

## CHAPTER III

### EXPERIMENTAL

#### Chemicals, Equipment and Glassware

##### Chemicals

Acrylamide, AM, (J.T Baker, electrophoresis grade) was obtained as crystalline powers and used without further purification.

1-vinyl-2-pyrrolidone, VP, (Fluka Chemika, analytical grade) was used as received.

Methanol, commercial grade from BDH, was puified by fractional distillation at atmospheric pressure.

Sodium hydroxide, analytical grade, from Merck, was used as received.

Acetone, analytical grade, from Merck, was used as received.

Potassium hydroxide, B.P. grade, from Carlo Erba, was used as received.

Sodium Chloride and magnesium chloride(both of analytical grade, Merck) were used as received.

##### Equipment and Glassware

Erlenmeyer flask, funnel, beakers, 3-necked round bottom flask, condenser, mechanical stirrer, heating mantle, water bath circulator, motor stirrer, analytical balance, reactor, grinder, freeze dryer, vacuum oven, and other general laboratory glassware.

Cobalt-60 source(Gamma cell 220 of 24,480 curies from Nordian International Inc., Canada).

## Procedure

### 1. Polymerization of acrylamide by gamma irradiation

Acrylamide(17.17 g) was dissolved in an acetone/deionized water solution(45/55 v/v) to yield a solution that contained 2.5M monomer. The reaction solution was transferred to the 250 cm<sup>3</sup> tube, and purged with nitrogen gas for 30 minutes. It was closed tightly with foil and parafin film, and then irradiated with a cobalt-60 irradiation source at a dose rate of  $1.19 \times 10^4$  Gy/h to various total doses. The unreacted monomer was removed by repeated washing of the precipitate with acetone. The polymer was then freeze-dried for 12 h. The dried product was ground into a power form and stored in a desiccator. To obtain a good yield of the polymer, important parameters on polymerization were carried out as follows :

#### 1.1 Effect of Total Dose(kGy) on Polymerization

The dose rate at  $1.19 \times 10^4$  Gy/h and with a total dose of 0.1 kGy was given to start this set of experiment. The subsequently total doses was increased by a 0.1 kGy interval to reach the maximum total dose of 2.0 kGy. The highest conversion value indicates the appropriate total dose for polymerization. The dried product was inspected with the FTIR spectrometer.

#### 1.2 Effect of Dose Rate on Polymerization

A fixed total dose obtained from Section 1.1 that gave the highest conversion was chosen for this set of experiment. Various dose rates of  $3.60 \times 10^3$ ,  $5.34 \times 10^3$  and  $1.19 \times 10^4$  Gy/h obtained from the source were used to irradiate the reaction mixture. The higher conversion value indicates the appropriate dose rate for the polymerization.

#### 1.3 Effect of the Concentration of AM on Polymerization

The dose rate of  $1.19 \times 10^4$  Gy/min and the optimum total dose of 1.4 kGy were fixed for the set of experiment. 0.5M to 3.5M of AM with an

increment of 0.5M were experimented by following the above procedure. The highest conversion value indicates the appropriate concentration of AM for the polymerization.

## 2. Hydrolysis of Polyacrylamide

Into a 500 cm<sup>3</sup> reactor, 5 g of polyacrylamide(PAM) derived from Section 1, was mixed with 100 cm<sup>3</sup> of 5% sodium hydroxide solution. The mixture was stirred with a mechanical stirrer at 400 rpm and the reaction was carried out at 60°C for 2 hours. It was then allowed to cool to room temperature. The reaction mixture was precipitated with methanol, filtered and washed thoroughly with methanol until pH 7 was reached. The resulting product was dried in a 65°C vacuum oven for 24 h. The dried product was ground into a powder form and stored in a desiccator. The degree of hydrolysis was then calculated.

To achieve the degree of hydrolysis which was suitable to copolymerize with 1-vinyl-2-pyrrolidone which could give the product with the highest water absorption value. The degree of hydrolysis governed by the functions of reaction time, temperature concentration of NaOH (%w/v) and quantity of polyacrylamide (g) are the important attributes for the subsequent copolymerization. The same experimental procedure as described above was carried out as follows:

2.1 A series of sodium hydroxide solution of 10, 15 and 20% w/v was used instead of 5% sodium hydroxide solution for the hydrolysis.

2.2 A series of temperature of 50, 70 and 80°C was used instead of 60°C for the hydrolysis.

2.3 A series of reaction time of 1, 3 and 4 h was used instead of 2 h for the hydrolysis.

2.4 A series of quantity of polyacrylamide 1, 3, 7, 9 g was used respectively, instead of 5 g polyacrylamide for the hydrolysis.

### 3. Copolymerization of partially hydrolyzed polyacrylamide with 1-vinyl-2-pyrrolidone

Into a 500 cm<sup>3</sup> reactor, 5 g of HPAM(71% hydrolysis which was derived from Section 2) mixed with 100 cm<sup>3</sup> of deionized water. The system was stirred at 400 rpm at room temperature for 30 minutes under the nitrogen atmosphere. 10 cm<sup>3</sup> of 1-vinyl-2-pyrrolidone was added into the HPAM solution. The mixture was stirred at 400 rpm under nitrogen atmosphere at room temperature for 15 minutes. The HPAM-1-vinyl-2-pyrrolidone mixture was removed into the 250 cm<sup>3</sup> tube, and purged with nitrogen gas for 15 minutes. It was closed tightly with foil and parafin film, and then irradiated under gamma rays at a dose rate of  $1.19 \times 10^4$  Gy/h to the total dose of 10 kGy. The reaction product was precipitated with methanol, filtered and dried at 65°C in a vacuum oven for 24 h. The dried product was ground into a powder form and stored in a desiccator.

To obtain a good yield of copolymer with a high water absorption value, important effects on copolymerization were carried out as follows:

#### 3.1 Effect of Total Dose (kGy) on Copolymerization

A fixed dose rate of  $1.19 \times 10^4$  Gy/h, and various quantities of total dose of 8, 9, 10, 11 and 12 kGy of gamma-rays were given respectively to the mixture of HPAM-1-vinyl-2-pyrrolidone as described in Section 3. The dried products were inspected with the FTIR spectrometry and water absorption capacity as described in Section 5 was consequently measured. The higher water absorption value indicates the appropriate total dose for the copolymerization of this system. Percentage conversion was also calculated.

#### 3.2 Effect of Dose Rate on Copolymerization

A , fixed total dose obtained from Section 3.1 to various dose rates of  $3.60 \times 10^3$ ,  $5.34 \times 10^3$ , and  $1.19 \times 10^4$  Gy/h obtained from the source was used to irradiate the HPAM-1-vinyl-2-pyrrolidone mixture. The maximum

water absorption capacity of the dried copolymer produced by each dose rate indicates the appropriate dose rate.

### 3.3 Effect of the Amount of HPAM on Copolymerization

Based on the technical information of the optimum total dose (Section 3.1) and the appropriate dose rate (Section 3.2), various amounts of HPAM of 5, 10, 15 and 20 g were each mixed with 100 cm<sup>3</sup> deionized water. The dried samples were inspected with the FTIR spectrometer and water absorption capacity was then determined.

### 3.4 Effect of the Quantity of 1-vinyl-2-pyrrolidone on Copolymerization

Various amounts of 1-vinyl-2-pyrrolidone of 5, 10, 15 and 20 cm<sup>3</sup> (0.47, 0.94, 1.41 and 1.88 M) were added to each of the HPAM mixture. The reaction mixture was stirred mechanically for 15 minutes under nitrogen atmosphere, and was removed into the 250 cm<sup>3</sup> tube purged with nitrogen gas for 15 minutes. Irradiations were carried out at the optimum total dose (Section 3.1) and dose rate (Section 3.2). The dried products were inspected with the FTIR spectrometer and water absorption capacity was then determined.

### 3.5 Effect of the Degree of Hydrolysis of Polyacrylamide on Copolymerization

The same experimental procedure as described in Section 3 was carried out, except a series of the degree of hydrolysis of polyacrylamide of 63, 72, 76, 77, 80 and 84% hydrolysis was used respectively instead of 71% hydrolysis.

## 4. Copolymer Characterization

### 4.1 Determination of Percent Conversion

The experimental procedures described in Sections 1 and 3 were carried out. The weight of polymer and copolymer were regarded as the

total amount of polymer obtained from the weight of monomer changed. Percent conversion was subsequently calculated.

#### 4.2 Determination of Degree of Hydrolysis

The degree of hydrolysis of the polyacrylamide was determined by Semi-Micro Kjeldahl method, which gave the nitrogen content. The difference of the nitrogen contents before and after hydrolysis was determined for the degree of hydrolysis.

### 5. Water Absorption/Retention Capacity of the Copolymer

#### 5.1 In Deionized Distillated Water

One hundred gram of deionized distilled water was added to 0.1 g of the dried partially hydrolyzed polyacrylamide(HPAM)-1-vinyl-2-pyrrolidone copolymer in a 150 cm<sup>3</sup> glass beaker and was allowed to stand for 30 minutes for swelling. The fully swollen copolymer was filtered through a 100-mesh aluminium screen for 3 hours and the drained water was weighed. The amount of water retained by the copolymer was calculated as in gram per gram of the dry copolymer. The viscosity of fully swollen copolymer was measured by Brookfield Viscometer Model DV-III.


#### 5.2 In Sodium Chloride and Magnesium Chloride Concentrations.

The same experimental procedure as described in Section 5.1 was carried out, except that a series of sodium chloride, and magnesium chloride solutions of 0.1, 0.5, 1.0 and 2.0 % w/v was used instead of deionized distilled water. The viscosity of fully swollen copolymer was measured by Brookfield Viscometer Model DV-III.

### 6. Water Absorption Rate of the Copolymer

The equipment for assessment of the water absorption rate was composed of a 100-mesh aluminium screen in a funnel that was connected with a graduated buret through a rubber tube. The level of aluminium screen

and that of the buret at the zero scale were the same. The deionized distilled water was filled into the buret until the water level was at the zero scale. The aluminium screen was found to be thoroughly wet. Then 0.1 g of dried copolymer was dropped onto the wet aluminium screen and then it was swollen immediately. The time required for 0.1 g of the product to fully wet, regarded as the wicking time, was recorded. The amount of water, which lessened from the zero level of the buret, expressed in gram of water per gram of the product within a specified time needed, was the water absorption rate.



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