

## CHAPTER III

### EXPERIMENTAL

#### 3.1 Chemicals, Equipments and Glasswares

##### 3.1.1 Chemicals

Acrylamide (AM), commercial grade, cordially provided by Siam Fine Chemie Co.,Ltd., was recrystallized twice from distilled dried methanol. Commercial grade methanol supplied by BDH was purified by fractional distillation at atmospheric pressure. Other chemicals shown in Table 3.1 were analytical grade and used as received.

**TABLE 3.1**

#### **Chemicals Used**

Chemical	Source
Water soluble starch (WSS)	Merck
Cassava starch	Thai Wah Co. ,Ltd.

TABLE 3.1 (continued)

## Chemicals Used

Chemical	Source
Glucose	Merck
Sodium ethylenediamine tetraacetate (NaEDTA)	Fluka
Sodium carbonate ( $\text{Na}_2\text{CO}_3$ )	Fluka
Potassium persulphate ( $\text{K}_2\text{S}_2\text{O}_8$ )	Fluka
Acetic acid ( $\text{CH}_3\text{COOH}$ )	Merck
Nitric acid ( $\text{HNO}_3$ )	Merck
Propylene glycol	BDH
Liquid $\text{N}_2$	Thai Industrial Gas Co.,Ltd.

3.1.2 Equipments and Glasswares

4-Necked, flat flange reaction vessel, mechanical stirrer, circulating water bath, magnetic stirrer, analytical balance, filtering system, evaporating system, distillating system, cooling system, crusher, desiccator, vacuum oven and other general laboratory glasswares and equipments were used in these studies.

### **3.2 Instruments**

Major instruments used in these studies were

- 1) 1760X Perkin-Elmer Fourier Transform Infrared Spectrophotometer (FTIR) .
- 2) DSC 7 Perkin-Elmer Differential Scanning Calorimeter .
- 3) TGA 7 Perkin-Elmer Thermogravimetric Analyser .
- 4) Teflon® PTFE-coated sheaths Type K Cole-Parmer, Thermocouple .
- 5) Logit SL200 Grant Datalogger, interfaced with microcomputer .
- 6) Abbe-type Bausch & Lomb precision Refractometer

### **3.3 Experimental : Preliminary Studies**

#### **3.3.1 Synthesis and Characterization of Starch-g-Polyacrylamide (S-g-PA) Via the Foamed Polymerization Process**

Polymerization was carried out in a 500-ml 4-necked, flat flange reaction vessel equipped with a mechanical and fitted with a top-supported type stirrer and a thermometer. Temperature was controlled constant using a water bath .

The basic recipe used for the foamed polymerization is given in

Table 3.2

TABLE 3.2

## Foamed Polymerization Recipe I

Substance	Quantity	Unit
Solvent : distilled water		
Acrylamide powder	4.45	Molar
Potassium persulphate aqueous solution	2.22	$\times 10^{-3}$ Molar
Water soluble starch powder	10.00	% Based on monomer weight
Foaming agent :		
Na <sub>2</sub> CO <sub>3</sub> powder	0.89	Molar
Mol ratio of Na <sub>2</sub> CO <sub>3</sub> : CH <sub>3</sub> COOH	1:2	Mol : Mol
Propylene glycol	0.28	% Based on monomer weight
NaEDTA aqueous solution	3.35	$\times 10^{-3}$ Molar
Initial polymerization temp.	40	°C
Polymerization time	15	Min.
Agitation rate	500-1500	Rpm.

· Foamed aqueous solution of starch monomer was prepared by dissolving  $\text{Na}_2\text{CO}_3$  powder in an aqueous starch gel at  $80^\circ\text{C}$ . The mixture was then allowed to cool down to room temperature, and a high concentration solution (I) was obtained. To (I), acrylamide monomer powder, NaEDTA and propylene glycol were added and blended until a gelation solution (II) had been prepared. To (II) was added slowly  $\text{CH}_3\text{COOH}$  while blending at 1000 rpm. Carbon dioxide bubbles was formed and filled the system. The blending was continued for additional 10-15 minutes. The reaction temperature was held at approximately  $40^\circ\text{C}$ , and those foamed aqueous gelated solution (III) was obtained.

Then a specified amount of 0.1 M solution of  $\text{K}_2\text{S}_2\text{O}_8$  initiator in 1.0 M nitric acid was added to (III) with continuous stirring at 500 rpm. The temperature of water bath was controlled at  $40^\circ\text{C}$  while the temperature of system was allowed to rise exothermically to a higher temperature. Copious quantity of vapor escaped during that time. The polymerization was allowed to complete for 15 minutes .

The product was cut into small pieces using a knife or scissors. Residual monomer was eliminated by extracting with methanol. Then, it was dried in vacuum at  $60^\circ\text{C}$  and crushed to powder. The starch-g-polymer was subjected to the analysis of the chemical structure using a FT-IR spectrophotometer.

### **3.3.2 Study of Degradation of Starch Backbone in the Presence of Alkali Foaming Agent**

65 ml of 10% aqueous solution of water soluble starch was prepared by dissolving the starch material into boiling water. 21.2 g of sodium carbonate powder was added and dissolved in the aqueous starch solution at 60°C for 15 min. The observation of reaction and product appearance was made. The experiment was repeated except that the studied temperatures of reaction were changed to be 80 and 100°C. After that the other carbohydrate materials, cassava starch and glucose were studied using the same procedure mentioned above. The results of each experiment were compared.

The solution in the presence of water soluble starch was evaporated and dried at 60°C. Separated from Na<sub>2</sub>CO<sub>3</sub>, the product was subjected to the analysis of chemical structure using a FT-IR spectrometer and thermal properties using DSC and TGA techniques.

### **3.3.3 Synthesis and Characterization of Polyacrylamide via the Foamed Polymerization Process**

Polymerization was carried out in the same reactor equipped with accessories described in Section 3.3.1. The recipe used for the foamed polymerization are given in Table 3.3

TABLE 3.3

## Foamed Polymerization Recipe II

Substance	Quantity	Unit
Solvent : distilled water		
Acrylamide aqueous solution	2.44	Molar
Potassium persulphate aqueous solution	1.22	$\times 10^{-3}$ Molar
Foaming agent :		
Na <sub>2</sub> CO <sub>3</sub> aqueous solution	0.50	Molar
Mol ratio of Na <sub>2</sub> CO <sub>3</sub> : CH <sub>3</sub> COOH	1 : 2	Mol : Mol
Propylene glycol	0.28	% Based on monomer weight
NaEDTA aqueous solution	1.83	$\times 10^{-3}$ Molar
Initial polymerization temp.	70	° C
Polymerization time	15	Min.
Agitation rate	500	Rpm.

Foamed aqueous solution of monomer was prepared by adding Na<sub>2</sub>CO<sub>3</sub> aqueous solution to the aqueous monomer solution in the presence of NaEDTA and propylene glycol with the continuous stirring at 500 rpm. The temperature was held at 30°C for 10 minutes. Then the

solution (I) was prepared. To (I) are added slowly acetic acid while stirring. Carbon dioxide bubbles was formed and filled the system. The mixed solution was allowed to continue further for 5 minutes, and the foamed aqueous solution (II) was obtained.

The solution temperature was raised up to  $70^{\circ}\text{C}$  within 5 minutes, and the specific amount of 0.1 M  $\text{K}_2\text{S}_2\text{O}_8$  initiator solution in 1.0 M nitric acid was added to (II) with agitation speed at 500 rpm. The temperature of water bath was held at  $70^{\circ}\text{C}$  while the temperature of system was allowed to rise exothermically to a higher temperature. The copious quantity of vapor escaped during that time. The polymerization was allowed to complete within 15 min.

The product was cut into small pieces and dissolved in distilled water. The polymer was precipitated from the solution using methanol, filtered, dried in vacuum at  $60^{\circ}\text{C}$  for 2 days and crushed to powder. The chemical structure of polymer was analysed using a FT-IR spectrophotometer.

### **3.4 Studies of the Kinetics of Isothermal Foamed Polymerization of Acrylamide**

#### **3.4.1 Initial Rate of the Foamed Polymerization**



The DSC 7 Perkin Elmer differential scanning calorimeter was dedicated for the studies. The foamed aqueous solution for the polymerization was prepared using the same recipe and procedures as described in details in Section 3.3.3, except that the scale of polymer synthesis was smaller and the temperature of solution prior to adding of the initiator solution was at 5°C. Approximately 10 mg of the solution was loaded into a standard Perkin-Elmer pan suitable for volatile samples, which was subsequently placed into the sample holder of the calorimeter. Temperature was previously set to 5°C for 10 minutes. The empty pan was used as reference. Temperature of the system was programmed to detect heat of the reaction in the scanning mode with the heating rate of 10°C/min from 50 to 150°C. The experiment was repeated 5 times. The mean standard deviation was within the limitation of  $\pm 5\%$ .

Then, the fresh foamed aqueous solution was detected the heat of reaction in the isothermal mode at 70°C. The experiment was repeated as in the scanning mode. The residual monomer content was determined calorimetrically. After each isothermal mode run the sample was heated from 50 to 150°C at a heating rate of 10°C/min. Each pan was checked for tightness and practically no leakage was observed. Calibration of the calorimeter was performed by the determination of the heat of fusion for Indium and Zinc.

The areas under the particular curves in the DSC

thermograms were calculated as the heat of reactions.

This information measured during the reaction was correlated to the monomer conversion and reaction rate which are functions of time according to the following equations

$$C = \frac{(\alpha)(\Delta H_I)}{(\Delta H_S)} \quad (3.1)$$

$$R_p = \frac{(dc)}{(dt)} \frac{[M]}{6000} \quad (3.2)$$

$$\alpha = \frac{\Delta H_{I,t}}{\Delta H_I} = \frac{\Delta a_t}{\Delta a_T} \quad (3.3)$$

- Where  $C$  (%) = The percent conversion at a given time in sec.  
 $R_p$  (mol/L-s) = The polymerization rate at a given time in sec.  
 $\alpha$  (%) = The percent conversion at a given time in sec. in isothermal exotherm
- $\Delta H_I$  (J/g) = The total isothermal exotherm
- $\Delta H_{I,t}$  (J/g) = The accumulated isothermal exotherm from  $t=0$  to the given time in sec.
- $\Delta a_t$  (J/g) = The accumulated area under the isothermal DSC curve from  $t=0$  to the given time in sec.
- $\Delta a_T$  (mJ) = The total area under isothermal DSC curve
- $\Delta H_S$  (J/g) = The total scanning exotherm which is the

total area under scanning DSC curve

$[M]$  (mol/L) = The initial concentration of monomer .

The typical percentage of conversion against time curve was done and shown subsequently in the Result and Discussion Sections. Conversion up to 5% only was used for the calculation of initial rate of polymerization.

### 3.4.2 Initial Rate Dependency on Monomer Concentration

The same procedures as described in Section 3.4.1 were carried out ,except that the monomer concentrations were varied from 2.44 to 3.66 mol/L.

The log-log plot of  $R_p$  vs. the monomer concentration was carried out. The slope of curve was calculated related to the monomer order according to Eq. (3.4)

$$\log R_p = n \log [M] + \log K [I]^m \quad (3.4)$$

where  $n$  = The monomer order which was the slope  
of curve of the equation,

$K$  (L/mol-s) = The overall rate constant,

$[I]$  (mol/L) = The initial concentration of initiator,

$m$  = The initiator order.

The other variables were similar to the ones in Section 3.4.1.

### 3.4.3 Initial Rate Dependency on Initiator Concentration

The same procedures described in Section 3.4.1 were again carried out, except that the initiator concentration was varied from 0.0012 to 0.0061 mol/L.

The log-log plot of  $R_p$  vs initiator concentration was also carried out. The slope of curve was calculated related to the initiator order according to Eq. (3.5).

$$\log R_p = m \log[I] + \log K [M]^n \quad (3.5)$$

The variables were similar to the ones in Section 3.4.2.

### 3.4.4 The Effect of Polymerization Temperature on Initial Rate

The same procedures as described in Section 3.4.1 were carried out, except that the polymerization temperature was varied from 70 to 90°C.

The Arrhenius plot of  $\log R_p$  vs.  $1/T$ , where  $T$  is

temperature in Kelvin, was done. The overall activation energy and average overall rate constant were calculated from the slope of curve and the Eqs.(3.6) and (3.7) showing the relationship of the plot.

$$\log R_p = \frac{-E_a}{R} \cdot \frac{1}{T} + \log [M]^n [I]^m + \log A \quad (3.6)$$

$$K = \frac{R_p}{[M]^n [I]^m} \quad (3.7)$$

- where  $E_a$  (kJ/mol) = The overall activation energy,  
 $K$  (L/mol-s) = The average overall rate constant,  
 $R$  (J/K-mol) = The gas constant,  
 $T$  = The temperature degree in Kelvin,  
 $A$  (L/mol-s) = The collision frequency factor.

### **3.5 Study of Thermal Effects of the Foamed Polymerization of Acrylamide**

#### **3.5.1 Temperature Profile during the Course of Polymerization in the Ampoule**

The same recipe and procedures as described in Section 3.3.3 were carried out, except that only 5 cm<sup>3</sup> of the foamed aqueous solution for the polymerization prepared in a 10 cm<sup>3</sup> glass

ampoule (diameter of 1 cm.). The polymerization time was 30 minutes. The temperature during the course of polymerization was detected using a thermocouple-data logger interfacing with IBM/PC computer system. The temperature versus time curve was obtained. The calibration of thermocouple was performed by determining the freezing point and boiling point of distilled water under atmospheric pressure .

### 3.5.2 Conversion Profile during the Course of Polymerization in Ampoules

The same procedures as described in Section 3.5.1 were carried out, except that many sets of polymerization were prepared. In each set, the polymerization was ceased under liquid nitrogen at different reaction times (0.5 min : 1 times) of polymerization (30 min).

The Abbe-type refractometer was used to measure the refractive index at 25°C of the products obtained at the particular reaction time. Calibration of the refractometer was achieved using n-hexadecane and 1-methylnaphthalene as standards according to ASTM D 1747-94.

The final percentage of conversion was determined by weighing the product of the final set, dissolving in distilled water. The polymer precipitated from methanol ,then filtered, dried under vacuum at 60°C ,followed by weighing of the polymer. Calculation of the percentage of conversion was achieved using the equation shown below.

$$\text{Percent conversion (\%)} = \frac{\text{Weight of polymer (g)} \times 100}{\text{Weight of monomer (g)}} \quad (3.8)$$

Compared to the final percentage of conversion, the difference between the refractive index of the initial set and the final set was used to calculate the conversion as a function of time based on the equation shown below

$$C = \frac{n_t - n_0 (C_f)}{n_{30} - n_0} \quad (3.9)$$

where  $C$  (%) = The percent conversion at a given time in min,

$n_t$  = The refractive index of product at a given time in min,

$n_0$  = The refractive index of product at initial time in min,

$n_{30}$  = The refractive index of product at final time in min,

$C_f$  = The final percentage of conversion.

The percent conversion against time curve was obtained. Conversion up to 5% only was used for the calculation of initial rate of polymerization based on the Eq. (3.2).

### 3.5.3 The Effect of Reaction Scale for the Polymer Synthesis on Temperature Profile and Conversion Profile

The same procedures as described in Sections 3.5.1 and 3.5.2 were carried out, except that the volume of foamed aqueous

solution was varied from 0.5 to 5.0 cm<sup>3</sup>.

#### **3.5.4 The Effect of Surface Area/Volume Ratio of Ampoules on Temperature Profile and Conversion Profile**

The same procedures as described in Sections 3.5.1 and 3.5.2 were carried out, except that the diameters of ampoules were varied from 1.0 to 2.0 cm.

#### **3.5.5 The Effect of Reaction Mass on Temperature Profile and Conversion Profile**

The same procedures as described in Sections 3.5.1 and 3.5.2 were carried out, except that the weight percentage of solvent was varied from 43.61 to 70.59 % . Table 3.4 shows the foamed polymerization recipe for the experiments in this section.



TABLE 3.4

## Foamed Polymerization Recipe III

Substance	Quantity	Unit
Solvent : distilled water	70.59-43.61	% Based on total solution weight
Acrylamide	2.44- <u>4.66</u>	Molar
Potassium persulphate aqueous solution	1.22-2.30	$\times 10^{-3}$ Molar
Foaming agent :		
Na <sub>2</sub> CO <sub>3</sub> aqueous solution	0.50- <u>0.92</u>	Molar
Mol ratio of Na <sub>2</sub> CO <sub>3</sub> : CH <sub>3</sub> COOH	1:2	Mol :Mol
Propylene glycol	0.28	% Based on monomer weight
NaEDTA aqueous solution	1.83-3.46	$\times 10^{-3}$ Molar
Initial polymerization temp.	70	° C
Polymerization time	30	Min.

\_\_\_\_\_ used in powder form