CHAPTER III

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 acetone, commercial grade from BDH, were purified by fractional distillation at atmospheric pressure.

Potassium acrylate, KA, was synthesized by neutralizing acrylic acid with potassium hydroxide in acetone in the presence of 4-methoxyphenol, a free radical inhibitor, as described by Variu, C., et al., and used without futher purification (26).

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

3.1.2 Equipment and Glassware

3-necked round bottom flask, magnetic stirrer, heating mantle, mechanical stirrer, water bath circulator, analytical balance, filtering system, desiccator, oven, and other general laboratory glassware and equipment.

3.2 Apparatus

Infrared spectrometer, Perkin-Elmer, model Perkin-Elmer 1430.
Bruker AC 200 MHz Fourier Tranform NMR Spectrometer.

Differential Scanning Calorimeter, Du Pont Instruments, model
DSC 910S, connected with Thermal Analyst 2000 microcomputer.
Scanning Electron Microscope, JEOL, JSM-T220A.

TABLE 3.1

Chemicals

Chemicals	Source
Ammonium persulfate ($(NH_4)_2S_2O_8$)	Merck
Isooctane	Carlo Erba
Magnesuim chloride hexahydrate ($MgCl_2.6H_2O$)	Merck
4-methoxyphenol	Fluka
N,N´-methylenebisacrylamide (N,N´-MBA)	Fluka
Potassium chloride (KCl)	Carlo Erba
Potassium hydroxide (KOH)	Merck
Sorbitane monosterate (Span 60)	Nacalai Tesque
N,N,N´,N´-tetramethylethylenediamine (TMEDA)	Nacalai Tesque

3.3 The Synthesis of Poly(acrylamide-*co*-potassium acrylate)

3.3.1 Optimum Concentration of the Monomer Solution

Polymerizations were carried out in a 250-ml 3-necked
round bottom reaction flask equipped with a reflux condenser, a
thermometer, a nitrogen-gas inlet and a top-supported mechanical
stirrer (Figure 3.1).

The basic recipe used for the inverse suspension
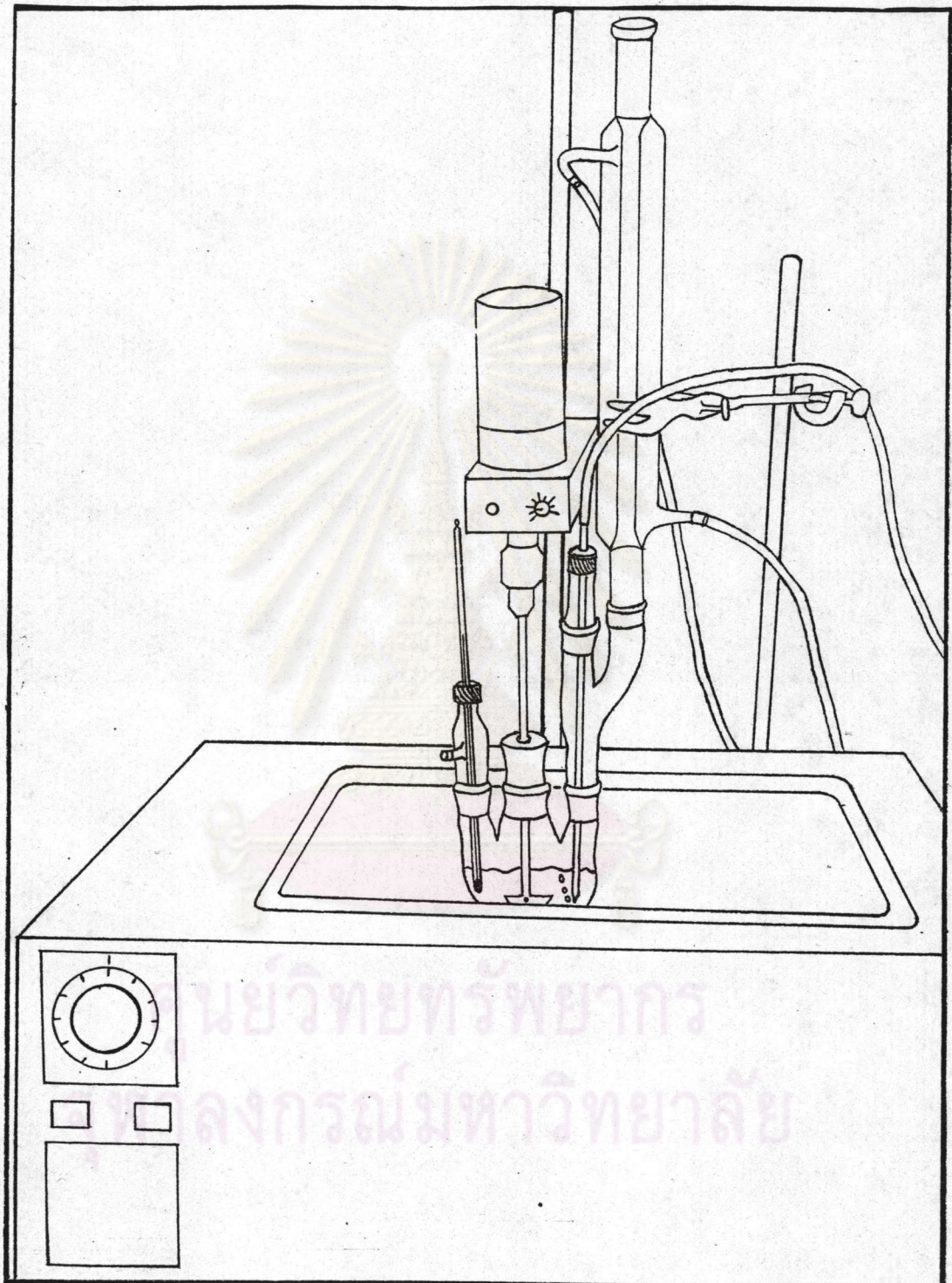copolymerization was shown in Table 3.2.

FIGURE 3.1 Inverse suspension polymerization setup

TABLE 3.2

Inverse Suspension Copolymerization Recipe

Dispersion medium	isooctane
Total monomer concentration (molar)	7
Molar ratio of aqueous Am:KA	vary from 10:90-90:10
Volume ratio of monomer solution:isooctane	1:1
Emulsifier; Span 60 (wt% based on isooctane)	1
$(NH_4)_2S_2O_8$ (g/l of the suspension)	1.4
Polymerization temperature (°C)	60
Polymerization time (hours)	2
Agitation rate (rpm)	600

Inverse suspensions of the monomer were prepared by adding the aqueous monomer solution to the isooctane-emulsifier mixture under stirring at 600 rpm and the system was allowed to sit for 30 minutes to disperse the monomer droplets in isooctane, attained temperature equilibrium at 60°C by using a thermal bath. Then a specified amount of initiator ($(NH_4)_2S_2O_8$), freshly dissolved in 1 cm^3 of doubly-distilled water, was injected through a silicone cap to start the polymerization. All polymerizations were of isothermal condition with a temperature control within 1°C. The polymerization was allowed to complete in 2 hours and ceased by adding 200 cm^3 methanol through the condenser to precipitate the copolymer under stirring at the same speed for 30 minutes. Poured the reaction mixture into a 600 cm^3 beaker, decanted and added 400 cm^3 of fresh methanol to the copolymer. Stirred overnight with a magnetic bar at 500 rpm. Filtered the mixture and dried the solid in an oven at 100°C for 1 hour.

3.3.2 Optimum Condition for the Polymerization Temperature

The same recipe and procedure as described in Section 3.3.1 were carried out, except for that the molar ratio of aqueous phase containing Am:KA was fixed at 79:21 and the polymerization temperature was varied from 40-60 °C in a 10 °C interval.

3.2.3 Optimum Concentration of the Initiator

The same recipe and procedure as described in Section 3.3.1 were carried out, except for that the molar ratio of aqueous phase of Am:KA was fixed at 79:21 and the $(NH_4)_2S_2O_8$ concentration was varied from 0.5-2.0 g/l of the suspension.

3.3.4 Optimum Quantity of the Crosslinking Agent

The same recipe and procedure as described in Section 3.3.1 were carried out, except for that the molar ratio of aqueous phase of Am:KA was fixed at 79:21 and a specific amount of N,N´-MBA (varied from 0.005 - 0.05 mole% based on the monomer), freshly dissolved in 1 cm^3 doubly-distilled water, was injected into the reaction flask after 5 minutes of the initiator injection.

3.4 The Synthesis of Crosslinked Poly(acrylamide-*co*-potassium acrylate) by the Redox Initiator

The same recipe and procedure as described in Section 3.3.4 were carried out and the concentration ratio of $(NH_4)_2S_2O_8$: TMEDA of 2:1 by weight was used as a redox initiating system at 45 °C for the reaction temperature.

3.5 Characterizations

The copolymer beads were subjected to various instrumental analyses as shown below.

3.5.1 Study of the Functional Groups in the Copolymer

The copolymer in a form of KBr disk, was scanned with a Perkin-Elmer 1430 Infrared Spectrophotometer to determine the functional groups of the bead.

3.5.2 Struture of the Copolymer

The copolymer was subjected to the analysis of the structure by ^{13}C-Solid State NMR. In order to obtain a high resolution of the NMR spectrum, 30 mg of the water-soluble material obtained from Section 3.3.1 was dissolved in 0.5 cm^3 D_2O, then scanned with an FT-NMR in the modes of ^{1}H-NMR and ^{13}C-NMR.

3.5.3 Study of Thermal Properties of the Copolymer

T_g and T_m of the copolymer were determined by DSC, using 3-5 mg of the copolymer which was equilibrated at 30 $^\circ$C, scanned with a heating rate of 10 $^\circ$C/minute and stopped at 350 $^\circ$C.

3.5.4 Surface morphology of the Copolymer Beads

SEM was introduced to study the surface morphology of the copolymer beads without cross-section.   The thickness of gold coated on the copolymer beads was 25 nm, and SEM was operated with 15 or 20 kV accelerating voltage, the working distance was 39 nm, and the specimen was tilted in SEM at 0 $^\circ$.

3.6 Water Absorbency of the Copolymer

3.6.1 In Distilled Water

150 g of distilled water was added to 0.1 g of dry polymer(A) in a 250-cm^3 glass beaker and it was allowed to stand for 30 minutes. The fully swollen polymer was filtered through 100-mesh wire for 3 hours and the remaining swollen polymer was weighed(B). The water absorbency was calculated by equation 5 shown below (24).

Water absorbency (g water/ g dry polymer) = (B—A)/A   eq.5

3.6.2 In Potassium Chloride and Magnesium Chloride Solutions

The same experimental procedure as described in Section 3.6.1 was carried out, except for that a series of potassium chloride and magnesium chloride solutions of 0.1, 0.5, 1.0, and 2.0 % wt/v was used instead of distilled water.