

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

- 1) Acrylamide, AM (99% pure) from Siam Resin & Chemical Co., Ltd.
 C_3H_5NO , clear, colorless solid, m.p. $84.5^\circ C$, b.p. $87^\circ C$ (2 mmHg)
 $M = 71.08 \text{ g mol}^{-1}$
- 2) Crotonic acid, CA analytical grade from Fluka (Buchs, Switzerland)
 $C_4H_6O_2$, clear, colorless solid, $M = 86.09 \text{ g mol}^{-1}$
- 3) Ammonium persulfate, analytical grade from Merk (Hohenbrunn, Germany)
 $(NH_4)_2S_2O_8$, solid, $M = 228.2 \text{ g mol}^{-1}$
- 4) *N,N'*-Methylenebisacrylamide, (N-MBA) analytical grade from Fluka (Buchs, Switzerland)
 $C_7H_{10}N_2O_2$, solid, $M = 154.17 \text{ g mol}^{-1}$
- 5) *N,N,N',N'*-tetramethylenediamine, analytical grade from Sigma-Aldrich (St. Louis, U.S.A.)
 $(CH_3)_2NCH_2CH_2N(CH_3)_2$, liquid, $M = 116.21 \text{ g mol}^{-1}$, $D = 0.775 \text{ g cm}^{-3}$

- 6) Methyl alcohol, BDH (Bangkok, Thailand)
Commercial grade was purified by fraction distillation at an atmospheric pressure.
 CH_3OH , liquid, b.p. $64\text{-}65^\circ\text{C}$, $M = 32.04 \text{ g mol}^{-1}$, $D = 0.791 \text{ g cm}^{-3}$
- 7) LF[®]127, analytical grade from BASF (Ludwigshafen, Germany)
white solid, $M = 9,9840\text{-}14,600 \text{ g mol}^{-1}$
- 8) Sodium hydrogen carbonate, analytical grade from Fluka (Buchs, Switzerland)
 NaHCO_3 , solid, $M = 84.01 \text{ g mol}^{-1}$
- 9) Potassium chloride, analytical grade from Fluka (Buchs, Switzerland)
 KCl , solid, $M = 74.56 \text{ g mol}^{-1}$
- 10) n-Heptane, analytical grade from J.T.Baker (New Jersey, USA)
 C_7H_{16} , colorless liquid, b.p. 96.0°C , $D = 0.684 \text{ g/cm}^3$
- 11) 2-Amino-6-methoxybenzothiazole-2-(*N*-ethylanilino)ethanol, (Basic blue 41) from Dystar Textilfarben Co., Ltd.
light blue powder, $M = 310 \text{ g mol}^{-1}$

3.2 Glassware

- a) Four-necked round bottomed flask, 500-cm³
- b) Spiral condenser
- c) Thermometer
- d) Volumetric flask
- e) Other general laboratory glassware

3.3 Equipment

- a) Flow meter : Cole Parmer, Illinois, USA
- b) Stirring type : Semicircular Teflon Paddle
- c) Water Bath : Mammert W 350, Swabach
Germany
- d) Oven : D7200, Tuttlingen, Germany
- e) Scanning Electron Microscope (SEM) : Jeol JSM-T 220, Tohoku, Japan
- f) Fourier Transform Infrared Spectrometer (FTIR) : Nicolet Impact 410, Madison,
USA
- g) Potentiostat : PGSTATO Autolab, Utrecht,
Netherlands
- h) UV-vis spectrophotometer : Specord S100, Darmstadt
Germany
- i) pH meter : Scoth CG 842, Mainz, Germany

j) Analytical Balance : Mettler AE 260, Greifensee
Switzerland

3.4 Procedures

3.4.1 The Synthesis of Poly[Acrylamide-co-(Crotonic acid)]

Copolymerization : A mixture of 100-cm³ aqueous solution containing acrylamide (AAm), crotonic acid (CA) monomer, crosslinker (N-MBA), initiator (ammonium persulfate, APS) was placed in a 500-cm³ four-necked round bottomed flask. This reaction flask equipped with a mechanical stirrer set at 250 rpm, a condenser, and an inlet tube for nitrogen gas, was immersed in a set temperature water bath (50°C). The ingredients were stirred gently by a small-bladed propeller for 5 minutes. Then 2 g of the foaming agent (sodium bicarbonate powder), stabilizer (Lutrol[®] F 127 of 0.05% w v⁻¹), and 0.2 cm³ of co-initiator (TEMED) were added sequentially. Foam formation and solution polymerization took place and was continued for 30 minutes. The resulting polymer was dewatered with methanol as a non-solvent, cut into small pieces, dried at 50°C for 24 hours in a vacuum oven to a constant weight and then milled. The basic reaction conditions set for preparing the superabsorbent polymer of poly[acrylamide-co-(crotonic acid)] are shown in Table 3.1.

Table 3.1 Conditions used in the polymerization reaction of poly(AAm/CA)

Ingredients	Amount
Distilled water (g)	100
Monomer (AAm:CA) ratios (% mol)	100:0, 98:2, 96:4, 94:6, 92:8, 90/10, 85/15, 80/20, and 70/30
Sodium bicarbonate (g)	2
Lutrol F [®] 127 (g)	0.5
<i>N,N'</i> -Methylenebisacrylamide, N-MBA (% wt)*	0.5, 1.0, 1.5, and 2.0
Ammonium persulfate, APS (% wt)*	0.5, 1.0, 1.5, and 2.0
TEMED (% wt)*	2
Reaction temperature (°C)	40, 50, 60, and 70
Agitation rate (rpm)	150, 200, and 250 rpm
Reaction time (min)	30

* %wt based on the monomers.

3.4.1.1 The Effect of Crotonic Acid (Percent Mole)

The experimental procedure as described above and Table 3.1 was carried out, with varying the CA mole percents of 0 to 30. The concentrations of the crosslinking agent and initiator were fixed at 1.0 and 1.0% wt, respectively.

3.4.1.2 The Effect of APS Concentration

In this experiment, the monomer ratios were fixed at 90/10 and 98/2, the APS concentration (% wt., based on monomer content) was varied when the concentration of TEMED was kept at 2% wt. based on the monomers.

3.4.1.3 The Effect of *N,N'*-methylenebisacrylamide Concentration

The ratio of AAm/CA was fixed at 98:2 and 90:10. The content of crosslinking agent was varied from 0.5 to 2.0% wt., based on monomer content. The preparation of P(AAm-co-CA) was carried by following the basic procedure in 3.4.1 and other reaction condition in Table 3.1.

3.4.1.4 The Effect of the Polymerization Temperature

The solution of monomers of AAm and CA were prepared in two different compositions (AAm/CA mole percent ratios, 90/10, 98/2) The concentration of the crosslinking agent (N-MBA), initiator (APS), and co-initiator (TEMED) were fixed at, 1.0% wt. , 1.0% wt., and 2.0% wt. respectively. These solution were synthesised by varying reaction temperature at 40, 50 , 60, and 70°C.

3.4.1.5 The Effect of Agitation Rate

The same experimental procedure as described above was carried out except that the agitation rate for the reation mixture was varied at 150, 200, and 250 rpm.

3.4.2 Characterization of the Copolymer

The newly synthesized copolymers were characterized as follows:

3.4.2.1 Identification of the Functional Groups of the Copolymers

The functional groups of the copolymers were identified using Fourier-Transform Infrared Spectrometry (FTIR) (Nicolet Infrared Spectrometer, model Impact 410). The copolymer was ground with the dried KBr powder. The KBr disc was dried again, pressed and subjected to the FTIR spectrometer.

3.4.2.2 Morphology of the Copolymers

The surface morphology of the copolymers was investigated using scanning electron microscopy (SEM), model JSM-T 220A, Japan JEOL without cross-section. The thickness of gold coated on the copolymer was 25 nm, and SEM was operated with an accelerating voltage 15 to 20 kV.

3.4.2.3 Determination of Swelling Properties of the Copolymers

a) Water Absorbency

The swelling measurements of the copolymer were carried out in water at room temperature. Distilled water 200 g was added to 0.1 g of the dry copolymer in a 400-cm³ glass beaker with a glass cover. The polymer was allowed to swell for 24 hours. The fully swollen gel was then separated from unabsorbed water by filtering through a 100-mesh sieve aluminum screen for 2 hours in a room temperature and the

swollen copolymer gel was weighed. The water absorbency was calculated as shown below:

$$\text{Water absorbency}(Q) = (B - A)/A \quad (3.1)$$

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

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

b) Equilibrium Volume Swelling

To determine the equilibrium volume swelling, it is necessary to place a sample of known density into a chosen solvent (in this research, heptane was used) until mass measurements indicate the cessation of the uptake of liquid by the polymer. If no extractable is present, and all the imbibed solvent causes swelling, the volume swelling, S, is given by

$$S = \frac{(B-A)/d_s}{A/d_p} \quad (3.2)$$

where A and B are the same parameters defined earlier, and d_s and d_p are the water density and polymer density, respectively.

3.4.2.4 Determination of Crosslinking Density of Acrylamide-co-(Crotonic Acid) Copolymers

The crosslinking densities of copolymer were determined using the Flory-Rehner theory (14), for a network as follows:-

$$\bar{M}_c = -V_1 d_p \frac{v_s^{1/3} - v_s/2}{\ln(1-v_s) + v_s + \chi v_s^2} \quad (3.3)$$

where,

\bar{M}_c is the number-average molar mass of the chain between crosslinks

V_1 is the molar volume ($\text{cm}^3 \text{mole}^{-1}$)

d_p is the polymer density (g cm^{-3})

v_s is the volume fraction of the polymer in the swollen gel (cm^3)

χ is the Flory-Huggins interaction parameter between the solvent and the polymer.

The swelling ratio (S) is equal to $1/v_s$. The polymer-solvent interaction parameter was estimated using following formula (14):

$$\chi = 0.431 - 0.311d_p - 0.036d_p^2 \quad (3.4)$$

Here, the crosslink density, q , is defined as mole fraction of the crosslink units.

$$q = \frac{M_o}{M_c} \quad (3.5)$$

where M_o is the molecular weight of the polymer repeating unit. The other important parameter of crosslink density, v_e , as the number of elastically effective chains totally included in a network per unit volume. v_e is simply related to q (19).

$$v_e = \frac{d_p N_A}{M_c} \quad (3.6)$$

where, N_A is the Avogadro's number. Then,

$$v_e = \frac{d_p N_A q}{M_c} \quad (3.7)$$

Since the hydrogel is a copolymeric structure and contains a crosslinker (CL), the molar mass of the polymer repeat unit, M_o , can be calculated with the following equation (19):

$$M_o = \frac{(m_{AAm} \times M_{AAm}) + (m_{CA} \times M_{CA}) + (m_{CL} \times M_{CL})}{m_{AAm} + m_{CA} + m_{CL}} \quad (3.8)$$

where m_{AAm} , m_{CA} and m_{CL} are the mass in g of acrylamide, crotonic acid and the crosslinker, and M_{AAm} , M_{CA} and M_{CL} are the molar mass in g mol^{-1} of acrylamide, crotonic acid and the crosslinker, respectively.

3.4.2.5 Determination of Density of Acrylamide-co-(Crotonic acid)

Copolymers

The determination of density of the copolymer was based on the displacement technique by following the ASTM D792 test method. The principle of this measurement was described in Appendix A.

3.4.2.6 Investigation of Electrochemical Behavior of the Redox Reaction System

The monomer, co-monomer, initiator, and crosslinking agent were investigated for redox characteristic by cyclic voltammetry technique.

General Procedure for the Investigation of the Redox Reaction

Each ingredient was dissolved in 100 cm³ of 0.1 M KCl solution or otherwise in a sequential addition. The sample solution was examined for the redox reaction in the electrochemical cell using the glassy carbon electrode as the working electrode, Ag/AgCl (Sat. KCl) as the reference electrode and platinum wire as the auxiliary electrode. General instructions for cyclic voltammetry are as follows:

1. A clean electrochemical cell was equipped with a Ag/AgCl (Sat. KCl) reference electrode, a glassy carbon working electrode, and a platinum auxiliary electrode as shown in Figure 3.1.
2. The sample solution to be analyzed, was filled in the cell; making sure that all three electrodes are immersed in solution.
3. The scan rate was set at 50 mV s⁻¹. and swept potential from -2.0 to 2.0 V.
4. A voltammogram of sample solution was plotted as current versus voltage graph.

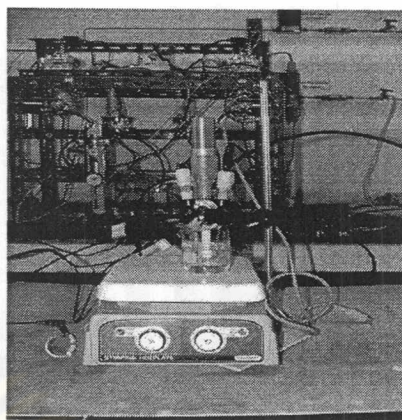
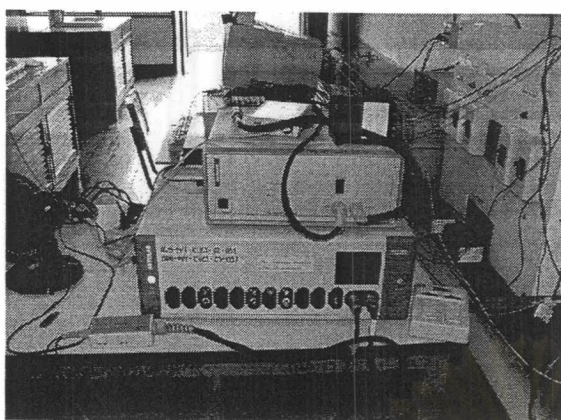
The concentration of each ingredient for the cyclic voltammetry measurement is shown in Table 3.2.

Table 3.2 The concentration of ingredient for cyclic voltammetry measurement

Ingredient	Concentration
Acrylamide	90% mol
Crotonic acid	10% mol
APS/TEMED	1% wt./ 2% wt.
N-MBA	1% wt.

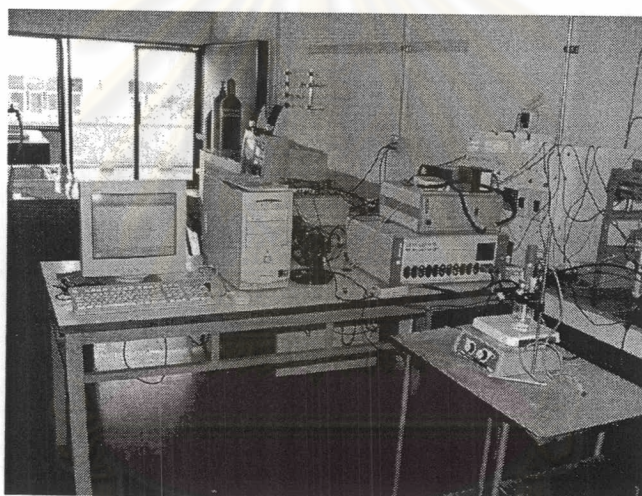


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a) Potentiostat, model Pastato Autolab

b) The reaction cell with three electrodes



c) Potentiostat connects with the reaction cell

Figure 3.1 Instrument for investigation of electrochemical behavior of the redox reaction system a) Potentiostat, model Pastato Autolab, b) The reaction cell with three electrodes, and c) Potentiostat connects with the reaction cell.

3.4.3 Kinetics of Absorption of the Synthesized Copolymer

3.4.3.1 In Distilled Water

Distilled water 200 g was added to 0.1 g of the dry copolymer in a 400-cm³ glass beaker with a glass cover. The polymer was allowed to swell first for 5 min. The fully swollen gel was then separated from the unabsorbed water by filtering through a 100-mesh sieve aluminum screen for 2 hr in room temperature and the swollen copolymer was then weighed. The similar experiments were carried out for each gel swelling time of 10, 20, 30, 40, 50, and 60 min, respectively.

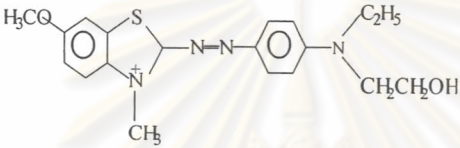
3.4.4 Application of the Superabsorbent Copolymer for Removing Dye Pollutants

3.4.4.1 Efficiency of Removing Dye Solution

Adsorption of cationic dyes in aqueous solution was investigated in a continuous adsorption equilibrium experiment. The effects of the initial concentration of dyes, pH of the medium and crotonic acid content on dye adsorption capacity were studied. Aqueous solutions containing different amounts of the dye (in a range of 5-50 mg dm⁻³) were treated with poly(AAm/CA) hydrogels at different pH (in a range of 2-7), adjusted with an acid of 0.1 M HCl and a base of 0.1 M NaOH. The dry poly(AAm/CA) of 0.1 g, was transferred into 200 cm³ of the aqueous dye solution and allowed to equilibrate for 24 hr at ambient temperature. These solutions were separated by decantation from the hydrogels. Spectrophotometric measurements were carried out at room temperature using a Specrod S100 model Ultraviolet-Visible

Spectrophotometer. The absorbencies of these solutions were read at the wavelengths given in Table 3.3. Distilled water was chosen as the reference. The equilibrium concentrations of the dye solutions were determined by means of the precalibrated scales.

Table 3.3 Some properties of the dyes

Name	Chemical Formula	Molar Mass	C.I. No.	λ_{\max} , nm
Basic blue 41		310	11105	610

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