

CHAPTER 3

EXPERIMENTAL

3.1 Chemicals, Equipment and Glassware

3.1.1 Chemicals

Acrylamide, AM, (99 % pure) and acrylic acid (99% pure) provided by Siam Resin & Chemical Co., Ltd. were used as received.

Methanol and normal hexane, commercial grade from Rungsap Chemical Co. Ltd., were purified by fractional distillation at an atmospheric pressure.

Other chemicals of analytical grade, as shown in Table 3.1, were used without further purification.

3.1.2 Equipment and glassware

Four-necked round bottle flask, spiral condenser, magnetic stirrer, heating mantle, mechanical stirrer, water bath circulator, reduced pressure filtering system, steel wire filtering, 100 mesh aluminium screen, analytical balance, desiccator, oven, and other general laboratory glassware and equipment.

TABLE 3.1

Chemicals

Chemicals	Source
Ammonium persulphate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$	Merck
Calcium chloride, (CaCl_2)	Merck
Magnesium chloride hexahydrate, $(\text{MgCl}_2 \cdot 6\text{H}_2\text{O})$	Merck
N,N'-Methylenebisacrylamide, (N,N'-MBA)	Fluka
Potassium chloride, (KCl)	Merck
Potassium hydroxide, (KOH)	Merck
Sodium chloride, (NaCl)	Merck
Sorbitan monopalmitate, (Span 40)	Kao
Sorbitan monostearate, (Span 60)	Nacalai Tesque
Sorbitan monooleate, (Span 80)	Kao
Boric acid	Merck
Citric acid	Merck
Tri-sodium phosphate	Merck
Potassium iodide	Merck
Potassium bromide	Merck

3.2 Apparatus

Fourier Transform Infrared Spectroscopy, Perkin Elmer 1760 X

Elemental Analyzer, PE 2400 series 2, Perkin Elmer

Scanning Electron Microscope, JEOL, JSM-T 220 A

Differential Scanning Calorimeter, Du Pont 2100

Viscometer, model RVT, Brookfield

3.3 The synthesis of potassium poly(acrylate-co-acrylamide)

3.3.1 Optimum total concentration and molar ratio of the monomer solution

A series of the copolymer superabsorbents were prepared by the following procedure:

Preparation of the dispersed phase: A predetermined amount of aqueous potassium hydroxide solution was carefully added to the acrylic acid which was thermally controlled not to be over heated than 40°C in order to obtain a 100% neutralized acrylic acid salt. Exact amounts of acrylamide, AM were dissolved in the above mentioned monomer solution in various molar ratios and total monomer concentrations at a fixed amount of a cross-linking agent, (N,N'-MBA). A specified amount of a thermal initiator, $((\text{NH}_4)_2\text{S}_2\text{O}_8)$, freshly dissolved in 2 cm^3 of distilled water, was added in the monomer solution, and stirred until a homogenous mixture was obtained.

Preparation of the continuous phase: Normal hexane was selected as an organic phase. The organic phase containing an appropriate proportion of water in an oil suspending agent, (Span 80: Sorbitan monooleate) was prepared in a 500 cm^3 round four-necked bottle flask, fitted with a mechanical stirrer, a nitrogen inlet, a spiral reflux condenser, a drip funnel and a thermometer, was heated to $60 \pm 1^{\circ}\text{C}$ by using a water bath, under stirring at 200 rpm while bubbling nitrogen gas over a 15-min period. To obtain the suitable reaction

condition, the set amounts of each chemical needed for different formulations were listed in Table 3.2.

Copolymerization: The mixed monomer solution was added dropwise at a predetermined flow rate ($10 \text{ cm}^3/\text{min}$ to obtain an isothermal polymerization), into the continuous phase while being agitated at 200 rpm. The reaction was allowed to proceed for 2 h to ensure a complete consumption of the monomers. The reaction was then stopped and water was removed from the copolymer by stirring the reaction mass in 300 cm^3 methanol in a 1000 cm^3 -beaker. The methanol solution was decanted and another 700 cm^3 of fresh methanol was again added to the reaction mass. The mixture was stirred overnight with a mechanical stirrer at same speed (200 rpm). The mixture was filtered and dried in an air oven 70°C for 6 h. The dried reaction mass was ground and was sievedly separated into portions.

3.3.2 Optimum concentration of the cross-linking agent

The same reaction procedure as described in Section 3.3.1 was carried out for various molar ratios of the monomers and the total concentration of monomers at the concentration of the cross-linker from 0-0.1 % weight of the water soluble monomer.

3.3.3 Optimum neutralization degree of acrylic acid

The same experimental procedure as described in Section 3.3.1 was carried out, except for that the molar ratio of the aqueous phase containing

AM:KA, and the suspending agent concentration were fixed at 60:40 molar, and 1.0% weight by volume of the oil phase, respectively, and the degree of neutralization of acrylic acid and cross-linking agent concentration were varied from 40-100%, and 0-0.075 % mole, respectively.

TABLE 3.2
Inverse suspension copolymerization recipe

Dispersion medium	n-hexane
Total monomer concentration (Molar)	5-10
Molar ratio of the monomers in aqueous solution, AM:KA	90:10-10:90
Volume ratio of mixed monomer solution : n-hexane	1:1.5
Suspending agent : Span 80 (% wt by volume based on n-hexane)	1
$(\text{NH}_4)_2\text{S}_2\text{O}_8$ (g/dm^3 of aqueous solution), Molar	1.4 (6.14×10^{-3})
$\text{N,N}'$ -MBA (cross-linking agent (% mole of monomer))	0.25 %
Polymerization temperature	60°C
Polymerization time	2 h
Agitation rate (rpm)	200

3.3.4 Optimum concentration of the initiator

The same procedure as described in Section 3.3.1 was carried out, except for that the molar ratio of aqueous phase of AA:KA, the cross-linking agent concentration, and the degree of neutralized AA were fixed at 60:40 molar, 0.025 % mole of monomer and 100% neutralized acrylic acid, respectively, and

the initiator, $((\text{NH}_4)_2\text{S}_2\text{O}_8)$ concentration was varied from 0.5-3.0 g/dm³ (2.19×10^{-3} to 1.32×10^{-2} M) of the aqueous phase.

3.3.5 Optimum concentration of the suspending agent

The same experimental procedure as described in Section 3.3.1 was carried out, except for that the molar ratio of aqueous phase containing AM:KA, the cross-linking agent concentration, and the degree of neutralization were fixed at 60:40 molar, 0.025 % mole of monomer, and 100% neutralized acrylic acid, respectively, and the suspending agent (Span 80) concentration was varied from 0.1-2% weight by the volume of the oil phase.

3.3.6 Type of the suspending agent

The same procedure as described in Section 3.3.1 was carried out, except for that the molar ratio of aqueous phase of AM:KA, the cross-linking agent concentration, the initiator concentration, and the degree of neutralized acrylic acid were fixed at 60:40 molar ratio, 0.025 % mole of monomer, 1.4 g/dm³ of aqueous phase and 100% neutralized acrylic acid, respectively, and the type of the suspending agent were Span 40, and Span 60.

3.4 Characterization of the copolymer

The synthesized copolymers were investigated for their obligated as below:

3.4.1 Identification of the functional groups of the copolymers

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

3.4.2 Determination of the thermal properties of the copolymers.

The copolymers were investigated with a Differential Scanning Colorimetry, Du Pont, model DSC 2100 for their thermal property. The measurements were carried out over a temperature range of 50 to 350 °C with a heating rate of 10 °C/min, under the N₂ flow rate of 10 cm³/min with a sensitivity of 100/Rg 500 μV. The weight of sample used was 15-25 mg.

3.4.3 Determination of surface morphology of the copolymers

The surface morphology of the copolymers were investigated by using a Scanning Electron Microscope (SEM), model JSM-T 220A 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.

3.4.4 Determination of copolymerization ratios of the initial monomer concentrations

The copolymerization ratios of initial monomers were determined by Elemental Analyzer, model PE 2400 series 2 of Perkin-Elmer, which measures the percentage ratio of C, H, and N. Detailed methods of calculation were described in Appendix A. The ratio of acrylamide and potassium acrylate was calculated by using the number of mole according to C, H, and N in the copolymer from the analysis results.

3.4.5 Determination of rheological properties of the copolymers

The copolymers, synthesized at various cross-linking agent concentrations were determined the viscoelastic properties by using a viscometer, Brookfield, model RVT, at 25^oC with spindle number 14 and speed 5 rpm. Theory and detailed method of calculation were described in Appendix B. The shear modulus of copolymers were calculated by using the viscosity of the swollen gel.

Sample preparation: 300 g of distilled water was added to 0.3 g of dry copolymer in a 600 cm³ glass beaker and it was allowed to stand for 30 min. The completely swollen copolymer was filtered through 100 mesh aluminium screen for 2 hours and the remaining swollen copolymer was measured the viscosity.

3.5 Water absorbency of the copolymers

3.5.1 In distilled water

150 g of distilled water was added to 0.1 g of the dry copolymer(A) in a 250 cm³ glass beaker and it was allowed to stand for 30 min. The completely swollen copolymer was filtered through 100 mesh aluminium screen for 3 hours and the remaining swollen copolymer was weighed(B). The water absorbency was calculated by equation shown below

$$\begin{aligned} \text{Water absorbency of copolymer (g of water /g of dry copolymer)} \\ = (B-A)/A \end{aligned} \quad (3.1)$$

3.5.2 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, potassium chloride, potassium iodide, potassium bromide, magnesium chloride, and calcium chloride solutions of 0.005, 0.05, 0.1, 0.3, 0.5, and 0.9 % wt/v were used instead of distilled water.[^]

3.5.3 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 mixing of 0.20 *M* boric acid, 0.05 *M* citric acid, and 0.10 *M* tri-sodium phosphate(0.10 *M* $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$).

3.6 Aqueous absorbing speed of the copolymer

The speed at which the copolymer absorbs aqueous fluid is an important property. It is characterized by a “vortex test”. This test was measured and reported in seconds by the procedure.

Fifty grams of physiological saline solution, 90% aqueous solution of sodium chloride, and a stirring rod were placed in a 100 cm³ beaker and the solution was stirred with a magnetic stirrer at a rate of 600 rpm. Into the beaker was charged 2.0 g of the water-absorbing resin which was later cause gellation by hygroscopic swelling. The gellation subdued the fluidity, precluding the agitation from inducing the swirl. The water-absorbing speed was expressed in terms of the time taken from the addition of water-absorbent resin sample until the cessation of swirl.