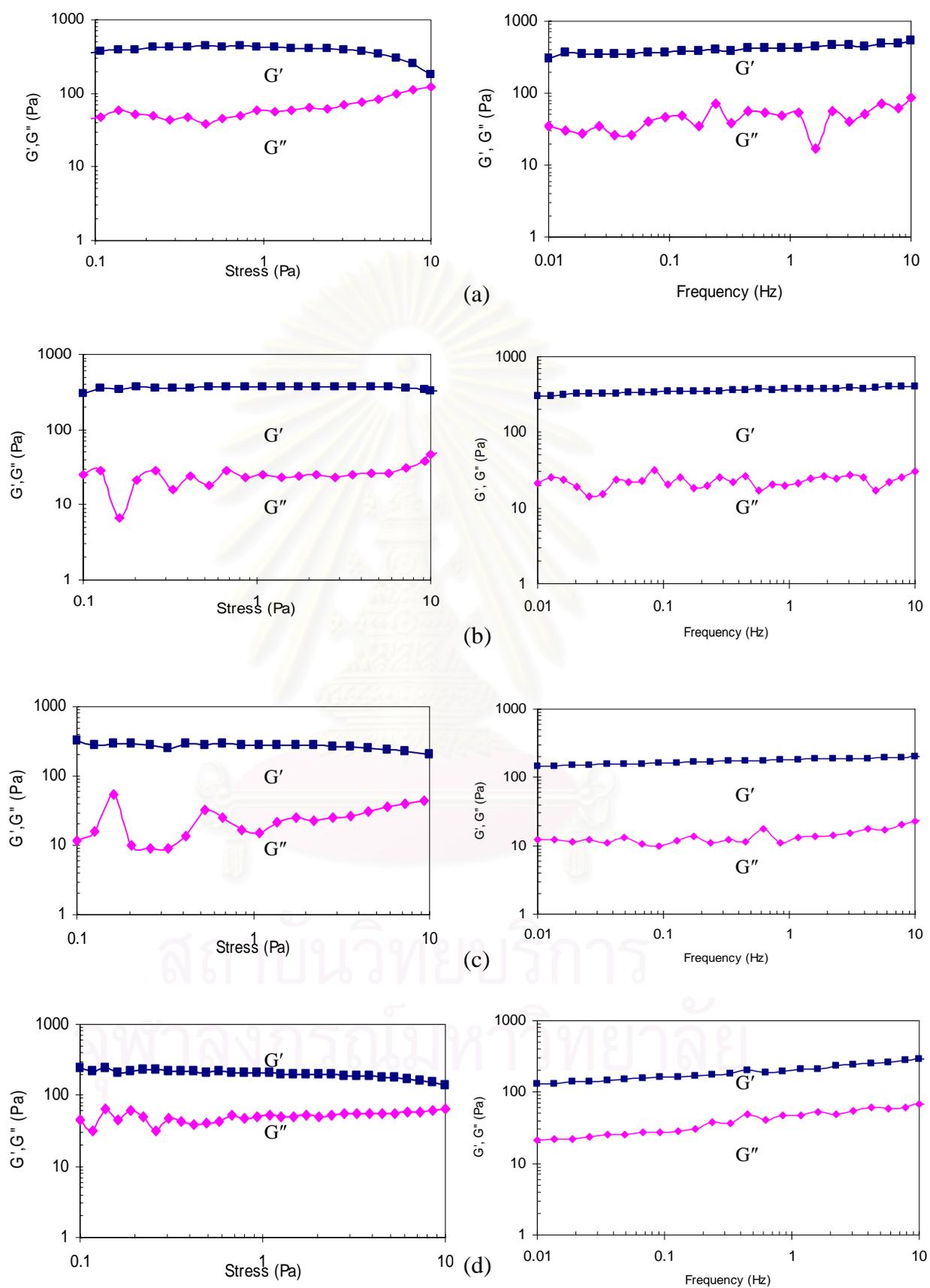
Figure 4.11 Stress sweep and frequency sweep of copolymeric hydrogels: (a) P(AM/AA),

(b) P(AM/CA), (c) P(AM/MA) and P(AM/IA)

Table 4.7 Equilibrium water absorbency *(Q)* of hydrogels swollen in Britton-Robinson buffer at various pHs

pH	Equilibrium Water absorbency (Q) (g g^{-1})			
	P(AM/AA)	P(AM/CA)	P(AM/MA)	P(AM/IA)
2	32 ± 1	32 ± 1	36 ± 1	27 ± 1
3	33 ± 1	33 ± 1	38 ± 2	28 ± 1
4	35 ± 1	33 ± 1	41 ± 2	47 ± 2
5	50 ± 2	34 ± 1	44 ± 1	64 ± 3
6	54 ± 2	35 ± 1	45 ± 1	70 ± 1
7	51 ± 1	35 ± 1	48 ± 2	76 ± 1
8	51 ± 1	37 ± 1	48 ± 2	80 ± 1
9	50 ± 2	37 ± 1	49 ± 1	81 ± 2

4.3 Determination of $\overline{M}_c$ and χ of Hydrogels

Data obtained from the swelling experiments as a function of pH (Table 4.7) were used to evaluate the values of average molecular weight between crosslinks ($\overline{M}_c$) and polymer-solvent interaction parameter (χ) by using Eqs. 2.2 and 2.3 which were derived to predict swelling behavior of monoprotic acid- and diprotic acid-containing hydrogels, respectively. If one defines the left-hand side of the equations, and the coefficient of $1/\overline{M}_c$ on the right-hand side of the Eqs. 2.2 and 2.3 to be constant values of A and B, respectively as described in Eq. 4.1, the plot of A against B correspondingly gives χ and $\overline{M}_c$ as the intercept and inverse slope via a linear regression analysis.

$$A = \chi + B\big/\overline{M}_c \qquad\qquad (4.1)$$

In this study, the related experimental parameters to be used with eqs. 2.2 and 2.3 are as follows: ionic strength of the swelling medium, $I = 1 \times 10^{-4}$ mol cm^{-3}, molar volume of the swelling medium, $V_1 = 18$ cm^{3}mol^{-1}, mol fraction of the ionic unit in the gel system, $f_i = 0.04$, the number of branches originating from a crosslinking site, $\phi = 4$. V_r is the average molar volume of polymer repeating units, and can be calculated as [54]:

$$V_r = M_r\big/\rho_2 \qquad\qquad (4.2)$$

where M_r is the molecular weight of the repeating unit in the hydrogels which can be determined from

$$M_r = \left[M_n(1 - f_i) + M_i(f_i) \right] \qquad\qquad (4.3)$$

where M_n is molecular weight of a neutral unit (acrylamide monomer), and M_i is the molecular weight of an ionic unit (ionic comonomer) in the gel system. v_{2r} is the volume fraction of the network after preparation which can be identified as [54]:

$$v_{2r} = c_o V_r \qquad\qquad (4.4)$$

where c_o is initial concentration of monomers (mol cm^{-3}). Table 4.8 contains the parameters essential for constructing the plot of Eq. 4.1 for each copolymeric

hydrogel as shown in Figure 4.12. The determined χ and $\overline{M}_c$ values of the hydrogels

from their swelling behavior are listed in Table 4.9.
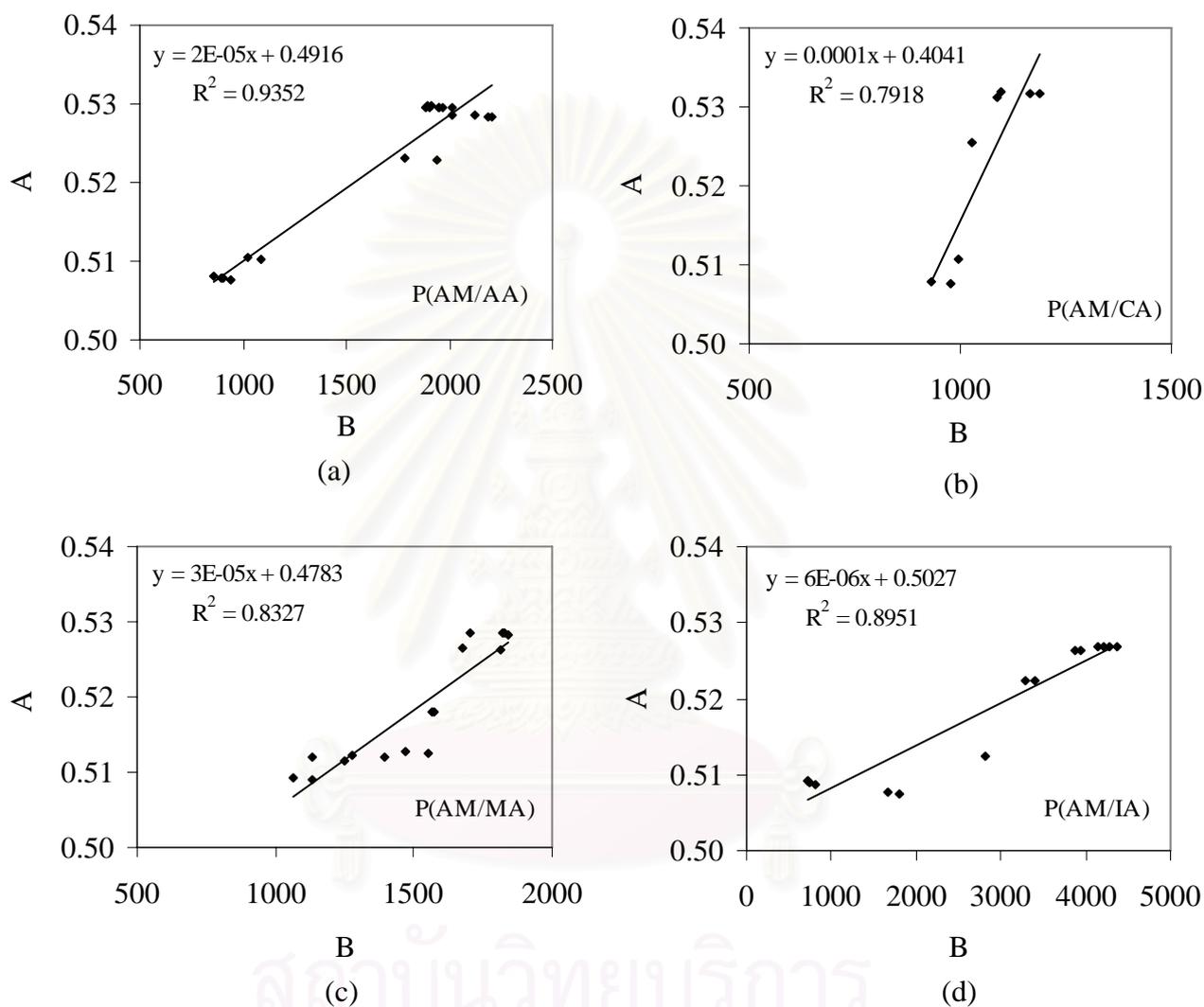
Figure 4.12 Determination of χ and $\overline{M}_c$ values from equilibrium swelling behaviors

of copolymeric hydrogels: (a) P(AM/AA), (b) P(AM/CA), (c) P(AM/MA) and (d)

P(AM/IA). Please see the text for the explanation of A and B.

Table 4.8 Essential parameters used to determine χ and $\overline{M}_c$ values from swelling experiment

hydrogels	M_r (g/mol)	V_r (cm^3/mol)	C_o (mol/cm^3)	v_{2r}
PAM	71.08	52.00	0.001	0.0519
P(AM/AA)	71.12	53.98	0.001	0.0537
P(AM/CA)	71.68	54.41	0.001	0.0543
P(AM/MA)	72.88	55.57	0.001	0.0555
P(AM/IA)	73.44	55.13	0.001	0.0550

Table 4.9 Flory polymer-solvent interaction parameter (χ) and average molecular weight between crosslinks ($\overline{M}_c$) of the hydrogels

Hydrogels	$\chi_{swelling}$	$\overline{M}_{c\ swelling}$ (g/mol)	$\overline{M}_{c\ rheology}$ (g/mol)	$M_{c\ stoi}$ (g/mol)
PAM	0.480*	37,000	219,000 ± 3,200	7,726
P(AM/AA)	0.491 ± 0.001	51,200 ± 2,800	119,000 ± 2,300	7,730
P(AM/CA)	0.404 ± 0.004	8,750 ± 150	202,000 ± 4,500	7,625
P(AM/MA)	0.477 ± 0.003	36,450 ± 50	265,000 ± 2,500	7,753
P(AM/IA)	0.503 ± 0.001	184,000 ± 3,400	250,000 ± 2,000	7,650

*literature reported [57-58]

The average molecular weight between crosslinks can also be determined via rheological measurements. The theory of polymer networks predicts the equilibrium

elastic modulus (G_e) for polymer gels obtained by solution crosslinking polymerization as shown in Eq. 4.5 [55].

$$G_e = \left(1 - \frac{2}{\phi}\right)\left(\frac{\rho_2}{\overline{M}_c}\right)RT\nu_{2r}^{2/3}\nu_{2m}^{1/3} \tag{4.5}$$

where ϕ is the functionality of the crosslinks ($\phi = 4$ for tetrafunctional networks), ρ_2 is the polymer network density, R is the gas constant, and T is the temperature. The front factor $(1-2/\phi)$ is for phantom network model. Equilibrium elastic modulus (G_e), obtained from rheological measurements of the hydrogels swollen in deionized water as reported in Table 4.10, was used to calculate $\overline{M}_c$. The values of ν_{2r} listed in Table 4.8 were also used to determine $\overline{M}_c$. The values of $\overline{M}_c$ estimated from rheological experiments were reported in Table 4.9.

   On the other hand, if one assumes that all MBA crosslinkers involve in the formation of effective crosslinks in the network, the stoichiometric molecular weight between crosslinks, $M_{c\,(stoi.)}$, was calculated by equation (4.6) [56].

$$M_{c\,(stoi.)} = M_r/2X \tag{4.6}$$

where X is crosslinking ratio which in the ratio of mole of crosslinker to mole of monomers.

   Likewise, for a comparison to network properties of the copolymeric hydrogels, $\overline{M}_c$ of PAM hydrogel calculated from swelling experiment (according to eq. 2.1 by using the literature reported χ value of the crosslinked PAM to be 0.48 [57,

58]) and rheological measurement were shown in Table 4.9. As indicated in Table 4.9, the experimentally-calculated $\overline{M}_c$ values from swelling and rheological measurements of all hydrogels are higher than their stoichiometric calculated value. This difference is attributed to the fact that a significant portion of divinyl crosslinker (MBA) is not employed in the crosslinking copolymerization. It has been well-known that gelation during free-radical crosslinking copolymerization occurs non-randomly, probably due to the cyclization and the multiple crosslinking reactions at pendant vinyl groups of MBA [59, 60]. In addition, several researchers found that high degrees of dilution of monomers during hydrogel preparation, and the higher crosslinker reactivity (11.5) may predominantly be accountable for these reactions, which lead to the inhomogeneous crosslinking distribution in the hydrogel and contribute to the decrease in elastic behavior of the hydrogel [59, 61, 62]. All these network imperfections may be responsible for an unsatisfactory basic assumption of tetrafunctional crosslinks.

Table 4.9 also points out that both experimental values of $\overline{M}_c$ determined from the swelling and rheological measurements were not in good agreement. This difference has been previously reported on the crosslinked polyacrylamide hydrogels immobilized with glucose oxidase [4]. The authors explained that $\overline{M}_c$ derived from thermodynamic swelling experiments is more reliable than the rheologically calculated $\overline{M}_c$. Entanglements (which tend to increase the modulus) and other chain defects, as closed loops and loose ends (which do not contribute to the network elasticity), have a stronger effect on the mechanical properties, and finally on the calculated values of $\overline{M}_c$ than on the swelling properties. The significant difference between the three $\overline{M}_c$ values derived from the stoichiometric calculation, swelling,

and rheological experiments reveals a rather heterogeneous structure of the hydrogels such as cyclization of polymer chains, formation of microgels in the pre-gel period which is trapped within the macrogels, pendant chain ends, and etc [5, 59].

The obtained $\overline{M}_c$ calculated from swelling experiment can be explained from the reactivity ratio of monomer pairs as follows.

Poly[(acrylamide-*co*-(crotonic acid)]

r_{AM} is 4.72-5.32 and r_{CA} is 0.11-0.12 [63], whereas r_{AM} and r_{MBA} are 0.64 and 1.77, respectively [64]. Due to low reactivity ratio of CA, it does not like to homopolymerize. Likewise, due to steric effects of MBA structure, MBA has low tendency to self-homopolymerize. Therefore, one may state that both AM and CA were crosslinked by MBA with the CA moiety at the chain end [7]. Moreover, hydrophobic nature of CA could limit the level of water absorption of the copolymer, which consequently gives higher G_e (when comparing to diprotic acid-containing copolymers).

Poly[(acrylamide-*co*-(acrylic acid)]

r_{AM} is 1.08-1.34 and r_{AA} is 0.29-0.34 [63]. Thus, higher amount of AA may incorporated within the copolymer network when compared to CA. Additionally, the hydrophilic nature of AA may create greater water absorption to P(AM/AA). Due to the high reactivity ratio of MBA, MBA tend to incorporate into the polymer chain and can crosslink both AM and AA. Since more ionic contents were included in the polymer, the growing chains presume more extended conformation which resulted in the larger $\overline{M}_c$.

Poly[acrylamide-*co*-(maleic acid)]

Maleic acid has low tendency to copolymerize and does not homopolymerize as a result of its 1,2-disubstituted vinyl structure [65]. However, in the presence of a monomer with a high polymerization tendency such as acrylamide, maleic acid randomly incorporated into the copolymer backbone [66]. This random incorporation of ionic moieties may lead to the lower degree in electrostatic repulsion of the charge groups. This might lead to the similar value of the calculated $\overline{M}_c$ from swelling experiments ($\overline{M}_{c\,\text{swelling}}$) of crosslinked PAM and crosslinked P(AM/MA). However, the presence of carboxylic groups in crosslinked P(AM/MA) enhances hydrophilicity of the system resulting in the increase in equilibrium swelling of the copolymer. The presence of absorbed water molecules in the copolymer could lead to the lower G_e value compared to the crosslinked PAM.

Poly[acrylamide-*co*-(itaconic acid)]

r_{AM} is 0.48-0.88 and r_{IA} is 1.24-1.65 [63]. High reactivity ratio of IA is from the presence of methylene group, connected to one carboxylic group, at the beta carbon. IA has more tendencies to incorporate into the growing chains due to its higher reactivity ratio over AM. As a result, IA might be incorporated as a block in the copolymer backbone. The presence of higher amount of negative charges from carboxylic groups along the backbone caused the growing chain extend more than the system of P(AM/MA) due to higher electrostatic repulsion. Thus, high $\overline{M}_c$ was obtained.

Table 4.10 Water absorbency (Q), equilibrium swelling by volume (q_v) and

equilibrium elastic modulus (G_e) of hydrogels swollen in deionized water

hydrogels	Q(g g^{-1})	q_v	G_e (Pa)
PAM	33 ± 1	46 ± 2	300
P(AM/AA)	131 ± 7	174 ± 10	350
P(AM/CA)	44 ± 2	59 ± 4	300
P(AM/MA)	160 ± 4	210 ± 6	150
P(AM/IA)	294 ± 6	393 ± 9	130

Table 4.10 indicated that Q inversely correlated with G_e. The presence of more water molecules inside the hydrogel increases the mobility of the network chains, and thus reduces the strength of the system.

4.4 Effect of the Equilibrium Degree of Swelling

The correlation of the extent of equilibrium water absorbency and the viscoelastic properties of each hydrogel was studied from the copolymeric hydrogels synthesized from the polymerization conditions designed as Set 2 and Set 3. Figures 4.13 and 4.14 show the stress sweep and frequency sweep of Set 2 and Set 3 for the copolymeric hydrogels, respectively. The equilibrium water absorbency and the equilibrium elastic modulus of P(AM/AA), P(AM/CA), P(AM/MA) and P(AM/IA) are shown in Table 4.11.
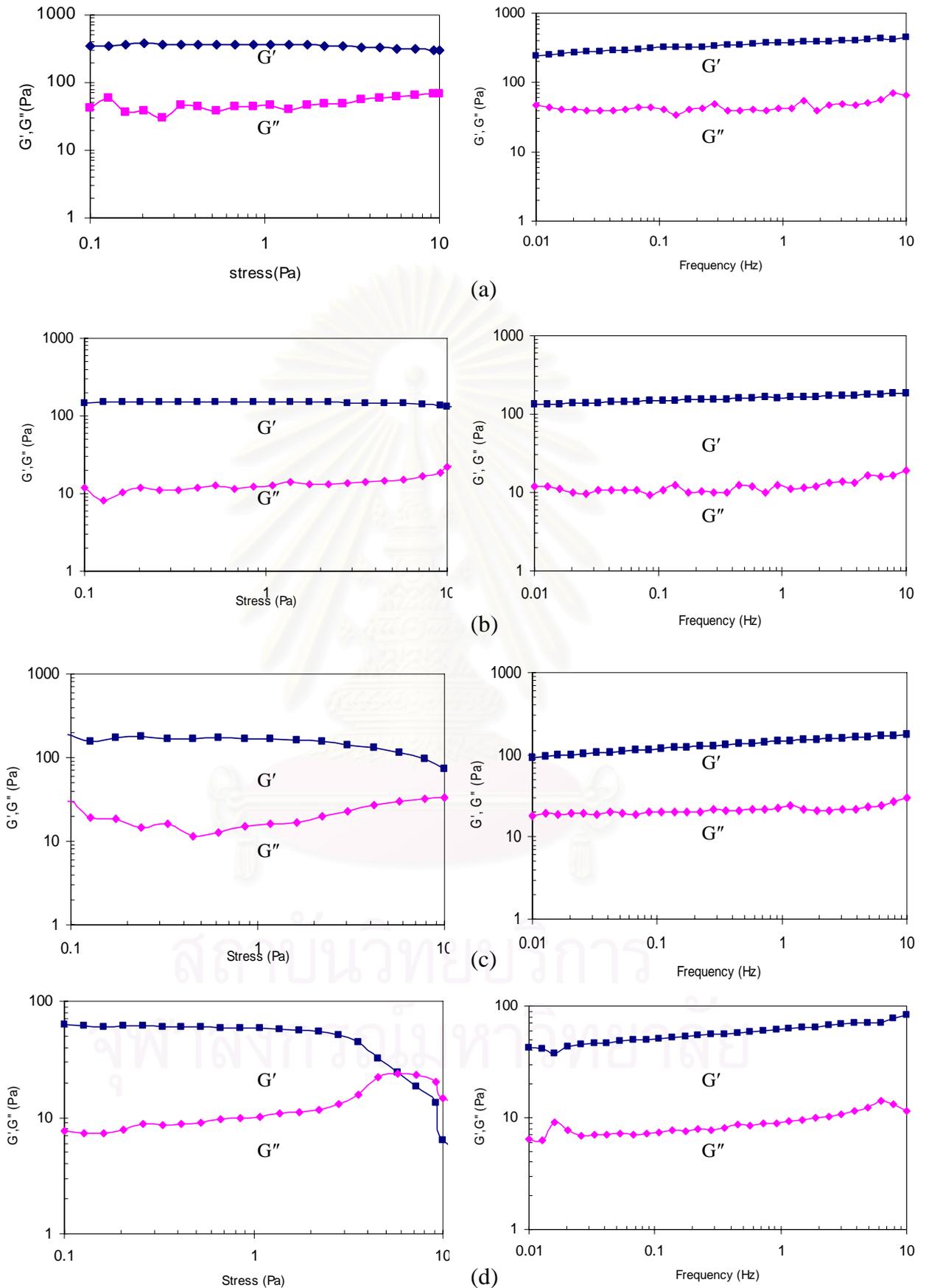
Figure 4.13 Stress sweep and frequency sweep of copolymeric hydrogels (Set 2): (a)

P(AM/AA), (b) P(AM/CA), (c) P(AM/MA) and (d) P(AM/IA)
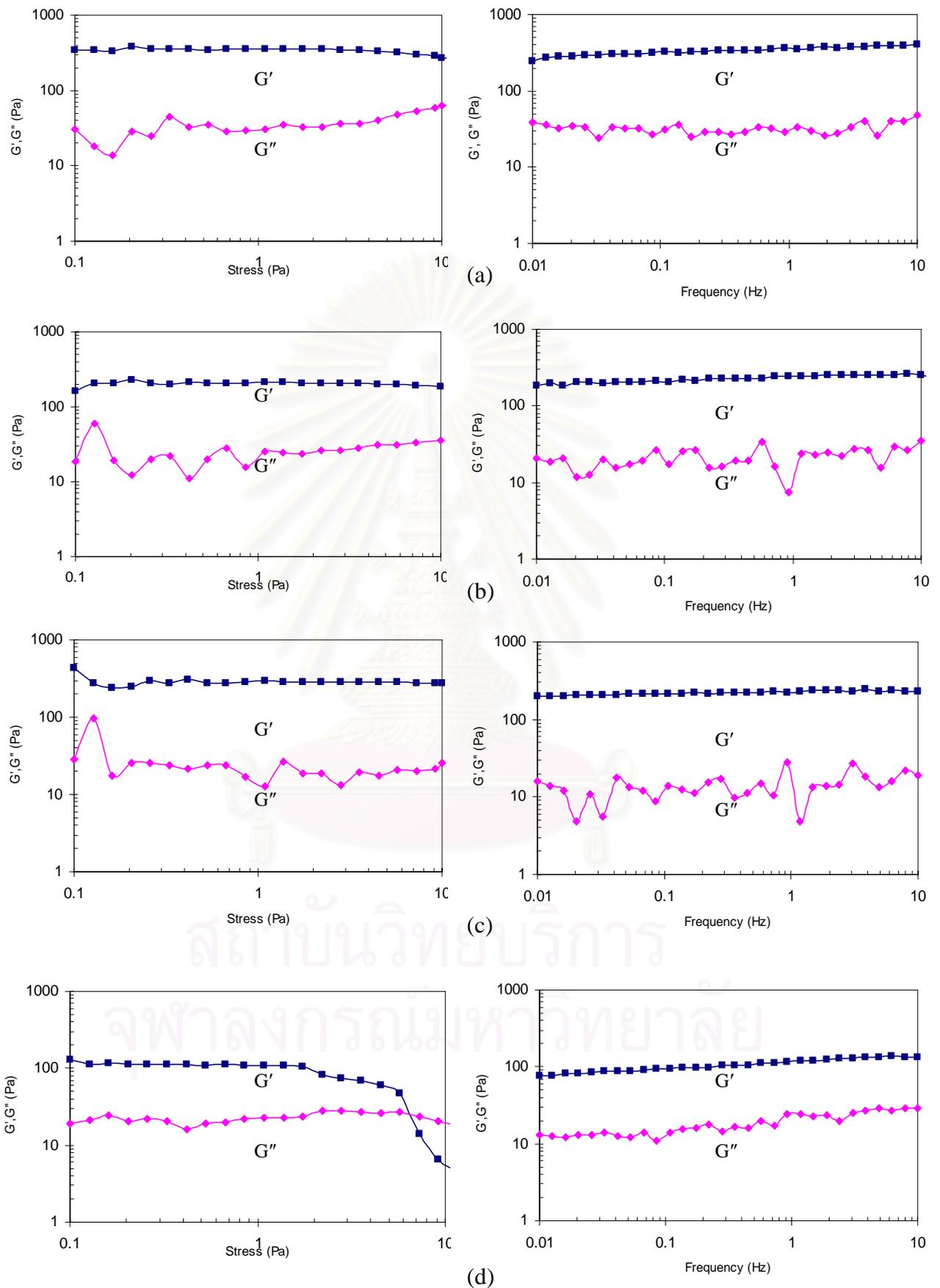
Figure 4.14 Stress sweep and frequency sweep of copolymeric hydrogels (Set 3): (a)

P(AM/AA), (b) P(AM/CA), (c) P(AM/MA) and (d) P(AM/IA)

As shown in Figures 4.13 and 4.14, the G′ value of all hydrogels is always higher than G″ for the whole frequency range studied. It is clear that G′ of the copolymers shows almost no dependence on the frequency. These features are characteristics of a "strong gel" (stable viscous liquid) [47]. The elastic behavior of the polymeric gel predominates over its viscous behavior, and the swollen gel also exhibits the mechanical rigidity.

Table 4.11 Equilibrium water absorbency (Q) of hydrogels swollen in deionized water

monomer	Equilibrium water absorbency (Q) (g g^{-1})			
	P(AM/AA)	P(AM/CA)	P(AM/MA)	P(AM/IA)
Set 2				
<150μm	166 ± 1	60 ± 3	371 ± 6	515 ± 7
150-300μm	173 ± 3	62 ± 4	354 ± 13	400 ± 14
G_e (Pa) Size <150μm	240	130	90	40
Set 3				
<150μm	117 ± 3	47 ± 2	39 ± 2	360 ± 7
150-300μm	130 ± 3	53 ± 3	41 ± 2	341 ± 6
G_e (Pa) Size <150μm	260	190	200	75

The results from Table 4.11 showed that the equilibrium water absorbency of Set 2 was higher than one of Set 3 because more ionic comonomer was employed in Set 2. Table 4.11 also shows that G_e of Set 3 was higher than that of Set 2. The G_e of

P(AM/AA) and P(AM/CA) are higher than those of the P(AM/IA) and P(AM/MA) which indicated that Q inversely correlated with G_e. In both Sets, the G_e values of P(AM/AA) were higher those that of P(AM/CA), even though water absorbency of P(AM/AA) hydrogel was much larger. This might be due to the higher amount of MBA added into the synthesis experiments of P(AM/AA) as compared to P(AM/CA) systems. However, as described previously that AA might be incorporated within the copolymeric network, while CA may locate at the copolymer chain ends. And additionally, AA is more hydrophilic in nature. Thus, this could lead to higher water absorbency of P(AM/AA) system despite the presence of higher amount of crosslinker.
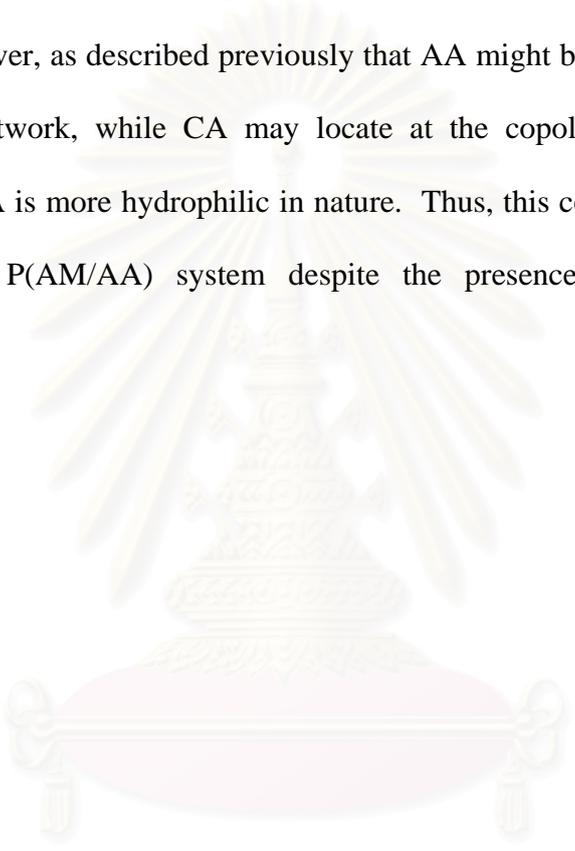
CHAPTER V

CONCLUSIONS AND RECOMMENATIONS

5.1 Conclusion

In this research, poly[AAm-*co*-AA], poly[AAm-*co*-CA], poly[AAm-*co*-MA] and poly[AAm-*co*-IA] hydrogels were prepared by solution polymerization using APS and TEMED as an initiator and coinitiator, respectively, and N-MBA as crosslinking agent. The findings can be concluded as follows:

1. The water absorbency of each hydrogel of poly[AAm-*co*-AA], poly[AAm-*co*-CA], poly[AAm-*co*-MA] and poly[AAm-*co*-IA] is higher than that of PAM.

2. The functional groups of the synthesized copolymeric hydrogels were characterized by RAMAN Spectroscopy. The results show that spectra of the copolymers give the characteristic absorption peaks of the O-H stretching at 3206-3200 cm^{-1}, the C-H stretching at 2922 cm^{-1} and the peak at 1651-1648 cm^{-1} of C=O stretching of COO^{-}. Moreover, the peaks at 3337-3334 and 1320-1316 cm^{-1} indicate the N-H stretching and C-N stretching of amide groups, respectively.

3. The surface appearance of synthesized copolymers was observed using SEM technique. The cellular structure with rough irregular surfaces and plenty of porous patterns control the ability to absorb and retain water.

4. The equilibrium water absorbency of poly[AAm-*co*-AA], poly[AAm-*co*-CA], poly[AAm-*co*-MA] and poly[AAm-*co*-IA] hydrogels can be achieved at 166±1 g g^{-1}, 60±3 g g^{-1}, 371±6 g g^{-1} and 515±7 g g^{-1}, respectively.

5. The rheological studies indicate that the elastic responses of poly[AAm-*co*-AA], poly[AAm-*co*-CA], poly[AAm-*co*-MA] and poly[AAm-*co*-IA] hydrogels are

stronger than their viscous responses. The copolymers have a higher storage modulus which agrees with the lower water absorption. It confirms that the low water absorbency is controlled by the rigid polymer chains. The copolymers are thus the strong gel.

6. The average molecular weight between crosslinks ($\overline{M}_c$) and polymer-solvent interaction parameter (χ) were determined from swelling data by using the equations based on Flory-Rehner swelling theory, and the approaches of Brannon-Peppas and Peppas on monoprotic acid-containing hydrogels. The equation modified by Şen and Güven was used for determining $\overline{M}_c$ and χ for the diprotic acid-containing hydrogels. Equilibrium elastic modulus was used to determine $\overline{M}_c$ based on the polymer network theory. Large difference between $\overline{M}_c$ from both measurements was observed. This difference in the basis of different theories indicates existence of an intrinsic heterogeneous structure within the hydrogels.

5.2 Recommendations for Future Work

Chapter IV contains the original manuscript material drafted for an international journal. Synthesis of superabsorbent polymers by solution polymerization would be further studied as follows:-

a) The absorbency under load should be measured because water absorbency correlate with strength of hydrogel.

b) Proton relaxation time by NMR should be investigated.
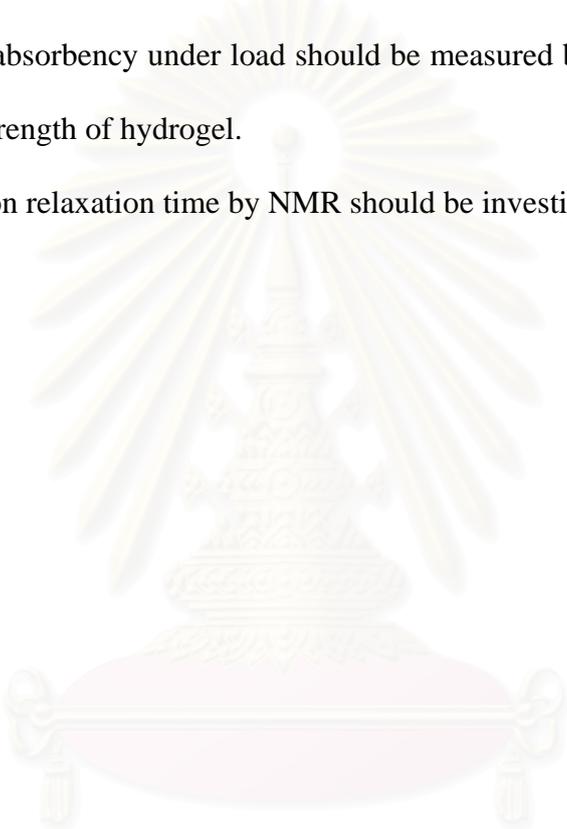
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APPENDICES

APPENDIX A

Determination of Average Molecular Weight between

Crosslinks

From Figure 4.12 and Equation 4.1, the plot of A against B correspondingly gives $\overline{M}_c$ and χ as the intercept and inverse slope via a linear regression analysis. The data of this experiment is shown in Table A-1 to Table A-4 for P(AM/AA), P(AM/CA), P(AM/MA) and P(AM/IA), respectively.

Table A-1 Data for determination of $\overline{M}_c$ and χ for P(AM/AA)

pH	A	B
2	0.5079	896.585
3	0.5077	942.663
4	0.5104	1037.567
5	0.5229	1860.209
6	0.5285	2110.891
7	0.5297	1860.209
8	0.5296	1921.689
9	0.5296	1921.689

Table A-2 Data for determination of $\overline{M}_c$ and χ for P(AM/CA)

pH	A	B
2	0.5079	903.053
3	0.5077	949.463
4	0.5107	968.042
5	0.5250	996.328
6	0.5306	1054.973
7	0.5313	1066.534
8	0.5312	1134.192
9	0.5311	1152.433

Table A-3 Data for determination of $\overline{M}_c$ and χ for P(AM/MA)

pH	A	B
2	0.5091	1101.070
3	0.5118	1189.689
4	0.5121	1332.994
5	0.5126	1512.636
6	0.5181	1570.279
7	0.5263	1743.683
8	0.5283	1773.61
9	0.5284	1824.974

Table A-4 Data for determination of $\overline{M}_c$ and χ for P(AM/IA)

pH	A	B
2	0.5091	720.739
3	0.5088	772.779
4	0.5076	1740.292
5	0.5124	2939.961
6	0.5223	3346.432
7	0.5263	3908.715
8	0.5267	4210.479
9	0.5268	4291.286

APPENDIX B

The data of feeding composition of all components, i.e. monomers, crosslinker, initiator, coinitiator, and water for the synthesized hydrogels are shown in Table B-1.

Table B-1 Feeding composition for the synthesized hydrogels

hydrogels	monomers		crosslinker	initiator	coinitiator	water
	AM (g)	comonomer	MBA (g)	APS (g)	TEMED (cm^3)	(cm^3)
PAM	7.108	-	0.0711	0.0711	0.14	100
P(AM/AA)	6.8238	0.27 cm^3	0.0713	0.0714	0.18	100
P(AM/CA)	6.8237	0.3446 g	0.0718	0.0717	0.18	100
P(AM/MA)	6.8238	0.4644 g	0.0730	0.0729	0.19	100
P(AM/IA)	6.8238	0.5204 g	0.0730	0.0735	0.19	100

VITA

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