CHAPTER III

EXPERIMENTAL

3.1 Chemicals

1. Styrene ($C_6H_5CH=CH_2$) : Eternal Resin
2. Divinylbenzene ($C_6H_4(CH=CH_2)_2$,63.5% DVB) : Merck
3. Methanol (CH_3OH) , Commercial Grade
4. Toluene (C_7H_8) , AR Grade : J.T. Baker
5. Benzoyl peroxide ($C_{14}H_{10}O_3$) , AR Grade : Merck
6. Poly(vinyl alcohol) molecular weight 100,000, degree of polymerization of 2,000, with a degree of hydrolysis, 86-89% : Fluka
7. Hydroquinone : Merck
8. Anhydrous sodium sulfate (Na_2SO_4) : Carlo erba
9. Sodium hydroxide (NaOH) : Carlo erba
10. Aluminium oxide, 100-125 mesh : Fluka
11. Distilled water

3.2 Glassware

1. 4-Necked flask, 500 cm^3
2. Nitrogen gas tube
3. Reflux condenser
4. Iodine flask
5. And other general laboratory glassware

3.3 Equipment

1. Stirring type : Semicircular, turbine-type blade, homemade

2. Oil bath	: Memmert, Germany
3. Mechanical stirrer	: Ika RW20, Germany
4. Scanning electron microscope (SEM)	: JSM-6400, Japan
5. Gas Chromatrograph	: Shimadzu GC-14B, Japan
6. Recorder	: Shimadzu C-R6A, Japan
7. Column 25% PEG-20M Uniport B, 60/80 mesh	: Shimadzu, Japan
8. Heating mantle	: Electrothermal, England
9. Soxhlet apparatus	
10. Stereomicroscope coupling with Luzex-F software program of Nireco QJ 8500	: Olympus SZH 10, Japan
11. FT-IR Spectrometer	: Perkin Elmer 1760X, USA.
12. Differential Scanning Calorimeter	: Perkin Elmer DSC 7, USA.

3.4 Procedures

3.4.1 Preparation of Monomer Phase

3.4.1.1 Purification of monomer: The monomer and 10% NaOH solution were poured in a separatory funnel and the mixture was shaken vigorously. The red aqueous phase was drained off. The same procedure was repeated until the aqueous solution turned colorless. The monomer was then washed with distilled water for removal of NaOH until the litmus paper did not change its original color. Then the monomer was dried with anhydrous Na_2SO_4 and was kept overnight (at lower 10°C) in a refrigerator.

3.4.1.2 Removal of the inhibitor: The monomer was stored at the lower 10°C, which was passed through a column packed with γ form aluminium oxide for removal of the inhibitor. Finally the monomer was sealed in a dark brown bottle

which was then stored in a refrigerator at the temperature lower than 10°C to prevent self- polymerization.

3.4.2 Preparation of Aqueous Phase

Dissolve Poly(vinyl alcohol) 0.018 g (0.09% by monomer weight) was dissolved in distilled water, 100 cm^3, in a flask and was stirred by a magnetic stirrer at room temperature.

3.4.3 Kinetics Study of the Styrene-Divinylbenzene Copolymer

3.4.3.1 Copolymerization

The styrene-divinylbenzene copolymer was prepared by suspension polymerization. The procedure of suspension polymerizations of styrene-divinylbenzene beads was summarized as shown in Figure 3.1.

The solution of the suspending agents was charged into a 500-cm^3 reaction flask and 40 cm^3 of distilled water was added. The monomer solution phase containing styrene, divinylbenzene as a crosslinker, benzoyl peroxide as an initiator and toluene as an organic solution was added to the flask, which was stirred at an agitation speed of 240 rpm., while maintaining the reaction temperature at 70°C. A typical charge solution consisted of: water (140 ml), styrene (92.5%), divinylbenzene (7.5 %), benzoyl peroxide (0.5% by monomer weight), organic solvent (100% by monomer weight), PVA (0.09% by monomer weight), was used for polymerization, based on 63.5% DVB and 32.9% EVB content of the commercial DVB composition. The monomer/water phase ratio throughout the experiments was fixed for 1:7 wt/wt and the polymerization was carried out under a nitrogen atmosphere.

3.4.3.2 Determination of the Residual Styrene-Divinylbenzene by GC Technique

A gas chromatograph (GC, Shimadzu GC-14B) equipped with a flame-ionization detector was employed. A packed column containing 25% PEG-20M Uniport B was used. A high purity nitrogen gas (99.99%) was used as the carrier gas under a pressure of 200 kPa. The injection port, oven and detector temperatures were

set at 180, 150 and 200°C, respectively. 1.0-μL sample was injected into the GC using syringe. A peak area was calculated using the software supplied by Shimadzu C-R6A.

Samples were picked up at the set interval, which were then rapidly quenched with hydroquinone (0.2 g) in an iodine flask. Toluene (60 cm^3) was added to extract the unreacted monomers. The sample was stored at 4°C for 20 minutes. The sample solution was analyzed for the unreacted monomers through a volumetric determination. The solid polymer was extracted with acetone in a soxhlet extractor for 10 hours and the solid portion was then dried in an oven at 50°C for 24 hours. The overall conversion of the monomers to the solid copolymer was determined gravimetrically. The dried weight of the polymer was then measured.

The residual monomer content in mole was also calculated with reference to the calibration curve. The monomer conversion was obtained from Eq (3.1).

$$\text{Percent monomer conversion} = (1 - m_r/m_I) \times 100 \qquad (3.1)$$

where m_r is the mole of the residual monomer determined by the GC technique, and
m_I is the initial mole of the monomer determined by calculation.

The scope of the polymerization was presented in Table 3.1.

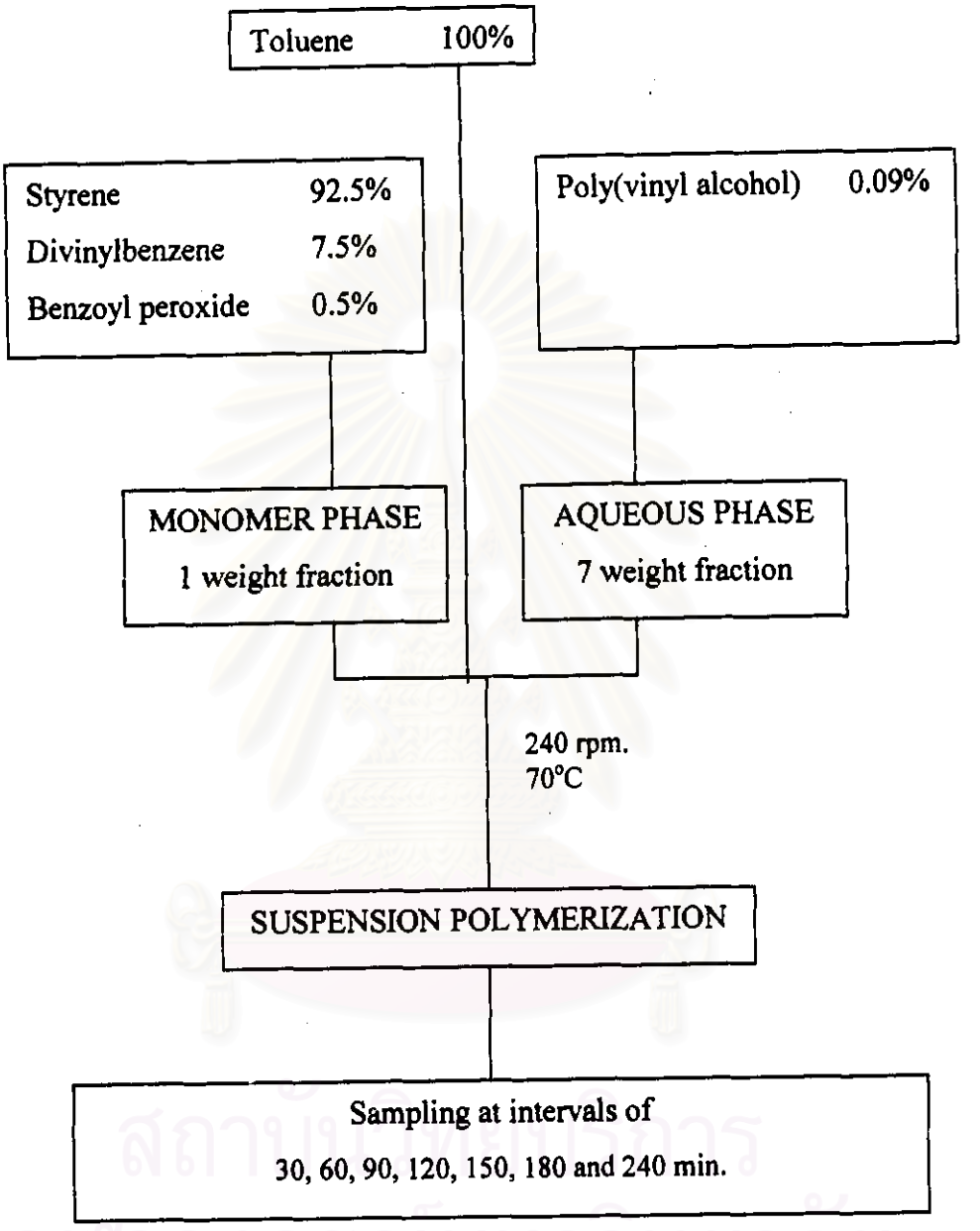

Figure 3.1 Diagram of Suspension Copolymerization of Styrene-Divinylbenzene Beads.

3.5 Characterization

The solid polymers from step 2 were subjected to various instrumental analyses as below.

3.5.1 Degree of Swelling Ratio

A dry polymeric sample weighed m_g in a test tube of total weight m_1, was immersed to swell in toluene at room temperature for 24 hours. After that, the test tube containing the swollen polymer was weighed, m_s, after toluene was separated. The swelling ratio, G, was calculated by the following equation:

$$G = \frac{m_s - m_1}{m_g} \tag{3.2}$$

3.5.2 Parameters Understudy for the Swelling Ratio

The styrene-divinylbenzene copolymer prepared by suspension polymerization for the preliminary investigation of the parameters involved was measured for degree of swelling ratio. Part of data was calculated for finding relationship of swelling weight with parameters by SPSS program.

Based on the ingredient and the condition for suspension polymerization in Table 3.1, the parameters involved in each recipe was undertaken for their influences on the swelling ratio. To determine the main parameters and their interaction on swelling, an SPSS program was used as a statistical tool.

3.5.3 Scanning Electron Microscope (SEM)

The crosslinked polymers were viewed for their surface morphology by scanning electron microscopy on the JSM-6400.

3.5.4 Particle Sizes [23]

The particle sizes of the crosslinked styrene-divinylbenzene beads were determined by counting more than 300 grains projected on an SZH 10 stereomicroscope coupling with the Luzex F package.

The Sauter mean diameter was calculated as

$$d = \frac{\Sigma f_i \overline{d_i^3}}{\Sigma f_i \overline{d_i^2}} \qquad (3.3)$$

where $\overline{d_i} = (d_i + d_{i+1})/2$ is the average diameter in the interval and f is the frequency of grains in the size range, d_i and d_{i+1}.

3.5.5 Determination of Glass Transition Temperature

The samples were prepared by drying at 50°C for a constant weight. Glass transition temperature and incremental changes in heat capacity at T_g were measured calorimetrically using a differential scanning calorimeter, programmed at a heating rate of 20°C/min. Large-volume stainless steel sample pans for the samples were used instead of the standard aluminum pans.

3.5.6 Infrared Spectroscopy

Infrared spectroscopy of the crosslinked styrene-divinylbenzene beads was carried out to detect the functional groups as well as the crosslinking sites of the polymeric beads.

3.6 Kinetics of absorption and desorption of the polymeric beads

One imbiber bead was placed in a mini petri dish (1.5x1 cm) to immerse and swell in the excess solvent. Time zero was the time when the bead was placed into the bulk solvent and the measurement of swelling kinetics was started, consequently. The bead remained spherical throughout the entire process and the variation in diameter was measured as a function of time by the stereomicroscope coupling with Luzex-F software program. The diameter of bead could be measured by clicking three points on the edge of the bead. The circle around the bead and the bead diameter were shown. The accuracy of the bead diameter measured from this method was 1×10^{-5} mm.

For desorption kinetics measurements, a fully swollen bead was placed on a piece of the filter paper substrate (38.5 cm^2) in a petri dish (1.5x1 cm) covered with a glass lid. It was covered to reduce evaporation and keep out of contaminating particles. Again, the bead remained spherical and the variation of diameter was measured as a function of time by the same stereomicroscope and computer software.

Table 3.1 Polymerization recipes and reaction conditions.

Ingredient	SAMPLE												
	A	B	C	D	E	F	G	H	I	J	K	L	M
Sty (%)	92.5	92.5	92.5	92.5	92.5	92.5	92.5	92.5	95.0	90.0	92.5	92.5	92.5
DVB (%)	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	5.0	10.0	7.5	7.5	7.5
Tol (%)	100	100	100	100	100	100	100	100	100	100	20	60	140
BPO (%)	0.1	0.5	1.5	2.0	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Temperature (°C)	70	70	70	70	60	80	70	70	70	70	70	70	70
Agitation (rpm.)	240	240	240	240	240	240	180	300	240	240	240	240	240
PVA (%)	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09
Water : Monomer (weight ratio)	7 : 1	7 : 1	7 : 1	7 : 1	7 : 1	7 : 1	7 : 1	7 : 1	7 : 1	7 : 1	7 : 1	7 : 1	7 : 1