การสังเคราะห์และการตรวจลักษณะเฉพาะของซุปเปอร์แอบซอร์แบนซ์ที่มีรูพรุนของพอลิ(อะคริลิกแอซิด-*โค*-อะคริลาไมด์)

นางสาวรัตนา วงศ์วัฒนเสถียร

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SYNTHESIS AND CHARACTERIZATION OF POROUS SUPERABSORBENTS OF POLY(ACRYLIC ACID-*CO*-ACRYLAMIDE)

Miss Rattana Wongwatthanasatiean

A Thesis Submitted in Partial Fulfillment of the Requirements
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รัตนา วงศ์วัฒนเสถียร : การสังเคราะห์และการตรวจลักษณะเฉพาะของซุปเปอร์แอบซอร์แบนซ์ที่มีรูพรุนของพอลิ(อะคริลิกแอซิด-*โค*-อะคริลาไมด์) อ. ที่ปรึกษาวิทยานิพนธ์ : ศาสตราจารย์ ดร. สุดา เกียรติกำจรวงศ์, 130 หน้า. ISBN 974-13-1338-1.

การสังเคราะห์ซุปเปอร์แอบซอร์แบนซ์พอลิเมอร์โดยกระบวนการพอลิเมอไรเซชันแบบสารละลาย ซึ่งใช้เวลาพอลิเมอไรซ์สั้นสำหรับอะคริลิกแอซิดและอะคริลาไมด์มอนอเมอร์ ในตัวเร่งปฏิกิริยารีดอกซ์ (แอมโมเนียมเพอร์ซัลเฟต / เอ็น, เอ็น,เอ็น, เอ็น-เททระเมทิลเอทิลีนไดแอมีน) ศึกษาชนิดของตัวเชื่อมขวาง (เอ็น, เอ็น-เมทิลีนบิสอะคริลาไมด์, เอทิลีนไกลคอลไดเมทาคริเลต และฟอร์แมลดีไฮด์) ในภาวะที่มีการเกิดฟองแก๊สคาร์บอนไดออกไซด์ระหว่างการเกิดปฏิกิริยาของกรดอะคริลิกและ $NaHCO_3$ และสเตบิไลซ์ด้วย PF127 และใช้รอบกวนที่ 250 รอบต่อนาที อุณหภูมิ 45 องศาเซลเซียส เวลา 30 นาที โคพอลิเมอร์ที่สังเคราะห์ได้นำมาดึงน้ำออกโดยตกตะกอนในเมทานอลที่มากเกินพอ แล้วอบให้แห้งโดยใช้เตาอบสุญญากาศ ที่อุณหภูมิ 50 องศาเซลเซียส 24 ชั่วโมง ศึกษาการดูดซึมน้ำ ณ ภาวะบวมตัวเต็มที่เทียบกับเวลาของไฮโดรเจลในน้ำกลั่น นอกจากนี้ยังศึกษาพฤติกรรมการบวมตัวของโคพอลิเมอร์ที่สังเคราะห์ได้ในสารละลายเกลือต่างๆ และในสารละลายบัฟเฟอร์ที่มีความเป็นกรด-เบสต่างๆ พฤติกรรมการบวมตัวของแอบซอร์แบนซ์นี้มีความสัมพันธ์กับโครงสร้างทางเคมี สัดส่วน และธรรมชาติของสารละลายเกลือต่างๆ

อิทธิพลของตัวแปรของปฏิกิริยาต่อการดูดซึมน้ำของโคพอลิเมอร์ที่สังเคราะห์ได้ โคพอลิเมอร์ที่ได้จากการสังเคราะห์โดยมีสัดส่วนโมลของอะคริลาไมด์ที่ 0.1, ความเข้มข้นของตัวริเริ่มปฏิกิริยาแอมโมเนียมเพอร์ซัลเฟตที่ 2.3×10^{-3} โมลต่อลูกบาศก์เดซิเมตร, เอ็น, เอ็น, เอ็น, เอ็น-เททระเมทิลเอทิลีนไดแอมีน 1.0×10^{-2} โมลต่อลูกบาศก์เดซิเมตร, กรดอะคริลิกที่ไม่ได้ทำให้เป็นกลาง, เอ็น, เอ็น-เมทิลีนบิสอะคริลาไมด์ 4.0×10^{-3} โมลต่อลูกบาศก์เดซิเมตร, PF127 0.06 เปอร์เซ็นต์โดยน้ำหนักต่อปริมาตร และ $NaHCO_3$ 2.48×10^{-1} โมลต่อลูกบาศก์เดซิเมตร ค่าการดูดซึมน้ำที่สูงที่สุดวัดได้ 2,196±14 เท่าของน้ำหนักแห้ง และสามารถดูดซึมน้ำได้ 1,628±14 เท่าของน้ำหนักแห้งภายในเวลา 10 นาที การคอมเพล็กซ์ของพอลิ(อะคริลิกแอซิด-*โค*-อะคริลาไมด์) กับสารช่วยตกตะกอน $Al_2(SO_4)_3.8H_2O$ โดยเกิดพันธะเคมีระหว่างไอออนโลหะและคาร์บอกซิลิกแอซิดหรือลิแกนด์เอไมด์ภายในพอลิเมอร์ สารช่วยตกตะกอนคอมเพล็กซ์พอลิเมอร์นี้ให้ประสิทธิภาพดีกว่าการใช้สารช่วยตกตะกอนที่ไม่ได้เกิดเป็นคอมเพล็กซ์

หลักสูตร ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต……………………………..………………….
สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่ออาจารย์ที่ปรึกษา…………………………………
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4172561823 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEY WORD: POROUS SUPERABSORBENT / ACRYLIC ACID / ACRYLAMIDE / REDOX INITIATOR

RATTANA WONGWATTHANASATIEAN : SYNTHESIS AND CHARACTERIZATION OF POROUS SUPERABSORBENTS OF POLY(ACRYLIC ACID-*CO*-ACRYLAMIDE).
THESIS ADVISOR : PROF. SUDA KIATKAMJORNWONG, Ph.D. 130 pp.
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A series of superabsorbent polymers was synthesized by solution polymerization using a short polymerizing time for acrylic acid(AA) and acrylamide(AM) monomer in a redox initiator (ammonium persulfate(APS)/ $N,N,N^{\prime},N^{\prime}$- tetramethylethylenediamine (TMEDA)) with various types of crosslinker ($N,N^{\prime}$-methylene bisacrylamide (N-MBA), ethyleneglycol dimethacrylate (EGDMA) or formaldehyde) in the presence of CO_2 gas bubbles formed by the chemical reaction of acrylic acid and $NaHCO_3$ stabilized by PF127 foam with a stirring speed of 250 rpm at the temperature 45°C for 30 min. The synthesized copolymers were dewatered by precipitation with excess methanol and drying at 50°C in a vacumm oven for 24 h. The absorption kinetic behavior for these hydrogels in distilled water was investigated. In addition, the water absorbencies of the synthesized copolymer in various saline and pH buffered solutions were investigated. The swelling behavior of these absorbents were related to their chemical structures, compositions, and the nature of external salt solutions.

The effects of the influential reaction parameters on water absorbency of the synthesized copolymers were investigated from which they were produced from the following recipe: 0.1 mole fraction of AM; 2.3×10^{-3} mol dm^{-3} APS; 1.0×10^{-2} mol dm^{-3} TMEDA; unneutralizated AA; 4.0×10^{-3} mol dm^{-3} N-MBA; 0.06% w/v PF127; and 2.48×10^{-1} mol dm^{-3} $NaHCO_3$. The highest water absorbency of the synthesized copolymer was 2,196±14 times its dry weight and can absorp up to 1,628±14 times its dry weight in 10 min. Complexation of poly(acrylic acid–*co*-acrylamide) with $Al_2(SO_4)_3\cdot 8H_2O$ coagulant could take place through the chemical bonding between the metal ion and carboxyl acid groups or amide ligands within the polymer. This complex polymeric flocculant(CPF) is more effective for water treatment than the non CPF.

Department…………………-………………………	Student's signature……………………………….
Field of study Petrochemistry and Polymer Science	Advisor's signature……………………………….
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ABBREVIATIONS

SAPs	Superabsorbent Polymers
AA	Acrylic acid
AM	Acrylamide
FTIR	Fourier Transform Infrared Spectroscopy
SEM	Scanning Electron Microscopy
T_g	glass transition temperature
s	second
min	minute
$g\ g^{-1}$	gram per gram
% w/v	percent weight by volume
^oC	degrees Celsius
kV	kilovolt
kcal	kilocalories
µm	micrometer
dm^3	cubic decimeter
cm^{-1}	reciprocal centimeter, wave number
rpm	round per minute
h	hour

kg	kilogram
mol dm^{-3}	mole per cubic decimeter
Q	water absorbency, liquid absorbency
f	functionality
%T	percentage transmittance
$\overline{M_n}$	the average molecular weight of the polymer before crosslinking
$\overline{M_c}$	the average molecular weight between crosslinks
M	the molecular weight of polymer repeat unit
k	the Boltzmann constant
T	temperature
χ_{12}	the Flory-Huggins interaction parameter between solvent and polymer
I	the ionic strength
S	the swelling ratio
q	the mole fraction of crosslinked units
q_m	the swolling ratio of the network at equilibrium
ρ_p	the polymer density

$\bar{\upsilon}$	the polymer specific volume
ϕ_p	the volume fraction of polymer in the swollen gel
V_o	the volume of the unswollen network
D	the diffusion coefficient
k_d	the rate constant for initiator decomposition
k_p	the rate constant for the propagation step
k_t	the rate constant for the termination step
k_{tc}	the rate constant for the termination step by combination
k_{td}	the rate constant for the termination step by disproportionation
N-MBA	*N,N'*-methylenebisacrylamide
PF127	Pluronic F127
APS	ammonium persulfate
TMEDA	*N,N,N',N'*-tetramethylethylenediamine
EGDMA	ethylene glycol dimethacrylate
CPF	complex polymeric flocculant
KPS	potassium persulfate
TEGDA	triethylene glycol diacrylate

BPO	benzoyl peroxide
PVA	poly(vinyl alcohol)
PEO	poly(ethylene oxide)
CMC	carboxymethyl cellulose
VP	vinyl pyrrolidone
HEMA	hydroxy ethylmethacrylate
SPAK	potassium salt of 3-sulfopropylacrylate
NIPAM	N-isopropyl acrylamide
AMPS	acrylamido-2-methyl-1-propanesulfonic acid
ATMS	2-(acryloyloxyethyl)trimethyl ammonium methylsulfate
SA	sodium acrylate
KA	potassium acrylate
TMMAAI	trimethyl methacrylamidopropyl ammonium iodide
DMAAPS	*N,N'*-dimethyl(acrylamidopropyl) ammonium propane sulfonate
DMAPS	dimethyl(methacryloyloxyethyl) ammonium propane sulfonate
MSAS	sodium methallylsulfonate

HSPAA	hydrolyzed starch-poly(acrylic acid) graft copolymer
HSPAN	hydrolyzed starch-polyacrylonitrile graft copolymer
PAA	partially crosslinked poly(acrylic acid) salt
MA	maleic acid
IB	isobutylene
U.S. Pat	United States of America Patent
EP	European Patent
Eur. Polym. J.	European Polymer Journal
J. Chem. Ed.	Journal of Chemistry Education
J. Polym. Sci.	Journal of Polymer Science
J. Polym. Sci. : Part A Polym. Chem.	Journal of Polymer Science Part A : Polymer Chemistry
J. Polym. Sci. : Part B Polym. Phys.	Journal of Polymer Science Part B : Polymer Physics
J. Appl. Polym. Sci.	Journal of Applied Polymer Science
DPST	Development and Promotion of Science and Technology

CHAPTER 1

INTRODUCTION

1.1 Scientific Rationale

Since the early 1970s the growth of the superabsorbent polymers (SAPs) industry and the competitive drive toward new and less costly designs requires polymers with improved properties. Superabsorbent polymers capable of absorbing and holding large amounts of water and used to absorb body fluids in a variety of personal care products, notably body diapers. These polymers absorb and hold under pressure because of the effectiveness of superabsorbent polymers, diapers have become an important component of disposable infant diapers, adult incontinence products, and fascinating substances because of using a superabsorbent polymer as a liquid storage medium. Many kinds of SAPs have been commercialized since they are widespreadly applied not only in the fields of personal care products, biosorbent, biomaterials, but also in soil for agriculture and horticulture, medicine for the drug delivery system, wastewater treatment, gel actuator, etc., where water absorbency or water retention is important.

Among superabsorbent polymer types, the crosslinked, partially neutralized poly (acrylic acids) are the principal superabsorbent polymer of commerce. SAPs are most commonly formed by free radical crosslinking polymerizations of hydrophilic acrylate or methacrylate monomers with small quantities of crosslinking agents containing two (or more) polymerizable double bonds.

1.2 Objectives of the Research Work

The objectives of this research are as follows:

1.2.1 To synthesize the poly(acrylic acid-*co*-acrylamide) by foamed solution polymerization. Influences of reaction parameters such as mole fraction of acrylamide: acrylic acid, degree of neutralization of acrylic acid, type of crosslinking agent, crosslinking concentration, etc., were studied.

1.2.2 To characterize some chemical and physical properties of the synthesized superabsorbent polymers.

1.2.3 To study absorption capacity of the resulting polymer.

1.2.4 To study kinetics of absorption of the synthesized superabsorbent polymers.

1.2.5 To apply the synthesized superabsorbent polymer to purifying wastewater.

1.3 Expected Benefit Obtainable for Development of This Research

1.3.1 To achieve the synthesized superabsorbent polymers with high water absorption rates and water absorption capacities possibly for thin disposable diapers and feminine napkin application.

1.3.2 To explain some influences of the reaction parameters in order to possibly transfer far-more developed technologies for the synthesis of effective superabsorbent polymers.

1.4 Scopes and Work Plan

The synthesis of superabsorbent polymer by solution polymerization, which is a highly flexible and versatile technique to produce superabsorbents with a high capacity of absorption acrylicacid (AA) and acrylamide (AM) are used as comonomers. They are polymerized by a thermal initiator with a crosslinking agent, in water at the temperature of 45°C for 30 min. The influences of reaction parameters on properties of synthesized copolymer are investigated. The important procedure to achieve a better result is as follows:

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

1.4.2 Synthesis of poly(acrylic acid-*co*-acrylamide) via an solution polymerization by changing the following parameters so as to attain an appropriate reaction condition:

a) The effect of mole fraction of monomer (acrylamide : acrylic acid) : 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9

b) The effect of reaction temperatures at: 45, 50, 55, 60, 65, and 70°C.

c) The effect of initiator concentration (mol dm^{-3}) of ammonium persulfate (APS): *N, N,N',N'*-tetramethylethylenediamine (TMEDA) at: $1.50.\times10^{-3}$: 1.0×10^{-2}, 2.0×10^{-3}: 1.0×10^{-2}, 2.30×10^{-3}: 1.0×10^{-2}, 3.0×10^{-3}: 1.0×10^{-2}, $3.50.0\times10^{-3}$: 1.0×10^{-2}, 4.4×10^{-3}: 1.0×10^{-2}, and 2.30×10^{-3}: 2×10^{-2}

d) The effect of crosslinking agent types: *N, N'*-methylenebisacrylamide (N-MBA), ethylene glycol dimethacrylate (EGDMA) and formaldehyde.

e) The effect of crosslinking concentration (mol dm^{-3}) at: 1.0×10^{-3}, 1.5×10^{-3} 2.0×10^{-3}, 2.5×10^{-3}, 3.0×10^{-3}, 3.5×10^{-3}, 4.0×10^{-3}, 4.5×10^{-3}, and 5.0×10^{-3}.

f) The effect of degree of neutralization of acrylic acid at: 0%, 40%, 60%, 80%, and 100%.

1.4.3 Characterization of the synthesized polymer by means of :

a) Identification of functional group and structure in the copolymer by Fourier transform infrared spectroscopy.

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

c) The water absorbency of the synthesized polymer in distilled water, universal buffer solution (APPENDIX B): pH 2-12 and electrolyte solutions: sodium chloride (NaCl), calcium chloride ($CaCl_2$), magnesium chloride ($MgCl_2.6H_2O$) potassium chloride (KCl), potassium iodide (KI), and potassium bromide (KBr) was determined.

d) The water absorbency of the synthesized polymer in urea solution.

e) The water absorbency of the synthesized polymer in various temperature of distilled water at: 35, 45, 55, 65, 75, and 85^{o}C.

1.4.4 Studying the kinetic of absorption of the copolymer in distilled water.

1.4.5 Application of the synthesized polymer in purifying water.

a) Prepare a complex polymeric flocculant (CPF)

b) Efficiency of Wastewater Treatment

1.4.6 Summarizing the result and preparing the report.

CHAPTER 2

THEORY AND LITERATURE REVIEW

2.1 Superabsorbent Polymer (SAPs)

Superabsorbent polymers (SAPs) are used in a wide range of health care applications. They are especially important as materials for absorbing and holding large amounts of fluid in personal care products such as infant diapers, feminine hygiene and incontinence products. Furthermore, they 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. SAPs are crosslinked networks of flexible polymer chains. The polymer chains each have a preferred size and orientation in space that depends on their environment and their own thermal motion, which keeps them in constant, random motion about an average location.

The commercially important SAPs are prepared by redox and thermal free-radical initiated polymerizations of acrylic acid and its salts, with small quantities of a croslinker containing two (or more) polymerizable double bonds such as N,N'-methylenebisacrylamide, triallylamine and analogs of the aforementioned acrylates, in aqueous solution or as a suspension of drops of aqueous solution in a hydrocarbon. Some of the commercially available polymers are graft terpolymers with starch or poly(vinyl alcohol) as the graft substrate. As mentioned above, SAPs have been mainly used and developed only in the limited field of disposable absorbing materials such as primarily in diapers and feminine hygiene applications. Commercially available products are summarized in Table 2.1 [1].

Table 2.1 Commercially Available Superabsorbent Polymer [1]

Maker	Trade Name	Composition
JAPAN		
Sanyo Kasei	SUNWET	HSPAA, PAA
Seitetsu Kagaku	AQUAKEEP	PAA
Kao	TURFINE	PAA
Sumitomo Kagaku	SUMIKAGEL	PVA-b-PAA
		PEO
	IGETAGEL P	Vinyl alcohol
		Sodium polyacrylate
Arakawa Kagaku	ARASORB	PAA
Nippon Shokubai	AQUALIC	PAA
	ACRYHOPE	PAA
Kurareisoprine	KI gel	MA-co-IB
Exlan	LANSIL	HPAN
Nippon Synthetic Chemical Industry	MIZUMOCHI ICHIBAN	PVA
Mitsubishi Petrochemical	DIAWET	PAA
Kurita Water Industries	GRASSPOWER	PAA
Meisei Kagaku	AQUAPLEN P 840	PEO
USA		
Dow Chemical	DRYTECH	PAA
Grain Processing	WATER-LOCK	HSPAN
Hercules	AQUALON	CMC
EUROPE		
BASF	LUQUASORB	PAA
Stockhausen	FAVOR	PAA

2.1.1 Physical Behavior of Superabsorbent Polymers

Superabsorbent polymers (SAPs) are crosslinked networks of flexible polymer chains. The most efficient water absorbers are polymer networks that carry dissociated, ionic functional groups. SAPs function by means of a diffusive mechanism. Diffusion is a molucular phenomenon wherein molecules move in a random, nonorganized manner as a result of their thermal energy. Increasing the temperature makes the molecules move faster, and the diffusive processes occur therefore at a faster rate. The molecules are in constant motion and will move from their average position in space toward regions of lower activity by purely statistical means. The absorption mechanism before and after swelling in a dilute salt solution of an example of a superabsorptive resin, in the case of a crosslinked polymer with sodium carboxylate groups is shown in Figures 2.1 and 2.2. Before absorption, long chains of polymers are interwoven and polymers make a three-dimensional structure by crosslinking between the chains to make a dense phase. These SAPs instantaneously absorb water and swell with dissolution of Na^+, owing to the hydrophilic ionic groups, and becoming a gel [2].

During absorption, water moves into a particle of superabsorbent polymer 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 superaborbent polymer network must also move, generally in a direction opposite to that of the water molecules, in order to accommodate the volume of the additional molecules of water. After absorption, the change in volume is apparent due to polymer molecules are much larger than water molecules, they diffuse much more slowly. Not only are the polymer molecules larger, but they are also connected one to the other by the crosslinks, so that the polymer does not eventually dissolve in the water and become useless as a superabsorbent.

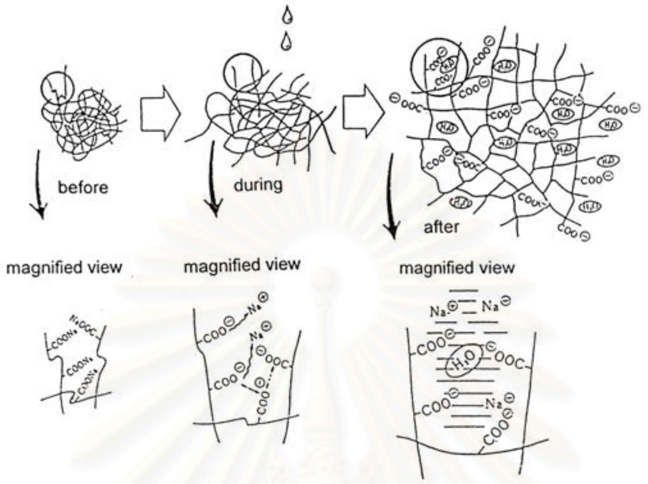


Figure 2.1 Water absorption in ionic polymer network. Sodium carboxylate groups are present in a stable salt form (before). Sodium cations (Na^+) leave carboxylate anions ($-COO^-$) bound to polymer chains, which then extend as a result of repulsion between anionic charge (during). Water molecules are taken in and retained in the polymer network (after).

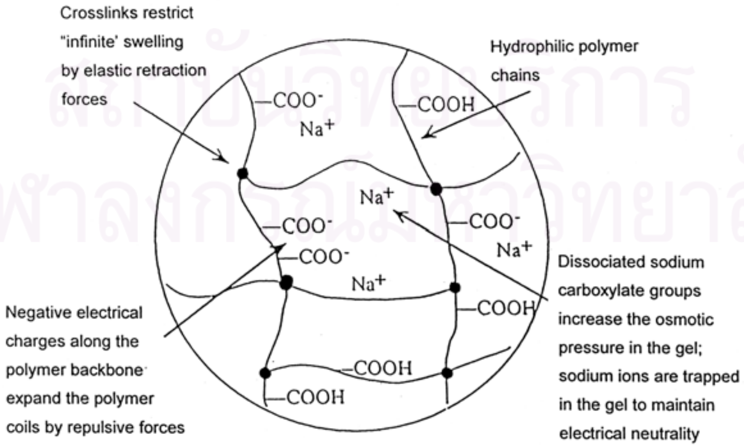


Figure 2.2 Mechanisms of swelling of superabsorbent polymers

2.1.2 Applications of Superabsorbent Polymers

Superabsorbent polymers possess a number of attributes that make them attractive in many different applications. Superabsorbent polymers have supplanted much of the traditional absorbents in infant diapers and have made significant improvements in the performance of feminine hygiene products and adult incontinence products as a result of superior water-absorbing properties. The basic property of water absorption has suggested the use of superabsorbent 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 and fertilizers may be incorporated into superabsorbent polymer to yield controlled release products.

Another characteristic of the swollen polymer is its rubbery nature, which has been 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 impart sealing properties to products that are in contact with water or aqueous solutions, for example, underground wires and cables [3]. In recent their applications are being extended into other industrial areas as shown in Table 2.2 [2].

Table 2.2 Possible Applications of Superabsortive Polymers

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

2.2 Polyacrylates by Free Radical Chain Polymerization

The structure of the polymeric network is ultimately determined by the method of synthesis. One of the most important types of addition polymerization is initiated by the action of free radicals, electrically neutral species with an unshared electron. All free radical addition (chain growth) polymerization have at least three basic reaction types occurring simultaneously during polymerization. These include: initiation reactions which continuously generate radicals; propagation reactions which are responsible for the growth of polymer chains by monomer addition to a radical center; and termination reactions between two radical centers which give a net consumption of radicals. Free radicals for the initiation of addition polymerization are usually generated by the thermal decomposition of organic peroxides or azo compounds. The initiator molecule, represented by I, undergoes a first-order decomposition with a rate constant k_d to give two free radicals, $R^{\bullet}$:

$$I \xrightarrow{k_d} 2R^{\bullet} \qquad (2.1)$$

The radical then adds a monomer by grabbing an elelctron from the electron-rich double bond, forming a single bone with the monomer, but leaving an unshared electron at the other end:

where $P_1^{\bullet}$ represents a growing polymer chain with 1 repeating unit.

$$R^{\bullet} + M \xrightarrow{k_i} P_1^{\bullet} \qquad (2.2)$$

In practice, not all the radicals generated in reaction 2.1 actually initiate chain growth as in reaction 2.2. Some recombine or are used up by side reactions.

The product of the addition reaction is still a free radical; it proceeds to propagate the chain by adding another monomer unit:

$$P_1^\bullet + M \xrightarrow{k_p} P_2^\bullet \tag{2.3}$$

$$P_2^\bullet + M \xrightarrow{k_p} P_3^\bullet \tag{2.4}$$

$$P_3^\bullet + M \xrightarrow{k_p} P_{(x+1)}^\bullet \tag{2.5}$$

Growing chains can be terminated in one of two ways. Two can bump togethre and stick, their unshared electrons combining to form a single bond between them (combination):

$$P_x^\bullet + P_y^\bullet \xrightarrow{k_{tc}} P_{(x+y)} \tag{2.6}$$

where $P_{(x+y)}$ is a dead polymer chain of (x+y) repeating units.

Or, one can abstract a proton from the penultimate carbon of the other (disproportionation).

$$P_x^\bullet + P_y^\bullet \xrightarrow{k_{td}} P_x + P_y \tag{2.7}$$

The relative proportion of each termination mode depends on the particular polymer and the reaction temperature, but in most cases, one or the other predominates.

Superabsorbents are prepared by free radical initiated polymerization of acrylic acid and its salt, with a crosslinker, in aqueous solution or in suspensions of aqueous solution drops in a hydrocarbon. These two principal processes, bulk solution polymerization and suspension polymerization, share many features. The monomer and crosslinker concentrations, the initiator type and concentrations, polymerization modifiers, the relative reactivities of the monomers, the basic polymerization kinetics and reaction temperature are all significant factors in both processes.

2.2.1 Monomer concentration

The concentration of monomer in the reaction solution affects the properties of the resulting polymer, the kinetic of the reaction and the economics of the process. High monomer concentration results in increasing toughness of the intermediate gel polymer as the polymerization progresses. The toughness of the gel affects the design of equipment, the size of gel particles produced during agitation of the reaction mass and the method of heat removal. In addition, chain transfer to polymer increases with monomer concentration, especially at a high extent of conversion, and this results in increasing amounts of branching and self-crosslinking reactions that affect product propertries. Chain-transfer agents are useful to combat these side-reaction [4]. Another factor influencing the choice of monomer concentration is that the efficient use of the crosslinker increases with monomer concentration because the solubility of crosslinkers typically not very water soluble often increases with monomer concentration due to the increasing organic content of the monomer phase.

A factor of considerable importance to the polymerization in large quantity and at high monomer concentration is the large heat of polymerization of acrylic acid. The monomer yields 18.5 kcal/mol upon polymerization, making a temperature control an important parameter. Lower monomer concentration lessens the potentially adiabatic temperature rise but also lowers the volumetric efficiency of the reaction equipment and affects the polymeization kinetics. Evaporative cooling at reduced pressure may be used to remove the heat of polymerization [5]. The heat has also been used to dry the polymer to a foamy mass [6]. If the suspension process is used, traditional methods of heat transfer can be used because a lower viscosity, liquid state is maintained. This can be an advantage when a precise temperature control is desired.

Because acrylic acid is inhibitedly stored against a premature polymerization with *p*-methoxyphenol and oxygen, either the *p*-methoxyphenol and oxygen must be removed from the monomer solution before a polymerization will proceed. The simplest method is to strip the dissolved oxygen from the solution with a stream of nitrogen gas. Alternatively, the oxygen must be reacted from the solution by a metal ion catalyzed reaction that forms hydroperoxides from the oxygen and monomer.

2.2.2 Initiators

The polymerization is initiated by a free radical in the aqueous phase, using thermally decomposable initiators, redox initiators or combinations. Redox systems used for the crosslinking copolymerization include couples of persulphate/bisulfite, persulphate/thiosulphate, persulphate/ascorbate and hydrogen peroxide/ascorbate. Thermal initiators include persulphates, 2,2’-azobis-(2-amidinopropane)-dihydrochloride, and 2,2$^{'}$-azobis(4-cyanopentanoic acid). Combinations of initiator are used when the polymerization takes place over a broad temperature range. In this case, it may be desirable to maintain a constant rate despite the change in temperature. Appropriate concentration of multiple initiators can provide the desired constant rate of polymerization [7].

In graft copolymerization of vinyl monomers to polysaccharide substrates, initiation is accomplished using a redox reaction of an oxidant, such as the oxidized form of a metal ion, with oxidizable groups of the polysaccharide. When the metal ion is reacted with the graft substrate before monomer is added, grafting efficiency is increased. In addition to initiating the polymerization reaction, initiators are a factor in reducing the levels of unreacted monomer during the drying step [8], and can contribute to undesirable chain cleavage reactions to occur when the gel is handled at higher temperatures. For example, a higher content of soluble polymer is found when sodium polyacrylate gels made by ammonium persulphate initiator are dried in a very hot oven [9].

2.2.3 Crosslinkers

Relatively small amounts of crosslinkers play the major role in modifying the properties of superabsorbent polymers. The crosslinkers typically used in superabsorbent polymers are di- and tri-acrylate ester such as 1,1,1-trimethylolpropanetriacrylate or ethylene glycol diacrylate. In addition to modifying the swelling and mechanical properties, the crosslinker affects the amount of soluble polymer formed during the polymerization. The tendency of a crosslinker to be depleted earlier in the polymerization is reflected in its reactivity ratio with acrylic acid or sodium acrylate. Early depletion of crosslinkers should cause higher soluble fraction in the product.

Unfortunately, reactivity ratios have not been directly determined for the crosslinker typically used in making superabsorbent polymers. However, these can be estimated from the reactivity ratios of structurally analogous monomers, using the Alfrey-Price Q-e scheme. This has been done for several crosslinker analogs, using the available Q-e values [10]. The results, shown in Table 2.1, suggest that crosslinkers similar to triallycitrate should yield polymers with a lower amount of soluble polymer while a crosslinker similar to ethylmethacrylate should yield higher amounts of soluble polymer. This prediction is confirmed in the results from polymerization, shown in Tables 2.3 – 2.4 [10].

Table 2.3 Crosslinker reactivity effect on gel fraction [10].

Crosslinker	**r_1**[a]	**gel fraction**[b]
Methylenebisacrylamide	2.8	0.986
Triallycitrate	2.8	0.981
Ethyleneglycol diacrylate	1.56	0.955
Ethyleneglycol dimethacrylate	0.74	0.789

[a] Taken as the average of the r_1 values for acrylic acid and sodium acrylate with the respective crosslinker analogs.

[b] Identical polymerization of 65 mole% neutralized acrylic acid with 0.145 mole% crosslinker, in aqueous solution at 32 mass% monomer, initiated with a sodium persulphate and sodium erythorbate redox couple at 28°C.

Table 2.4 Reactivity ratios for structural analogs of crosslinkers [10].

Monomer/Crosslinker analog	**r_1**	**r_2**
1. Acrylic acid		
triallycitrate	5.636	0.049
acrylamide(bisacrylamide)	2.676	0.324
ethyl methacrylate(diacrylate)	1.514	0.576
ethyl methacrylate(dimethacrylate)	0.585	1.024

Table 2.4 Reactivity ratios for structural analogs of crosslinkers [10] (continue).

Monomer/Crosslinker analog	r_1	r_2
2. Sodium acrylate		
acrylamide	2.852	0.355
ethy acrylate	1.598	0.631
ethyl methacrylate	0.902	1.173

The choice of crosslinker will also depend on the method used to neutralize the carboxylic acid groups. A high pH process step may require a hydrolytically stable crosslinker, such as tetraallyoxyethane, rather than a diacrylate ester. In a suspension polymerization process, the availability of the crosslinker in the aqueous phase will be controlled by the partition coefficient of the crosslinker between the aqueous phase and the hydrocarbon, a continuous phase. The partition coefficient will depend on the extent of neutralization and on the nature of the hydrocarbon e.g., whether aromatic or aliphatic. The solubility of the crosslinker in the monomer solution also affects the efficiency of crosslinking in solution polymerization. Efficiency of crosslinking will also depend on steric hindrance and reduced mobility at the site of pendent double bond, the tendency of a given crosslinker to undergo intermolecular addition (cyclopolymerization) and the solubility of the crosslinker that can depend on the extent of neutralization, as noted above. As a result of a combination of factors such as these, different crosslinkers can exhibit much different effectiveness in the crosslinked product. An example is given in Figure 2.3, in which the effectiveness of crosslinking is compared for triallyamine and 1,3-butyleneglycol diacrylate. The amount of crosslinker has been normalized in each case for the functionality of the crosslinker, using the normalizing factor (1-2/f) where f is the functionality of the crosslinker. In Figure 2.3, the functionality of 1,3-butyleneglycol diacrylate is 4 and the functionality of triallyamine is 6. Several times more triallyamine is needed than diacrylate to achieve the same swelling ratio.

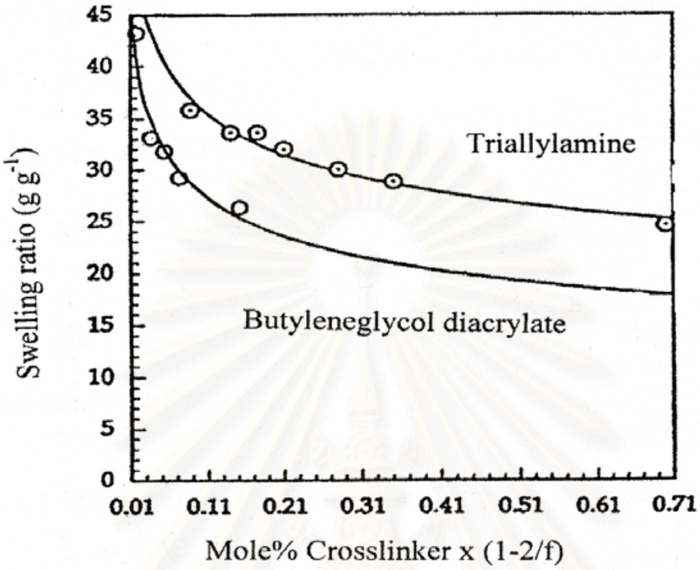


Figure 2.3 Dependence of the swelling ratio on the crosslink density and the functionality of the crosslinker. The two crosslinkers differ in efficiency [10].

2.2.3.1 *Chemical Crosslinking[11]*

The most severe mechanism for decreasing molecular freedom is chemical crosslinking-linking the polymer chains together through covalent or inonic bonds to form a network. Occasionally the term curing is used to denote crosslinking. There are a number of ways crosslinking can be brought about, but basically they fall into two categories:

(1) crosslinking during polymerization by the use of polyfunctional instead of difunctional monomers, and

(2) crosslinking in a separate processing step after the linear (or branched) polymer is formed.

The crosslinks may contain the same structural features as the main chains, which is usually the case with the former, or they may have an entirely different structure, which is more characteristic of the latter. A number of extreme changes accompany crosslinking. If previously soluble, the polymer will no longer dissolve (except in the case of some ionically crosslinked polymers). In the presence of solvent, a crosslinked polymer swells as solvent molecules penetrate the network. The degree of swelling depends on the affinity of solvent and polymer for one another, as well as on the level of crosslinking. It may be recalled that a solvent-swollen crosslinked polymer is called a gel. Covalently crosslinked polymer also lose their flow properties. They may still undergo deformation, but the deformation will be reversible; that is, the polymer will exhibit elastic properties. Ionically crosslinked polymers will flow at elevated temperatures, however.

With network polymers it is common to speak of the crosslink density, that is, the number of crosslinked monomer units per main chain. The higher the crosslink density, the more rigid the polymer. Very high crosslink densities lead to embrittlement. Because crosslinking reduces segmental motion, it is frequently empolyed to increase the glass temperature.

2.2.3.2 *Physical Crosslinking [11]*

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

2.2.3.3 *Crosslink Density [12]*

One of the most important structure parameters characterizing crosslinked polymers is $\overline{M_c}$, the average molecular weight between crosslinks, which is directly related to the crosslink density. The magnitude of $\overline{M_c}$ significantly affects the physical and mechanical properties of crosslinked polymers and its determination has great practical significance. Equilibrium swelling is widely used to determine $\overline{M_c}$. Early research by Flory and Rehner laid the foundations for the analysis of equilibrium swelling. According to the theory of Flory and Rehner, the $\overline{M_c}$ for a perfect network can be written as in Equation 2.8.

$$\overline{M_c} = -V_1 \rho_p \frac{\left(\phi_p^{1-3} - \phi_p / 2\right)}{\left[\ln(1-\phi_p) + \phi_p + \chi_{12}\phi_p^2\right]} \tag{2.8}$$

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

V_1 is the molar volume of the solvent

ρ_p is the polymer density

ϕ_p is the volume fraction of polymer in the swollen gel

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

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

$$q = \frac{M}{\overline{M_c}} \tag{2.9}$$

where M is the molecular weight of polymer repeat unit. We defined q in Equation 2.9 in order to simplify a direct comparison with the mole fraction of divinyl monomers in copolymerization.

2.2.4 Neutralization

The monomer and crosslinker are dissolved in water at a desired concentration, usually from about 10% –70%. The acrylic acid usually is partially neutralized before the polymerization is initiated [13], but the crosslinked polymer can be neutralized after the polymerization is complete [14]. From a technical point of view, pre-neutralized technique is preferred due to the relative ease of neutralizing the liquid monomer solution.

Inexpensive bases, such as sodium hydroxide and sodium carbonate, are used as neutralizing agents. A choice would be made based on consideration of the pH of the base solution and the resulting potential for hydrolyzing crosslinker, the solubility limits of the base in water and on the solubility of the monomer salt in water. For example, potassium acrylate is more soluble in water than is sodium acrylate.

2.2.5 Other polymerization additives

Under appropriate conditions, almost anything in the reaction mass may act as a chain transfer agent, including initiator, monomer, solvent and dead polymer. Chain transfer agents may be used to control network properties through a control of polymer backbone molecular mass. A variety of chain transfer agents are known for water soluble monomer systems [15]. Examples are mercapto compounds [16-19], formic acid [20], carbon tetrachloride, isopropanol [21], monobasic sodium phosphate and hydropersulfite salts [22]. Some of these have also been used in a crosslinking system [23-25]. Typically, a higher swelling capacity is obtained when chain transfer agents are used, as predicted by theory [2]. Chain transfer agents and other radical scavengers can also help prevent oxidative degradation of the polymer after it has been hydrated during use [26]. In addition, chain transfer may be used to minimize the branching and self-crosslinking reactions that have been reported during polymerization at a higher monomer concentration [27].

Chelating agents are useful to help control the variable concentrations of metal ions that are present in the water used as reaction solvent. These metal ions, notably iron, catalyze many free radical reactions. When their concentration is variable, initiation is irregular and possibly uncontrollable. Metal ions can also catalyze reactions of the initiators that lead to nonradical product; this wastes the initiator and can cause incomplete conversion of the monomer to polymer.

2.2.6 Kinetics

To be useful as superabsorbents, linear polymers must be crosslinked to form gels. Two general approaches exist for crosslinking. The first method is through co-polymerization of acrylic acid with a second monomer, which has multiple vinyl groups, to form a gel directly in the polymerization process. The second approach is via crosslinking of a polymer by reacting with a di-functional molecule, similar to a rubber curing reaction. The first approach is discussed in the following section.

Adequate description of a crosslinking co-polymerization requires at least a summary of co-polymerization in general. The model outlined was developed by Alfrey and Goldfinger and extended to systems containing many monomers by Walling and Briggs [28]. The model itself is known as the Mayo-Lewis model and is the most widely used model for co-polymer systems.

The model is based on the concept that the nature of the very last monomer added to the growing chain controls its reactivity. In a simple co-polymerization of two monomers, M_1 and M_2, there are four possible propagation events. The growing chain with a monomer 1 moiety on the end $RM_1^\bullet$ can react with another molecule M_1 with a rate constant k_{p11} or with a molecule M_2 with a rate constant k_{p12}. Likewise, when monomer 2 moiety $RM_2^{\bullet}$ is at the end of the growing chain, it can add to M_1 with a rate constant k_{p21} or to M_2 with a rate constant k_{p22} as shown in Equations 2.10-2.13.

$$RM_1^{\bullet} + M_1 \xrightarrow{k_{p11}} RM_1M_1^{\bullet} \tag{2.10}$$

$$RM_1^{\bullet} + M_2 \xrightarrow{k_{p12}} RM_1M_2^{\bullet} \tag{2.11}$$

$$RM_2^{\bullet} + M_1 \xrightarrow{k_{p21}} RM_2M_1^{\bullet} \tag{2.12}$$

$$RM_2^{\bullet} + M_2 \xrightarrow{k_{p22}} RM_2M_2^{\bullet} \tag{2.13}$$

The reactivity ratio r_1 and r_2 are defined by Equations 2.14-2.15

$$r_1 = \frac{k_{p11}}{k_{p12}} \tag{2.14}$$

$$r_2 = \frac{k_{p22}}{k_{p21}} \tag{2.15}$$

When $r_1 > 1$, radical $RM_1^{\bullet}$ preferentially resets with monomer M_1 (i.e., homopolymerizes), instead of monomer M_2. Very frequently $r_1 < 1$, which indicates $RM_1^{\bullet}$ preferentially reacts with monomer M_2. This latter behavior can lead to alternating co-polymers. The reactivity ratio can also be zero, indicating that a monomer will not homopolymerize.

Consider a co-polymerization of a di-functional vinyl crosslinker, after incorporation of one double bond, a new species forms that was not present in the original monomer solution. This species has a pendant double bond, as well as some other unique characteristics that confound the kinetic analysis of a crosslinking copolymerization. Most obvious is that the new species, which is now a macromolecular reactant, and so its diffusion to the growing radical chain is slowed more by the increasing viscosity resulting from the polymerization than is the diffusion of monomeric reactant [29].

2.3 Specific Polymerization Techniques

Commercial polyacrylate superabsorbent polymers are prepared using a large variety of techniques, but they can be grouped into five general categories:

2.3.1 Solution Polymerization

The polymerization of acrylic acid or sodium acrylate with a crosslinking agent in aqueous solution would seem to be a straightforward process. The monomer and crosslinking agent are dissolved in water at a desired concentration, usually from about 10%-70%, since polymerization of undiluted acrylic acid is extremely dangerous due to the high heat of polymerization and rapid polymerization kinetics. The monomer solution is deoxygenated by bubbling an inert gas through the solution, or by a series of evacuations and repressurizations with an inert gas, the desired free radical initiator is added and the temperature is brought to the appropriate point for polymerization to begin. However, the use of this technique in industrial practice is complicated by a variety of factors, the solution to which is the subject of numerous patents.

2.3.2 Graft Copolymerization

Water soluble polymers such as starch and poly(vinyl alcohol) are grafted into superabsorbents in order to modify the properties. Certain processes benefit from increased viscosity of the monomer solution, and the water soluble, graft substances can serve this purpose [30,31]. Historically, the “superslurper” absorbents were made from acrylonitrile grafts to starch, and the currently used acrylic acid grafts to starch appear to have developed from the earliers work. Special initiators are useful to increase grafting efficiency with polymers containing hydroxyl sites. Metal ions, such as cerium, complex with the hydroxyl sites and serve as a locus for the nascent free radical formed by oxidation of the substrate. For example, starch has been reacted with a partially neutralized acrylic acid and a diacrylate ester crosslinking agent, using Ce^{4+} as a free radical initiator. The gel like reaction product was dried and pulverized [32]. Graft copolymers can also be prepared using an inverse suspension polymerization [33].

2.3.3 Crosslinking after Polymerization

In this technique, the polyacrylate is formed in a first step, as a soluble polymer, which is then reacted in a second step with a suitable crosslinking agent. These are any of a hung variety of compounds which can react with carboxylic groups including amines, alcohols, epoxides and polyvalent metal ions. A benefit of this technology is that the absorbent polymer can be formed in to a desired shape by mixing the soluble polymer and crosslinking agent and curing in place, for example onto fibers or ont the surface of a sheet of tissue. Drawbacks to this technology are the handing of the viscous solutions of polymer and their through mixing with the crosslinking agent and any catalysis required [10].

2.3.4 Suspension Polymerization

Suspension polymerization is a system in which monomer are suspended as the discontinuous phase of droplets in a continuous phase and polymerized. The reactor product is a slurry of suspended polymer particles. The monomer suitable for suspension polymerizatin usually can be polymerized by free radical mechanism. The continuous phase is usually water, as most monomer are relatively insoluble in water. The terms pearl polymerization and bead polymerization describe the smooth, spherical particles from some suspension polymerization.

2.3.5 Inverse suspension Polymerization

Inverse suspension polymerization, which recently have attained commercial importance, begin with concentrated aqueous solution of monomers dispersed in hydrophobic organic solvents. The technique is particularly useful with acrylamide, methacrylamide, acrylic acid, methacrylic acid, salts of the corresponding acids, and quaternary ammonium monomers such as quaternized diethylaminoethyl methacrylate and vinylbenzyl trimethylammonium chloride and their mixtures. Generally 50%-80% monomer in concentrated solution with water is dispersed along with water soluble initiators such as persulphates, hydrogen peroxide, and redox activators of these. As external phases one may use aliphatic hydrocarbons or less frequently toluene, xylene or chlorinated hydrocarbons [34]. This system is different from suspension polymerization in phase of monomer solution, solubility of initator in organic phase and aqueous phase as shown in Figure 2.4.

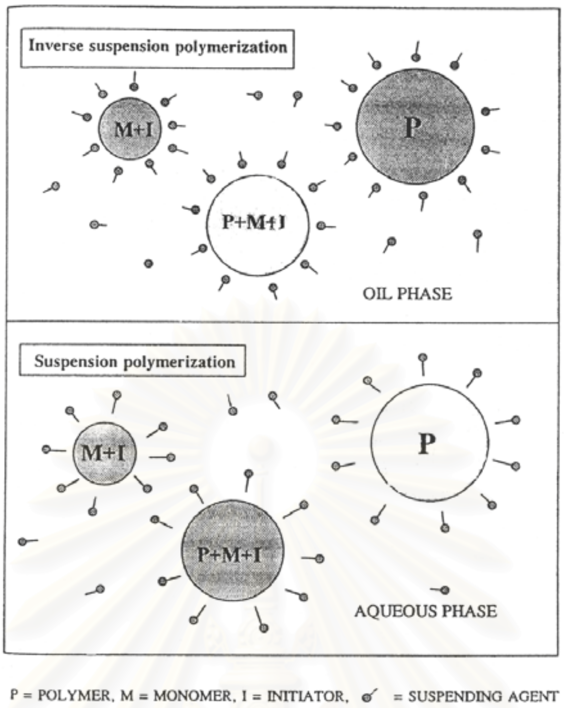


Figure 2.4 Comparison of the difference of inverse suspension polymerization and suspension polymerization

2.4 Complex Polymeric Flocculant (CPF)

Natural materials were recently employed in the treatment of wastewater, such as immobilized biopolymers for removing metal ions from wastewater, chitosan for treating wastewater in papermaking, and polysaccharide for treatment of wastewater from swine farms, but more of the organic polymer flocculants are those containing polyelectrolytes. Polyelectrolytes are synthetic polymers having many ionizable functional groups along the polymer chain such as poly(methacrylic acid) or polycations such as quaternary polyallylamine, or their mixture. CPF is a chemical bond between inorganic and organic coagulants. Often coagulation and flocculation are used interchangeably, although a distinction should be made. Coagulation refers to the process of destabilization of the colloid particles by the addition of some material to the water. Flocculation refers to the collision and aggregation of the destabilized particles into large flocs. Flocculation describes only the transport step involving the collision frequency and hydrodynamics of floc formation after the particles have become destabilized.

Processes commonly used to treat wastewater are listed in Table 2.5.

Table 2.5 Wastewater treatment processes in common use [35]

Purpose	Process	Comments
Turbidity removal	Coagulation Flocculation Sedimentation Filtration: Depth Precoat	Often used for domestic water treatment
Dissolved-solids removal	Precipitation ion exchange	Often used to remove hardness
	Distillation Reverse osmosis	Reduction in total-dissolved-solids (TDS)
Dissolved-organic removal	Activated-carbon adsorption	Used for removal of color, tasted, and odors and low concentrations of toxic organics
	Chemical oxidation	Chlorine, ozone, permanganate or peroxide used to oxidize organics
Cooling	Cooling towers	
Disinfection	Chlorination	Most common method in United States
	Ozonation	Effective, leaves no residual products, more expensive than chlorination

Treatment processes and systems for wastewater renovation can be classified in a number of ways. The most common method is to characterize them by function, e.g., precipitation, bioxidation, or adsorption. The coagulation-flocculation process is shown qualitatively in Figure 2.5. The coagulant is added to the influent wastewater with a rapid mixing and high turbulence and is initially in destabilizing the particles. The rapid mixing continues either in the same process vessel or in a separate one to promote the initial flocculation by collision of the primary particles. Once these primary particles have combined together to give larger aggregates, they flow into a slow mixing tank to allow the aggregates to grow into flocs of sufficient size to separate out by sedimentation, dissolved air flotation, or filtration. The flocculation process involves both a rapid mixing step to promote dispersion and initial aggregation of the primary particles and a slow mixing step where the aggregates can grow without high shear forces. Since the particles can grow by several orders of magnitude during flocculation, each of these steps is modeled separately.

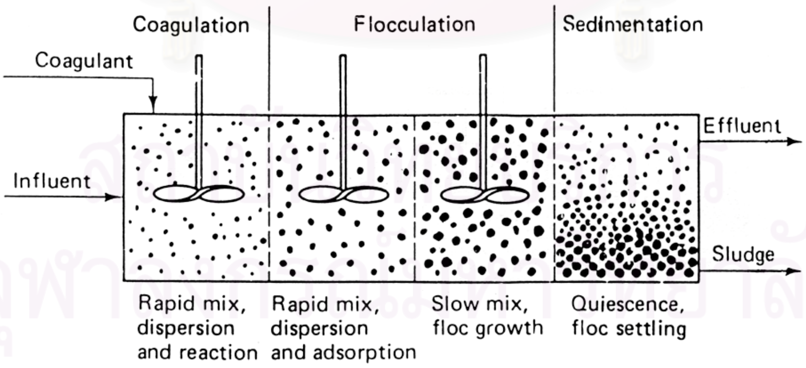


Figure 2.5 Coagulation/Flocculation process sequence.

Flocculation tanks are intended to promote interparticle contacts. These contacts can occur either by random Brownian motion or by the forced collision of the colloid particles due to velocity gradients established by fluid mixing. The latter method, often called orthokinetic flocculation, is the dominant mechanism of particle contact in the rapid mixing tanks. O’Melia [36] has derived a first-order model for batch flocculation involving a collision efficiency factor, η, the volume of colloidal particles per unit volume of suspension, Ω, and a mean velocity gradient, υ_g. If N_p^o is the number of separate particles initially, then the number of separate particles remaining, N_p, after time t becomes

$$\mathrm{n}\left[\frac{N_p}{N_p^0}\right] = \frac{-4}{\pi}\eta\Omega\upsilon_g t \tag{2.16}$$

The mean velocity gradient has been given by Camp and Stein [37] as

$$\upsilon_g = \left(\frac{P}{V\mu}\right)^{1/2} \tag{2.17}$$

Where P is power input to the fluid in the vessel

V is liquid volume in the vessel

μ is viscosity of the fluid

Coagulants are usually added to a wastewater and thoroughly mixed for up to 30 min before the slow mixing and sedimentation begins. Ogedengbe [38] has shown that the dimensionless group, $\upsilon_g t$, is a useful design parameter in the rapid-mix step as predicted by Equation 2.16. Using cationic polymers on domestic wastewater, he found that various combinations of υ_g up to 500 s^{-1} and mixing times up to 25 min yielding constant $\upsilon_g t$ values gave constant levels of residual turbidity. Values of $\upsilon_g t$ commonly vary between 10^4 and 10^6 in wastewater treatment systems, depending upon the coagulant used.

The slow mixing step is often done in paddle type mixers for up to 60 min to allow the small flocs to combine into larger ones. Fiedler and Willus [39] have modeled this process with a second-order expression containing a delay time to give

$$\frac{1}{N_p} - \frac{1}{N_p^0} = k_f \left(t - t_0\right) U\left(t - t_d\right) \tag{2.18}$$

Where k_f is an empirical rate constant

U is a step function: $U=0$ for $t \le t_d$, $U = 1$ for $t > t_d$

t_d is a delay time

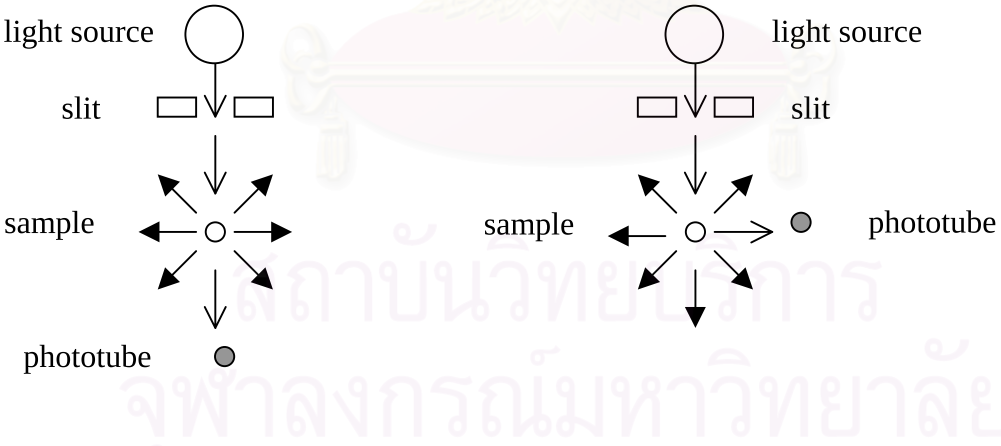
The delay time, t_d, is inversely proportional to the initial colloidal concentration, N_p^0, and must be experimentally determined for any wastewater. The rate constant k_f is usually independent of colloid concentration but is influenced by both the time of mixing and the speed of the paddle type mixer. Mixing time between 15-45 min and speeds between 30-50 rpm give relatively constant values of k_f.

Some physical measurements commonly made in wastewater analysis do not require the use of expensive instruments. Two methods used to evaluate turbidity are discussed below.

Turbidimetry: The method in which ordinary white light transmitted through a finely divided suspension is compared with that transmitted by a standard suspension is known as trubidimetry.

Nephelometry: Nephelometric methods are also employed to measure turbidity. In this method, light is allowed to strike a suspension at right angles to the eye of the observer or photoelectric cell of the instrument. The light reflected by the dispersed particles (Tyndall effect) is recorded. When this principle is employed, very low turbidities can be determined in filtered water, and this is one of the major advantages of nephelometry.

In the instrument of the turbidimetry, a light source illuminates the sample and one or more photoelectric detectors are used with a readout device to indicate the intensity of light passing through a solution to be measured, as indicated in Figure 2.6. The higher the turbidity, the smaller the quantity of light transmitted. In nephelometry, on the other hand, the detecting cell is placed at right angles to the light source to measure light scattered by the turbidity particles.



Turbidimeter **Nephelometer**

Figure 2.6 Schematic diagrams of a turbidimeter and a nephelometer

2.5 Literature Survey

Recent researches on the synthesis of superabsorbent polymer and important physical property development are listed as below:

Liu and Rempel [40] prepared the high water-absorbent copolymer comprising acrylic acid and acrylamide in the presence of a crossinking agent, monofunctional aldehyde, by a solution polymerization technique via a potassium metabisulfite redox initiation system. The copolymer formed absorbed about 900 g water/g dry copolymer. They found that the absorption behavior of the supersorbents related to their chemical composition and the nature of the solvent.

Rangaraj et al., [41] synthesized homopolymers and copolymers of acrylamide and acrylic acid by the free radical solution polymerization technique using hydrogen peroxide, potassium persulfate, and benzoyl peroxide as initiators. The copolymers were purified by removing homopolymers. The homopolymers and copolymers were characterized by infrared (IR), ^{13}C-nuclear magnetic resonance (NMR), ^{1}H-NMR, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and viscosity measurements.

Abe, et al., [42] synthesized thermosensitive polymer beads by inverse suspension polymerization of aqueous monomer solution containing N-acryloylpyrrolidine (APR), *N*,*N'*-methylenebisacrylamide, a crossliking agent, and ammonium peroxysulphate (APS) and *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA) as a redox initiator system. The polymerization temperature was maintained at 20^{o}C for 2 h. The polymerization conditions such as dispersion medium, dispersing agent, monomer, and initiator concentration were investigated. Fine spherical gels with diameters of 50-500 μm were obtained in high yield. The swelling volume of these gels in water continually decreased by raising atmospheric temperature and vice versa. The degree of swelling increased for gel synthesized with a lower degree of crosslinking or with lower monomer concentration. The degree of swelling was high in water and alcohols, the gel swelled even in non-polar organic solvent, although the degree of swelling was low. The pore radius distribution of the gel was determined by aqueous size exclusion chromatographic method to investigate the relation between pore characteristics of the gel and polymerization conditions. Monomer concentration has a large effect on pore size, porosity, and pore volume of the gels. On the other hand, degree of crosslinking had little effect on these pore characteristics.

Dubrovskii, et al., [43] synthesized superabsorbent hydrogels (SAHs) by copolymerization of acrylamide (AM) and acrylic acid (AAc) in the presence of *N*,*N'*-methylenebisacrylamide or by γ-radical crosslinking of the high molecular AM-AAc copolymer in aqueous solution. The polymerization was initiated with ammonium persulphate : tetramethylethylendiamine (2:1) in 20% aqueous solution of the monomer at 45^{o}C. The modified swelling theory had been used to develop a system of experimental and computational methods for the evaluation of supergel network parameter.

Omidian, et al., [44] synthesized, characterized and modified acrylic based superabsorbents, which were synthesized through the well-known process of inverse suspension polymerization. The dispersion was stabilized using a mixture of micromolecular and macromolecular stabilizers. High swelling and appropriate absorption kinetics were obtained, provided that the parameters, including initial monomer and crosslinking agent concentrations, a range of neutralization degree, an initiating and stabilizing system, a monomer addition rate, the temperature and the nature of the organic phase were considered. The water absorbent efficiency of the synthesized polymer, in which crosslinking agent concentration was higher than the synthesized polymer, in which the crosslinking agent was the oil soluble crosslinking agent, ethyleneglycol dimethacrylate (EGDMA). By replacing some of the base monomer in a modified system with acrylamide, the rate of water absorption progressively increased at the expense of reducing absorbing capacity.

Yao and Zhou [45] prepared a series of novel copolymer superabsorbents based on acrylamide, sodium allylsulfonate, sodium acrylate, and *N,N'*-methylenebisacrylamide at a copolymerization temperature at 35°C. The resulting superabsorbents had a fast swelling rate. The absorbency increased to a maximum, 437 times its dry copolymer weight as the crosslinking agent concentration increased, 5×10^{-3} mole dm^{-3}, but an excess of crosslinking agent led to a decrease swelling. Their water retention was observed under the pressures of 1-10 kg cm^{-3} and temperatures at 60°C and 100°C, respectively. The water retention of soil had been enhanced using the poly(acrylamide-*co*-sodium allylsulfonate-*co*-sodium acrylate) superabsorbent; its use is for an enhancement of bean growth.

Smith and Lind [46] improved absorption under pressure and fast absorption rate properties of superabsorbent polymer which was obtained by polymerizing a solution containing carboxylic acid monomers or water soluble salts, and a crosslinking agent. The most preferred crosslinking agents were bis-acrylamide such as *N,N'*-methylenebisacrylamide, the di, tri or polyesters of unsaturated mono or polycarboxylic acid polyols, such as trimethylolpropane triacrylate, the di or tri glycidyl ethers of polyols such as ethyleneglycol dialycidyl ether, the multi-substituted allyl amines such as diallyl amine and triallyl amine, or their mixtures. A blowing agent, preferred carbonate blowing agents was $MgCO_3$, $(NH_4)_2CO_3$, Na_2CO_3, and their mixture and a polymerization initiator are added, individually or in combination, to the solution to form a carbonated monomer solution. A polymerization initiator was then added to the carbonated monomer solution which was then polymerized at the temperature ranging from about 0^oC to 130^oC, forming a microcellular hydrogel. The hydrogel was ground into gel pieces and dried at temperatures ranging from about 85^oC to 210^oC. A mixture was formed from 100 parts by weight of the polymer and about 0.001 to 30 parts by weight of a crosslinking agent. The polymer was reacted with the crosslinking agent to crosslinked molecular chains existing on a surface of the polymer, forming the superabsorbent polymer.

Kiatkamjornwong and Phunchareon [47] synthesized high water absorbing copolymers of poly(potassium acrylate-*co*-acrylamide) by an inverse suspension copolymerization. Potassium acrylate and acrylamide were used as comonomers, and *N*,*N’*-methylenebisacrylamide as a crosslinker polymerized by ammonium persulfate in n-hexane, each was emulsified by a series of sorbitan surfactants with a relatively lower concentration of 1.0% w/v at 60^oC for 2 h. The water absorption depended highly on the pH of the buffer solution and the type of the saline solution. The copolymers exhibited a shear-thinning behavior at both low and high shear rates.

Chen et al., [48] synthesized superporous hydrogels based on monomers: acrylic acid (AA), acrylamide (AM), *N*-isopropyl acrylamide (NIPAM), vinylpyrrolidone (VP), hydroxyethylmethacrylate (HEMA), potassium salt of 3-sulfopropyl acrylate (SPAK), 2-

acrylamido-2-methyl-1-propanesulfonic acid (AMPS), 2-(acryloyloxyethyl) trimethyl ammonium methylsulfate (ATMS) and hydroxypropyl methacrylate (HPMA) , *N*,*N’*-methylene bisacrylamide (N-MBA) as crosslinking agent, ammonium persulfate (APS) and *N*,*N*,*N’*,*N’*-tetramethylethylenediamine (TEMED) as coinitiatior and Pluronic F127 (PF127) as foam stabilizer. Crosslinking polymerization of monomer in a test tube (20 mm outer diameter x 150 mm in length) and presence of carbon dioxide gas bubbles, which were generated by a reaction of sodium bicarbonate with an acid. The use of the $NaHCO_3$/acid system allowed easy control of the timing for gelation and foam formation. PF127 was the best foam stabilizer for most of the monomer systems. The resulting superabsorbents gave a fast swelling rate. The swelling ratio (Q) is 368±34 times its dry copolymer weight. The average diameter of the pores of superporous hydrogels is approximately 150 μm, and some pores are as large as 300 μm.

Liu et al., [49] prepared a novel flocculant, a method consisting of a poly (acrylamide-*co*-acrylic acid) complexed with an inorganic coagulant (aluminium sulfate, ferric sulfate, or calcium oxide) through the chemical bond between metal ions and carboxyl acid groups or amide ligands within the polymer. Poly(acrylamide-*co*-acrylic acid) was synthesized using benzoyl peroxide (BPO) as an initiator in a mixed solvent of benzene and acetone as an organic phase at 70^{o}C in nitrogen atmosphere for 4 h under stirring. The advantages of this complex polymeric flocculant over common polymeric flocculants included fast precipitation, easy dosage control, and more satisfactory performance.

Lee and Huang [50] prepared a series of xerogels based on sodium acrylate (SA), cationic comonomer trimethyl methacrylamidopropyl ammonium iodide

(TMMAAI), and *N*,*N'*-methylenebisacrylamide (NMBA) by inverse suspension polymerization. The water absorbency and the swelling behavior for these highly absorbent polymers in deionized water and various saline solution are studied. The water absorbency increased when a small amount of TMMAAI monomer was introduced into the SA gel and decreased with increasing concentration of crosslinking agent.

Lee and Tu [51] prepared a series of xerogels based on sodium acrylate (SA), *N*,*N*-dimethy(acrylamidopropyl) ammonium propane sulfonate (DMAAPS) or dimethyl (methacryloyloxyethyl) ammonium propane sulfonate (DMAPS), and *N*,*N'*-methylene bisacrylamide (NMBA) by inverse suspension polymerization. The water absorbencies of these two copolymeric gel series were improved effectively by copolymerizing SA with a small amount of zwitterionic monomer (DMAAPS or DMAPS). The water absorbency of the gel containing DMAPS is larger than that of the gel containing DMAAPS when the amount of zwitterionic monomer in the copolymeric gel is less than 0.8 mol%, but a contrary result is observed when the zwitterionic monomer content is more than 0.8 mol%. The tendency of the absorbency for these gels in the dilute solution is in the order of $Cu^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+}$ for the $CuCl_2$, $ZnCl_2$, $CoCl_2$, and $NiCl_2$ aqueous solution, respectively.

Zhou et al., [52] synthesized hydrogels of acrylamide (AM), sodium methallylsufonate (MSAS), sodium acrylate (AA), and *N*,*N'*-methylenebisacrylamide (BisA) in aqueous solution using 1.33×10^{-3} mol dm^{-3} potassium persulfate (KPS)/3.0×10^{-3} mol dm^{-3} of *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA) as the redox initiator. These gels, which absorbed about 125 times their own weight in distilled water, and 21 times in 0.9% NaCl solution. Conversion and absorbency increase with the MSAS concentration. Further increase of the MSAS concentration leads to a decrease in absorbency.

Chen and Zhao [53] prepared polyacrylate superabsorbents by *in situ* aqueous solution polymerization in a polyethylene bag, which was submerged in a 70^{o}C water bath. The monomer mixture was polymerized *in situ* for 2 h and a polymeric gel was then formed. Using potassium persulfate (KPS) as an initiator and triethylene glycol diacrylate (TEGDA) as a crosslinking agent, the water absorbency increases linearly with increases of the initiator content. The water absorbency is changed slightly when the bath temperature is between 50^{o}C and 60^{o}C and water absorbency increases continuously when the bath temperature is between 60^{o}C and 80^{o}C. Water absorbency increased linearly with increase of the content of a chain-transfer agent of isopropanol.

Chen and Shen [54] investigated the swelling behaviors of polyacrylate superabsorbent in mixtures of water and hydrophilic solvents, including methanol, ethanol, ethylene glycol, glycerol, acetone, dimethyl formamide, and dimethyl sulfoxide. The addition of hydrophilic solvent in water reduced the water absorbency of the superabsorbent. The equilibrium absorbency was very high when the solubility parameter of the solvent-water mixture was more than 20, whereas the absorbing capacity of the superabsorbent was very low then the solubility parameter was less than 17.5. The polarity fraction of solvents did not have any obvious influence on equilibrium absorbency, but not enough polarity fraction might affect the absorbing rate.

CHAPTER 3

EXPERIMENTAL

3.1 Chemicals, Equipment and Glassware

3.1.1 Chemicals

a) Acrylamide, AM (99% pure) from Siam Resin & Chemical Co., Ltd.

C_3H_5NO, clear, colorless solid

m.p. 84.5°C, b.p. 87°C (2 mmHg)

$M = 71.08\ g\ mol^{-1}$

b) Acrylic acid, AA (99% pure) from Siam Resin & Chemical Co., Ltd.

$C_3H_4O_2$, liquid

m.p. 12-15 °C

$M = 72.06\ g\ mol^{-1}$

$D = 1.047\text{-}1.051\ g\ cm^{-3}$

c) Aluminum sulfate octahydrate, analytical grade from Fluka (Buchs, Switzerland)

$Al_2(SO_4)_3.8H_2O$, solid

$M = 486.43\ g\ mol^{-1}$

d) Ammonium persulfate, analytical grade from Merck (Hohenbrunn, Germany)

$(NH_4)_2S_2O_8$, solid

M = 228.20 g mol^{-1}

e) *N,N'*-Methylenebisacrylamide, (N-MBA) analytical grade from Fluka (Buchs, Switzerland)

$C_7H_{10}N_2O_2$, solid

M = 154.17 g mol^{-1}

f) *N,N,N',N'*-tetramethylethylenediamine, analytical grade from Sigma-Aldrich (St. Louis, U.S.A.)

$(CH_3)_2NCH_2CH_2N(CH_3)_2$, liquid

M = 116.21 g mol^{-1}

D = 0.775 g cm^{-3}

g) Formaldehyde , analytical grade from Fluka (Buchs, Switzerland)

HCHO , liquid

M = 30.03 g mol^{-1}

D = 1.09 g cm^{-3}

h) Ethylene glycol dimethacrylate, analytical grade from Fluka (Buchs, Switzerland)

$CH_2C(CH_3)COOCH_2CH_2OCOC(CH_3)CH_2$, liquid b.p. 98-100^{o}C

M = 198.22 g mol^{-1}

D = 1.050 g cm^{-3}

i) Sodium hydroxide, Merck (Darmstadt, Germany)

pellets, the percentage of neutralization of acrylic acid

NaOH, pellets

M = 40.00 g mol^{-1}

j) Methyl alcohol, BDH (Bangkok, Thailand)

commercial grade was purified by fractional distillation at an atmospheric pressure.

CH_3OH, liquid

b.p. 64-65^{o}C

M = 32.04 g mol^{-1}

D = 0.791 g cm^{-3}

k) PF127, analytical grade from BASF (Ludwigshafen, Germany)

solid

M = 9,840-14,600 g mol^{-1}

l) Sodium hydrogen carbonate, analytical grade from Fluka (Buchs, Switzerland)

$NaHCO_3$, solid

M = 84.01 g mol^{-1}

m) Sodium chloride, analytical grade from Merck (Darmstadt, Germany)

$NaCl$, solid

M = 58.44 g mol^{-1}

n) Calcium chloride, analytical grade from Fluka (Buchs, Switzerland)

$CaCl_2$, solid

M = 110.99 g mol^{-1}

o) Magnesium chloride hexahydrate, analytical grade from Fluka (Buchs, Switzerland)

$MgCl_2.6H_2O$, solid

M = 203.31 g mol^{-1}

p) Potassium chloride, analytical grade from Fluka (Buchs, Switzerland)

KCl, solid

M = 74.56 g mol^{-1}

q) Potassium iodide, analytical grade from Fluka (Buchs, Switzerland)

KI, solid

M = 166.01 g mol^{-1}

r) Potassium bromide, analytical grade from Fluka (Buchs, Switzerland)

KBr, solid

M = 119.01 g mol^{-1}

s) Boric acid , analytical grade from Fluka (Buchs, Switzerland)

H_3BO_3, solid

$M = 61.83\ g\ mol^{-1}$

t) Citric acid monohydrate, analytical grade from Fluka (Buchs, Switzerland)

$HOC(COOH)(CH_2COOH)_2.H_2O$

$M = 210.14\ g\ mol^{-1}$

u) Tertiary sodium phosphate dodecahydrate, analytical grade from Fluka (Buchs, Switzerland)

$Na_3PO_4.12H_2O$

$M = 380.12\ g\ mol^{-1}$

3.1.2 Equipment and glassware

a) analytical balance: Precisa 300A, Switzerland

b) magnetic stirrer: Snijders, Tilburg, Holland

c) mechanical stirrer: Ika-Ruhrwerke RW20, Staufen, Germany

d) water bath circulator: WBU 45 memmert, Schwabach, W-Germany

e) oven: Hotpack, U.S.A.

f) blender/mill : Pyramid, Bangkok, Thailand

g) other general laboratory glassware and equipment

- four-necked round bottomed flask
- spiral condenser
- desiccator
- heating mantle
- 100 mesh aluminium screen

3.2 Apparatus

a) Fourier Transform Infrared Spectroscopy, (FTIR), Perkin Elmer 1760X, U.S.A.

b) Scanning Electron Microscope, (SEM), JEOL, JSM-6400, Japan

c) Turbidity Meter, 2100P, U.S.A.

3.3 The synthesis of poly(acrylic acid-*co*-acrylamide)

3.3.1 Optimum mole fraction of monomer (acrylamide: acrylic acid)

A series of the copolymer surperabsorbents was prepared by following procedure:

Copolymerization: A mixture (100 ml) of a specific amount of aqueous solution of acrylic acid (neutralized by NaOH), acrylamide monomer, crosslinker (N-MBA), an initiator (ammonium persulfate:*N,N,N',N'*-tetramethylethylenediamine), a stabilizer (PF127) and a foaming agent ($NaHCO_3$) was prepared in a 500 ml four-necked round bottomed flask equipped with a mechanical stirrer (with a rate of 250 rpm.), a spiral condenser, and a thermometer at 45^{o}C (in water bath) in nitrogen atmosphere for 30 minutes. The resulting polymer was dewatered with methanol, cut into small pieces, dried at 50^{o}C for 24 h in a vacuum oven to a constant weight and then milled.

3.3.2 Optimum reaction temperature

The same experimental procedure as described in Section 3.3.1 was carried out, except for the mole fraction of AM: AA, the percentage of neutralization of acrylic acid, and the crosslinking agent concentration were fixed at 0.1, 40% neutralization, and 4.0×10^{-3} mol dm^{-3}, respectively, and the polymerization temperature was varied at: 45, 50, 55, 60, 65, 65 and 70^{o}C.

3.3.3 Optimum concentration (mol dm^{-3}) of initiator of ammonium persulfate: *N,N,N',N'*-tetramethylethylenediamine

The same experimental procedure as described in Section 3.3.1 was carried out, except for the mole fraction of AM: AA, the percentage of neutralization of acrylic acid, and the crosslinking agent concentration were fixed at 0.2, 40% neutralization, and 6.30×10^{-3} mol dm^{-3}, respectively, and the concentration of initiator (mol dm^{-3}) of ammonium persulfate: *N,N,N',N'*-tetramethylethylenediamine was varied at $1.50.\times10^{-3}$: 1.0×10^{-2}, 2.0×10^{-3}: 1.0×10^{-2}, 2.30×10^{-3}: 1.0×10^{-2}, 3.0×10^{-3}: 1.0×10^{-2}, $3.50.0\times10^{-3}$: 1.0×10^{-2}, 4.4×10^{3}: 1.0×10^{-2}, and 2.30×10^{-3}: 2×10^{-2}

3.3.4 Type of the crosslinking agent

The same experimental procedure as described in Section 3.3.1 was carried out, except for the mole fraction of AM: AA, the percentage of neutralization of acrylic acid, and the crosslinking agent concentration were fixed at 0.1, 40%neutralization, and 4×10^{-3} mol dm^{-3}, respectively, and the type of crosslinking agent from *N,N'*-methylenebisacrylamide (N-MBA) was changed to ethylene glycol dimethacrylate (EGDMA) and formaldehyde.

3.3.5 Optimum concentration of the crosslinking agent

The same experimental procedure as described in Section 3.3.1 was carried out, except for the mole fraction of AM: AA was fixed at 0.1, and the percentage of neutralization of acrylic acid at 40% neutralization. The concentration of crosslinking agent (mol dm^{-3}) was varied 1.0×10^{-3}, 1.5×10^{-3} 2.0×10^{-3}, 2.5×10^{-3}, 3.0×10^{-3}, 3.5×10^{-3}, 4.0×10^{-3}, 4.5×10^{-3}, and 5.0×10^{-3}.

3.3.6 Optimum degree of neutralization of acrylic acid

The same experimental procedure as described in Section 3.3.1 was carried out, except for the mole fraction of AM: AA, the crosslinking agent concentration were fixed at 0.2, and 4.0×10^{-3} mol dm^{-3}, respectively, and the percentage of neutralization of acrylic acid was varied from 0%, 40%, 60%, 80% and 100%.

3.4 Characterization of the copolymer

The synthesized copolymers were investigated for their obligation as below:

3.4.1 Identification of the function groups of the copolymers

The functional groups of the copolymers were investigated using Fourier-Transform Infrared Spectrometer (FTIR) Perkin-Elmer Infrared Spectrometer, model 1760X). The copolymer was ground with the dried KBr powder. The KBr disc was dried again, pressed and subjected to the FTIR spectrometer.

3.4.2 Determination of surface morphology of the copolymers

The surface morphology of the copolymers was investigated by using a Scanning Electron Microscope (SEM), model JSM-T 220 A JEOL without cross-section. The thickness of gold coated on the copolymer was 25 nm, and SEM was operated with a 15 or 20 kV accelerating voltage.

3.5 Water absorbency of the copolymers

3.5.1 In distilled water

Distilled water 400 g was added to 0.1 g of the dry copolymer in a 600 ml glass beaker and it was allowed to stand for 30 min. The swollen gel was then separated from unabsorbed water by screening through 100-mesh sieve aluminium screen for 2 h and the remaining swollen copolymer was weighed. The water absorbency was calculated as shown below:

$$Water \quad absorbency(Q) = \frac{B - A}{A} \tag{3.1}$$

Where A is the weight of the dry polymer (g)

B is the weight of the water swollen gel (g)

3.5.2 In buffer solutions

The same experimental procedure as described in Section 3.5.1 was carried out, except for that a series of buffer solutions ranging from pH 2 to 12 was used instead of distilled water at room temperature. The buffer solutions of pH 2 to 12 were prepared from universal buffer (APPENDIX B).

3.5.3 In salt solutions

The same experimental procedure as described in Section 3.5.1 was carried out, except for that a series of sodium chloride (NaCl), calcium chloride ($CaCl_2$), magnesium chloride ($MgCl_2.6H_2O$), potassium choride (KCl), potassium iodide (KI) and potassium bromide (KBr) solutions of 0.05, 0.10, 0.50, and 0.9% w/v were used instead of distilled water.

3.5.4 In urea solution

The same experimental procedure as described in Section 3.5.1 was carried out, except for that urea solutions of 0.01, 0.02, 0.03, 0.04, 0.05, and 0.10% w/v were used instead of distilled water.

3.6 Kinetics of absorption of the synthesized copolymer

3.6.1 In distilled water

Distilled water 400 g was added to 0.1 g of dry copolymer in a 600-ml glass beaker and it was allowed to stand for 10 min. The swollen gel was then separated from unabsorbed water by screening through 100-mesh sieve aluminium screen for 2 h and the remaining swollen copolymer was weighed. The similar experiments were each carried out for gel swelling times of 20, 30, 40, 50, and 60 min, respectively.

3.7 Application of Superabsorbent copolymer in Wastewater Treatment

3.7.1 Preparation of a complex polymeric flocculant

A mixture of resulting polymer (5.4 g) with aluminum sulfate (inorganic flocculant) (41.6 g) at 45^{o}C in nitrogen atmosphere was prepared by stirring for 30 min. The reaction was performed in a four-necked round bottle flask equipped with a mechanical stirrer and a reflux condenser. The complex flocculant formed was dewatered with methanol, cut into small pieces and vacuum-dried at 50°C, left overnight to a constant weight and then milled.

3.7.2 Efficiency of Wastewater Treatment

A certain amount of inorganic flocculant or complex flocculant was added into 1 dm^3 wastewater taken from the Withayapatthana Building, Chulalongkorn University. Under mechanical stirring rate at 100 rpm, 5 min. The transmittance of the upper liquid in the container was measured at different time by turbidity meter (2100P). The effect of flocculant dosage was examined.

CHAPTER 4

RESULTS AND DISCUSSION

The copolymers were synthesized by a foamed aqueous solution polymerization of water soluble monomeric material, initiated by adding a redox initiator, exothermically polymerizing the monomeric material to form a foamed gel, and comminuting the gel. After adding the monomers, the foamed gel took place within 10 min. The polymerization was allowed to proceed to completion of the reaction for another 20 min. Because polymerization temperature was increased resulting from an exothermic reaction of acrylic acid/acrylamide mixture, the foamed gel became comminuting gel.

The polymerization started from carbon dioxide gas generated from the reaction of acrylic acid and sodium bicarbonate. The dissolution of a gas bubble immersed in a liquid is driven by a difference in concentration, the gas bubble acrossed the bubble's boundary and entered into the surrounding liquid solution. In this liquid, the gas bubble is transported by the process of diffusion and convection due to motion of the bubble's boundary. The concentration of the gas bubble in the liquid tends to zero, except at the bubble's boundary where it is constant. The gaseous phase is first supposed to contain only one species, which is chemically different from the liquid. The bubble grows and departs from the liquid surface. The growth of a bubble was unattainable because of the complicated thermal and hydrodynamic interaction of the gaseous and liquid phases (ambient fluid) at the bubble wall. The bubble growth is controlled by the rate at which energy is transferred through the liquid to the gaseous-liquid interface, including the effects of radial convection in the liquid. The mechanisms associated with gaseous bubble growth at a plane heated surface are not understood nearly as well as unbounded growth in an infinite pool. This is due to the fact that it is exceedingly difficult to control the temperature and flow field in the vicinity of growing bubbles during experimental investigations due to natural convection and liquid motions induced by other bubbles.

The interfacial liquid temperature is decreasing due to a net loss of thermal energy by conduction out of the liquid and into the gaseous bubble, coupled with conduction and advection of thermal energy away from the bubble and into the bulk liquid, the maximum temperature with in the boundary layer decreases and moves further out from the bubble interface.

When $NaHCO_3$ powder was added into the solution, followed immediately by the PF127 foam stabilizer, carbon dioxide was generated from the solution. The carbon dioxide bubbles were stabilized by PF127. The bubbles were accommodated by the monomers, initiator radicals and crosslinker. The initial polymerization should take place in the gaseous phase from which the clean and unique polymer chains were produced.

After the bubbles had been destabilized, they fell into the solution. Afterwards, the polymerization was continued in the aqueous phase until a foamed was achieved. The foamed polymerization could possibly be depicted as a combined polymerization of bulk polymerization and solution polymerization. This technique reduces primary terminary of free radical (radical recombination of the polymerization regime), which gives the narrow molecular weight distribution. Because the polymer chains were produced initially in the gaseous phase, the kinetic chain length of such polymers is relatively long, and the conversion time to foamed gel is thus shorter than other radical polymerization techniques.

4.1 Effect of mole fraction of acrylamide

The result of water absorbency test of the copolymer synthesized by solution polymerization of various mole fractions of acrylamide (AM) is in Table 4.1 and Figure 4.1.

Table 4.1 Effect of mole fraction of AM on the water absorbency (*Q*) of the synthesized copolymers at 0.1 mole fraction of AM (mole fraction = [AM]/[AA]+[AM])

Mole fraction of AM	Water absorbency (*Q*) $g\ g^{-1}$
0.10	1,452±15
0.20	1,335±12
0.30	1,132±30
0.40	986±14
0.50	1,051±26
0.60	892±18
0.70	975±22
0.80	806±18
0.90	586±25

Reaction Condition: [APS] = 2.30×10^{-3} mol dm^{-3}, [TMEDA] = 1.0×10^{-2} mol dm^{-3}, [N-MBA] = 4.0×10^{-3} mol dm^{-3}, [PF127] = 0.06% w/v, [$NaHCO_3$] = 2.48×10^{-1} mol dm^{-3}, 40% degree of neutralization of AA; at 45°C, 250 rpm,30 min. Three repeats were carried out.

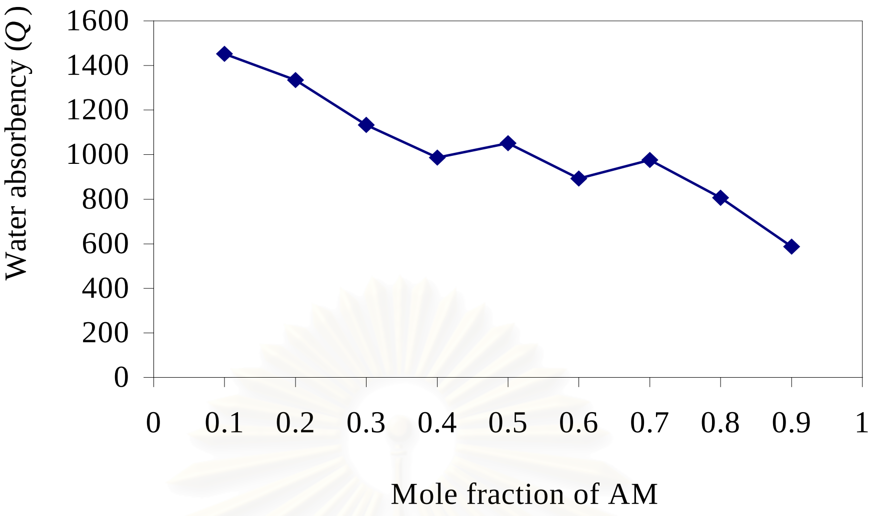


Figure 4.1 Effect of mole fraction of AM on the water absorbency of the synthesized copolymer

The synthesized copolymers of acrylamide (AM) and acrylic acid (AA) are swollen in water on the account of the hydrophilic pendants (amide and carboxylic groups) in their structure, especially the synthesized copolymer, which mole fraction of AM and AA at 0.1 and 0.9, respectively, at 40% degree neutralization of acrylic acid and 4.0×10^{-3} mol dm^{-3} crosslinking agent, N-MBA, produced the high water absorbency value of 1,452±15 times its dry weight. The water absorption ability was decreased with increasing the mole fraction of AM because chain transfer to polymer was increased with monomer concentration, especially at the mole fraction of AM at 0.9 the water absorbency value was 586±25 times its dry weight, because the chain transfer reaction results in increasing amounts of branching and self-crosslinking reactions that affect the product properties [10].

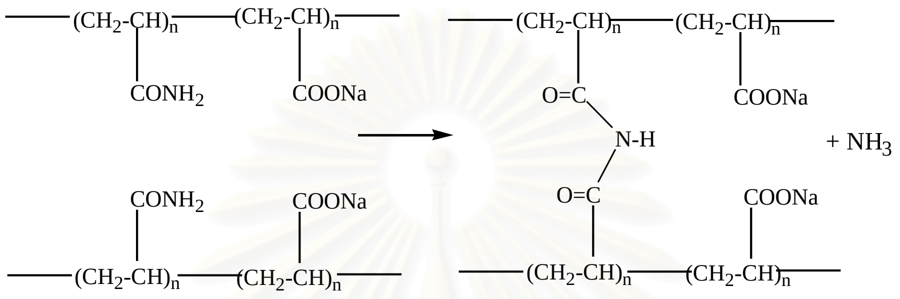
The critical mole fraction of AM at 0.1 and non neutralization of acrylic acid produced the optimum superabsorbent polymer; the result indicated that one of the side reactions could be crosslinking reaction of the copolymer with an appropriate crosslinking agent whose concentration is 4.0×10^{-3} mol dm^{-3}. Actually, the structure of the copolymer should consist of more acrylamide units than acrylate units owing to the higher hydrophilicity of the carboxylate group. The reactivity of AM is lower than that of sodium acrylate. The copolymerization reactivity ratio of acrylamide and sodium acrylate were 0.78 and 1.35, respectively [55]. In contrast, if the flexibility of polymer chain was an important factor, the water absorbency should have decreased with increasing concentration of acrylate units in the polymer chain since the glass transition temperature (T_g) of sodium acrylate is higher than that of acrylamide, i.e., 194^{o}C and 165^{o}C, respectively [55, 56].

The water absorbency ability of the all synthesized copolymers containing various ratios of monomer of AA and AM, in the absence of the crosslinking agent was higher than those with the crosslinking agent, because the former contained both soluble and insoluble polymers with poor gel strength. The insolubility of the copolymer is possibly due to the formation of a gel in the absence of any crosslinking monomer, which may be described as the following side reactions:

a) Polymerizing highly concentrated solutions of acrylic acid, may cause an auto-crosslinking through a hydrogen abstraction from the polymer backbone followed by radical combination [57, 58].

b) Chain transfer to polymer may occur during the polymerization [10].

c) The occurrence of imidization that usually takes place in the polymerization of acrylamide in concentrated solution and at high temperature and pH [59]. The imidization of the amide pendants in the copolymer is shown below:



(4.1)

The absorbency of the crosslinked polymer can be explained in term of swelling. Swelling is a diffusion phenomenon driven by the affinity of the molecules of the swelling material for the molecules of the contracting fluid. The swelling equilibria of ionized hydrogels are determined by a balance of three main forces [60, 61]:

1) The free energy of mixing of the network chains with solvent.
2) The net osmotic pressure within the network, resulting from the mobile counterions surrounding the fixed-charge groups (ion swelling pressure).
3) The elastic retractile response of the network (elastic swelling pressure).

Forces (1) and (2) favor hydrogel swelling, where force (3) opposes it. A classical crosslinked network has a swelling limit controlled by a balance between the thermodynamic forces due to polymer-solvent interactions and the entropic force of coiled polymer chains.

The swelling equilibrium is dependent on the entropy of dilution, the heat of dilution, and the entropy of the polymer network. For a given polymer-solvent system the equilibrium swelling is a function of the crosslink density. The relationship involving the equilibrium swelling ratio, Q, defined as the ratio of the final swollen volume to the original unswollen volume of the network, was derived by Flory [62]. If the crosslink density is not too high and the solvent is a good solvent, the following approximated relationship was obtained.

$$Q^{5/3} = \frac{(1/2 - \chi_1) 2\overline{M_c}}{V_1 \rho_0 \upsilon_{2,r}^{2/3} \left(1 - 3\overline{M_c} / \overline{M_n}\right)} \tag{4.2}$$

Where χ_1 is the polymer-solvent interaction parameter,

V_1 is the molar volumer of solvent,

$\upsilon_{2,r}$ is the polymer fraction at crosslinking,

$\overline{M_c}$ is the molecular weight of polymer chain between crosslinks, and

$\overline{M_n}$ is the initial molecular weight of the uncrosslinked polymer

The parameter that describes the basic structure of the hydrogel is the molecular weight between crosslinks, $\overline{M_c}$. This parameter defines the average molecular size between two consecutive functions regardless of the nature of those junctions. Additional parameters of importance in structural analysis of hydrogels are the crosslinking density, ρ_x , which is related to $\overline{M_c}$ as defined by Equation 4.3 [63].

$$\rho_x = \frac{1}{\upsilon \overline{M_c}} \tag{4.3}$$

Where $\overline{\upsilon}$ is the specific volume of the polymer. Determination of the crosslink density is described in APPENDIX A.

From Equations 4.2 and 4.3, Q is inversely related with the crosslink density, ρ_x.

4.2 Effect of the polymerization temperature

The water absorbency of the crosslinked copolymers synthesized with varied temperature for the solution polymerization is shown in Table 4.2 and Figure 4.2 while the concentrations of crosslinking agent, and other ingredients are fixed.

Table 4.2 Effect of the polymerization temperature on the water absorbency (Q) of the synthesized copolymer at 0.1 mole fraction of AM

Temperature (^{o}C)	**Water absorbency (Q) g g^{-1}**
45	1,452±15
50	1,325±12
55	1,247±14
60	1,198±10
65	1,085±18
70	975±12

Reaction Condition: [APS] = 2.30×10^{-3} mol dm^{-3}, [TMEDA] = 1.0×10^{-2} mol dm^{-3}, [N-MBA] = 4.0×10^{-3} mol dm^{-3}, [PF127] = 0.06% w/v, [NaHCO$_3$] = 2.48×10^{-1} mol dm^{-3}, 0.1 mole fraction of AM, 40% degree of neutralization of AA; at 250 rpm, 30 min. Three repeats were carried out.

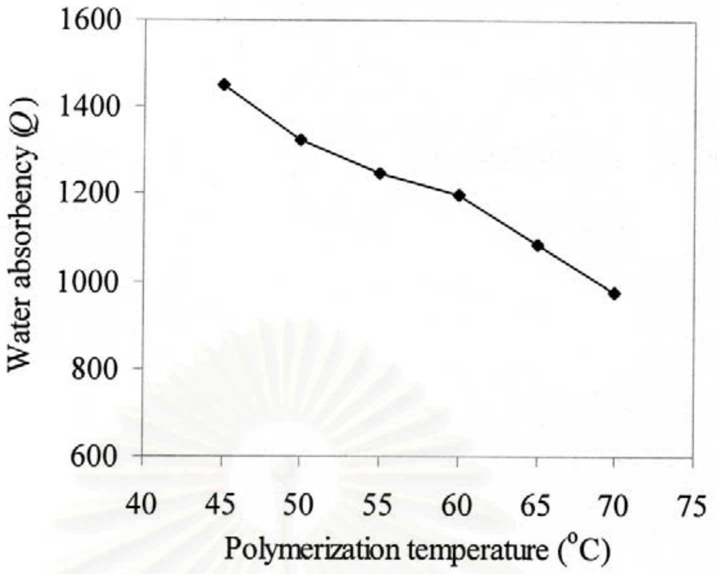


Figure 4.2 Effect of the polymerization temperature on the water absorbency (*Q*) of the synthesized copolymer

It is well known that in radical polymerization started by thermal decomposition of an initiator where transfer reactions are negligible, as temperature is increased, the rate of polymerization is strongly enhanced and the molecular weight of the polymer is reduced because of increase of the rate termination and transfer reactions [66]. The effect of polymerization temperature on the absorption capacity of the synthesized copolymer is shown in Figure 4.2. The water absorbency (*Q*) of the synthesized copolymer is decreased when polymerization temperature is increased. Because an increase of polymerizing temperature decreases the molecular weight with increasing a large amount of short kinetic chains. These short chains reduce the water absorption capacity. Therefore, increasing the polymerization temperature results in decrease in the absorption capacity, which is probably caused by changes in the copolymer composition with temperature due to a change in the length of the polymer chains.

4.3 Effect of the initiator concentration

The water absorbency of the crosslinked copolymers synthesized with various initiator (APS:TMEDA) concentrations for the solution polymerization is shown in Table 4.3 and Figure 4.3.

Table 4.3 Effect of the initiator concentration on water absorbency (*Q*) of the synthesized copolymers at 0.2 mole fraction of AM

Initiator concentration, (mol dm^{-3})	**Water absorbency (*Q*) g g^{-1}**
APS(1.50×10^{-3}) : TMEDA(1.0×10^{-2})	975±15
APS(2.0×10^{-3}) : TMEDA(1.0×10^{-2})	1,054±12
APS(2.30×10^{-3}) : TMEDA(1.0×10^{-2})	1,117±14
APS(3.0×10^{-3}) : TMEDA(1.0×10^{-2})	1,020±8
APS(3.50×10^{-3}) : TMEDA(1.0×10^{-2})	957±12
APS(4.40×10^{-3}) : TMEDA(1.0×10^{-2})	947±9
APS(2.30×10^{-3}) : TMEDA(2.0×10^{-2})	904±12

Reaction Condition: [N-MBA] = 6.30×10^{-3} mol dm^{-3}, [PF127] = 0.06% W/V, [$NaHCO_3$] = 2.48×10^{-1} mol dm^{-3}, 40% degree of neutralization of AA; at 45°C, 250 rpm, 30 min. Three repeats were carried out.

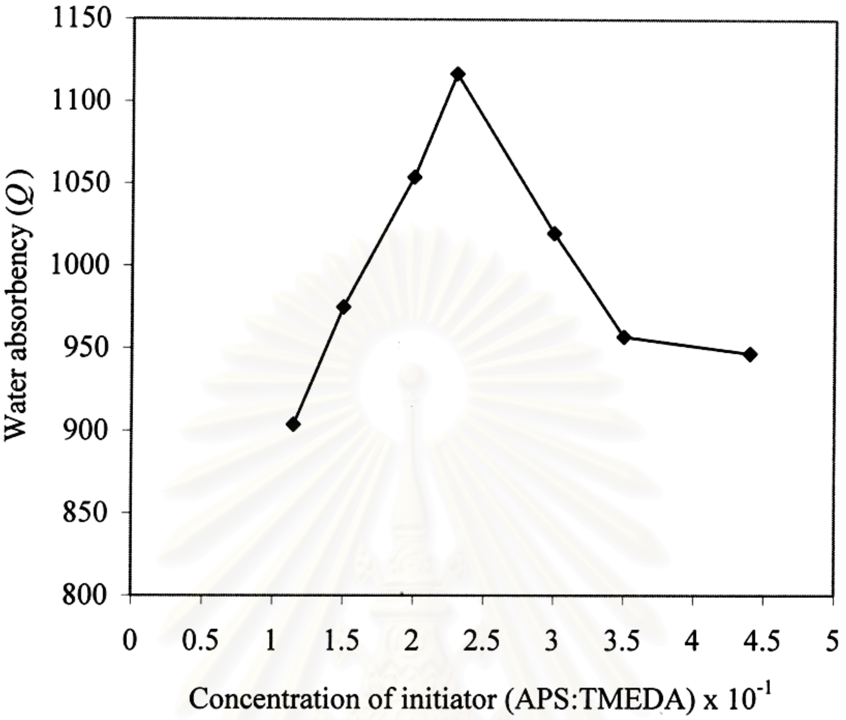
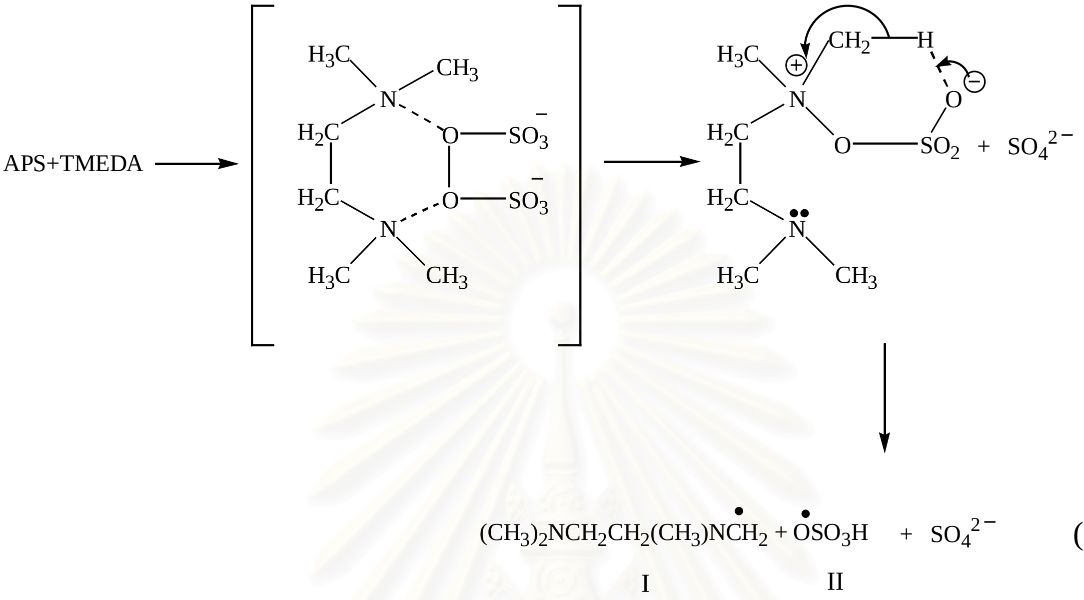


Figure 4.3 Effect of the initiator concentration on water absorbency (*Q*) of synthesized copolymer

The copolymers, synthesized by APS (2.30×10^{-3} mol dm^{-3}): TMEDA (1.0×10^{-2} mol dm^{-3}) gave the optimum result which has the highest water absorbency. Figure 4.3 shows the effect of the initiator concentration on water absorbency. The water absorbency increases linearly with the increase of initiator ratio of APS: TMEDA at 0.23 and then decreases with the increasing initiator ratios. As mentioned above, the rate of polymerization depended on the concentrations of monomers and initators, for a bimolecular termination. When APS-TMEDA is used as redox initiator for free radical polymerization, the free radical (I) is one of the initial free radicals responsible for the initiation of vinyl polymerization in addition to sulfate free radical (II). The following mechanism represents the production of initial radicals for the polymerization:



(4.4)

4.4 Effect of type and concentration of the crosslinker

The water absorbency of the superabsorbent polymers, synthesized by 0.1 mole fraction of AM with 2.30×10^{-3} mol dm^{-3} APS, 1.0×10^{-2} mol dm^{-3} TMEDA, 40% neutralization and various types of crosslinking agent was shown Table 4.4 and Figure 4.4.

Table 4.4 Effect of types of crosslinking agent on the water absorbency (*Q*) of the synthesized copolymers at 0.1 mole fraction of AM

Types of crosslinker	Water absorbency (*Q*) g g^{-1}
A1	1,452±15
A2	922±10
A3	238±12
A4	27±5

A1 is N-MBA, A2 is EGDMA, A3 is formaldehyde and A4 is no crosslinker

Reaction Condition: [APS] = 2.30×10^{-3} mol dm^{-3} , [TMEDA] = 1.0×10^{-2} mol dm^{-3}, [PF127] = 0.06% w/v, [Crosslinker] = 4.0×10^{-3} mol dm^{-3}, [$NaHCO_3$] = 2.48×10^{-1} mol dm^{-3}, 40% degree of neutralization of AA; at 45°C, 250 rpm, 30 min. Three repeats were carried out.

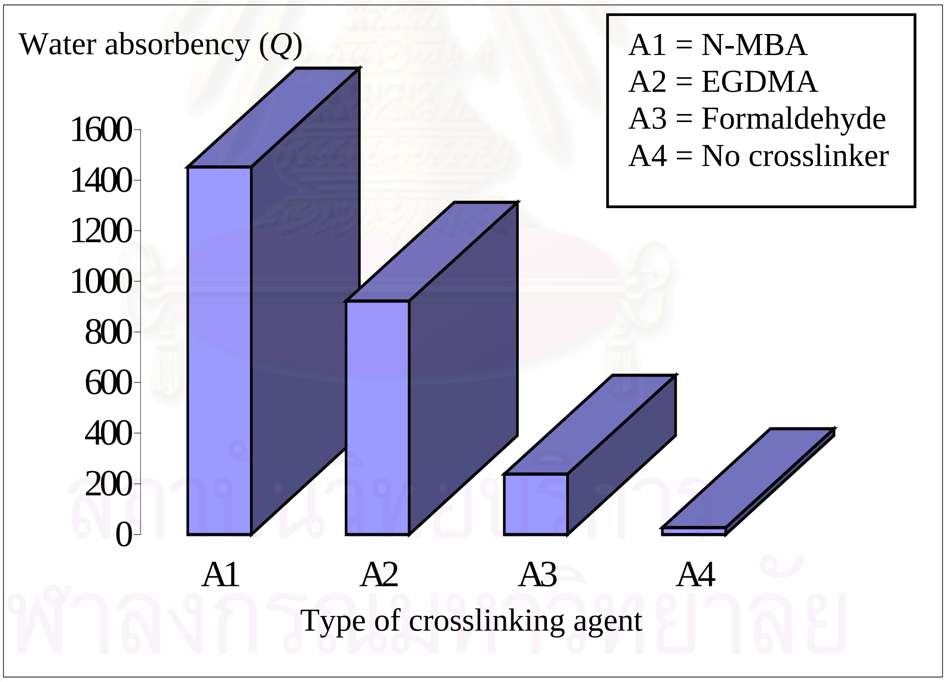
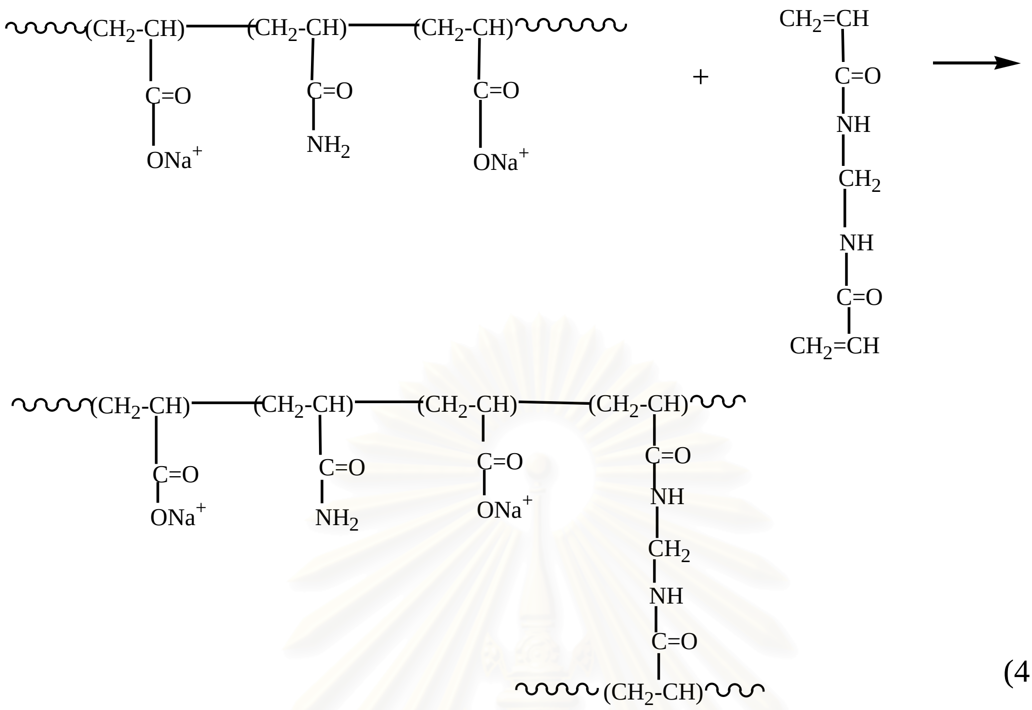
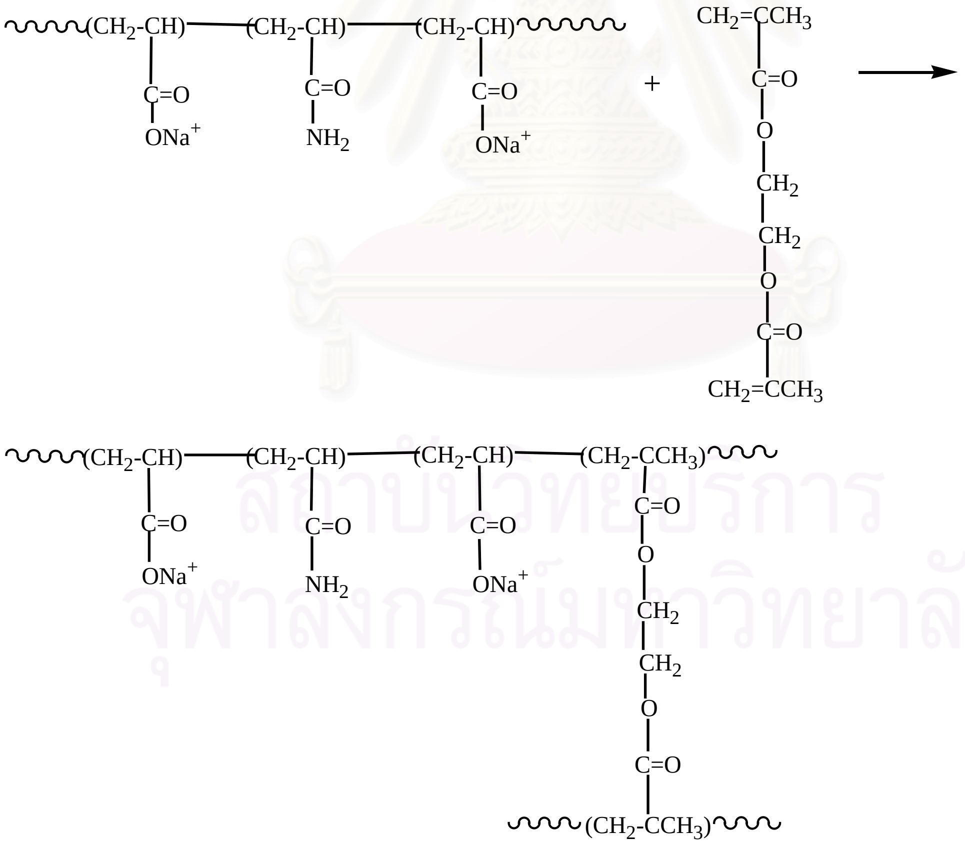


Figure 4.4 Effect of types of crosslinking agent on the water absorbency (*Q*) of the synthesized copolymer

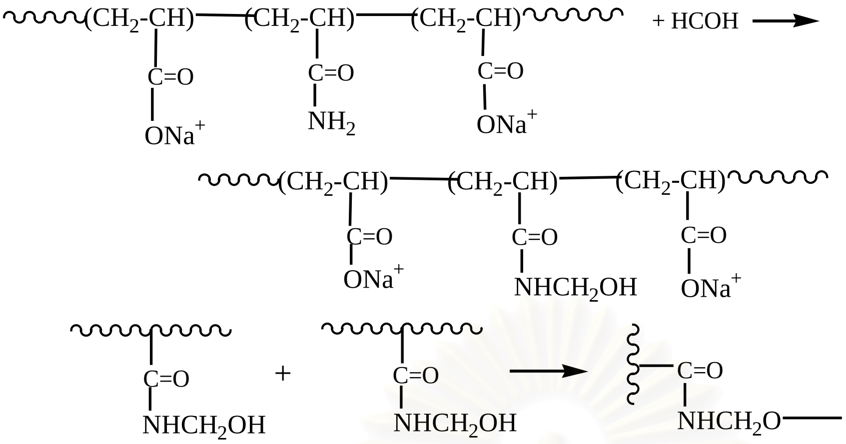
The water absorbency of the copolymers in the presence of N-MBA as a crosslinking agent is higher than those of EGDMA and formaldehyde. The water absorbency of EGDMA crosslinked copolymer is higher than that resulted from formaldehyde, because the efficiency of crosslinking depends on steric hindrance and reduced mobility at the site of pendent double bond, the tendency of a given crosslinker to undergo intermolecular addition, and the solubility of the crosslinker. The copolymer crosslinked with N-MBA at 0.1 mole fraction of AM and 40% degree of neutralization of acrylic acid gave a water absorbency values of 1,452±15 which is higher than copolymers synthesized in the absence of the crosslinking agent. In the absence of the crosslinking agent, more soluble copolymers are produced that can not absorb fluid effectively. However, in the presence of high crosslinking agent concentrations, more crosslinks are formed that lowers the swelling of the gel as well. In general, crossliking agents have been employed to help improve the gel strength of the swollen gel but it is very effective to reduce the water absorbency. As a result of a combination of such factors, different crosslinkers can exhibit much different effectiveness in the crosslinked product. The following represents the synthesis of the copolymer by free radical copolymerization using a redox initiator with N-MBA crosslinking agent as shown in Equation 4.5, EGDMA crosslinking agent as shown in Equation 4.6 and formaldehyde crosslinking agent as shown in Equation 4.7.



(4.5)



(4.6)



(4.7)

Table 4.5 Effect of concentration of crosslinking agent on the water absorbency (*Q*) of the synthesized copolymer

Concentration of N-MBA, (mol dm^{-3})	**Water absorbency (*Q*) g g^{-1}**
1.0×10^{-3}	312±12
1.50×10^{-3}	350±8
2.0×10^{-3}	378±5
2.50×10^{-3}	403±18
3.0×10^{-3}	542±20
3.50×10^{-3}	871±16
4.0×10^{-3}	1,452±15
4.50×10^{-3}	502±10
5.0×10^{-3}	335±12

Reaction Condition: [APS] = 2.30×10^{-3} mol dm^{-3}, [TMEDA] = 1.0×10^{-2} mol dm^{-3}, [PF127] = 0.06% w/v, [$NaHCO_3$] = 2.48×10^{-1} mol dm^{-3}, 40% degree of neutralization of AA, mole fraction of AM = 0.1; at 45°C, 250 rpm, 30 min. Three repeats were carried out.

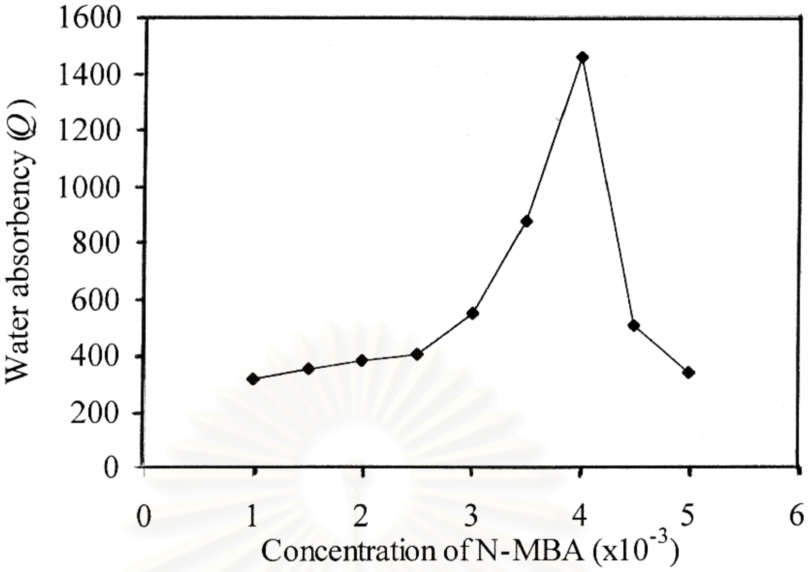


Figure 4.5 Effect of concentration of crosslinking agent on the water absorbency (*Q*) of the synthesized copolymer

Relatively small changes in crosslinker density can play a major role in modifying the properties of superabsorbent polymers. Figure 4.5 illustrates the relationship between water absorbency and crosslinker (N-MBA) concentration. It is clear that the gel absorbency is diminished at low N-MBA concentration because of an increase of soluble material. A maximum water absorbency of 1,452±15 is obtained at the N-MBA concentration of 4.0×10^{-3} mol dm^{-3}. On the other hand, excessive crosslinking reaction also decreases gel absorbency [64, 65].

4.5 Effect of the degree of neutralization of acrylic acid

The water absorbency of the crosslinked copolymers synthesized with various mole fractions of AM and the degree of neutralization of acrylic acid are shown in Table 4.6 and Figure 4.6.

Table 4.6 Effect of mole fraction of AM and the degree of neutralization of acrylic acid on the water absorbency (*Q*) of the synthesized copolymers

Mole fraction of AM	**Water absorbency (*Q*) at the degree of neutralization of AA, g g^{-1}**				
	0%	**40%**	**60%**	**80%**	**100%**
0.10	2,196±14	1,452±15	1,215±18	1,170±20	1,053±16
0.20	1,576±16	1,335±12	1,144±22	1,141±14	1,232±14
0.30	1,265±21	1,132±30	1,027±16	1,263±12	635±22
0.40	1,217±18	986±14	875±24	731±8	817±12
0.50	1,140±25	1,051±26	743±12	918±9	812±14
0.60	767±9	892±18	719±9	448±9	834±9
0.70	958±22	975±22	541±6	733±12	717±10
0.80	591±16	806±18	515±12	760±15	722±16
0.90	578±14	586±25	348±5	568±14	368±6

Reaction Condition: [APS] = 2.30×10^{-3} mol dm^{-3}, [TMEDA] = 1.0×10^{-2} mol dm^{-3}, [N-MBA] = 4.0×10^{-3} mol dm^{-3}, [PF127] = 0.06% w/v, [$NaHCO_3$] = 2.48×10^{-1} mol dm^{-3}; at 45°C, 30 min. Three repeats were carried out.

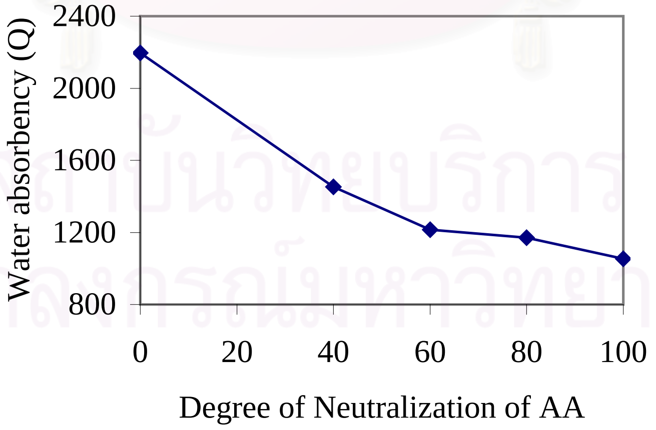


Figure 4.6 Effect of the degree neutralization of AA on the water absorbency (*Q*) of synthesized copolymer at 0.1 mole fraction of AM

Figure 4.6 shows the effect of the degree of neutralization of AA on water absorbency. The water absorbency decreases with the increase of degree of neutralization of AA. There exists a maximum water absorbency at a degree of neutralization of 0%. Flory decribed the mechanism of the swelling of ionic network [67]. If the polymer chains making up the network contain ionizable groups, the swelling forces may be greatly increased as a result of the localization of charges on the polymer chains. When the crosslinked copolymer is neutralized with sodium hydroxide, the negatively charged carboxyl groups attached to the polymer chains set up an electrostatic repulsion, which tends to expand the network. The concentration of sodium ions also increases with the increase of degree of neutralization of AA. Sodium ions, by screening the negative charges of carboxyl groups, reduce the electrostatic repulsion tremendously.

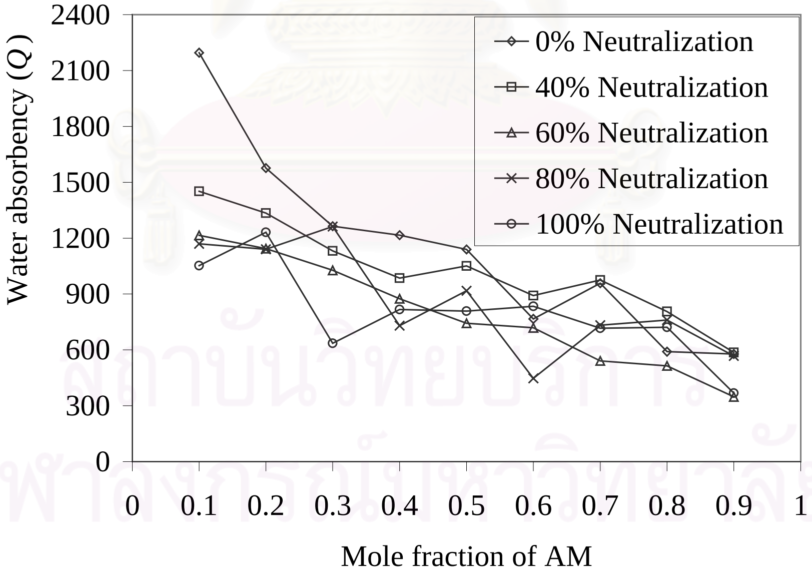


Figure 4.7 Effect of mole fraction of AM and degree neutralization of AA on the water absorbency (*Q*) of synthesized copolymer

The water absorbency of synthesized copolymer not only depends on the degree of neutralization of AA, but also depends on the mole fraction of AM. Because the electrostatic repulsion may be increased with the increase of the mole fraction of AM, resulting in the increased water absorbency (*Q*).

4.6 The buffer effect on swelling behavior

The influence of solution pH (2-12) on water absorbency of the synthesized copolymers, produced by the solution polymerization of 0.2 mole fraction of AM, 2.45×10^{-3}mol dm^{-3} APS, 1.00×10^{-2} mol dm^{-3} TMEDA, 4.19×10^{-3} mol dm^{-3} N-MBA and 40% neutralization degree of acrylic acid in a universal buffer (APPENDIX B) solution system alters the water absorbency as shown in Table 4.7 and Figure 4.8.

Table 4.7 The effect of pH on water absorbency (*Q*) of the synthesized copolymers at room temperature

pH of buffer solution	**Water absorbency(*Q*) g g^{-1}**
pH 2	59±5
pH 3	98±14
pH 4	147±18
pH 5	162±12
pH 6	141±10
pH 7	142±15
pH 8	154±9
pH 9	126±12
pH 10	118±15
pH 11	139±14
pH 12	122±6

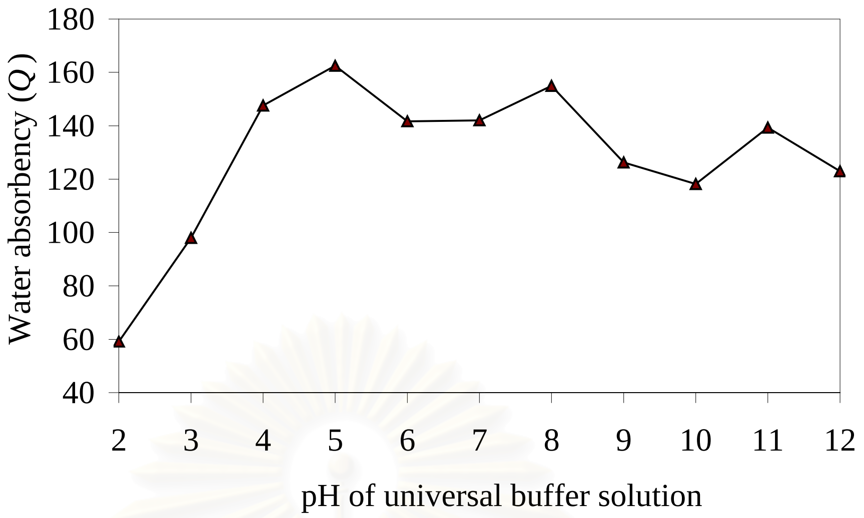


Figure 4.8 The effect of pH of the universal buffer solution on the water absorbency (*Q*) of the synthesized copolymer

The swelling capacity of the copolymer is very dependent on pH, and concentration of the absorbed liquid. The swelling of synthesized copolymer was found to increase significantly from pH 2 to pH 5 and the water absorbency then reaches a maximum at pH 5, then slightly decreases when increasing the pH to 10.

At pH below 4 the water absorbency of the crosslinked polymer is less since the carboxylate groups of these hydrogels have all combined with a H^+ ion to become un-ionized and the amide side chains of the acrylamide become hydrolyzed to be the carboxylic group, thus decreasing the charge density of anions on the network. The concomitant decreases in the mobile counterion content of the network sharply decrease the internal osmotic pressure, which retards the observed swelling transitions. For the un-ionized and nonpolar molecules, Brownian motion of the individual segments largely determines the shape of the polymer molecules. The degree of dissociation and consequently the charge density of the polymer molecules will be controlled by the ionization constants for these functional groups and by the pH of medium.

The opposite behavior occurs in the weak acid and basic solutions in the pH range 5-12. As increasing the pH, the concentration of the base cations in the outer solution and the concentration of the base anion inside of network will also increase. Those cations will be attracted into the gel to balance the osmotic pressure occurred from the anion of base-hydrolyzed acrylamide and carboxylate groups. Those cations will replace the mobile H^+ ions. The gel, of course, acts as an ion exchanger. New H^+ ions will be supplied by water. The concentration of mobile ions in the gel will thus increase more rapidly than those in the outer solution and the ion swelling pressure will increase.

Normally, hydrogels are also classified into three categories by their ionic character [65]. In particular, anionic hydrogels prepared by the copolymerization of acrylic acid are important for industrial products that are used widely as superabsorbent hydrogels. Cationic ones, however, have not been much developed as industrial products. Nonionic ones are very useful, since they can absorb water in a wide range of pH and there is no ionic interaction between the solutes in water and gel matrix.

Sodium cation in the universal buffer can interact with anions on the network, thus decreasing the charge density of anions on the network that retard the ion exchange between H^+ ions from inside and outside the gel network. This result is far lower than the water absorbency of copolymer in distilled water, because of the ionic contents.

Theoretical framework developed to describe the equilibrium swelling characteristic of networks were Flory-Rehner model, Peppas-Merrill model, and Peppas-Luchy model [69]. The developed model for the anionic polymeric network interacting cross-linked with solvents present and exhibiting a non-Gaussian chain length distritution, the complete equilibrium expression is shown in Equation 4.8:

$$\frac{V_1}{4I}\left(\frac{\upsilon_{2,s}}{\bar{\upsilon}}\right)\left(\frac{K_a}{10^{pH}+K_a}\right)^2 = \left(\ln\left(1-\upsilon_{2,s}\right)+\upsilon_{2,s}+\chi_1\upsilon_{2,s}^2\right)+$$

$$\frac{\left(\frac{V_1}{(\bar{\upsilon})(\overline{M}_c)}\right)\left(1-\frac{2\overline{M}_c}{\overline{M}_n}\right)\upsilon_{2,s}\left(\left(\frac{\upsilon_{2,s}}{\upsilon_{2,r}}\right)^{1/3}-\frac{1}{2}\left(\frac{\upsilon_{2,s}}{\upsilon_{2,r}}\right)\right)\left(1+\frac{1}{N}\left(\frac{\upsilon_{2,s}}{\upsilon_{2,r}}\right)^{1/3}\right)^2}{\left(1-\frac{1}{N}\upsilon_{2,s}^{2/3}\right)^3} \qquad (4.8)$$

Where V_1 is the molar volume of the swelling agent

I is ionic strength

$\upsilon_{2,s}$ is the polymer volume fraction in the equilibrium-swollen polymer

$\upsilon_{2,r}$ is the polymer volume fraction in the sol-called relaxed polymer state

χ_1 is the Flory polymer-solvent interaction parameter

N is the effective number of bond vectors between consecutive crosslinks

$\overline{M}_n$ is the number average molecular weight before crosslinking

$\overline{M}_c$ is the number average molecular weight between crosslinking

$\bar{\upsilon}$ is the specific volume of the polymer

Based on Equation 4.8, the molar volume of the swelling agent is increased with increasing pH of the solution.

The swelling equilibria of ionized hydrogels are determined by a balance of three primary forces. The main forces that favor hydrogel swelling are the free energy of mixing of the network chains with solvents and the ionic osmotic pressure generated from mobile counterions to charged ions in the network (Donnan equilibrium) [70]. For this result, the latter force is plausibly explained as follows:

The simplest part of the theories attributes the ion swelling pressure to the difference between the osmotic pressure of freely ions in the gel and the outer solution, the distribution of the ions between the gel and the outer solution forms Donnan equilibrium. Within this theory, the ionic forces depend only on the ionic composition of the solvent and on the concentration of fixed ionizable group in the gel but not on the properties of the neutral network [70].

4.7 Swelling behavior in salt solution

The salt effect is clearly evidenced as a result of the osmotic pressure differential between the internal solution in the gel and external solution, due to the different ion concentration. The water intake by the gel reduced the osmotic pressure until an ion concentration equilibrium was reached.

The superabsorbent copolymer obtained earlier with the highest water absorbency (2,196±14) was selected to test the salt effect in various concentrations of NaCl, KCl, KI, KBr, $MgCl_2$ and $CaCl_2$ solutions. The influences of salt solutions upon liquid absorbency of the copolymer are summarized in Table 4.8 and Figure 4.9.

Table 4.8 Effect of different salt solutions on the liquid absorbency (*Q*) of the synthesized copolymers at 0.1 mole fraction of AM

Concentration of salt solution (%w/v)	**Liquid absorbency (*Q*), g g^{-1}**					
	NaCl	**KCl**	**KI**	**KBr**	**MgCl$_2$**	**CaCl$_2$**
0.00	2,196±14	2,196±14	2,196±14	2,196±14	2,196±14	2,196±14
0.05	398±6	482±8	662±10	589±12	228±10	174±12
0.10	305±4	385±5	512±12	451±8	164±12	105±8
0.50	222±5	268±6	369±8	315±6	75±8	48±5
0.90	180±10	204±8	298±4	246±5	60±10	36±5

Reaction Condition: [APS] = 2.30×10^{-3} mol dm^{-3}, [TMEDA] = 1.0×10^{-2} mol dm^{-3}, [N-MBA] = 4.0×10^{-3} mol dm^{-3}, [PF127] = 0.06% w/v, [NaHCO$_3$] = 2.48×10^{-1} mol dm^{-3}, non-neutralizedAA; at 45°C, 250 rpm, 30 min. Three repeats were carried out.

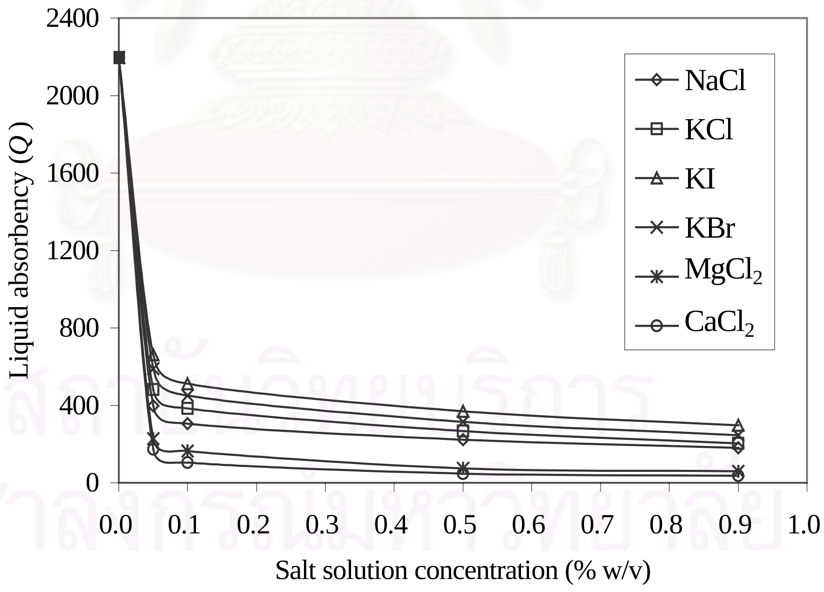


Figure 4.9 Effect of different salt solution on the liquid absorbency (*Q*) of synthesized copolymer

A water absorbent system consists of a quantity of polymer network with a variable quantity of aqueous component. The osmotic pressure attributable to the polymer network is driving force for the water absorption and, consequently, swelling. At swelling equilibrium, the chemical potentials of water in the polymer equals that of water surrounding the polymer. Therefore, absorbent polyelectrolyte polymers cannot imbile as much salt water as pure water [62].

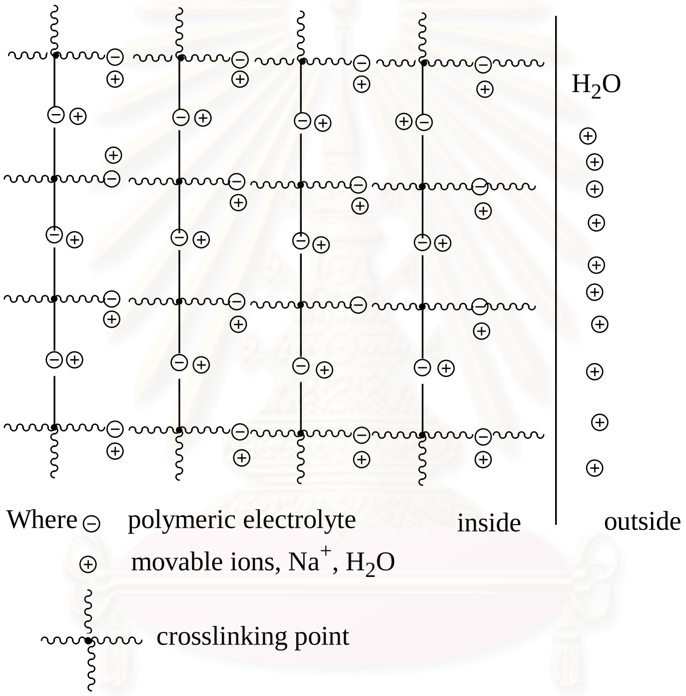


Figure 4.10 Ionic network of a superabsorbent polymer

The absorbency of a SAP has been defined by Flory as the swelling ratio, q_m, of the crosslinked polyelectrolyte network system as shown in Equation 4.9 [67].

$$q_m^{5/3} = \frac{\left(i/2\upsilon_u I^{*1/2}\right)^2 + (1/2-\chi_1)/\upsilon_1}{\upsilon_e/V_0} \tag{4.9}$$

$$q_m^{5/3} = \frac{\left\lfloor \left(i/2\upsilon_u I^{*1/2}\right)^2 + \left(1/2-\chi_1\right)/\upsilon_1 \right\rfloor \left(\overline{M}_c/\rho_c\right)}{\left(1-2\overline{M}_c/\overline{M}_n\right)} \qquad (4.10)$$

Where q_m is the swelling ratio of the network at equilibrium

i is the degree of ionization multiplied by the valency of the fixed charge in the network

υ_u is the molar volume of a structure unit

I^* is the ionic strength of external solution

χ_1 is the interaction parameter between the network and the solvent

υ_1 is the molar of the solvent

υ_e is the effective number of chains in the network

V_o is the volume of the unswollen network

$\overline{M_c}$ is the average molecular weight of network chains

ρ_p is the density of polymer, and

$\overline{M_n}$ is the average molecular weight of the polymer before crosslinking

In Equation 4.9, the first and second terms in the right side represent the contribution of ionic charges in the network and in the solution, and the contribution of the affinity between the polymer network and the solvent, respectively. The term of i/υ_u is the concentration of fixed charge referred to the unswollen networks and term of υ_e/V_o is crosslinking density which refers to the number of effectively crosslinked chains in unit volume.The term on the bottom of the right side represents the crosslink density of the network. Equation 4.9 explains the absorbing behavior of a SAP very well and can conveniently be used for designing a SAP since it gives basic ideas about what the main chain structure and the crosslink density of SAP should be for a particular application. The term $(1-2\overline{M_c}/\overline{M_n})$ in Equation 4.10 expresses the correction for the network imperfection resulting from chain ends [67]. The network imperfection is higher when $\overline{M_n}$ is smaller and this also means there are more chain ends in the networks. It is predicted from Equation 4.10 that networks with more chain ends have higher swelling ratio, q_m, when $\overline{M_c}$ is the same value.

Figure 4.9 shows the absorbency dependency of poly(acrylic acid-*co*-acrylamide) on the concentration of salt aqueous solutions. The absorbency decreases as the concentration of the salts increases; this is clearly explained by the increase of $I^{*1/2}$ in Equation 4.9.

Table 4.9 Ionic strength of the salt solutions at various concentration

Concentration of salt solution (% w/v)	**Ionic strength *, (mol-ion dm^{-3})**					
	NaCl	**KCl**	**KI**	**KBr**	**MgCl$_2$**	**CaCl$_2$**
0.05	8.55×10^{-3}	6.70×10^{-3}	3.01×10^{-3}	4.20×10^{-3}	7.38×10^{-3}	13.51×10^{-3}
0.10	17.1×10^{-3}	13.4×10^{-3}	8.61×10^{-3}	8.40×10^{-3}	14.8×10^{-3}	27.0×10^{-3}
0.50	85.6×10^{-3}	67.1×10^{-3}	43.1×10^{-3}	42.0×10^{-3}	73.8×10^{-3}	135.1×10^{-3}
0.90	154.0×10^{-3}	120.7×10^{-3}	54.2×10^{-3}	75.6×10^{-3}	132.9×10^{-3}	243.3×10^{-3}

*$I = 1/2\Sigma(C_iZ_i^2)$; where I is the ionic strength, C_i is the ionic concentration, and Z_i is charge on each individual ion [71].

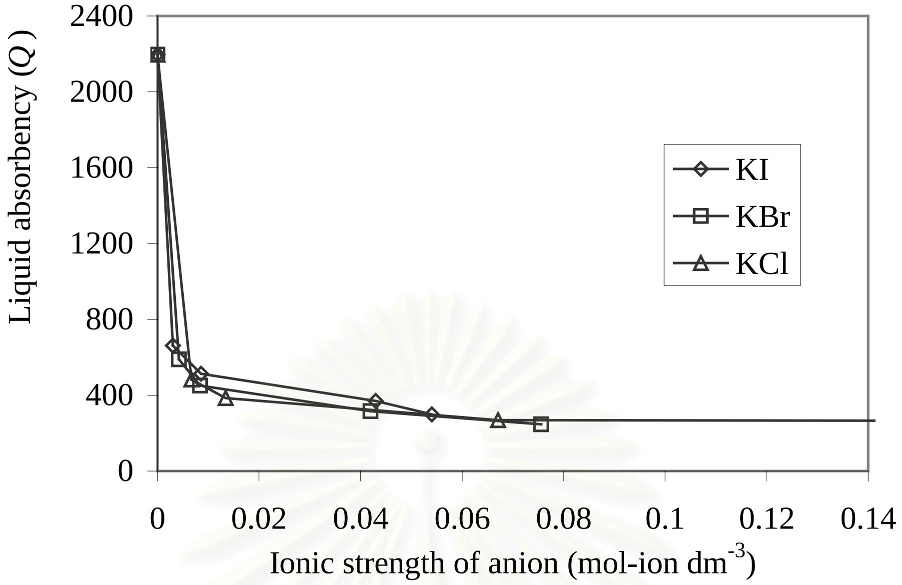


Figure 4.11 Effect of the anion of the salt solution on liquid absorbency (*Q*) of the synthesized copolymer

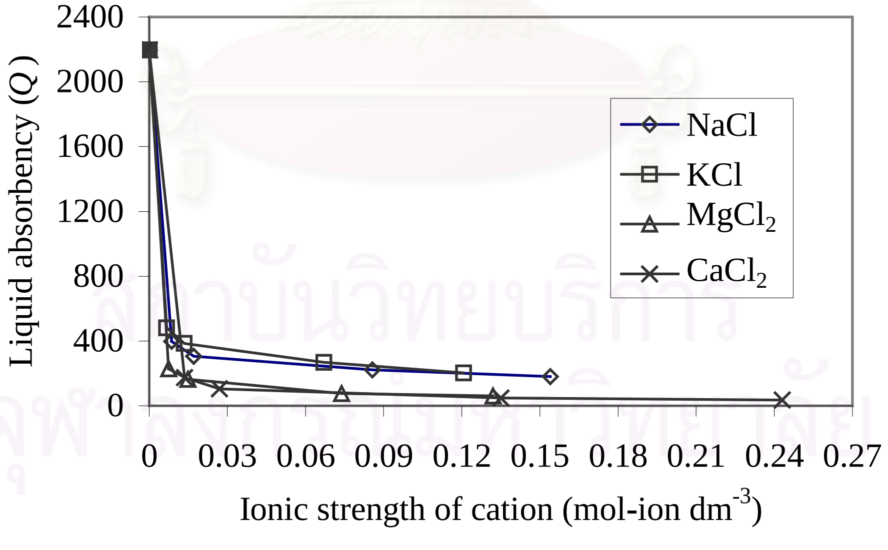


Figure 4.12 Effect of the cation of the salt solution on liquid absorbency (*Q*) of the synthesized copolymer

The result shows the tendency that the water absorbency decreases as the salt concentration increases due to the ionic strength (I) of the salt solution. At low ionic strength (large Debye lengths), repulsions are long-range interaction and the gel expansion to minimize the repulsion free energy; as ionic strength rises (small Debye lengths), repulsions are shielded and the gel dewash [72]. The ion concentration and ionic strength of the salt solutions are calculated in Table 4.9.

On observing the cases of $MgCl_2$ and $CaCl_2$ the water absorbency decreases when increases $MgCl_2$ and $CaCl_2$ concentrations. This suggests that the equilibrium osmotic pressure is reached earlier in the presence of the divalent ion as result of the higher ionic strength of the $MgCl_2$ and $CaCl_2$ solution comparing with that of other salt solutions at the same concentration. The drop will occur at lower salt concentrations in the divalent case. In addition, the divalent Mg^{2+} and Ca^{2+} ions may crosslink the gel by salt formation with the carboxylate groups on adjacent chains or chain segments of the copolymer. Consequently, the crosslink density of the network increases [73, 74].

At the same ionic strength value, the water absorbency of copolymers in various salt solutions containing different cations and anions are shown in Figures 4.11-4.12. The water absorbency of copolymer is relatively equal, except for the results of $MgCl_2$ and $CaCl_2$ solutions, the divalent salts differ because Mg^{2+} and Ca^{2+} can react with the free carboxylic sites of the gel by a chelate formation to give additionally divalent carboxylate groups on the backbone.

4.8 Swelling behavior in urea solution

The highest water-absorbing copolymer obtained earlier with liquid absorbency (2,196±14) was selected to test the salt effect in various urea concentrations. The influences of salt solutions upon liquid absorbency of the copolymer are summarized in Table 4.10 and Figure 4.13.

Table 4.10 The effect of urea solution on liquid absorbency (*Q*) of the synthesized copolymers at 0.1 mole fraction of AM

Concentration of urea solution (% w/v)	**Liquid absorbency (*Q*) $g\ g^{-1}$**
0.00	2,196±14
0.01	1,691±22
0.02	1,875±25
0.03	1,645±18
0.04	1,797±20
0.05	1,627±15
0.10	1,686±10

Reaction Condition: [APS] = 2.30×10^{-3} mol dm^{-3}, [TMEDA] = 1.0×10^{-2} mol dm^{-3}, [N-MBA] = 4.0×10^{-3} mol dm^{-3}, [PF127] = 0.06% w/v, [$NaHCO_3$] = 2.48×10^{-1} mol dm^{-3}, non-neutralized AA, at 45°C, 250 rpm, 30 min. Three repeats were carried out.

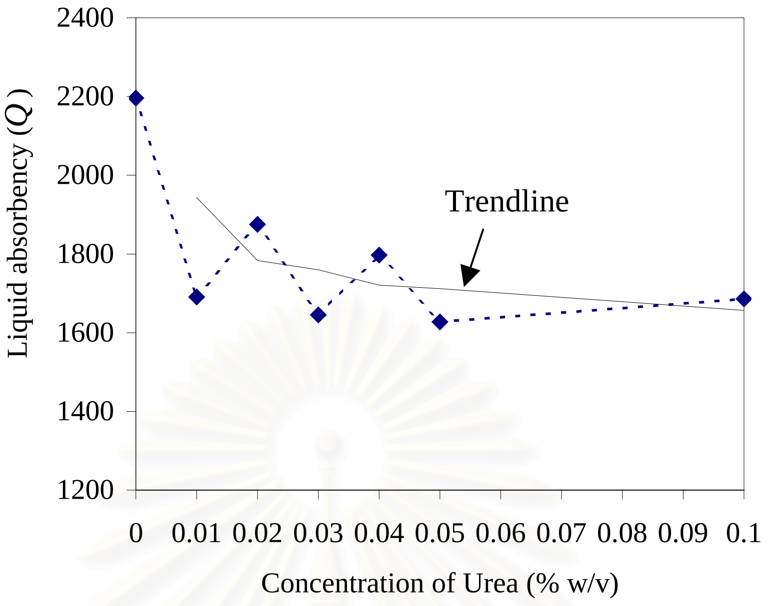


Figure 4.13 Effect of urea solution on the liquid absorbency (*Q*) of synthesized copolymer

Figure 4.13 shows the urea absorption of the synthesized copolymer generally used for hygiene applications. Although the concentration of urea is as high as 0.1% w/v, the copolymer still has the high water (1,686±10 g g^{-1}); since the residual acid groups in the synthesized copolymer can react with alkaline substances very effectively. This property is very beneficial in diapers.

4.9 The effect of temperature on water absorbency (*Q*)

Water absorbency of the superabsorbent polymers, synthesized by 0.1 mole fraction of AM with 2.30×10^{-3} mol dm^{-3}, APS, 1.0×10^{-2} mol dm^{-3} TMEDA , and various temperatures of water, is shown in Table 4.11 and Figure 4.14. Three repeats were carried out.

Table 4.11 The effect of water temperature on water absorbency of the synthesized copolymer

Temperature (^{o}C)	**Water absorbency (*Q*) g g^{-1}**
35	2,196±14
45	2,150±12
55	2,085±25
65	1,919±18
75	1,898±20
85	1,787±14

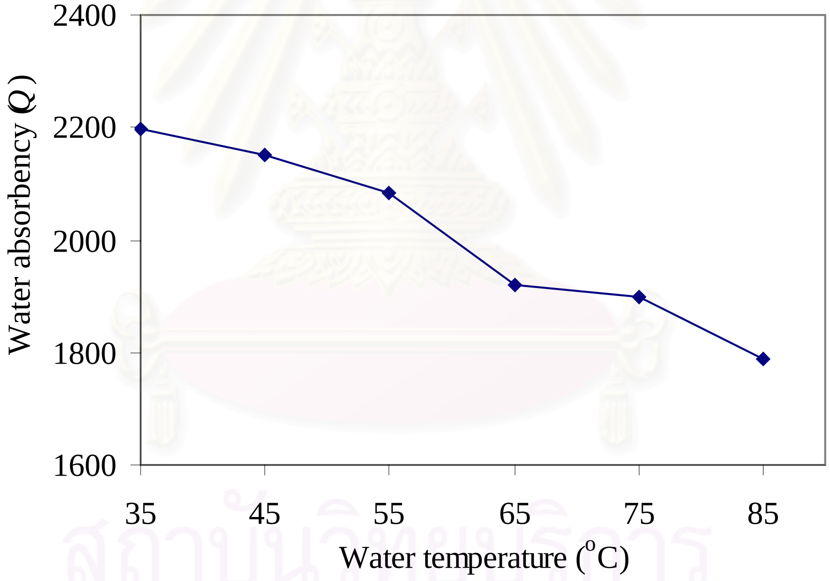


Figure 4.14 The effect of water temperature on water absrobency (*Q*) of the synthesized copolymer

Figure 4.14 shows that at the water temperature higher than 35^{o}C, the water absorption decreases steadily. This indicates a release of water-soluble materials, i.e., the copolymers have a lower crosslinking degree. When the gel is cool, the swollen state is thermodynamically stable. The gel formed by the synthesized copolymer seems to be a thermosensitive polymer gel.

Superabsorbent polymers are used under conditions in which the system temperature may change over time. For example, in a diaper, the superabsorbent polymer will first be bathed in a salt and urea solution, that is at the internal temperature of the human body, but the resulting gel will cool slowly in contact with the external environment. The extent and rate of cooling will depend on the climate and other environment. The diffusion coefficients of polymer in solution are temperature dependent, and this should be reflected in the absorption rate of superabsorbent polymers. The diffusion coefficient, D, may be related to the temperature and molecular weight of the polymer by the following equation:

$$D = \frac{kT}{CM^{a}} \tag{4.11}$$

Where D is the diffusion coefficient,

k is the Boltzmann constant,

T is the temperature,

C is a number characteristic of the polymer structure,

M is the molecular weight of the polymer, and

a depends on the solvent quality [75].

4.10 Swelling Kinetics

The swelling process is a diffusive process, with water diffusing into the polymer as the polymer chains relax and diffuse outwardly into the liquid. The polymer chains must diffuse and move for the volume of the polymer to increase. Because of the diffusive mechanism, a principal factor in swelling kinetic is the size of the polymer particle, its morphology and its shape.

The swelling kinetics of superabsorbent polymer can be studied by application of a first-order kinetic expression based upon Fick’s second low of diffusion [76]. For a spherical particle, the diffusion equation reduces to Equation 4.12. The rate of swelling is first-order in the amount of swelling capacity remaining at any time, as given by Equation 4.13.

$$\frac{\partial C}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(rD\frac{\partial C}{\partial r}\right) \tag{4.12}$$

$$\frac{dQ}{dt} = k\left(Q_{\max} - Q\right) \tag{4.13}$$

Where D is the diffusion coefficient of C,

C is concentration of the diffusing species,

r is the diffusion path length,

Q_{max} and Q are the swelling capacities at equilibrium,

t is any time,

k is the swelling rate constant, which depends on particle size and on the diffusion coefficient.

The values of Q are given as the ratio of the mass of liquid absorbed to the dry mass of the polymer. The first-order swelling behavior is commonly observed for the swelling of networks. Taking the definite integral between the limits of swelling capacity equal to zero and Q_{max} yields

$$Q(t) = Q_{\max}(1 - e^{-kt}) \tag{4.14}$$

In this model of the dynamic swelling processes, the structure features of the polymer and system that affect the maximum swelling capacity influence the rate through the Q_{max} term.

In practical applications, not only is a higher absorption capacity required of the absorbent, but also a higher absorbing rate. The synthesized copolymer is also characterized by its high swelling kinetics. The results are presented in Table 4.12 and Figure 4.15.

Table 4.12 Swelling kinetics of the synthesized copolymer

Time (min)	**Water absorbency (*Q*) g g^{-1}**
10	1,628±14
20	2,125±10
30	2,196±12
40	2,212±18
50	2,254±25
60	2,308±22

Reaction Condition: [APS] = 2.30×10^{-3} mol dm^{-3}, [TMEDA] = 1.0×10^{-2} mol dm^{-3}, [N-MBA] = 4.0×10^{-3} mol dm^{-3}, [PF127] = 0.06% w/v, [$NaHCO_3$] = 2.48×10^{-1} mol dm^{-3}, 0.1 mole fraction of AM, at 250 rpm,30 min. Three repeats were carried out.

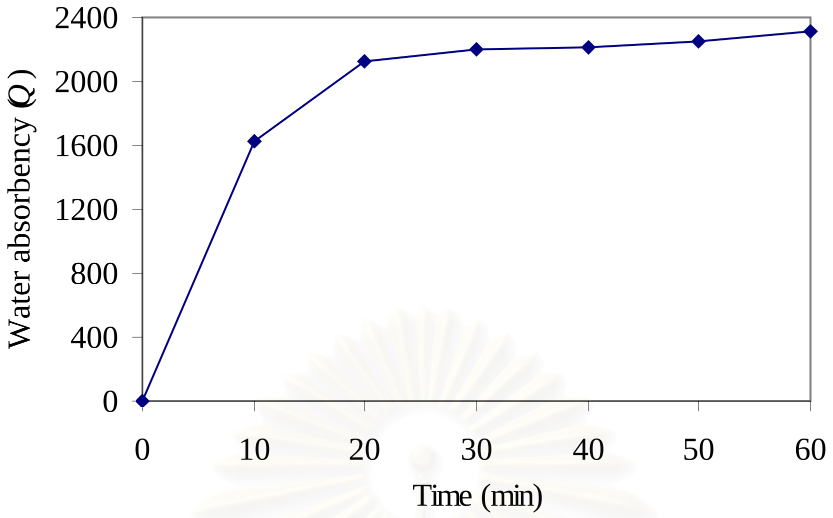


Figure 4.15 Swelling kinetics of the synthesized copolymer

The synthesized copolymer can absorb water up to 1,628±14 g per g of the dry copolymer within 10 min. The dependence of swelling time on equilibrium swelling arises because the mass of liquid absorbed during the swelling rate measurement depends on the equilibrium swelling capacity of the polymer. As the equilibrium swelling capacity increases, less polymer is used in the test so that each sample reaches the same relative swelling extent at the specific time.

4.11 Characterization

4.11.1 Fourier Transform Infrared Spectroscopy (FTIR)

The functional groups of the synthesized copolymer were investigated by Fourier Transform Infrared Spectroscopy (FTIR). The spectra are shown in Figures 4.19-4.25 and assignment in Table 4.13.

The result shows that FTIR spectra of the synthesized copolymers is resemble that of the poly(acrylic acid), polyacrylamide and poly(acrylic acid-*co*-acrylamide) as shown in Figures 4.16-4.18, respectively. The spectrum of the copolymer confirms the existence of the carboxylate and carboxamide functionalities

Table 4.13 Assignments for the FTIR spectrum of the synthesized copolymer

Wave number (cm^{-1})	**Assignment**
3,433	O-H stretching
3,225	N-H stretching
2,944	Aliphatic C-H stretching
1,722	C=O stretching of –COOH
1,677	C=O stretching of $–CONH_2$
1,575	C=O asymmetric stretching for the carboxylate ion
1,452	C-H asymmetric bending
1,403	C=O symmetric stretching for the carboxylate ion
1,321	C-N aliphatic stretching

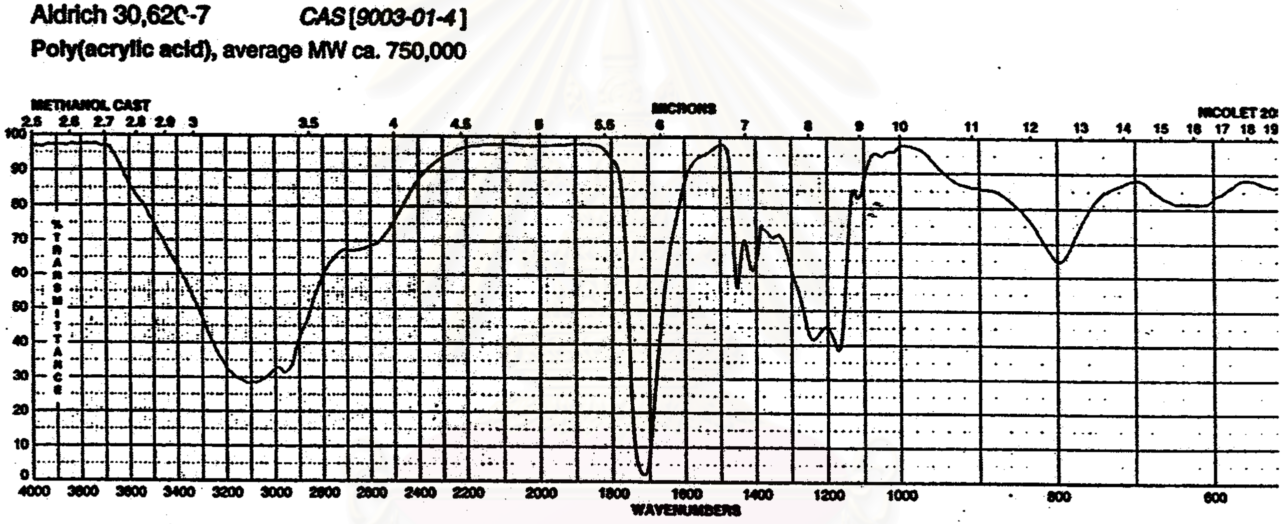


Figure 4.16 FTIR spectrum of poly(acrylic acid)

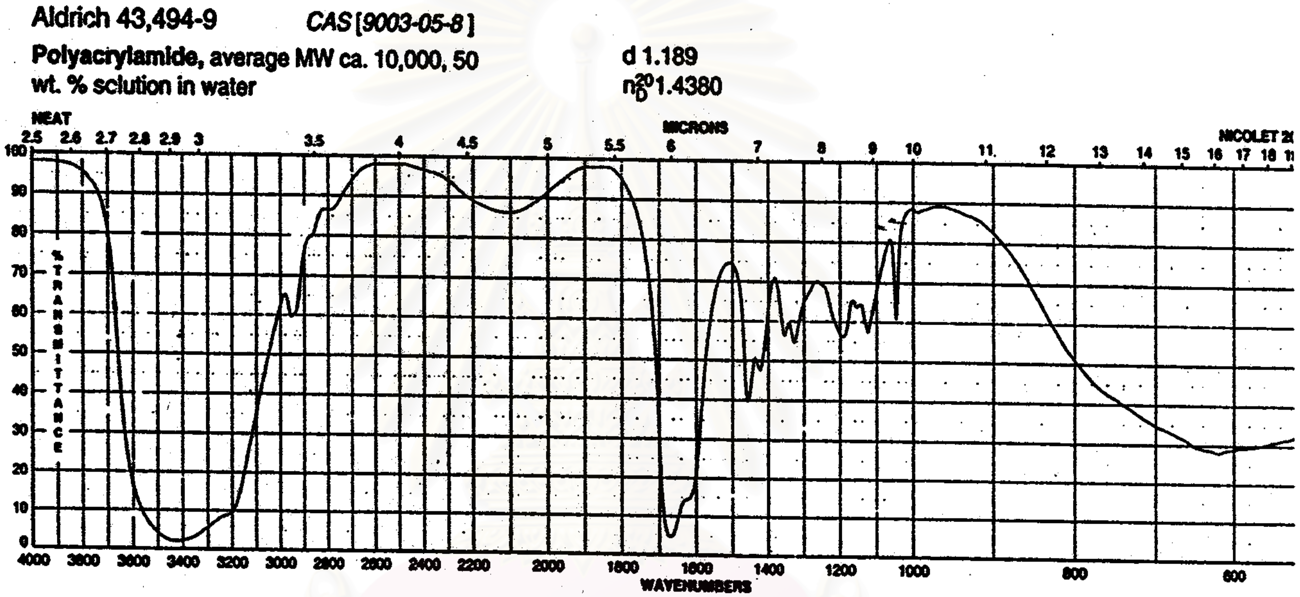


Figure 4.17 FTIR spectrum of polyacrylamide

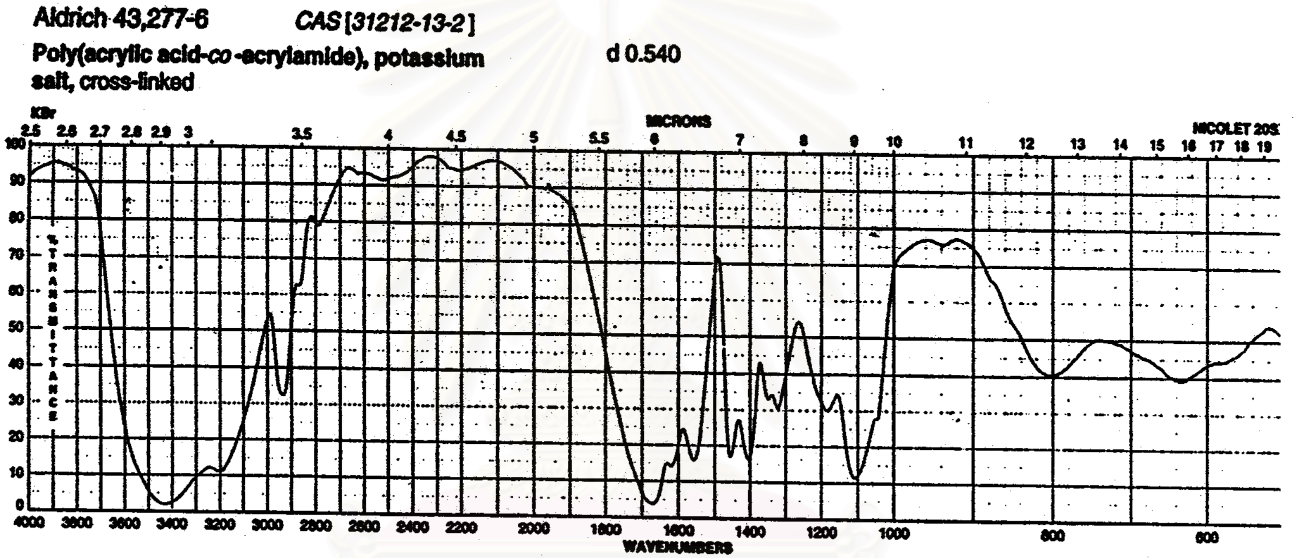


Figure 4.18 FTIR spectrum of poly(acrylic acid-*co*-acrylamide)

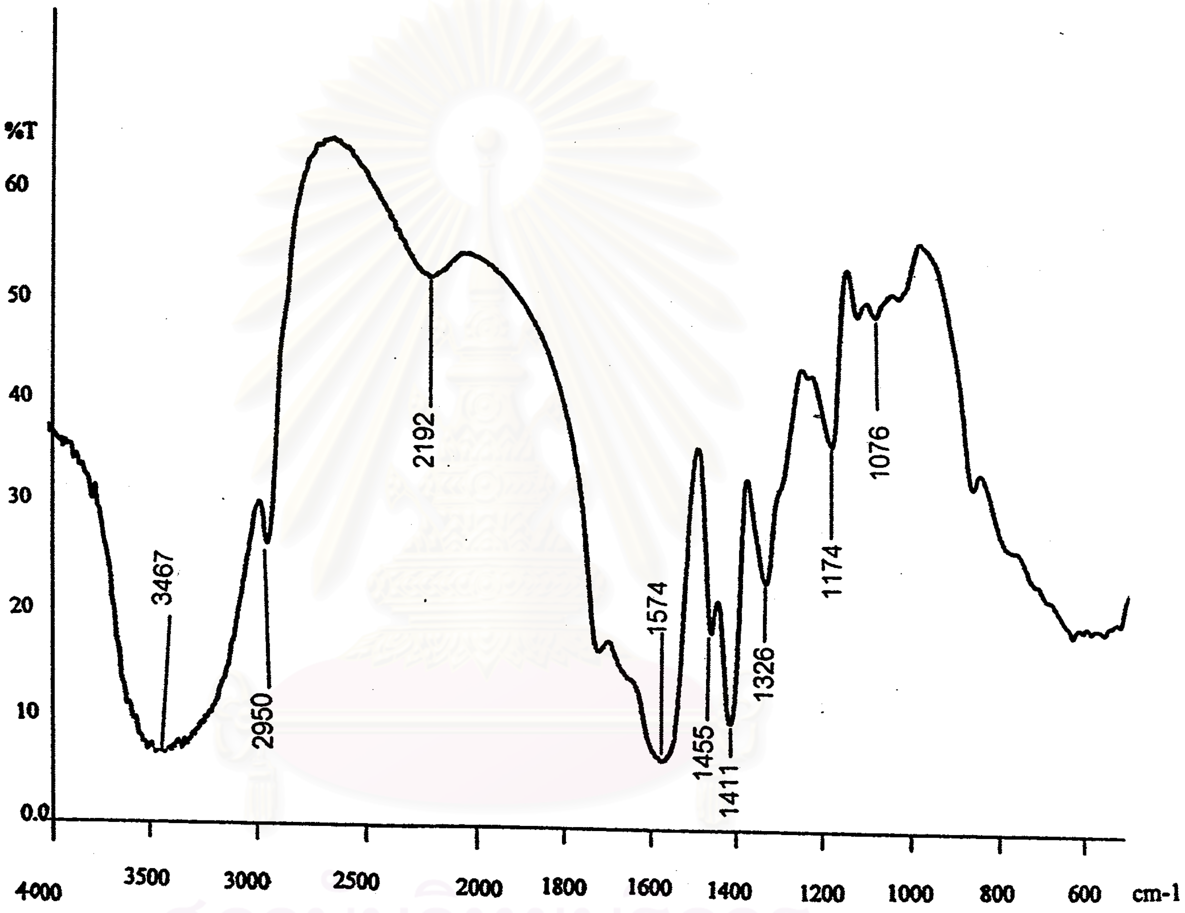


Figure 4.19 FTIR spectrum of poly(acrylic acid) synthesized with N-MBA crosslinking agent

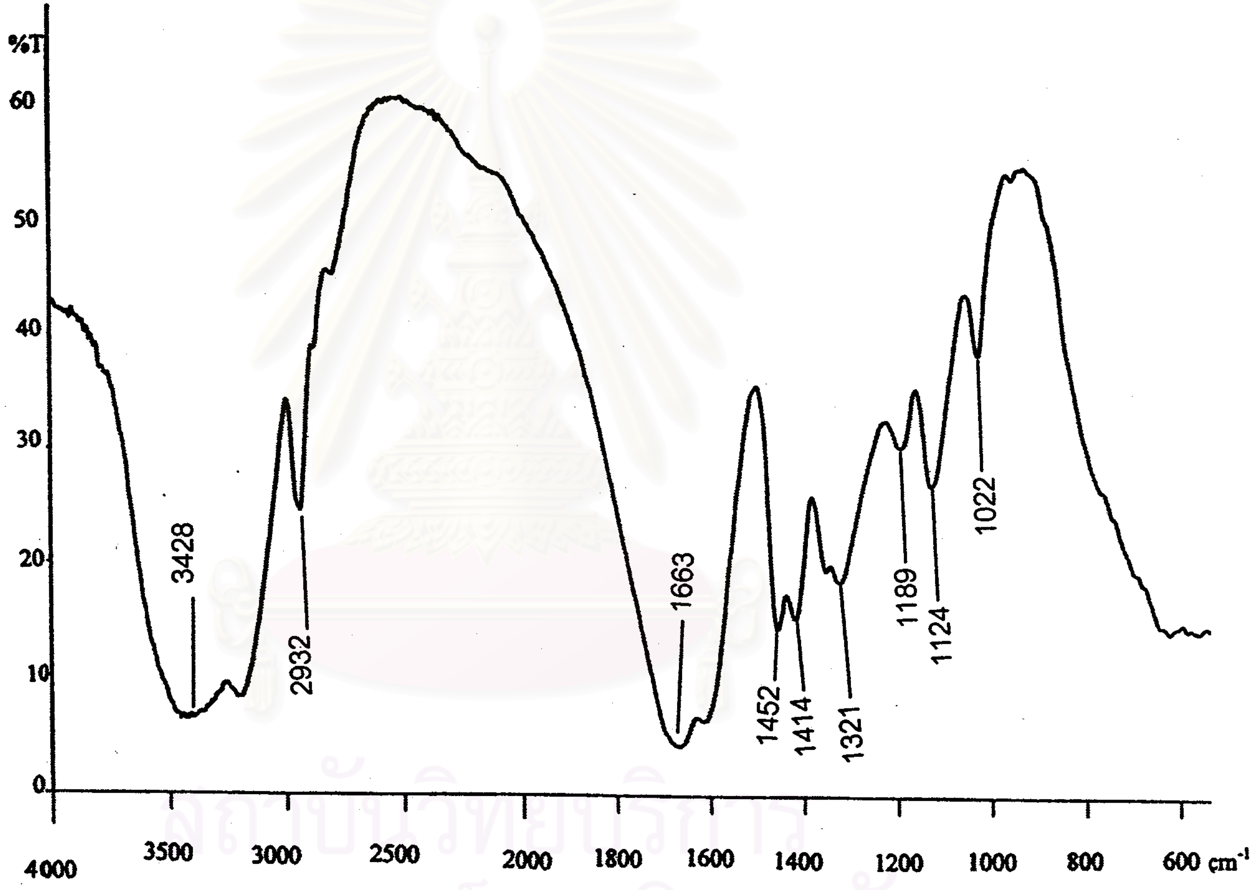


Figure 4.20 FTIR spectrum of polyacrylamide synthesized with N-MBA crosslinking agent

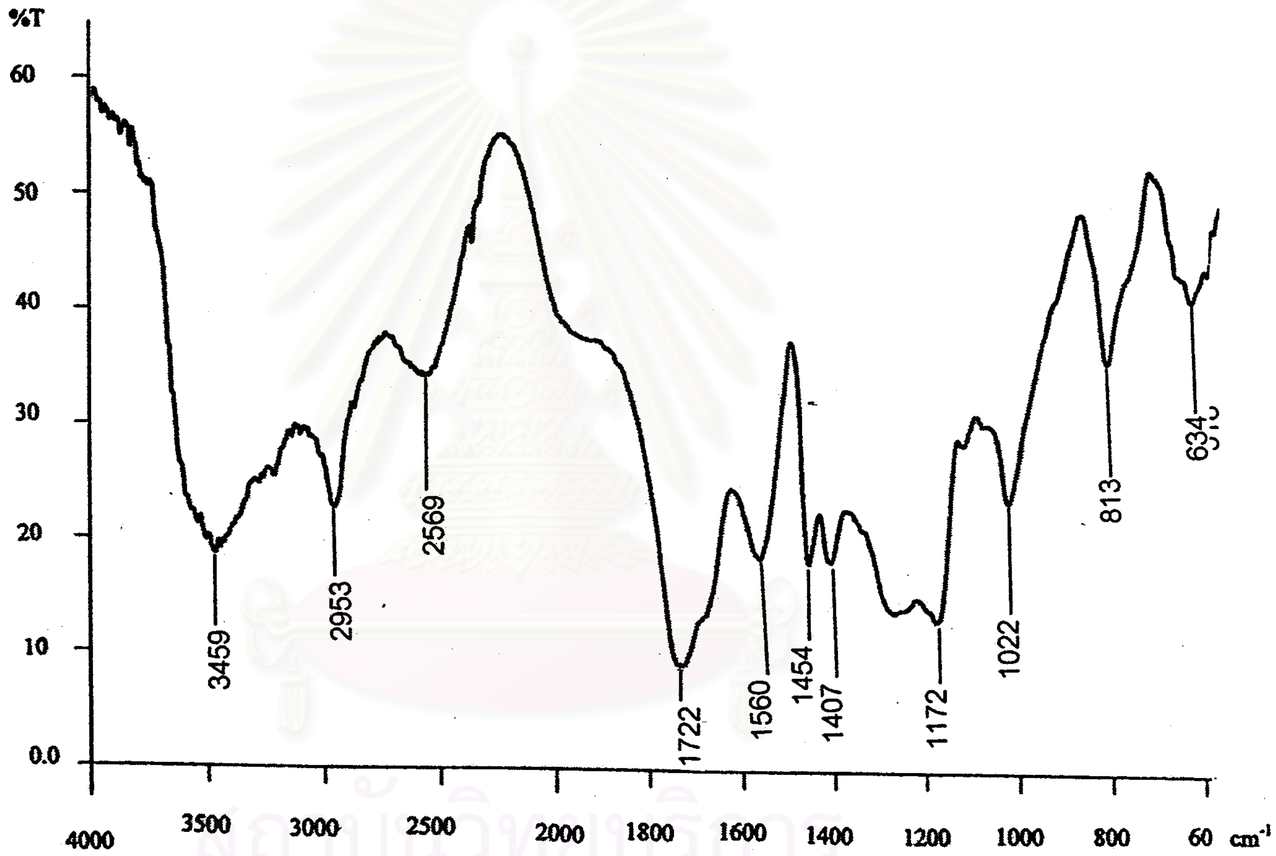


Figure 4.21 FTIR spectrum of poly(acrylic acid-*co*-acrylamide) synthesized with N-MBA crosslinking agen

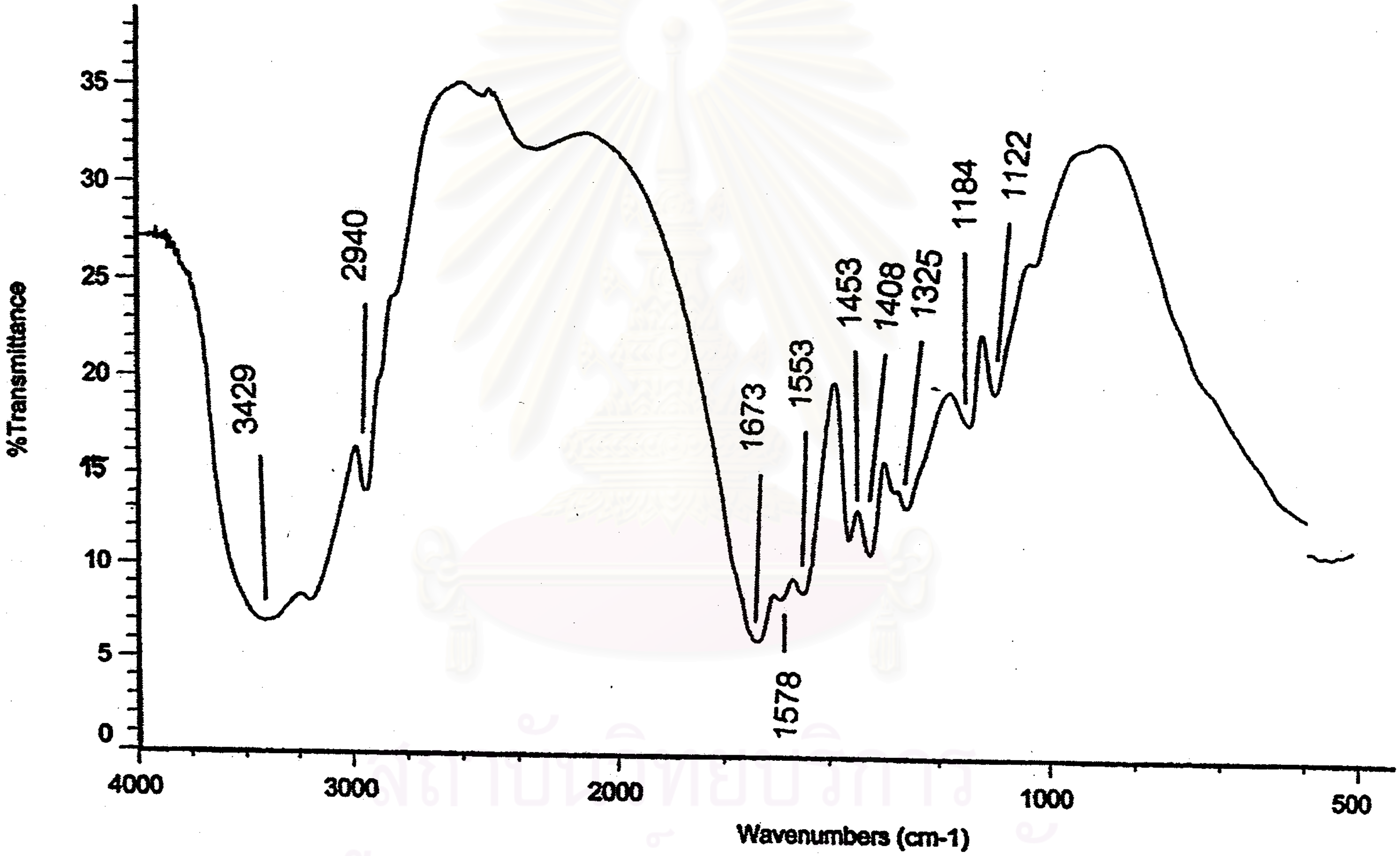


Figure 4.22 FTIR spectrum of poly(acrylate-*co*-acrylamide) synthesized with N-MBA crosslinking agent

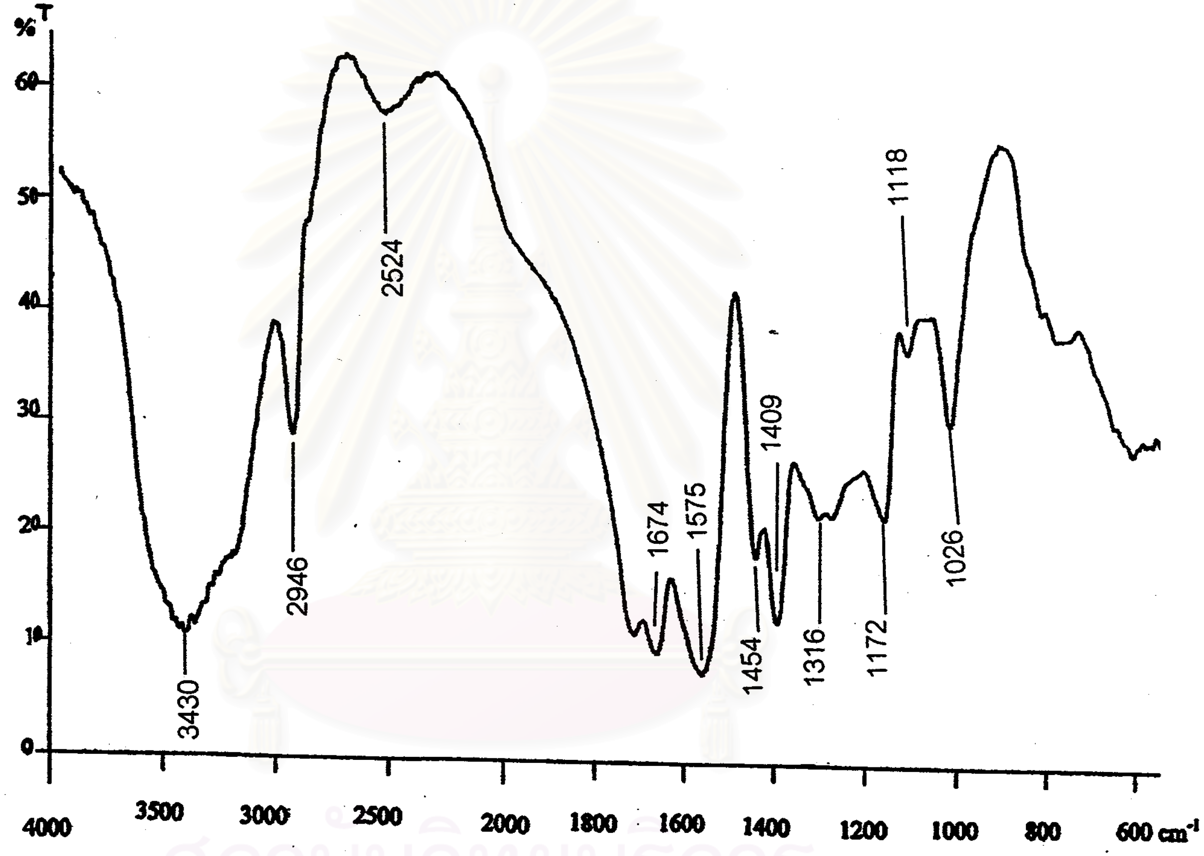


Figure 4.23 FTIR spectrum of poly(acrylic acid-*co*-acrylamide) synthesized with EGDMA crosslinkiagent

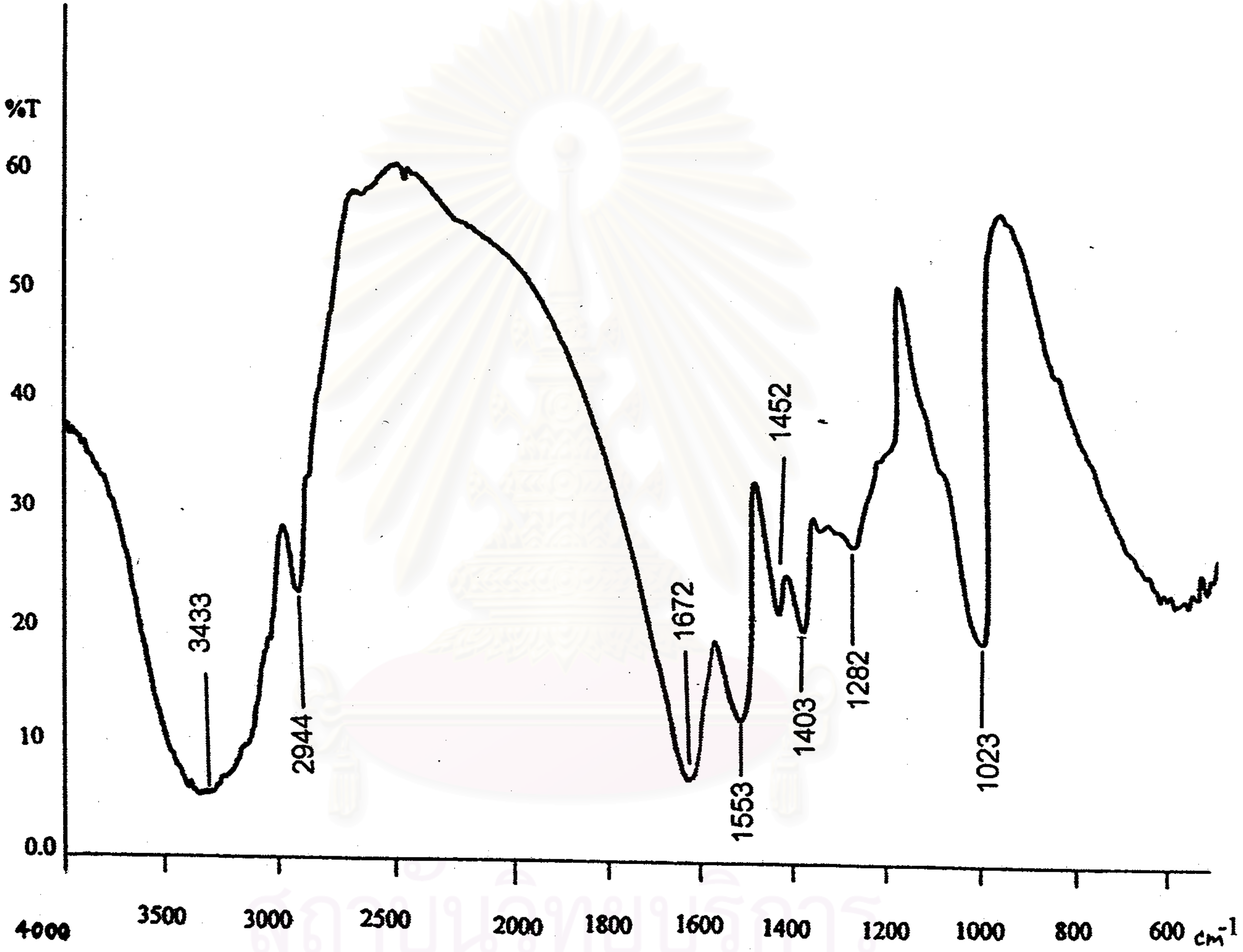


Figure 4.24 FTIR spectrum of poly(acrylic acid-*co*-acrylamide) synthesized with formaldehyde crossking agent

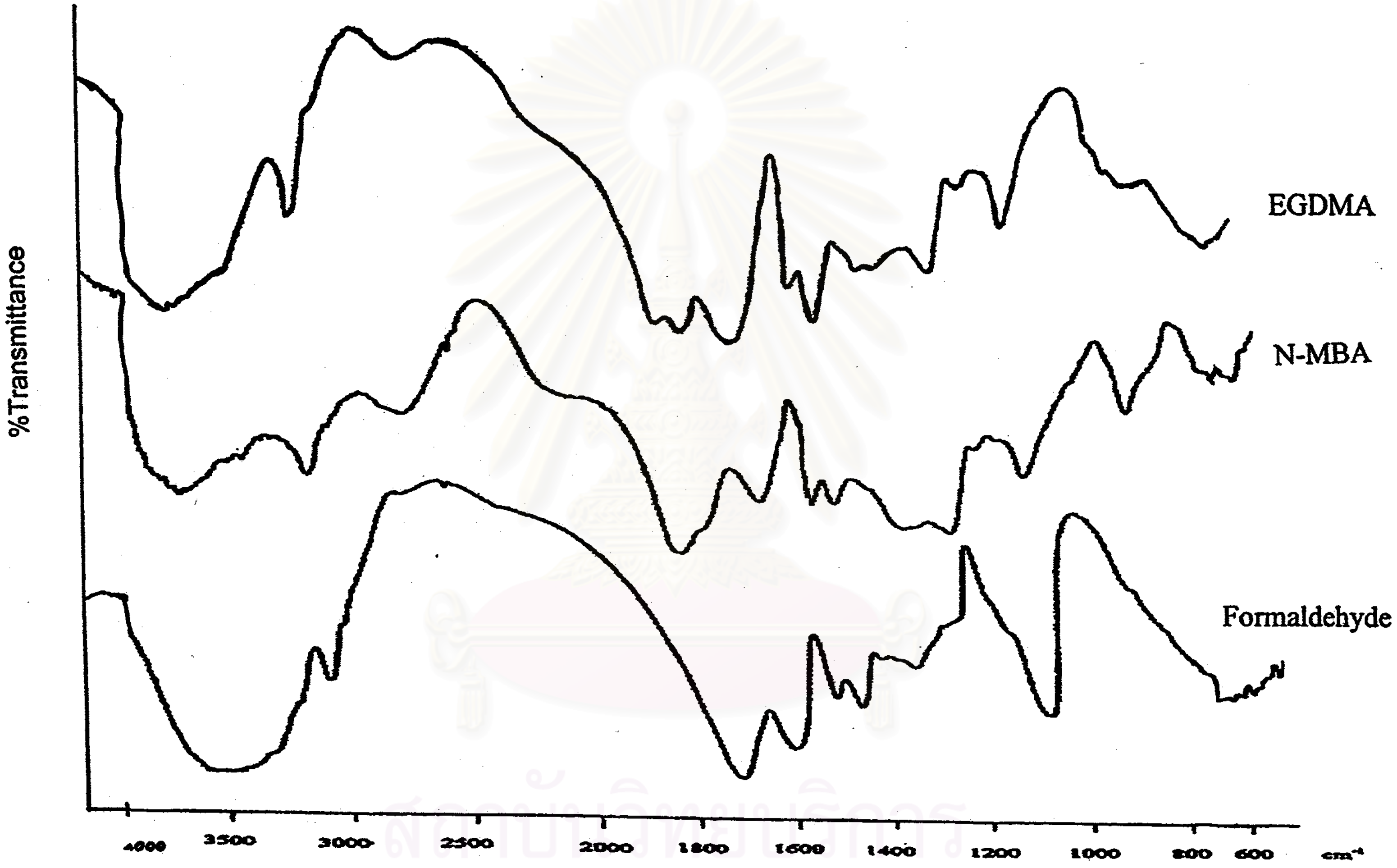


Figure 4.25 FTIR spectra of poly(acrylic acid-*co*-acrylamide) compared with various crosslinking ag

4.11.2 Surface morphology of the synthesized copolymers

The synthesized copolymers were investigated by SEM technique to observe the surface appearance. The electron micrographs of the crosslinked copolymers, with different types of the crosslinking agent are shown in Figures 4.26-2.28. Polymer particles from the foamed solution polymerization were irregular in shape. The SEM micrographs of the synthesized copolymer crosslinked with N-MBA gave good absorbency. The copolymers are microporous with a broad network and many flexibly cellular structure than other crosslinked copolymer. On the other hand, the SEM micrographs of the synthesized copolymers crosslinked with EGDMA have fine network structures and smooth. Moreover, the water absorbency of the synthesized copolymers crosslinked with EGDMA is higher than the synthesized copolymers crosslinked with formaldehyde. Hence the water absorbency not only depend on the porous of copolymers but also depend on the type of crosslinking agents.

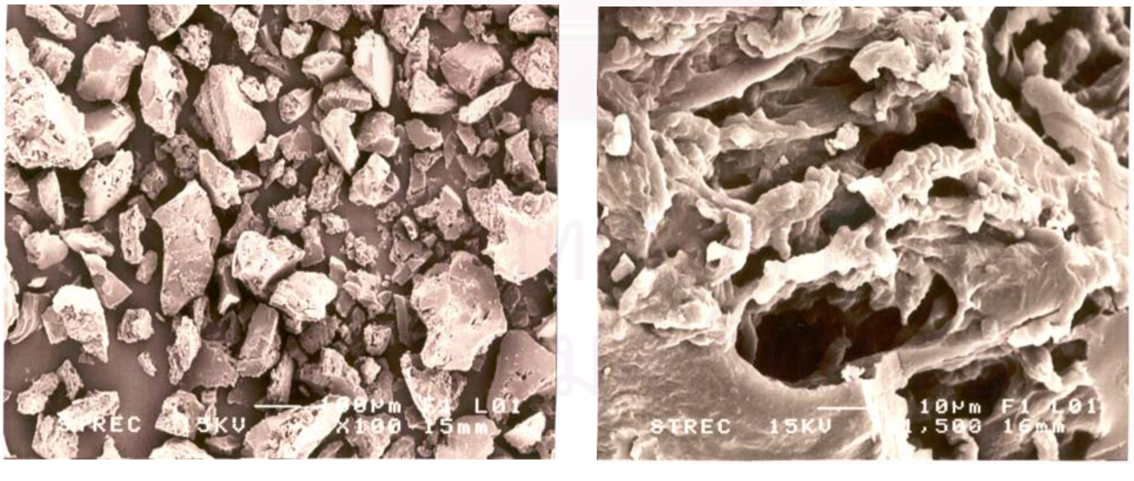


Figure 4.26 SEM micrograph of poly(acrylic acid-*co*-acrylamide) synthesized with N-MBA crosslinking agents (Water absorbency = 2,196±14 g g^{-1})

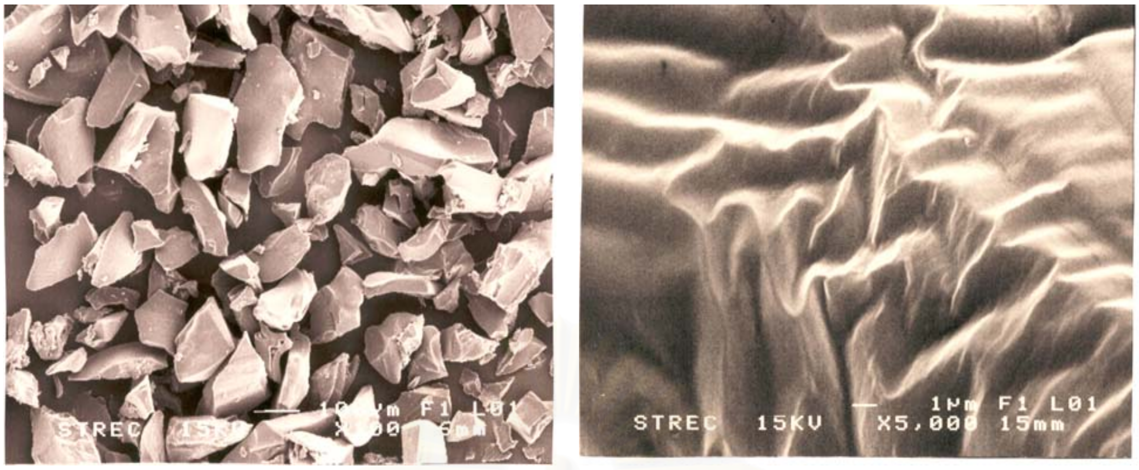


Figure 4.27 SEM micrograph of poly(acrylic acid-*co*-acrylamide) synthesized with EGDMA crosslinking agents (Water absorbency = 922±10 g g^{-1})

Figure 4.28 SEM micrograph of poly(acrylic acid-*co*-acrylamide) synthesized with formaldehyde crosslinking agents (Water absorbency = 238±12 g g^{-1})

The SEM micrograph of the uncrosslinked copolymer is shown in Figure 4.29. Polymer particles of uncrosslinked copolymer has same irregular in shape as crosslinked copolymer but its surface has pore which not same the crosslinked copolymer. So that water absorbency of uncrosslinked is less than crosslinked copolymer.

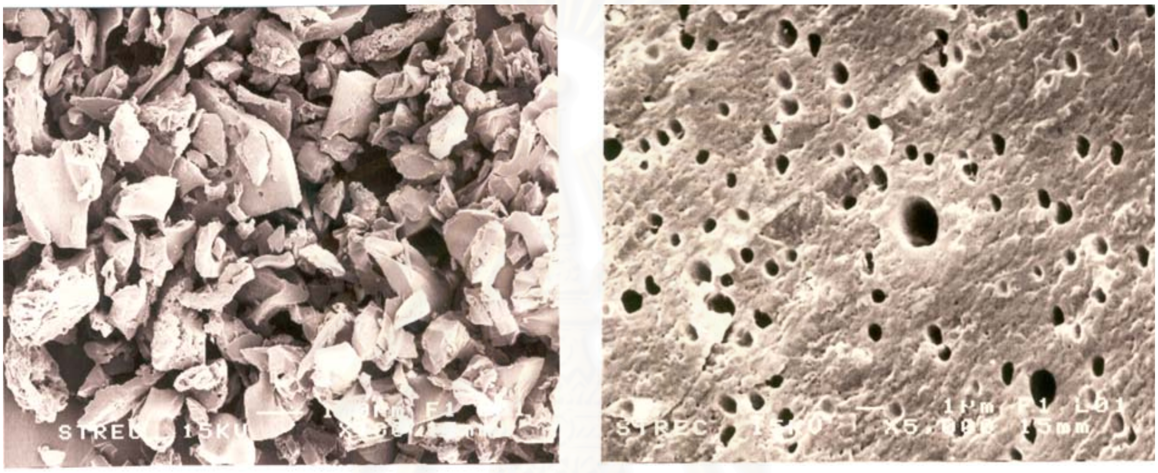


Figure 4.29 SEM micrograph of poly(acrylic acid-*co*-acrylamide) synthesized in absence of the crosslinking agents (Water absorbency = 27±5 g g^{-1})

4.12 Application of superabsorbent copolymer in wastewater treatment

4.12.1 The Structure of Complex Polymeric Flocculant (CPF)

The structure of CPF contains poly(acrylic acid-*co*-acrylamide) and an inorganic flocculant is shown in Figure 4.30. The FTIR spectra of aluminium sulfate and CPF are shown in Figures 4.31-4.32.

It can be seen from the IR spectra that the vibration absorption of the functional groups within the complex polymers differs from that of the pure polymer, that is the CPF was not a simple mixture of organic polymer and inorganic coagulant. The stretching vibration of C=O of carboxyl group in the polymer was extremely weak in the complex, but the asymmetric and symmetric vibrations of the O-C-O at 1,668 and 1,597 cm^{-1} appeared, which implied that the carboxyl group had been ionized to the carboxyl root ion. From the spectrum, it could also be found that the vibration of C=O, C-N in amide units shifted from 1,722 and 1,560 cm^{-1} to 1,668 and 1,465 cm^{-1}, respectively, which represented that the coordination between the amide group and the metal ion had already formed.

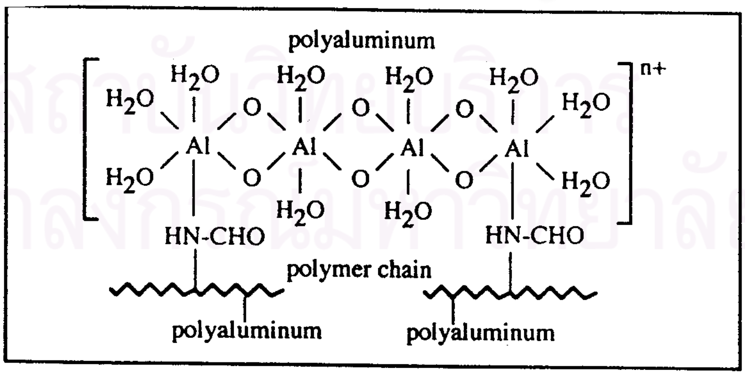


Figure 4.30 Proposed Structure of CPF

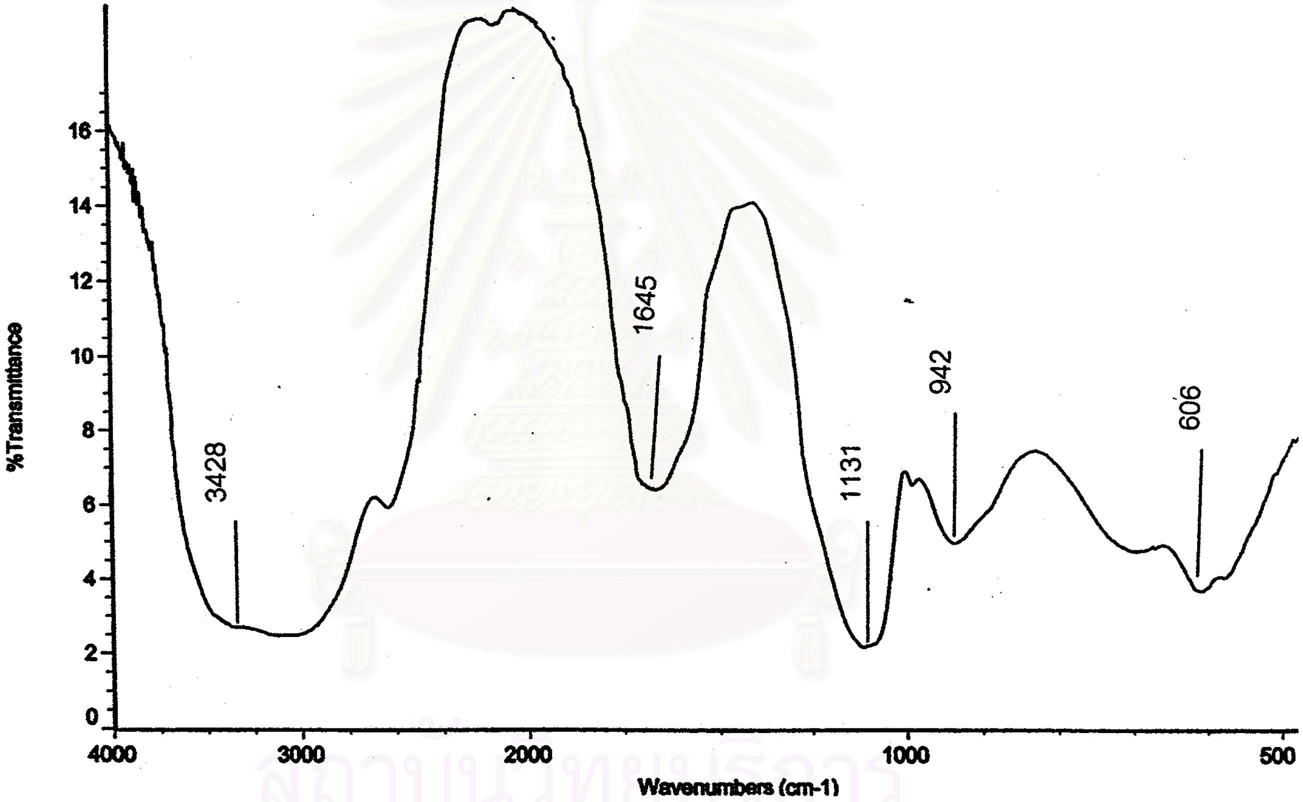


Figure 4.31 FTIR spectrum of aluminium sulfate

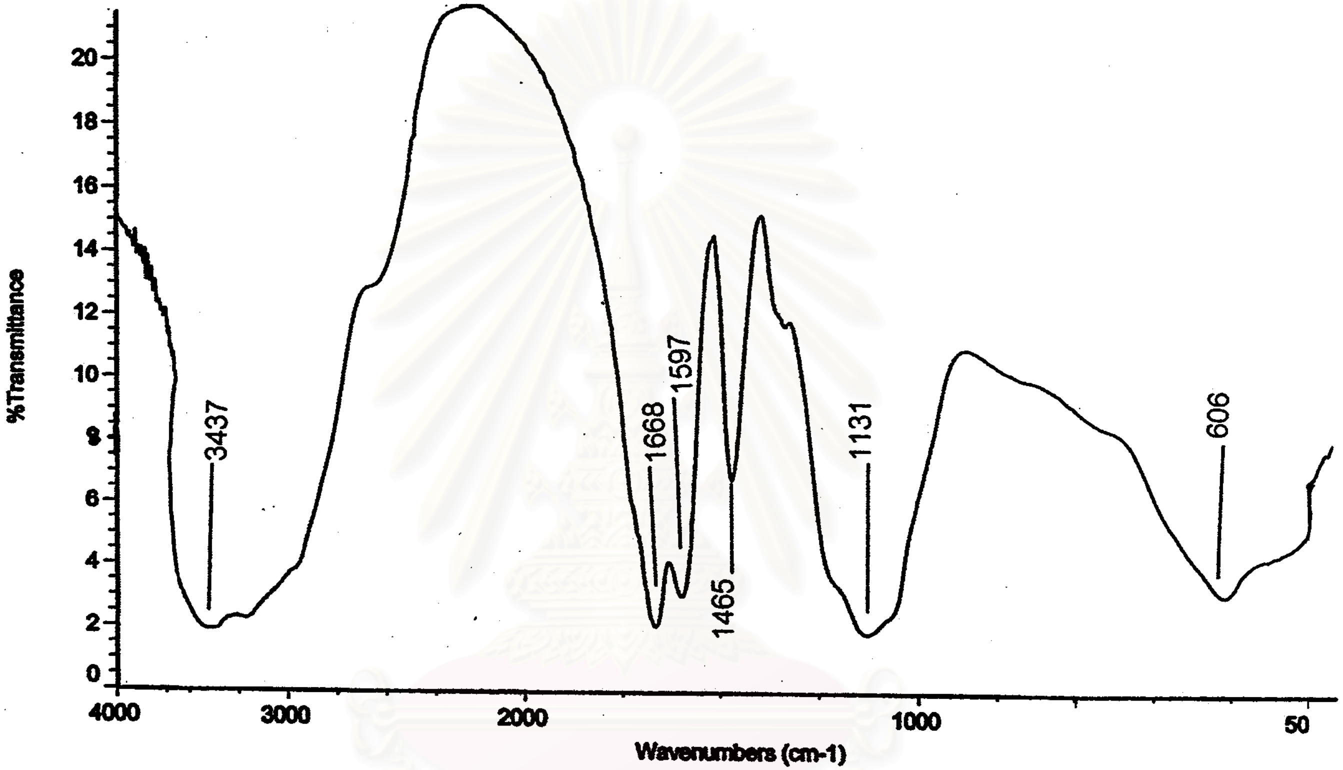


Figure 4.32 FTIR spectrum of CPF

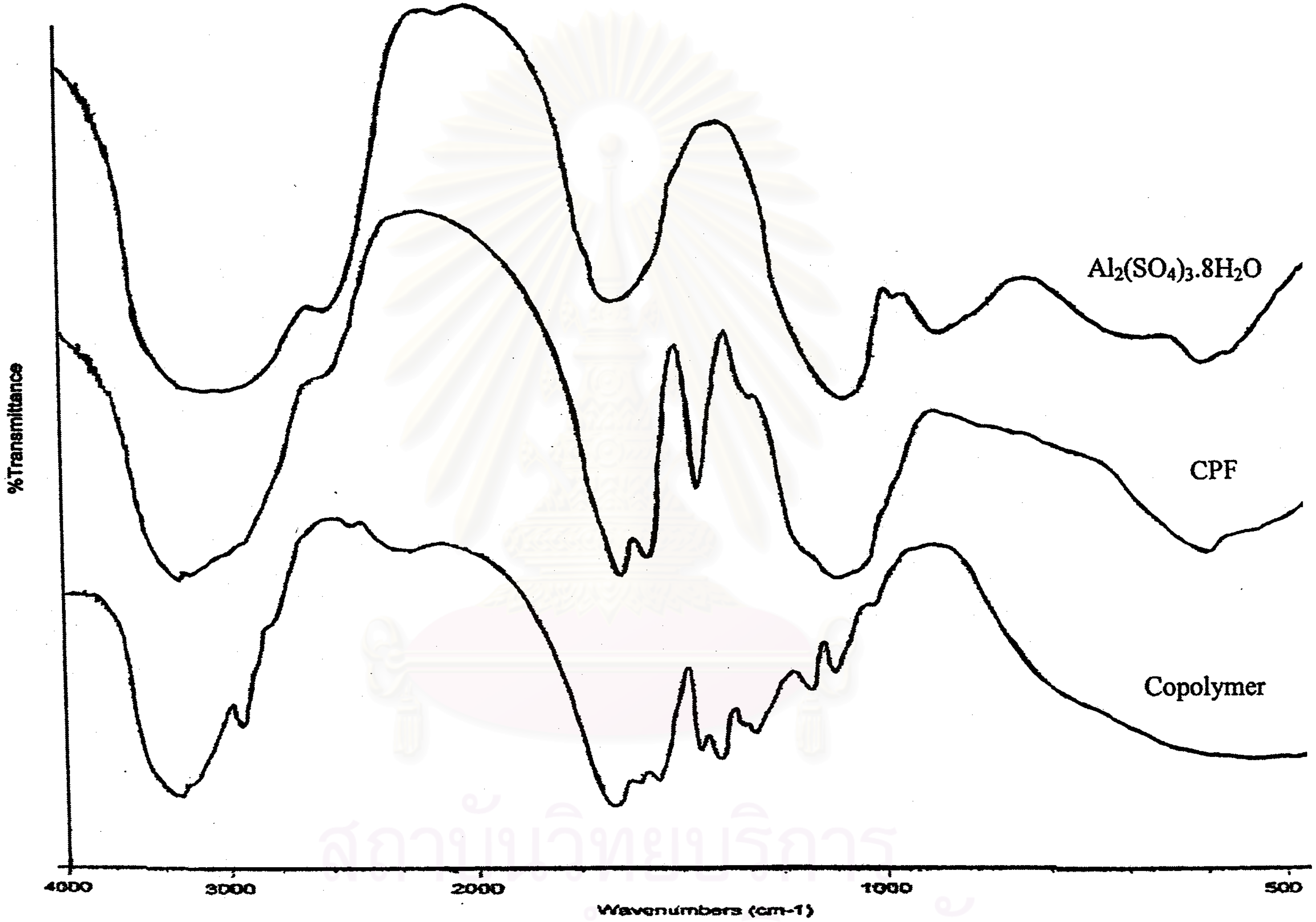


Figure 4.33 FTIR spectra of CPF compared with $Al_2(SO_4)_3.8H_2O$ and copolymer

The SEM micrograph of CPF was compared with pure aluminium sulfate as shown in Figures 4.34 -4.35. The surface of CPF is similar to that of the pure copolymer, whereas the particle sizes of CPF are smaller than those of pure copolymer, which may be caused by aluminium sulfate coordinate in the sturcture of CPF.

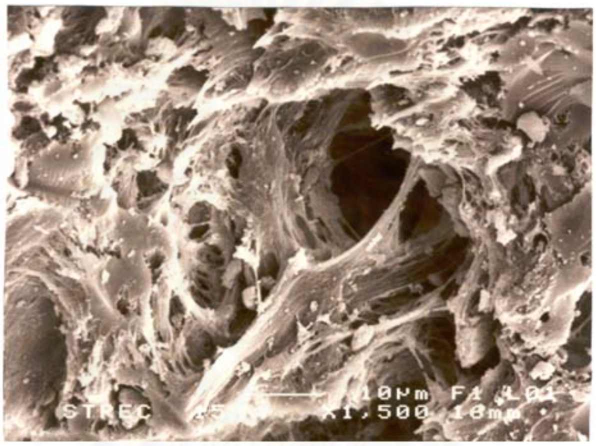


Figure 4.34 SEM micrograph of CPF

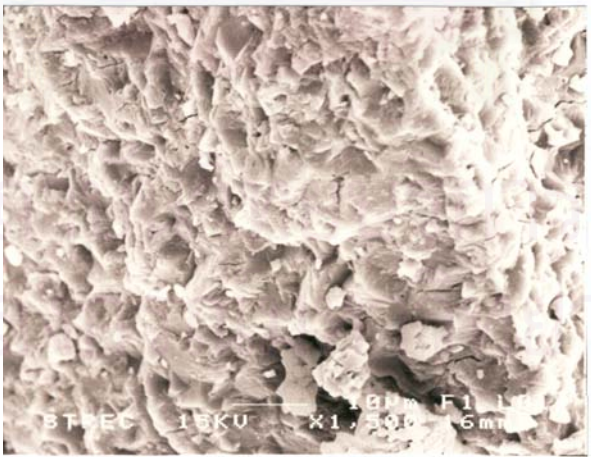


Figure 4.35 SEM micrograph of pure aluminium sulfate

4.12.2 Effect of Structure and Dosage on Coagulation

Under stirring, a certain amount of inorganic flocculants (aluminium sulfate) and CPF was added into the wastewater taken from the pool at Vithayapatthana Building in Chulalongkorn University (1 dm^3). The turbidity of the upper liquid in the container was measured at different times by a 2100P Turbidimeter. The effect of CPF dosage on turbidity of the water is shown in Table 4.14 and Figure 4.36. It can be seen that the complex polymeric flocculant was more efficient than aluminium sulfate alone, which was reflected in the low turbidity of the treated wastewater. Only the dosages from 0.03 to 0.1 g dm^{-3} (based on the wastewater amount) of the complex polymeric flocculant were often effective.

Table 4.14 Effect of the dose rate of CPF and aluminuim sulfate on turbidity of the wastewater

Dose of CPF (g dm^{-3})	**Turbidity (NTU)**	**Dose of Aluminium Sulfate (g dm^{-3})**	**Turbidity (NTU)**
0.0000	35.6	0.0000	35.6
0.0308	32.0	0.0616	33.2
0.0446	31.1	0.0892	32.7
0.0534	29.3	0.1068	31.5
0.0586	26.0	0.1172	30.8
0.0656	25.9	0.1312	30.2
0.0786	24.4	0.1572	28.4
0.0856	21.0	0.1712	26.8
0.0958	18.1	0.1916	23.6
0.1046	11.0	0.2092	21.8

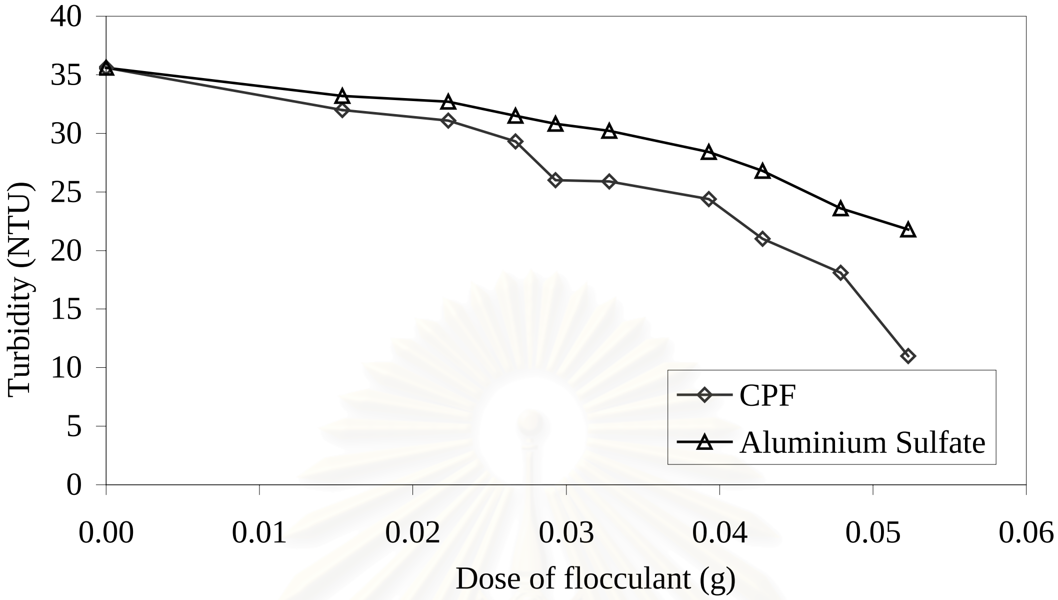


Figure 4.36 Effect of dosage of flocculant on Turbidity

The behavior of the complex flocculation can be concluded by the following characteristics. It is well known that colloidal particles can be stabilized by double electric-layer repulsion force (Figure 4.37). To induce the particles to aggregate, two distinct steps may occur: the repulsion forces-reducing step and the particles-contacting step. CPF contains an ion bond between inorganic and organic components that the polyions may be hydrolyzed in water solution at once and may remain oppositely charged along the polymer chain. When a certain type of CPF is added to wastewater in sufficient amounts, it can be dispersed rapidly because of the soluble polymer chain with same charge. Meanwhile, the inorganic parts hydrolyze so that precipitates take place momentarily. Colloids may serve as condensation nuclei for these precipitates or may become enmeshed as the precipitates settle. Removal of colloids in this manner is frequently referred to as sweep-floc coagulation. The charged precipitates can also compress the double layer of colloids and decrease their surface charge by the interaction of the opposite charge, adsorption, and charge neutralization. So an optimum pH may exist for each coagulant to reduce the colloids zeta potential. Neutralization of surface charge also depends on adsorption of colloids on precipitates, which will promote a precipitate formation of polymer bridges. This bridging action results in the formation of a floc particle having a favorable settling characteristic. Such a process is shown in Figure 4.38.

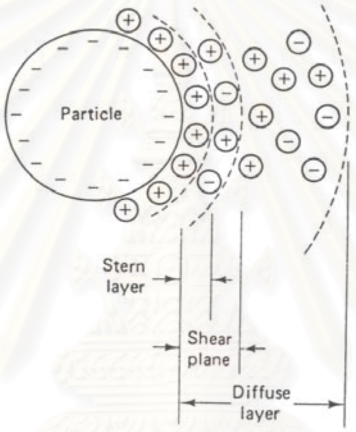


Figure 4.37 Double-layer charge distribution

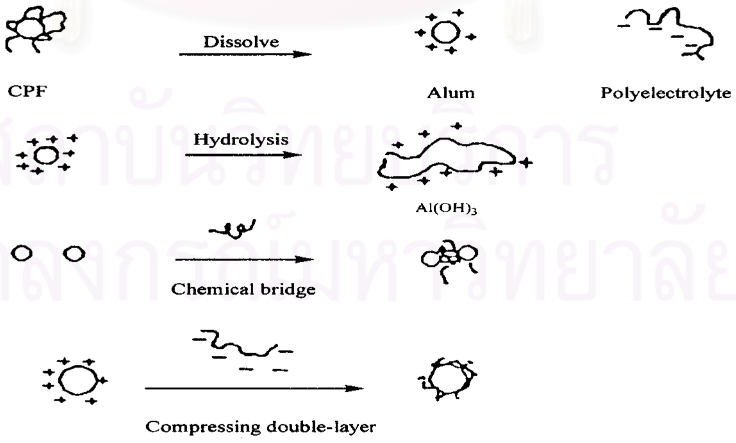


Figure 4.38 The mechanism of flocculation of CPF

The complex polymeric flocculant consists of inorganic and organic components that combine to gather because of the ionic bond of metal ions with the oppositely charged poly(acrylic acid) root, and the coordination bond of transition metal ion with the polymeric ligands. In an aqueous solution, the organic-component polymeric acid can be ionized to cause the polymer chain to extend, which can be assumed as a rod because of the electrical repulsion within the polymer chain. For the mechanical mixture, the organic-component polymeric acid cannot be ionized immediately from the polyacid so that most of the polymers remain a helical structure, which cannot offer a chemical bridge effect. Except for the complex flocculant, the polyacid was ionized in a bulk state, so that the polymeric flocculant over common polymeric flocculants included fast precipitation, easy dosage control, and more satisfactory performance.

CHAPTER 5

CONCLUSION AND SUGGESTION

5.1 Conclusion

The petroleum-based superabsorbent polymers have many types, which apperently progressed ahead the laboratory and usually disclosed in the patent literature are poly(acrylic acid) salts, polyacrylamide, polyether-based nonionic xerogellants, hydrolyzed polyacrylonitrile, poly(vinyl alcohol-*co*-sodium acrylate), and poly (isobutylene-*co*-disodiummaleate). In this research, the copolymers of acrylamide(AM) and acrylic acid were synthesized by foam solution polymerization and characterized the functional groups of the copolymer by FTIR. The spectrum reveals that the functional groups of the copolymer, which confirms the existence of the carboxylate and carboxamide functionalities, are similar to those of poly(acrylic acid-*co*-acrylamide) and poly(acrylamide). These synthesized copolymers are used for improved handling of fine coal, water absorption in underground wet areas, agriculture, nappies, feminine hygiene products, incontinence pads, mineral processing, oil service, printing inks, coating and specialties, paper and textiles, and pollution control. The present research can be concluded as follows:

1. The mole fraction of AM was varied from 0.1-0.9 and the concentration of crosslinking agent was fixed at 4.0×10^{-3} mol dm^{-3} with 40% degree neutralization of

acrylic acid. The AM at 0.1 mole fraction could produce a water insoluble copolymer having the water absorbency of 1,452±15 times its dry weight.

2. The water absorbency of the copolymer having N-MBA as a crosslinking agent was the highest when comparing to the other crosslinking agents of EGDMA or formaldehyde or those without a crosslinking agent. The concentration of N-MBA crosslinker at 4.0×10^{-3} mol dm^{-3} presented a optimum concentration.

3. The effect of polymerization temperature on water absorbency of the synthesized copolymer was less when the polymerization temperature was increased because of the molecular weight decreased and the relative amount of the polymer chain end increased.

4. The appropriate degree of neutralization of acrylic acid at 0% produced the best crosslinking copolymer having the water absorbency of 2,196±14 g g^{-1}.

5. The concentration of the redox initiator APS(2.30×10^{-3} mol dm^{-3}):TMEDA (1.0×10^{-2} mol dm^{-3}) gave the optimun result to achieve the highest water absorbency (1,117±14 g g^{-1}).

6. The crosslinked copolymers were measured for the water absorbency by swelling in distilled water and buffer solutions. The best water absorbing copolymer, which gave water absorbency of 2,196±14 times its dry weight in distilled water, was selected to test the effect of buffer solution upon absorbency of the synthesized copolymer. The liquid absorbency of the copolymer was found to increase with increasing pH of external solution until pH 5 and remained slightly changed afterwards

because of the nature of copolymer as an anionic type of polymer and the osmotic pressure balance between inside and outside of the copolymer gel.

7. The synthesized copolymers were measured for the absorbency by swelling in saline solutions for liquid absorbency. The liquid absorbency decreased rapidly as the salt concentration increased due to the increasing ionic strength of the solution, which affected the equilibrium osmotic pressure of the system. In case of the divalent cation, for example, Mg^{2+} and Ca^{2+} ions, the osmotic pressure equilibrium should reach earlier than in potassium and sodium aqueous solutions. The Mg^{2+} and Ca^{2+} ions may crosslink the gel by a salt formation with the carboxylic groups on adjacent chains or chain segments of the copolymer which lowered the liquid absorbency comparing with the that in potassium and sodium aqueous solutions.

8. The synthesized copolymers were measured for the absorbency by swelling in urea solutions for liquid absorbency. The concentration of urea at 0.1% W/V has the highest water absorbency (1,686±10) since the residual acid group in the synthesized copolymer can react with alkaline substances very effectively.

9. The synthesized copolymers were measured for the absorbency by swelling in various temperature of distilled water for water absorbency. The water absorption decreases steadily since the diffusion coefficient, D, related to the temperature and molecular weight of the polymer.

10. The kinetic absorption of the synthesized copolymer could absorp up to 1,628±14 times its dry weight in 10 min. The dependence of the swelling time on

equilibrium swelling arised because the mass of liquid absorbed during the swelling rate measurement depended on the equilibrium swelling capacity of the polymer.

11. The application of poly(acrylic acid-*co*-acrylamide) in purifying water by complexing with the inorganic flocculant of aluminium sulfate denoted as a CPF. The CPF is more effective than aluminium sulfate or the absorbing polymer alone because the CPF is consisted of both inorganic and organic components that combine to gether. In an aqueous solution, the organic component of the polymeric acid can ionize in the bulk state to cause the polymer chain to extend, so that the polymeric flocculant included fast precipitation, easy dosage control, and more satisfactory preformance.

12. The functional groups of poly(acrylic acid-*co*-acrylamide) were characterized by FTIR spectroscopy. The infrared absorption spectrum showed the significant absorption peaks at 3,437 cm^{-1} demonstrating the N-H stretching; 2,950 cm^{-1} demonstrating the aliphatic C-H stretching; 1,672 cm^{-1} demonstrating the C=O streching of the $–CONH_2$; 1,553 cm^{-1} demonstrating the C=O asymmetric stretching for the carboxylate ion; 1,452 cm^{-1} demonstrating the C-H asymmetric bending; 1,403 cm^{-1} demonstrating the C=O symmetric stretching for the carboxylate ion and 1,320 cm^{-1} demonstrating the C-N aliphatic stretching.

13. The CPF gave the FTIR spectrum, which contains the characteristic peaks at 3,467 cm^{-1} (broad and strong peaks) demonstrating the intramolecular H bond of polymeric moiety; 1,668 cm^{-1} demonstrating the C=O stretching of the primary $–CONH_2$; 1,597 cm^{-1} demonstrating the N-H bending; 1,465 cm^{-1} demonstrating the scissoring mode of $–CH_2–$; 1,131 cm^{-1} demonstrating the sulfate ion, and 606 cm^{-1} demonstrating the C-S stretching.

14. The surface morphology of the synthesized copolymer was studied by SEM. The SEM micrographs reveal that lumps are observed on the synthesized copolymer without the crosslinking agent, the synthesized copolymer with the crosslinking agent, and the CPF. The cellular structure with rough irregular surfaces and plenty of porous pattern than those was found in the crosslinked copolymers than without crosslinking agent, and the CPF surface is similar to that of crosslinked copolymers.

5.2 Suggestions for future work

The synthesis of superabsorbent polymers by solution polymerization would be further studied as follows:-

a) The influence of stirring intensity on the polymerization should be investigated.

b) Other kind of redox initiators should be used in place of APS:TMEDA.

c) The molecular weight and molecular weight distribution should be determined by the traditional size exclusion chromatography.

d) The absorption capacity under pressure and stability test should be investigated.

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APPENDICES

APPENDIX A

Determination of Crosslink Density

The effective crosslink density, ρ_x is defined as the concentration of elastically active chains (chains which are deformed by an applied stress) in the polymer network, and is usually reported on the basis of moles of chains per cubic centimeter of dry polymer.Network structure can also be described with a number of closely related terms. For example, when linear polymers are crosslinked, it is often desirable to express crosslinking in terms of the number average molecular weight of the polymer before crosslinking, $\overline{M_n}$, and the number average molecular weight between crosslinks, $\overline{M_c}$. These quantities can be related to the crosslink density as follows:

$$\rho_x = \left(1/\overline{\upsilon M_c}\right)\left(1 - 2\overline{M_c}/\overline{M_n}\right) \qquad \text{(A-1)}$$

Where $\overline{\upsilon}$ is the polymer specific volume. The factor $(1\text{-}2\overline{M_c} / \overline{M_n})$ is a correction for network imperfections such as dangling ends. In the case of an ideal network, this factor reduces to one. This correction is difficult to apply to networks formed by copolymerization/crosslinking reactions since an appropriate value of $\overline{M_n}$ may be difficult to determine. In many cases, howerer, $\overline{M_n}$ is much greater than $\overline{M_c}$, and equation can be simplified to the following:

$$\rho_x = \frac{1}{\overline{\upsilon M_c}} = \frac{1}{V_m Z} \qquad \text{(A-2)}$$

Where Z is the degree of polymerization between crosslinks.

APPENDIX B

Preparation of Universal Buffer Solutions

Mixing the two solutions as below according to the instructions indicated in Table B-1 to prepare 1,000 cm^3 of a buffer solution of the disired pH.

Solution 1: Dissolve 12.37 g of anhydrous boric acid, H_3BO_3, and 10.51 g of citric acid, $H_3C_6H_5O_7.H_2O$, in distilled water and dilute to 1,000 cm^3 in a volumetric flask. This makes a 0.20 mol dm^{-3} boric acid and a 0.05 mol dm^{-3} citric acid solution.

Solution 2: Dissolve 38.01 g of $Na_3PO_4.12H_2O$ in distilled water and dilute to 1,000 cm^3 in a volumetric flask. This makes a 0.10 mol dm^{-3} tertiary sodium phosphate solution.

Table B-1 Preparation of universal buffer solutions

Desired pH	Solution 1, cm^3	Solution 2, cm^3	Ionic Strength, mol-ion dm^{-3}
2	97.5	2.5	$2.51x10^{-3}$
3	88	12	$6.06x10^{-3}$
4	77.5	22.5	$9.61x10^{-3}$
5	67	33	$1.34x10^{-2}$
6	59	41	$1.60x10^{-2}$
7	49.5	50.5	$1.90x10^{-2}$
8	42.5	57.5	$2.12x10^{-2}$
9	34.5	65.5	$2.36x10^{-2}$
10	27	73	$2.58x10^{-2}$
11	22	78	$2.72x10^{-2}$
12	8.5	91.5	$3.10x10^{-2}$

VITA

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